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Interfacial Phenomena in Electrocatalysis

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Preface

This Volume analyzes and discusses several important recent developments in the study of interfacial phenomena at the metal/solution interface and their role in Electrocatalysis. The six chapters are written by internationally recognized experts in these areas and address both fundamental properties of the metal/solution interface and the practical implications of these phenomena in electrocatalysis.

The Chapter by N. Garcia, V. Climent and J. Feliu provides a lucid and authoritative overview of the use of laser-pulsed induced temperature variations at the platinum single-crystal/aqueous solution interphases and of the rigorous analysis of these experiments via Gibbs thermodynamics to extract new and very valuable information on the structure and reactivity of the metal/solution interphase. The authors show how some key interfacial properties can be evaluated directly via this elegant analysis, such as the entropy of charge-transfer adsorbed species, the entropy of formation of the interfacial water network and the potential of water reorientation.

The Chapter by G. Tsirlina provides a lucid historical evolution of our understanding of Pt metal electrochemistry and electrochemical surface thermodynamics from the days of Frumkin to the modern era of sophisticated surface science techniques. This exciting review links theory and experiment, poorly and well defined surfaces and the thermodynamics of adsorption with the most recent results obtained with modern in situ spectroscopic and microscopic techniques.

The amazing new horizons opened by the use of X-ray absorption Spectroscopy (XAS) for in situ or operando studies of the electrode/electrolyte interphase in a working fuel cell are presented in a lucid and concise chapter by C. Roth and D. Ramaker. It is shown how via the use of EXAFS and the newer $\Delta\mu$ XANES technique one can now monitor individually the surface concentrations of atop CO, opd and upd H, bridge-bounded and fcc O and even OH, all possibly present on Pt and PtRu surfaces during cycling in acidic PEM fuel cells media.

The Chapter by C. Bianchini provides a comprehensive and authoritative overview of recent advances on the use of Pd-based electrocatalysts in direct alcohol fuel cells. The Chapter shows lucidly how the dilution of Pd with non-noble metals in a smart catalytic architecture can lead to inexpensive and highly active anode electrodes which can knock down the main barriers for the commercialization of direct alcohol/fuel cells (DAFC).

The cathodic oxygen reduction (ORR) electrocatalysis on chalcogenides is discussed in an authoritative Chapter by N. Alonso-Vante. Several new findings are discussed related to the design, genesis and ORR mechanism on these materials which are promising catalysts for Pt replacement in the future.

A promising approach for avoiding CO poisoning of PEMFCs is higher operating temperatures and the Chapter by M. Daletou, J. Kallitsis and S. Neophytides discusses the use of new polymeric membrane materials which allow for PEMFC operation up to 180°C. This is shown to enhance anodic and cathodic electrocatalysis with minimal material degradation problems and thus appears quite promising for future practical applications.

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Temperature Effects on Platinum Single-Crystal/Aqueous Solution Interphases. Combining Gibbs Thermodynamics with Laser-Pulsed Experiments

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I. INTRODUCTION

The rigorous analysis of the effect of temperature variations on interfacial properties is a key tool to provide new and valuable information on the structure and reactivity of the metal|solution interphase. The entropy of the components that form the interphase is a unique probe of their structural properties. Therefore, this experimental data is particularly useful for the validation of molecular models of electrified interphases. In addition, the use of fast temperature perturbations is especially suitable for the selective characterization of different interfacial components, based on their different response time towards the temperature change. In this way, the entropic properties of double-layer phenomena and charge-transfer adsorption processes can be evaluated separately. It will be shown in this chapter that the combina-

tion of Gibbs thermodynamics with results from laser-induced temperature jump experiments, allows the evaluation of key interfacial properties, such as the entropy of charge-transfer adsorbed species, the entropy of formation of the interfacial water network, and the potential of water reorientation.

Despite the importance of the analysis of temperature effects, the vast majority of studies at electrochemical interphases are performed under isothermal conditions. A notable exception is the classical thermodynamic work by Harrison, Randles and Schiffrin,¹ where the concept of the entropy of formation of the interphase was first introduced. After that work, different experimental approaches were taken for the evaluation of the entropy of formation of the interphase of mercury electrodes in contact with different aqueous solutions.²⁻⁵ In addition, these results further promoted the development of several models for the state of water on the mercury|solution interphase.⁶⁻⁹ Moreover, it is also worth mentioning that this method of analysis was later successfully extended to the study of gold and silver single-crystals.¹⁰⁻¹²

Comparatively, fewer studies deal with temperature effects at the platinum|solution interphase. The reason for this is that the occurrence of the ubiquitously present charge-transfer adsorption processes (such as hydrogen, anion and OH adsorption) complicates the interpretation of the experimental results. Consequently, the concept of the entropy of formation of the interphase is not directly applicable to platinum group metals. Alternatively, temperature effects on charge-transfer adsorption processes can be studied by using an isotherm. Obviously, the suitability of this approach relies on the fact that the process under study fulfills the selected isotherm. For this reason, the approach proposed by Conway,¹³ and later generalized by Jerkiewicz,¹⁴ is expected to be widely applicable to many adsorption processes, and has been followed by most of the thermodynamic studies on temperature effects. This approach allows the evaluation of the standard entropy change associated to charge-transfer adsorption processes. Interestingly, these results can be then compared to statistical mechanics calculations, thus providing information of the state of order/disorder of the adsorbed species. This method of analysis was later applied to the study of single-crystal platinum surfaces.¹⁴⁻¹⁷ In these later works, the thermodynamic characterization of the charge-transfer adsorption processes was completed through the evaluation of the standard enthalpy chang-

es, which provide a measure of the strength of the bond of the adsorbate with the surface. These results were compared with the values of the bond energy at the platinum|gas interphase, thus providing evidence of the effect of the environment (electrochemical vs. UHV conditions) on the energetics of the adsorption process.

The authors of this chapter have pioneered the application of the method of analysis using Gibbs thermodynamics to the study of temperature effects on platinum electrodes.^{18,19} For this purpose, it is first necessary to derive the Gibbs thermodynamic equations describing temperature effects in the presence of charge-transfer adsorption processes. The definition of the entropy of formation of the interphase has to be modified in order to take into account the occurrence of charge-transfer processes. Moreover, this derivation shows that the entropy of formation of the interphase for platinum group metals can be split in two contributions, namely, the entropy of formation of the double-layer and the entropy change associated to charge-transfer adsorption processes. The separation of these contributions can be done with the help of laser-induced temperature jump experiments.^{18,20} This analysis takes advantage of the fact that double-layer phenomena are usually much faster than charge-transfer adsorption processes. In this way, the temperature coefficient of the potential drop across the double-layer can be evaluated under conditions of *frozen* coverage of charge transfer adsorbed species. Interestingly, the sign of this coefficient provides evidence on the net orientation of the interfacial water network. A negative coefficient is associated with a net orientation of interfacial water with the hydrogen towards the metal, while the opposite orientation would produce positive values.²¹ A zero value for this coefficient corresponds to a situation where the net orientation of water is parallel to the surface. Moreover, this situation coincides with a maximum value of the entropy of formation of the double-layer. In conclusion, these laser-pulsed experiments can be used to evaluate the potential of maximum entropy of formation of the double-layer, which, in turn, can be identified with the potential of water reorientation.²⁰⁻²⁶ This relationship provides a unique insight on the interaction of liquid water with platinum single-crystal surfaces, under electrochemical conditions.

Furthermore, the combination of the results of the temperature coefficient of the double-layer potential, with free charge density data, allows the evaluation of the entropy of formation of the double-

layer.¹⁸ In turn, these results can be used to evaluate the entropy of formation of the interfacial water network. On the other hand, the combination of the results of the temperature coefficient of the interfacial potential with total charge density data, provides the entropy of formation of the overall interphase. Finally, the comparison of the entropy of formation of the interphase with that of the double-layer, provides a new method for the evaluation of the entropy of charge-transfer adsorbed species. This new approach is advantageous with respect to the more common method of analysis employing a generalized isotherm, because it overcomes the use of a-priori assumptions about the adsorption process under study.

This chapter is organized as follows. Section II describes the method of analysis of temperature effects, based on the use of an isotherm and reviews some experimental results. Then, Section III provides a full derivation of the Gibbs thermodynamic equations describing temperature effects on metal|solution interphases, in the presence and absence of charge-transfer processes. The use of these equations is illustrated in Section IV with the separation of temperature effects on double-layer and charge-transfer processes for the case of Pt(111) in perchloric acid solutions. First, the entropies of formation of the interphase, the double-layer and the interfacial water adlayer are evaluated in Sections IV.1, IV.2, and IV.3, respectively. Then, in Section IV.4, this data is used to obtain the entropy of hydrogen and OH on Pt(111), which are compared in Section IV.5 with the entropies calculated using the generalized adsorption isotherm. Finally, Section V reviews recent results on the application of the laser-induced temperature jump method for the evaluation of the behavior of interfacial water on single-crystal platinum electrodes. Special emphasis is given to the determination of the potential of maximum entropy of formation of the double-layer, since it essentially corresponds to the potential of water reorientation. First, the fundamentals of the technique are explained in Section V.1, and the proposed interpretation of the experimental data, in Section V.2. Then, recent results obtained with the three basal planes, Pt(111), Pt(100) and Pt(110), are discussed in Section V.3. Afterwards, the effect of the systematic introduction of step sites on Pt(111) stepped surfaces is analyzed in Section V.4. Finally, results on the deposition of foreign metal adatoms on Pt(111) are presented in Section V.5, and some implications for the understanding of the en-

hancement of the electrocatalytic activity on these surfaces are briefly discussed.

II. ANALYSIS OF TEMPERATURE EFFECTS BASED ON THE USE OF AN ISOTHERM

Traditionally, the analysis of adsorption processes has been mainly performed through the application of a selected type of isotherm. In this way, the fit of the experimental data recorded under isothermal conditions, provides the values of the standard Gibbs energy of adsorption and, in some cases, the energy of interaction between adsorbed species. On the other hand, the fit of experimental data recorded at different temperatures can be used to obtain a more complete understanding on the energetics of the process under study, through the evaluation of the enthalpy and entropy change associated to the adsorption. Obviously, in these fitting procedures, the selection of a suitable type of isotherm is critical to obtain meaningful values of the energetic parameters. In relation to the fit of experimental data recorded under isothermal conditions, a wide variety of isotherms have been proposed, but most thermodynamic works of adsorption processes employ the empirical *square-root isotherm* proposed by Parsons,²⁷ since this isotherm has been specially designed to be applicable to any type of adsorption process. On the other hand, except for the initial work by Breither,²⁸ which calculated the equivalent pressure of H_2 corresponding to different equilibrium hydrogen coverages, and the work by the present authors employing Gibbs thermodynamics,^{18,19} the thermodynamic studies of adsorption processes as a function of temperature follow the method of analysis based on the application of an isotherm, which was first proposed by Conway,¹³ and later completed by Jerkiewicz.¹⁴ In the following, the fundamentals of this method of analysis will be described in Section II.1. Then, the application of this method will be illustrated for the case of hydrogen and OH adsorption on Pt(111) from 0.1 M $HClO_4$ solutions, in Section II.2. Finally, some of the most relevant experimental results on platinum single-crystals will be briefly reviewed in Section II.3.

1. Method of Analysis Employing a Generalized Isotherm

The first complication in the study of the effect of temperature on adsorption processes is the selection of a suitable design of electrochemical cell. The electrochemical measurements can be performed in:

- (1) an isothermal cell, in which the working and reference electrodes are kept at the same temperature; or
- (2) in a non-isothermal cell (also known as thermal cell), in which only the temperature of the working electrode is varied, while the temperature of the reference electrode is maintained constant.

Consequently, two different temperature coefficients of the electrode potential can be obtained: the isothermal and the thermal temperature coefficient. The thermodynamic implications of these coefficients were clearly established by de Bethune,²⁹ who also evaluated the values of the temperature coefficients of a wide variety of reference electrodes. While the use of a non-isothermal cell presents the clear advantage that only the temperature effect on the reaction on the working electrode is evaluated, it also presents the problem that the measurements will be interfered by the appearance of a thermodiffusion potential, arising from temperature differences within the electrolyte solution. This thermodiffusion potential can be experimentally minimized (by using, for example, a saturated potassium chloride bridge for the liquid unions)²⁹ or, alternatively, the effect of the thermodiffusion potential can be subtracted by calculating its numerical value from:³⁰

$$\frac{\Delta E_{\text{Thermodiffusion}}}{\Delta T} = -\frac{1}{F} \sum_i \frac{t_i}{z_i} \hat{S}_i \quad (1)$$

where t_i , z_i and $\hat{S}_i$ are the transport number, the charge (with its sign) and the Eastman entropy of transport of the ion i , respectively. For didactic purposes, appendix 1 illustrates the estimation of thermodiffusion potentials of some commonly used solutions, by the application of Eq. (1).

On the other hand, the use of isothermal cells presents the advantage that the appearance of thermodiffusion potentials is strictly

avoided. Moreover, Conway demonstrated that this type of experimental data can be used to evaluate, in an unambiguous way, the thermodynamic properties of the global reaction of the electrochemical cell.¹³ For this purpose, one only needs to establish the half-cell reaction taking place on the working electrode. For example, for hydrogen adsorption:



Then, if a RHE reference electrode is employed, the corresponding half-cell reaction will be:



Therefore, the global reaction of the electrochemical cell will be hydrogen adsorption from H_2 :



Application of the equilibrium conditions to Eqs. (2) and (3) gives:

$$\tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{\text{e}^-} = \mu_{\text{H}_{\text{ads}}} \rightarrow F\Delta_{\text{S}}^{\text{M}}\phi = \mu_{\text{H}^+}^0 + RT \ln a_{\text{H}^+} + \mu_{\text{e}^-}^0 - \mu_{\text{H}_{\text{ads}}} \quad (5)$$

$$\frac{1}{2} \mu_{\text{H}_2} = \tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{\text{e}^-} \rightarrow F\Delta_{\text{S}}^{\text{Ref}}\phi = \mu_{\text{H}^+}^0 + RT \ln a_{\text{H}^+} + \mu_{\text{e}^-}^0 - \frac{1}{2} \mu_{\text{H}_2} \quad (6)$$

where $\mu_i(\tilde{\mu}_i)$ is the (electro)chemical potential of species i ; $\Delta_{\text{S}}^{\text{M}}\phi$ and $\Delta_{\text{S}}^{\text{Ref}}\phi$ are the potential drops across the interphase of the working and reference electrodes, respectively; F is the Faraday constant; μ_i^0 is the standard chemical potential of species i ; and a_{H^+} is the proton activity in solution. With this, it is clear that the potential of the electrochemical cell, E , is given by:

$$FE = F\left(\Delta_{\text{S}}^{\text{M}}\phi - \Delta_{\text{S}}^{\text{Ref}}\phi\right) = -\mu_{\text{H}_{\text{ads}}} + \frac{1}{2} \mu_{\text{H}_2} = -\Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2} \quad (7)$$

where $\Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}$ is the chemical molar Gibbs energy change associated to the global reaction of the cell (Eq. 4). It is worth noting that Eq. (7) can also be easily obtained by taking into account that, since the electrochemical cell as a whole is in equilibrium, the total Gibbs energy of the system (which includes chemical and electrical contributions) should be zero.

At this point, it should be noted that the chemical potential of adsorbed hydrogen species can be represented by:

$$\mu_{\text{H}_{\text{ads}}} = \mu_{\text{H}_{\text{ads}}}^0 + RT \ln \left(\frac{\theta_{\text{H}}}{1 - \theta_{\text{H}}} \right) + r(\theta_{\text{H}}) \quad (8)$$

where θ_{H} is the normalized hydrogen coverage (i.e., the surface concentration of hydrogen species with respect to saturation), and the term $r(\theta_{\text{H}})$ accounts for all deviations with respect a Langmuir-type behavior. For example, for a Frumkin isotherm, $r(\theta_{\text{H}}) = \omega_{\text{H-H}} \theta_{\text{H}}$, where $\omega_{\text{H-H}}$ is the lateral interaction parameter (that is, the interaction energy between neighboring hydrogen species). On the other hand, the chemical potential of H_2 in the RHE reference electrodes will be given by:

$$\mu_{\text{H}_2} = \mu_{\text{H}_2}^0 + RT \ln f_{\text{H}_2} \quad (9)$$

where f_{H_2} is the fugacity of H_2 . Then, combination of Eqs. (7), (8) and (9) gives:

$$\begin{aligned} \Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2} = \mu_{\text{H}_{\text{ads}}}^0 + RT \ln \left(\frac{\theta_{\text{H}}}{1 - \theta_{\text{H}}} \right) + r(\theta_{\text{H}}) - \frac{1}{2} \mu_{\text{H}_2}^0 \\ - \frac{1}{2} RT \ln f_{\text{H}_2} = -FE \end{aligned} \quad (10)$$

The goal of this study is to evaluate the molar Gibbs energy of hydrogen adsorption at the standard state:

$$\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0 = \mu_{\text{H}_{\text{ads}}}^0 - \frac{1}{2} \mu_{\text{H}_2}^0 \quad (11)$$

The standard state for the bulk species is an ideal hypothetical solution with unity activity/fugacity coefficient, and 1 M concentration/1 atm partial pressure; and for the adsorbed species, the standard state is an ideal hypothetical adsorbed adlayer with $\theta^0 = 1/2$ and zero interactions between adsorbed species.³¹ In order to evaluate $\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0$, it is convenient to define a formal molar Gibbs energy of hydrogen adsorption, $\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$, that fulfils the following generalized isotherm:

$$\frac{\theta_{\text{H}}}{1 - \theta_{\text{H}}} = \sqrt{f_{\text{H}_2}} \exp \left(\frac{-\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f - FE}{RT} \right) \quad (12)$$

where $\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ is related to $\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0$ by:

$$\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f = \Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0 + r(\theta_{\text{H}}) = \frac{1}{2} RT \ln f_{\text{H}_2} - FE - RT \ln \left(\frac{\theta_{\text{H}}}{1 - \theta_{\text{H}}} \right) \quad (13)$$

In conclusion, $\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ can be calculated from the combination of the experimental results of values of potential, E , and hydrogen coverages, θ_{H} , as obtained in an isothermal cell. In this calculation, the fugacity of H_2 can be considered equal to unity. The values of hydrogen coverages can be calculated from integration of the voltammetric curves (see below, Section II.2).

Once values of $\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ have been evaluated as a function of the hydrogen coverage and the temperature, $\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0$ values can be obtained from the extrapolation of $\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ to the zero coverage limit (at constant temperature):

$$\Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0 = \lim_{\theta_{\text{H}} \rightarrow 0} \Delta \bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f \quad (14)$$

because the interaction term $r(\theta_{\text{H}})$ is expected to vanish in the limit of an infinitely dilute adsorption state. Moreover, a Frumkin type of lateral interaction parameter, $\omega_{\text{H-H}}$, can be obtained from the derivative of $\Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ with the hydrogen coverage (at constant temperature):

$$\omega_{\text{H-H}} = \left(\frac{\partial \Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f}{\partial \theta_{\text{H}}} \right)_T \quad (15)$$

The standard entropy change, $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^0$, can be evaluated in two slightly different ways. One can evaluate $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^0$ from the effect of temperature on $\Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0$, according to:

$$\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^0 = - \frac{d\Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0}{dT} \quad (16)$$

Alternatively, $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^0$ can be obtained from the evaluation of $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ by:

$$\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^f = - \left(\frac{\partial \Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f}{\partial T} \right)_{\theta_{\text{H}}} \quad (17)$$

Next, the extrapolation of $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ to the zero coverage limit provides $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^0$. In published work on adsorption processes on platinum single-crystal, essentially the same results are usually obtained by both procedures.^{16,17,20,32,33}

Finally, the standard entropy of adsorption, $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^0$, can be obtained from:

$$\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^0 = \Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^0 + T\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^0 \quad (18)$$

Alternatively, $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^0$ can also be calculated through the calculation of $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ by:

$$\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^f = -F \left(\frac{\partial(E/T)}{\partial(1/T)} \right)_{\theta_{\text{H}}} \quad (19)$$

Then, the extrapolation of $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ to zero coverage, provides $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^0$. As in the case of $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^0$, both methods of evaluation of $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^0$ provide nearly the same results.^{16,17,20,32,33}

The Eq. (19) for the evaluation of $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ can be demonstrated as follows. The right-hand side of Eq. (19) can be rewritten as:

$$-F \left(\frac{\partial(E/T)}{\partial(1/T)} \right)_{\theta_{\text{H}}} = -FE + TF \left(\frac{\partial E}{\partial T} \right)_{\theta_{\text{H}}} \quad (20)$$

On the other hand, $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ can be obtained from combination of $\Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ and $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ by:

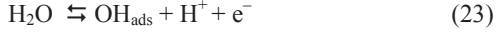
$$\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^f = \Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f + T\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^f \quad (21)$$

In turn, $\Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ and $\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^f$, can be written as a function of E by using Eqs. (13) and (17). With this, and using $f_{\text{H}_2} \approx 1$:

$$\begin{aligned} \Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^f &= \left[-FE - RT \ln \left(\frac{\theta_{\text{H}}}{1 - \theta_{\text{H}}} \right) \right] \\ &+ T \left[F \left(\frac{\partial E}{\partial T} \right)_{\theta_{\text{H}}} + R \ln \left(\frac{\theta_{\text{H}}}{1 - \theta_{\text{H}}} \right) \right] = -FE + TF \left(\frac{\partial E}{\partial T} \right)_{\theta_{\text{H}}} \end{aligned} \quad (22)$$

To finish, it is convenient to describe the application of this method of analysis to the study of an oxidative reaction on the working

electrode. Probably, the most relevant example is the adsorption of OH, which in acidic solutions takes place through:



Therefore, if an RHE reference electrode is employed, the global reaction of the electrochemical cell will be:



Following the same arguments as for the case of hydrogen adsorption, it is shown that the molar Gibbs energy change associated to the global reaction of the cell (reaction 24), $\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}$, is related to the electrode potential, E , by:

$$\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2} = \mu_{\text{OH}_{\text{ads}}} - \mu_{\text{H}_2\text{O}} + \frac{1}{2} \mu_{\text{H}_2} = FE \quad (25)$$

In this case, the standard molar Gibbs energy change will be given by:

$$\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 = \mu_{\text{OH}_{\text{ads}}}^0 - \mu_{\text{H}_2\text{O}}^0 + \frac{1}{2} \mu_{\text{H}_2}^0 \quad (26)$$

Considering that the chemical potential of adsorbed OH species can be represented by:

$$\mu_{\text{OH}_{\text{ads}}} = \mu_{\text{OH}_{\text{ads}}}^0 + RT \ln \left(\frac{\theta_{\text{OH}}}{1 - \theta_{\text{OH}}} \right) + r(\theta_{\text{OH}}), \quad (27)$$

where θ_{OH} is the normalized OH coverage, the following expression for the generalized isotherm is obtained:

$$\frac{\theta_{\text{OH}}}{1 - \theta_{\text{OH}}} = \frac{a_{\text{H}_2\text{O}}}{\sqrt{f_{\text{H}_2}}} \exp \left(\frac{-\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f + FE}{RT} \right) \quad (28)$$

where $a_{\text{H}_2\text{O}}$ is the water activity, and $\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f$ is the formal Gibbs energy change of the global reaction of the cell (reaction 24):

$$\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f = \Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 + r(\theta_{\text{OH}}) = RT \ln a_{\text{H}_2\text{O}} - \frac{1}{2}RT \ln f_{\text{H}_2} \quad (29)$$

$$+ FE - RT \ln \left(\frac{\theta_{\text{OH}}}{1 - \theta_{\text{OH}}} \right)$$

In conclusion, considering that the activity of water and the fugacity of H_2 are both essentially unity, values of $\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f$ can be calculated from the experimental data of E and θ_{OH} values. With this, the standard thermodynamic properties can be calculated in a similar way as for hydrogen adsorption. Below we summarize the expressions for OH adsorption, analogous to Eqs. (14) to (19):

$$\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 = \lim_{\theta_{\text{OH}} \rightarrow 0} \Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f \quad (30)$$

$$\omega_{\text{OH-OH}} = \left(\frac{\partial \Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f}{\partial \theta_{\text{OH}}} \right)_T \quad (31)$$

$$\Delta\bar{S}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 = - \frac{d\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^0}{dT} \quad (32)$$

$$\Delta\bar{S}_{\text{OH}_{\text{ads}}/\text{H}_2}^f = - \left(\frac{\partial \Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f}{\partial T} \right)_{\theta_{\text{H}}} \quad (33)$$

$$\Delta\bar{H}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 = \Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 + T\Delta\bar{S}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 \quad (34)$$

$$\Delta\bar{H}_{\text{OH}_{\text{ads}}/\text{H}_2}^f = F \left(\frac{\partial (E/T)}{\partial (1/T)} \right)_{\theta_{\text{OH}}} \quad (35)$$

2. Application to Hydrogen and Hydroxyl Adsorption on Pt(111)

In the following, the application of the method of analysis using a generalized isotherm will be illustrated with the thermodynamic characterization of hydrogen and OH adsorption on Pt(111) from 0.1 M HClO₄ solutions. Figure 1 shows cyclic voltammograms for Pt(111) in 0.1 M HClO₄, as measured at 283 and 323 K in an isothermal cell. The change of temperature produces small, but reproducible changes on the voltammetric profiles. The first step in the analysis of the experimental results is the evaluation of the hydrogen and OH normalized coverages. This can be done by considering that both hydrogen and OH adsorption are negligible at potentials within the double-layer region ($\approx 0.4 < E < \approx 0.5$ V vs. RHE), and considering that double-layer contributions can be subtracted by employing a constant baseline, with a value given by the capacity measured within the double-layer region:

$$\theta_i = \frac{1}{Q_{ML}} \int_{E=0.5V}^E \frac{j(E) - j(E=0.5)}{\nu} dE \quad (36)$$

where j is the voltammetric current, ν is the scan rate, Q_{ML} is the charge associated to the adsorption of one monolayer [$Q_{ML} = 241$ and $110 \mu\text{C cm}^{-2}$ for hydrogen and OH adsorption on Pt(111), respectively], and it has been considered that, at $E = 0.5\text{V}$, $\theta_H = \theta_{OH} = 0$.

The results of the evaluation of the hydrogen and OH normalized coverages at 283 and 323 K are shown in Fig. 2, as a function of the applied potential, E . Figure 3 shows the results of $\Delta\bar{G}_{H_{ads}/H_2}^f$ and $\Delta\bar{G}_{OH_{ads}/H_2}^f$, calculated using Eqs. (13) and (29), respectively, at six different temperatures between 273 and 323 K, plotted as a function of the normalized coverage. It is observed that both $\Delta\bar{G}_{H_{ads}/H_2}^f$ and $\Delta\bar{G}_{OH_{ads}/H_2}^f$ exhibit a linear dependence on coverage, for coverages between ≈ 0.05 and ≈ 0.6 . At lower coverages, $\Delta\bar{G}_{H_{ads}/H_2}^f$ and $\Delta\bar{G}_{OH_{ads}/H_2}^f$ deviate from this tendency, probably due to the large

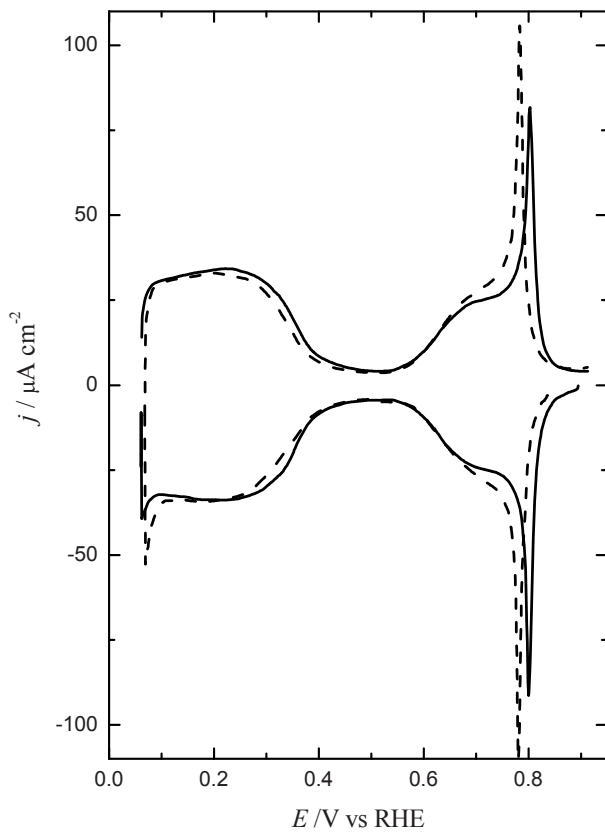


Figure 1. Cyclic voltammogram of a Pt(111) electrode in 0.1 M HClO_4 solution, at 283 (solid line) and 323 K (dashed line), as recorded in an isothermal cell. Scan rate: 50 mV/s. Adapted from Refs. 16, 17, and 19.

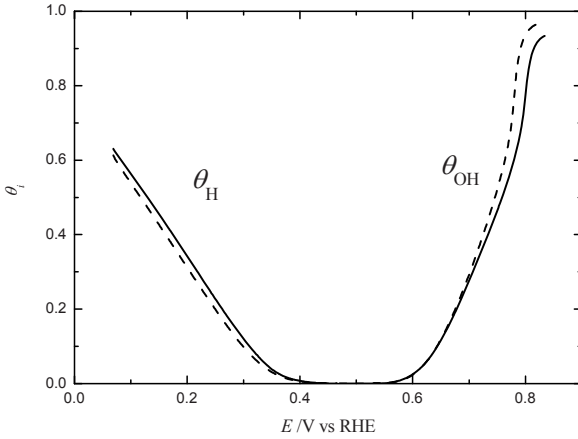


Figure 2. Hydrogen and OH normalized coverages on Pt(111) from 0.1 M HClO₄, at 283 (solid line) and 323 K (dashed line). Adapted from Refs. 16, 17 and 19.

uncertainty in θ_i values, which affects the calculation of $\Delta\bar{G}_{\text{H}_{\text{ads}}/\text{H}_2}^f$ and $\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f$ through the term $RT\ln[\theta_i/(1 - \theta_i)]$. On the other hand, $\Delta\bar{G}_{\text{OH}_{\text{ads}}/\text{H}_2}^f$ clearly deviates from this linear tendency for $\theta_{\text{OH}} > 0.6$, indicating that the magnitude of lateral interactions between neighboring OH species, $\omega_{\text{OH-OH}}$, changes at these OH coverages (Eq. 31). From the fit of $\Delta\bar{G}_{i/\text{H}_2}^f$ vs. θ_i within the linear region, the values of $\Delta\bar{G}_{i/\text{H}_2}^0$ are obtained from the intercept (Eqs. 14 and 30), while the value of the lateral interaction parameter, ω_{i-i} , at low-medium coverages is obtained from the slope (Eqs. 15 and 31). The results of this calculation are shown in Fig. 4.

With this, from the fit of $\Delta\bar{G}_{i/\text{H}_2}^0$ vs. temperature, the standard entropy of adsorption, $\Delta\bar{S}_{i/\text{H}_2}^0$, is calculated (Eqs. 16 and 32). This gives

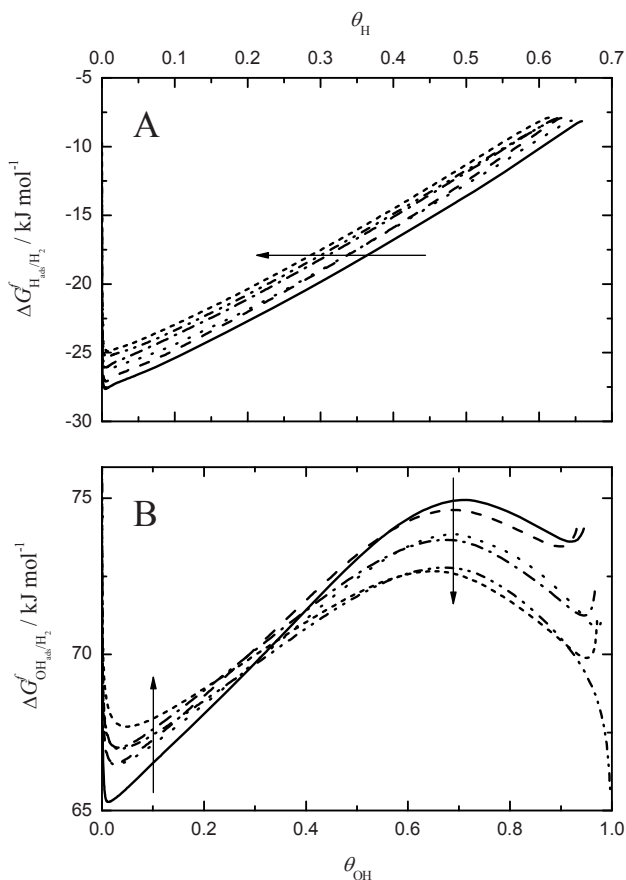


Figure 3. Formal Gibbs energies of hydrogen and OH adsorption on Pt(111) from 0.1 M HClO_4 , at six different temperatures between 273 and 323 K, associated to the following global reactions of the cell: A) $\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$, B) $\text{H}_2\text{O} \rightleftharpoons \text{OH}_{\text{ads}} + \frac{1}{2} \text{H}_2$; plotted as a function of the normalized coverages. The arrows indicate the direction of increasing temperature. Adapted from Refs. 16, 17 and 19.

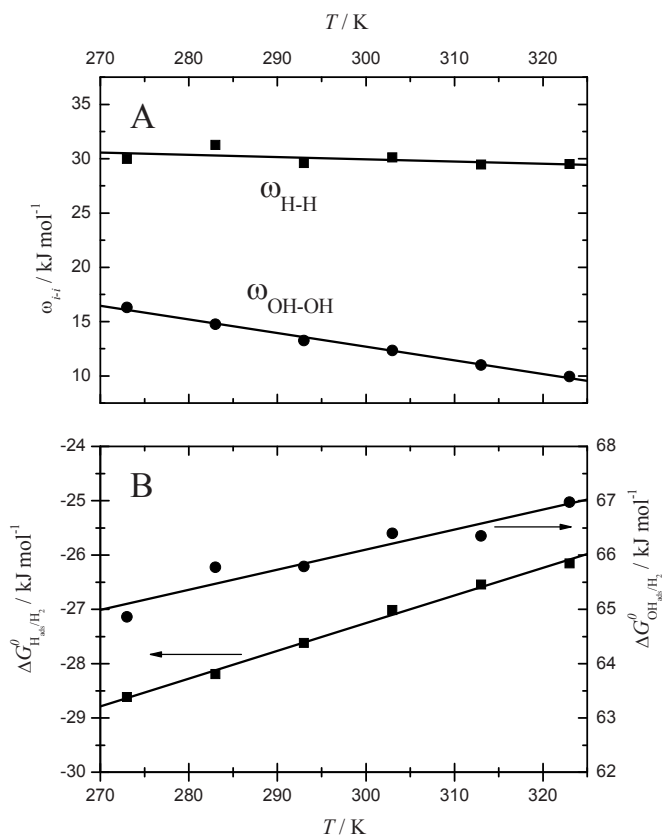


Figure 4. Interaction energy parameter (A) and standard Gibbs energy of adsorption (B) for hydrogen (squares) and OH (circles) on Pt(111) from 0.1 M HClO_4 , plotted as a function of the temperature. Lines are the linear fit of the experimental data. Adapted from Refs. 16, 17 and 19.

$\Delta\bar{S}_{\text{H}_{\text{ads}}/\text{H}_2}^0 = -51$ and $\Delta\bar{S}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 = -37 \text{ J mol}^{-1} \text{ K}^{-1}$. Analogously, the fit of ω_{i-i} vs. temperature provides the magnitude of the entropic contribution to the lateral interaction, $d\omega_{\text{H-H}}/dT \approx -20$ and $d\omega_{\text{OH-OH}}/dT \approx -125 \text{ J mol}^{-1} \text{ K}^{-1}$. And finally, the standard enthalpy of adsorption, $\Delta\bar{H}_{i/\text{H}_2}^0$, can be obtained from combination of $\Delta\bar{G}_{i/\text{H}_2}^0$ and $\Delta\bar{S}_{i/\text{H}_2}^0$ data (Eqs. 18 and 34), giving $\Delta\bar{H}_{\text{H}_{\text{ads}}/\text{H}_2}^0 = -43$ and $\Delta\bar{H}_{\text{OH}_{\text{ads}}/\text{H}_2}^0 = 55 \text{ kJ mol}^{-1}$.

3. Review of Experimental Results on Platinum Single-Crystals

Table 1 summarizes some of the most relevant results from thermodynamic studies on platinum single-crystal surfaces. In order to facilitate the comparison of thermodynamic data corresponding to different adsorption reactions, values of the thermodynamic properties at the standard state ($\Delta\bar{G}^0$, $\Delta\bar{H}^0$ and $\Delta\bar{S}^0$) are provided. Values of the lateral interaction parameter (ω), and its temperature dependence ($d\omega/dT$) are also given in Table 1. While the lateral interaction parameter measures the magnitude of the lateral interactions, its temperature dependence reflects the entropic contributions to the lateral interactions. Therefore, the enthalpic contribution to the lateral interaction energy, can be obtained from $\omega - T d\omega/dT$.

It should be noted that, in some works, only the numerical values of the formal thermodynamic properties ($\Delta\bar{G}^f$, $\Delta\bar{H}^f$ and $\Delta\bar{S}^f$) are given. Then, the values of the standard thermodynamic properties in Table 1 have been obtained by graphical extrapolation to the zero coverage limit, or, alternatively, the values of the formal thermodynamic properties at a low enough coverage have been used. In some particular cases, the formal thermodynamic properties have only been evaluated at certain coverage, and then, the value of coverage is indicated in brackets after the thermodynamic quantity. Similarly, when the value of the thermodynamic property corresponds to some special conditions, these are indicated in brackets.

Table 1
Standard Thermodynamic Properties of Selected Adsorption Processes on Platinum Single-Crystal Surfaces,
as Evaluated from the Analysis of Voltammetric Data at Different Temperatures by Means of the
Application of a Generalized Isotherm.

Reaction	Electrode	Electrolyte	$\Delta\bar{G}^0$ kJ mol ⁻¹	$\Delta\bar{S}^0$ J mol ⁻¹ K ⁻¹	$\Delta\bar{H}^0$ kJ mol ⁻¹	ω kJ mol ⁻¹	$(d\omega/dT)$ J mol ⁻¹ K ⁻¹	Ref.
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(111)	0.1 M HClO ₄	-28	-51	-43	29	-10	20
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(111)	0.1 M HClO ₄	-27	-48	-41	28		16
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(111)	0.1 M HClO ₄	-27	-48	-42	29		32
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(111)	0.05 M H ₂ SO ₄	-26	-65	-45	27		33
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(111)	0.05 M H ₂ SO ₄	-28	-48	-42	31		32
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(111)	0.1 M NaOH	-22	-63	-41	36		32
$\text{H}_2\text{O} \rightleftharpoons \text{OH}_{\text{ads}} + \frac{1}{2} \text{H}_2$	Pt(111)	0.1 M HClO ₄	66	-37	55	13	-117	17, 20
						($\theta_{\text{OH}} \leq 0.6$)		
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(100)	0.1 M HClO ₄	-37	-49	-51	5.6	-18	20
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(100)	0.1 M HClO ₄	-36	-56	-53	9		16
$\text{H}_2\text{O} \rightleftharpoons \text{OH}_{\text{ads}} + \frac{1}{2} \text{H}_2$	Pt(100)	0.1 M HClO ₄	41	10	44	14	20	17
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(110)	0.1 M HClO ₄	-12	-100	-42	-2.7	-102	20
$\frac{1}{2} \text{H}_2 \rightleftharpoons \text{H}_{\text{ads}}$	Pt(110)	0.1 M HClO ₄	-15	-70	-36	-4		16
			($\theta_{\text{H}} = 0.65$)	($\theta_{\text{H}} = 0.65$)	($\theta_{\text{H}} = 0.65$)	(323 K)		

III. GIBBS THERMODYNAMIC EQUATIONS DESCRIBING TEMPERATURE EFFECTS IN THE PRESENCE AND ABSENCE OF CHARGE-TRANSFER PROCESSES

As previously mentioned, the present thermodynamic analysis is based on the concept of the entropy of formation of the interphase, introduced by Harrison, Randles and Schiffrin,¹ as the difference in entropy of the components of the interphase when they are forming part of it, and when they are present in the bulk of their respective phases. In the following, the derivation for fully polarizable electrodes¹ will be extended to the situation where charge-transfer processes are present. However, the Guggenheim model for the interphase will be used here and, therefore, the interphase will be considered as a region of finite thickness, comprising all inhomogeneities between the two phases.³⁴ The present derivation follows, when appropriate, the seminal work about temperature effects given by Parsons.³⁵ The starting point is the Gibbs-Duhem equation for an interphase:

$$-d\gamma = \sum_i \Gamma_i d\tilde{\mu}_i + S^\sigma dT - V^\sigma dp \quad (37)$$

where γ is the interfacial tension; the symbol $\sum_i$ refers to the summation over all species i present at the interphase, $\mu_i(\tilde{\mu}_i)$ is the (electro)chemical potential of species i ; Γ_i is the surface concentration of species i at the interphase; S^σ is the entropy per unit area of the interphase; V^σ is the volume per unit area of the interphase; T is the absolute temperature; and p is the pressure. For the interphase between a platinum electrode and an acid, inert electrolyte solution (such as a perchloric acid solution), the equilibria of charge-transfer adsorption of hydrogen and OH species and water dissociation have to be considered:

$$\tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{\text{e}^-} = \mu_{\text{H}} \quad (38)$$

$$\mu_{\text{H}_2\text{O}} = \mu_{\text{OH}} + \tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{\text{e}^-} \quad (39)$$

$$\mu_{\text{H}_2\text{O}} = \tilde{\mu}_{\text{H}^+} + \tilde{\mu}_{\text{OH}^-} \quad (40)$$

Taking into account the above relationships, Eq. (37) can be rewritten as:

$$\begin{aligned} -d\gamma = & -\left(\frac{\sigma_{\text{M}}}{F} - \Gamma_{\text{H}} + \Gamma_{\text{OH}}\right)d\tilde{\mu}_{\text{e}^-} \\ & + \left(\Gamma_{\text{H}} + \Gamma_{\text{H}^+} - \Gamma_{\text{OH}} - \Gamma_{\text{OH}^-}\right)d\tilde{\mu}_{\text{H}^+} \\ & + \left(\Gamma_{\text{H}_2\text{O}} + \Gamma_{\text{OH}} + \Gamma_{\text{OH}^-}\right)d\mu_{\text{H}_2\text{O}} + \Gamma_{\text{M}}d\mu_{\text{M}} \\ & + \sum_{i \neq \text{e}^-, \text{H}^+, \text{OH}^-, \text{H}_2\text{O}, \text{M}} \Gamma_i d\tilde{\mu}_i + S^\sigma dT - V^\sigma dp \end{aligned} \quad (41)$$

where σ_{M} is the electronic charge density on the metal, $\sigma_{\text{M}} = -F\Gamma_{\text{e}^-}$, which is usually referred to as the free charge density. At this point we will separate the chemical and the electrical contributions to the electrochemical potentials and we will introduce the electroneutrality condition:

$$\begin{aligned} -d\gamma = & Qd\Delta_{\text{S}}^{\text{M}}\phi - \frac{Q}{F}d\mu_{\text{e}^-} \\ & + \left(\Gamma_{\text{H}} + \Gamma_{\text{H}^+} - \Gamma_{\text{OH}} - \Gamma_{\text{OH}^-}\right)d\mu_{\text{H}^+} \\ & + \left(\Gamma_{\text{H}_2\text{O}} + \Gamma_{\text{OH}} + \Gamma_{\text{OH}^-}\right)d\mu_{\text{H}_2\text{O}} \\ & + \sum_{i \neq \text{e}^-, \text{H}^+, \text{OH}^-, \text{H}_2\text{O}, \text{M}} \Gamma_i d\mu_i + \Gamma_{\text{M}}d\mu_{\text{M}} + S^\sigma dT - V^\sigma dp \end{aligned} \quad (42)$$

where $\Delta_{\text{S}}^{\text{M}}\phi$ is the potential difference across the interphase and Q is the total charge density:

$$Q = \sigma_{\text{M}} - F\Gamma_{\text{H}} + F\Gamma_{\text{OH}} \quad (43)$$

Next, the two remaining dependent variables in Eq. (42) can be eliminated through the Gibbs-Duhem equations for the solution and metal phases:

$$d\mu_M = -\bar{S}_M dT + \bar{V}_M dp \quad (44)$$

$$d\mu_{H_2O} = -\frac{\bar{S}_{sol}}{\chi_{H_2O}} dT + \frac{\bar{V}_{sol}}{\chi_{H_2O}} dp - \frac{\chi_{H^+}}{\chi_{H_2O}} d\mu_{H^+} - \sum_{j \neq H_2O, H^+, OH^-} \frac{\chi_j}{\chi_{H_2O}} d\mu_j \quad (45)$$

where $\bar{S}_M$ and $\bar{V}_M$, and $\bar{S}_{sol}$ and $\bar{V}_{sol}$, are the absolute molar entropy and volume of the metal and solution phases, respectively; χ_j is the molar fraction of species j ; and the variable j refers to all species present at the solution phase. Combination of Eqs. (42), (44) and (45) gives:

$$-d\gamma = Qd\Delta_S^M \phi - \frac{Q}{F} d\mu_e + \Gamma_{H,H_2O} d\mu_{H^+} + \sum_{i \neq e^-, H^+, OH^-, H_2O, M} \Gamma_{i,H_2O} d\mu_i + \Gamma_{S,H_2O,M} dT - \Gamma_{V,H_2O,M} dp \quad (46)$$

where Γ_{i,H_2O} is the relative surface concentration of species i at the interphase; $\Gamma_{S,H_2O,M}$ is the relative entropy per unit area of the interphase; and $\Gamma_{V,H_2O,M}$ is the relative volume per unit area of the interphase. These thermodynamic quantities are given by:

$$\Gamma_{H,H_2O} = \Gamma_H + \Gamma_{H^+} - \Gamma_{OH} - \Gamma_{OH^-} - \left(\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-} \right) \frac{\chi_{H^+}}{\chi_{H_2O}} \quad (47)$$

$$\Gamma_{i,H_2O} = \Gamma_i - \left(\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-} \right) \frac{\chi_i}{\chi_{H_2O}} \quad (48)$$

$$\Gamma_{S,H_2O,M} = S^\sigma - \left(\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-} \right) \frac{\bar{S}_{sol}}{\chi_{H_2O}} - \Gamma_M \bar{S}_M \quad (49)$$

$$\Gamma_{V,H_2O,M} = V^\sigma - \left(\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-} \right) \frac{\bar{V}_{sol}}{\chi_{H_2O}} - \Gamma_M \bar{V}_M \quad (50)$$

Moreover, at a constant solution composition and pressure, taking into account that $d\mu_i = -\bar{S}_i dT$, where $\bar{S}_i$ is the absolute molar entropy of species i , Eq. (46) can be re-written as:

$$-d\gamma = Q d\Delta_S^M \phi + \left(\frac{Q}{F} \bar{S}_{e^-} - \Gamma_{H,H_2O} \bar{S}_{H^+} - \sum_{i \neq e^-, H^+, OH^-, H_2O, M} \Gamma_{i, H_2O} \bar{S}_i + \Gamma_{S, H_2O, M} \right) dT \quad (51)$$

Then, using Parsons' function, $\xi = Q \Delta_S^M \phi + \gamma$, to change the electrical independent variable, the following expression is obtained:

$$-d\xi = -\Delta_S^M \phi dQ + \left(\frac{Q}{F} \bar{S}_{e^-} - \Gamma_{H,H_2O} \bar{S}_{H^+} - \sum_{i \neq e^-, H^+, OH^-, H_2O, M} \Gamma_{i, H_2O} \bar{S}_i + \Gamma_{S, H_2O, M} \right) dT \quad (52)$$

Finally, cross-differentiation of the above equation gives:

$$\left[\frac{\partial \left(\Gamma_{S, H_2O, M} - \sum_{i \neq e^-, H^+, OH^-, H_2O, M} \Gamma_{i, H_2O} \bar{S}_i - \Gamma_{H, H_2O} \bar{S}_{H^+} \right)}{\partial Q} \right]_{T, p, c_i} + \frac{1}{F} \bar{S}_{e^-} \quad (53)$$

$$= - \left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{Q, p, c_i}$$

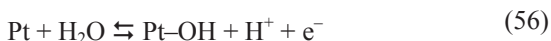
where c_i is the concentration of species i in solution. As previously mentioned, the entropy of formation of the interphase, ΔS , is defined as the difference in entropy of the components of the interphase when they are forming part of it and when they are in the bulk of their respective phases.¹ However, the expression for ΔS given in Ref. 1 for the study of temperature effects on mercury electrodes:

$$\Delta S_{\text{Hg}} = S^\sigma - \sum_i \Gamma_i \bar{S}_i \quad (54)$$

is not adequate for platinum electrodes, as a result of the occurrence of charge-transfer adsorption processes (such as hydrogen and OH adsorption). Therefore, in order to derive a proper expression for ΔS in this case, one should take into account that hydrogen adsorption involves the consumption of protons from the solution and electrons from the metal:



Hence, the entropy of “hydrogen species in the bulk” should be understood as the sum of the entropy of proton and electron species in the solution and metal phases, respectively. Thus, the appropriate term for the entropy in the bulk phases will be $\Gamma_{\text{H}} (\bar{S}_{\text{H}^+} + \bar{S}_{\text{e}^-})$. Analogously, OH adsorption in acid media involves water and proton species in solution and electrons in the metal:



Therefore, the corresponding term for the entropy in the bulk phases will be $\Gamma_{\text{OH}} (\bar{S}_{\text{H}_2\text{O}} - \bar{S}_{\text{H}^+} - \bar{S}_{\text{e}^-})$. In conclusion, the entropy of formation of the interphase in the presence of hydrogen and OH adsorption processes will be given by:

$$\begin{aligned} \Delta S = S^\sigma + \frac{Q}{F} \bar{S}_{\text{e}^-} - (\Gamma_{\text{H}} + \Gamma_{\text{H}^+}) \bar{S}_{\text{H}^+} - (\Gamma_{\text{OH}} + \Gamma_{\text{OH}^-}) (\bar{S}_{\text{H}_2\text{O}} - \bar{S}_{\text{H}^+}) \\ - \Gamma_{\text{H}_2\text{O}} \bar{S}_{\text{H}_2\text{O}} - \Gamma_{\text{M}} \bar{S}_{\text{M}} - \sum_{i \neq \text{e}^-, \text{H}^+, \text{OH}^-, \text{H}_2\text{O}, \text{M}} \Gamma_i \bar{S}_i \end{aligned} \quad (57)$$

It is worth noting that the above expression for ΔS includes a term corresponding to the entropy of electrons. This term was explicitly neglected in Ref. 1, but recent work has demonstrated that this term should be included because electrons are involved in the

formation of the interphase.³⁶ Taking into account Eqs. (47)-(49) and the following expression for the entropy of the solution:

$$\bar{S}_{\text{sol}} = \chi_{\text{H}_2\text{O}} \bar{S}_{\text{H}_2\text{O}} + \chi_{\text{H}^+} \bar{S}_{\text{H}^+} + \sum_{j \neq \text{H}_2\text{O}, \text{H}^+, \text{OH}^-} \chi_j \bar{S}_j \quad (58)$$

the expression for ΔS (Eq. 57) can be re-written as a function of the thermodynamic available magnitudes:

$$\Delta S = \Gamma_{\text{S,H}_2\text{O,M}} + \frac{Q}{F} \bar{S}_{\text{e}^-} - \Gamma_{\text{H,H}_2\text{O}} \bar{S}_{\text{H}^+} - \sum_{i \neq \text{e}^-, \text{H}^+, \text{OH}^-, \text{H}_2\text{O,M}} \Gamma_{i,\text{H}_2\text{O}} \bar{S}_i \quad (59)$$

Furthermore, the combination of Eqs. (53) and (59) gives:

$$\left(\frac{\partial \Delta S}{\partial Q} \right)_{T,p,c_i} = - \left(\frac{\partial \Delta_{\text{S}}^{\text{M}} \phi}{\partial T} \right)_{Q,p,c_i} \quad (60)$$

where $\left(\frac{\partial \Delta_{\text{S}}^{\text{M}} \phi}{\partial T} \right)_{Q,p,c_i}$ is the temperature coefficient of the potential

drop across the interphase. In conclusion, the entropy of formation of the interphase can be determined from the integration of the temperature coefficient of the interfacial potential over the total charge density, up to a constant of integration.

On the other hand, it is convenient to define the entropy of formation of the double-layer, ΔS_{dl} , as the difference in entropy of the components of the interphase, with respect to the entropy in the bulk phases, but without the entropy change due to charge-transfer adsorption processes. Hence, ΔS_{dl} equals the entropy associated to the formation of the interphase, but under conditions of frozen charge-transfer adsorption processes. It will be shown later that these conditions can be achieved if the temperature change is performed very fast (in the submicrosecond time scale) with the help of pulsed laser irradiation. Consequently, the definition of ΔS_{dl} will differ from that of ΔS , because the terms corresponding to the entropy of “hydrogen and OH species in the bulk” [that is, the terms $\Gamma_{\text{H}} (\bar{S}_{\text{H}^+} + \bar{S}_{\text{e}^-})$ and $\Gamma_{\text{OH}} (\bar{S}_{\text{H}_2\text{O}} - \bar{S}_{\text{H}^+} - \bar{S}_{\text{e}^-})$ in Eq. 57] will be

replaced by the actual entropy values of adsorbed hydrogen and OH at the interphase (that is, by $\Gamma_{\text{H}} \bar{S}_{\text{H}}^{\text{ads}}$ and $\Gamma_{\text{OH}} \bar{S}_{\text{OH}}^{\text{ads}}$, respectively, where $\bar{S}_{\text{H}}^{\text{ads}}$ and $\bar{S}_{\text{OH}}^{\text{ads}}$ are the absolute molar entropies of adsorbed hydrogen and OH species):

$$\Delta S_{\text{dl}} = S^{\sigma} + \frac{\sigma_{\text{M}}}{F} \bar{S}_{\text{e}^{-}} - \Gamma_{\text{H}^{+}} \bar{S}_{\text{H}^{+}} - \Gamma_{\text{OH}^{-}} (\bar{S}_{\text{H}_2\text{O}} - \bar{S}_{\text{H}^{+}}) \quad (61)$$

$$- \Gamma_{\text{H}_2\text{O}} \bar{S}_{\text{H}_2\text{O}} - \Gamma_{\text{H}} \bar{S}_{\text{H}}^{\text{ads}} - \Gamma_{\text{OH}} \bar{S}_{\text{OH}}^{\text{ads}} - \Gamma_{\text{M}} \bar{S}_{\text{M}} - \sum_{i \neq \text{e}^{-}, \text{H}^{+}, \text{OH}^{-}, \text{H}_2\text{O}, \text{M}} \Gamma_i \bar{S}_i$$

Comparison of Eqs. 57 with 61 shows that ΔS and ΔS_{dl} are related by:

$$\Delta S = \Delta S_{\text{dl}} + \Gamma_{\text{H}} (\bar{S}_{\text{H}}^{\text{ads}} - \bar{S}_{\text{H}^{+}} - \bar{S}_{\text{e}^{-}}) + \Gamma_{\text{OH}} (\bar{S}_{\text{OH}}^{\text{ads}} - \bar{S}_{\text{H}_2\text{O}} + \bar{S}_{\text{H}^{+}} + \bar{S}_{\text{e}^{-}}) \quad (62)$$

where $\Gamma_{\text{H}} (\bar{S}_{\text{H}}^{\text{ads}} - \bar{S}_{\text{H}^{+}} - \bar{S}_{\text{e}^{-}})$ and $\Gamma_{\text{OH}} (\bar{S}_{\text{OH}}^{\text{ads}} - \bar{S}_{\text{H}_2\text{O}} + \bar{S}_{\text{H}^{+}} + \bar{S}_{\text{e}^{-}})$ equal the entropy change associated to hydrogen and OH adsorption, respectively.

Strictly speaking, ΔS_{dl} is not a truly thermodynamic quantity, since it corresponds to a situation where charge-transfer adsorption processes are not in equilibrium. Therefore, in order to derive the thermodynamic relationships for ΔS_{dl} , the equilibrium conditions for hydrogen and OH adsorption (Eqs. 38 and 39) should not be employed. Instead, under conditions of constant surface concentration of hydrogen and OH species (i.e., Γ_{H} and Γ_{OH} constant), $d\mu_{\text{H}} = -\bar{S}_{\text{H}}^{\text{ads}} dT$ and $d\mu_{\text{OH}} = -\bar{S}_{\text{OH}}^{\text{ads}} dT$. Consequently, following a similar thermodynamic derivation to that given above, the electrocapillary equation (Eq. 37) can be rewritten as:

$$-d\gamma = \sigma_{\text{M}} d\Delta_{\text{S}}^{\text{M}} \phi + \Delta S_{\text{dl}} dT \quad (63)$$

With this, it is easy to show that the entropy of formation of the double-layer is related to the temperature coefficient of the potential drop across the double-layer, $\left(\frac{\partial \Delta_{\text{S}}^{\text{M}} \phi}{\partial T} \right)_{\sigma_{\text{M}}, \Gamma_{\text{H}}, \Gamma_{\text{OH}}, P, \mathcal{E}_i}$, by:

$$\left(\frac{\partial \Delta S_{\text{dl}}}{\partial \sigma_{\text{M}}} \right)_{T, p, c_i} = - \left(\frac{\partial \Delta S^{\text{M}} \phi}{\partial T} \right)_{\sigma_{\text{M}}, \Gamma_{\text{H}}, \Gamma_{\text{OH}}, p, c_i} \quad (64)$$

In conclusion, the entropy of formation of the double-layer can be determined from the integration of the temperature coefficient of the double-layer potential over the free charge density, up to a constant of integration. It is worth noting that this temperature

coefficient is related to $\left(\frac{\partial \Delta S^{\text{M}} \phi}{\partial T} \right)_{Q, p, c_i}$ by:

$$\begin{aligned} \left(\frac{\partial \Delta S^{\text{M}} \phi}{\partial T} \right)_{Q, p, c_i} &= \left(\frac{\partial \Delta S^{\text{M}} \phi}{\partial T} \right)_{\sigma_{\text{M}}, \Gamma_{\text{H}}, \Gamma_{\text{OH}}, p, c_i} \\ &+ \left(\frac{\partial \Delta S^{\text{M}} \phi}{\partial \Gamma_{\text{H}}} \right)_{T, p, c_i} \left(\frac{\partial \Gamma_{\text{H}}}{\partial T} \right)_{p, c_i} + \left(\frac{\partial \Delta S^{\text{M}} \phi}{\partial \Gamma_{\text{OH}}} \right)_{T, p, c_i} \left(\frac{\partial \Gamma_{\text{OH}}}{\partial T} \right)_{p, c_i} \end{aligned} \quad (65)$$

Finally, it should be emphasized that, according to Eq. (64), the potential where the temperature coefficient of the double-layer potential is zero, corresponds to a maximum in the entropy of formation of the double-layer.

IV. ANALYSIS OF TEMPERATURE EFFECTS BASED ON GIBBS THERMODYNAMICS

As demonstrated in the previous Section, temperature effects on platinum|solution interphases can be rigorously characterized through the evaluation of the entropies of formation of the interphase and double-layer. Moreover, these results can be employed to obtain an independent evaluation of the entropy of charge-transfer adsorbed species.

The approach employing Gibbs thermodynamics presents some advantages with respect to the method of analysis that employs a generalized isotherm:

- (1) It does not assume any type of isotherm for the process under study, as opposed to the application of a generalized iso-

therm, which assumes that a Langmuirian type of isotherm is fulfilled (see Eqs. 8, 12, 27 and 28)

- (2) Double-layer effects can be separated in a rigorous way, as opposed to previous studies employing a generalized isotherm, where a constant baseline is usually used to subtract the double-layer capacity.^{16,17,20,32,33}
- (3) No assumption about the values of charge numbers is required, as opposed to the analysis employing a generalized isotherm, where it is assumed that the charge number involved in the adsorption process equals the charge of the adsorbing species in solution (see, for example, Eqs. 12 and 28).

Nevertheless, the method of analysis proposed in this Section also has its limitations:

- (1) It requires additional experimental data, such as CO displacement experiments at different temperatures and laser-pulsed measurements.
- (2) It involves a more complex mathematical treatment of data, and hence it can produce a higher magnification of the experimental dispersion.

In the following, the application of this method of analysis will be illustrated for the case of Pt(111) in 0.1 M HClO₄ solution. First, the evaluation of the entropies of formation of the interphase, double-layer and the interfacial water network will be described in Sections IV.1, IV.2 and IV.3, respectively. Then, these results will be employed to evaluate the absolute molar entropy of adsorbed hydrogen and OH on Pt(111), in Section IV.4. Finally, these results will be critically compared with those obtained with a generalized isotherm in Section IV.5.

1. Entropy of Formation of the Interphase of Pt(111) in 0.1 M HClO₄ Solution

The entropy of formation of the interphase, ΔS , can be evaluated from the integration of the temperature coefficient of the interfacial potential, $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{Q,p,c_i}$, over the total charge density, Q , up to

a constant of integration (Eq. 60). Consequently, the evaluation of ΔS requires first the evaluation of Q and $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{Q,p,c_i}$ data. Total

charge density data for Pt(111) in 0.1 M HClO₄ solutions have been obtained from the integration of cyclic voltammograms:

$$Q = \int_{E^*}^E \frac{j}{\nu} dE + Q^* \quad (66)$$

where j is the voltammetric current, ν is the scan rate, and Q^* equals the total charge density at a potential E^* , that can be calculated from the charge displaced during CO adsorption under potentiostatic conditions.^{37,38} Results of the total charge density curves for Pt(111) in 0.1 M HClO₄ solutions, at 283 and 323 K, as measured in an isothermal cell, are shown in Fig. 5A.

At this point, it should be noted that when an isothermal cell is used, the temperature changes will affect both the reference and working electrode potential drops. In order to use the equations of the previous Section, written in terms of $\Delta_s^M \phi$, the effect of temperature on the reference potential should be eliminated. This can be done by correcting the measured potential values for the shift of the reference potential with the temperature, according to:

$$E(\text{vs. RHE at } 298\text{K}) = E(\text{vs. RHE at } T) + \frac{d\text{RHE}}{dT}(T - 298\text{K}) \quad (67)$$

Where E (vs. RHE at 298 K) and E (vs. RHE at T) account for the potential values of the working electrode measured vs. a RHE reference electrode at 298 K and at the same temperature T as the working electrode, respectively; and $\frac{d\text{RHE}}{dT}$ is the temperature

coefficient of the 0.1 M HClO₄ RHE electrode. Although the latter is not available, it can be approximated to the temperature coefficient of the RHE electrode measured in 0.1 M HCl by de Bethune, +0.640 mV/K.²⁹

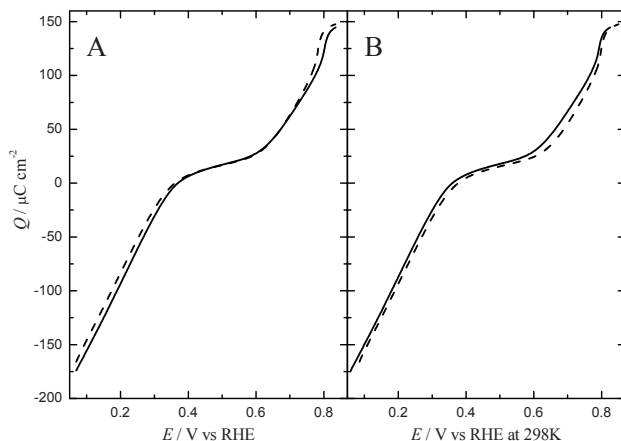


Figure 5. Total charge density curves for Pt(111) in 0.1 M HClO₄ solution, at 283 (solid line) and 323 K (dashed line), plotted in a potential scale: A) with the RHE reference electrode at the same temperature as the working electrode; B) with the RHE at 298 K in all cases. Adapted from Ref. 19.

Once total charge density curves are referred to a constant-temperature reference electrode, this data can be used to evaluate the temperature coefficient of the potential drop across the interphase, $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{Q,p,c_i}$. This is done by interpolating values of poten-

tial at a constant total charge (corresponding to horizontal sections in Fig. 5B) and plotting the results against the temperature. The slope of this plot equals $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{Q,p,c_i}$. Selected results are shown

in Fig. 6A.

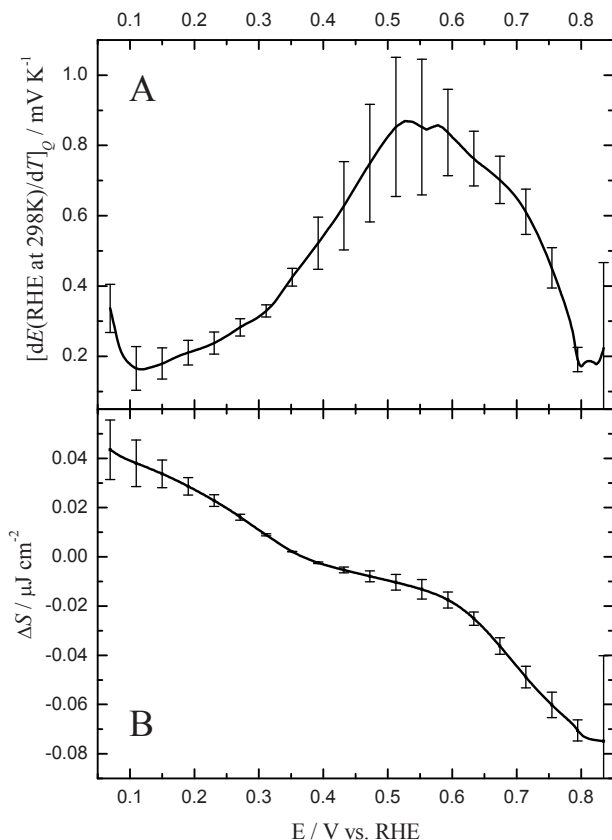


Figure 6. Temperature coefficient of the interfacial potential (A), and entropy of formation of the interphase (B), for Pt(111) in 0.1 M HClO_4 solution at 298 ± 2 K. Error bars in (A) correspond to the standard deviation of the fit of potential values at constant charge vs. temperature. Error bars in (B) correspond to the propagation of the error in the temperature coefficient of the interfacial potential, according to the method described in Ref. 95. Figure adapted from Ref. 19.

Finally, the entropy of formation of the interphase, ΔS , is obtained from integration of $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{Q, p, c_i}$ over the total charge density, up to a constant of integration. This constant of integration has been arbitrarily taken as zero at the potential of zero total charge, E_{pztc} . Therefore, the resulting ΔS values correspond to the difference in the entropy of formation of the interphase at a potential E , with respect to the E_{pztc} . Selected results of ΔS are shown in Fig. 6B.

2. Entropy of Formation of the Double-Layer of Pt(111) in 0.1 M HClO₄ Solution

The entropy of formation of the double-layer, ΔS_{dl} , can be evaluated from the integration of the temperature coefficient of the double-layer potential, $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{\text{OH}}, p, c_i}$, over the free charge density, σ_M , up to a constant of integration (Eq. 64). Consequently, the evaluation of ΔS_{dl} requires first the evaluation of σ_M and

$$\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{\text{OH}}, p, c_i} \text{ data.}$$

Free charge density data for Pt(111) in 0.1 M HClO₄ solution was evaluated in Ref. 20 from the integration of the double-layer capacities reported in Ref. 39. Noteworthy, this evaluation of double-layer capacities takes advantage of the fact that, in perchloric acid solutions, the only charge-transfer adsorption processes that take place on Pt(111) are hydrogen and OH adsorption. Since these processes involve proton species in solutions, the surface concentration of hydrogen and OH are linked to the derivative of the chemical potential of proton ions (see, for example, Eq. 42). As a result, double-layer capacities can be evaluated from the thermodynamic analysis of the effect of pH on total charge density data in $(0.1 - x) \text{ M KClO}_4 + x \text{ M HClO}_4$ solutions (see Appendix 2).

Figure 7A compares the results of the double-layer capacity, $C_{dl} = \frac{d\sigma_M}{dE}$, with the total capacity, $C_{tot} = \frac{dQ}{dE}$, for Pt(111) in 0.1 M HClO₄. It is observed that both capacities are essentially equal within the double-layer region ($\approx 0.35 < E < 0.5$ V vs. RHE), evidencing that both hydrogen and OH adsorption are essentially negligible at these potentials. Then, at $E < 0.35$ V, $C_{tot} > C_{dl}$ due to hydrogen adsorption; and at $E > 0.5$ V, $C_{tot} > C_{dl}$ due to OH adsorption.

Next, free charge densities have been obtained from integration of C_{dl} values, and considering that the potential of zero free charge, E_{pzfc} , can be identified with the E_{pztc} , in view of the fact that the later ($E_{pztc} = 0.37$ V) is located within the double-layer region (where $\Gamma_H \approx \Gamma_{OH} \approx 0$). Noteworthy, the results from laser-pulsed measurements give support to this identification of $E_{pzfc} \cong E_{pztc}$ (see below, Section V.3). Figure 7B shows the results of the evaluation of free charge densities on Pt(111) in 0.1 M HClO₄, together with the corresponding total charge density data. It is observed that within the double-layer region, $\sigma_M \approx Q$, since at these potentials, both hydrogen and OH adsorption are very small. Then, at $E < 0.35$ V, $Q < \sigma_M$ due to hydrogen adsorption. And finally, at $E > 0.50$ V, $Q > \sigma_M$ due to OH adsorption.

On the other hand, $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ could be obtained, in principle, from the analysis of free charge density curves at different temperatures, in an analogous way as $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{Q, p, c_i}$ was determined from the analysis of total charge density curves at different temperatures. Nevertheless, this method of evaluation of $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ is extremely difficult from an experimental

point of view. First, the evaluation of double-layer capacities at a single temperature requires the realization of a large number of high quality experiments. For example, around 60 voltammograms were acquired for the evaluation of the double-layer capacities in Fig. 7A.³⁹ In addition, the evaluation of free charge density data

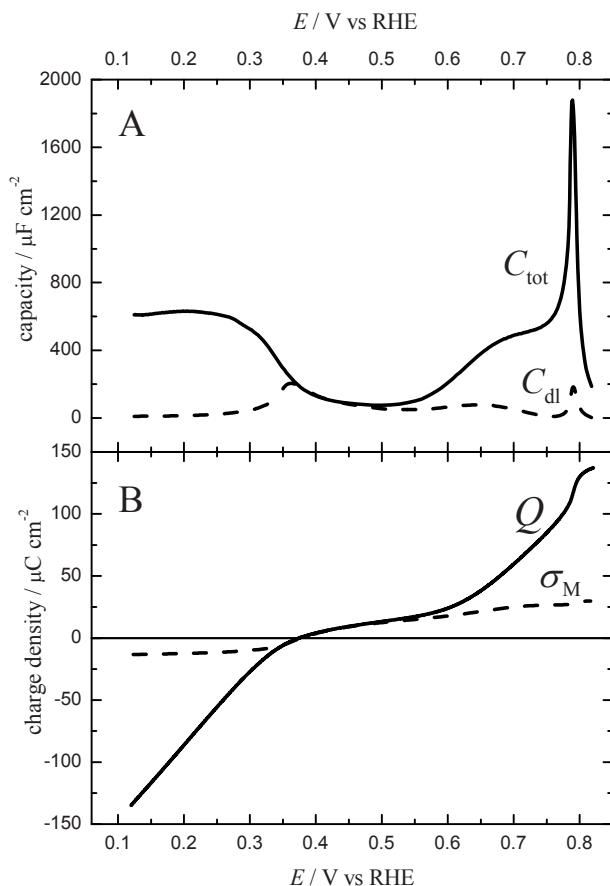


Figure 7. Comparison of: A) the double-layer capacity, C_{dl} , with the total capacity, C_{tot} ; B) the free charge density, σ_M , with the total charge density, Q ; for Pt(111) in 0.1 M HClO_4 solution at 298 ± 2 K. Adapted from Ref. 18.

from the integration of double-layer capacities at different temperatures, would require that the E_{pzfc} at different temperatures was determined by an independent method, and none of these experimental data is currently available. Finally, the effect of a tempera-

ture change on the interfacial properties is usually small, mainly because the experimentally available temperature range is limited (typically, between 273 and 330 K) and therefore, the relatively high uncertainty of the free charge density values does not allow achieving reliable evaluations of their temperature dependence.

Alternatively, $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ can be evaluated from the

analysis of laser-pulsed experiments. Although this methodology is explained in detail in Section V, at this stage it is convenient to take a leap and borrow some results from that Section and just use them at this point. In this way, Fig. 8 shows the results of

$\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ for Pt(111) in 0.1 M HClO₄. It is observed

that $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ changes sign at $E_{pzfc} = E_{pztc} = 0.37$ V.

Noteworthy, the sign of $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ provides evidence on

the net orientation of the interfacial water network (see Section V.2). Accordingly, at $E < E_{pztc}$, the interfacial water network exhibits a net orientation with the hydrogen towards the metal, and at $E > E_{pztc}$, the interfacial water molecules reorient to achieve a net orientation with the oxygen towards the metal.

Figure 8 also includes the result of $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{Q, p, c_i}$ for Pt(111)

in 0.1 M HClO₄, for comparison purposes. In addition, this figure includes the results of the surface concentrations of hydrogen and OH, determined from the thermodynamic analysis of the effect of the proton concentration on total charge density data (see Appen-

dix 2). It is observed that $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ and

$\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{Q, p, c_i}$ values are close within the double-layer region, as a

result of the fact that the surface concentrations of hydrogen and

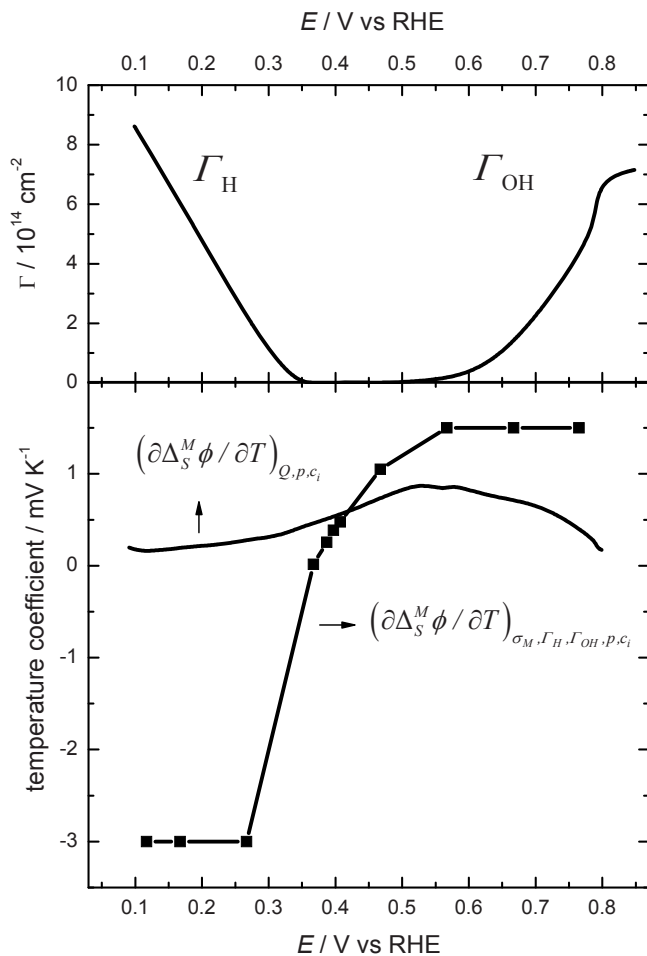


Figure 8. Temperature coefficient of the electrode potential, $(\partial \Delta_S^M \phi / \partial T)_{Q,p,c_i}$, and temperature coefficient of the double-layer, $(\partial \Delta_S^M \phi / \partial T)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$, for Pt(111) in 0.1 M HClO_4 at 298 ± 2 K. Values of hydrogen and OH Gibbs excesses are shown in the upper graph for the sake of comparison. Adapted from Ref. 18.

OH species are small. Conversely, these quantities clearly deviate within the hydrogen and OH adsorption regions. These deviations are related to the effect of temperature on hydrogen and OH adsorption (Eq. 65). Nevertheless, the interpretation of these deviations is not straightforward. In this regard, the comparison of ΔS with ΔS_{dl} is more instructive.

ΔS_{dl} can be obtained from the integration of $\left(\frac{\partial \Delta S^M_s \phi}{\partial T} \right)_{\sigma_M, F_H, F_{OH}, p, c_i}$ over the free charge density, up to a constant of integration. This constant of integration will be taken as zero at $E_{pzfc} = E_{pztc}$. Figure 9 compares the results of ΔS_{dl} with ΔS . It is observed that the curve ΔS_{dl} vs. E exhibits a bell-shape. Furthermore, the potential where the ΔS_{dl} vs. E exhibits a maximum essentially corresponds to the $E_{pzfc} = E_{pztc} = 0.37$ V. This is a consequence of the fact that $\left(\frac{\partial \Delta S^M_s \phi}{\partial T} \right)_{\sigma_M, F_H, F_{OH}, p, c_i}$ changes sign at $E_{pzfc} =$

$E_{pztc} = 0.37$ V. Moreover, this evidences that the degree of disorder of the double-layer is closely related to the free charge density on the metal. Furthermore, it will be shown below in Section IV.3, that the potential of maximum ΔS_{dl} essentially corresponds to the potential of reorientation of the interfacial water network. Indeed, considering a very simplistic model of the water adlayer, with only two possible configurations (up and down), it is expected that the maximum configurational entropy will correspond to a situation where the surface concentrations of up and down molecules are the same. Consequently, the decrease of ΔS_{dl} values at $E < 0.37$ V is related to the fact that water molecules reorient, in order to achieve a net polarization with the hydrogen towards the metal, as the free charge density on the metal becomes more negative. Similarly, the decrease of ΔS_{dl} values at $E > 0.37$ V can be ascribed to the reorientation of interfacial water molecules towards the oxygen-towards-the-metal orientation as the free charge density on the metal becomes more positive.

On the other hand, Fig. 9 shows that $\Delta S \approx \Delta S_{dl}$ within the double-layer region, as expected from the fact that both hydrogen and

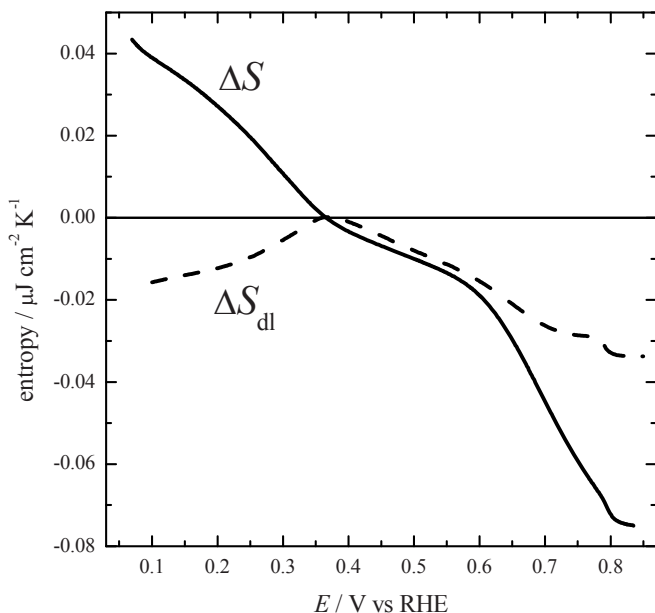


Figure 9. Entropy of formation of the interface, ΔS , and of the double-layer, ΔS_{dl} , for Pt(111) in 0.1 M HClO_4 solution at 298 ± 2 K. Adapted from Ref. 18.

OH adsorption are very small at these potentials. Then, within the hydrogen adsorption region, ΔS and ΔS_{dl} display opposite trends.

This is a direct result of the fact that $\left(\frac{\partial \Delta S^M \phi}{\partial T} \right)_{Q,p,c_i}$ and

$\left(\frac{\partial \Delta S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ have opposite signs at these potentials. The

fact that, within the hydrogen adsorption region, $\Delta S > \Delta S_{dl}$, evidences that the process of hydrogen adsorption involves a positive entropy change [i.e., the term $(\bar{S}_H^{\text{ads}} - \bar{S}_{H^+} - \bar{S}_{e^-})$ in Eq. (62) is positive]. Conversely, within the OH adsorption region, $\Delta S < \Delta S_{dl}$, evidencing that the process of OH adsorption involves a negative

entropy change [i.e., the term $(\bar{S}_{\text{OH}}^{\text{ads}} - \bar{S}_{\text{H}_2\text{O}} + \bar{S}_{\text{H}^+} + \bar{S}_{\text{e}^-})$ in Eq. (62) is negative]. In Section IV.4, the results of ΔS and ΔS_{dl} will be employed to obtain a rigorous, independent evaluation of $\bar{S}_{\text{H}}^{\text{ads}}$ and $\bar{S}_{\text{OH}}^{\text{ads}}$ values.

3. Entropy of Formation of the Interfacial Water Network on Pt(111) in 0.1 M HClO₄ Solution

The entropy of formation of the double-layer, ΔS_{dl} , can be split into three contributions:^{36,40}

- (1) the entropy of formation of the diffuse double-layer, $\Delta S_{\text{dl}}^{2\text{-sol}}$;
- (2) the entropy of formation of the interfacial water network, $\Delta S_{\text{dl}}^{\text{w}}$; and
- (3) the entropy of formation of the electric double-layer inside the metal, i.e., the contribution to ΔS_{dl} from the metal electrons, $\Delta S_{\text{dl}}^{\text{e}}$.

$\Delta S_{\text{dl}}^{2\text{-sol}}$ can be calculated by means of the Gouy-Chapman model, according to:

$$\Delta S_{\text{dl}}^{2\text{-sol}} = - \int_0^{\sigma_{\text{M}}} \left(\frac{\partial \phi_2}{\partial T} \right)_{\sigma_{\text{M}}} d\sigma_{\text{M}} \quad (68)$$

where ϕ_2 is the potential at the plane of closest approach of the ions belonging to the diffuse double-layer (i.e., the outer Helmholtz plane). For a 1:1 electrolyte:⁴¹

$$\phi_2 = \frac{2kT}{e} \sinh^{-1} \left(\frac{\sigma_{\text{M}}}{\sqrt{8kT\varepsilon\varepsilon_0 N_{\text{A}} c}} \right) \quad (69)$$

where e is the absolute value of the charge of an electron, ε is the dielectric constant of water, ε_0 is the permittivity of free space, N_{A} is the Avogadro's number and c is the electrolyte concentration.

Therefore, $\left(\frac{\partial \phi_2}{\partial T}\right)_{\sigma_M}$ can be calculated by numerical differentiation of ϕ_2 with temperature, by using Eq. (69), and taking into account that ε is also temperature-dependent ($\varepsilon = 78.36$ at 298 K, $d\ln\varepsilon/dT = -45.88 \cdot 10^{-4} \text{ K}^{-1}$)⁴⁰. Then, ΔS_{dl}^{2-sol} can be evaluated by using Eq. (68). Finally, the entropy of formation of the inner double-layer can be obtained from:

$$\Delta S_{dl}^{M-2} = \Delta S_{dl} - \Delta S_{dl}^{2-sol} \quad (70)$$

As above mentioned, ΔS_{dl}^{M-2} contains contributions from the entropy of formation of the interfacial water network, ΔS_{dl}^w , and the entropy of formation of the electric double-layer inside the metal, ΔS_{dl}^e . ΔS_{dl}^e can be estimated from the thermal coefficient of the work function of the metal, $d\Phi/dT$. (For Pt(111), $d\Phi/dT \approx -1.5 \cdot 10^{-4} \text{ eV K}^{-1}$.)⁴² Considering that $d\Phi/dT$ is essentially independent of the charge density, the contribution to ΔS_{dl} from the entropy of metal electrons can be estimated as:³⁶

$$\Delta S_{dl}^e \approx \left(\frac{\partial \Phi}{\partial T}\right) \sigma_M \quad (71)$$

With this, ΔS_{dl}^w can be obtained from:

$$\Delta S_{dl}^w = \Delta S_{dl} - \Delta S_{dl}^{M-2} - \Delta S_{dl}^e \quad (72)$$

Figure 10 plots the results of ΔS_{dl}^w , ΔS_{dl}^{M-2} and ΔS_{dl} , against the free charge density. It is observed that the difference between ΔS_{dl}^w and ΔS_{dl} is relatively small, thus supporting the qualitative interpretation of ΔS_{dl} in terms of the state of disorder of the interfacial water network (Sections IV.2 and V.2). Similarly, the present result also gives support to the interpretation of

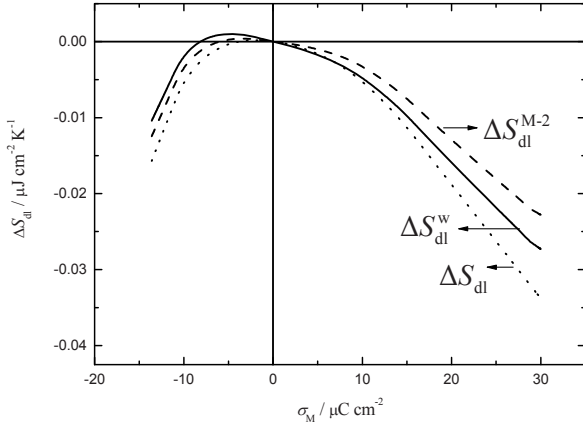


Figure 10. Entropies of formation of: the double layer, ΔS_{dl} , the inner double-layer, ΔS_{dl}^{M-2} , and the interfacial water network, ΔS_{dl}^w , plotted against the free charge density, for Pt(111) in 0.1 M HClO_4 solution at 298 ± 2 K. Adapted from Ref. 18.

$\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ as an evidence of the net orientation of the interfacial water molecules (Sections IV.2 and V.2), since it shows that $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ essentially determines ΔS_{dl}^w , according to:

$$-\int_0^{\sigma_M} \left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} d\sigma_M = \Delta S_{dl} \approx \Delta S_{dl}^w \quad (73)$$

Moreover, it is observed that the maximum of the three curves in Fig. 10 is located very close to $\sigma_M = 0$. Therefore, the potential of maximum ΔS_{dl}^w , ΔS_{dl}^{M-2} and ΔS_{dl} , is very close to the E_{pzfc} . Close

inspection of this data indicate that maximum $\Delta S_{\text{dl}}^{\text{w}}$ values are achieved at slightly negative charge densities ($\sigma_{\text{M}} \approx -4 \mu\text{C cm}^{-2}$), but this increase in $\Delta S_{\text{dl}}^{\text{w}}$ values, with respect to the value at $\sigma_{\text{M}} = 0$, is within the uncertainty of their determination.

In conclusion, the present results show that the entropy of the interfacial water network on Pt(111) is nearly dominated by the free charge density. The state of maximum disorder corresponds to $\sigma_{\text{M}} \approx 0$, $E \approx E_{\text{pzfc}}$. Then, at $\sigma_{\text{M}} < 0$, the entropy of the interfacial water network decreases, due to the fact that the interfacial water molecules achieve a net polarization with the hydrogen end towards the metal. Conversely, at $\sigma_{\text{M}} > 0$, the orientation with the oxygen end towards the metal becomes the most favorable. Noteworthy, the fact that water reorientation on Pt(111) takes at $\sigma_{\text{M}} \approx 0$, $E \approx E_{\text{pzfc}}$ evidences that specific interactions between water molecules and the Pt(111) surface play a minor role on the orientational behavior of the interfacial water network. That is, water structures with net orientations with the hydrogen and with the oxygen towards the metal seem to experience similar specific interactions with the Pt(111) surface. These conclusions will be discussed in more detail in Section V.3.

4. Absolute Molar Entropy of Hydrogen and OH on Pt(111)

The derivation in Section III demonstrates that the absolute molar entropy of charge-transfer adsorption species can be obtained, in a rigorous way, from the combination of ΔS and ΔS_{dl} data. According to Eq. (62), the absolute molar entropy of hydrogen and OH species can be obtained from:

$$\bar{S}_{\text{H}}^{\text{corr}} \equiv \frac{\Delta S - \Delta S_{\text{dl}}}{\Gamma_{\text{H}}} + \bar{S}_{\text{H}^+} + \bar{S}_{e^-} \text{ (hydrogen adsorption)} \quad (74)$$

$$\bar{S}_{\text{OH}}^{\text{corr}} \equiv \frac{\Delta S - \Delta S_{\text{dl}}}{\Gamma_{\text{OH}}} + \bar{S}_{\text{H}_2\text{O}} - \bar{S}_{\text{H}^+} - \bar{S}_{e^-} \text{ (OH adsorption)} \quad (75)$$

where the superscript corr in $\bar{S}_{\text{H}}^{\text{corr}}$ and $\bar{S}_{\text{OH}}^{\text{corr}}$ is used to stress that double-layer effects are corrected by using the results of ΔS_{dl} .

Nevertheless, it should be kept in mind that the evaluation of ΔS_{dl} involves a number of uncertainties. For this reason, it is convenient to evaluate the effect of ΔS_{dl} data on the results of the molar entropies of adsorbed hydrogen and OH species. For this purpose, it is convenient to define effective absolute molar entropies of adsorbed hydrogen and OH species, $\bar{S}_H^{\text{eff}}$ and $\bar{S}_{OH}^{\text{eff}}$, which will contain contributions from the entropy change of double-layer phenomena coupled to the adsorption process under study. These quantities are obtained by assuming $\Delta S_{dl} = 0$ in Eq. (62), and solving the values of $\bar{S}_H^{\text{ads}}$ and $\bar{S}_{OH}^{\text{ads}}$.

$$\bar{S}_H^{\text{eff}} \equiv \frac{\Delta S}{\Gamma_H} + \bar{S}_{H^+} + \bar{S}_{e^-} \quad (\text{hydrogen adsorption}) \quad (76)$$

$$\bar{S}_{OH}^{\text{eff}} \equiv \frac{\Delta S}{\Gamma_{OH}} + \bar{S}_{H_2O} - \bar{S}_{H^+} - \bar{S}_{e^-} \quad (\text{OH adsorption}) \quad (77)$$

It should be noted that these methods of evaluation of the entropy of adsorbed hydrogen and OH species provide *integral* molar entropies, which are defined as the entropy of the adlayer divided by the number of moles of adsorbed species.⁴³ Conversely, *differential* molar entropies are defined as the derivative of the entropy of the adlayer with the number of moles of adsorbed species.⁴³ Clearly, with the available experimental data, the evaluation of integral molar entropies involves a smaller uncertainty, in comparison to differential molar entropies.

For the evaluation of $\bar{S}_H^{\text{corr}}$, $\bar{S}_{OH}^{\text{corr}}$, $\bar{S}_H^{\text{eff}}$ and $\bar{S}_{OH}^{\text{eff}}$ by Eqs. (74)-(77), respectively, the following values of $\bar{S}_{H^+}$, $\bar{S}_{e^-}$ and $\bar{S}_{H_2O}$ will be used. First, the entropy of electrons can be considered negligible: $\bar{S}_{e^-} \approx 0$.¹³ Moreover, for a 0.1 M HClO₄ solution, the activity coefficient of water can be considered very close to unity, and hence, $\bar{S}_{H_2O}$ can be considered equal to $\bar{S}_{H_2O}^0 = 69.8 \text{ J mol}^{-1} \text{ K}^{-1}$.¹³ Finally, the molar entropy of proton species will be given by:

$$\bar{S}_{\text{H}^+} = \bar{S}_{\text{H}^+}^0 - \frac{d(RT \ln a_{\text{H}^+})}{dT} = \bar{S}_{\text{H}^+}^0 - R \ln a_{\text{H}^+} - RT \frac{d(\ln a_{\text{H}^+})}{dT} \quad (78)$$

where $\bar{S}_{\text{H}^+}^0 = -18.8 \text{ J mol}^{-1} \text{ K}^{-1}$,¹³ and the values of the proton activity and its temperature dependence can be taken from those in 0.1 M HCl: $a_{\text{H}^+} = 0.07967$ and $\frac{d(\log a_{\text{H}^+})}{dT} \approx -0.0002181 \text{ K}^{-1}$.²⁹ Putting these numbers together, one obtains:

$$\bar{S}_{\text{H}^+} = \bar{S}_{\text{H}^+}^0 - R \ln a_{\text{H}^+} - RT \frac{d(\ln a_{\text{H}^+})}{dT} \approx -18.8 + 21.02 + 1.24 = 3.5 \frac{\text{J}}{\text{mol K}} \quad (79)$$

The results of $\bar{S}_{\text{H}}^{\text{eff}}$, $\bar{S}_{\text{OH}}^{\text{eff}}$, $\bar{S}_{\text{H}}^{\text{corr}}$ and $\bar{S}_{\text{OH}}^{\text{corr}}$ are compared in Fig. 11. In order to facilitate the discussion of these results, it is convenient to calculate the theoretical entropy values corresponding to an ideal adlayer, in the limiting cases of fully mobile and totally immobile adsorbates, $\bar{S}_i^{\text{mob}}$ and $\bar{S}_i^{\text{im}}$, respectively. The statistical mechanics treatment shows that the absolute integral molar entropy of a fully mobile adlayer is given by (see Appendix 3):

$$\bar{S}_i^{\text{mob}} = R \left[2 + \ln \left(\frac{2\pi m_i kT}{h^2} \frac{1}{c_s \theta_i} \right) \right] \quad (80)$$

where m_i is the atomic mass of the adsorbed species i , c_s corresponds to the surface density of adsorption sites, θ_i is the normalized coverage of the species i , and the other symbols have their usual meaning. On the other hand, the absolute integral molar entropy of a fully immobile adlayer is essentially given by the configurational entropy, since the vibrational contribution is very low.^{16,17} Accordingly (see Appendix 3):

$$\bar{S}_i^{\text{im}} \approx -R \ln \left(\frac{\theta_i}{1 - \theta_i} \right) - \frac{R}{\theta_i} \ln(1 - \theta_i) \quad (81)$$

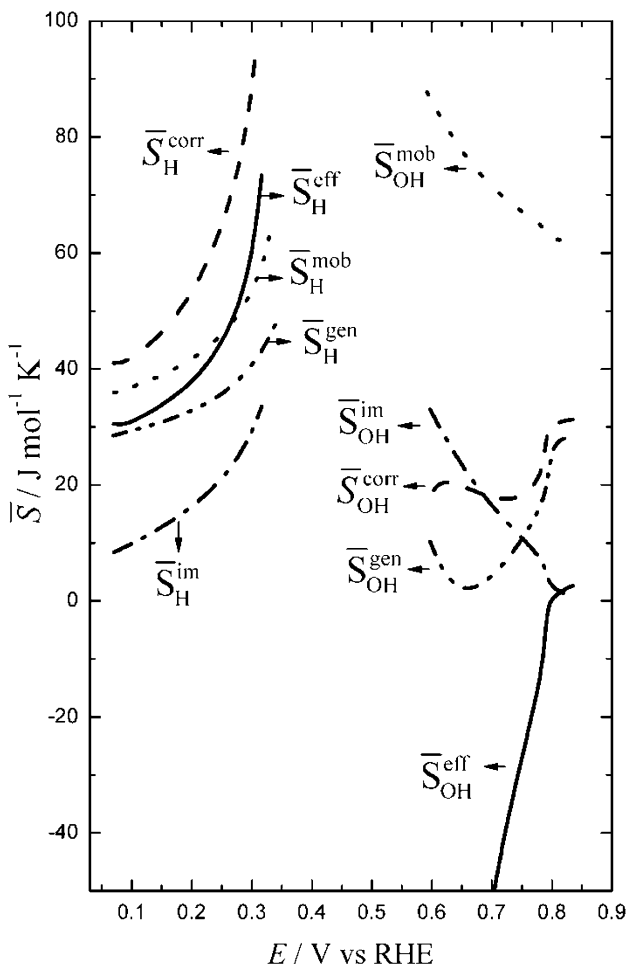


Figure 11. Absolute molar entropies of adsorbed hydrogen and OH species on Pt(111), as evaluated by different approximations: $\bar{S}_i^{\text{eff}}$ (solid lines), $\bar{S}_i^{\text{corr}}$ (dashed lines) and $\bar{S}_i^{\text{gen}}$ (dashed-dotted-dotted lines). The results for the theoretical entropy values of $\bar{S}_i^{\text{mob}}$ (dotted lines) and $\bar{S}_i^{\text{im}}$ (dashed-dotted lines) are also included for the sake of comparison. Adapted from Ref. 18.

For the calculations of $\bar{S}_i^{\text{mob}}$ and $\bar{S}_i^{\text{im}}$, coverages are obtained from Γ data in Fig. 8, as $\theta = \Gamma / \Gamma_{\text{sat}}$, where Γ_{sat} is the saturation value of the surface concentration of hydrogen and OH, $\Gamma_{\text{sat,H}} = 1.5 \cdot 10^{15}$ and $\Gamma_{\text{sat,OH}} = 7.2 \cdot 10^{14}$ ions cm^{-2} . The results are included in Fig. 11.

It is observed that both $\bar{S}_{\text{H}}^{\text{corr}}$ and $\bar{S}_{\text{H}}^{\text{eff}}$ are quite close to $\bar{S}_{\text{H}}^{\text{mob}}$, indicating that adsorbed hydrogen species on Pt(111) are very mobile. In this regard, quasielastic helium atom scattering (QHAS) measurements⁴⁴ indicate that the activation energy for surface diffusion of hydrogen on Pt(111) is only ca 6.6 kJ mol^{-1} , and several density functional theory (DFT) calculations report that the adsorption energy of hydrogen on Pt(111) is similar for all adsorption sites,⁴⁵⁻⁴⁷ thus indicating that the surface diffusion should be facile.

On the other hand, in relation to OH adsorption, the calculated values of $\bar{S}_{\text{OH}}^{\text{eff}}$ are always negative, evidencing that OH adsorption on Pt(111) is coupled to double-layer processes involving a negative entropy change. However, when ΔS_{dl} values are used to correct the contribution from double-layer phenomena, the resulting $\bar{S}_{\text{OH}}^{\text{corr}}$ values become positive, as it is to be expected. In addition, it is observed that $\bar{S}_{\text{OH}}^{\text{corr}}$ values are clearly closer to $\bar{S}_{\text{OH}}^{\text{im}}$ than to $\bar{S}_{\text{H}}^{\text{mob}}$, indicating that adsorbed OH species are rather immobile. This agrees with the observation of hindered translational modes for OH on Pt(111) by high-resolution electron energy loss spectroscopy (HREELS).⁴⁸ However, $\bar{S}_{\text{OH}}^{\text{corr}}$ and $\bar{S}_{\text{OH}}^{\text{im}}$ exhibit clear deviations (except at around $E \approx 0.65$ V), and display opposite dependences on potential, evidencing that the state of OH on Pt(111) is more complex than an ideal hard-sphere adlayer, with zero or very small interactions, assumed for the statistical mechanics calculations. Moreover, the increase of $\bar{S}_{\text{OH}}^{\text{corr}}$ with potential suggests that the mobility of OH species increases with the OH coverage. This finding is quite surprising, since one expects that, in general, the mobility of adsorbed species decreases with coverage. However, it should be noted that the mechanism of OH surface diffusion takes

place through proton exchange reactions, and therefore, the mechanism of this reaction is complex.⁴⁹

5. Comparison with Results from the Application of a Generalized Isotherm

It is interesting to compare the present results of the entropy of adsorbed hydrogen and OH on Pt(111), obtained in Section IV.4 using Gibbs thermodynamics, with the results obtained in Section II.2 using a generalized isotherm. For this purpose, first of all, it should be noted that the method of analysis employing a generalized isotherm provides the values of the standard entropy change associated to the global reaction of the cell. Therefore, for hydrogen and OH adsorption on Pt(111) from 0.1 M HClO₄:

$$\Delta \bar{S}_{\text{H/H}_2}^0 = \bar{S}_{\text{H}}^{0,\text{gen}} - \frac{1}{2} \bar{S}_{\text{H}_2}^0 \quad (82)$$

$$\Delta \bar{S}_{\text{OH/H}_2}^0 = \bar{S}_{\text{OH}}^{0,\text{gen}} + \frac{1}{2} \bar{S}_{\text{H}_2}^0 - \bar{S}_{\text{H}_2\text{O}}^0 \quad (83)$$

where the superscript gen is used to stress that the entropy values have been obtained by the use of a generalized isotherm. Therefore, from the results of $\Delta \bar{S}_{\text{H/H}_2}^0$ and $\Delta \bar{S}_{\text{OH/H}_2}^0$ in Section II.2, the values of $\bar{S}_{\text{H}}^{0,\text{gen}}$ and $\bar{S}_{\text{H}}^{0,\text{gen}}$ can be easily obtained by using Eqs. (82) and (83), and the tabulated values of $\bar{S}_{\text{H}_2}^0 = 129.6$ and $\bar{S}_{\text{H}_2\text{O}}^0 = 69.8 \text{ J mol}^{-1} \text{ K}^{-1}$.¹³ This gives $\bar{S}_{\text{H}}^{0,\text{gen}} \approx 14$ and $\bar{S}_{\text{OH}}^{0,\text{gen}} \approx -32 \text{ J mol}^{-1} \text{ K}^{-1}$. Then, in order to get the absolute molar entropy values at a given equilibrium state, different to the standard state, one has to add the terms corresponding to the configurational entropy and the entropic contributions of the interaction energy between adsorbates. In the case of the differential absolute molar entropy of adsorbed species, this can be done by using the well-known expression (see Appendix 3):

$$\bar{S}_i^{\text{gen, diff}} = \bar{S}_i^{0,\text{gen}} - \frac{d\omega}{dT} \theta - R \ln \left(\frac{\theta}{1-\theta} \right) \quad (84)$$

However, the derivation in Appendix 3 shows that the integral absolute molar entropy of adsorbed species at a given coverage, θ , is given by:

$$\bar{S}_i^{\text{gen}} = \bar{S}_i^{0,\text{gen}} - \frac{1}{2} \frac{d\omega}{dT} \theta_i - R \ln \left(\frac{\theta_i}{1 - \theta_i} \right) - \frac{R}{\theta_i} \ln(1 - \theta_i) \quad (85)$$

Therefore, all the data required for the evaluation of $\bar{S}_H^{\text{gen}}$ and $\bar{S}_{\text{OH}}^{\text{gen}}$ has been obtained in Section II.2. It should be recalled that in this method of analysis, values of coverages are obtained from integration of the voltammograms, considering that double-layer effects can be subtracted by a constant baseline. Then, the combination of the coverage data with the results of $\bar{S}_H^{0,\text{gen}} \approx 14$ and $\bar{S}_{\text{OH}}^{0,\text{gen}} \approx -32 \text{ J mol}^{-1} \text{ K}^{-1}$, and the results of $d\omega_{\text{H-H}}/dT \approx -20$ and $d\omega_{\text{OH-OH}}/dT \approx -125 \text{ J mol}^{-1} \text{ K}^{-1}$, provides the values of $\bar{S}_H^{\text{gen}}$ and $\bar{S}_{\text{OH}}^{\text{gen}}$. The results of this calculation are included in Fig. 11.

Figure 11 shows that $\bar{S}_H^{\text{gen}}$ values are close, but somewhat lower than $\bar{S}_H^{\text{eff}}$ and $\bar{S}_H^{\text{corr}}$. This (small) deviation is mainly due to the fact that in the calculation of $\bar{S}_H^{\text{gen}}$, the double-layer capacity is subtracted as a constant baseline. If the entropy of adsorbed hydrogen is evaluated by the method of analysis using Gibbs thermodynamics, but assuming that the double-layer capacity is constant, then the resulting entropy values (not shown) agree well with $\bar{S}_H^{\text{gen}}$. In conclusion, the method of analysis employing a generalized isotherm is suitable for the study of hydrogen adsorption on Pt(111), but the method of correction of the double-layer contributions by assuming a constant double-layer capacity is less appropriate than the use of the results of ΔS_{dl} data.

On other hand, in relation to OH adsorption, the results of $\bar{S}_{\text{OH}}^{\text{gen}}$ values agree well with $\bar{S}_{\text{OH}}^{\text{corr}}$ at $E > 0.75 \text{ V}$, but exhibit clear deviations at lower potentials. This deviation is, as in the case of hydrogen adsorption, originated by the different double-layer correction employed in both mathematical treatments. If one calculates the entropy of adsorbed OH by using Gibbs thermodynamics, but assuming a constant double-layer capacity, then the resulting

entropy values (not shown) are in good agreement with $\bar{S}_{\text{OH}}^{\text{gen}}$. In conclusion, the use of the method of analysis employing a generalized isotherm is justified for OH adsorption on Pt(111), but the method of subtraction of double-layer effects as a constant baseline is inappropriate. Indeed, Fig. 11 shows that values of $\bar{S}_{\text{OH}}^{\text{gen}}$ at low-medium OH coverages ($E < 0.75\text{V}$) are unrealistically low, since they fall below the theoretical value of a fully immobile adlayer, $\bar{S}_{\text{OH}}^{\text{im}}$. This evidences again the advantage of the use of ΔS_{dl} data to correct double-layer effects.

V. WATER REORIENTATION ON SINGLE-CRYSTAL ELECTRODES FROM NANOSECOND LASER-PULSED EXPERIMENTS. POTENTIAL OF MAXIMUM ENTROPY OF DOUBLE-LAYER FORMATION

If one is challenged with the study of the effect of the temperature on a metal solution interphase, the first approach that will probably come to mind is the use of a thermostated bath or a jacketed cell to control the temperature of the whole system. Then, the whole battery of electrochemical techniques, including cyclic voltammetry and CO charge displacement experiments, can be applied at different temperatures to scrutinize the effect of this variable on the measured properties. This is the usual choice employed in almost all of the studies reviewed above. This approach leads to equilibrium thermodynamic properties such as the temperature coefficient of the potential drop across the interphase, as explained in Section IV.1.

Another, less obvious, approach to change the interfacial temperature is to deposit selectively the heat locally into the metal|solution interphase. This method produces an increase of the temperature of the metal|solution interphase under study, while the temperature of the other components of the electrochemical cell (including the reference electrode) remains unchanged. Thus, these experiments are performed in a non-isothermal configuration. The clear advantage of this experimental approach is the possibility of producing a very fast thermal perturbation, by using a pulsed heat source, since the volume of solution heated can be made very

small. The sudden change of the temperature can be done by using short laser pulses, and the technique is called laser-induced temperature jump method. In this approach, two situations can arise: If the temperature change is performed faster than the characteristic response time of a given electrochemical reaction, kinetic information can be obtained from the relaxation of the potential with time. This technique is especially suitable for the study of very fast electrochemical processes, since, as no current flows during this experiment, the limitation imposed by the finite time constant of the cell is avoided. On the other hand, if the response time of the electrochemical reaction is much faster than the time scale of the temperature change, the reaction will remain at equilibrium and thermodynamic properties can be measured without much difference with the conventional approach that uses the thermostatic bath. Still, the measurements can be done much faster since no time is needed to heat the whole volume of the solution.

The real advantage of this approach is attained in the case of platinum electrodes where the time scale of the perturbation is selected to achieve the separation of double-layer and charge-transfer adsorption processes, by taking advantage of the fact that the double-layer response is usually much faster than charge-transfer adsorption phenomena. If the laser-pulsed experiments are performed under experimental conditions so that charge-transfer processes remain essentially frozen during the measurement time-scale, then the laser-induced potential transient reflects the temperature coefficient of the potential drop across the double-layer,

$$\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} . \text{ Finally, if the rate of charge-transfer process-}$$

es is fast enough to respond to the temperature change, the laser-induced potential transient will show two contributions with different response time, one virtually instantaneous response, related to the temperature coefficient of the double-layer, and the response from charge transfer processes, with a response time given by the standard rate constant of the process. The separation of both contributions can be achieved by introducing kinetic relationships into the analysis of the laser-induced potential transients, as explained in Section V.1.

Remarkably, the temperature coefficient of the double-layer potential provides information on the net orientation of interfacial

water (see below, Section V.2). As a result, the laser-induced temperature jump method constitutes a powerful technique to characterize the behavior of water molecules in contact with platinum electrodes. It should be emphasized that the study of interfacial water molecules at metal|aqueous solution interphase constitutes a big experimental challenge. In most experimental techniques, the response of interfacial water molecules is buried within the interference from an overwhelming higher number of bulk water molecules. Fortunately, bulk water molecules do not contribute to the measurements of potential variations, and therefore, the laser-induced potential transients reflect selectively the response from interfacial water.

The behavior of interfacial water molecules on platinum single-crystal electrodes, under electrochemical conditions, has been characterized for the first time by means of the laser-induced temperature jump method. The fundamentals of this method and the proposed interpretation of the experimental results will be described in Section V.1 and V.2. Then, recent results on the three platinum basal planes will be discussed in Section V.3. Afterwards, the application of this technique to Pt(111) stepped surfaces will be explained in Section V.4. And finally, results on the effect of the chemical modification of the surface composition of Pt(111) by adatom deposition will be presented in Section V.5.

1. Fundamentals of the Laser-Induced Temperature Jump Method

The laser-induced temperature jump method was developed by Benderskii for the study of mercury electrodes,^{3,50} and was first applied to the study of single-crystal electrodes by Climent et al.²⁰⁻²⁶ This technique is based on the use of short laser pulses to suddenly increase the temperature of a metal|water interphase, in the microsecond time-scale. The wavelength of the laser pulses (in the present experiments, $\lambda = 532$ nm) is selected so that the possibility of electron photoemission can be ruled out (see Appendix 4), and therefore, the only effect caused by the laser illumination is a local increase of temperature. Considering that the laser energy is instantaneously converted into heat at the electrode surface, the temperature change induced by the laser pulse at the interphase can be estimated from (see Appendix 4):

$$\Delta T = \Delta T_0 \left(\frac{\sqrt{t} - \sqrt{t - t_0}}{\sqrt{t_0}} \right) \quad t > t_0 \quad (86)$$

where t_0 is the duration of the laser pulse (in the present experiments, $t_0 = 5$ ns) and ΔT_0 is the maximum temperature change (in the present experiments, $\Delta T_0 \approx 35$ K).

The experimental response towards the laser pulse, under coulometric conditions, is a displacement of the electrode potential from its initial value: $\Delta E = E - E_i$, where E is the electrode potential and E_i is the initial electrode potential (i.e., at $t = 0$). This potential change is essentially given by the response of the interphase. Another contribution is due to the existence of a thermodiffusion potential, between the heated solution at the surface of the electrode and the cold solution near the reference electrode, but this contribution is small under the present experimental conditions, and will be corrected on the bases of the estimation of the thermodiffusion potential described in Appendix 1.

The interfacial response towards the laser heating involves two main contributions:

- (1) The response of the double-layer, associated to the temperature coefficient of the double-layer potential,

$$\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, P, c_i}$$

- (2) The contribution from charge-transfer adsorption processes, resulting from the modification of their equilibrium coverage.

Noteworthy, the double-layer response is, in general, virtually instantaneous within the time scale of the laser-pulsed measurements. Accordingly, under conditions where the contribution from charge-transfer processes is negligible, the laser-induced potential transients, ΔE , would be given by:

$$\Delta E = \left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, P, c_i} \Delta T \text{ (instantaneous double-layer response)} \quad (87)$$

With this, and taking into account that the laser-induced temperature change can be calculated by Eq. (86), the value of

$\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ can be determined from the fit of the measured ΔE values vs. $(\sqrt{t} - \sqrt{t - t_0})$.

On the other hand, the contribution from charge-transfer processes to the laser-induced transients will only be significant if:

- (1) their equilibrium coverage is changed by the laser pulses, and
- (2) their kinetics are fast enough.

Consequently, in order to evaluate the value of

$\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$, one can select experimental conditions under

which the charge-transfer processes are too slow to contribute to the laser-induced response. This can be done by decreasing the concentration of the corresponding species in solution. For instance, hydrogen and OH adsorption on platinum electrodes in 0.1 M $\text{KClO}_4 + 1 \text{ mM HClO}_4$ solutions remain nearly frozen within the time scale of the laser measurements ($t < 10 \mu\text{s}$), and hence the measured potential change represents mainly the response of the double-layer (see below, Section V.3). Indeed, this approach has been taken for the interpretation of the laser-pulsed measurements in Sections V.4 and V.5.

Alternatively, one can perform a full analysis of the laser-induced transients measured at several concentrations of charge-transfer adsorption species. In this way, one can characterize both

the value of $\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ and the kinetics of charge-transfer

adsorption processes. This approach has been followed in Section V.3 for the analysis of the laser-induced transients for Pt(111), Pt(100) and Pt(110) in $(0.1 - x) \text{ M KClO}_4 + x \text{ M HClO}_4$ solutions, where x equals 10^{-4} , 10^{-3} , 10^{-2} and 0.1. This has been achieved through the simulation of the laser-induced transients, according to the following equations. First, the kinetics of hydrogen and OH

adsorption have been modeled by means of Butler-Volmer equations with Frumkin interactions:

$$\text{Pt} + \text{H}^+ + \text{e}^- \rightleftharpoons \text{Pt-H}$$

$$\frac{d\theta_{\text{H}}}{dt} = k_{\text{H}}^0 \left\{ \begin{array}{l} (1 - \theta_{\text{H}}) c_{\text{H}^+} \exp \left[-\frac{0.5}{RT} (FE^{\text{SHE}} + \Delta \bar{G}_{\text{H}}^0 + \omega_{\text{H-H}} \theta_{\text{H}}) \right] \\ - \theta_{\text{H}} \exp \left[\frac{0.5}{RT} (FE^{\text{SHE}} + \Delta \bar{G}_{\text{H}}^0 + \omega_{\text{H-H}} \theta_{\text{H}}) \right] \end{array} \right\} \quad (88)$$

$$\text{Pt} + \text{H}_2\text{O} \rightleftharpoons \text{Pt-OH} + \text{H}^+ + \text{e}^-$$

$$\frac{d\theta_{\text{OH}}}{dt} = k_{\text{OH}}^0 \left\{ \begin{array}{l} (1 - \theta_{\text{OH}}) \exp \left[\frac{0.5}{RT} (FE^{\text{SHE}} - \Delta \bar{G}_{\text{OH}}^0 - \omega_{\text{OH-OH}} \theta_{\text{OH}}) \right] \\ - \theta_{\text{OH}} c_{\text{H}^+} \exp \left[\frac{0.5}{RT} (-FE^{\text{SHE}} + \Delta \bar{G}_{\text{OH}}^0 + \omega_{\text{OH-OH}} \theta_{\text{OH}}) \right] \end{array} \right\} \quad (89)$$

where θ is the normalized coverage; k^0 is the standard rate constant; E^{SHE} is the electrode potential measured vs. an SHE reference electrode; $\Delta \bar{G}^0$ is the Gibbs energy of adsorption at $\theta = 0$; and ω is the lateral interaction parameter. The effect of temperature on k^0 values has been taken into account through:

$$k^0 = k_{T=298\text{ K}}^0 \exp \left(\frac{E_{\text{a}}}{R \cdot 298\text{ K}} - \frac{E_{\text{a}}}{RT} \right) \quad (90)$$

where E_{a} is the activation energy of the reaction, and $k_{T=298\text{ K}}^0$ is the standard rate constant at 298 K. Similarly, the effect of temperature on $\Delta \bar{G}^0$ has also been included, according to:

$$\Delta \bar{G}^0 = \Delta \bar{H}^0 - T \Delta \bar{S}^0 \rightarrow \Delta \bar{G}^0 = \Delta \bar{G}_{T=298\text{ K}}^0 - \Delta \bar{S}^0 (T - 298\text{ K}) \quad (91)$$

where $\Delta \bar{H}^0$ and $\Delta \bar{S}^0$ are the enthalpy and entropy of adsorption at $\theta = 0$; and $\Delta \bar{G}_{T=298\text{ K}}^0$ accounts for the value of $\Delta \bar{G}^0$ at 298 K.

The values of the thermodynamic properties associated to hydrogen and OH adsorption (namely, $\Delta\bar{G}^0$, $\Delta\bar{S}^0$ and ω) have been obtained from the analysis of voltammetric data as a function of temperature, by means of the application of a generalized isotherm. However, since this analysis is performed by using voltammetric data recorded in an isothermal cell, the resulting thermodynamic values correspond to the adsorption reactions under isothermal conditions. Conversely, the laser-pulsed measurements are performed under non-isothermal conditions. Consequently, the simulation of the laser-induced transient should be performed by employing the thermodynamic data corresponding to a non-isothermal cell. For this purpose, the potential values measured in an isothermal cell, referred to a RHE reference electrode at the same temperature as the working electrode, should be converted to a potential scale where the reference electrode is a RHE at 298 K (see Section IV.1). This is equivalent to recalculate the entropy values according to:

$$\Delta\bar{S}_{\text{non-isothermal}}^0 = \Delta\bar{S}_{\text{isothermal}}^0 + z\Delta\bar{S}_{\text{RHE}} \quad (92)$$

where $\Delta\bar{S}_{\text{non-isothermal}}^0$ and $\Delta\bar{S}_{\text{isothermal}}^0$ are the entropy changes associated to the adsorption reactions under non-isothermal and isothermal conditions, respectively; $z = 1$ for hydrogen adsorption and $z = -1$ for OH adsorption; and $\Delta\bar{S}_{\text{RHE}}$ is the entropy change associate

to the reaction on the RHE electrode, $\Delta\bar{S}_{\text{RHE}} = F \frac{d\text{RHE}}{dT}$, where

$\frac{d\text{RHE}}{dT}$ is the temperature coefficient of the 0.1 M HClO₄ RHE.

As before, this later value can be taken from the results of de Bethune on a 0.1 M HCl RHE,²⁹ giving $\frac{d\text{RHE}}{dT} \approx 0.640 \text{ mV K}^{-1}$,

$$\Delta\bar{S}_{\text{RHE}} \approx 61.75 \text{ J mol}^{-1} \text{ K}^{-1}.$$

With this, the simulation of the laser-induced transients has been achieved as follows. As above mentioned, two main effects contribute to the measured laser-induced variation of potential, ΔE . On the one hand, the response from the double-layer is given by the product of the temperature coefficient of the double-layer po-

tential, $\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$, and the laser-induced temperature

change, ΔT . On the other hand, the contribution from charge-transfer reactions originates from the modification of the equilibrium coverage, $\Delta \theta$. Then, since the laser-pulsed experiments are performed under coulostatic conditions (i.e., Q is constant), this modification of the hydrogen or OH coverage produces a corresponding variation on the free charge density, $\Delta \sigma_M$:

$$\Delta Q = \Delta(\sigma_M - F\Gamma_H + F\Gamma_{OH}) = 0 \rightarrow \begin{aligned} \Delta \sigma_M &= F\Delta\Gamma_H \text{ (H adsorption)} \\ \Delta \sigma_M &= -F\Delta\Gamma_{OH} \text{ (OH adsorption)} \end{aligned} \quad (93)$$

Thus, a variation on the equilibrium hydrogen or OH coverage by $\Delta \theta$, produces a variation on the free charge density of $(zQ_{ML}\Delta \theta)$, where $z = 1$ for hydrogen and $z = -1$ for OH adsorption, and Q_{ML} is the charge density associated to adsorption at saturation. With this, the corresponding variation on the electrode potential will be given by $\left(z \frac{Q_{ML}\Delta \theta}{C_{dl}} \right)$, where C_{dl} is the double-layer capacity. In summary, the laser-induced potential transient will be given by:

$$\Delta E = \left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} \Delta T + z \frac{Q_{ML}\Delta \theta}{C_{dl}} \quad (94)$$

Consequently, the laser-induced potential transients can be simulated by the numerical solution of the combination of the Eqs. (88) to (92) and (94). This has been done with a fifth-order Runge-Kuta method with adaptative stepsize implemented in Fortran.⁵¹ As will be shown in Section V.3, this method of analysis is satisfactory for the simulation of laser induced transients for Pt(111), Pt(100) and Pt(110) in $(0.1 - x)$ M $KClO_4 + x$ M $HClO_4$ solutions, with $x = 0.1, 10^{-2}, 10^{-3}$ and 10^{-4} . From these simulations, both the temperature coefficient of the double-layer potential,

$\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$, and the standard rate constant of hydrogen

and OH adsorption, k_H^0 and k_{OH}^0 , are evaluated.

2. Interpretation of the Laser-Pulsed Measurements

A particularly interesting result from the laser-pulsed measurements deals with the determination of the potential where the laser-induced response is negligible. At this potential,

$\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ is negligible. Moreover, according to the

derivation in Section III (Eq. 64), this potential also corresponds to an extremum in the ΔS_{dl} vs. σ_M curve. For the experimental situations studied here, this extremum is a maximum, since

$\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ changes from negative to positive as the

charge density (potential) is increased. In conclusion, the potential of zero response towards the laser heating corresponds to the potential of maximum entropy (E_{pme}) of double-layer formation.

It was shown in Section IV.3 that $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ is

closely related to the entropy of formation of the interfacial water network (Eq. 73), and the potential of water reorientation is very

close to the potential where $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} = 0$. Consequently,

the E_{pme} of double-layer formation can be identified with the potential of water reorientation. This conclusion can also be reached with somewhat different arguments, as shown below.

As already mentioned above, the sign of $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$

provides evidence on the net orientation of interfacial water. In order to demonstrate so, it is convenient to separate the different

contributions to the electrode potential, E^M . In the absence of specific adsorption phenomena, this gives:^{52,53}

$$E^M \equiv \Delta_S^M \phi - \frac{\mu_{e^-}}{F} + \text{constant} \equiv \frac{\Phi}{e} + \delta\chi^M - g^S(dip) + g(ion) + \text{constant}' \quad (95)$$

where Φ is the work function of the metal, $\delta\chi^M$ is the modification of the surface potential of the metal (electron spill-over) produced by the presence of solvent, $g^S(dip)$ is the surface dipole due to the excess of polarization of the solvent molecules at the metal|solution interphase, and $g(ion)$ is the contribution of ions to the potential drop across the double-layer. In concentrated electrolyte solutions, the potential drop across the diffuse double-layer can be neglected, and hence $g(ion)$ can be defined as $g(ion) = \frac{\sigma_M d}{\epsilon \epsilon_0}$,

where d is the thickness of the inner double-layer, σ_M is the free charge density, ϵ is the relative dielectric constant of water at the inner double-layer, and ϵ_0 is the permittivity of free space. Derivation with temperature at constant charge gives the thermal coefficient of the double-layer potential:

$$\begin{aligned} \left(\frac{\partial \Delta E^M}{\partial T} \right)_{\sigma_M} &\equiv \left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} + \frac{\bar{S}_{e^-}}{F} \\ &\equiv \frac{1}{e} \frac{d\Phi}{dT} + \frac{d(\delta\chi^M)}{dT} - \frac{d[g^S(dip)]}{dT} \end{aligned} \quad (96)$$

In the above equation, it has been taken into account that the constant in Eq. (95) does not vary with the temperature, and also, that the temperature dependence of the ionic contribution, $g(ion)$, can be considered as zero, since d and ϵ are molecular properties that should be only weakly dependent on the temperature.⁵⁴

The first term in the right-hand side of Eq. (96) corresponds to the thermal coefficient of the work function of the electrode, and it is usually small (for a Pt(111) electrode: $(d\Phi/dT)/e \approx -0.15 \text{ mV/K}$).⁴² The second term is usually considered to be negli-

gible.³⁶ Consequently, it can be concluded that the thermal coefficient of the double-layer potential is mainly determined by the temperature dependence of the dipole potential of the solvent network, $d[g^S(dip)]/dT$.

Furthermore, the sign of $d[g^S(dip)]/dT$ provides evidence on the net orientation of the water network at the interphase, $g^S(dip)$. This is because an increase in the temperature will induce a disordering of the water network, thus decreasing the absolute value of $g^S(dip)$. Therefore, when water molecules are oriented with the hydrogen towards the metal, giving a positive contribution to the overall potential drop ($g^S(dip) < 0$), the effect of the increase of temperature will be to decrease this positive contribution, resulting in a negative contribution to dE^M/dT . Following the same arguments, when the net orientation of the water network is with the oxygen towards the metal, ($g^S(dip) > 0$) its response towards the laser heating will result in a positive contribution to dE^M/dT . Finally, between these situations, there is a potential value where $d[g^S(dip)]/dT = 0$, which will correspond to the potential where $g^S(dip) = 0$. This potential of water reorientation will correspond to a maximum configurational entropy of the water adlayer, and can be identified with the E_{pme} .

The following Sections will summarize some recent results on the application of the laser-induced temperature jump method to characterize the net orientation of interfacial water on platinum single-crystal electrodes, under electrochemical conditions.

3. Pt(111), Pt(100) and Pt(110)

The behavior of interfacial water on the three platinum basal planes, under electrochemical conditions, has been studied, for the first time, by means of the laser-induced temperature jump method.²⁰ Moreover, the comparison of these results with charge density data has contributed to the understanding of the electrostatic and chemical interactions governing the reorientation of the interfacial water network on platinum electrodes. Below we provide a brief summary of the main results of this study.

The laser-pulsed measurements on Pt(111), Pt(100) and Pt(110) were performed in $(0.1 - x)$ M $KClO_4 + x$ M $HClO_4$ solutions, where x equals 10^{-4} , 10^{-3} , 10^{-2} and 0.1. These solution compositions were selected in order to minimize the extent of anion

specific adsorption. In addition, the use of solutions of different pH is useful to identify the contributions from the double-layer and charge-transfer processes to the laser-induced potential transients, as explained in Section V.1. Figure 12 shows the cyclic voltammograms for Pt(111), Pt(100) and Pt(110), in 0.1 M HClO₄ and 0.1 M KClO₄ + 1 mM HClO₄ solutions. The characteristic profiles of the voltammograms reveal that the surfaces are highly well-ordered, and virtually free of uncontrolled contaminants. Figure 13 shows laser-induced potential transients for Pt(111), Pt(100) and Pt(110) in 0.1 M KClO₄ + 1 mM HClO₄ and 0.1 M HClO₄ solutions, at selected potentials. Under the experimental conditions in Fig. 13, the laser-induced transients exhibit a small (or negligible) contribution from hydrogen and OH adsorption kinetics, and therefore, they mainly reflect the temperature coefficient of the double-

layer potential, $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, F_H, F_{OH}, p, c_i}$ (see Section V.1). It is ob-

served that, in all cases, transients are negative at low potentials, and they become positive at higher potentials. According to the discussion in Section V.2, this evidences that the interfacial water network on the three platinum basal planes, exhibits a net orientation with the hydrogen towards the metal at low potentials, and then, as the applied potential increases, the interfacial water molecules turn over to the oxygen-towards-the-metal orientation. Moreover, it is observed that the potential of water orientation, as determined from the potential of zero transient or E_{pme} , is very sensitive to the surface structure.

On the other hand, at certain selected potentials, the laser-induced transients for platinum electrodes in 0.1 M HClO₄ solutions exhibit clear contributions from kinetics of charge-transfer processes. As a result, the laser-induced transients exhibit a non-monopolar decay and, in some cases, a marked bipolar shape is observed. Figure 14 illustrates this behavior. Figure 14A shows that, for the three platinum basal planes, transients at $E = 0.10$ V vs. RHE exhibit a bipolar shape, with a sharp negative peak at very short times, $t < 0.5$ μ s, and a broader positive contribution at

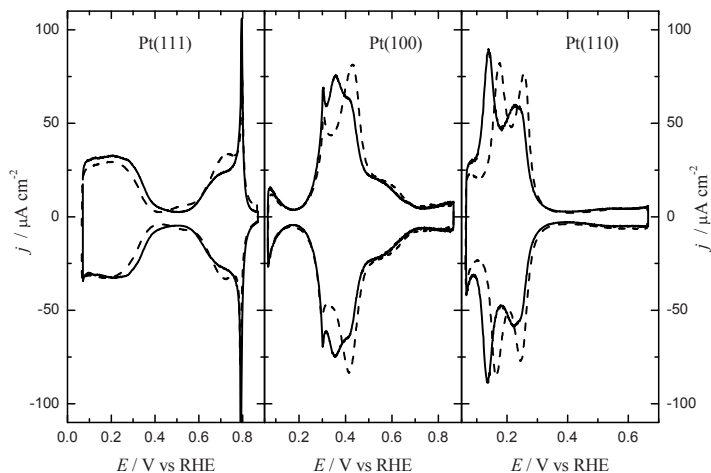


Figure 12. Cyclic voltammograms for Pt(111), Pt(100) and Pt(110) in 0.1 M HClO_4 (solid lines) and 0.1 M KClO_4 + 1 mM HClO_4 (dashed lines). Scan rate: 50 mV/s. Adapted from Ref. 20.

longer times, $t > 1 \mu\text{s}$. Interestingly, the time scale where the positive contribution takes place, strongly depends on the platinum surface structure. This is due to the different kinetics of hydrogen adsorption on the three basal planes, as will be shown below. On the other hand, Fig. 14B shows that the laser-induced transient for Pt(110) at $E = 0.35 \text{ V vs. RHE}$ shows a very marked bipolar shape, whose origin will be described below. Finally, Fig. 14C shows that the laser-induced transient for Pt(111) at $E = 0.75 \text{ V vs. RHE}$ exhibits a noticeable bipolar shape, which can be ascribed to the kinetics of OH adsorption, as will be shown below.

The bipolar shape of the laser-induced transients within the hydrogen adsorption region (Fig. 14A), has been explained as follows.^{20,23} The negative fast contribution can be ascribed to the

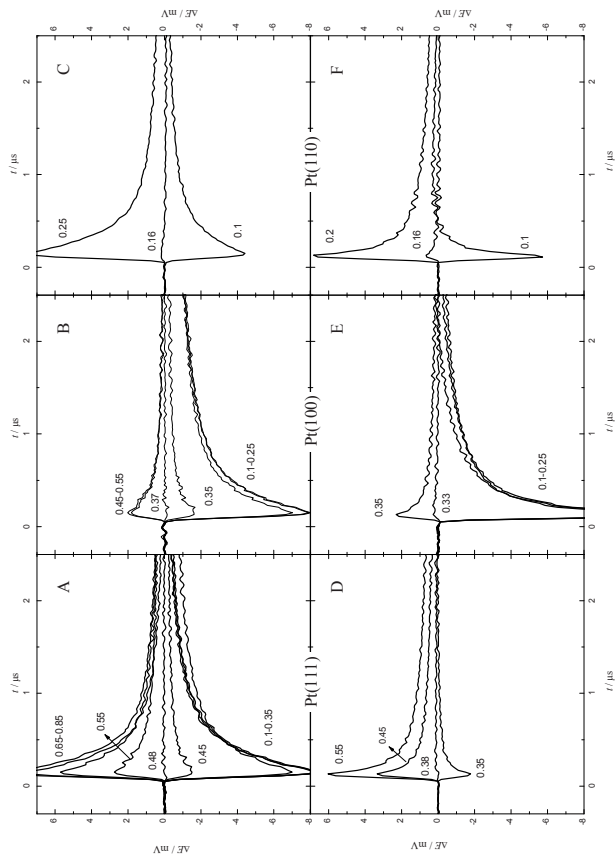


Figure 13. Laser-induced transients for Pt(111), Pt(100) and Pt(110) in 1 mM HClO₄ + 0.1 M KClO₄ (A,B,C) and 0.1 M HClO₄ (D,E,F), at selected potentials vs. RHE. Adapted from Ref. 20.

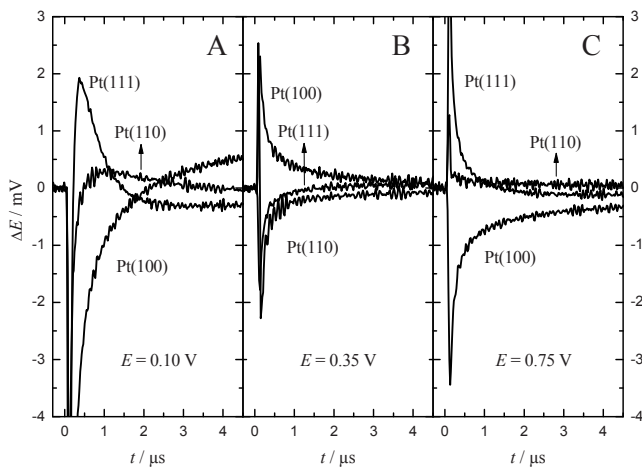


Figure 14. Comparison of the laser-induced transients obtained for Pt(111), Pt(100) and Pt(110) in 0.1 M HClO_4 at (A) $E = 0.10$ V, (B) $E = 0.35$ V, and (C) $E = 0.75$ V vs. RHE. Adapted from Ref. 20.

double-layer response, and its negative sign implies that the thermal coefficient of the double-layer potential, $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$,

is negative. This initial change of the potential induces a subsequent increase on the hydrogen coverage. Since hydrogen adsorption withdraws electrons from the surface, this second process produces a positive displacement of the potential at longer times (see Section V.1, Eq.94). As a consequence of these opposing effects (namely, the double-layer response and hydrogen adsorption) the transients in Fig. 14A exhibit a bipolar shape.

When the proton concentration is decreased, the rate of hydrogen adsorption is slowed down (Eq. 88). As a result, the simulation of the transients at different pH's allows the characterization of both the hydrogen adsorption kinetics and the thermal coefficient of the double-layer potential, as explained in Section V.1.

Figure 15 illustrates this behavior through the comparison of the simulations with the experimental data for Pt(111) at $E = 0.10$ V vs. RHE in $(0.1 - x)$ M $\text{KClO}_4 + x$ M HClO_4 solutions, where x equals 10^{-4} , 10^{-3} , 10^{-2} and 0.1 . Reasonable good agreement is observed between the simulated and experimental curves. Noteworthy, the four curves in Fig. 15A have been obtained with the same value of the thermal coefficient of the double-layer potential

$$\left[\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, P, C_i} = -3 \text{ mV/K} \right] \text{ and the standard rate constant for}$$

hydrogen adsorption ($k_H^0 = 10^{4.5} \text{ s}^{-1}$). The only parameter that was varied is the proton concentration.

Following this strategy, the standard rate constant for hydrogen adsorption on Pt(100) and Pt(110) have also been evaluated, concluding that $k_H^0 \approx 10^{3.4}$ and $10^{4.8} \text{ s}^{-1}$, respectively. Similarly, the kinetics of OH adsorption on Pt(111) have also been characterized.

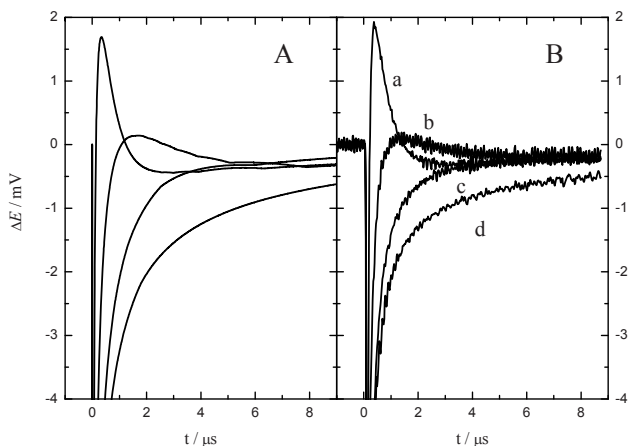


Figure 15. Comparison of the simulated (A) with experimental (B) laser-induced transients for Pt(111) at $E = 0.10$ V vs. RHE. A) Simulated curves with $\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, P, C_i} = -3 \text{ mV/K}$ and $k_H^0 = 10^{4.5} \text{ s}^{-1}$. B) Experimental curves in $(0.1 - x)$ M $\text{KClO}_4 + x$ M HClO_4 , where x equals: a) 0.1 , b) 10^{-2} , c) 10^{-3} and d) 10^{-4} . Adapted from Ref. 20.

Figure 16 compares the results of the simulations with the experimental laser-induced transients, for Pt(111) at $E = 0.75$ V vs. RHE in perchlorate solutions of pH = 1–4. For these calculations, constant values for the thermal coefficient of the double-layer potential $\left[\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} = 1.5 \text{ mV/K}\right]$ and the standard

rate constant for OH adsorption [$k_{OH}^0 = 10^{4.7} \text{ s}^{-1}$] have been employed. The calculated and experimental curves exhibit clear deviations for pH = 1 at $t > 1 \mu\text{s}$, likely due to the oversimplifications involved in the description of the OH adsorption process by means of Butler-Volmer equations with Frumkin-type interactions (Eq. 89). However, it is reasonable to assume that the present analysis is adequate for the estimation of the thermal coefficient of the double-layer, within the OH adsorption region.

Finally, as above mentioned, it is observed that laser-induced transients for Pt(110) at $E = 0.35$ V vs. RHE in 0.1 M HClO_4 solu-

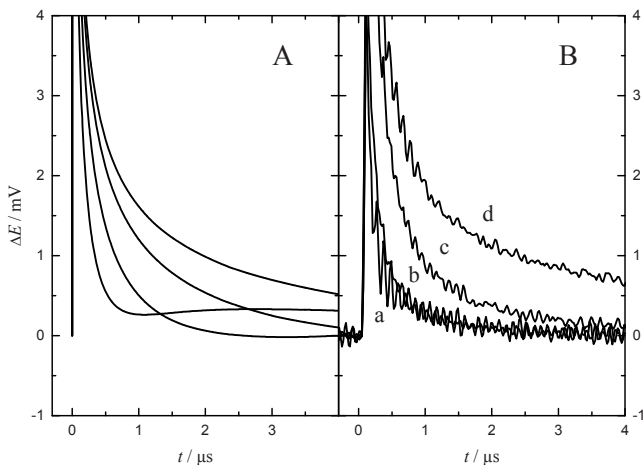


Figure 16. As in Fig. 15, but at $E = 0.75$ V vs. RHE, and calculated curves with $\left(\frac{\partial \Delta_s^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} = 1.5 \text{ mV/K}$ and $k_{OH}^0 = 10^{4.7} \text{ s}^{-1}$. Adapted from

Ref. 20.

tion (Fig. 14B) exhibit a marked bipolar shape, with a fast, positive contribution at $t < 0.1 \mu\text{s}$, followed by a slower, negative contribution at longer times. The origin of this bipolar shape cannot be ascribed to the kinetics of hydrogen or OH adsorption, since this shape prevails in a broad potential window (0.35–0.65V), where no charge-transfer processes are observed in the voltammograms of Fig. 12. Consequently, this bipolar shape has to be ascribed to the fact that the reorganization of the interfacial water adlayer exhibits a relatively slow response time. As a result, the evaluation of the thermal coefficient of the double-layer potential, under these conditions, is very uncertain, since its value will be given by the sum of two contributions of opposite sign. Interestingly, a similar behavior is observed for Pt(111) stepped surfaces, and will be discussed in Section V.4.

In summary, the careful analysis of laser-induced transients for the three platinum basal planes in $(0.1 - x) \text{ M KClO}_4 + x \text{ M HClO}_4$ solutions have allowed decoupling the double-layer response and hydrogen and OH adsorption contributions. In this way, the thermal coefficient of the double-layer potential,

$\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$, has been evaluated. Selected results are

shown in Fig. 17. As explained in Section V.2,

$\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$ is essentially given by the induced change in

polarization of the interfacial water network, which in turn is given by the net orientation of interfacial water. In view of Fig. 17, it is concluded that, in all cases, water exhibits a net orientation with the hydrogen towards the metal at low enough potentials. Then, when the applied potential is increased, the oxygen towards the metal orientation is favored. In addition, a clear effect of the surface structure on the value of potential of water orientation [as

determined from the potential where $\left(\frac{\partial \Delta_S^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} = 0$, or

potential of maximum entropy, E_{pme}] is observed. The pH-dependence of E_{pme} values is also strikingly different for the three basal planes. The origin of these differences is discussed below.

As a result of the electrostatic interaction of water dipoles with the electric field at the interphase, the net orientation of the interfacial water network is expected to be strongly influenced by the electronic charge density on the metal. In this regard, it should be recalled that for platinum electrodes, due to the existence of adsorption processes involving charge-transfer, it is necessary to distinguish between two types of charge (see Section III, Eq. 43). While the free charge is the actual electronic charge on the metal, the total charge takes into account the charge involved in charge-transfer adsorption processes. Unfortunately, free charge density values have been only evaluated for Pt(111) (Section IV.2). However, total charge density data has been determined with high precision for the three platinum basal planes, with the help of the CO displacement technique.²⁰ Selected results are included in Fig. 17.

In view of the comparison of the results of $\left(\frac{\partial \Delta_S^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$

with charge density data in Fig. 17, it is concluded that both quantities are closely related. Accordingly, the net orientation of the interfacial water adlayer on the three platinum basal planes is clearly correlated with the total charge density. In particular, it is observed that the potential of water reorientation, as identified

with the E_{pme} or potential where $\left(\frac{\partial \Delta_S^M \phi}{\partial T}\right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i} = 0$, is fairly

close to the potential of zero total charge, E_{pztc} . Figure 18 compares the E_{pme} with the E_{pztc} for the three basal planes, plotted as a function of the logarithm of the proton concentration. It should be recalled that, for Pt(111), $E_{pzfc} \cong E_{pztc}$ (see Section IV.2). This is due to the fact that the E_{pztc} is located within the double-layer region. Furthermore, the fact that, for Pt(111), the E_{pme} and the E_{pztc} are essentially equal, gives support to this assignment. Moreover, the fit of E_{pme} and E_{pztc} values vs. the logarithm of the proton concentration gives a slope of -0.060 V/dec. This value of the slope is due to the variation of the value of the RHE reference electrode with the proton concentration. If E_{pme} and E_{pztc} values are given vs. an SHE scale, then it is concluded that both E_{pme} and E_{pztc} values are essentially independent of the proton concentration. In turn, this corroborates that the extent of hydrogen and OH adsorption is essentially negligible at these potentials (Eq. 122).

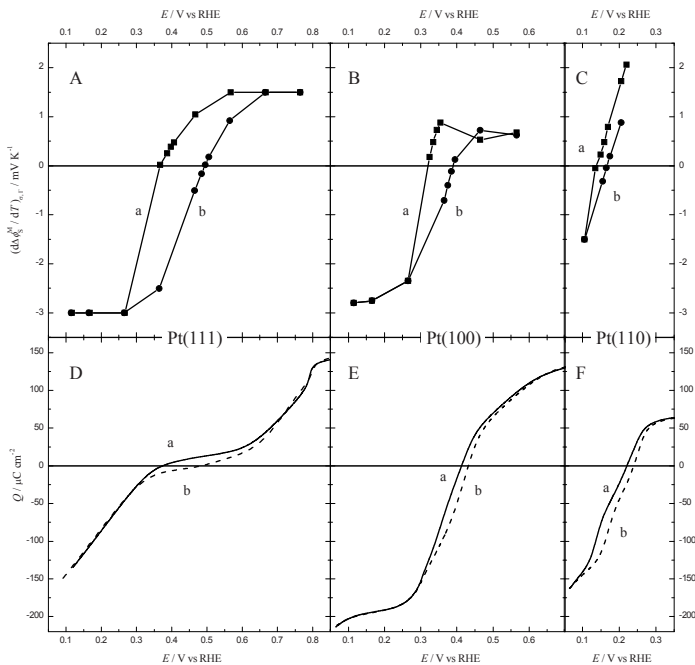


Figure 17. Temperature coefficient of the double-layer potential (A, B,C) and total charge density data (D,E,F) for Pt(111), Pt(100) and Pt(110) electrodes in: a) 0.1 M HClO_4 , b) 0.1 M $\text{KClO}_4 + 1 \text{ mM HClO}_4$. Adapted from Ref. 20.

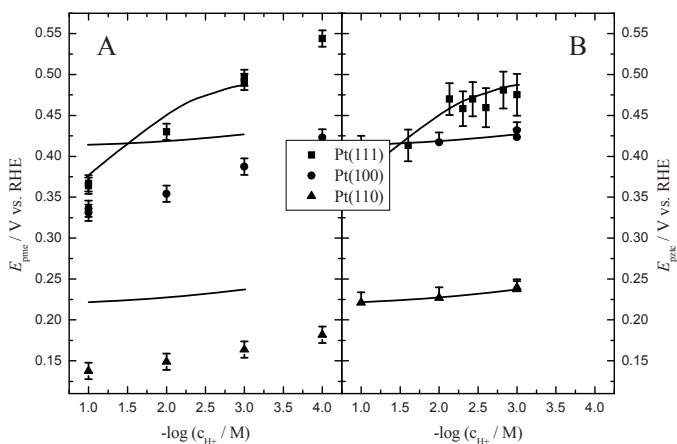


Figure 18. Values of E_{pme} (A) and E_{pztc} (B) for Pt(111), Pt(100) and Pt(110) electrodes in $(0.1 - x)$ M $\text{KClO}_4 + x$ M HClO_4 solutions, plotted against the logarithm of the proton concentration. Lines indicate the tendencies of E_{pztc} values, and they are reproduced in the left figure in order to facilitate the comparison. Adapted from Ref. 20.

Noteworthy, the relationship between the E_{pme} and the E_{pzfc} gives insight into the chemical interactions between water molecules and the platinum surface. If, in the absence of electrostatic interactions (i.e., at $\sigma_{\text{M}} = 0$), water adsorption was favored with the oxygen towards the metal, then the E_{pme} would be lower than the E_{pzfc} , since negative charge would be needed to compensate this chemical, preferential interaction, and to achieve the degree of maximum disorder of the water adlayer. The opposite would be true for a preferential orientation with the hydrogen towards the metal, which would lead to $E_{\text{pme}} > E_{\text{pzfc}}$. In conclusion, the close similarity between the E_{pme} and the E_{pzfc} for Pt(111) indicates that interfacial water molecules on Pt(111) exhibit a small net orientation at $\sigma_{\text{M}} = 0$. That is, chemical interactions play a minor role on the net orientation of the interfacial water network on Pt(111). In this regard, DFT calculations showed that the adsorption energies of water monolayers on Pt(111) in the oxygen-towards-the-metal and the hydrogen-towards-the-metal orientations are very simi-

lar,⁵⁵⁻⁵⁷ indicating that the actual structure of the water adlayer on the Pt(111) at $\sigma_M = 0$ can be a mixture of these configurations.

Unfortunately, the comparison of E_{pme} and E_{pzfc} values cannot be performed for Pt(100) and Pt(110) electrodes, because the corresponding E_{pzfc} values are not available at present. For these surface structures, the E_{pme} and the E_{pztc} are located in a potential region where hydrogen and OH coadsorb, as evidenced by the fact that their dependence on pH is less than 0.06 V/dec (see Eq. 122): the variation of E_{pme} values against the logarithm of the proton concentration is -0.030 V/dec for Pt(100) and -0.015 V/dec for Pt(110), while the corresponding slope for E_{pztc} values is -0.008 and -0.009 V/dec, respectively. However, the relative position of E_{pme} values, for the three basal planes, agrees well with the difference in work function values: the difference of E_{pme} values for Pt(100) and Pt(110), with respect to Pt(111), is ca 0.1 and 0.3 V, respectively, while the change in work function is 0.09 eV and 0.26 eV.^{58,59} This agreement suggests that the E_{pme} for Pt(100) and Pt(110) are close to the E_{pzfc} , despite the presence of coadsorbed hydrogen and OH. Accordingly, the net orientation of the interfacial water network at $\sigma_M = 0$ would be small. This agrees with DFT calculations of water monomers on the three platinum basal planes, concluding that water adsorbs with its molecular plane nearly parallel to the surface.⁶⁰

4. Pt(111) Stepped Surfaces

It is well-known that fundamental studies with the three platinum basal planes [Pt(111), Pt(100) and Pt(110)] are very valuable for the molecular-level understanding of the electrochemical reactivity. Nevertheless, from a practical point of view, the behavior of such electrodes is still very different from that observed in polycrystalline materials and nanoparticles. For this reason, the knowledge obtained with these basal plane electrodes cannot be directly extrapolated to real catalysts. In this regard, the use of stepped single-crystal electrodes has proven very useful to bridge the gap between the low index single crystals and the real electrodes.

Pt(111) stepped surfaces consist of a succession of (111) terraces, separated by monoatomic steps of (111) or (100) symmetry. Depending on the symmetry of the step site, these surfaces are

denoted as Pt(S)[$n(111) \times (111)$] or Pt(S)[$n(111) \times (100)$], where n is the number of atomic rows on the terraces. The Miller indices of these sets of surfaces are Pt($n, n, n - 2$) and Pt($n + 1, n + 1, n - 1$), respectively.

Figure 19 shows the cyclic voltammograms for Pt(111), Pt(755) and Pt(555) in 0.1 M HClO₄ and 1 mM HClO₄ + 0.1 M KClO₄ solutions. The same characteristic features are observed in both solution compositions, the most important being the peak that appears in the hydrogen adsorption region as a consequence of the introduction of step sites. This peak has been usually ascribed to hydrogen adsorption on the step sites,^{61,62} but the results of the laser-induced temperature jump method suggest that this voltammetric process also involves the competitive coadsorption of strongly-bonded water or oxygenated species.²⁶

The careful analysis of the laser-induced transients for Pt(111) stepped surfaces evidences the existence of two potential values where the double-layer temperature coefficient change sign from negative to positive. According to the preceding thermodynamic analysis, this implies the existence of two relative maxima in the entropy of formation of the double layer, or in brief, the presence of two E_{pme} 's.²⁶ The first E_{pme} is close to the peak potential of the step voltammetric peak, and it is absent for Pt(111). Therefore, this E_{pme} can be ascribed to a local E_{pme} associated with the steps. On the other hand, the second E_{pme} takes place within the double-layer region, and it is similar to that of Pt(111). Thus, it can be attributed to the local E_{pme} of the terraces.

The existence of two local E_{pme} 's is likely related to local E_{pzfc} 's. Accordingly, the reorientation of interfacial water would be closely related to the change of sign of the free charge density on step and terrace sites. In this regard, the presence of local E_{pztc} 's on Pt(111) stepped surfaces has been demonstrated by a kinetic study of N₂O reduction.⁶³ However, it should be pointed out that the local E_{pme} 's cannot be ascribed to the local reorientation of water molecules adsorbed on the step or terrace sites, since the laser-induced transient reflects the response of the whole water adlayer. In this regard, the present results evidence the presence strong cooperative effects in the interfacial water network. That is, the change of sign of the local free charge density on the steps (or terrace) sites, induces the reorientation of the nearby water mole-

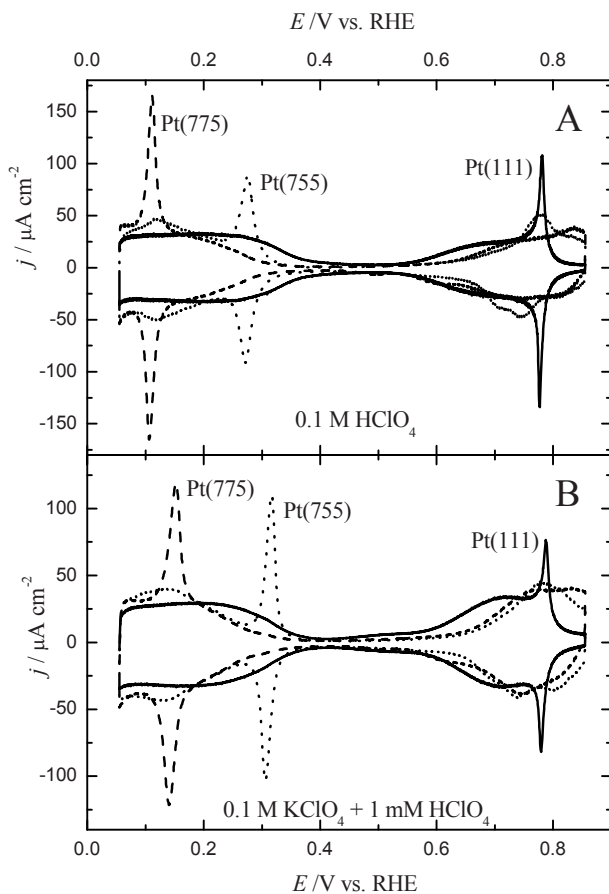


Figure 19. Cyclic voltammograms for Pt(111), Pt(775) and Pt(755) in (A) 0.1 M HClO_4 and (B) $0.1 \text{ M KClO}_4 + 1 \text{ mM HClO}_4$. Scan rate: 50 mV/s . Adapted from Ref. 26.

cles, and this fact, in turn, triggers the reorientation of the whole interfacial water adlayer.

Interestingly, the two local E_{pme} 's exhibit a distinctly different dependence on the step density, as illustrated in Fig. 20. It is ob-

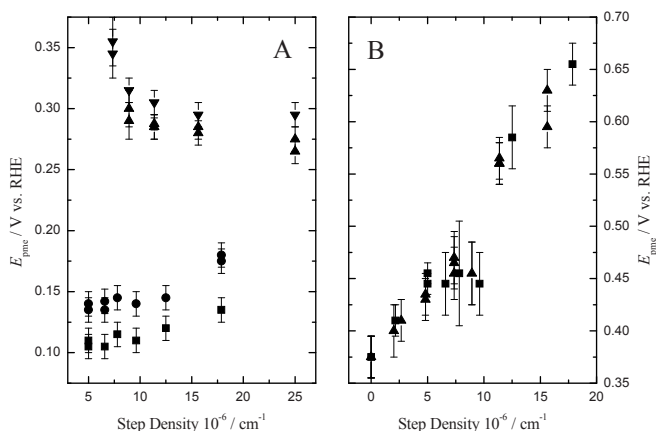


Figure 20. Values of E_{pme} associated to (A) the step and (B) terrace sites, for Pt(S)[$n(111)x(111)$] (squares, circles) and Pt(S)[$n(111)x(111)$] (up- and down-triangles) surfaces, in 0.1 M HClO_4 (squares, up-triangles) 0.1 M $\text{KClO}_4 + 1 \text{ mM HClO}_4$ (circles, down-triangles), plotted as a function of the step density. Adapted from Ref. 26.

served that, while the local E_{pme} associated with the steps is essentially independent of the terrace length, the E_{pme} associated with the terraces clearly increases as the terraces become narrower. Thus, it can be concluded that the interaction of interfacial water with platinum step sites is, effectively, one-dimensional. Conversely, the interaction of interfacial water with platinum terrace sites is clearly sensitive to the bidimensional order.

Finally, the presence of steps produces also a significant decrease on the reorganization rate of the interfacial water adlayer, at potentials within the double-layer region. This effect is more marked at $\text{pH} = 3$ than at $\text{pH} = 1$. This leads to the observation of potential transients with long relaxation times after the laser heating, at potentials near the E_{pme} associated with the terraces. The shape of these transients can be mathematically described with the following equation (see Appendix 5):

$$\Delta E = \xi_1 \Delta T(t) + \frac{\xi_2}{\tau} \int_0^t \Delta T(t') \exp\left(-\frac{t-t'}{\tau}\right) dt' \quad (97)$$

corresponding to a response composed of two contributions: a virtually instantaneous response, whose temperature coefficient equals ξ_1 , and a slower response with characteristic response time τ and temperature coefficient ξ_2 . ΔT is the temperature change at the interphase, which can be estimated from Eq. (86). Similar results have also been observed for Pt(110) (see Section V.3), which can also be considered as a highly stepped surface: Pt(S)[2(111)x(111)]. Analysis of the transients with Eq. (97) reveals that τ markedly increases with the step density and decreases with the pH. First, regarding the effect of the step density, since cooperative effects play a major role on the reorientation dynamics of the interfacial water network, it is believed that the slowing-down of the reorientation rate is related to the fact that the hydrogen-bonding between adjacent water molecules becomes weaker in the presence of steps. Indeed, DFT calculations show that lateral interactions between neighboring water molecules, as estimated from the difference in adsorption energy of a monolayer and a monomer, are much smaller for Pt(110) than for Pt(111): 0.128 and 0.218 eV, respectively.^{56,64}

On the other hand, for both Pt(110) and Pt(111) stepped surfaces, it is observed that the reorientation kinetics of the water adlayer becomes slower as the proton concentration decreases. This behavior could be explained by an acid-catalysis mechanism. In order to check this hypothesis, the laser-induced transients of Pt(110) in $(0.1 - x)$ M $\text{KClO}_4 + x$ M HClO_4 solutions, where x equals 10^{-4} , 10^{-3} , 10^{-2} and 0.1, were fitted with expression (97). The result shows that, as expected for an acid-catalysis mechanism, the reaction rate is proportional to the proton concentration, and hence, the response time is inversely proportional to the proton concentration. Figure 21 compares the simulated and experimental curves. The good agreement between these curves corroborates the hypotheses of an acid-catalysis mechanism.

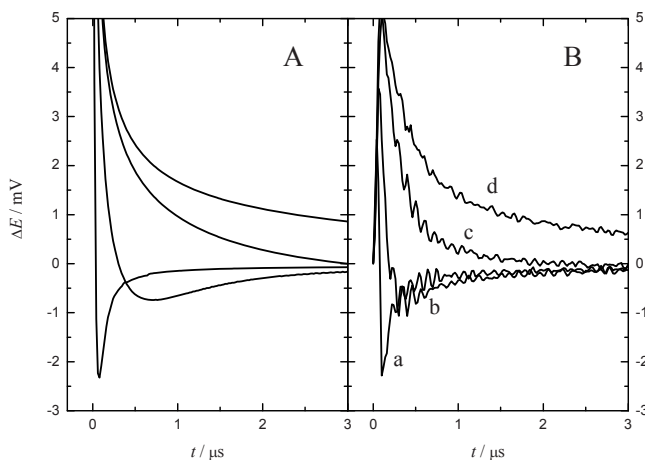


Figure 21. As in Fig. 15, but for Pt(110) at $E = 0.35$ V vs. RHE, and calculated curves consisting on an virtually instantaneous response with $\xi_1 = 1$ mV/K and a slower response with $\xi_2 = -1.2$ mV/K and response time $\tau = (0.004/c_{\text{H}^+}) \mu\text{s}$. Adapted from Ref. 20.

5. Adatom Modified Surfaces

The development of new electrocatalytic materials by deposition of foreign adatoms on a host metal is currently a very active area of research in electrochemistry. In this regard, most of the studies have been focused on platinum as a substrate, due to the very high reactivity of this metal for fuel-cell reactions. Still, a surface modifier is necessary to improve the catalytic activity and stability of the electrode and to avoid side poisoning reactions. It has been shown that the modification of platinum surfaces with submonolayer amounts of elements of the p-block of the periodic table leads, in many cases, to electrode materials with greatly improved catalytic properties.⁶⁵⁻⁶⁷

Nevertheless, the molecular-level understanding of the catalytic enhancement is, in general, not well established. In this regard, three main effects are usually invoked to explain the catalytic enhancement: the electronic (ligand) effect, associated with chang-

es in the electronic properties of the substrate; the ensemble (geometrical) effect, related to changes in the occupancy of adsorption sites of a given geometry; and the bifunctional effect, where the surface species provide one of the necessary reactant sites. The separation of these effects is usually difficult.^{67,68} However, it has been shown that the laser-induced temperature method provides valuable information on the electronic effects associated with adatom deposition.²¹

Figure 22 shows selected laser-induced transients for a Pt(111) electrode modified by the deposition of selenium and lead in 0.1 M $\text{KClO}_4 + 1 \text{ mM HClO}_4$ solutions. Under these conditions, the laser-induced transients essentially reflect the temperature coefficient of the double-layer, $\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, F_H, F_{OH}, p, c_i}$, as explained in

Section V.1. The effect of selenium and lead deposition is illustrated in Fig. 22 because these cases provide representative examples for all studied adatoms. Results for the unmodified Pt(111) are also included in this figure for the sake of comparison.

In all cases, it is observed that the laser-induced transients are negative at low enough potentials, indicating that interfacial water molecules exhibit a net orientation with hydrogen towards the metal. Then, as the potential is increased, the oxygen-towards-the-metal orientation is favored and the laser-induced potential transients become positive. The potential where the transients change sign corresponds to the E_{pme} , as above explained in Section V.2. Noteworthy, the value of the E_{pme} depends strongly on the surface composition of the electrode. Therefore, it is particularly interesting to evaluate the effect of the adatom coverage on E_{pme} .

Values of E_{pme} for selenium, sulfur, bismuth and lead modified Pt(111) electrodes in 0.1 M $\text{KClO}_4 + 1 \text{ mM HClO}_4$ solutions, are plotted in Fig. 23 as a function of the adatom coverage. Close inspection of this graph shows that a small, but measurable increase in E_{pme} values is induced by all studied adatoms at low coverages. The origin of this behavior is not clear. The disruption of a hypothetical preferential structure with the oxygen towards the metal on the bare Pt(111) at $E = E_{\text{pzfc}}$ was tentatively proposed to explain this behavior in Ref. 21. Accordingly, the E_{pme} of the bare Pt(111) would be lower than the E_{pzfc} , and the disruption of this

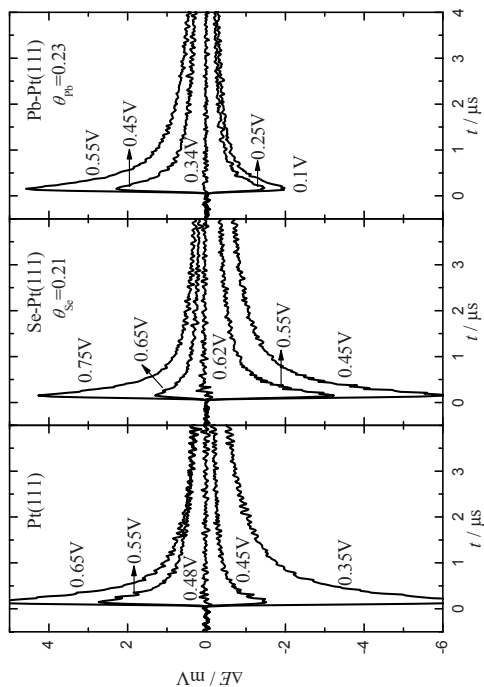


Figure 22. Laser-induced transients for a bare, Se-modified and Pb-modified Pt(111) electrodes in 0.1 M KClO_4 + 1 mM HClO_4 , at selected potentials vs. RHE. Adapted from Ref. 21.

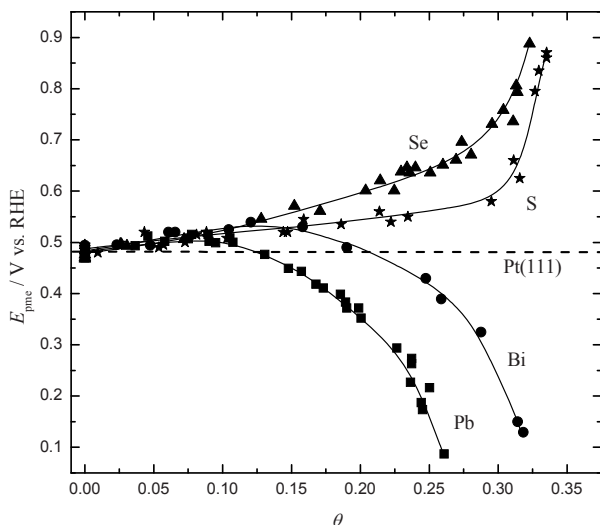


Figure 23. Values of E_{pme} for adatom-modified Pt(111) electrodes in 0.1 M KClO_4 + 1 mM HClO_4 , plotted as a function of the adatom coverage. Pb: squares, Bi: circles, Se: triangles, S: stars. The dotted, zero-slope line corresponds to the mean E_{pme} value of the unmodified Pt(111). Adapted from Ref. 21.

hypothetical preferential structure by adatom deposition would produce an increase in E_{pme} values, in order to approach the E_{pzfc} . Nevertheless, the analysis in Section V.3 demonstrated that for the bare Pt(111), $E_{\text{pme}} \approx E_{\text{pzfc}}$. Unfortunately, the uncertainty in the determination of these fundamental quantities is not enough to decide on the validity of this hypothesis. Therefore, the clarification of this point seems to require the development of alternative experimental methods for the characterization of the interfacial water structure on platinum single-crystal electrodes.

On the other hand, the results obtained in the medium-high coverage region have a more straightforward explanation. In this region, two different behaviors are observed, represented by S and

Table 2
Work Function Values, Φ , and Electronegativities, χ , of
Elements Studied in the Present Work

	Φ/eV	χ
Bi	4.29 ^a	1.9 ^c
Pb	4.01 ^a	1.81 ^c
Se	5.9 ^b	2.55 ^c
S	6.2 ^d	2.58 ^c
Pt	5.40 ^a	2.2 ^c

a: from Ref. 92, b: from Ref. 93, c: from Ref. 81, d: estimated from χ_s in Ref. 94

Se, on the one hand, which displace the E_{pme} towards higher values, and Bi and Pb, on the other hand, which clearly decrease the E_{pme} .

These trends can be easily explained by considering the differences in work function values and electronegativities (see Table 2) between the adatom and the platinum substrate: more electropositive adatoms (Bi and Pb) shift the E_{pme} towards lower potential values, while more electronegative adatoms (Se and S) displace the E_{pme} towards higher potential values. This effect can be explained by taking into account the formation of surface dipoles induced by the adatom adsorption. The more electropositive adatoms will tend to retain a partial positive charge density, thus favoring the reorientation of interfacial water with the oxygen towards the metal. Opposite arguments hold for the more electronegative adatoms, whose partial negative charge density will favor the hydrogen-towards-the-metal orientation.

According to the above explanation, the effect of adatom deposition on the potential of water reorientation is dominated by electrostatic effects. Other possible effects, such as chemical interactions between water molecules and the adatoms, seem to play a minor role, in view of the good correlation between the displacement of E_{pme} values and the adatom electronegativity. Accordingly, the main effect of adatom deposition would be to displace the E_{pzfc} (or equivalently, the work function)⁵² of the adatom-modified surface. Indeed, marked decreases of the work function of Pt(111) due to lead⁶⁹ and bismuth⁷⁰ deposition have been reported. This decrease is consistent with the formation of surface dipoles with negative charge on the metal and positive charge on the adatom, as proposed to explain the decrease on E_{pme} values by Bi and Pb

deposition. However, adsorption of sulfur at a saturation coverage of $\theta_s = 0.33$ produces a negligible change of the work function of a Pt(111) electrode, and a maximum decrease of ≈ -0.3 eV is observed at $\theta_s \approx 0.2$.^{71,72} These changes are not in accordance with the trend of the E_{pme} observed in the present work. This discrepancy is probable related to the very different experimental conditions associated to the electrochemical and UHV measurements.

An alternative method to study electronic effects induced by adatom modification on platinum electrodes is based on the analysis of the vibrational frequencies of coadsorbed CO. This method is based on the fact that the CO stretching frequency is sensitive to the ability of the substrate to backdonate electronic density towards the antibonding $2\pi^*$ orbital. This backdonation results in a weakening of the C $\equiv$ O bond and decreases the vibrational frequency. Accordingly, a decrease (increase) on the E_{pzfc} of the substrate would lead to a decrease (increase) of the CO stretching frequency. Indeed, under electrochemical conditions, it has been shown that bismuth⁷³⁻⁷⁶ and lead⁷⁷ adsorption on Pt(111) causes a displacement of the CO stretching frequency to lower values, while sulphur causes an increase on the CO vibrational frequency. These trends are in agreement with the proposed explanation for the change of the E_{pme} by adatom deposition.

In summary, the application of the laser-induced temperature jump method to adatom modified Pt(111) electrodes provides novel information of the behavior of interfacial water on bimetallic surfaces. Moreover, the evolution of the potential of water reorientation with the adatom coverage provides experimental evidence on the sign of the surface dipole induced by the adatom adsorption. The formation of this surface dipole results from the fact that more electropositive (electronegative) adatoms retain a partial positive (negative) charge density. Consequently, local variations of the E_{pzfc} values are induced by the adatom adsorption, modifying the electronic properties of the substrate. The resulting effect on the electronic density on the substrate is important to understand the so-called electronic or ligand effect in catalysis.^{78,79}

Another important effect governing the reactivity of bimetallic surfaces is the bifunctional effect. For example, bismuth adsorption on Pt(111) produces a marked decrease of the onset potential for CO oxidation.⁷⁵ This catalytic enhancement has been explained

by the adsorption of oxygenated species on the bismuth adatoms, thus providing the oxidizing reactant for CO oxidation. Incidentally, bismuth deposition also favors the reorientation of interfacial water with the oxygen towards the metal, which takes place at lower potentials than on the bare Pt(111). It is reasonable to consider that both effects are related, since it may be expected that the oxygen-towards-the-metal orientation may favor water dissociation to form oxygenated species on the surface. In conclusion, the new information about the interaction of solvent molecules with the electrode surface obtained from nanosecond-laser-pulsed experiments has demonstrated to be valuable to provide a deeper understanding of some general trends observed in electrocatalysis.

VI. CONCLUSIONS

In this chapter, we have tried to demonstrate that the use of temperature as an additional variable opens a new door to a wealth of valuable information with regard to interfacial studies of platinum single-crystal electrodes. Of course, this will not come as anything new to the physical chemist, since the importance of temperature as a thermodynamic variable is a textbook precept that does not need to be emphasized now. However, conceptual difficulties in the analysis of the experimental results obtained with variable temperatures have restricted the number of studies in this field.

A similar situation happened before with the application of the electrocapillary equation to interfacial studies. After a vast number of studies that applied it to mercury | electrolyte interphases, the application to solid electrodes was hampered by the existence of conceptual difficulties, especially in the case of platinum group metals due to charge-transfer phenomena.

Apart of giving a solid thermodynamic basis for the analysis of temperature variation on interfacial studies, we have shown in this chapter how a methodology based on temperature jump perturbation techniques can result in significant advantages, not only in terms of convenience from the experimental point of view, but also in the possibility of selectively separate processes based on their different characteristic response time.

When the interference of charge-transfer phenomena is eliminated by selecting an appropriate time window for the experiments,

purely double-layer information becomes accessible. This leads to the collection of data relevant for the understanding of the role of water in the formation of the interfacial region. The last Section of the chapter gives an example of the relevance of this information for the understanding of the role of water in electrocatalysis.

ACKNOWLEDGMENTS

Financial support from the MEC (Spain) through project CTQ 2006-04071/BQU is gratefully acknowledged. NG thanks the MEC (Spain) for the award of a postdoctoral fellowship.

GLOSSARY

C_{dl}	double-layer differential capacity
C_{tot}	total differential capacity
c_S	surface density of adsorption sites
d	thickness of the inner double-layer
E	electrode potential, measured vs. a reference electrode
e	absolute value of the charge of an electron ($e = 1.60218 \cdot 10^{-19} \text{ C}$)
E^M	absolute electrode potential ($E^M \equiv \Delta_S^M \phi - \frac{\mu_e}{e} + \text{constant}$)
E_{pme}	potential of maximum entropy
E_{pzfc}	potential of zero free charge
E_{pztc}	potential of zero total charge
F	Faraday's constant ($F = 96485 \text{ C mol}^{-1}$)
$g^S(dip)$	surface dipole due to the excess of polarization of the solvent molecules at the metal solution interphase
$g(ion)$	contribution of ions to the potential drop across the double-layer
k	Boltzmann's constant ($k = 1.38065 \cdot 10^{-23} \text{ J K}^{-1}$)
k^0	standard rate constant of a charge-transfer adsorption process
m_i	atomic mass of adsorbed species i
N_A	Avogadro's number ($N_A = 6.02214 \cdot 10^{23} \text{ mol}^{-1}$)
p	pressure

Q	total charge density
Q_{ML}	charge density associated to a charge-transfer adsorption process at saturation
R	molar gas constant ($R=8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$)
$\bar{S}_i$	absolute integral molar entropy of species i
$\bar{S}_i^{ads}$	absolute integral molar entropy of adsorbed species i
$\bar{S}_i^{corr}$	corrected (subtracting double-layer contribution) absolute integral molar entropy of adsorbed species i
$\bar{S}_i^{eff}$	effective (without double-layer correction) absolute integral molar entropy of adsorbed species i
$\bar{S}_i^{gen}$	absolute integral molar entropy of adsorbed species i , obtained from the mathematical treatment employing a generalized isotherm
$\bar{S}_i^{im}$	theoretical absolute integral molar entropy of adsorbed species i for the case of a fully immobile adlayer
$\bar{S}_i^{mob}$	theoretical absolute integral molar entropy of adsorbed species i for the case of a fully mobile adlayer
S^σ	entropy per unit area of the interphase
T	absolute temperature
t	time
$\bar{V}_i$	absolute molar volume of species i
V^σ	volume per unit area of the interphase
z	charge number associated to a charge-transfer adsorption process ($z = 1$ for hydrogen and $z = -1$ for OH adsorption)
ΔE	laser-induced potential transient.
$\Delta \bar{G}^0$	standard molar Gibbs energy change associated to a charge-transfer adsorption process.
$\Delta \bar{G}^f$	formal molar Gibbs energy change associated to a charge-transfer adsorption process.
$\Delta \bar{H}^0$	standard molar enthalpy change associated to a charge-transfer adsorption process.
$\Delta \bar{H}^f$	formal molar enthalpy change associated to a charge-transfer adsorption process.
$\Delta \bar{S}^0$	standard molar entropy change associated to a charge-transfer adsorption process.

$\Delta \bar{S}^f$	formal molar entropy change associated to a charge-transfer adsorption process.
ΔS	entropy of formation of the interphase.
ΔS_{dl}	entropy of formation of the double-layer.
ΔT	laser-induced temperature change.
ΔT_0	maximum laser-induced temperature change.
$\Delta_s^M \phi$	potential difference across the interphase
$\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{Q, p, c_i}$	temperature coefficient of the potential drop across the interphase.
$\left(\frac{\partial \Delta_s^M \phi}{\partial T} \right)_{\sigma_M, \Gamma_H, \Gamma_{OH}, p, c_i}$	temperature coefficient of the potential drop across the interphase under frozen conditions of the adsorbed species .
ϵ_0	permittivity of free space ($\epsilon_0 = 8.85419 \cdot 10^{-12} \text{ F m}^{-1}$)
ϵ	relative dielectric constant of water ($\epsilon = 78.36$ at 25°C)
Φ	work function.
$\delta \chi^M$	modification of the surface potential of the metal produced by the presence of solvent
Γ_i	surface concentration of species i at the interphase
$\Gamma_{i, \text{H}_2\text{O}}$	relative surface concentration of species i at the interphase
$\Gamma_{S, \text{H}_2\text{O}, M}$	relative entropy per unit area of the interphase
$\Gamma_{V, \text{H}_2\text{O}, M}$	relative volume per unit area of the interphase
γ	interfacial tension
$\tilde{\mu}_i$	electrochemical potential of species i
μ_i	chemical potential of species i
θ_i	normalized coverage of species i
σ_M	electronic charge density on the metal or free charge density.
ω	lateral interaction parameter

APPENDIX 1. **EVALUATION OF THE THERMODIFFUSION** **POTENTIAL OF SOME COMMONLY USED SOLUTIONS**

As described in Section II.1, thermodiffusion potentials can be estimated by Eq. (1) in the text.³⁰

$$\frac{\Delta E_{\text{Thermodiffusion}}}{\Delta T} = -\frac{1}{F} \sum_i \frac{t_i}{z_i} \hat{S}_i \quad (98)$$

where t_i , z_i and $\hat{S}_i$ are the transport number, the charge (with its sign) and the Eastman entropy of transport of the ion i , respectively. In the following, the application of this equation will be illustrated with some examples of commonly used solutions. Table 3 summarizes the ionic entropies of transport of some common ions (H^+ , K^+ , SO_4^{2-} and ClO_4^-), taken from Ref. 30. On the other hand, transport numbers are tabulated for some solution compositions (see, for example, Ref. 80). For other cases, they can be estimated from the mobilities of the ions in infinitely diluted solutions, as:

$$t_i = \frac{|z_i| c_i u_i}{\sum_i |z_i| c_i u_i} \quad (99)$$

where c_i is the concentration of the ion in the solution under study and u_i are the mobilities of the ions in infinitely diluted solutions, which can be taken from standard tables (for example, from Ref.

Table 3
Ionic Entropies of Transport of Selected Ions.³⁰

Ion	$\hat{S}_i / \text{J mol}^{-1} \text{K}^{-1}$
H^+	39.44
K^+	4.40
Na^+	7.14
ClO_4^-	-3.10
SO_4^{2-}	26.96
OH^-	53.90

Table 4
Transport Numbers of Some Commonly Used Solutions.

Solution	t_{H^+}	t_{K^+}	$t_{ClO_4^-}$	$t_{SO_4^{2-}}$	t_{OH^-}
0.1 M HClO ₄	0.849 ^a		0.151 ^a		
0.1 M H ₂ SO ₄	0.819 ^a			0.181 ^a	
0.1 M NaOH		0.202 ^b			0.798 ^b
0.1 M K ₂ SO ₄ + 1 mM H ₂ SO ₄	0.022 ^b	0.466 ^b		0.512 ^b	
0.09 M KClO ₄ + 10 mM HClO ₄	0.208 ^b	0.393 ^b	0.4 ^b		
0.1 M KClO ₄ + 1 mM HClO ₄	0.024 ^b	0.507 ^b	0.469 ^b		
0.1 M KClO ₄ + 0.1 mM HClO ₄	0.0025 ^b	0.52 ^b	0.477 ^b		

a) taken from Ref. 80; b) estimated from the mobilities of the ions in infinitely diluted solutions from Ref. 81.

81). Transport numbers of ions composing some commonly used solutions are summarized in Table 4. Finally, Table 5 provides the results of the evaluation of thermodiffusion potentials by Eq. (98), and using the parameters in Tables 3 and 4.

Table 5
Thermodiffusion Potentials of Some Commonly Used Solutions.

Solution	$\left(\frac{\Delta E_{\text{Thermodiffusion}}}{\Delta T} \right) / \text{mV K}^{-1}$
0.1 M HClO ₄	-0.381
0.1 M H ₂ SO ₄	-0.337
0.1 M NaOH	0.431
0.1 M K ₂ SO ₄ + 1 mM H ₂ SO ₄	0.041
0.09 M KClO ₄ + 10 mM HClO ₄	-0.115
0.1 M KClO ₄ + 1 mM HClO ₄	-0.048
0.1 M KClO ₄ + 0.1 mM HClO ₄	-0.04

APPENDIX 2

THERMODYNAMIC METHOD FOR THE EVALUATION OF THE HYDROGEN AND OH SURFACE CONCENTRATIONS AND THE DOUBLE-LAYER CAPACITY, FOR PLATINUM ELECTRODES IN MIXED HClO₄ AND KClO₄ SOLUTIONS

The following derivation was inspired by the combination of the works of Frumkin and Petrii⁸² and the thermodynamic analysis performed by Parsons and Dutkiewicz⁸³ and Hurwitz⁸⁴ for a series of solutions with a constant ionic strength. The Gibbs-Duhem equation for the interphase between a platinum electrode and an acid, inert electrolyte solution (Eq. 46), under conditions of constant temperature and pressure, will be used as the starting point:

$$-d\gamma = Qd\Delta_S^M\phi - \frac{Q}{F}d\mu_{e^-} + \Gamma_{H,H_2O}d\mu_{H^+} + \sum_{i \neq e^-, H^+, OH^-, H_2O, M} \Gamma_{i,H_2O}d\mu_i \quad (100)$$

where Γ_{i,H_2O} are the relative surface concentration of species i at the interphase, and are given by (Eqs. 47 and 48):

$$\Gamma_{H,H_2O} = \Gamma_H + \Gamma_{H^+} - \Gamma_{OH} - \Gamma_{OH^-} - \left(\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-} \right) \frac{\chi_{H^+}}{\chi_{H_2O}} \quad (101)$$

$$\Gamma_{i,H_2O} = \Gamma_i - \left(\Gamma_{H_2O} + \Gamma_{OH} + \Gamma_{OH^-} \right) \frac{\chi_i}{\chi_{H_2O}} \quad (102)$$

For mixed solutions of HClO₄ and KClO₄ of constant ionic strength [such as (0.1 - x) M KClO₄ + x M HClO₄ solutions, where x varies between 10⁻³ and 0.1], it has been shown that the activity coefficients remain essentially constant.⁸⁵ Accordingly, the chemical potential of perchlorate anions remains essentially constant, and hence:

$$d\mu_{ClO_4^-} \approx 0 \quad (103)$$

In addition, for these solution compositions, the chemical potential of proton and potassium cations are linked by:

$$\frac{d\mu_{K^+}}{d\mu_{H^+}} = \frac{c_{H^+}}{c_{K^+}} \frac{dc_{K^+}}{dc_{H^+}} = -\frac{c_{H^+}}{c_{K^+}} \quad (104)$$

Introducing these results in Eq. (100) gives:

$$-d\gamma = Qd\Delta_s^M \phi - \frac{Q}{F} d\mu_{e^-} + \left(\Gamma_{H,H_2O} - \frac{c_{H^+}}{c_{K^+}} \Gamma_{K^+,H_2O} \right) d\mu_{H^+} \quad (105)$$

Then, combination of Eqs. (101), (102) and (105) gives:

$$-d\gamma = Qd\Delta_s^M \phi - \frac{Q}{F} d\mu_{e^-} + \left(\Gamma_H + \Gamma_{H^+} - \Gamma_{OH} - \Gamma_{OH^-} - \frac{c_{H^+}}{c_{K^+}} \Gamma_{K^+} \right) d\mu_{H^+} \quad (106)$$

At this point, following previous works of Parsons and Dutkiewicz⁸³ and Hurwitz⁸⁴, it can be considered that proton, hydroxide and potassium ions may only be adsorbed on the diffuse part of the double-layer.³⁹ That is, it will be considered that these ions only experience long-range coulombic interactions among each other and with the electrode, and any specific short-range effect is negligible small. As a result, their surface concentration will be proportional to their bulk concentration in solution. For this reason, the surface concentration of hydroxide ions will be negligible:

$$\Gamma_{OH^-} \approx 0 \quad (107)$$

And the surface concentration of proton and potassium cations will be linked by:

$$\frac{\Gamma_{H^+}}{\Gamma_{K^+}} \approx \frac{c_{H^+}}{c_{K^+}} \quad (108)$$

Introducing these results in Eq. (106) gives:

$$-d\gamma = Qd\Delta_S^M\phi - \frac{Q}{F}d\mu_{e^-} + (\Gamma_H - \Gamma_{OH})d\mu_{H^+} \quad (109)$$

Finally, for the present purposes, it is convenient that potential values are measured vs. an external reference electrode (such as a SHE electrode). Then, taking into account that these E (vs. SHE) values are related to the potential drop across the interphase, $\Delta_S^M\phi$, by:⁵²

$$E(\text{vs. SHE}) \equiv \Delta_S^M\phi - \frac{\mu_{e^-}}{F} + \text{constant} \quad (110)$$

it is obtained that:

$$-d\gamma = QdE(\text{vs. SHE}) + (\Gamma_H - \Gamma_{OH})d\mu_{H^+} \quad (111)$$

The above equation provides a method of evaluation of the difference in the surface concentration of hydrogen and OH species.^{18,86} First, values of the surface energy, γ , are obtained, up to a constant of integration, from:

$$\gamma - \gamma_{\text{ptc}} = - \int_{E_{\text{ptc}}}^E QdE(\text{vs. SHE}) \quad (112)$$

With these results, the quantity $(\Gamma_H - \Gamma_{OH})$ can be obtained from:

$$\Gamma_H - \Gamma_{OH} = - \left(\frac{\partial \gamma}{\partial \mu_{H^+}} \right)_{E(\text{vs. SHE})} \quad (113)$$

Alternatively, the same analysis can be performed using charge density, instead of potential, as the electrical independent

variable. This is done by using Parson's function, $\xi = \gamma + QE$, giving:

$$-d\xi = -E(\text{vs. SHE})dQ + (\Gamma_{\text{H}} - \Gamma_{\text{OH}})d\mu_{\text{H}^+} \quad (114)$$

$$\xi - \xi_{\text{pztc}} = \int_{E_{\text{pztc}}}^E QdE(\text{vs. SHE}) \quad (115)$$

$$\Gamma_{\text{H}} - \Gamma_{\text{OH}} = - \left(\frac{\partial \xi}{\partial \mu_{\text{H}^+}} \right)_Q \quad (116)$$

In conclusion, the quantity $(\Gamma_{\text{H}} - \Gamma_{\text{OH}})$ can be obtained from either Eq. (113) or Eq. (116). Then, for the case of Pt(111) in perchloric acid solutions, the individual values of Γ_{H} and Γ_{OH} can be obtained by taking into account that, in the double-layer region, $\Gamma_{\text{H}} \approx \Gamma_{\text{OH}} \approx 0$.^{18,86}

On the other hand, the double-layer capacities can be evaluated as follows.³⁹ Taking into account that the total charge density, Q , is given by (Eq. 43):

$$Q = \sigma_{\text{M}} - F\Gamma_{\text{H}} + F\Gamma_{\text{OH}} \quad (117)$$

Eq. (111) can be rewritten as:

$$-d\gamma = QdE(\text{vs. SHE}) + \left(\frac{\sigma_{\text{M}} - Q}{F} \right) d\mu_{\text{H}^+} \quad (118)$$

Then, cross derivation of the above equation gives:

$$\left(\frac{\partial Q}{\partial \mu_{\text{H}^+}} \right)_{E(\text{vs. SHE})} = \frac{1}{F} \left(\frac{\partial (\sigma - Q)}{\partial E(\text{vs. SHE})} \right)_{\mu_{\text{H}^+}} \quad (119)$$

And using the Euler relation: $\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial x}{\partial y}\right)_z = -1$, one may write:

$$\left(\frac{\partial Q}{\partial E(\text{vs. SHE})}\right)_{\mu_{\text{H}^+}} \left(\frac{\partial E(\text{vs. SHE})}{\partial \mu_{\text{H}^+}}\right)_Q \left(\frac{\partial \mu_{\text{H}^+}}{\partial Q}\right)_{E(\text{vs. SHE})} = -1 \quad (120)$$

Combination of Eqs. (119) and (120) gives:

$$\begin{aligned} \left(\frac{\partial E(\text{vs. SHE})}{\partial \mu_{\text{H}^+}}\right)_Q &= -\frac{\left(\frac{\partial Q}{\partial \mu_{\text{H}^+}}\right)_{E(\text{vs. SHE})}}{\left(\frac{\partial Q}{\partial E(\text{vs. SHE})}\right)_{\mu_{\text{H}^+}}} = -\frac{\frac{1}{F} \left(\frac{\partial(\sigma - Q)}{\partial E(\text{vs. SHE})}\right)_{\mu_{\text{H}^+}}}{\left(\frac{\partial Q}{\partial E(\text{vs. SHE})}\right)_{\mu_{\text{H}^+}}} \\ &= \frac{1}{F} \left(1 - \frac{C_{\text{dl}}}{C_{\text{tot}}}\right) \end{aligned} \quad (121)$$

where $C_{\text{dl}} = \frac{d\sigma_{\text{M}}}{dE}$ is the double-layer capacity and $C_{\text{tot}} = \frac{dQ}{dE}$ is the total capacity. Finally, rearrangement of Eq. (121) gives:

$$\frac{C_{\text{dl}}}{C_{\text{tot}}} = 1 - F \left(\frac{\partial E(\text{vs. SHE})}{\partial \mu_{\text{H}^+}}\right)_Q \quad (122)$$

In conclusion, the above equation demonstrates that double-layer capacities can be evaluated from the analysis of the effect of pH on total charge density curves for Pt(111) in $(0.1 - x)$ M KClO_4 + x M HClO_4 solutions.³⁹

APPENDIX 3

STATISTICAL MECHANICS DERIVATION OF SELECTED THERMODYNAMIC PROPERTIES OF MODEL ADSORPTION PROCESSES

Consider the adsorption of a single type of particle in a lattice of N adsorption sites. For simplicity, consider that the only interactions between adsorbed particles are those between nearest neighbors (although the present derivation can be easily extended to a situation with more complex interactions).⁸⁷ In the mean-field approximation, it is considered that the number of nearest neighbors of a test particle equals $Z\theta$, where Z is the number of nearest neighbors positions ($Z = 4$ for a square lattice, $Z = 6$ for a triangular lattice), and θ is the coverage. Therefore, the interaction energy of a test particle will be given by $Z\varepsilon_{\text{nn}}\theta$, where ε_{nn} is the interaction energy between two particles adsorbed on nearest neighbors positions. Then, the total interaction energy of the system is obtained by multiplying $Z\varepsilon_{\text{nn}}\theta$ by the total number of particles, which equals $N\theta$, and dividing by 2 (in order to avoid double counting of pairs), thus giving $\frac{1}{2}NZ\varepsilon_{\text{nn}}\theta^2$. On the other hand, the total adsorption energy will be given by $N\theta\varepsilon_{\text{ads}}$, where ε_{ads} is the adsorption energy of a single particle, and $N\theta$ is the total number of particles. In conclusion, the total internal energy of the system will be given by:

$$U_{\text{lattice}} = N\theta\varepsilon_{\text{ads}} + \frac{1}{2}NZ\varepsilon_{\text{nn}}\theta^2 \quad (123)$$

Then, in order to calculate the Helmholtz energy of the system, F_{lattice} , one has to add the configurational entropy of the lattice, which is given by:⁸⁷

$$S_{\text{conf lattice}} = k \ln \left[\frac{N!}{(N\theta)!(N - N\theta)!} \right] \quad (124)$$

Thus giving:

$$\begin{aligned}
 F_{\text{lattice}} &= U_{\text{lattice}} - TS_{\text{conf lattice}} \\
 &= N\theta\epsilon_{\text{ads}} + \frac{1}{2}NZ\epsilon_{\text{nn}}\theta^2 - kT \ln \left[\frac{N!}{(N\theta)!(N-N\theta)!} \right]
 \end{aligned} \tag{125}$$

Using the Stirling's approximation, F_{lattice} can be simplified to:

$$\begin{aligned}
 F_{\text{lattice}} &= N\theta\epsilon_{\text{ads}} + \frac{1}{2}NZ\epsilon_{\text{nn}}\theta^2 - kTN \ln N + kTN\theta \ln(N\theta) \\
 &\quad + kT(N-N\theta) \ln(N-N\theta)
 \end{aligned} \tag{126}$$

With this, the chemical potential of adsorbed species, μ_{ads} , can be obtained from:

$$\mu_{\text{ads}} = \left(\frac{\partial F_{\text{lattice}}}{\partial (N\theta)} \right)_T = \epsilon_{\text{ads}} + Z\epsilon_{\text{nn}}\theta + kT \ln \left(\frac{\theta}{1-\theta} \right) \tag{127}$$

With this, the differential entropy of adsorbed species, S^{diff} , can be obtained from:⁴³

$$S^{\text{diff}} = - \left(\frac{\partial \mu}{\partial T} \right)_{\theta} = S^0 - Z\theta \frac{d\epsilon_{\text{nn}}}{dT} - k \ln \left(\frac{\theta}{1-\theta} \right) \tag{128}$$

where $S^0 = -\frac{d\epsilon_{\text{ads}}}{dT}$ is the entropy of adsorption at the standard state. It is easy to show that Eq. (128) is equivalent to Eq. (84) in the text, if one takes into account that:

- (1) S^{diff} and S^0 refer to the entropy of adsorption per particle, while $\bar{S}_i^{\text{gen, diff}}$ and $\bar{S}_i^{0, \text{gen}}$ refer to the entropy of adsorption per mol of adsorbed particles. Therefore, $\bar{S}_i^{\text{gen, diff}} = S^{\text{diff}} N_A$ and $\bar{S}_i^{0, \text{gen}} = S^0 N_A$, where N_A is the Avogadro's number.
- (2) When only nearest-neighbors interactions are present, the interaction parameter is given by $\omega = Z\epsilon_{\text{nn}} N_A$.

On the other hand, in order to calculate the integral entropy of adsorption, first one has to evaluate the total entropy of the whole lattice, S_{lattice} . This can be done from:⁴³

$$\begin{aligned} S_{\text{lattice}} &= - \left(\frac{\partial F_{\text{lattice}}}{\partial T} \right)_{\theta} \\ &= N\theta S^0 - \frac{1}{2} NZ\theta^2 \frac{d\varepsilon_{\text{nn}}}{dT} + kN \ln N - kN\theta \ln(N\theta) \\ &\quad - k(N - N\theta) \ln(N - N\theta) \end{aligned} \quad (129)$$

Then, the integral entropy of adsorbed species, S^{int} , is obtained from:⁴³

$$S^{\text{int}} = \frac{S_{\text{lattice}}}{N\theta} = S^0 - \frac{1}{2} Z\theta \frac{d\varepsilon_{\text{nn}}}{dT} - k \ln \left(\frac{\theta}{1-\theta} \right) - \frac{k}{\theta} \ln(1-\theta) \quad (130)$$

It is easy to show that the above equation is equivalent to Eq. (85) in the text, taking into account that $\bar{S}_i^{\text{gen}} = S^{\text{int}} N_A$, $\bar{S}_i^{0,\text{gen}} = S^0 N_A$ and $\omega = Z\varepsilon_{\text{nn}} N_A$.

With these results, the expressions for the differential and integral configurational entropy can be obtained straightforwardly, by taking $S^0 = 0$ and $\frac{d\varepsilon_{\text{nn}}}{dT} = 0$ in Eq. (128) and (130):

$$S^{\text{conf diff}} = -k \ln \left(\frac{\theta}{1-\theta} \right) \quad (131)$$

$$S^{\text{conf int}} = -k \ln \left(\frac{\theta}{1-\theta} \right) - \frac{k}{\theta} \ln(1-\theta) \quad (132)$$

Clearly, Eq. (132) is equivalent to Eq. (81) in the text, with the only difference that $S^{\text{conf int}}$ refers to the entropy per particle, while $\bar{S}_i^{\text{im}}$ refers to the entropy per mol of particles, and therefore, $\bar{S}_i^{\text{im}} = S^{\text{conf int}} N_A$.

On the other hand, the expressions for the differential and integral entropies for a totally mobile adlayer can be obtained as follows. The partition function of a two-dimensional gas is given by:⁴³

$$Q_{2D \text{ gas}} = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \sigma^2 \right)^N \quad (133)$$

where N is the number of particles of the system; m is the mass of one particle; σ^2 is the area occupied by one particle (ie. the area of the surface); and all other symbols have their usual meaning. The Helmholtz energy of the system can be obtained from:

$$F_{2D \text{ gas}} = -kT \ln Q_{2D \text{ gas}} = kT \ln N! - kTN \ln \left(\frac{2\pi mkT}{h^2} \sigma^2 \right) \quad (134)$$

Using Stirling's approximation, the above equation can be simplified to:

$$F_{2D \text{ gas}} = kTN \ln N - kTN - kTN \ln \left(\frac{2\pi mkT}{h^2} \sigma^2 \right) \quad (135)$$

With this, the chemical potential of the particle can be obtained from:

$$\mu_{2D \text{ gas}} = \frac{dF_{2D \text{ gas}}}{dN} = -kT \ln \left(\frac{2\pi mkT}{h^2} \frac{\sigma^2}{N} \right) \quad (136)$$

Then, considering that σ^2 is not temperature-dependent, the differential entropy of the particle can be obtained from:⁴³

$$S^{\text{mob diff}} = -\frac{d\mu_{2D \text{ gas}}}{dT} = k \left[1 + \ln \left(\frac{2\pi mkT}{h^2} \frac{\sigma^2}{N} \right) \right] \quad (137)$$

Finally, taking into account that $\frac{\sigma^2}{N} = \frac{1}{c_s \theta}$, where c_s is the surface density of adsorption sites and θ is the normalized coverage, the above equation can be rewritten as:

$$S^{\text{mob diff}} = k \left[1 + \ln \left(\frac{2\pi mkT}{h^2} \frac{1}{c_s \theta} \right) \right] \quad (138)$$

On the other hand, in order to calculate the integral entropy of the particle, one has to evaluate first the total entropy of the system, which is given by:

$$S_{2D \text{ gas}} = -\frac{dF_{2D \text{ gas}}}{dT} = kN \left[2 + \ln \left(\frac{2\pi mkT}{h^2} \frac{\sigma^2}{N} \right) \right] \quad (139)$$

With this, the integral entropy of the particle can be obtained from:

$$S^{\text{mob int}} = \frac{S_{2D \text{ gas}}}{N} = k \left[2 + \ln \left(\frac{2\pi mkT}{h^2} \frac{\sigma^2}{N} \right) \right] = k \left[2 + \ln \left(\frac{2\pi mkT}{h^2} \frac{1}{c_s \theta} \right) \right] \quad (140)$$

It is easy to show that the above equation is equivalent to Eq. (80) in the text, with the only difference that $S^{\text{mob int}}$ refers to the entropy per particle, while $\bar{S}_i^{\text{mob}}$ refers to the entropy per mol of particles.

APPENDIX 4 LASER HEATING

The application of the laser-induced temperature jump method requires that the only effect of the laser pulses is the heating of the electrode surface, resulting in a sudden temperature change at the interphase. In this regard, the laser pulses employed in the experiments described in Section V (wavelength of 532 nm, duration of

5 ns and fluence of 8 mJ cm^{-2}) have been selected so that the possibility of electron photoemission can be ruled out. This can be demonstrated as follows. The energy of the photons of the 532 nm laser beam is $h\nu = 2.33 \text{ eV}$. Therefore, one-photon photoemission will only take place in materials whose work function value is lower than 2.33 eV. Fortunately, the work function of a platinum electrode, at the operative potentials, is clearly higher than this value. In the worse case, when the applied potential is equal to zero vs. a SHE electrode, then the work function of the working electrode will be equal to the work function of the SHE reference electrode,⁵² whose value is $\sim 4.6 \text{ eV}$.⁸⁸ On the other hand, the possibility of two-photon photoemission can also be discarded, for the low laser fluences employed in the experiments in Section V. Moreover, a two-photon process would exhibit a quadratic dependence on the laser fluence, and the experimental results in Section V exhibit a nearly lineal dependence on the laser fluence.

The variation of temperature induced by the laser pulses can be estimated through a very simple model, by considering that the fraction of the energy of the laser pulse that is not reflected on the surface, is converted immediately into heat at the surface of the electrode.^{50,89,90} Then, the temperature change can be calculated by solving the following partial differential equation:

$$\frac{\partial^2 \Delta T}{\partial x^2} = \frac{1}{\alpha_i} \frac{\partial \Delta T}{\partial t} \quad (141)$$

subject to the following boundary conditions:

$$-\kappa \frac{\partial \Delta T}{\partial x} \Big|_{x=0^+} = q - q' \text{ (heat flux into the metal)} \quad (142)$$

$$-\kappa_1 \frac{\partial \Delta T}{\partial x} \Big|_{x=0^-} = -q' \text{ (heat flux into solution)} \quad (143)$$

$$\Delta T(x, t = 0) = 0 \quad (144)$$

$$\lim_{x \rightarrow \pm\infty} \Delta T(x, t) = 0 \quad (145)$$

In this model, the surface of the metal is located at $x = 0$, $x < 0$ correspond to the solution and $x \geq 0$ to the metal; q is the flux of heat absorbed at the surface of the electrode, i.e., the part of the radiation that is not reflected:

$$q = (1 - R)I \quad (146)$$

where I is the laser intensity (considered spatially uniform) and R is the reflectivity of the surface. q' is the heat flux conducted into the solution and κ , α and κ_1 , α_1 are the thermal conductivity and the thermal diffusivity of the metal and the aqueous solution, respectively ($\alpha = \kappa/\rho c$, where ρ is the density and c is the heat capacity).

Applying Laplace Transform to Eq. (141), the following ordinary differential equation is obtained:

$$\frac{1}{\alpha_i} \left\{ s \overline{\Delta T}(x, s) - \Delta T(x, t = 0) \right\} = \frac{\partial^2 \overline{\Delta T}}{\partial x^2} \quad \begin{array}{ll} \alpha_i = \alpha & \text{for } x \geq 0 \\ \alpha_i = \alpha_1 & \text{for } x < 0 \end{array} \quad (147)$$

where $\overline{\Delta T}$ is the transformed temperature change. Taking into account the initial condition (Eq. 144); Eq. (147) can be integrated, separately for $x \geq 0$ and $x < 0$, giving:

$$\begin{aligned} \overline{\Delta T} &= A e^{\sqrt{\frac{s}{\alpha}} x} + B e^{-\sqrt{\frac{s}{\alpha}} x} & \text{for } x \geq 0 \\ \overline{\Delta T} &= A' e^{\sqrt{\frac{s}{\alpha_1}} x} + B' e^{-\sqrt{\frac{s}{\alpha_1}} x} & \text{for } x < 0 \end{aligned} \quad (148)$$

The condition that $\overline{\Delta T}$ should remain finite for $x \rightarrow \pm\infty$ (Eq. 145) gives $A = B' = 0$. The relation between B and A' is obtained from the condition of continuity of $\overline{\Delta T}$ at $x = 0$:

$$\lim_{x \rightarrow 0^+} \Delta T(x, t) = \lim_{x \rightarrow 0^-} \Delta T(x, t) \quad (149)$$

thus giving $A' = B$.

At this point, the boundary conditions (142) and (143) will be applied:

$$-\kappa \frac{\partial \overline{\Delta T}}{\partial x} \Big|_{x=0^+} = \bar{q} - \bar{q}' = \kappa B \sqrt{\frac{s}{\alpha}} \quad (150)$$

$$-\kappa_1 \frac{\partial \overline{\Delta T}}{\partial x} \Big|_{x=0^-} = -\bar{q}' = -\kappa_1 B \sqrt{\frac{s}{\alpha_1}} \quad (151)$$

With these two equations, $\bar{q}'$ and B can be eliminated from Eq. (148):

$$\overline{\Delta T} = \bar{q} \left[\frac{\kappa}{\sqrt{\alpha}} + \frac{\kappa_1}{\sqrt{\alpha_1}} \right]^{-1} \frac{1}{\sqrt{s}} e^{-\sqrt{\frac{s}{\alpha}} x} \quad (152)$$

To calculate the change of the temperature in the real space we must take inverse Laplace transform of Eq. (152). This can be accomplished with the use of the convolution theorem and the following result:

$$L^{-1} \left\{ \frac{1}{\sqrt{s}} e^{-a\sqrt{s}} \right\} = \frac{1}{\sqrt{\pi t}} e^{-\frac{a^2}{4t}} \quad (153)$$

giving:⁵⁰

$$\Delta T(t) = \left[\frac{\kappa}{\sqrt{\pi\alpha}} + \frac{\kappa'}{\sqrt{\pi\alpha'}} \right]^{-1} \int_0^t q(t') \frac{1}{\sqrt{t-t'}} \exp\left(-\frac{x^2}{4\alpha t}\right) dt' \quad (154)$$

At the surface of the electrode, $x = 0$, the following expression is obtained:

$$\Delta T(t, x = 0) = \left[\frac{\kappa}{\sqrt{\alpha}} + \frac{\kappa_1}{\sqrt{\alpha_1}} \right]^{-1} \int_0^t \frac{q(t-t')}{\sqrt{\pi t'}} dt', \quad (155)$$

For a uniform pulse radiation:

$$q(t) = \begin{cases} 0 & \text{if } t > t_0 \\ (1-R)I & \text{if } t < t_0 \end{cases} \quad (156)$$

where I is the laser intensity and t_0 the pulse width, Eq. (155) simplifies to:

$$\Delta T = \frac{2(1-R)I}{\sqrt{\pi}} \left[\frac{\kappa}{\sqrt{\alpha}} + \frac{\kappa_1}{\sqrt{\alpha_1}} \right]^{-1} (\sqrt{t} - \sqrt{t-t_0}) \quad t > t_0 \quad (157)$$

Substituting $t = t_0$ in the above equation, the maximum temperature change achieved at the surface of the electrode, ΔT_0 , is obtained:

$$\Delta T_0 = \frac{2(1-R)I}{\sqrt{\pi}} \left[\frac{\kappa}{\sqrt{\alpha}} + \frac{\kappa_1}{\sqrt{\alpha_1}} \right]^{-1} \sqrt{t_0} \quad (158)$$

For $I = 1.6 \text{ MWcm}^{-2}$ and $t_0 = 5 \text{ ns}$ a maximum $\Delta T_0 = 35 \text{ K}$ is predicted for the platinum|water interphase, considering $R = 0.55$.⁹¹ Moreover, combination of Eqs. (157) and (158) gives Eq. (86) in the text:

$$\Delta T = \Delta T_0 \left(\frac{\sqrt{t} - \sqrt{t-t_0}}{\sqrt{t_0}} \right) \quad t > t_0 \quad (159)$$

To finish, it is worth mentioning that temperature transients calculated with different degrees of approximation were compared in reference ²², showing that at $t > 0.05 \mu\text{s}$ the results agree well.

APPENDIX 5

LASER-INDUCED TRANSIENTS WITH FIRST-ORDER KINETICS

Consider that the laser-induced potential change, ΔE , contains two contributions:

$$\Delta E = \Delta E_1 + \Delta E_2 \quad (160)$$

Consider that the first contribution, ΔE_1 , is virtually instantaneous. Accordingly, ΔE_1 will be given by the product of the temperature coefficient of this process, ξ_1 , and the laser-induced temperature change, ΔT :

$$\Delta E_1 = \xi_1 \Delta T(t) \quad (161)$$

Consider that the second contribution follows first-order kinetic. Accordingly, the potential relaxation will be given by:

$$\frac{d\Delta E_2}{dt} = -\frac{1}{\tau} [\Delta E_2 - \xi_2 \Delta T] \quad (162)$$

where ξ_2 is the corresponding temperature coefficient and τ is the characteristic response time. Using Laplace transforms techniques, Eq. (162) can be rewritten as:

$$\Delta E_2 = \frac{\xi_2}{\tau} \int_0^t \Delta T(t') \exp(t - t') dt' \quad (163)$$

In conclusion, the laser-induced potential transient will be given by:

$$\Delta E = \xi_1 \Delta T(t) + \frac{\xi_2}{\tau} \int_0^t \Delta T(t') \exp(t - t') dt' \quad (164)$$

which is equal to Eq. (97) in the text.

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Surface Thermodynamics of Metal/Solution Interface: the Untapped Resources

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I. INTRODUCTORY REMARKS

Platinum metals electrochemistry is closely associated with electrocatalysis. This wide and highly mobile field is occupied by extremely different types of researchers, who consider electrocatalytic phenomena at various levels, from industrial to atomic. All of them are fighting for one and the same result (roughly, as high as possible activity and stability of the catalyst), but they surely see the events at catalyst/solution interface by different eyes. Some researchers approached electrocatalytic field from the classical electrochemistry side, but a lot of people were involved from other areas of chemistry and physics. This situation is typical for electrochemical material science, with its mounting increase of publications around mainstreams and some risk of a gradual loss of fundamentals. However it is not over yet to remind some of them.

Electrochemical surface thermodynamics is a boundless science. For ideally polarisable (*mercury-like*) electrodes it is to a great extent fixed in textbooks and courses. On the contrary, for

perfectly polarisable electrodes (assuming coadsorption of ions and atoms) thermodynamical knowledge is less disseminated, still available mostly in original papers and brief reviews.¹⁻⁴ Today this knowledge is connected mostly with hydrogen-adsorbing platinum group metals.

In what follows, only a small portion of platinum interfacial electrochemistry is discussed. The boundaries of this review are very sharp:

- (a) aqueous solutions,
- (b) inorganic adsorbates (with accenting adsorption of anions, with only selective information about cations adsorption),
- (c) equilibrium interface (no faradaic processes are discussed),
- (d) pure metals (not alloys or surfaces modified by foreign metal adatoms).

However just inside these boundaries we have a hope to find key information concerning reaction zone of electrocatalytic processes, as hydrogen- and oxygen-containing species, as well as supporting inorganic anions, are unavoidable components of any interface in fuel cells and other important configurations. The basic problems of catalytic activity and reactivity prediction are still by and large based on the separation of *electronic* and *structural* factors (if possible) and understanding of their interrelation (if exact separation fails). This problem traces its roots to the period when only macroscopic observations were possible, and any experimentally measured quantity reflected the interplay of numerous molecular level factors. At that stage thermodynamic relationships were applied to construct a self-consistent description of various observations. During a modern period, when electrocatalytic studies are already well equipped with various microscopic and spectroscopic techniques, people operate with precise information about certain molecular aspects, but it is still impossible to get the complete set of data about all details of reaction layer. This means that some details should be understood or assumed indirectly, in particular from comparison with thermodynamic quantities.

Some details discussed in this review are of more routine importance, as the total charge quantity is actively used for in situ determination of electrodes true surface area of various perfectly polarisable electrodes.⁵

Even with the restriction of content mentioned above it is impossible to collect the literature exhaustively. To overcome this problem, some recent reviews related to application of various in situ techniques are cited instead of numerous original papers. Publications of active research groups working systematically in the field are cited selectively (if these studies present a long-term series, typically the latest papers are mentioned). Citations of rarely available papers are more sizeable (still not exhaustive), to avoid a loss of original sources. Illustrations attempt to present some less known data in a compact form.

II. PREHISTORY AND VISIBLE HORIZON

The pronounced progress of platinum electrochemistry is indebted to the existence of platinized platinum, Pt/Pt (first applied by Kolraush⁶). Starting from 1930s Frumkin initiated a systematic study of Pt/Pt, including comparison of hydrogen adsorption at metal/solution and metal/gas interfaces.⁷⁻⁹ Most important results are available in his review,¹⁰ including the grounds in favor of monolayer hydrogen coverage at zero RHE potential and discussion of experimental data in terms of Temkin isotherm. Other highly dispersed platinum materials (Adams platinum resulting from reduction of PtO₂, platinum black, skeletal platinum) were studied as well. Their specific surface areas were in the range of 10–40 m²·g⁻¹, but after stabilization (ageing) in solution the usual values were of the order of m²·g⁻¹. Systematic comparison of various dispersed platinum materials was reported later.^{11,12} Despite of pronounced difference in fabrication protocols, all dispersed materials demonstrate similar hydrogen adsorption isotherms, with significant distinction from smooth polycrystalline platinum. For the latter, complete hydrogen desorption takes place at lower potentials (*lower bonding energy*). In the absence of modern techniques for structural characterization and with the use of a limited number of electrochemical techniques it was hardly possible to get more information about structural/morphological effects, which later appeared in the centre of attention.

Electrochemistry of other platinum group metals was also roughly characterized before 1960s (see, e.g., Refs. 13–15 for Rh

and Ir, and Ref. 16 for Os and Ru). The studies of Pd formed a separate area,^{17,18} because hydrogen absorption in metal bulk attracted a principal attention, not interfacial processes. Separation of hydrogen adsorption and absorption for dispersed metals is rather complicated.

When the fact of hydrogen adsorption on platinum metals was well documented, a search for self-consistent models started, aimed to description of surface hydrogen coverage dependence on electrode potential and temperature. Breiter was the first who studied the temperature dependence of hydrogen adsorption on smooth platinum, rhodium and iridium.^{13,14,19} He demonstrated a possibility to present experimental dependences typical for polycrystalline platinum by combination of two Frumkin isotherms²⁰ (see below in Section IV.5).

To do the same with dispersed platinum metals, one had to overcome its fast ageing at elevated temperatures, accompanied by decrease of true surface area. This problem was addressed²¹ by measuring galvanostatic charging curves and rather fast voltammograms ($0.2\text{--}0.5\text{ V s}^{-1}$) of preliminary aged Pt/Pt, and 15–20% increase of the charge in H UPD region was found when temperature was increased from 20 to 80°C. This effect (absent for smooth Pt and powder-type dispersed materials)¹² was assigned to higher accessibility of specific surface regions, like narrow pores. An alternative hypothesis of hydrogen penetration into Pt bulk had never found solid confirmation. For other dispersed platinum metals, no anomalous increase of hydrogen coverage was observed.

The data on coverage-dependent differential heat of hydrogen adsorption and coverage-potential dependences formed a set of the most early quantitative thermodynamic information reported for both smooth platinum metals and electrodeposited dispersed Pt, Rh, and Ir in acidic and alkaline solutions. The following tendencies appeared to be general:

- (a) the heat of adsorption decreases with hydrogen surface coverage;
- (b) coverage of 0.3–0.4 separates the regions with more and less sharp decrease mentioned above, and simultaneously separates two voltammetric desorption peaks (both features are the most pronounced for platinum);

- (c) heat of adsorption decreased in a sequence $\text{KOH} > \text{H}_2\text{SO}_4 > \text{HCl}$ (at least at low and mid coverage, for which the accuracy was better).

The particular disagreements found for the behavior of *two forms* of hydrogen at smooth and dispersed platinum were probably induced by a limited accuracy of data treatment, as well as by still not exactly proven assumption of complete coverage at zero RHE potential.

Looking back one can easily notice that before mid 1960s the thermodynamics of adsorption phenomena on platinum was considered mostly in terms of temperature dependence. This traditional approach was not specific for electrochemical thermodynamics, but there was no serious basis to involve other parameters. Another remarkable point is discussion exclusively in terms of hydrogen adsorption, under more or less transparently formulated assumption of complete charge transfer with formation of uncharged adatom. It is slightly strange: future surface thermodynamics was outlined already in 1936,^{8,9} and its principal point was the interplay of ionic and atomic adsorption, but even 30 years later ionic contribution was still accounted only as very formal subtraction (*double layer correction*). When the idea of this interplay was first presented by Frumkin in more comprehensive form,²² it met immediately Breiter's support.²³

The main reason of slow intervention of the evident atomic-ionic interplay concept was a lack of experimental techniques to discover contributions of various coexisting adsorbates. Further development consisted in subsequent separation of strongly interrelated contributions from hydrogen adatoms, various ions, and (much later) water molecules. Running a few steps forward from early temperature dependences, we should refer to the most recent advancement: temperature effect on in situ scattering X-ray spectroscopy (SXS) response of platinum, currently available for very few systems,²⁴ confirms temperature-induced adsorbate reordering and temperature-dependent adsorbate-induced surface reconstruction/deformation. By involvement of these phenomena into general consideration of interfacial equilibria we really have a chance *to complete the picture*, and to arrange a solid link between observations and atomic/molecular models. The progress depends

equally on high-level experimental techniques²⁵⁻³² and reflecting, again and again, on the reliable electrochemical data.

The early thermodynamic data are effective quantities related simultaneously to hydrogen adsorption and numerous accompanying phenomena, but they are still not hopeless for deeper analysis. In addition we should not underestimate the importance of this early period for accumulating the experimental experience,³³ as platinum metals electrochemistry requires rather specific techniques of surface and solution preparation, to avoid contaminations.

Terminology originating from this early period appeared to be rather stable. Namely, the conditional separation of the overall potential interval into *hydrogen region*, *double layer region*, and *oxygen region* still holds much favor, as well as the names *strongly bonded* and *weakly bonded* for hydrogen adsorbed at higher and lower potentials (or for lower and higher hydrogen coverages). These historic names are still actual for polycrystalline platinum (with some reservations). UPD (underpotential deposition) notion appeared later, owing to Schmidt and Gygax studies of metal submonolayers on foreign supports,^{34,35} and became widespread after the first conceptual paper publication.³⁶ However it took some time to realize that hydrogen adsorption with charge transfer at positive RHE potentials (hydrogen adatoms formation) presents the same phenomenon. Now H UPD became a usual term, which never hinders the use of historic notions.

III. A BREAKTHROUGH: FRUMKIN-PETRII SURFACE THERMODYNAMICS

1. Rarity: Equilibrium Techniques to Study Adsorption

The initial approach to platinum surface thermodynamics^{7-9,37} was based on mercury-like double layer experience. In particular the adsorption of H^+ ions was treated as purely electrostatic, which means the complete replacement of these ions by any other cations when the latter are in large excess. This assumption works when H^+ : cation molar ratio is below 0.1, and valid at least for $pH \leq 3$ and salt concentrations up to 1 M.

Rather concentrated set of basic equations was published in a large conference paper²² and simultaneously in a brief Frumkin's note.³⁸ The results of versatile experimental verification of this theory were briefly reviewed in Ref. 39 and then subsequently in Refs 1–4. Important review of experimental facts collected before the 1960s can be found in Ref. 10, Section 4. Finally, the last Frumkin's book⁴⁰ completed and published by Damaskin and Petrii contains a representative selection of data and the most reliable tabulated values.

The interrelation of techniques applied to determine basic quantities is shown schematically in Fig. 1. The most evident are the total charge Q_t and the total capacity C_t : one can get both quantities from usual electrochemical techniques under (quasi) equilibrium conditions. The establishment of equilibrium can be controlled or estimated from dependence on current density (for chronopotentiometry) or scan rate (for voltammetry). For the former technique, it is possible to measure the equilibrium curves by interrupting polarization from time to time and waiting when potential becomes constant. This approach (equilibrium charging curves, called now the galvanostatic intermittent titration technique, GITT) had been first applied in the study of hydrogen sorption by palladium.¹⁷ To measure the free electrode charge Q_f associated with ionic adsorption exclusively, the direct measurements of Gibbs surface excess of ions were applied by means of the radiotracer technique. Independently, Γ_{H^+} value could be determined under some circumstances from the changes of solution pH induced by adsorption.

The principal interrelations of the basic quantities are well-known and explained in earlier reviews.^{1–4} The general approach is based on 3D electrocapillary curve, with its two planar intersects corresponding to two Lippmann equations for constant chemical potentials $\mu_H = \text{const}$ and $\mu_{H^+} = \text{const}$, see Refs. 41–43 for additional explanations. Here we mention the most important ratio:

$$Q_t = -F\Gamma_H = Q_f - FA_H \quad (1)$$

where A_H and Γ_H are the surface concentration and Gibbs adsorption of hydrogen adatoms, respectively. The total charge Q_t is what we need to spend when increasing the electrode surface for one

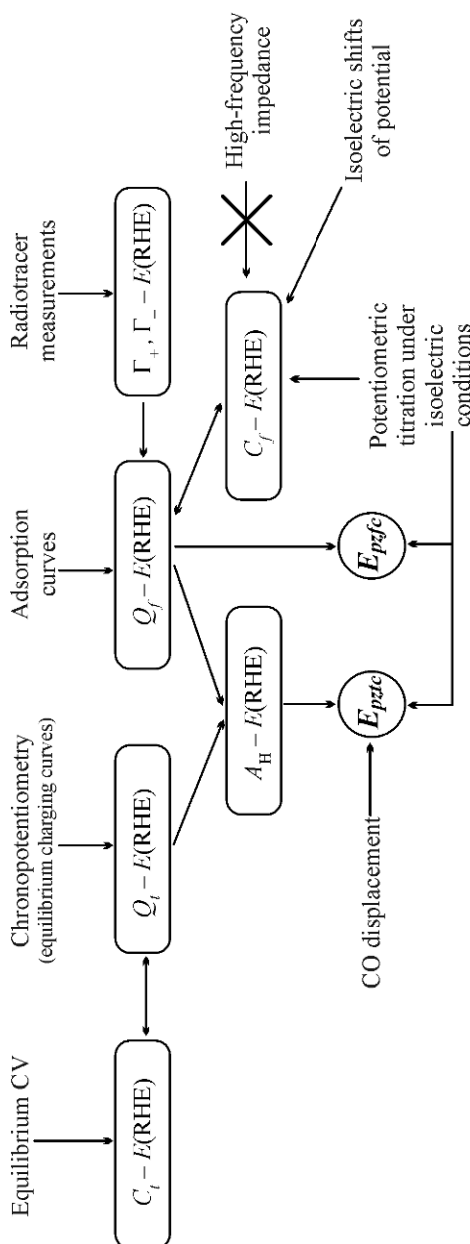


Figure 1. General scheme of the experimental verification applied in Frumkin-Petii surface thermodynamics to electrodes with high surface area. CO displacement represents the most informative currently developed technique for smooth electrodes.

square unity (to say, 1 cm^2) under condition $\mu_{\text{H}^+} = \text{const.}$, i.e., at fixed pH. For the free charge Q_f , it is possible to provide the experimental conditions when $Q_f = F\Gamma_{\text{H}^+}$: it is true for acidic solutions with excess of supporting salt electrolyte, when

- (a) all hydronium ions are displaced from ionic double layer, and
- (b) chemical potentials of all ions are constant.

Additional reservation consists in

- (c) the absence of hydronium specific adsorption; it is already beyond thermodynamics, and should be always taken into account when some physical models are considered in combination with thermodynamic data.

The majority of original results in 1960-70s were reported just for diluted acids with excess salt additives. For pure acid solutions, the important simple link between Q_f and Γ_{H^+} disappeared, and the scheme of experimental verification had to be more complex. In addition to basic quantities, a number of differential quantities can be determined experimentally. The technique of isoelectric potential shifts⁴⁴ gives the derivative $\left(\frac{\partial \Gamma_{\text{H}^+}}{\partial E(\text{RHE})} \right) \mu_{\text{H}^+}$. It provides a

meaning of the equilibrium ionic double layer capacity C_f for certain solution composition because no charge is spent for formation or desorption of hydrogen adatoms. Similar values corresponding to the constancy of other basic quantities were determined from similar potential shifts $\left(\frac{\partial E}{\partial \mu_{\text{H}^+}} \right)_{\Gamma_{\text{H}^+}}$ and $\left(\frac{\partial E(\text{RHE})}{\partial \mu_{\text{H}^+}} \right)_{Q_f}$ in experi-

ments with replacement of one solution by another. Relative replacement techniques could be applied to determination of ions adsorption, see a systematic series.⁴⁵⁻⁴⁷

For correct arrangement of these experiments, a lot of routine details had to be controlled, to avoid artefacts. Special cells with separated compartments allowed to replace solutions independently in the chambers of working and reference electrodes, as well as in the bridge between these solutions. Contributions from molecular hydrogen had to be minimized, especially in the vicinity of zero

RHE potential, when the amount of molecular hydrogen in equilibrium with hydrogen adatoms is already high enough. These details are explained at great length in the early papers.^{44,48,49}

To measure the quantities related to free charge, and to escape the effect of oxygen traces in experiments with solution replacement, one needs to use electrodes of very high true surface areas (1–10 m²), which is possible if the geometric area of the electrodes covered by the layer of dispersed electrodeposited platinum metals runs up to dozens of cm². For this configuration, the accuracy of Γ_{H} -determination is ca. $\pm 2 \mu\text{C}\cdot\text{cm}^2$. Radiotracer techniques available in the 1960s required only one order lower true surface areas, with the obligatory operation of taking the electrode out of the cell. This is the reason why the role of radiochemical data in the studies of equilibrium adsorption was initially rather limited. However in mid 1970s the improvement of this technique increased its contribution to the area, see e.g., Refs 50–52 and Section IV.2 below.

The most laborious experiments related to free charge determination turned out to be more effective when the technique of potentiometric titration under isoelectric conditions was worked out.⁵³ Using the cell shown in Fig. 2, it became possible to collect the data without solution replacement and to avoid the establishment of certain potential in the hydrogen region by equilibrating the system with hydrogen gas.

The two subsequent sections address frequently missed or misunderstood aspects of Frumkin-Petrii thermodynamics.

2. True Double Layer Capacity

It is usually believed that high frequency capacitance obtained from impedance spectroscopy can represent ionic double layer capacity. However in general this is not the case for platinum electrode, this is the reason why one arrow in Fig. 1 (in the left) is crossed. In contrast to C_f measured under equilibrium conditions (by means of isoelectric potential shifts), non-equilibrium impedance response can contain a contribution from A_{H} (and/or A_{O} , surface concentration of oxygen-containing species). These contributions are determined by A_{H} and A_{O} potential derivatives and their free electrode charge derivatives, and in general can be either positive, or negative.

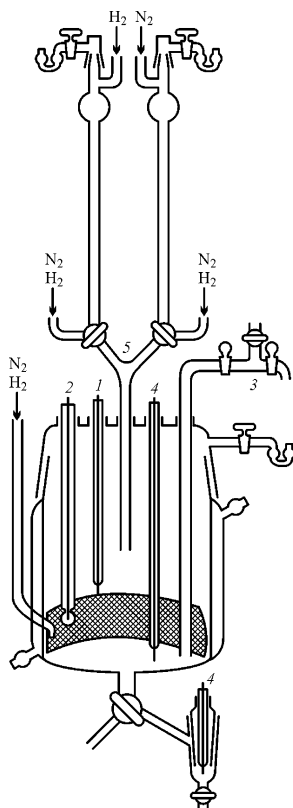


Figure 2. Schematic representation of the cell used for potentiometric titration under isoelectric conditions.⁵³ Working electrode (gauze with a layer of electrodeposited dispersed metal) (1), glass electrode (2), salt bridge for connection with the reference electrode compartment (3); counter electrodes (4); a set of burettes for deaerated solutions of acid and base containing the excess of supporting electrolyte (5). This technique allows avoiding solution replacement in the course of measurements of isoelectric potential shifts. Reprinted from Ref. 53, Copyright (1974) with permission of Nauka Publ.

The role of true double layer capacity in so-named *double layer correction* of total capacity was specially considered in a rarely available paper,⁵⁴ with illustrations reproduced in Fig.3. Curves 2 demonstrate that ionic contributions to total capacity in the hydrogen potential region are non-monotonous, and deviate from horizontal dashed line (extrapolation of current in double layer region, typically used for approximate correction). For chloride, and especially for bromide solutions, the ionic contribution to total capacity in the hydrogen region surely exceeds the contribution formally estimated from horizontal interpolation. In particular, this formal procedure results in pronounced underestimation of true surface area determined from H-UPD charge (up to 15–20%).

For sulfuric acid solution, there is a sort of mutual compensation of ionic contributions in the regions of weakly and strongly bonded hydrogen (C_f in these regions is below and above horizontal line, respectively, see Fig.3a). Another aspect of this compensation is as follows: the observed double layer capacity at $E(\text{RHE}) > 0.4$ V is essentially higher than ionic capacity because oxygen-containing species start to adsorb. Curves 3 and 4 in Fig. 3a demonstrate the results of approximate and more reliable correction. The corresponding difference is slightly higher than usual coulometric accuracy (at least 5%). Similar problems arise when other UPD-based techniques are applied to true surface area determination.⁵

Figure 3a presents also an example of negative true double layer capacity. In this case the sign is changed mostly due to a high negative contribution from A_O derivatives. It is the most obvious illustration to keep the reader from considering high-frequency capacity values (never negative in the absence of faradaic reactions) as C_f . An example of negative true double layer capacity in a wider potential interval is known for iridium: in alkaline solution the sign changes already at ca. 0.1 V RHE.⁵⁵

Another useful illustration goes from comparison of true and high-frequency capacity values. Namely, application of Dolin-Ershler scheme to impedance data for 40 Hz–50 kHz frequency range⁵⁶ results in 2–3 times lower values of double layer capacity in the region of high hydrogen coverage, as compared to curves 2 in Figs.3 a-c. The specific shape of capacity peaks determined by anion nature is qualitatively the same, but several details are smoothed or even lost in high-frequency data.

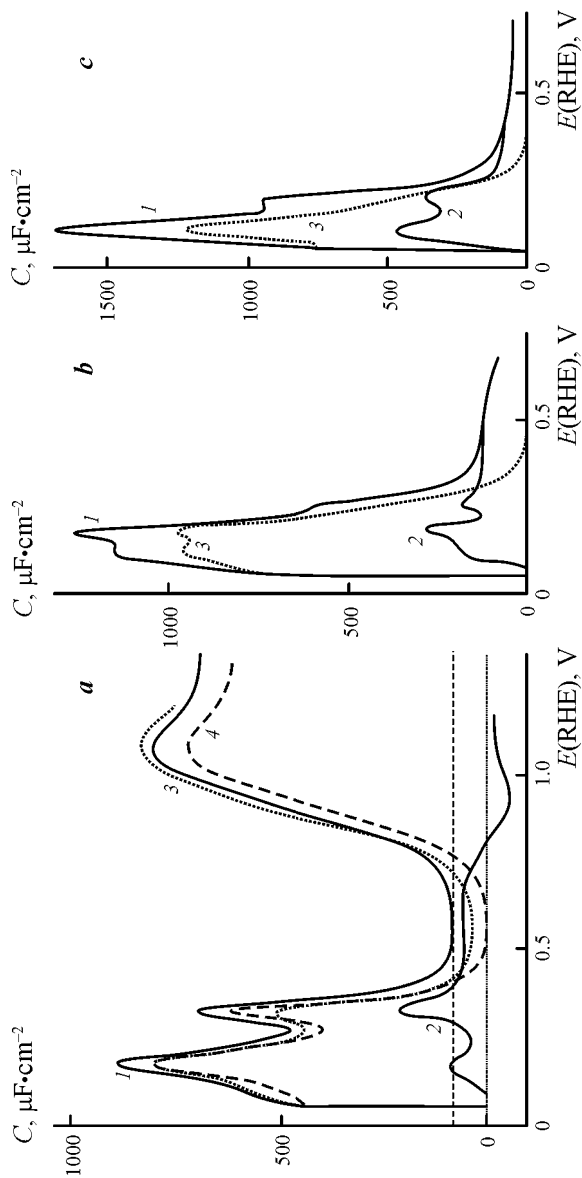


Figure 3. Cyclic voltammograms representing total capacitances C_t (1), and true double layer capacitances C_f (2) in 1 N H_2SO_4 (a), HCl (b) and HBr (c). Dashed lines (3) correspond to the difference of curves (1) and (2). In Figure 2a, dashed curve 4 corresponds to formal double layer correction (applied under assumption of purely double layer intermediate region between hydrogen and oxygen adsorption regions). From Ref. 54, with modifications.

A sharp right peak of sulfate contribution to C_f (curve 2 in Fig. 3a) is an interesting feature, as it somewhat reminds the famous Clavilier's butterfly at voltammograms of Pt(111)^{57,58}, the most intriguing feature of platinum single crystalline electrochemistry. It is a sort of *screened butterfly*: for the majority of disordered polycrystalline materials this feature finds itself inside the hydrogen region. It is surely sensitive to surface structure, which was never controlled in early equilibrium experiments. To estimate its possible position along the potential axis, we collect three sulphate adsorption curves definitely measured by various techniques and on different platinized platinum electrodes in sulfate solutions of close composition⁵⁹⁻⁶¹ (Fig. 4a). Figure 4b presents two limiting cases of *screened butterfly* obtained by differentiation of these equilibrium curves. The difference in curves 1 and 2 in Fig. 4b is far beyond inaccuracy of our treatment.

Probably some unusual voltammetric features of certain polycrystalline platinum samples, like the *third hydrogen peak*,⁶² can result from structure-sensitive sulfate adsorption.

3. Potentials of Zero Charge: General Trends

One of the most psychologically embarrassing aspects of platinum metals electrochemistry is the existence of two types of potentials of zero charge (pztc and pzfc for total and free charges, solid and open circles in Fig. 5 respectively). Figure 5a compares some data for Pt, Ir and Rh in solutions of various pH, and Fig. 5b collects the data for platinum (most actively studied) in solutions of various anionic composition. Other symbols in Fig. 5 mark several representative values for single crystals. The experimental approach to determine these values was discussed in a general context of zero charge problem in Ref. 63. The basis of this approach is CO displacement technique, which the Alicante group started developing jointly with Clavilier.^{64,65} It was consequently developed and improved by Feliu and co-workers, and a number of their results⁶⁶⁻⁷² plotted in Fig. 5 are discussed below in Section IV.2.

The number of platinum group metals in Fig. 5a is limited to three because other metals are less studied. For Pd, complications appear because of hydrogen absorption at potentials below ca. 0.1–0.15 V (RHE). This interval is so wide because highly defective dispersed palladium absorbs a lot of hydrogen in the α -phase, to

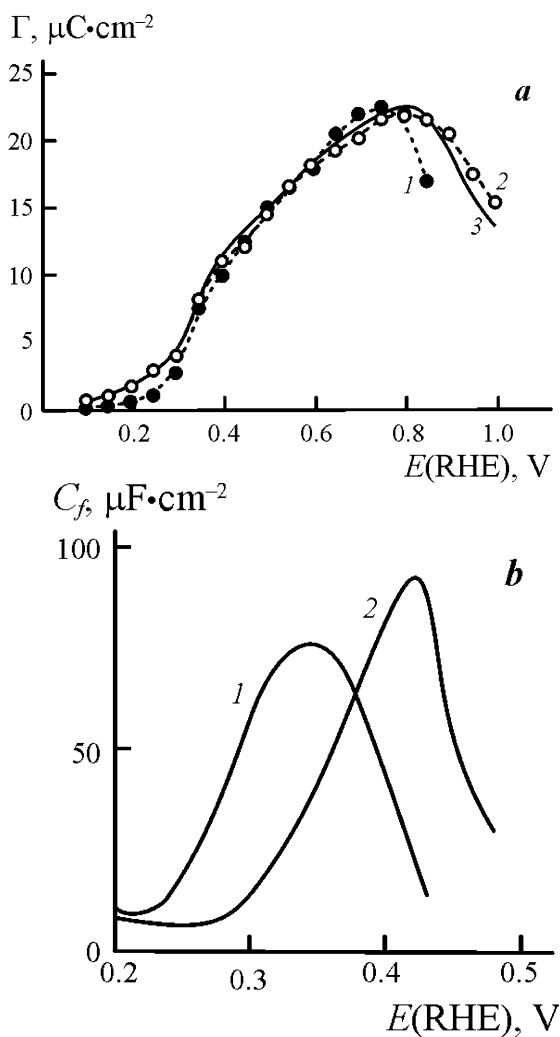


Figure 4. Equilibrium data on sulfate adsorption (a) and two limiting versions of their potential derivatives (b) for 3 - 10 mM H_2SO_4 with 0 - 10 mM additives of Na_2SO_4 . Curves 1-3 (a) for this treatment are taken in original form from PhD theses of L.Yu. Lukyanycheva (conductivity technique, curve 1), Zh. N. Malysheva (radiotracer technique, curve 2), V.V.Topolev (adsorption curves technique, curve 3); corresponding published plots are in smaller format,⁵⁹⁻⁶¹ and can contain some distortions.

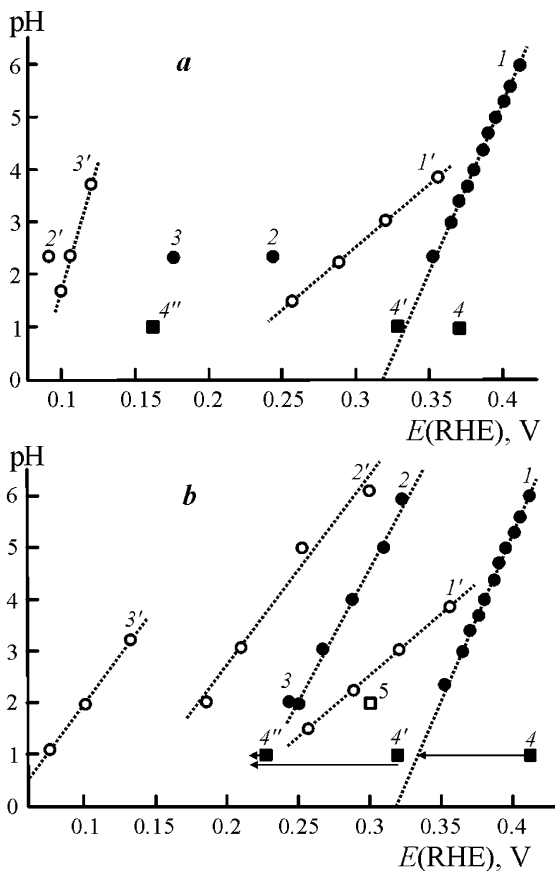


Figure 5. Potentials of zero total (solid symbols) and free (open symbols) charges of various dispersed electrodeposited metals in sulfate solutions (a) and of platinized platinum electrode in solutions of different anionic composition (b). The data for Pt (a - 1, 1'), Ir (a - 2, 2') and Rh (a - 3, 3') are plotted jointly with later determined values of the pztc of Pt(100) (a - 4)⁶⁶, Pt(111) (a - 4')⁶⁷ and Pt(110) (a - 4'')⁶⁸ in 0.1 M H_2SO_4 . The data for polycrystalline electrodeposited platinum in sulfate (b - 1, 1'), chloride (b - 2, 2') and bromide (b - 3, 3') are compared with pztc values for Pt(100) (b - 4)⁶⁹, Pt(111) (a - 4')⁷² and Pt(110) (a - 4'')⁶⁸ in 0.1 M HClO_4 . Arrows demonstrate the shifts of pztc with the density of (111) steps. Triangle (b - 5) demonstrates the estimate of pzfc of platinized platinum in perchlorate solution.⁷⁰ Original Refs for 1-3 and 1'-3' can be found in the text, Section III.3.

say nothing about formation of concentrated hydride β -phase below 0.06 V (RHE).^{73,74} Limitations result from the fact that the charge spent for equilibrium hydride formation is usually much higher than for any interfacial process. Despite of these troubles, a number of adsorption experiments with palladium were successful.^{75,76} Zero charge potentials are available for 0.05 M sulphate solution of pH 3. Unfortunately, there are no data for other metals in exactly the same solution, but it is evident that both pztc and pzfc of Pd are closer to the same values for Pt than for other metals.⁷⁵

Complications with ruthenium are induced by *early* oxygen adsorption, as well as by the shift of research interest to its catalytically outstanding alloy with platinum (see recent review).⁷⁷ Only one paper⁷⁸ contains some data on free electrode charge of electrodeposited Ru and Pt-Ru in alkaline and acidic chloride medium. The most important result is the shift of pzfc for Pt-Ru (ca. 0.06 V towards less positive values), as compared to Pt under the same conditions. As can be judged from some curves, pzfc of pure (non-oxidized) Ru finds itself in the region of negative RHE potentials.

For osmium, *early oxidation* problems are even more pronounced, and no systematic thermodynamic study was completed. A number of important experimental facts about electrodeposited osmium (or better to say, osmium oxohydroxide?) electrochemistry are collected in Ref. 79.

Summary of the data in Fig. 5b is also incomplete, and two other types of solutions should be mentioned. For perchloric acid solutions, application of a number of techniques shown in Fig. 1 is complicated by chloride formation taking part in parallel with H UPD, see below in Section IV.4. Nevertheless, the dependences of platinum free electrode charge on potential for 0.005 M H_2SO_4 + 0.5 M Na_2SO_4 and 0.01 M HClO_4 + 1 M NaClO_4 were compared.⁷⁰ The values of pzfc are very close (~ 0.3 V RHE), despite of lower perchlorate adsorption. Zero charge potentials of both types were also measured in fluoride-based solutions of pH 2.4 (0.3 M HF + 0.12 M KF), representative papers of this series are Refs. 80 and 81. Both pztc and pzfc of platinum and rhodium are found to be ca. 0.03 V more positive than in sulfate solutions of the same pH (with slightly different ionic strength). These results for both relatively weakly adsorbing anions, perchlorate and fluo-

ride, are in agreement with general tendency demonstrated in Fig. 5b.

The data on zero charge potentials in alkaline solutions are mostly available for platinum and rhodium,⁸²⁻⁸⁴ being closely related to the studies of oxygen adsorption. Oxygen UPD phenomena is beyond the frames of this review, but some intersections are inescapable, as just for these systems an interesting phenomenon of *inverted* pzfc is the most pronounced.

In fact, only the values of so-named *normal* pzfc are given in Fig. 5 and discussed above, but (as it was predicted already in 1930s) two pzfc can exist in each system. The second (*inverted*) pzfc results from oxygen adsorption and its contribution to free charge, this is why its shift to less positive potentials in RHE scale with pH is expected. The pH dependence of electrode charge required a lot of experimental efforts, and initially was approached from *acidic* and *alkaline* edges.⁸⁵⁻⁸⁷ Owing to improvement of isoelectric potential shifts technique and the arrangement of titration under isoelectric conditions^{53,88-92} it became possible to cover the overall pH interval and to get the reliable dependences of pztc and *normal* pzfc on solution pH (both dependences for Pt in chloride media are presented in Fig. 6a).

Direct experimental observations of both pzfc in solutions of certain composition were reported for the following systems: for Ir in alkaline iodide-containing solutions;⁹³ for Pt in sulphate solution, pH 6;⁵² for Rh in chloride solutions, pH 5–9;⁹² for Ru in chloride solution, pH 2.⁷⁸

There are also many examples of free charge vs. potential curves demonstrating the pronounced decrease of free charge in the oxygen adsorption region, when more positive *inverted* pzfc is approached, but not attained. An example for rhodium is presented by curves 1–3 in Fig. 6b. The subsequent curves 4–7 at higher pH already contain two zero points. The most surprising behavior in this series (curves 8 and 9 at the most high pH) is the absence of pzfc in potential interval under study. The same type of curves was observed in earlier studies of alkaline solutions.^{55,83} It is important that strongly adsorbing bromide or iodide additives induced the appearance of the *lost* region of positive free charge, due to their ability to compete with adsorbed oxygen. We do not discuss iodide-containing systems now, as many of them are strongly irre- for both relatively weakly adsorbing anions, perchlorate and fluo-

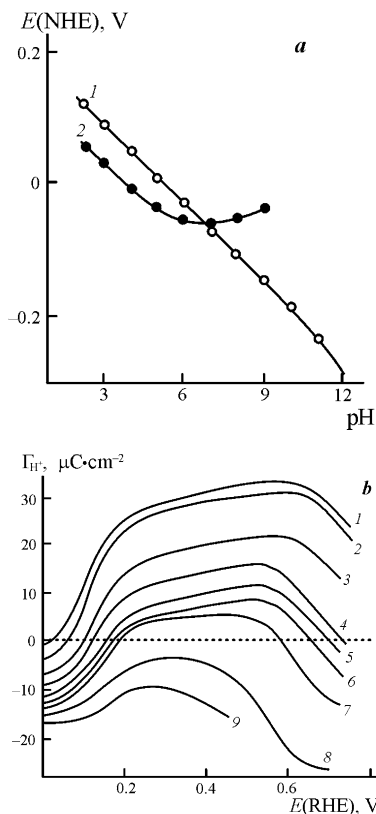


Figure 6. Some trends for potentials of zero charge as a function of solution composition: (a) pH dependences of platinum pztc (1) and pzfc (2) in 0.1 M KCl;⁹⁰ (b) example of pzfc inversion for rhodium in 0.1 M KCl; free charge curves are presented for pH 3(1), 4 (2), 5 (3), 6 (4), 7 (5), 8 (6), 9 (7), 10 (8), 11 (9);⁹² (c) (see p. 126) platinum pzfc dependence on salt concentration c and anion nature in 3 mM HCl + c M KCl (1), 3 mM HBr + c M KBr (2), 3 mM KOH + c M KBr (3), 3 mM KOH + c M KI (4).¹⁰³ In Refs 90, 92, pH was adjusted with HCl or KOH. Reprinted from Refs. 90(a), 92(b), and 103(c), Copyright (1975), (1976) and (1977), respectively, with permission of Nauka Publ.

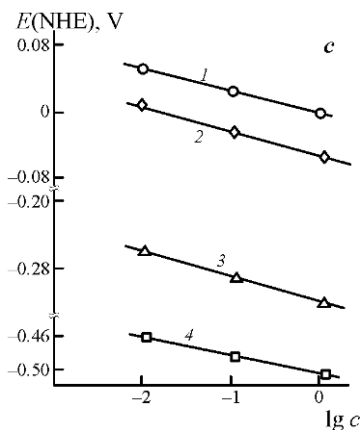


Figure 6. Continuation.

librium with hydrogen, but works as a sort of *surface modifier* (see representative Refs. 94 and 95).

Qualitatively, the initial hypothesis never contradicted the data on normal and inverted pzfc: residual negative charge of oxygen atoms (or hydroxide adsorption with charge transfer) decreases the adsorption of anions and supports the adsorption of cations. Finally the charge of adsorbed ions changes its sign, which means that the free electrode charge passes a new zero point. When superposition of hydrogen and oxygen adsorption is very pronounced (e.g., in alkaline media), the anomalous adsorption of cations starts at lower potentials, and these systems usually demonstrate no pzfc in the overall potential range. Attempts to support this hypothesis by quantitative data induced the interest to cations adsorption.

This topic should be separated, as it opens the door to the large area related to surface thermodynamics on metals modified by foreign adatoms. In the 1970s, the knowledge of metal UPD was still limited, and both electrostatically adsorbing cations and that adsorbing with pronounced charge transfer were studied in a similar manner. It is worth to mention a visual comparison of platinum pzfc shifts of the opposite sign in sulfate medium induced by iodide and thallium adatoms.⁹⁵ More weakly adsorbing cations only slightly affect platinum and rodium pzfc: 20 mV shift to more

positive values is observed when one goes from Li^+ to Cs^+ ;⁹⁶⁻⁹⁹ comparable or even smaller shifts are induced by alkaline earth cations,¹⁰⁰ and it does not correlate with cation charge and surface coverage. Namely, the effect increases when going from barium to zinc,¹⁰¹ despite of comparable Gibbs adsorptions of both cations. Most probably the reason is Zn UPD. Interplay of the effects of adsorbed cations and hydrogen adatoms was noticed, but never considered quantitatively.

Cations adsorption is of interest for interpretation and prediction of pzc dependences on salt concentration, considered in a general form in Ref. 102. Experimental data for solutions of various anionic composition¹⁰³ (Fig. 6c) demonstrate no pronounced slope difference for anions of essentially different adsorption behavior. All slopes are very low (even lower than expected in the absence of Esin-Markov effect studied earlier for similar systems.)¹⁰⁴ The decrease of slope can result from two contributions (decrease of cations adsorption with potential and displacement of hydrogen with increase of anion concentration). This result means that the straightforward interpretation of Esin-Markov coefficients for platinum metals (if any) should take into account that these values can be underestimated.

It is easy to see that a self-consistent thermodynamical consideration of hydrogen and ions adsorption ignored (at least in an explicit form) the existence of water at the interface. In reality water is expected to participate in all interfacial events, and can contribute to both *atomic* and *ionic* quantities if its orientation/location is changed with electrode charge and adsorbate coverage. This is a natural weak spot to be understood by some additional means.

General trends of zero charge potential behavior for electrodeposited platinum metals were formulated 20 years prior to the period of active thermodynamical studies of single crystalline surfaces. In what follows we try to catch similarities and disagreements missed or scarcely discussed earlier.

IV. SINGLE CRYSTALS AND *OLD* PLATINUM ELECTROCHEMISTRY TRY TO MEET HALF-WAY

1. From Poorly to Well-Defined Surfaces

Platinized platinum and relative dispersed electrodeposited metals of 1960s–1970s were extremely poorly-defined materials of complex structure. Protocols for electrode fabrication were of the same type as the standards of technical galvanics.¹⁰⁵ In particular, galvanostatic deposition was typically used, and concentration of chloride bath was not fixed precisely because of several subsequent depositions from one and the same portion of solution. Nowadays we know a lot about dependence of the structure of electrodeposited platinum on deposition potential and bath composition (see Ref. 106 and Refs. therein). Late data on SEM, TEM and XRD of platinum electrodeposits demonstrate that galvanostatic modes applied to prepare the electrodes for thermodynamic studies corresponded to very low RHE potentials (sometimes even below zero) and had to result in formation of rather loose agglomerates of 10–20 nm size crystals with relatively low defectiveness, weak mutual coalescence, and slightly pronounced bulk texture. Lamellar shape of platinum crystals formed in this region of deposition potentials is typical, but nobody can be sure about reproducibility of structural details when depositing at constant current. The specific surface areas were close to $10 \text{ m}^2 \cdot \text{g}^{-1}$ or higher, when the thickness was few μm .

A long period, between Will's pioneering studies of platinum single crystals¹⁰⁷ in 1965 and Clavilier's invention of the technique to prepare well-ordered platinum low-index surfaces^{57,58,108} in 1980, still remained *poly Pt epoch*, as all the results published for single crystalline electrodes were reconsidered later. During the next decade major attention was devoted to thorough coulometric analysis of voltammetric data and attempts to separate hydrogen and anions contributions (well-known Clavilier's papers^{109,110} can be mentioned as a very relative end of this period). In the 1990s, the most active period started: Aldaz, Feliu and coauthors created a worldwide school of single crystal electrochemistry based experimentally on Clavilier's technique. Simultaneously, a lot of important studies were carried out with larger commercial single crystals, a famous example is Ref. 111. This approach (initially

most popular in USA) is predominantly electrocatalytic, and now it places emphasis on bimetallic systems.

Two groups of electrode materials (electrodeposited platinum metals and single crystals) missed each other for a long time, and people simply certified the pronounced difference of electrochemical responses for poly Pt and single crystals. Some occasions to recognize each other appeared already in XXI century, when a lot of better characterized polycrystalline materials became available.

2. Potentials of Zero Charge – Occasion to Draw Together

Single crystal electrochemistry started to approach surface thermodynamics from attempts to get the basic quantities shown in Fig. 1. Application of a number of already known techniques was impossible because the surface areas of single crystals are several orders lower than required for tracing adsorption phenomena by any *bulk* technique applied to solution (changes of solution composition resulting from adsorption are negligible even if the volume is very low).

Under these circumstances two principal approaches were possible: to increase a sensitivity of techniques or to work out the alternative tools. The former approach was successful only for radiotracer techniques,¹¹² but their application is limited to certain ions and is typically helpless for hydrogen adsorption studies. Among alternative (purely electrochemical) techniques, the most successful was surely CO displacement recently reviewed in Ref. 72. There are also other probes besides CO (see, e.g., the comparison of CO and N₂O probes).⁶⁶

Displacement techniques were helpful for collecting the data on the total charge and corresponding pztc for low index and stepped single crystal surfaces in solutions of various composition. For pure acids (mostly studied by this technique) the quantitative comparison with Frumkin-Petrii school data is limited by the difference in pH and solution composition. If to consider extrapolation of sulfate series (curve 1 in Fig. 5a), pztc values for dispersed Pt/Pt appear to be closer to pztc of Pt(111) (point 4'). It is suggestive to join this coincidence and the *screened butterfly* discussed above in Section III.2, and to assume that the surface of electrodeposited platinum contains (111) terraces, but we should keep ourselves from too straightforward conclusions: for stepped surfaces,

pztc's should be more negative.^{66,68,69,72} In view of this fact the similarity of Pt/Pt and Pt(100) pztc's (point 4 in Fig. 5a) should be also considered. At the same time, the pztc for Pt(110) (point 4'' in Fig. 5a) is much more negative.

The values for two Pt and Rh single crystal surfaces in 0.5 M H₂SO₄ were compared.¹¹³ Surface crystallography effects on pztc values are qualitatively the same: 0.38 V for Pt(100) versus 0.15 V for Pt(110) and 0.14 V for Rh(100) versus 0.10 V for Rh(110). The authors accented the location of all pztc points inside hydrogen adsorption region, but the quantitative difference was not analysed (in later papers as well). Comparison of single crystalline and electrodeposited Rh (its pztc is presented by point 3 in Fig. 5a) results in approximately the same conclusion like for platinum: polycrystalline material behaves more likely as (100) than as (110). Recent data of Wandlowski's group¹¹⁴ for three low index Rh surfaces in 0.1 M H₂SO₄ demonstrate pztc sequence another than a sequence for platinum: Rh(111) (0.105–0.120 V) ≤ Rh(110) (0.110–0.130 V) < Rh(100) (0.140–0.155 V). Current hypothesis consists in a key role of strong sulphate adsorption on Rh(111) in the negative shift of pztc. This observation is very promising for interpretation of various surface crystallography manifestations affected by metal nature.

Unfortunately, for a majority of systems the available techniques for pzfc determination are still limited to high surface area electrodes and solutions with excess of supporting salt electrolyte, and there is a very small chance to compare with single crystals. However deep analysis of thermodynamic relationships and a proper choice of solution gives a principal possibility to determine pzfc if it is located in purely double layer region,^{71,72} and this is the case for Pt(111) in perchloric acid. For this interface, pzfc appeared to be very close to its earlier known pztc (marked by point 4' in Fig. 5b). This finding at first sight contradicts previous *polycrystalline* trend: for platinum and rhodium at pH below 5–6 pzfc is always lower than pztc. At low pH, the difference amounts to several dozens of mV and decreases with pH. For sulfate media, extrapolation of these dependences to pH 0–1 results in pzfc values of 0.22–0.23 V RHE. A single available point for perchlorate solution (point 5 in Fig. 5b) is very close to sulfate pzfc value (curve 1' in Fig. 5b), being evidently shifted from pztc in the same

solution. As there are no other systems to compare, we cannot judge whether it is some fundamental difference.

The values of pztc for low-index platinum surfaces in perchlorate medium (points 4, 4', and 4'' in Fig. 5b) are more positive than in sulfuric acid, but the dependence on surface crystallography follows the same trend. Horizontal arrows demonstrate the negative shifts of pztc with step density for stepped surfaces of all terrace orientations (shift is very small for originally stepped Pt(110) and attains 0.1 V for two other surfaces). From detailed analysis with inclusion of high vacuum data⁶³ one can assume that for pzft the negative shift can be even more pronounced, and it is confirmed by very few values reported now for stepped surfaces.⁷² The general trend of halide ions effect is the same for single crystals and electrodeposited platinum, as can be concluded from available total charge curves.^{71,115}

Basically, the comparison of zero charge potentials gives very rough notion concerning similarities and difference in thermodynamic behavior of single crystals and highly disordered metals. However even being affected by numerous factors, this comparison demonstrates that metal nature and strongly adsorbing anions nature play a major role for materials of any surface structure. Further clarification requires additional experimental facts for single crystals, especially the reliable pH dependences of zero charge potentials. To address this problem experimentally, it is important first to clarify the behavior of adsorbed OH species on single crystal electrodes.¹¹⁶

Another challenge is to widen the knowledge concerning other metals, besides platinum. Good examples of Ru^{117,118} and Ir¹¹⁹ single crystal electrochemistry were published, but systematic thermodynamic treatment is still absent.

As for already existing data on zero charge potentials and related values, they are of great interest for the studies of more and more complex real less characterized materials.

3. From Well-Defined Surfaces to More and Less Defined Materials

A rather natural idea is to present the behavior of polycrystalline surfaces as an additive behavior of their fragments having different

crystallographic orientations. There are dozens of examples where such attempts seemed to be successful.

A possibility to consider polycrystalline platinum surface as some combination of low index surfaces or as some disordered single crystalline surface surely cannot be immediately concluded from the values of zero charge potentials exclusively. Experiments with some *intermediate* model systems more or less *reduceable* to simple additive combinations of several planes, or of terraces and steps, are of increasing interest. Microfacetted electrodes,^{120,121} various types of nanoparticles prepared by precise non-electrochemical techniques,^{122,123} non-coalesced electrodeposited particles,¹²⁴ and single platinum *microspheres* deposited on micro-electrodes,¹²⁵ as well as highly ordered templated electrodeposits¹²⁶ can be considered as most ordered real platinum materials helpful to discover structural effects at atomic level. However they all are still *too simple* to compare with, to say, platinized platinum, and attempts to electrodeposit the dispersed metallic multilayers of more and more ordered type^{106,127} are also relevant.

Very specific type of platinum materials hopefully able to form a bridge between less and more ordered surfaces is the so-called facetted polycrystal. Since the pioneering work of Cerviño et. al.¹²⁸ in the 1980s, the electrochemical faceting procedure of different metal surfaces to produce preferred crystallographic orientations was widely employed and investigated. The application of fast repetitive periodic potential pulses in different potential ranges to produce faceting of platinum, gold, palladium, rhodium is a highly reproducible procedure developed by Arvia and coworkers.¹²⁹⁻¹³³ The structure and morphology of this sort of electrodes is already well characterized by scanning electron and scanning tunnelling microscopy (as well as their catalytic properties).¹³⁴⁻¹³⁶ The mechanisms of faceting processes is also clarified.¹³⁷ A similar type of surface treatment was proposed later,¹³⁸⁻¹⁴⁰ and some comparison with what was previously and carefully studied by Arvia's team for a huge number of systems surely makes sense, as the faceting process involves very similar phenomena. Representative examples of early and more recent electrochemical faceting studies can be found in Refs. 141, 142. Recent review on faceting and roughening of metals is also available.¹⁴³ The main goal to involve these materials is to collect as manifold as possible experimental arguments supporting contribu-

tion of faceted regions and intermediate areas into electrochemical responses.

However it is evidently senseless to reduce single crystal electrochemistry to material science, a tool to solve some puzzles of real materials, but it is easy to see that appealing to various materials widens a field of vision. The same is with inadequacy of idea to put this area in frames of classical thermodynamic scheme. Following its own way, single crystal experiments collect more and more information about behavior of all adlayer components, but keeping some traditions of data treatment would not be out of place for this advanced field. The subsequent Sections touch briefly three points of most visible intersection.

4. Adsorption of Anions

A sort of asymmetry is observed in the studies of ions adsorption on platinum group metals: anions attract more attention than cations. The reason is probably a prevalence of acids among electrolytes, and just the sulphuric acid remained one of the most popular for a long period. It was stated already in Ref. 9 that platinum capacity in the double layer region exceeds the capacity of ionic double layer in sulfuric acid. This was confirmed more directly by comparison of the slope of galvanostatic charging curves and the values of sulphate adsorption:¹⁴⁴ more than a half of capacity formally determined from electrochemical data could not be attributed to sulphate adsorption. However this ratio estimated by various means, as well as the observed double layer capacity, were not quantitatively reproducible for various polycrystalline materials, leading to the assumption that competitive adsorption of sulfate and OH species is very sensitive to surface structure.

Unbelievable progress in sulfate adsorption studies took place during the single crystalline era, especially after direct visualization of adlayer and phase transition in 2D sulfate adlattice on Pt(111).¹⁴⁵ Partly similar observations were reported for Ir(111).¹⁴⁶ In addition, quantitative agreement of sulfate surface coverage on Pt(111) determined by radiotracer technique¹¹² and results of thermodynamic analysis¹⁴⁷ made Pt(111) a really famous electrode and inspired the studies of more general problem: order-disorder in adlayer. It was a real shift to atomic level electrochemistry.

Parallel events in the field of in situ IR spectroscopy (for a review of sulfate IR studies, see Ref. 26) resulted in a coupled shift to molecular level: bi-sulfate anion was recognized in sulfate adlayer even in solutions with predominating sulfate. It was completely new situation, when chemical equilibrium is affected by adsorbate-surface interaction. In usual terms of solution equilibria, the effect corresponds to increase of pK_a from its bulk value (ca. 2) to 3.3–4.7 (pK_a is potential-dependent).¹⁴⁸ To agree this situation with *bulk* thermodynamics, one should simply use electrochemical potential instead of chemical. The phenomena of adsorption-induced protonation is relative to UPD, when adsorbate-surface interaction shifts redox equilibria. In more *molecular* terms, the species determined as bi-sulfate ions are probably interfacial ion pairs,¹⁴⁹ i.e., the phenomenon can be considered as coadsorption. This situation is screened in purely thermodynamic analysis, as excess surface protonation is hidden in Gibbs adsorptions of sulfate and H^+ . However it becomes important for any further model consideration, as it can affect lateral interactions and the order in the adlayer. The excess adsorption-induced protonation of various anions is a very attractive field. In particular it is the only chance to explain why multicharged oxoanions can form complete monolayers on platinum.^{150,151}

This unique sulfate developments attracted more attention to reference systems with weaker adsorbing anions. Fluoride and perchlorate looked the best candidates for a long period, despite both require special efforts to keep the surface pure.¹⁵² Double layer capacity values and the data for various anions adsorption are always very sensitive to impurities in acids (the problem was specially addressed recently in Ref. 153). Perchlorate *self-contamination* by reductive chloride formation takes place at positive RHE potentials on Pt and especially on Rh. Kinetics of these processes was studied systematically by Horanyi and co-workers (see Ref. 154 for earlier references). At Rh electrode, the reduction starts already at ~ 0.5 V RHE, when for Pt measurable amounts of chloride appear only after polarization at potentials closer to zero RHE. According to Ref. 155, for typical modern experiments with single crystals the concentration of chloride in 0.1 M $HClO_4$ does not exceed 0.01 μM , leading to negligible effects on voltammograms. However for long-term experiments contamination can be much higher. The only available perchlorate adsorption data for

electrodeposited platinum⁷⁰ were surely obtained in presence of chloride impurities. Actually, no chloride in solution was found (analytical technique applied in Ref. 70 provided sensitivity not better than 0.01 mM), but the directly determined quantity of adsorbed chloride was rather high (several $\mu\text{C}\cdot\text{cm}^{-2}$, with a maximum at $E(\text{RHE}) = 0.4 \text{ V}$), so the reported data on perchlorate adsorption can be affected by this fact.

An important detail consists in suppression of perchlorate reduction by sulfate and chloride in mixed solutions. For sulfate-containing systems, it is also important to remember that when chloride appears it suppresses sulfate adsorption and induces smoothing of ascending branch of adsorption vs. potential curves.¹⁵⁶ In any case a search for other reference with weakly adsorbing anions is reasonable.

Among most weakly adsorbing anions, trifluorosulphonic anion⁵⁹ and tetrafluoroborate¹⁵⁷ were considered (Fig. 7). BF_4^- highest adsorption value on platinized platinum in 0.01 M HBF_4 solution hardly exceeds $3 \mu\text{C}\cdot\text{cm}^{-2}$. To compare, the maximal value for sulphate in 0.005 M H_2SO_4 is close to $20 \mu\text{C}\cdot\text{cm}^{-2}$; for fluoride in 0.14 M HF , $12 \mu\text{C}\cdot\text{cm}^{-2}$ maximal adsorption was reported.^{80,81} Trifluorosulphonic anion adsorption on platinized platinum from 0.005 M solution never exceeds $5 \mu\text{C}\cdot\text{cm}^{-2}$.⁵⁹ (Trifluoroacetate adsorption was studied for comparison,⁵⁹ and was found to be close to sulphate adsorption). All these values correspond to 0.6–0.7 V RHE. Weak adsorption of CF_3SO_3^- anion recently attracted attention,^{158,159} and the abovementioned data can be helpful.

Adsorption phenomena in H_3PO_4 are of special interest in view of the role of this electrolyte in fuel cell research and development. Early studies^{160,161} induced the suspicion that phosphate adsorption on polycrystalline platinum is irreversible, at least in certain (rather wide) potential region. Manifestations of slow destructive phosphate adsorption were found, probably relative to well-known adsorption behavior of nitrate on platinum group metals.^{162,163} The study of phosphate adsorption is surely of interest for basic problem of adsorption-induced protonation. Recent data for Pt(111) indicate no irreversibility, but it is not obligatory contradiction. For metal UPD, there are several examples (thallium UPD on Pt is typical)¹⁶⁵ of reversible behavior at single crystals, despite of completely irreversible adatoms deposition on polycrystalline surfaces.

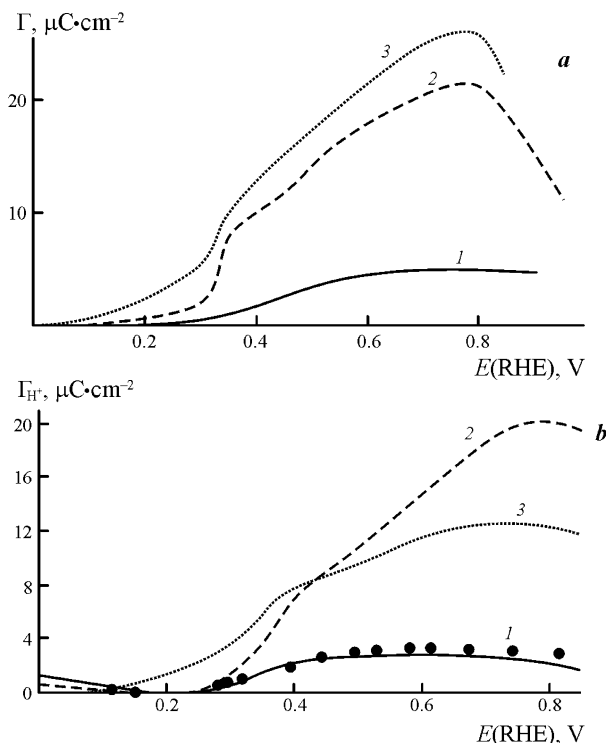


Fig. 7. Less known data on weak anions adsorption on platinum obtained by the conductivity technique. Curves 2 are given for comparison, measured in 2.5 mM H_2SO_4 by the same technique at the same electrodes. (a) Trifluoromethanesulfonic anion adsorption from 5 mM $\text{CF}_3\text{SO}_3\text{H}$ solution (curve 1)⁵⁹, compared also with the data for 5 mM CF_3COOH (curve 3). (b) Fluoroborate adsorption from 6 mM HBF_4 solution (curve 1)¹⁵⁷ compared with the available earlier data of isoelectric potential shifts for Γ_{H^+} in 10 mM HBF_4 solution (points). To compare roughly with fluoride adsorption,⁸¹ curve 3 for 0.14 M HF is presented (the activity of hydronium ion in this solution is the same as in 10 mM H_2SO_4). Reprinted from Refs. 59 (a) and 157 (b), Copyright (1981) and (1977), respectively, with permission from Nauka Publ.

Direct experimental results on anions Gibbs adsorption, even if obtained for poorly characterized dispersed platinum, are still of interest for comparison. The effect of potential on the difference of these values for some anions (in particular sulfate and perchlorate)

illustrates the trends of competitive anions and adatoms adsorption, being qualitatively the same for poly Pt and single crystals.

5. Adsorption Isotherms

Temkin isotherm¹⁶⁶ (considered for a long time as the most suitable to describe hydrogen adsorption on platinum, at least at mid coverage) assumes admittedly that interactions in adlayer are repulsive. Early Breiter's analysis²⁰ in terms of Frumkin isotherm, despite of less satisfactory fit, discovered that the attraction in adlayer is also possible, and more probable for *strongly bonded* hydrogen at low coverage. To compare Breiter's fitting with numerous recent applications of Frumkin isotherm, one should remember that in Ref. 20 the equation of this isotherm was applied in original Frumkin's form,¹⁶⁷ i.e., positive attraction constant corresponded to attraction, not to repulsion, and was twice lower than currently habitual parameter g .

Present-day results for poly Pt in the same 0.5 M H₂SO₄ solution, e.g., based on the estimates of hydrogen coverage from integrated IR band intensities,¹⁶⁸ confidently give positive g of ca. 3.1, i.e., the result of an opposite sign. It is easy to guess that the difference goes from separation of hydrogen from anions. The latter were actually "mixed up" with hydrogen in Ref. 20.

Appearance of the data for platinum single crystals stimulated many attempts to apply Frumkin isotherm, in order to provide some quantitative characteristics of lateral interactions in adlayer. Even straightforward double layer correction and fitting of coverage versus potential curves for a single temperature (see, e.g., Ref. 169 and citations in this paper) discovers the pronounced difference in g values for hydrogen on Pt(111) from much lower values for Pt(100) and Pt(110). The former value always exceeds 10 in both sulphuric and perchloric media, when both latter values are usually close to each other and even low negative g values were reported. To improve the agreement of Frumkin isotherm with experimental curves, more complicated approach (*local Frumkin isotherms*) was proposed,¹⁶⁹ with ironic conclusive comment *the analysis would be only as good as the experimental data*. We should add that the analysis would be as reasonable as the degree of relation of starting corrected values to hydrogen surface coverage.

The approach based on the treatment of temperature dependences^{111,170} is more solid, even with the same approximate double layer correction. It confirms very high g values (this time 16-18)¹¹¹ for Pt(111). However the most serious progress resulted from extraction of entropy terms and application of generalized isotherms, in combination with precise double layer correction based on thermodynamic treatment of voltammetric data.¹⁷¹⁻¹⁷³ Entropy term played a role of effective diagnostical tool, as it discovered the role of water ordering in lateral interaction. This finding provides the direct link to both molecular modeling and interpretation of spectral information related to water at the interface. By these means, the third important adlayer component, besides hydrogen and anions, ceased to be invisible by purely electrochemical techniques.

To adjust the approach based on Frumkin isotherm to deconvolution of experimental curves, the approximations by Gaussian (for repulsive interactions) and Lorentzian (for attractive interactions) were proposed.¹⁷³ This approach was helpful to estimate partial contributions from terraces and steps of certain orientation by means of deconvolution of CVs for various high index surfaces. It is interesting to compare contributions from ionic adsorption (known directly for Pt of high roughness factor, as exemplified by Fig. 3) with deconvolution based on formal application of Frumkin isotherm.¹⁷³ Deconvolution of Breiter's curves and comparison with his fitting parameters can be also of interest, to understand what form of adsorbate is critical for switching from attractive to repulsive fitting parameter. At this stage deconvolution approach already works for ordered platinum nanoparticles with a complex voltammetric response.¹²²

Computational efforts to describe lateral interactions and compare the results with experiment in terms of isotherms started much earlier¹⁷⁴ than the experimental information was well prepared. Qualitatively, these initial results obtained in frames of lattice-gas model are interesting, as they demonstrate a possibility of attractive H-H interactions in the case of coadsorption with repulsing anions. Modelling of mixed adlayers at various computational levels was systematically developed by Koper and coworkers,¹⁷⁵⁻¹⁷⁷ and now represents a rather general approach. It can be probably applied to mixed adlayers with short-range interactions of completely different type, earlier considered at phenomenological level (mixed ionic¹⁷⁸ or organic¹⁷⁹ adlayers).

We escape to discuss here a number of hydrogen adsorption isotherms reported on the basis of rather formal kinetic data analysis for hydrogen reactions, like in Refs. 180 and 181. Most frequently the values of surface coverage in this type of studies are extracted from current-time or current-overpotential dependences simply as fitting parameters, and correspond to so-called hydrogen OPD, i.e., the reactive form of adsorbed hydrogen. Ionic double layer effect is ignored under these circumstances.

Besides adsorption isotherms, a model of two parallel capacitors was applied in the 1960s to describe the free charge vs. potential dependence for platinum metals.¹⁸⁵ The authors attempted to take into account contributions of hydrogen and oxygen adatoms in a manner earlier typical for consideration of organic species adsorption. The number of approximations appeared to be too high for further applications, but rereading of this paper 40 years after publication demonstrates that the approach (and the analogy itself) can be of particular interest for analysis of true charge transfer problem addressed in the next Section.

6. The First Step towards True Charge Transfer

Charge transfer in adlayers presents a subject of dramatic everlasting misunderstandings. To discuss this phenomenon it is necessary first to define the location of transferred charge, i.e., to state that it joins the electronic collective of metal (or leaves it). As there is no experimental tools to observe directly any *boundary* between electrons in metal and solution edge, the only possibility to study true charge transfer is to measure some signal sensitive to free electrons in metal. This is the meaning assumed by Lorenz, who introduced the notion of adsorption with charge transfer.^{186,187} In the 1970s, a sharp discussion of so-named *electrosorption valency* γ took place between Frumkin et al.^{188,189} and Vetter and Schultze.¹⁹⁰⁻¹⁹³ It was finally agreed that γ presents a formal charge transfer coefficient, which relation to basic Lorenz's quantity depends on a plenty of unknown interfacial details, including adsorbate location and its effect on solvent molecules inside the double layer.

The precise values of γ for various adsorbates on platinum single crystals are available now (see examples in Refs 114, 147), and it is probably a challenge to compare their behavior with two

practically forgotten differential quantities available for platinized platinum from combinations of directly measured thermodynamic quantities. These so-named differential contributions of hydrogen atoms (X),

$$X = \left(\frac{\partial E}{\partial A_{\text{H}}} \right)_{\Gamma_{\text{H}^+}} \quad (2)$$

and ions (Y)

$$Y = \left(\frac{\partial E}{\partial \Gamma_{\text{H}^+}} \right)_{A_{\text{H}}} \quad (3)$$

to interfacial potential drop were first discussed in Ref 22, and later calculated more accurately¹⁹⁴ for Pt and Rh (E is the potential in respect to fixed reference electrode, not RHE). The equations for X and Y combine:

- (a) isoelectric potential shifts,
- (b) the slopes of charging curves, $\left(\frac{\partial Q_t}{\partial E(\text{RHE})} \right)_{\mu_{\text{H}^+}}$ and
- (c) the values of the $\left(\frac{\partial \Gamma_{\text{H}^+}}{\partial \mu_{\text{H}^+}} \right)_{E(\text{RHE})}$ derivative.

To determine (c), one should treat a set of adsorption curves for a pH interval as wide as possible.⁸⁷ The accuracy of this treatment is not too high, but the reliability of final X and Y values can be checked by comparison with the ratio $X/(X+Y)$ determined independently from another type of data.^{82,87}

Despite of numerous accuracy problems going from recalculations of different experimental values into X and Y , the final result is of high qualitative significance: it confirms the existence of at least two physically different forms of hydrogen adatoms on polycrystalline platinum. Positive X values (corresponding to the negative residual charge on hydrogen adatom) are typical for low and mid surface coverage. At high surface coverage, X changes the sign, i.e., the residual charge on the hydrogen adatom becomes

positive. In original papers the effect was presented in terms of hypothetical *dipole of adsorbed hydrogen*.¹⁹⁴ It is important that for polycrystalline Rh, with its single narrow hydrogen adsorption-desorption peak at voltammograms, no changes of X sign were found in the overall interval of surface coverage: X was always positive, indicating negative residual charge of adatoms.

Absolute values of X in sulfate medium were found to be ca. two orders lower as compared to ionic contribution Y . Despite both values are referred to differential effects of introducing the species into adlayer, this difference allows very rough (surely cautious) estimate of the order of residual charge values: hundredth of the electron charge. *Residual* corresponds to conditional (not physical), but fixed metal/adlayer boundary. For halide-containing solutions, the difference is already closer to one order of magnitude, i.e., the residual charge is higher. Other (less pronounced) trends in X and Y behavior were discussed in relation to dependence of zero charge potentials on metal nature and solution composition.¹⁹⁴ This analysis looks self-consistent, but to apply it to exact understanding of charge distribution in the interfacial region one needs to link all charge-related quantities to any independently determined true charge transfer coefficients.

Information on true charge transfer in 1 M HCl and HBr solutions is available from electroreflectance data¹⁹⁵ owing to plasma mechanism of optical signal generation in these solutions. This mechanism was grounded by comparing the experimental electroreflectance spectra with the spectra calculated in frames of plasma electroreflectance theory. This approach cannot be applied in the same manner to any arbitrary system without preliminary analysis. Figs. 8 a,b present the dependence of true charges $|q|$ on adsorbed halide ions (grey areas between two curves in each plot present the interval of possible $|q|$ values, see explanations in Ref. 195 about the attainable accuracy). The potential scales of Figs 8 a, c and 8 b,d are the same, in order to show that for both chloride and bromide systems the behavior of differential X values taken from Ref. 194 (curves 1 in Figs. 8 b, d) is well correlated with decrease and increase of $|q|$. It is also notable that Y behavior correlates with $|q|$,

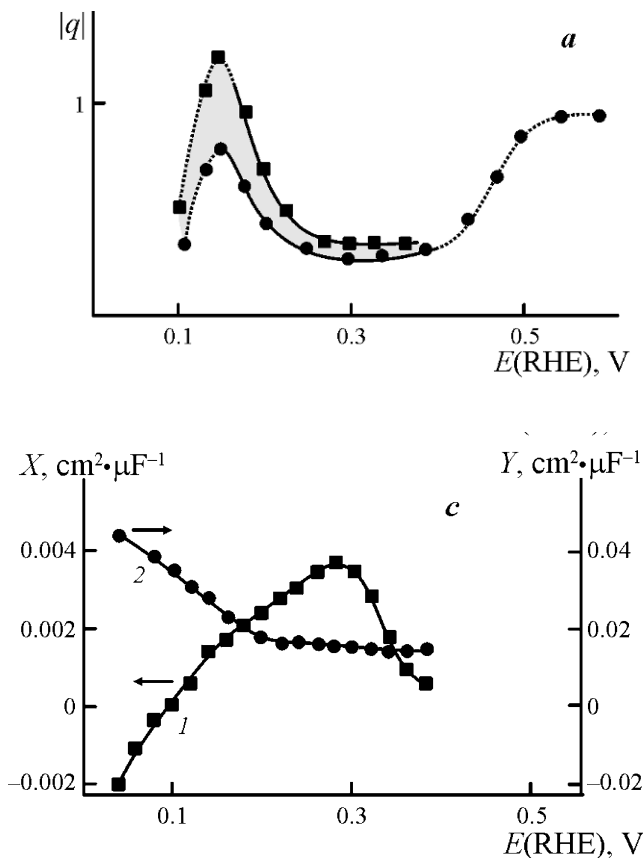


Figure 8. Comparison of true charge transfer coefficients q for chloride (a) and bromide (b) estimated from plasma electroreflectance data¹⁹⁵ (smooth polycrystalline Pt) with X and Y values¹⁹⁴ in solutions of the same anionic composition (c – chloride, d – bromide, dispersed electro-deposited platinum). The area between two curves (a, b) corresponds to unavoidable scatter (boundaries present to limiting versions of q recalculation). Dashed fragments (a) correspond to the region of lower accuracy, as compared to the overall potential region. Reprinted from Refs. 195 (a, b) and 194 (c, d), Copyright (1990) and (1969), respectively, with permission of Nauka Publ.

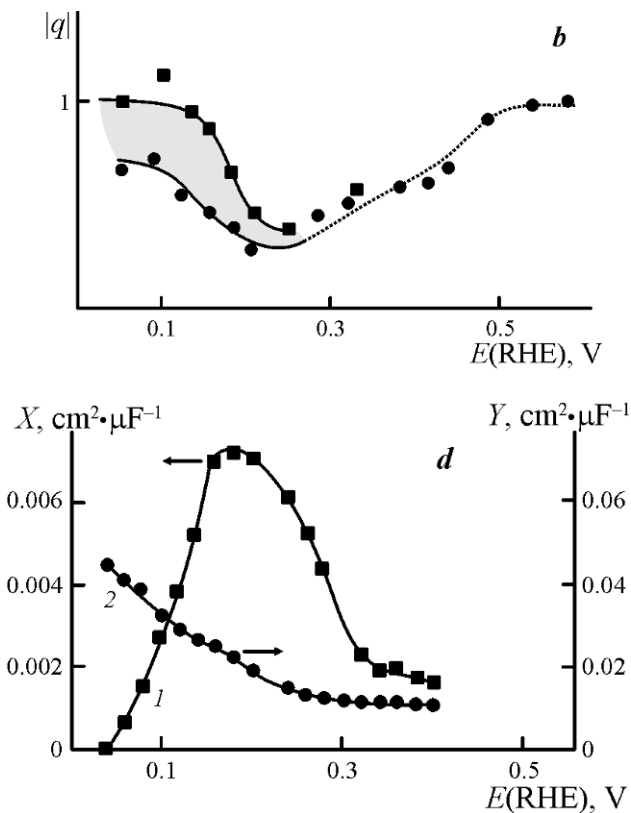


Figure 8. Continuation.

but not with X , i.e., behavior of hydronium ions is coupled mostly with halide ions, not with adatoms. Of course plasma electroreflectance signal can not recognize the nature of atom from which the charge is transferred, so the changes of $|q|$ can involve partial charge transfer from hydrogen adatoms as well, but we are first interested in mysterious true charge transfer value.

Further quantitative analysis is hardly reasonable, as the data for comparison should be obtained at exactly one and the same electrode and solution. At this stage we can only conclude from this comparison that the true charge transfer can be used for cali-

bration of the data on formal charge transfer. It looks more visually in differential form with conditional separation of hydrogen atom and ion, but calibration of this sort is basically possible for electrosorption valency as well. The bottleneck is to find the reliable spectroscopic signals sensitive to true charge transfer.

Phenomenological model of effective charge transfer coefficients is presented in Ref. 196. Its application to available thermodynamic data surely can not result in any true charge transfer coefficients, but provides independent possibility to estimate differential effects of solution composition on the electrode charge values. General trends agree with the trends going from X and Y analysis.

Differential values of Y can be also useful for interpretation of electrosorption valency in terms of sulfate versus bi-sulfate adsorption,¹⁹⁷ as one of mostly untapped resources of platinum electrochemistry. However the main progress is expected from combination of precise electrochemistry, thermodynamic analysis, and independent physical information supported by an appropriate theoretical basis, with necessary links provided by computational community. The final Section contains some brief notes in this respect.

V. REALISTIC AND VISIONARY DREAMS

Fast progress of platinum computational electrochemistry is stimulated by electrocatalysis, and the studies of CO adsorption predominate.¹⁹⁸ Accumulated experience is extremely useful for modeling the reversible adsorption at the interface, but today the latter looks like a tiny brook in the vicinity of computational mainstream. The closest layer going from electrocatalysis is theoretical/ computational prediction of electrocatalytic activity in hydrogen reactions,^{199,200} as it requires the modeling of hydrogen adatoms. The main problem in this case is comparison with experiment, because a lot of factors besides adlayer structure affect the observed reaction rates.

It is surely attractive to model first the structure of adlayers, and to verify the results using more or less direct information from X-ray techniques³⁰ and probe microscopy.^{28,29,32} However the important physical features of the interface can be missed in this

analysis. *Structural* results are necessary to check whether computational approach is realistic, and to supplement further steps.

A field well-prepared to be the second step is experimental modeling of electrochemical interface in vacuum systems²⁰¹⁻²⁰⁴ (see also Section 4 in Ref. 205). These systems give a chance to separate interactions in adlayer (even *artificial*) from any effects going from the solution side. In addition, owing to direct work function measurements in vacuum experiments, one can hope to check the adaptability of certain approaches involved in computational modeling of metal electronic structure. Experimental verification of these approaches with the use of data for real electrochemical systems is usually ambiguous, as the result is simultaneously affected by the uncertainty of solution model. Finally, a strong advantage of vacuum experiments is their already formed stable link with real electrochemical phenomena, constructed in the 1990s by Weaver.²⁰¹⁻²⁰³ The data on work functions are available for platinized platinum as well,^{206,207} so some feedback with classical data for this electrode material is possible. Current attempts to model the potential of zero charge for platinum/solution interface^{208,209} can be probably linked in more natural manner just to experiments done in vacuum.

In situ optical techniques should be considered as a very important tool, because of their natural compatibility with the usual configuration of electrochemical cells. The limiting factor is always a model of optical signal, and a lot of important experimental results for platinum/solution interface still wait for physically grounded interpretation.

Laser pulse experiments²¹⁰⁻²¹³ form rather informative link between surface thermodynamics and interfacial molecular features, despite the nature of this technique is still macroscopic, and approximations in separating contributions from dipole, ionic, and surface potential terms are unavoidable. However these approximations are of different nature as compared to classical beyond-thermodynamical assumption. Namely, the experimentally available potential of maximal entropy (pme, considered as a value correlating with pzfc) reflects mostly order-disorder effects, like solvent reorientation. Molecular modeling of *temperature jump* was already reported for mercury electrode,²¹⁴ giving the transparent explanation of pioneering experimental results of Benderski and Velichko for mercury²¹⁵ in terms of hydrogen bonding in water

adlayer. This computational approach can be also helpful for estimating the difference of pme and pzfc.

Among other optical techniques, reflectance spectroscopy and electroreflectance studies were actively applied to study platinum electrode surface already 40 years ago.^{216,217} Before the beginning of 1990s these studies were mostly *polycrystalline* (see Refs. in 195, 218–220), as no well-defined single crystal surfaces were available. These works were concentrated on the assignment of optical signals to certain adsorbates, in particular to various *forms of adsorbed hydrogen*. The specific features of these forms could be explained either by structural factors, or by anions coadsorption, or by charge transfer peculiarities, and the existing theoretical approaches were unable to unriddle this puzzle (however some attempts were reported).²¹⁹ A strong effect of oxygen adatoms on the reflectance²¹⁹ is still waiting for serious interpretation.

When single crystalline period started, the attention of electrochemical community was already reswitched from optical to in situ X-ray spectroscopic and probe microscopic techniques. Very few electroreflectance results were reported during this period. The earliest data for three low index platinum surfaces²²¹ were not interpreted in detailed manner. For Pt(111) in sulfate medium, no pronounced signal was observed for hydrogen, excluding butterfly region.²²² For perchloric solutions, electroreflectance was also sensitive selectively to the region of anions highest contribution to electrochemical response.²²¹ The effects were later reproduced for (111) facets of a platinum microsphere²²³: sensitivity of optical signal to surface crystallography was found to be much higher than for voltammetry.

During the same period in situ IR spectroscopy started its active development. Nowadays the multivarious versions of this technique are widely applied in routine electrocatalytic studies, with predominating attention to adsorption of organic species.²⁶ However Bewick's IR studies of hydrogen adsorption on Pt poly²²⁴ and on single crystals of several platinum metals²²⁵ should not be forgotten.

Second harmonic generation (SHG) of platinum/solution interface was pioneered by Corn and coworkers,²²⁶⁻²³¹ who managed to get the response of hydrogen adatoms and coadsorbed anions despite platinum signal is rather low as compared with SHG of Cu, Ag and Au. Further steps²³²⁻²³⁴ resulted in a number of particular

findings, mostly used as supplementary information for the studies of organic species adsorption. Possibilities to use SHG for true charge transfer characterization are strongly dependent on signal generation mechanism, which is rarely studied systematically. Simplified contribution in frames of a jellium model gives a semi-quantitative tool to estimate the sign and degree of charge transfer (see discussion in Refs. 150,151). In particular, for polycrystalline platinum the direction of charge transfer for weakly and strongly adsorbed hydrogen appears to be opposite, in (still apparent) agreement with previous consideration¹⁹⁴ of hydrogen adatom contribution to potential drop.

A single attempt was done to use the so-named electroscattering, a modulation technique worked out by analogy with electroreflectance. Its application to Pt poly surfaces faceted in Arvia's style, in combination with linear optics, discovered the inhomogeneity of hydrogen adlayers at relatively low coverage, which was sensitive to microscopic surface morphology.²³⁵

Recent progress in interfacial optics surely results from combination of linear and non-linear (mostly SFG and SHG) optical techniques.^{120,121} At this stage the approach to data interpretation still remains correlative, but a number of newly determined thermodynamic quantities for single crystalline interfaces are involved in these correlations, along with usual coulometrically estimated surface coverages for various adsorbates. SFG application to various platinum/solution interfaces was recently reviewed.³¹ SFG is able to provide a reliable separation of contributions from hydrogen (Pt-H band), anions and water molecules,^{236,237} and already discovered various types of potential-dependent lateral water bonding. Combination of these results and progress of laser pulse experiments can be highly resultive, but today the data of these two techniques are available for platinum surfaces of different structure.

A challenging problem is to address the effect of adsorbed hydrogen on NMR response of small platinum particles (see Section 3.1.3.2 in Ref. 27). EQCM probably presents a separate possibility to get microscopic information if applied less straightforwardly (not reduced to a weighting instrument). This technique is sensitive to hydrogen adsorption and able to tell the difference of sulfate and perchlorate coadsorption with hydrogen (see Ref. 238 for a brief review of earlier works). Recently developed EQCM

theory coupled with modified EQCM technique (admittance measurements)²³⁹ gives a principal chance to extract local viscosity in the vicinity of interface, an enigmatic feature closely related to the structure of adsorbed water.

Platinum/solution interface is also studied by some techniques with less comprehensible background, like contact electric resistance.²⁴⁰ Probably the progress of other techniques can later result in some clarification of the meaning of these data. The same is related to immersion techniques applied to determine the potentials of zero charge.²⁴¹ Who knows, probably what looks mistaken now can be helpful later, when the nature of disagreement of various techniques shall be interpreted.

No other way out is immediately seen to amplify interactions of electrochemical and spectroscopic techniques, than single-minded computational efforts. If these efforts are concentrated on the modeling of several certain experimentally available signals in frames of unified computational approaches, it is helpful for all consortium. From experimental side, it is highly desirable to apply various techniques to one and the same systems. Usually the quantities more complex for experimental determination are simultaneously more favorable for computational modeling, and vice versa. It can not be helped, but it makes science and life more intriguing.

VI. CONCLUDING REMARKS

This brief review is limited to consideration of platinum group metals in aqueous solutions. Thermodynamic approaches should work in other protic solvents. However these solvents are always of organic nature, and the experimental measurements of any thermodynamic quantities are complicated by irreversible dissociative adsorption of organic species. Another interesting field, still separated, is platinum electrochemistry in aprotic media.²⁴²⁻²⁴⁷

Surface thermodynamics of perfectly polarizable electrodes forms a basis for various amphyfunctional approaches being of interest for electrochemistry of oxides²⁴⁸ and functionally modified electrodes.²⁴⁹ Beyond platinum metals electrochemistry, this approach is also important for gold, silver and copper when OH adsorption with charge transfer takes place at these surfaces.

The links between our knowledge about ideally and perfectly polarizable electrodes should be thoroughly maintained, as water and ions adsorption are common phenomena for these types of systems. For ideally polarizable (*mercury-like*) electrodes, pzc (pzfc) data are available for much higher number of metals, and the roles of electron work function and water adsorption are more apparent.^{250,251}

Frumkin's portrait, jokingly ascribed to Picasso (Fig. 9), was designed by Oleg A. Petrii with assistance of Rein V. Marvet in 1965, i.e., a year before the start of active experimental studies of platinum surface thermodynamics. Correspondingly, this work of art reflects mostly the mercury period of Frumkin school, but the specific asymmetric contour of the face is already formed by platinum-related curves: charging curve from the right and potential shift from the left. Frumkin isotherm, representing the central fragment (nose), consolidates two periods. It is difficult to imagine how the current situation in platinum electrochemistry can be presented in similar style, as many faces with uniquely refined features took part in its development. We already need a whole portrait gallery, and if sooner or later arranged it will surely accumulate this Picasso masterpiece.

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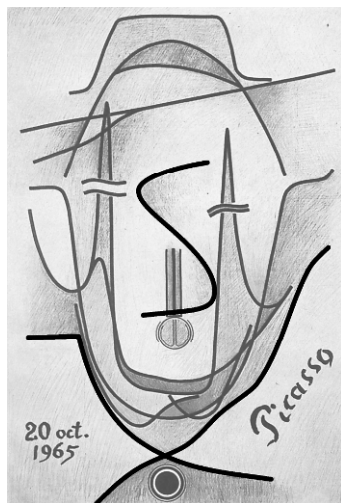


Figure 9. Scientific portrait of A. N. Frumkin representing 1965 state-of-the-art. Features of platinum electrochemistry already became faintly visible: lower part of the face is outlined by potential shift curve (from the right) and charging curve (from the left) of platinum electrode; nose is formed by Frumkin isotherm (S-shaped, corresponding to high lateral attraction). Other features go mostly from mercury electrochemistry, symbolized by a capillary with a mercury drop in the center. Curves, from top to bottom: potential dependences of organic species adsorption (hat) and surface tension (crown of the head); Tafel plots for hydrogen evolution (wrinkle at the forehead); differential capacity curves, including sharp peaks of organic species desorption with splits (eyes), surrounded by *anionic pit* (polarogram of anion electroreduction on the negatively charged surface); intersecting potential energy terms of reactant and product (chin). Rotating ring disc electrode (as adornment at the neck) completes the image. Designed by Oleg A. Petrii with assistance of Rein V. Marvet, originally without thickened curves; first published in 1989 (colored version).²⁵² With modifications.

notice some *critical points* in interrelations of *old* platinum electrochemistry and current research.

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XAS Investigations of PEM Fuel Cells

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I. INTRODUCTION

Polymer-electrolyte membrane (PEM) fuel cells are still far from an area-wide market launch due in part to long-term stability, reliability and cost issues. A more detailed knowledge of the underlying reaction mechanisms is expected to further their application, as it would allow for the design of tailor-made catalysts. However, this will only be possible by complementing traditional in situ studies on single-crystals in electrochemical cells with more sophisticated metal/electrolyte interfacial studies by novel spectroscopic methodologies, which can provide complementary insights into the behaviour of commercial catalysts under real fuel cell operating conditions. This review will focus on the advances of X-ray absorption spectroscopy (XAS) in applied fuel cell research utilizing several examples. XAS enables both the nanoparticle morphology and the adsorbate coverage and binding site to be investigated with just one technique. The latter is possible when complementing the conventional extended X-ray absorption

fine structure (EXAFS) analysis with the more novel $\Delta\mu$ XANES approach.

In current catalytic reactors, fuel cells and water electrolyzers, there is a critical need for new catalysts that not only enhance reaction rates but are more durable and less costly. As pointed out in recent literature¹, there is a need for a substantial increase in the ability to design, characterize, and test new catalysts, particularly nanostructured catalysts with specifically tailored properties. The growing awareness of environmental issues during the last decade has dramatically increased the demand for highly-efficient, low emission processes that turn both fossil and renewable fuels into clean energy. In this respect, fuel cells appear to be a key technology for the twenty-first century, as they present an attractive alternative for both stationary as well as mobile energy applications. However, polymer-electrolyte membrane (PEM) fuel cells, perhaps the closest to market of the many types of fuel cells under study, are still far from an area-wide market launch because of long-term stability and reliability problems experienced under the severe conditions of the fuel cell environment. Moreover, costly and rare noble metals are applied almost exclusively in catalyzing the anode and cathode reactions to date, and a successful non-precious metal substitute is still not in view even after much research.

It is a widely accepted fact that only a detailed understanding of the underlying reaction mechanisms occurring at the electrodes will lead to rational design of new, cost-efficient and stable catalysts. Traditional *in situ* studies on single-crystals in electrochemical cells, probing the electrocatalytic activity of different crystal facets, have provided much information in this field. For example, the CO adsorption and oxidation reaction on Pt low-index surface sites has been studied for decades and is still of significant scientific interest.^{2,3,4} However, in the future novel spectroscopic methodologies will become more useful, as they provide complementary insights into the behaviour of commercial catalysts under real fuel cell operating conditions.

Numerous investigations have contributed to the detailed structural characterization of nanoscaled catalysts before application.^{5,6,7,8,9} However, the information obtained in these studies does not seem to be quite enough for rational catalyst design, in part because the catalyst structure must be adapted to the real fuel cell environment. For example, what does it help to know the anode

catalyst is oxidized as-received, when its oxides are reduced immediately when in contact with the anode feed in a direct methanol fuel cell?¹⁰ And moreover, is the oxidized as-received catalyst more active than its in-situ reduced counterpart? If so, then synthesizers of optimum catalysts should find ways to stabilize the pristine oxide phase during operation. Another question is, what should one expect, when *unstable* bimetallic nanoparticle catalysts are exposed to different atmospheres during real fuel cell operation? In-situ X-ray absorption spectroscopy on a standard Pt-Ru catalyst revealed significant structural fluctuations,^{11,12} e.g., Pt moving to the particle surface in hydrogen, whereas ruthenium dominates at the surface in oxygen. Thus bimetallic nanoparticles clearly appear susceptible to changes of morphology in different atmospheres already during preparation; how much more so in a real fuel cell environment? And what is the preferred morphology for optimum performance in a fuel cell at either the anode or the cathode?

In order to get answers to these questions, the ability to better characterize catalysts and electrocatalysts in situ under actual reactor or cell operating conditions (i.e., *operando* conditions) with element specificity and surface sensitivity is crucial. However, there are very few techniques that lend themselves to the rigorous requirements in electrochemical and in particular fuel cell studies (Fig. 1). With respect to structure, in-situ X-ray diffraction (XRD) could be the method of choice,¹³ but it has severe limitations for very small particles. Fourier transform infra red (FTIR),^{14,15} and optical sum frequency generation (SFG) directly reveal the adsorption sites of such *probe* molecules as CO,⁴ but cannot provide much information on the adsorption of O and OH. To follow both structure and adsorbates at once (i.e., with extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), respectively), only X-ray absorption spectroscopy (XAS) has proven to be an appropriate technique. This statement is supported by the comparatively large number of in situ XAS studies that have been published during the last decade.^{16,17,18,19,20,21,22,23,24,25} XAS is highly versatile, since in situ measurements can be carried out in different environments, different

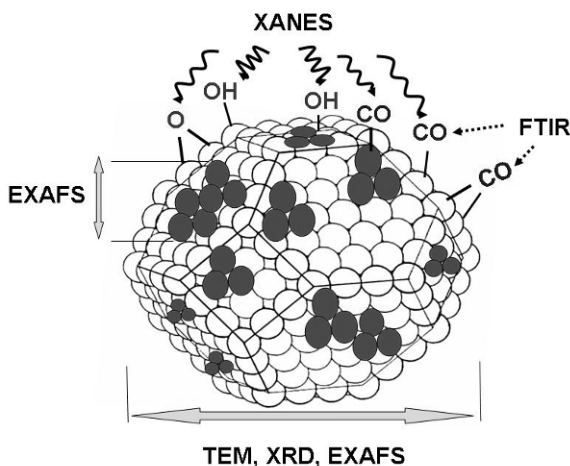


Figure 1. Illustration of the adsorbate coverages and structural information that can be obtained by the indicated in situ spectroscopic techniques (acronyms defined in the text).

atmospheres and at various temperatures. Thus, a variety of problems in fuel cell research can be addressed, e.g., temperature-dependent structural changes of the catalysts,^{11,12} the effect of different electrode potentials^{21,22} and the impact of H, OH and CO adsorption on the catalyst structure.

XAS has traditionally been rather limited in gleaning the effective surface chemistry involved in catalysis (i.e., weakly-bound adsorbate interactions) due to its bulk-averaging nature. This limitation has been alleviated by the “ $\Delta\mu$ ” XANES analysis technique pioneered by Koningsberger and Ramaker,^{26,27,28,29} and has turned XAS into a truly surface sensitive technique (see Fig. 2a). Only recently, the $\Delta\mu$ XANES technique has been applied to the adsorption of H, O, and OH on Pt³⁰ and Pt-M (M=Cr, Fe, Co, and Ni)²⁸ cathodes in an electrochemical cell, as well as CO, O and OH on alloyed Pt-Ru electrodes. Results recently obtained have been successful in providing detailed binding site information for adsorbed CO simultaneously with OH,³¹ and even coverage levels

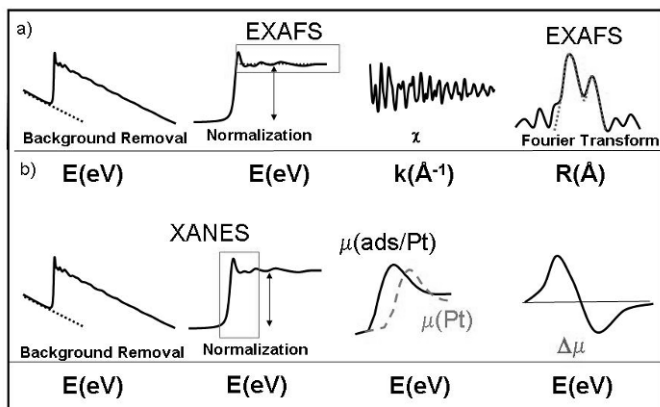


Figure 2. Illustration of the EXAFS and $\Delta\mu$ XANES analysis procedures. Energy alignment is critical in the difference technique and is needed to eliminate the slight *wandering* in photon energy that exists in any photon beam coming from a synchrotron. The Pt L_3 foil spectra taken simultaneously with each sample run are aligned and then the actual sample spectra are shifted by the exact same energy required to align the foil spectra. Reprinted from Ref. 49, Copyright (2005) with permission from Authors.

of active and inactive H (overpotential deposited (opd) and underpotential deposited (upd) H, respectively), and the role that co-adsorbed CO has on opd H. It has been applied to non-Pt catalysts^{32,33} and even to the competition for halide ion adsorption with O(H) adsorption on operating Pt/C cathodes.³⁴ This site-specific surface spectroscopy can be used in conjunction with EXAFS measured concurrently (see Fig. 2b). The EXAFS provides short range atomic order information such as average cluster size, its average cluster homogeneity, bond distances and other morphology changes.

This review will give a short introduction to the EXAFS and $\Delta\mu$ XANES techniques and then focus on various investigations in PEM fuel cells. The advantages and limitations of XAS in fuel cell research will be compared to other characterization techniques, and then investigations of specific Pt-Ru anode catalysts presented. In the light of these recent results, the suitability of the XAS approach to reveal fundamental steps in the reaction mechanisms will be discussed.

II. RELATIONSHIP OF XAS TO OTHER SURFACE SCIENCE AND IN SITU TECHNIQUES

Table 1 provides a summary of the wealth of experimental techniques utilized in the study of catalysts, which allow for the investigation of nanoparticle morphology, nanoparticle shape and / or adsorption at the atomic level.

For the investigation of the nanoparticle structure, X-ray diffraction (XRD), transmission electron microscopy (TEM) and anomalous small angle X-ray scattering (ASAXS) come to mind. By Rietveld analysis of powder diffraction patterns the crystalline phases present in the sample can be identified, and using the full-width half-maximum (FWHM) of the reflection peaks, nanoparticle sizes can be estimated.^{5,6,35} Apart from nanoparticle size, TEM also offers particle shape information, size distribution, and can be used in imaging, diffraction and analysis mode³⁶. But while XRD and ASAXS can be used in situ, TEM investigations, like most methods using electron probes, rely on UHV and thus cannot be used in situ, although recently a special sample holder was developed, which allows for quasi in situ investigations at very low pressures.³⁷ However, XRD and ASAXS also have their limitations, since XRD relies on the extent of coherent scattering regions in the sample (sufficient long-range order) and thus does not provide information on particles with sizes smaller than 2 nm. ASAXS requires synchrotron radiation and a complex mathematical analysis routine, but can give some indication of particle size distribution.³⁸

Modern surface science techniques, such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), offer information about the catalysts surface and the identity of adsorbed species (e.g., O, H, CO, etc.), and have frequently been used to study metal surfaces. However, most require an ultrahigh vacuum (UHV) or other ex situ environment which can introduce problems. For example, XPS, an ex situ technique, shows that most of the alloying elements; e.g., Ru, Sn, Mo, and even the Pt are oxidized under UHV³⁹ conditions, while they are not in an electrochemical environment; indeed recent in situ XANES results prove this.⁴⁰ Temperature programmed desorption (TPD) can provide binding energies of nearly all molecules, but does not give information on the binding sites and is not an in situ method, as it

Table 1
Comparison of Various Experimental Techniques Utilized to
Study Catalysts.

Technique	Information obtained	In situ	Disadvantages/Advantages
XAS (XANES/EXAFS)	Ads. binding site and particle size	Yes	-Synchrotron required -Complex theoretical analysis
XRD	Crystal structure	Yes	-Long range order required -Complex theoretical analysis
TEM	Crystal structure and cluster shapes and size	No	-Direct imaging of clusters -Simultaneous imaging -Diffraction, and analysis -UHV required
(A)SAXS	Cluster size	Yes	-Synchrotron required -Complex theoretical analysis
XPS/AES	Electronic structure	No	-UHV required
TPD,ECTDMS	Ads. binding energy	No	-UHV required
Vibrational spectroscopies			
ATR, IRAS	Binding of atoms and molecules	Yes	-Noisy differential / difference techniques -3-fold site vibrations invisible
IR/Raman	Binding of atoms and molecules	Yes	-Huge bulk electrolyte absorption
HREELS	Binding of atoms and molecules	No	-UHV required
SHG, SFG, SNIFTIRS	Binding of atoms and molecules	Yes	-Noisy differential / difference techniques -3-fold site vibrations invisible -Mirror surfaces required
NIS	Binding of atoms and molecules	No	-High surface areas required because of small cross-section for scattering
DRIFTS, FTIR-DRS	Binding of probe molecules	Yes	-Cannot see atomic adsorbates such as O and H - Requires fine powder samples

requires a vacuum. Electrochemical thermal desorption mass spectroscopy (ECTDMS) is a very powerful technique for the identification of reaction intermediates, but offers only limited value in the detection of surface adsorbates.⁴¹

Vibrational spectroscopy involving infra-red (IR) and Raman absorption are powerful techniques providing detailed information on different binding sites, and bond stretching frequencies, but they are severely hindered because of the large absorption of light by the bulk water of the electrolyte. Several attempts to eliminate this absorption by taking differences or differentials (such as in the Subtraction and Normalization FTIR (SNIFTIR), Second Harmonic Generation (SHG), attenuated total reflectance (ATR), and Sum Frequency Generation (SFG) techniques) have been developed, but these often still produce noisy data, and because of dipole selection rules cannot see vibrations coming from the dominant adsorbate species in the three-fold binding sites. Although providing detailed site information on CO compact ad-layers on Pt and PtM,^{42,43,44} SNIFTIRS encounters difficulties when used on porous electrodes.⁴¹ Other vibrational techniques such as High Resolution Electron Energy Loss Spectroscopy (HREELS) and Neutron Inelastic Scattering (NIS) enable non-dipole transitions to be seen, but they are not in situ techniques.

In spite of the limitations indicated above, surface infrared spectroscopic techniques are frequently used to monitor adsorbed species on solid surfaces. From the vibrational properties of the adsorbed molecules, information can be obtained regarding the geometry of the adsorbed molecules and the strength of adsorption. The geometry can be evaluated using the surface selection rule, which states, that only vibrations with dipole perpendicular to the surface are visible in the IR spectrum. From the shift of individual infrared bands compared to the gas phase, the strength of adsorption (physisorption, chemisorption via donation-backdonation) can be estimated. In the case of probe molecules like CO, the frequency shift of main vibrations is also often considered as an indicator for the respective adsorption site (e.g. on top or bridged), however, this attribution is an indirect one. Apart from the requirement of mirror surfaces, another significant limitation of the above methods (indeed all the methods including XAS) is that they can only be applied to catalyst poisons or long lived

intermediates, i.e., to adsorbates that stick to the surface long enough to be measured.

An exception among the surface infrared techniques is DRIFTS (diffuse reflection infrared Fourier transform spectroscopy), which unlike the other infrared techniques does not require smooth and reflective surfaces but can be applied to powder samples.⁴⁵ In this way, studies using real catalysts under relevant reaction conditions (> 1 bar, elevated temperatures) became feasible. However, relatively fine, homogeneous powders are required, and therefore, it is often necessary to grind the catalyst, which may induce unwanted structural changes in return. DRIFTS in principal does not require vacuum, however, vibrational bands of adsorbed species are often masked by bands of gas phase molecules. DRIFTS can be considered an ideal tool to study adsorbed CO on transition metal catalysts. The CO molecule has a strong dipole moment, which results in strong infrared adsorption bands. Moreover, in most cases strong and characteristic shifts of the C-O-stretching vibration occur, allowing for the estimation of the strength of adsorption and the likely surface site, as mentioned above.

In situ FTIR diffuse reflection spectroscopy (FTIR-DRS) has been routinely used to track various adsorbates, but the specific adsorption sites (e.g., on the Pt or Ru site) cannot be determined with this technique.⁴⁶ Further it cannot be used to track OH and H adsorption, which are both of significant importance in electrochemical studies. To our knowledge, adsorbed OH has not yet been directly observed on any Pt anodes except via the $\Delta\mu$ XANES technique. Thus, the evidence for OH formation had to come previously from the coincidence of the potential for the onset of water activation and the CO oxidation peak in CV curves (e.g., see Fig. 6 below).

Compared to the many methods described above, the strength of XAS lies in the fact that it is so far the only method which can simultaneously provide information on catalyst structure and adsorption properties at the molecular level. Thus, it gives direct proof of the structure-activity correlation. Moreover, it is the only technique to provide direct insight into H and OH adsorption on catalytic powders.

III. DATA ANALYSIS: $\Delta\mu$ XANES, FEFF CALCULATIONS, AND EXAFS

1. $\Delta\mu$ XANES Technique

(i) *Methodology*

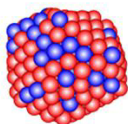
It is a well-known phenomenon that the Pt L_3 , or other metal core-level, XANES is sensitive to the adsorption of various adsorbates, as is shown schematically in the analysis procedure in Fig. 2b. The total absorption signal from XAS after pre-edge background removal is normally referred to as μ . First the pre-edge background is removed, followed by normalization over the 20 to 100 eV range (relative to the edge) typically for XANES analysis. The normalized data are then energy calibrated using foil data of the same material studied (e.g., Pt foil, Ru, foil etc. for Pt or Ru edges, etc.). This energy calibration is the most crucial for the success of the $\Delta\mu$ XANES technique, as full cancellation of the atomic contribution (i.e., that contribution coming from the atom itself and not containing any bonding information) in the XANES must be achieved when taking the difference to obtain $\Delta\mu$. This atomic contribution dominates the spectrum so that the isolated $\Delta\mu$ is typically only about 3–5% of the total μ signal. However, the small $\Delta\mu$ is not generally a problem here, since the noise level after smoothing is generally much smaller (around 0.2%). The oscillations utilized in EXAFS are even smaller than that in the XANES, particularly at large k ranges, and yet EXAFS is a well established technique, with its beginnings well over 25 years ago when less brilliant light sources were available. As the high brilliance of modern synchrotrons becomes more readably accessible, the noise levels and reproducibility of the data are expected to improve, making the $\Delta\mu$ technique even more powerful.

Figure 2b shows two different XANES spectra. Here $\mu(\text{Ad/Pt})$ is the Pt L_3 edge spectrum in the presence of the adsorbate and $\mu(\text{Pt})$ the L_3 edge spectrum at some different potential or current, where the adsorbate coverage is either much smaller, or at least very different from the initial spectrum so that the effect of the adsorbate can be isolated. The $\Delta\mu$ technique can therefore be considered a subtractive technique with the difference, $\Delta\mu$, given as:

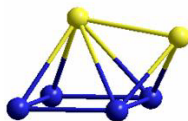
Experiment

Theory

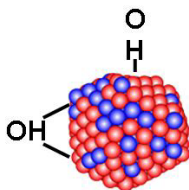
Pt(-Ru) cluster:



Calculation:



Pt(-Ru) cluster plus OH:



Calculation:

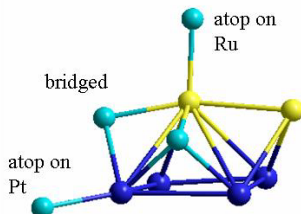


Figure 3. Illustration of the $\Delta\mu$ technique where the difference $\mu(\text{OH}/\text{PtRu}) - \mu(\text{PtRu})$ is taken in both the experimental and theoretical approaches. The μ 's are obtained from XAS data for the experiment and from FEFF8 for the theory. The usual Pt_4Ru_2 cluster utilized to model the much bigger PtRu experimental clusters are shown. The bottom theoretical clusters show an O atom in an atop, bridged, and 3-fold fcc sites on Pt and an atop site on Ru.

$\Delta\mu = \mu(\text{Ad}/\text{M}) - \mu(\text{M}_{\text{clean}})$ (see Figs. 2b and 3). Essentially, careful normalization^{47,48} and subtraction of the XANES signals at different applied potentials from the *clean* potential (i.e., the double layer), or at different temperatures or pressures in a reactor, will result in a spectrum that has completely eliminated the underlying chemically un-reactive bulk signal. Hence the resulting $\Delta\mu$ line shapes reflect the chemistry, site symmetry, and magnitude of adsorbed species on the surface. It should be further noted that contributions in μ coming from surface sites not available for adsorption (e.g., those in contact with the support or with neighboring particles, those covered by surface islands or just not in the region of the required electrochemical 3-phase boundary) will cancel out when taking the difference, so the $\Delta\mu$ technique can even give an

indication of the accessible surface Pt sites as shown previously.^{31,49,50}

A noteworthy point to be stressed is the incredible sensitivity of the $\Delta\mu$ technique. While direct analysis of the -50 to 50 eV XANES spectrum can reveal the presence of *strongly* interacting ligands, such as direct metal-oxygen covalent bonds, this type of interpretation is limited by the extent of the change in the white line region. Only qualitative information can be obtained from changes in the white-line intensity, for instance, it is not easily possible to distinguish between O and CO adsorption just from the white-line.⁵¹ However, identification of both the O and CO coverage is essential in fuel cell studies, when one wants to investigate the effect of CO poisoning and Pt surface oxidation. The $\Delta\mu$ analysis technique pushes the sensitivity to fractions of a percent, picks up different adsorbed species, and allows for direct spectroscopic observation of weakly adsorbed species.

One problem that often enters when determining the experimental $\Delta\mu$ is incomplete cancellation of the background; i.e., the $\Delta\mu$ appears to have a non-zero slope or exist on top of a slowly varying contribution over a wide energy range. This *residual background* can easily be removed by performing a Savitzky-Golay⁵² smooth of the $\Delta\mu$ data using 30–50% of the points. This is similar to the post-edge background removed in the normal EXAFS analysis (see Section III.2); but now it can extend continuously through the edge region and well below the edge, since the step at the edge in μ has been removed by taking the difference. The same Savitzky-Golay smoothing—but now with say 2–3 points—can be used to decrease the noise level if needed.

The resulting experimental difference spectra obtained by the $\Delta\mu$ technique do not offer much information by themselves. Indeed, they require proper interpretation by comparing theoretical $\Delta\mu$ spectra to the experimentally derived curves, such as illustrated in Fig. 3. Good agreement of the experimental $\Delta\mu$ signature with the theoretical $\Delta\mu$ signature confirms the validity of the entire technique, and sometimes allows the binding site to be determined, since a strong dependence on binding site is found in specific cases. To generate the theoretical $\Delta\mu$ spectrum, first a theoretical XANES spectrum of a 3-dimensional model of the *clean* (adsorbate-free) cluster is generated using the structural information

gleaned from a full analysis of the experimental EXAFS spectrum of the material of interest. The closer the model structure is to the experimental one, the more likely the theoretical *signature* will match the experimental data. XANES spectra obtained by covering the afore-mentioned *clean* cluster model with differing adsorbed species in different adsorption geometries, e.g., atop or bridge-bonded, are then subtracted from the clean theoretical XANES spectrum to obtain the theoretical $\Delta\mu$. Comparison between experiment and theory then allows for interpretation of the experimental $\Delta\mu$ to provide adsorbate information such as the coverage and binding site geometry.

Theoretical calculations using the FEFF⁵³ code are performed to calculate μ for the model clusters and prove the significance of the experimental $\Delta\mu$ results by comparing with the resultant theoretical $\Delta\mu$. FEFF8 performs real-space full multiple scattering calculations utilizing a muffin-tin potential calculated with the Hedin-Lundquist exchange correlation approximation, and implements self-consistent field potentials for the determination of the Fermi-level and the charge transfer. A core-hole is included on the absorber atom in order to mimic the final state of the photon absorption process. Thus, the difference $\Delta\mu$ between a spectrum with and without an adsorbate can be calculated by performing the same $\Delta\mu$ difference as obtained experimentally; i.e., $\Delta\mu = \mu(\text{Ad/Pt}_6) - \mu(\text{Pt}_6)$, where for illustrative purposes here, Pt_6 is a cluster of 6 Pt atoms as shown in Fig. 3, assuming all six atoms in the cluster are Pt in this case.

The Pt_6 cluster has been used most often,⁵⁴ as this highly asymmetrical cluster provides for all of the possible common binding sites (fcc, hcp, bridged, and atop), does not introduce any *surface resonances* which might arise from a more symmetric cluster, and yet is sufficiently large to account for the change in Pt-Pt scattering and new Pt-Ad scattering introduced by the adsorber atom.²⁶ Agreement between the theoretical and experimental signatures, although generally not quantitative, is sufficient to identify the binding site. Since the experimental data is an average over a wide array of particles sizes and shapes in the catalyst, any further attempt to improve on the model cluster to find more quantitative agreement between the experimental and theoretical signatures is deemed to be fruitless. Although the XAS process samples all Pt

atoms in the beam's cross-sectional area, it is assumed that the μ of Pt atoms not bonded to the adsorbate (i.e., the spectators) would not change so that $\Delta\mu$ would be zero for these atoms. Although this latter assumption may not be rigorously correct for the small Pt_6 cluster, because the charge or electron distribution of nearby Pt atoms may be altered by the adsorbate;⁵⁵ in general the much larger (and therefore more metallic) clusters in the experimental catalysts are believed to make this effect small.²⁶ This is due to the *leveling out* of charges across a more extended metallic surface.

Since the absorption μ equals $\mu_o(1+\chi)$, the total signature $\Delta\mu$ can be expressed as

$$\Delta\mu = \Delta\mu_o + \Delta(\mu_o\chi_{\text{Pt-Pt}}) + \mu_{o,\text{Ad/Pt}}\chi_{\text{Pt-Ad}} \quad (1)$$

where $\Delta\mu_o$ represents the change in the *atomic* XAFS due to the adsorbate coverage, $\Delta(\mu_o\chi_{\text{Pt-Pt}})$ is the change in the Pt-Pt total scattering induced by chemisorption, $\mu_{o,\text{Ad/Pt}}$ is the free atom absorption (including atomic XAFS) in the presence of the adsorbate and $\chi_{\text{Pt-Ad}}$ is the additional Pt-Ad scattering. FEFF8 calculations reveal that the second term (i.e., the change in the Pt-Pt scattering) generally dominates the total and therefore it provides the adsorbate binding site sensitivity. One can understand this by noting that if an adsorbate binds in a 3-fold fcc site for example, that the Pt-Pt bonds immediately below this adsorbate weaken significantly, while if it binds in an atop site, this change in Pt-Pt binding is much smaller. The additional scattering arising from the adsorbate (the last term) is remarkably independent of binding site, and its shape is also remarkably independent of adsorbate although its size depends markedly on the scattering strength of the adsorbate. Thus for example this term will be much larger for an O atom than for a H atom; indeed this is the dominant difference between the $\Delta\mu$ signature for a H vs. O adsorbate. The $\Delta\mu_o$ term is generally the smallest of the three terms, but of the three terms $\Delta\mu_o$ is probably the least well determined by the FEFF8 calculation on the small Pt_6 cluster. This is because the other terms are very much localized on the nearest atoms involved in the adsorption, while the $\Delta\mu_o$ term includes the effects of charge rearrangement within the clusters as a result of the adsorption and therefore involves most of the

other atoms in the cluster. We have found that this term is exaggerated in the FEFF8 calculations on the Pt_6 cluster as already noted above. Therefore as in previous work,²⁶⁻³¹ the $\Delta\mu_0$ contribution was not included for H/Pt, but is included in the signatures for CO and O. Further, it is only the $\Delta\mu_0$ term which enters when the photon absorbing atom is removed from the atom directly bonded to the adsorbate (i.e., the spectator atoms), so that by excluding the contribution from the spectators as noted above, we are also reducing the size of the $\Delta\mu_0$ term for all adsorbates. We find this gives generally much better agreement with experiment.

(ii) Characteristic $\Delta\mu$ signatures

In this Section the $\Delta\mu$ technique will be illustrated utilizing one of the most common systems in electrochemistry, a polycrystalline Pt electrode in acidic electrolyte as investigated in an electrochemical cell. Of course, this situation is also very much similar to a porous gas diffusion electrode, which is generally applied in a low-temperature fuel cell, and will also be discussed below. In these experiments, several adsorbates could come down onto the Pt surface, depending on potential and other working conditions, and compete for adsorption sites including H, O, OH, and CO. A strength of the $\Delta\mu$ XANES technique is that the competition between these different adsorbates for free Pt sites can now be followed during operation.

(a) O and OH adsorption in an electrochemical cell

As an example of some $\Delta\mu$ signatures, the theoretical results in Fig. 4 show the importance of changes in the Pt L_3 XANES region due to the influence of chemisorbed O with increasing coverage. When O species are adsorbed in an atop position vs. the 3-fold (fcc) surface sites, the Pt-Pt scattering changes in a different way as discussed above, so that the total becomes sensitive to the specific adsorption site. As the theoretical calculations show, it is possible to distinguish between atop and n-fold O by their so-called fingerprints. Oxygen in the atop position has been assumed to correspond to OH (since the scattering from H is negligible), while oxygen in an n-fold position is treated as O. This is consis-

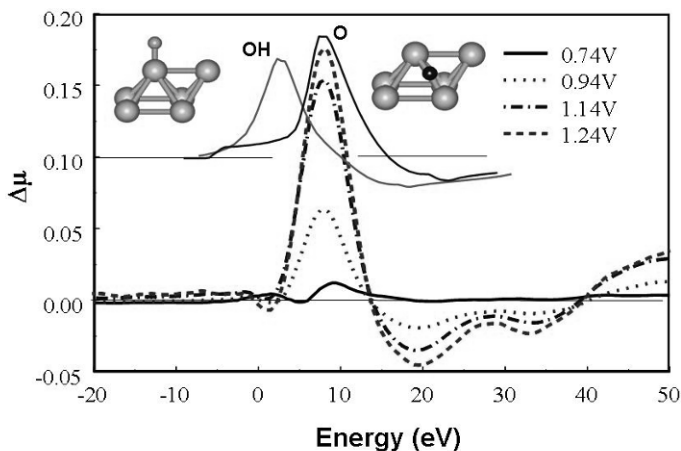


Figure 4. Pt L₃-edge $\Delta\mu$ for Pt at the indicated potentials in HClO₄ using 0.54 V as reference obtained from Ref. 29. Theoretical signatures from FEFF 8.0 obtained in the manner described in the text are shown for OH (atop) and O(3-fold) binding sites. Note the increasing magnitude with potential showing the increase in relative coverage with potential and the change-over from a mix of OH and O at 0.74 V to mostly O at higher potential.

tent with chemical intuition and density functional theory calculations,⁵⁶ which show that OH prefers to be singly coordinated, whereas O prefers a doubly- or triply-coordinated position. Unfortunately, for bridged, fcc and hcp sites, overlapping fingerprint curves are obtained (not shown), making it impossible to distinguish among these sites. However, the sensitivity of the $\Delta\mu$ XANES technique is sufficient to distinguish adsorbed atop OH species from n-fold O,²⁹ which is critical in this work. Figure 4 also shows how the amplitude of the $\Delta\mu$ signature increases with increasing O coverage, and for the most part we assume that the $\Delta\mu$ magnitude is representative of relative adsorbate coverage, although we have discussed deviations from this previously.^{31,50,57}

It is also possible to identify the neighbour atoms to the OH adsorption sites. It has been observed in previous work that the signature curves are significantly affected when OH is adsorbed atop of a Pt atom near another *foreign* metal atom such as Ni, Co or Ru. The fingerprint is found to be shifted downward in energy

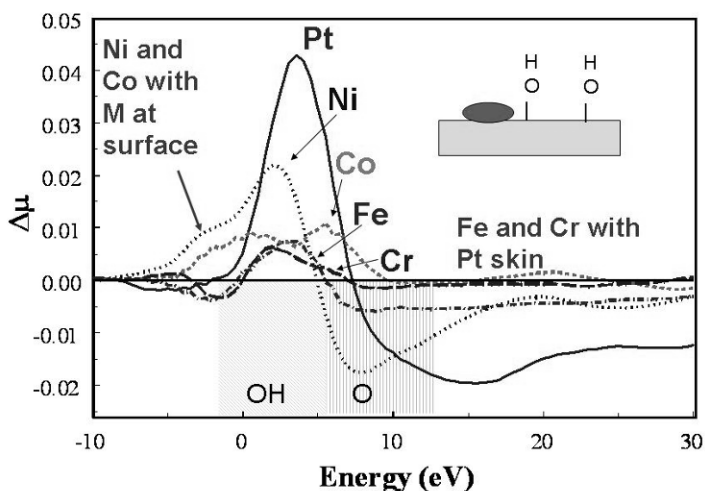


Figure 5. $\Delta\mu$ magnitudes for PtM (M = Fe, Cr, Ni, and Co) bimetallic catalysts and pure Pt in H_2SO_4 at 0.84 V prepared as described in Ref. 28. The region where the maximum is observed for OH and O on Pt is indicated. Note the presence of the additional shoulder below 0 V when M atoms are on the surface (case for PtNi and PtCo), and the absence of these shoulders in the case of a Pt skin (case for PtFe and PtCr). Thus OH/Pt near a M island can be distinguished from OH/Pt distant from these islands.

compared to OH adsorbed at a Pt site surrounded only by platinum atoms (see Fig. 5). Thus, the $\Delta\mu$ XANES can provide the following information:

- (1) it gives a measure of the coverage and kind of adsorbates found on the surface,
- (2) it indicates the binding site (e.g., atop OH or n-fold O), and
- (3) in the case of atop OH, it even indicates, if the Pt site has another atom (e.g., Ru) as a neighbour instead of all Pt neighbours.

The latter feature renders the $\Delta\mu$ XANES a suitable technique to unravel complex reaction mechanisms and synergetic actions, as they are often active in bimetallic catalysts. One example might be the bifunctional mechanism in CO poisoning of Pt-Ru fuel cell anodes, which will be discussed in detail below.

(b) *CO, H, and OH signatures on an active fuel cell catalyst*

The accuracy of the $\Delta\mu$ method depends on the availability of a good reference spectrum, most favourably a spectrum obtained from the blank, adsorbate free metallic surface. Unfortunately, for in-situ measurements in a working fuel cell the situation is not so straightforward, as it is difficult to find an appropriate reference spectrum where no species, or at least a controlled amount, are adsorbed on the surface. The specific measures taken for methanol and reformat operation in a working fuel cell, i.e., when there is CO, H and O[H] co-adsorption, are described below. More specifically, we illustrate the $\Delta\mu$ XANES technique to follow the coverage of specific adsorbates on carbon supported Pt and different Pt/Ru bimetallic systems in pure H₂, in simulated reformat (150 ppm CO in H₂) and in direct methanol operation as a function of current in an operating PEM fuel cell.

So what are the different adsorbates expected for a Pt and a Pt/Ru electrode, respectively, when put into fuel cell operation? Figure 6 shows the voltammogram of a polycrystalline Pt electrode in acidic solution. The features observed at potentials close to 0 V vs. RHE belong to the hydrogen evolution reaction (HER; negative going cycle) and the hydrogen oxidation reaction (HOR; positive going cycle), together involving the overpotential deposited hydrogen (H_{opd}), where the hydrogen molecule gets adsorbed on the platinum surface and dissociates into two hydrogen atoms. In the underpotential region (H_{upd}) between ca. 0 and 0.3 V vs. RHE, the electron transfer is catalyzed turning the adsorbed hydrogen atom into a proton and an electron. The three distinct features in the voltammogram are attributed to hydrogen adsorbed on different crystal facets with probably different adsorption energies. When ruthenium is introduced, however, the characteristic hydrogen adsorption region changes and becomes less pronounced as shown in Fig. 6.

So far, the exact nature of the adsorbed H_{opd} involved in the HOR/HER reactions on the Pt surface has been subject to controversial discussions. Some studies corroborated the idea that the H_{upd} and H_{opd} are in the same Pt binding site, but with H_{opd} having a weaker binding energy.^{58,59} However, spectroscopic evidence for an atop H binding site appearing at higher H coverage has been reported by several other investigations.^{60,61,62} Thus, strong evi-

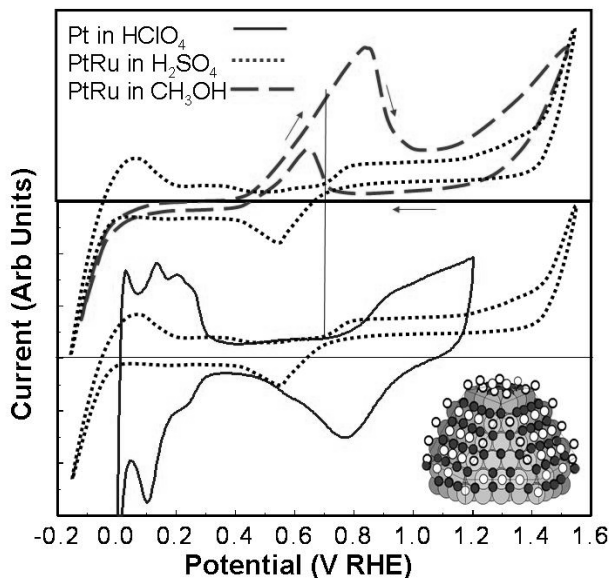


Figure 6. Comparison of representative CV data for the indicated catalysts. The Pt data were obtained from Ref. 28 and the PtRu data from Ref. 64. Note the earlier onset of OH/Pt in the PtRu catalysts compared with Pt, arising from an apparent ligand effect by the Ru on the Pt. In addition, the methanol oxidation occurs primarily in the region where OH is on the surface indicating the necessity for CO oxidation to uncover Pt sites for the methanol oxidation to occur. Schematic of H_{opd} (atop in white) and H_{upd} (3-fold in black) on a Pt crystal shown in lower right. Note the absence of H_{opd} on the Pt(111) surface.

dence exists from optical spectroscopy that the H_{opd} is ontop H (meaning atop H in the presence of full coverage of fcc H) in a binding site different from the H_{upd}. In a study⁶³ using the $\Delta\mu$ XANES, H was found in an ontop binding site on Pt and attributed to the H_{opd} intermediate directly involved in the hydrogen evolution and oxidation. An illustration of a Pt cluster covered with H_{opd} and H_{upd} is shown in Fig. 6. In agreement with literature reports⁶³ the Pt (111) facet is depicted without adsorbed H_{opd}.

In fuel cell operation, the different H adsorbates should also be present on the Pt and Pt/Ru surface, although it is expected that the reaction kinetics (Volmer-Tafel and Volmer-Heyrovski kinet-

ics) are affected by the surface morphology (smooth well-defined surfaces vs. real supported powder catalysts) and the experiment design (liquid electrolyte vs. polymer electrolyte) etc.⁶³ When pure hydrogen is replaced by either reformat or methanol as anode feed in the fuel cell, additional adsorbates will be found on the surface. Depending on the potential, hydrogen will have to compete with both CO and O[H] for adsorption sites. CO attaches strongly to platinum surfaces, which is well-known as the CO poisoning effect on electrocatalytically active surfaces. Since CO adsorbs in an atop site, both hydrogen and O[H] are expected to compete with the stronger adsorbate CO for adsorption sites or to interact with each other. On Ru sites, competition between CO and O[H] for adsorption sites should already start at lower electrode potentials, since Ru is reported to catalyze the water activation at potentials significantly more negative than Pt. Moreover, ruthenium sites, like Pt, should also be active for H and CO oxidation, although less so than Pt. When co-adsorption of different adsorbates takes place on the catalyst surface, problems can be encountered in the analysis, as the experimentally observed signatures in the spectra will overlap with each other.

Figure 7 shows Pt $L_3 \Delta\mu$ data for a PtRu catalyst in 0.3 M methanol using the data obtained at 0.4 V in the cathodic sweep direction as the reference. As suggested by the CV plot⁶⁴ for methanol in Fig. 6, less CO and O should be present at this potential. Figure 7 also shows theoretical signatures for CO, OH, and O in order to identify the changes seen in the experimental results with potential. Clearly CO is leaving as O species build up on the surface. Note the 3 peak structure between 0 and 6 eV. From the discussion above concerning OH and O, the peaks correspond respectively to atop OH/Pt near a Ru island, atop OH/Pt away from the islands, and bridged or fcc/hcp bonded O/Pt. These 3 O(H) peaks can be separated from the CO signature by simply scaling out the CO contribution as determined around 10 eV. Then the magnitudes of the isolated O(H) signature can be estimated from the individual peak heights and their build-up followed with potential. Figure 8 shows similar Pt $L_3 \Delta\mu$ data for 0.3 M methanol but for a PtSn catalyst.⁵⁰ Note that now below 0.54 V, both H_{upd}

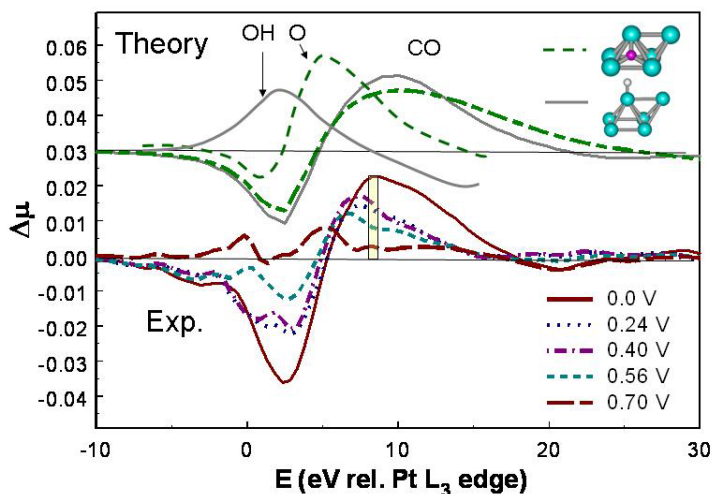


Figure 7. Pt L₃-edge $\Delta\mu$ data for PtRu Watanabe sample using 0.40 V on the backward cathodic sweep as the reference. Theoretical signatures from FEFF 8.0 obtained in the manner described in the text are shown for CO adsorbed in atop and n-fold sites and for OH (atop) and n-fold (O). Shaded area indicates region utilized to determine relative CO $\Delta\mu$ magnitudes or coverages.

and CO are observed. Estimates of the amount of each can be made from the magnitudes at the indicated regions in Fig. 8. The difference between Figs. 7 and 8, showing the presence of H_{upd} or lack of it, results from the different behaviour of a PtRu vs. PtSn catalysts, the Pt-CO bond apparently much weaker on the PtSn clusters enabling H to displace the CO at low potentials. In this example, one can clearly see the possibilities of the new technique. It has been known for a long time that Pt-Ru and Pt-Sn show distinctly different activities in reformate and methanol operation. The reasons for this behaviour, however, were largely unknown and vaguely referred to as arising from different mechanisms. With the help of the $\Delta\mu$ XANES analysis, a more weakened CO-bond on the PtMo catalyst is indicated compared to PtRu allowing H replacement at potentials below 0.3 V.⁵⁰ This obviously aids with the CO removal in reformate, but much less so in methanol operation mode because the anode exists at higher potentials in

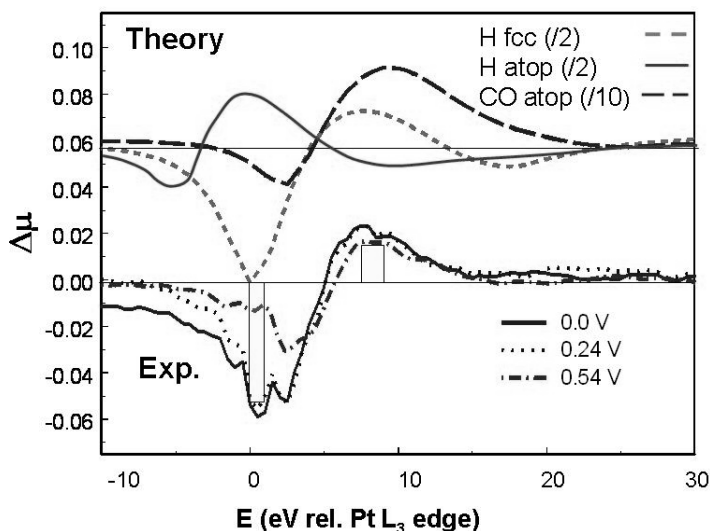


Figure 8. Pt L_3 edge $\Delta\mu$ spectra for a Pt_4Mo catalyst prepared as described in Ref. 50 using 0.4 V on the return cathodic scan as the reference in obtaining $\Delta\mu$. Experimental data are compared with theoretical signatures from FEFF 8.0 (scaled as indicated) obtained as illustrated in Fig. 3 for CO adsorbed in an atop site, and for atop and fcc H. Shaded area indicates energy regions utilized to determine relative CO and U_{upd} $\Delta\mu$ magnitudes or coverages. Only fcc H_{upd} is seen experimentally here.

methanol. Thus, by identifying basic mechanisms, the $\Delta\mu$ XANES technique can help in the design of tailor-made catalysts for specific requirements.

In simulated reformat (H_2 with 100 ppm CO), determination of the simultaneous relative abundances of H_{opd} , H_{upd} , and CO, is even more complicated than in methanol operation. In the case of an operating fuel cell using reformat, the anodic surface is always at low potential, comparable to the situation in the known H adsorption region. Therefore, we assume that the surface has to be covered to some extent with H_{upd} at all currents. When using pure H_2 as fuel, the only adsorbate seen with the $\Delta\mu$ technique under these conditions is H in an atop position on an already H n-fold covered surface (i.e., H_{opd} covered with H_{upd}). This is because at low potential the H_{upd} contribution cancels out in the $\Delta\mu$, since the H_{upd} coverage is relatively constant. Further, the highest operation

current is chosen as the reference current, as this is the current, at which the potential is highest, and therefore the H_{opd} coverage should be lowest. In the simulated reformat case, however, CO is found to displace n -fold H, resulting in an experimental signature for $\Delta\mu$ depending on the extent of this exchange. Consequently, the experimental $\Delta\mu$ observed in reformat operation needs to be fit to all three species, H n -fold, CO and H ontop, with linear regression in the range 0 to 35 eV. Details on this regression technique have been presented elsewhere.⁵⁷

2. Methodology for EXAFS Technique

Since the EXAFS analysis technique is a much better known and a more established technique, we will present far fewer details on this approach. Many standard reference texts,^{65,66} papers,⁶⁷ and web sites⁶⁸ exist fully describing this technique and well-known software packages, such as the IFEFFIT package and others,⁶⁹ are available to analyze data. Figure 2a shows the basic essentials, whereby again the XAS data must have a background removed, then normalized, and energy calibrated much as described for the XANES. FEFF8 calculations are again performed on model clusters, and the many parameters such as the mean free path, scattering amplitudes and phases are provided internally. In this work, we limit ourselves to two paths; namely the Pt-Pt and Pt-M scattering for PtM bimetallic catalysts. Usually four variables are obtained for each path, namely the Pt-M coordination number, N_{PtM} , the bond length, R_{PtM} , the Debye-Waller factor, σ , and the E_0 parameter, which establishes the inner potential. Assuming that both the Pt and M atom XAS data were measured, one can then obtain 4 coordination numbers, 2 at each edge namely the Pt-Pt, Pt-M, M-Pt, and M-M coordination numbers. These are the critical parameters that will be used to propose an average nanoparticle morphology.

Figure 9b shows as an example a fit of two paths, the PtPt and PtRu, to a PtRu ETEK catalyst.³¹ The large intensity of the separate PtPt and PtRu contributions at 2.5 Å compared with the total shows the high level of interference between these two paths right at $R = 2.5$ Å. This is further revealed by the difference between a pure Pt and Pt₃Ru catalysts compared with the somewhat better mixed PtRu ETEK or PtRu Watanabe catalysts in Fig. 9a. This

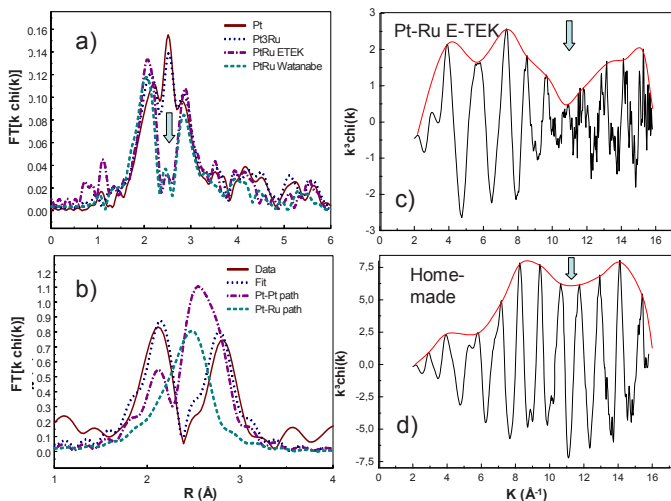


Figure 9. a) FT for Pt and PtRu samples prepared as described in Ref. 31, showing destructive interference of PtPt and PtRu scattering for the more *alloyed* PtRu E-TEK and PtRu Watanabe catalysts. b) Representative fit for PtRu E-TEK sample with indicated paths showing larger overlap of PtPt and PtRu contributions. c) Destructive interference of PtPt and PtRu scattering already visible in k -space as exhibited by large drop in amplitude (indicated by red line) around $k = 11$. d) Smaller destructive interference in k -space for a PtRu catalyst synthesized in our lab indicating it is much less *alloyed*.⁷⁰

large interference can sometimes make the fitting procedure difficult, but it does reveal the significant sensitivity of the EXAFS to these separate paths. Figures 9c and 9d show that this interference can be seen already in k -space by the large dip in amplitude around $k = 11 \text{ Å}^{-1}$.⁷⁰

We now describe the procedures used by us^{31,57} and others^{71,72,73,74} to estimate the morphology of the PtM clusters from the obtained four coordination numbers. Hwang et al.^{73,74} utilize a technique quite similar to ours described below to determine the experimental morphology (i.e., trial and error until an optimal model is reached), but define some useful parameters as follows: $J_{\text{Pt}} = N_{\text{PtRu}} / (N_{\text{PtPt}} + N_{\text{PtRu}}) * 200$ and $J_{\text{Ru}} = N_{\text{RuPt}} / (N_{\text{RuRu}} + N_{\text{RuPt}}) * 200$ for PtRu 1:1 catalysts. Then $(J_{\text{Pt}}, J_{\text{Ru}})$ equals (0,0) for a completely separated structure, (100,100) for a fully *alloyed* structure, and

(200,200) for an onion ring structure. Further one can expect values of (<100,<100) for a homophilic structure and (>100,>100) for a heteroatomic-rich structure. Hwang et al.^{73,74} find the clusters in a commercial ETEK 30 and Johnson-Mathey 30 catalysts to be (40,78) and (26,48) respectively (i.e., more homophilic in general) with the Ru more on the outer reaches of the cluster as we find below.

Stoupin et al.^{71,72} assume a core structure surrounded by a more amorphous shell rich in Ru, and therefore determine a parameter $s_{\text{Ru}} = (n - (1-D)/x_{\text{Ru}})/D$, where D is the dispersion (fraction of atoms at the surface) determined assuming spherical particles and based on the estimated particle size from the EXAFS (or XRD) results, and n is the nominal molar ratio (Pt_nRu , perhaps determined from XRF). Here s_{Ru} represents the relative composition of the surface (i.e., it is the fraction of Ru atoms relative to the total on the surface), and x_{Ru} is an estimate of the relative composition of the core using in situ EXAFS results. Their final results suggest that the surface of a PtRu ETEK cluster is rich in Ru, and is heavily oxidized, similar to Hwang's and our conclusions.

In work reported previously by us,^{31,57} appropriate models were developed for the structure or morphology of the average PtRu cluster for three different catalysts based on the EXAFS results, using the ATOMS code⁷⁵ to generate different cluster models. The nearest neighbor coordination of each atom divided by the total number of atoms of that type then gives the average coordination number. We assumed oxidized Ru removed Ru-Ru scattering since the presence of an O atom between the Ru atoms or even in its close proximity is known to strongly reduce the metal-metal scattering,^{29,76} thus oxidized Ru atoms had zero Ru-Ru coordination. For the 1:1 alloys here, we have three coordination numbers to suggest something about the morphology of the clusters. Only three numbers are available here because in our earlier work, N_{PtRu} was forced to be equal to N_{RuPt} during simultaneous fitting of both edges, but more recently we have relaxed this restriction to allow different molar ratios and some of the Ru to be effectively removed by full oxidation.

The optimal models for three catalysts, the PtRu ETEK, the PtRu Watanabe, and the Pt_3Ru Watanabe, are shown in Fig. 10, using our technique. However, their uniqueness can be legitimately questioned. That is why we include Fig. 11 to illustrate just

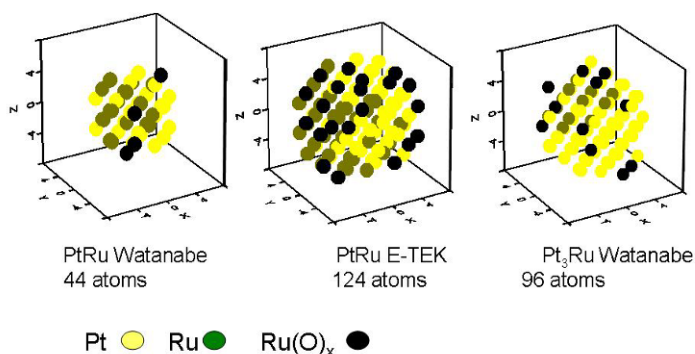


Figure 10. Average cluster size and morphology determined from EXAFS modeling for 3 different PtRu clusters prepared as described in Ref. 31. The PtRu Watanabe clusters are smaller with the Ru mostly in the metallic state, the Ru in the larger PtRu E-TEK clusters are heavily oxidized.

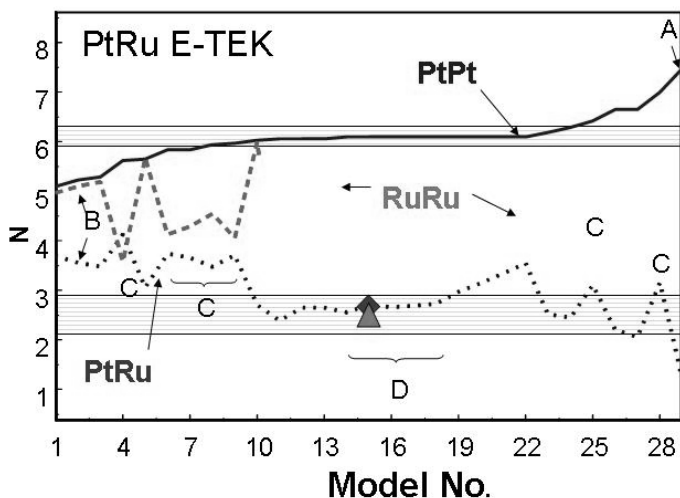


Figure 11. Various models for the PtRu E-TEK catalyst used to arrive at optimum morphology.³¹ Shaded areas represent $\pm 5\%$ deviation from experimental EXAFS fits. For clarity, lower error bar encompasses both Ru-Ru and Pt-Ru (Ru-Pt and Pt-Ru forced to be equal in the EXAFS fit).

how sensitive the coordination numbers are to the different assumed Pt and Ru morphologies by showing a number of models considered for the PtRu ETEK sample. The upper shaded band in Fig. 11 represents a $\pm 5\%$ deviation from the EXAFS $N_{\text{Pt-Pt}}$, while for clarity, the lower shaded band encompasses the same window for both $N_{\text{Pt-Ru}}$ and $N_{\text{Ru-Ru}}$. The models marked A represent highly segregated configurations; essentially a small Pt particle joined to a small Ru particle. Models marked B, by contrast, correspond to extremely well-alloyed morphologies. Models marked C contain a higher order Pt core (Pt_nRu where $n > 1$) with a Ru skin of various depths. Finally, models marked D are those deemed acceptable; the only models discovered for which all three coordination numbers fall in or near the acceptable windows. As can be seen, many models may accurately reproduce two coordination numbers, but few can accurately model all three numbers.

Of the 29 models shown in Fig. 11, models 14 through 18 most closely approximate the experimental values. Of these, models 14, 15, 16 and 18 are identical except for the degree of oxidation, and model 17 is only very slightly different. All contain around 120 atoms, with a Pt_2Ru core comprising approximately 60 atoms, a somewhat segregated PtRu layer of around 40 atoms, and a Ru *skin* of around 20 atoms. The best fit is obtained by model 16, which consists of a Pt_2Ru core of 63 atoms, a somewhat segregated PtRu layer of 40 atoms, and a Ru *skin* of 21 atoms. The entire Ru skin is oxidized in model 16, one-third of the total Ru atoms present. The larger cluster has only 70% of its atoms at the surface, and about 40% of the Ru atoms, those at the surface, are oxidized. Based on these optimal models (Fig. 10), which of course should be regarded as average and representative only, one can briefly characterize the difference between the three electrocatalysts under the conditions existing in the cell corresponding to non-adsorption (0.58 V for Pt L_3 edge, 0.04 V for Ru K edge in 1 M HClO_4). The PtRu ETEK clusters are relatively large with the Ru and Pt atoms poorly mixed and the Ru oxidized on the surface. The PtRu Watanabe clusters are much smaller with the Pt and Ru more evenly mixed (alloyed), the Ru atoms more monodispersed, and relatively less of the Ru oxidized at the surface. Finally, the Pt_3Ru Watanabe clusters are intermediate in size with the Ru more alloyed. However, the much larger Pt:Ru ratio leaves large components of pure Pt, and a considerable amount of Ru oxidized at the surface. These

qualitatively different morphologies help to explain the different CO oxidation regimes found from the XANES data.

In summary, although several procedures for estimating cluster morphology are noted above, the basic premise is as follows:

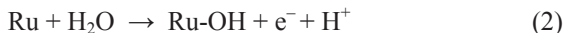
- (1) The EXAFS measurements must be done in situ because in air all of the more reactive M atoms at the surface such as Ru, Sn, Mo will be oxidized, and even much of the Pt will be covered by O. After insertion and reaction with the electrolyte most of these oxides are removed from the Pt, and perhaps even in part from the more reactive M islands on the surface.
- (2) The preferred measurement potential is around 0.2–0.5 V, where the adsorbate coverages are minimal; although CO will certainly be present in methanol.
- (3) Even though the catalysts may have the nominal Pt_nM composition, most often the amount of M atoms seen in the EXAFS analysis will be much less than expected. This is because of the greater oxidation level of the M atoms relative to Pt. In a fully oxidized MO_x island very little M-M, M-Pt, and even Pt-M coordination will be visible, since all M atoms in such a MO_x oxide are surrounded by O atoms. Thus the different coordination numbers represent not only the level of mixing of the Pt and M atoms, but also the extent of oxidation. Indeed, how this amorphous oxide layer is treated represents the primary difference between the above reported techniques.

IV. RESULTS ILLUSTRATING THE INTERPLAY BETWEEN CLUSTER MORPHOLOGY AND ADSORBATE COVERAGE

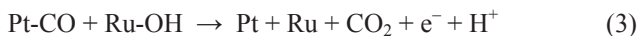
1. Mechanisms for Enhanced CO Tolerance in Pt-M Catalysts

Before discussing specific results, we review the current mechanisms responsible for the enhanced CO tolerance seen for Pt-M catalysts. Two widely accepted mechanisms for the oxidation of CO

from the Pt-Ru surface have been proposed in the literature.^{77,78,79,80,81} The bifunctional mechanism (BF) involves activation of water at the Ru surface to yield Ru-OH:



This hydroxide is tightly bound; however, the more mobile CO is assumed to migrate across the surface to react with this OH according to Eq. (2):



In contrast, the direct mechanism, enabled by the ligand or electronic effect, (called Dsl = direct surface ligand and Dil = direct interior ligand below depending on whether the ligand effect on the Pt comes from surface Ru or interior Ru atoms) holds that Ru modifies the electronic structure of the Pt by donating electron density, thus either weakening the Pt-CO bond and thereby allowing CO to be more easily oxidized, or by enhancing Pt-H₂O activation and thereby allowing the reaction of OH and CO directly on the Pt. The bifunctional mechanism is generally acknowledged as being dominant,^{82,83} however in a study of tolerance to CO in reformat systems,⁸¹ the electronic effect was suggested to be important. Additionally, the ligand effect has been shown to have a large effect on Pt atoms near Ru islands for Ru/Pt(111), whereas Pt atoms far from these islands are only minimally affected (i.e., Dsl > Dil).⁸⁴ Current state of the art Pt-Ru electrocatalysts rely on the *bifunctional approach*; however, as reported previously,¹⁹ a simple bifunctional catalyst with good nucleation of oxygenated species at low overpotential will fail for methanol oxidation, despite its excellent CO oxidation characteristics, as has been shown previously for Pt-Sn electrocatalysts^{19,85} and for Pt-Mo.⁸⁶

2. PtM Catalysts in 0.3 M Methanol

Figure 12 shows the $\Delta\mu$ amplitudes of the PtRu ETEK and PtRu Watanabe catalysts in 0.3 M methanol as described above. These $\Delta\mu$ amplitudes represent relative changes in coverage with potential, and show the general trend revealed already in Fig. 7 with increasing O(H) coverage as the CO coverage decreases. Numbers

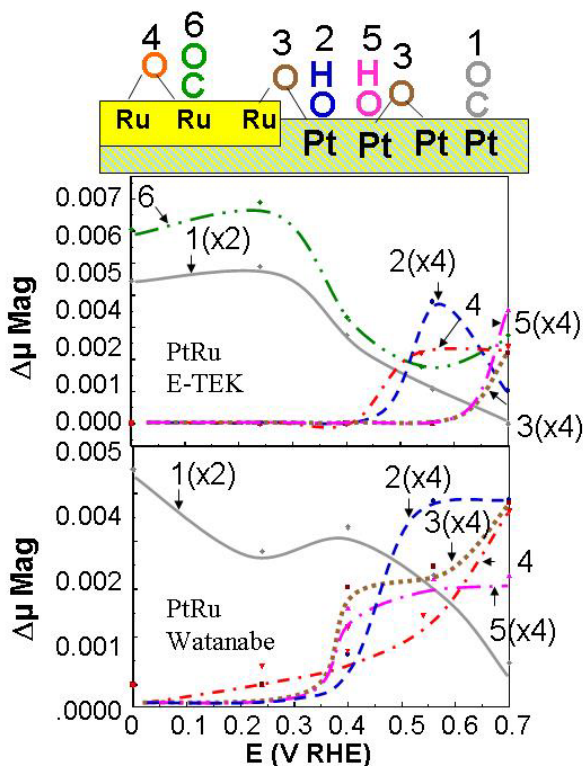


Figure 12. $\Delta\mu$ XANES magnitudes or relative coverages (obtained by the heights of the shaded areas in Figs. 7 and 8 and similar plots not shown) for the numbered CO, OH and O adsorbates on the indicated catalysts, whose average cluster models were shown in Fig 10. Magnitudes are scaled ($\times n$) to give all plots similar heights.

1–6 in Fig. 12 mark the different adsorbate configurations that can be obtained on a Ru island covered Pt catalyst and distinguishable by the $\Delta\mu$ XANES. While atop CO is visible either on a Pt or a Ru site (by examining both the Pt L_3 and Ru K absorption edges), OH is visible at Pt in the vicinity of a Ru neighbour, i.e., at a Ru island edge, or away from any Ru sites on the Pt terraces. Bridge-bonded O, however, is visible collectively either on two Pt, two Ru or to a Pt/Ru mixed site. Figure 12 shows that the different morphologies

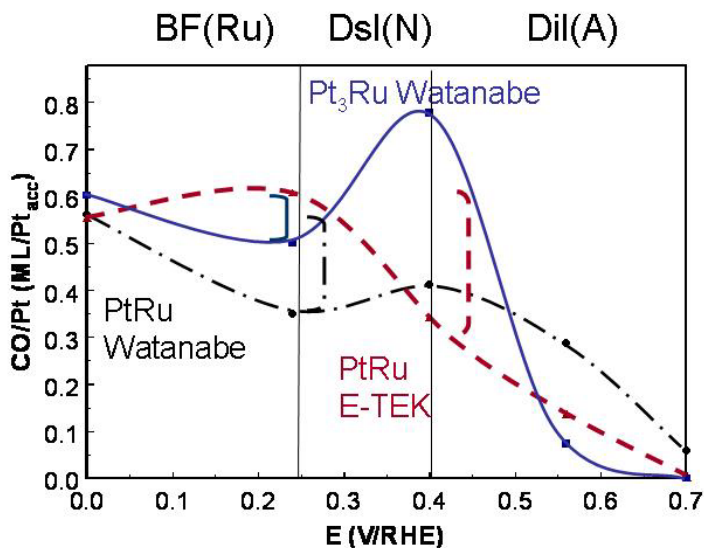


Figure 13. Estimated CO/Pt coverages in 0.3 methanol for the catalysts depicted in Fig. 10, and the indicated regions where each CO oxidation mechanism dominates, as determined by the binding site of the active OH in the CO oxidation. The brackets indicate the net amount of CO stripped via either the BF or Dsl mechanism due to mobile CO moving toward the Ru islands.

of the two different catalysts give quite different coverage trends. For instance, atop adsorbed CO on a Ru island site is only observed for PtRu E-TEK, but not for the PtRu Watanabe catalyst. Moreover, OH on Pt is not observed on the PtRu E-TEK catalyst below 0.6 V, whereas the other catalyst shows OH adsorption at Pt sites already at potentials shortly above 0.3 V.

Figure 13 compares just the CO coverages obtained for all three catalysts, and the different regions where the CO is stripped from the Pt surface as obtained from the $\Delta\mu$ XANES analysis. The mechanism which dominates in each potential region is indicated with the label BF, Dsl and Dil; these were defined by Eqs. (2) and (3) and described in the text above. The letter in parentheses indicates the source of the active OH (on the Ru, or on the Pt but Near or Away from surface Ru islands), which really differentiates the mechanisms. The potential region where each mechanism domi-

nates is determined primarily by the reactivity of various sites to water activation as reported earlier.³¹ The more reactive Ru sites will become active below 0.25 V, Pt sites near the Ru islands will *ignite* between 0.25–0.4 V and Pt sites away from Ru above 0.4 V. Since the CO coverage is depicted in the figure, we are actually looking for a decrease in coverage, where the respective region in which that *loss* occurs indicates the most active mechanism for the respective catalyst. Figure 13 shows that both Watanabe samples exhibit a significant BF stripping component below 0.3 V, consistent with OH coming onto the Ru surface in this region. However, this fractional component is larger in the PtRuW case than in the Pt₃RuW case as indicated by the brackets in Fig. 13. This is consistent with the larger fraction of Ru in the former case, so that more CO/Pt is in the vicinity of the Ru islands. In contrast, the E-TEK sample exhibits a large Dsl component and no BF component.

These data strongly indicate that the BF mechanism for CO oxidation is enhanced by the formation of smaller Ru islands with adsorption of CO in competition with OH adsorption at low potential, while the bigger more metallic Ru islands are fully oxidized and adsorb no CO or OH. However, larger Ru islands are found to impose an increased ligand effect on the nearby Pt atoms enabling CO oxidation via OH directly adsorbed on the Pt. This interplay between Pt and Ru, apparently determined by the relative size of the Ru islands and Pt particles as suggested above, has been discussed previously. For example, DFT calculations by Koper et al.⁸⁷ and by Desai and Neurock⁸⁸ show a weakening of the CO-Pt bond with addition of Ru and strengthening of the CO-Ru bond with addition of Pt, pointing to this interplay. Several other groups have published experimental data suggesting that the CO poisoning and hence reactivity depended on the Ru distribution and/or island size^{7,89} but the data in Fig. 13 give the clearest evidence of these effects.

These data further suggest a reason for the different efficacy of PtRu catalysts in reformat vs. methanol. Since the BF mechanism operates at lower anode potential than the direct ligand mechanisms, more homogeneously alloyed PtRu catalysts with smaller Ru islands should be more effective in reformat and less well-mixed alloys (with large Ru islands) better in methanol fed

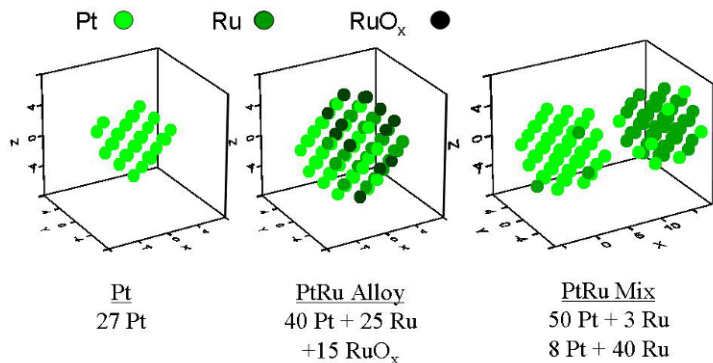


Figure 14. Structural models estimated from EXAFS analysis for the indicated electrocatalysts prepared as described in Ref 57. The PtRu Mix catalyst was prepared by mechanically mixing Pt/C and Ru/C powder, with some atoms of the *other* element thereby being deposited on each cluster surface.

fuel cells, because the operating anode potential is higher in methanol. Similar analysis of data for PtMo and PtSn alloys in methanol shows that the relative importance of the bifunctional and electronic mechanisms is quite different for these alloys compared to PtRu, thus accounting for the well-known difference between the higher efficiency of PtRu for methanol oxidation vs. PtMo for CO stripping.⁵⁰ With the information obtained above, the optimum structure of catalysts can be predicted for particular fuels much easier. Furthermore, even predictions of catalysts behaviour in other than the experimental conditions studied might be made.

3. Operando Fuel Cell Studies: Hydrogen Oxidation in 100 ppm CO

Figure 14 shows the estimated average morphology of three different catalysts used to study the HOR in 100 ppm CO in a working fuel cell. As a plain Pt reference, a standard carbon-supported Pt catalyst from E-TEK (20 wt.% on Vulcan XC-72) was chosen and compared with both a traditional carbon-supported PtRu bimetallic electrocatalyst also from E-TEK (20 wt.% Pt:Ru (1:1) on Vulcan XC-72; *PtRu Alloy*) as well as a so-called carbon-supported PtRu mixture catalyst (*PtRu Mix*). The latter was produced by mechani-

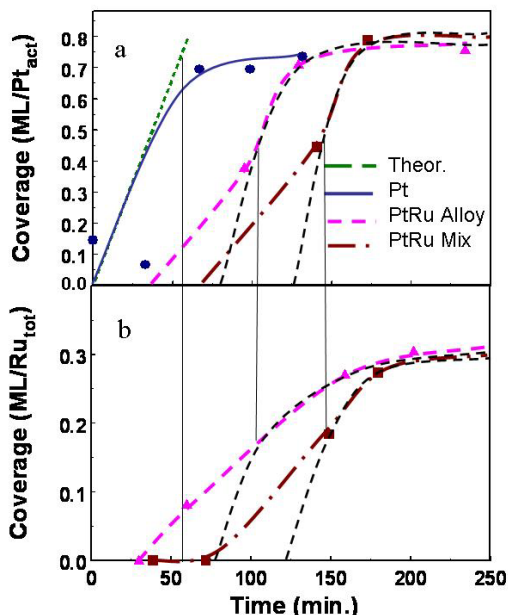


Figure 15. CO coverage on Pt (a) and Ru (b) in H_2 (with 100 ppm CO) on the three indicated catalysts shown in Fig. 14 as a function of CO exposure time. The dotted lines estimate the coverage assuming the mobility of the CO drops off extremely fast with CO coverage. Vertical lines are to guide the eye showing that the CO/Ru reaches the asymptote at the same time as the CO/Pt.

cally mixing carbon-supported Pt and carbon-supported Ru (both from E-TEK) in an agate mortar, resulting in Pt nanoparticles with a small Ru surface component and similarly composed Ru particles with some Pt on the surface.

The corresponding estimated morphologies presented in Fig. 14 were obtained using the EXAFS cluster modelling technique described above. As also discussed in the previous paragraphs, the nanoparticle morphology is crucial to the catalyst's activity, and CO poisoning will strongly depend on the ruthenium distribution and island size.

Figure 15 shows the growth rate of CO as a function of time in an operating PEM fuel cell containing 100 ppm CO in H_2 for

these three catalysts.⁵⁷ The CO growth rate found for pure Pt (marked theory) is entirely consistent with the experimental parameters (i.e., flow rate of H₂, Pt loading, fraction of active Pt, etc.), so that steady state is reached at approximately 55 min. However, the CO growth rate for both PtRu samples is quite different and quite unexpected. Assuming a major fraction of the CO/Pt is non-mobile (leaving only a small fraction of CO/Pt sites presumably near the Ru islands to be oxidized by OH via the BF mechanism), one would expect the CO coverage to increase at the same rate as that for pure Pt, but go to an asymptote at a fraction of the full coverage, representing the fraction of non-mobile sites. The remaining sites would stay uncovered. However, Fig. 15 paints an entirely different picture; the entire active Pt surface is eventually covered by CO regardless of the presence of Ru. Only the point at which this asymptotic CO coverage is reached is delayed, apparently due to the BF or DsL mechanism involving the Ru.

The slower rate of CO accumulation on the PtRu samples suggests that at low CO/Pt coverage, all of the CO is mobile. This is indicated by the initiation time required to see the first adsorbed CO on the bimetallic surface. However, as the CO coverage increases, more of it becomes immobile until the rate of growth of the CO poisoning (marked by the vertical lines) equals that of pure Pt above 0.4 ML CO.⁵⁷ The dotted lines in Fig. 15 estimate the CO coverage assuming the mobility of the CO drops off extremely fast with CO coverage above 0.4 ML. The mobility of the CO on Pt and Ru appears to behave more like normal automotive traffic patterns where at low coverage the CO is *free-flowing* enabling the BF mechanism to operate fully. As the CO coverage increases, the *traffic* goes into synchronous mode, allowing the CO to move only at the rate of the slowest CO, much like occurring in an auto traffic jam. However, the apparent decline in CO mobility drops to zero on both the Ru and the Pt at approximately the same time (110 and 150 min for the PtRu Alloy and PtRu Mix respectively as indicated by the vertical lines in Fig. 15). One might have expected this point on Ru to appear at a significantly later time or not at all if the BF mechanism is fully operational at all coverages on Ru, since the water activation to form OH is generally expected to occur on the Ru in the classic BF mechanism. These results suggest that the initial *traffic jam* appears on the Ru islands, thus slowing down the

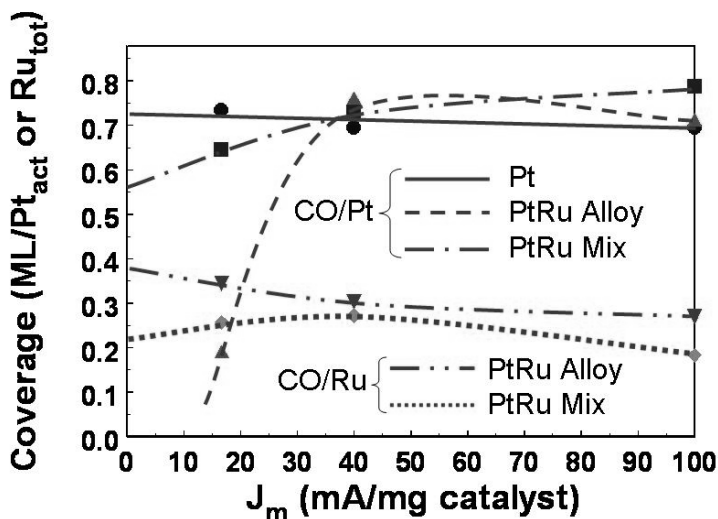


Figure 16. Equilibrium CO coverage on both Pt and Ru as a function of current on the three indicated catalysts illustrated in Fig. 14.

CO oxidation on both the Ru and the Pt simultaneously. This is a somewhat unexpected result, and one that needs further study. The apparent greater effectiveness of the small amount of Ru on the Pt surfaces in the PtRu Mix catalyst vs. the PtRu Alloy catalyst, as exhibited in Fig. 15, is consistent with the effect of Ru island size as noted above for methanol. Small Ru islands, such as those in the PtRu Mix catalysts, cause the BF mechanism to be more effective at lower overpotentials, whereas larger islands promote the ligand effects. Consequently, more OH can be provided by the smaller islands on the PtRu Mix, before the CO mobility finally goes into synchronous mode and poisons these sites.

Figure 16 further confirms these relative ligand effects and reactivity by showing the *steady-state* coverage of CO on both Pt and Ru, now as a function of low current rather than with time at higher currents, as in Fig. 15. Note that the CO/Pt coverage for the PtRu Alloy sample drops off drastically at low current, while that for PtRu Mix shows only a slight decrease, and pure Pt shows none at all. Clearly, the Ru ligand effect is stronger in the PtRu

Alloy with the larger Ru islands, so much so as to weaken the Pt-CO bond and therefore decrease the CO coverage by H replacement at low potential. Recall that the PtRu Alloy has a much greater fraction of Ru in the cluster interior than PtRu Mix so we cannot completely rule out some effect of the interior Ru atoms, but as stated above this interior ligand effect appears to be much less effective.

V. CONCLUSIONS

X-ray absorption spectroscopy is an attractive in situ technique that, along with measurements in electrochemical cells in liquid electrolyte, even allows for *operando* studies in a working fuel cell. The more conventional EXAFS data analysis technique has been complemented by the newer $\Delta\mu$ XANES technique. With the latter it is now possible to determine adsorbate, specific adsorption sites and adsorbate coverage, which helps a great deal to unravel the mechanisms operating in electrochemical systems. Atop CO, opd and upd H, bridge-bonded or fcc O, and even OH, all possibly present on a Pt surface during cycling in acidic media, can now be monitored individually. The strength of XAS lies in its ability to provide information on nanoparticle morphology and adsorbate coverages with one technique. Thus, it enables us to directly probe the structure-activity relationship even in bimetallic catalysts, e.g., a PtRu system.

The PtRu results presented here and similar $\Delta\mu$ XANES studies reported elsewhere reveal or at least confirm the following morphology-adsorbate relationships:

- (1) Smaller Ru islands experience a *reverse* ligand effect from the Pt which reduces their reactivity. Thus both CO and OH competitively adsorb on their surfaces and the bifunctional CO oxidation mechanism is operative. Larger Ru islands are highly reactive and thus are more oxidized in aqueous environment making them inactive for CO oxidation. However these oxidized islands exert a strong ligand effect on the nearby Pt making CO oxidation active with the OH on these nearby sites.

- (2) Ru atoms in the core, and therefore not oxidized, exert relatively little ligand effect on the surface Pt atoms with respect to OH adsorption from water activation, but may weaken the Pt-CO bond allowing hydrogen replacement at low potentials.
- (3) Sn and Mo islands in Pt_nSn and Pt_nMo catalysts are apparently fully oxidized and exert a strong ligand effect on the Pt-CO bond thus enabling a strong H replacement at low potentials.³¹
- (4) CO oxidation can occur via the bifunctional mechanism, the ligand mechanism, or via a hydrogen replacement mechanism, and the morphology and island type strongly determines which of these is more important.

The XAS studies reported here and similar studies have also revealed new information on the behaviour of adsorbates; namely the following:

- (1) The coverage of overpotential-deposited H (H_{opd}) (an intermediate in the hydrogen oxidation reaction) is strongly dependent on current in a fuel cell, and CO poisoning at even 100 ppm levels strongly alters the coverage of this intermediate.^{57,63}
- (2) The mobility of the CO is strongly dependent on the CO coverage. At coverage well below 0.4 ML, almost all CO is apparently mobile, but above 0.4 ML, this mobility drops off surprisingly fast; reminiscent of typical auto traffic jam models. Furthermore, the *traffic jam* appears to occur on the Ru islands at about the same point as on the Pt.

Finally, combined $\Delta\mu$ XANES and EXAFS studies have recently been reported on other more complex electrocatalysts, including RuS_x ,^{32,33,90} $RhSe$,⁹¹ Au/SnO_x ,⁹² Pt/NbO_x ,⁹³ and $Pt/TPPTP/C$ (TPPTP = triphenyl phosphine triphosphate)⁹⁴ catalysts. The $\Delta\mu$ XANES has also been used to study the effects of anion adsorption on Pt including bisulfate⁹⁵ and Cl ,³⁴ differentiate the various oxidation states of S during the electrochemical oxidation of S on Pt⁹⁶, and identify acetaldehyde-like intermediates during ethanol oxidation on Pt.⁹⁷ In all of these studies, unprecedented new details on the coverage and binding sites of adsorbates in situ have been revealed. Further, similar XAS studies in gas phase cat-

alytic reactors have been reported; including H on supported Pt clusters in zeolites and various flat supports⁹⁸ as well as ethylene on Pt and its different molecular geometries (atop π -bonded, bridged di- σ bonded, and a dehydrogenated vertical ethylidyne species) as the temperature was increased, revealing the ability of the $\Delta\mu$ technique to differentiate between different bonding geometries⁹⁹ on Pt, and even ethylene-type intermediates in the hydroepoxidation of propene over Au.¹⁰⁰ We expect a much wider application of the combined $\Delta\mu$ XANES and EXAFS techniques in the future.

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Advanced course by B. Ravel <http://leonardo.phys.washington.edu/ravel/course>
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<http://www.esrf.fr/computing/scientific/exafs/>
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Palladium-Based Electrocatalysts for Alcohol Oxidation in Direct Alcohol Fuel Cells

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I. INTRODUCTION

Palladium is emerging as an attractive replacement for platinum in a number of electrochemical applications, including low-temperature fuel cells, electrolyzers and sensors. Palladium is more abundant in nature and less expensive than platinum.¹ However, cost-associated issues are not the main driving force behind the increasing interest in palladium as it remains a rare noble metal whose introduction for a broad technological use would lead to an irreversible increase in its market price.

The real attraction for Pd-based electrocatalysts is originated by the fact that, unlike Pt-based electrocatalysts, they can be highly active for the oxidation of a large variety of substrates in alkaline environment where also non-noble metals are sufficiently stable for electrochemical applications.

The dilution of Pd with non-noble metals in a smart catalytic architecture capable of rapidly and stably oxidizing alcohols on anode electrodes would knock down the main barriers to the commercialization of *direct alcohol fuel cells* (DAFC), especially those fed with primary alcohols, higher than methanol, and polyalcohols. Indeed, apart from methanol for which there exist platinum based catalysts capable of producing current densities of several tens of mW cm^{-2} ,² the higher alcohols like ethanol and polyalcohols like glycerol are difficult to oxidize on platinum or platinum alloyed with either noble or non-noble metals.³⁻⁶

Besides allowing for the use of Pt-free catalysts at both anode and cathode,⁹ the DAFCs operating in alkaline media are attracting increasing industrial interest also due to new developments in the design of anion-exchange membranes.¹⁰⁻¹⁷ In fact, the drawback of traditional alkaline fuel cells to undergo electrolyte carbonation is strongly minimized by the use an anion conductive membrane, while the advantages in operating in alkaline conditions are manifold and include:

- Usability of both noble and non-noble metals to manufacture the electrocatalysts.
- Improved kinetics at both cathode and anode, in particular low anodic over-voltages for alcohol oxidation.
- Alcohol cross-over from anode compartment to cathode compartment reduced by electro-osmotic drag of hydrate hydroxyl ions.
- Easier water management as water is formed at the anode side where an aqueous solution already exists, while the electro-osmotic drag transports water away from the cathode preventing its flooding.
- Reduced risk of corrosion of the materials, including catalysts and carbons.
- Reduced adsorption of spectator ions that might limit electrocatalysis.

The progress achieved over the last five years in the design of Pd-based electrocatalysts for the oxidation of alcohols in alkaline media is reviewed in this chapter, which is particularly concerned with renewable substrates such as ethanol and glycerol.

II. SYNTHETIC PROCEDURES TO Pd-BASED ELECTROCATALYSTS FOR ALCOHOL OXIDATION

Current synthetic methods for the preparation of Pd-based electrocatalysts for anodes of DAFCs are manifold, including reduction of high-valent metal compounds with chemical agents, colloidal metal deposition, electrodeposition and transmetalation reactions.

Electroless procedures involve the adsorption of a palladium compound (PdCl_2 , K_2PdCl_4 or H_2PdCl_4), alone or in conjunction with other metal compounds, onto a porous, electro-conductive material. The following reduction reaction is commonly carried out in aqueous dispersion with an appropriate reducing agent, which may also act as templating agent to favor the formation of nano-sized metal particles (NaBH_4 , ethylene glycol, hydrazine, tannic acid, formic acid, formaldehyde, hydrogen gas).¹⁸⁻²⁰

A large variety of conductive materials have been used to support Pd nanoparticles prepared by electroless procedures, these include carbon blacks like Vulcan XC-72, alone¹⁸ or in combination with either nanocrystalline metal oxides (NiO , CeO_2 , Co_3O_4 , Mn_3O_4)^{21,22} or tungsten carbide nanocrystals,²³ carbon microspheres,²⁴ coin-like hollow carbons,²⁵ ultrahigh-surface hollow carbon spheres,²⁶ carbonized porous anodic alumina,²⁷ carbonized TiO_2 nanotubes,²⁸ single- and multi-walled carbon nanotubes^{19,29} and activated carbon nanofibers.¹⁹

Common techniques for the characterization of the electrocatalysts include High Resolution Electron Microscopy (HRTEM), Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS), Energy Dispersive Spectroscopy (EDS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Near Edge X-ray Absorption Spectroscopy (XANES), X-Ray Powder Diffraction (XRPD), Infrared and Raman Spectroscopy (IR, RS).

The metal particles obtained by electroless procedures are generally well dispersed and crystalline with dimensions in the range from 3 to 25 nm, while the XRPD patterns show face-centered cubic (fcc) lattice structures with diffraction peaks at the Bragg angles of 40.10° , 46.40° and 68.08° , corresponding to the (111), (200) and (220) facets of palladium crystal. Typical TEM micrographs and XRPD patterns of Pd nanoparticles supported on

various carbon materials are shown in Figs. 1 and 2 for Vulcan-XC 72 (C), multi-walled carbon nanotubes (MWCNT), activated carbon fibers (ACF) and ultrahigh surface area hollow carbon spheres (HCS). Figure 3 illustrates a SEM micrograph of Pd particles supported on carbonized and pulverized anodic alumina (CPAA) featured by excellent electrocatalytic activity for ethanol oxidation (*vide infra*).²⁷

In alternative to the reduction of metal salts or compounds adsorbed on conductive materials, surfactant-stabilized colloidal Pd can be independently prepared *via* the Bönnerman method and later mixed with a carbon black.¹⁶ A TEM micrograph of a Pt-Pd/C catalyst prepared using this method is given in Figure 4 together with the corresponding histogram of particle distribution. Binary Pt-Pd/C and ternary Pt-Pd-Bi/C catalysts have been prepared by the water-in-oil microemulsion method, involving the reduction of different microemulsions of metal salts, successively added to a conductive carbon.¹⁷

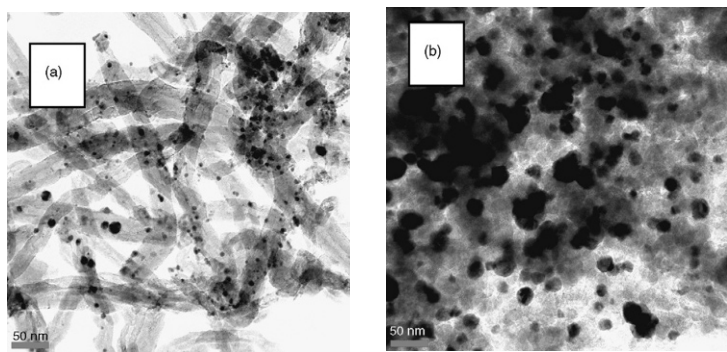


Figure 1. XRD patterns and TEM images of (a) Pd/MWCNT, (b) Pd/C and (c) Pd/ACF (ACF = activated carbon fiber). Bars are 50 nm for images (a and b) and 20 nm for image (c). Reprinted from Hai Tao Zheng, Yongliang Li, Shuixia Chen, and Pei Kang Shen, "Effect of support on the activity of Pd electrocatalysts for ethanol oxidation," *Journal of Power Sources*, **163** (2006) 371-75, Copyright (2006), with permission from Elsevier.

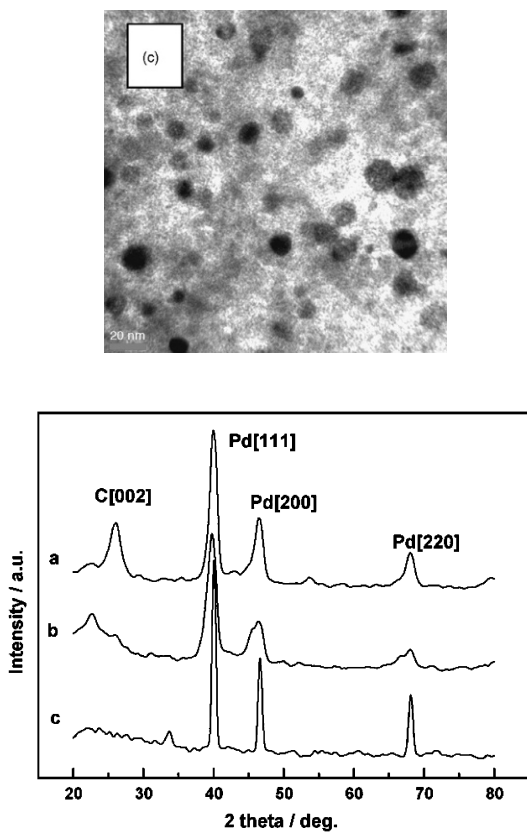


Figure 1. Continuation.

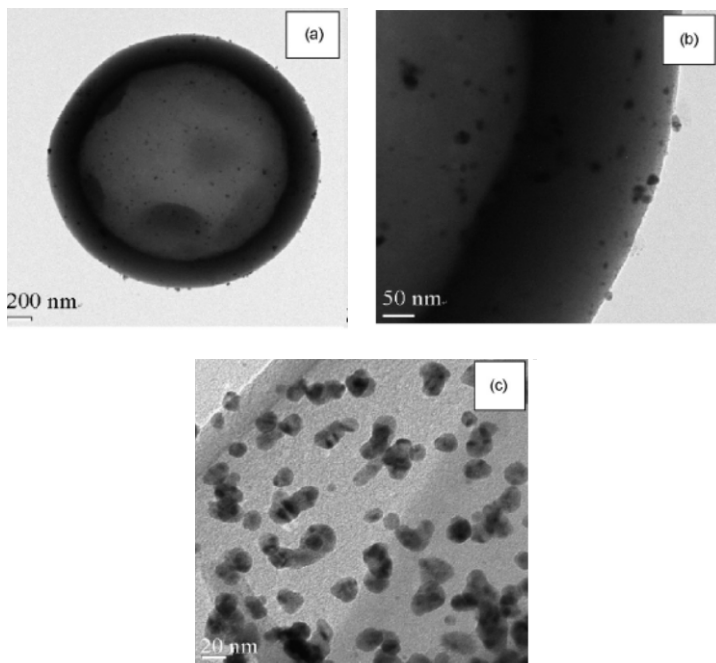


Figure 2. (a) TEM image of Pd/HCS (HCS = ultrahigh surface area hollow carbon spheres) (bar 200 nm), (b) the distribution of Pd on the surface of HCS (bar 50 nm) and (c) the enlarged TEM image of Pd/HCS (bar 20 nm). Reprinted from Feng Ping Hu, Zhenyou Wang, Yongliang Li, Changming Li, Xin Zhang and Pei Kang Shen, "Improved performance of Pd electrocatalyst supported on ultrahigh surface area hollow carbon spheres for direct alcohol fuel cells," *Journal of Power Sources*, **177** (2008) 61-66, Copyright (2008) with permission from Elsevier.

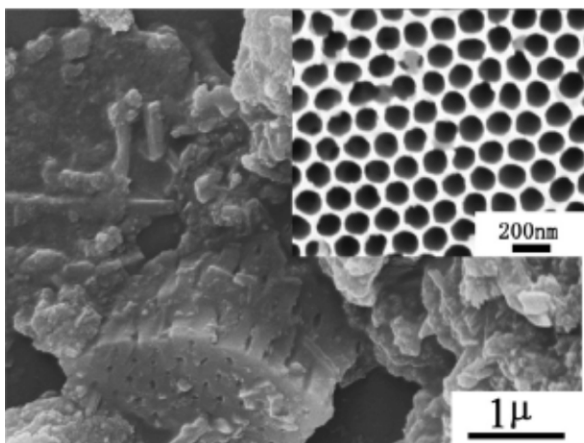


Figure 3. SEM micrograph of the carbonized and pulverized PAA after Pd deposition. Inset: SEM micrograph of PAA prepared in 0.3 M oxalic acid at 60 V. Reprinted from Zhenyou Wang, Fengping Hu and Pei Kang Shen, "Carbonized porous anodic alumina as electrocatalyst support for alcohol oxidation," *Electrochemistry Communications*, **8** (2006) 1764-68, Copyright (2006) with permission from Elsevier.

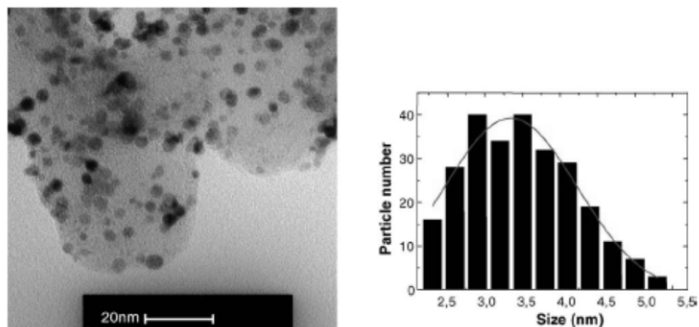


Figure 4. TEM micrograph particle size distribution of Pt-Pd (1:1) 20 wt%. Reprinted from C. Coutanceau, L. Demarconnay, C. Lamy and J.-M. Léger, "Development of electrocatalysts for solid alkaline fuel cell (SAFC)," *Journal of Power Sources*, **156** (2006) 14-19, Copyright (2006), with permission from Elsevier.

Electrochemical methods for the preparation of anode electrocatalysts for DAFCs involve either the electrodeposition of one metal at a time, eventually followed by the electrodeposition of other metals, or the contemporaneous electrodeposition of two or more metals. Highly ordered Pd nanowires arrays (Fig. 5) have been prepared by template-electrodeposition on glassy carbon electrodes,³⁰ while cyclic potential sweep techniques have been used to prepare Pd thin films on polycrystalline Pt or Au substrates.³¹ Ni-Pd electrodes for methanol oxidation have been prepared by electrodeposition onto titanium discs using a $\text{PdCl}_2/\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ bath.³²

The spontaneous deposition of noble metals onto less noble metal particles or metal surfaces is emerging as a viable technique for creating new catalyst architectures as well as allowing one to introduce single noble metal sites over the surface of a non-noble metal phase.³³⁻³⁶ A schematic representation of the spontaneous deposition of a high-valent metal *via* redox transmetalation is shown in Fig. 6 for a hypothetical non-noble metal phase supported on a conductive material.

Some applications of the spontaneous deposition technique to the preparation of Pd-based electrocatalysts for fuel cells have been recently reported,³⁶⁻⁴⁰ among these there are examples of active anode catalysts in DAFCs.^{36,40} Their preparation commonly proceeds by simply stirring a water solution of either a Pd^{II} or Pd^{IV} salt in the presence of an appropriate electropositive metal phase. For example, stirring a water solution of K_2PdCl_4 in the presence of Vulcan-supported Ni-Zn and Ni-Zn-P alloys gives the highly efficient electrocatalysts Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C.^{36,40}

The characterization of the latter materials by HRTEM (Fig. 7), EXAFS (Fig. 8), XPRD (Fig. 9) and XANES has unambiguously shown their surface to contain small (0.5–1 nm), highly dispersed and crystalline Pd and Ni clusters, as bimetallic aggregates, Ni-O as well as single Pd sites, likely stabilized by interaction with oxygen atoms from the nickel oxide.

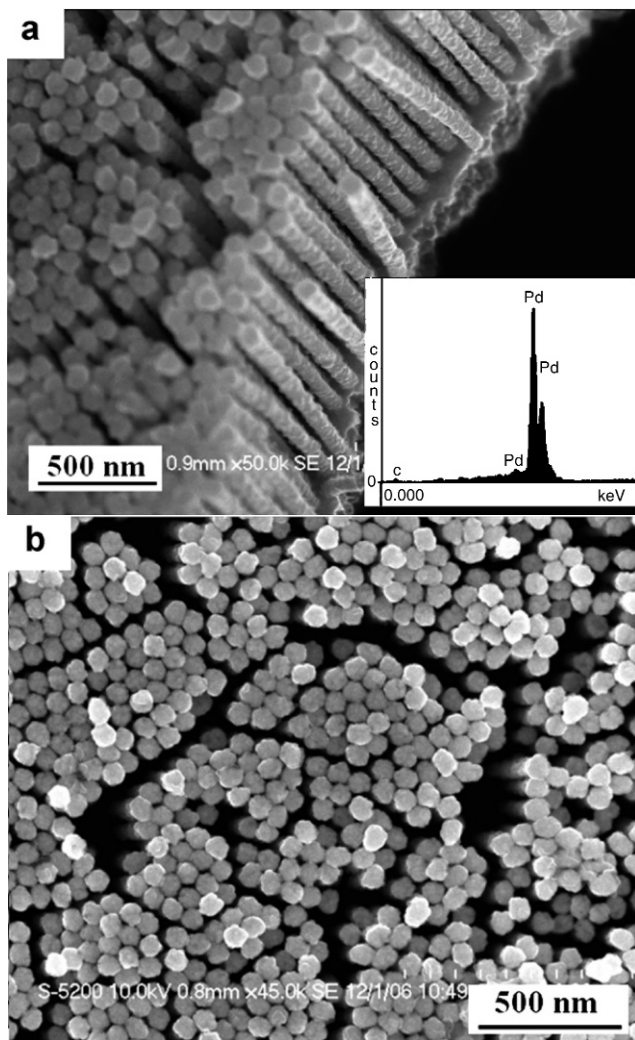


Figure 5. (a) and (b) SEM images of Pd nanowire arrays (EDS spectrum in the inset). Reprinted from Hong Wang, Changwei Xu, Faliang Cheng and Sanping Jiang, "Pd nanowire arrays as electrocatalysts for ethanol electrooxidation," *Electrochemistry Communications*, **9** (2007) 1212-1214, Copyright (2007) with permission from Elsevier.

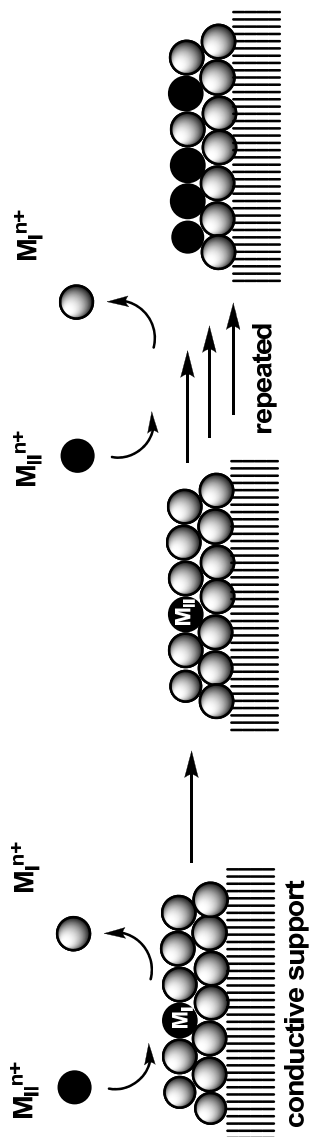


Figure 6. Schematic metal_{II} deposition onto metal_{II} particles via redox transmetalation.

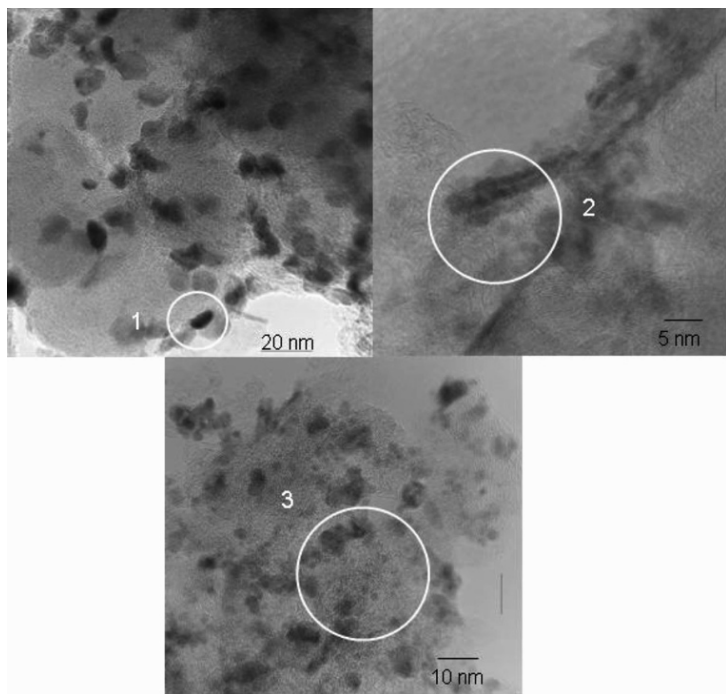


Figure 7. HRTEM micrographs of Pd-(Ni-Zn-P)/C at different magnifications. Spot of EDS analysis in circles, with Pd/Ni relative compositions as detected by the integrated peak area: 1) Pd; 2) Ni; 3) Ni:Pd = 1:1. Everywhere minor O contribution.³⁶ Reprinted from Ref. 36, Copyright (2009) with permission from Wiley-VCH.

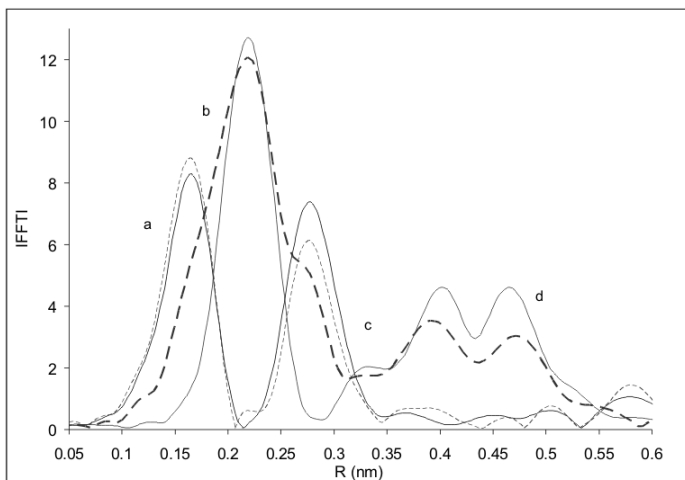
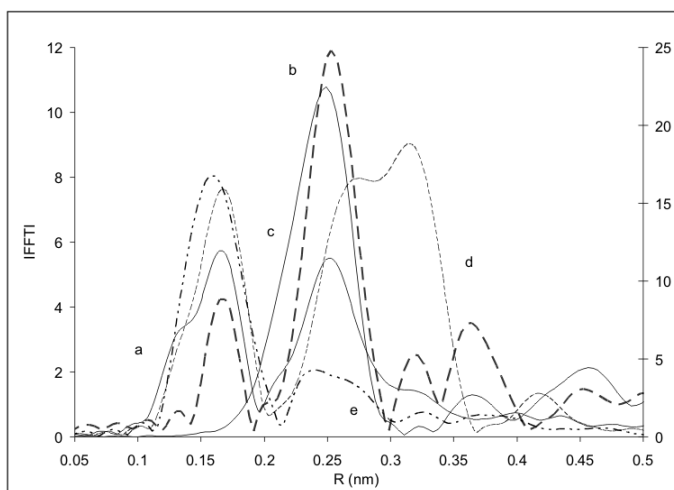
**a****b**

Figure 8. a) Ni K-edge Fourier Transformed EXAFS spectra (not phase corrected) of: a) (—) Pd-(Ni-Zn-P)/C; b) (---) Pd-(Ni-Zn)/C; c) (···) NiO and d) (—) Ni foil reference standards. b) Pd K-edge Fourier Transformed EXAFS spectra (not phase corrected) of: a) Pd-(Ni-Zn-P)/C; b) Pd-(Ni-Zn)/C; reference standards: c) Pd foil (right axis); d) PdO and e) Pd(acac)₂. Reprinted from Ref. 36, Copyright (2009) with permission from Wiley-VCH.

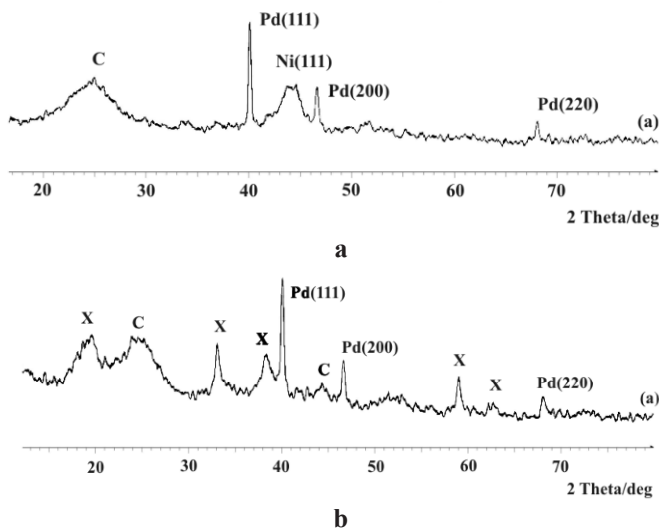


Figure 9. XRD patterns of a) Pd-(Ni-Zn)/C and b) Pd-(Ni-Zn-P) (x-rated peaks are due to the Ni-Zn-P support). Reprinted from Ref. 36, Copyright (2009) with permission from Wiley-VCH.

III. ALCOHOL OXIDATION ON Pd-BASED CATALYSTS

Primary alcohols with a higher molecular weight than methanol are arousing major interest as fuels in DAFC for various reasons, among which their low toxicity, high boiling point, high specific energy and, most importantly, the capacity of some of them to be renewable.¹⁻⁴ Included in this group are ethanol and glycerol. The former can be massively produced from biomass feedstocks originating from agriculture (first-generation bio-ethanol), forestry and urban residues (second-generation bio-ethanol). Glycerol is the byproduct of biodiesel synthesis and, as such, is inexpensive and largely abundant.

In the following Sections the most relevant studies of alcohol oxidation in both half cells and single monoplanar fuel cells using electrodes containing Pd-based electrocatalysts are reviewed.

1. Electrochemical Studies in Half Cell

Electrodes coated with nanostructured Pd catalysts are generally active for alcohol oxidation in alkaline media, but both the type of the support material and the co-presence of other metals or metal oxides can remarkably affect the catalytic performance in terms of activity and electrochemical stability.

The effect of the carbon support on the activity of nanostructured Pd catalysts for ethanol oxidation has been systematically investigated by P. K. Shen and coworkers using PdCl_2 as metal precursor and various reducing agents. A number of supports have been considered, including Vulcan XC-72,¹⁹ MWCNTs,¹⁹ ACFs,¹⁹ carbon microspheres (CMS)²⁴ and ultrahigh surface-area hollow carbon spheres (HCS).²⁶ The cyclic voltammograms (CVs) relative to the ethanol oxidation on Pd nanoparticles supported on the first three materials are reported in Fig. 10 that also shows the CV of a Pt/C electrode for comparative purposes (trace c). Under comparable experimental conditions ($200 \mu\text{g cm}^{-2}$ Pd), the Pd/MWCNT catalyst is clearly more active than Pd/ACF or Pd/C as well as more electrochemically stable as shown by the chronopotentiometric tests reported in Fig. 11. Consistent with the higher catalytic activity of Pd/MWCNT, its Nyquist plot shows a lower reaction resistance as compared to Pd/ACF and Pd/C.¹⁹ The smaller size and higher dispersion of the Pd nanoparticles in Pd/MWCNT have been claimed by P. K. Shen et al. as the factors accounting for the higher catalytic activity of this catalyst as compared to Pd/ACF and Pd/C.¹⁹

It is worth noticing that, under comparable experimental conditions, the Pt/C electrode is not only much less active, in terms of both onset potential of ethanol oxidation and peak current density (Fig. 10), but it is also less stable showing extensive potential oscillation as well as faster attainment of the oxygen-discharge overpotential (Fig. 11). According to some authors, the oxidation of ethanol on Pt in alkaline media is thwarted by fast electrode passivation because of the formation of a thick Pd-O layer upon reaction with ethoxy radicals.⁴¹ Other authors have argued that strong CO binding to the Pt sites, even when the catalyst is promoted by the addition of metal oxides, is the principal reason for electrode deterioration.⁴² Indeed, Pt-based

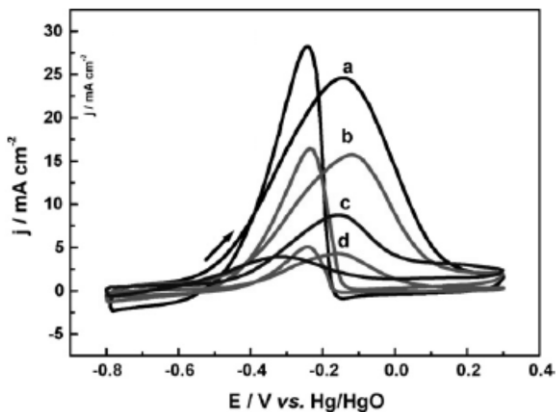


Figure 10. Cyclic voltammograms of the Pd-based electrodes and Pt/C in 1 M KOH solution containing 1 M ethanol at a sweep rate of 50 mVs^{-1} at room temperature, Pd loading: 0.2 mg cm^{-2} . (a) Pd/MWCNT, (b) Pd/C, (c) Pt/C and (d) Pd/ACF. Reprinted from Hai Tao Zheng, Yongliang Li, Shuixia Chen, and Pei Kang Shen, "Effect of support on the activity of Pd electrocatalysts for ethanol oxidation," *Journal of Power Sources*, **163** (2006) 371-75, Copyright (2006), with permission from Elsevier.

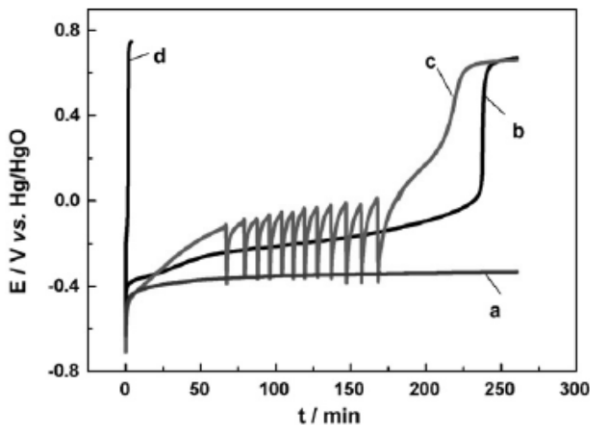


Figure 11. Chronopotentiometric curves of ethanol oxidation on (a) Pd/MWCNT, (b) Pd/C, (c) Pt/C and (d) Pd/ACF at 1.0 mA cm^{-2} in 1 M ethanol + 1 M KOH solution. Reprinted from Hai Tao Zheng, Yongliang Li, Shuixia Chen, and Pei Kang Shen, "Effect of support on the activity of Pd electrocatalysts for ethanol oxidation," *Journal of Power Sources*, **163** (2006) 371-75, Copyright (2006), with permission from Elsevier.

catalysts are more amenable than Pd-based catalysts to cleave C-C bonds also in alkaline media.^{12,42,43}

A further evidence of the ability of MWCNTs to contribute to the formation of excellent Pd electrocatalysts for alcohol oxidation has been reported by Bianchini, Serp and coworkers.²⁹ These authors have synthesized a nanostructured Pd/MWCNT catalyst by treatment with H_2 of MWCNT-adsorbed $Pd_2(dba)_3$ (dba = benzylideneacetone) and have evaluated its performance for the oxidation of methanol, ethanol and glycerol in 2 M KOH solutions. The catalyst exhibits high activity for the oxidation reaction of all alcohols even at metal loadings as low as $17\text{--}20\text{ }\mu\text{g cm}^{-2}$. In the half cell, glycerol provides the highest peak current density (54 mA cm^{-2}), while ethanol shows the lowest onset potential ($-0.75\text{ V vs. Ag/AgCl/KCl}_{\text{sat}}$) (Fig. 12).

On the other hand, the Pd/MWCNT electrode is electrochemically stable only for the oxidation of ethanol as the oxidation reactions of methanol and glycerol are featured by a fast increase of the overpotential (Fig. 13).

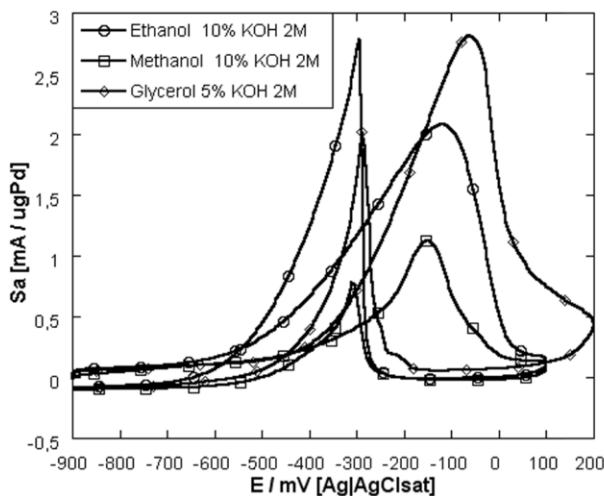


Figure 12. Cyclic voltammograms of methanol, ethanol and glycerol oxidation on a Pd/MWCNT electrode in 2 M KOH. Pd loading: $17\text{ }\mu\text{g cm}^{-2}$. Scan rate: 50 mV s^{-1} . Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.

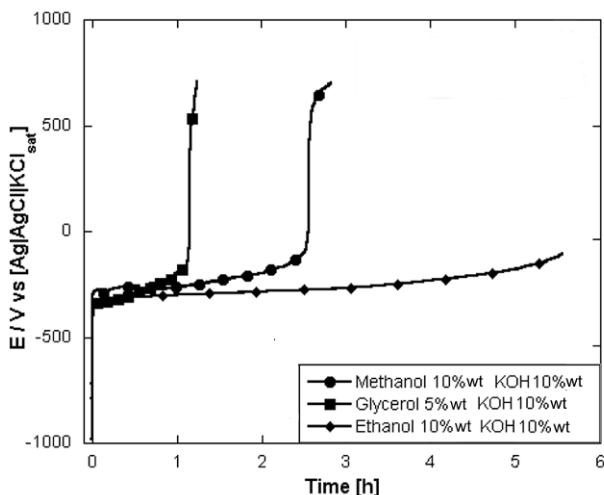


Figure 13. Chronopotentiometric traces of methanol (10 wt%), ethanol (10 wt%) and glycerol (5 wt%) oxidation on a Pd/MWCNT electrode at 3.46 mA cm^{-2} in 2 M KOH. Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.

The degradation of the Pd/MWCNT electrode during methanol and glycerol oxidation has been ascribed to the formation of adsorbed CO .^{5,6,9,29} Indeed, ethanol is selectively oxidized to acetic acid, transformed into acetate ion in the alkaline environment of the reaction, whereas methanol and glycerol give carbonate via CO intermediate.²⁹ In particular, methanol is fully oxidized to carbonate, while glycerol gives C_3 hydroxy carboxylates and bi-carboxylates, but also oxalate, formate and carbonate via C-C bond breaking reactions (*vide infra*). Given for granted that the formation of CO_{ads} increases the polarization of the Pd/MWCNT electrode during glycerol oxidation, it alone can hardly account for its much faster deactivation as compared to methanol oxidation (Fig. 13). In fact, the products derived from glycerol via C-C bond cleavage paths, leading to CO_{ads} , constitute a minor fraction (30-40%) of the overall transformation of this substrate.²⁹

On a speculative basis, it has been suggested that the large polarization of the Pd/MWCNT electrode during glycerol

oxidation may be due to strong interactions between the electrode surface and the products of the partial oxidation, which include hydroxyacids such as glycolic and glyceric acids and keto acids such as tartronic acid (*vide infra*).^{29,44,45}

Bianchini, Serp and coworkers have also observed a remarkable effect of the MWCNTs on the alcohol diffusion.²⁹ As shown in Figure 14a, a linear $Sa_p/(V^{1/2} s^{-1/2})$ relationship, typical of an electrochemical reaction under diffusion control, features the oxidation of ethanol on PD/MWCNT at scan rates lower than 350 mV s^{-1} (Sa_p = specific peak current density). Above this scan rate, the slope decreases tending to a plateau, which has been ascribed to a reaction limited by other factors than substrate diffusion, for example the very low density of catalytic centers due to the extremely low Pd loading ($17 \mu\text{g cm}^{-2}$) as well as the slow desorption of the acetate product.²⁹ A much narrower window of diffusion-controlled kinetics was observed for the oxidation of glycerol (Fig. 14b), the independence of the peak current density on the voltage scanning frequency being attained already at scan rates above 50 mV s^{-1} and ascribed to the concomitant action of

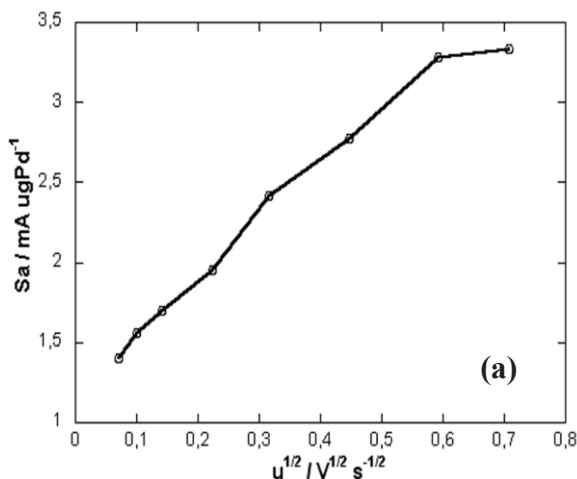


Figure 14. Plots of the anodic peak current density against the square-root of the scan rate for the oxidation on the Pd/MWCNT electrode of a) ethanol, b) glycerol and c) methanol (10 wt% MeOH & 2 M KOH; 20 wt% MeOH & 2 M KOH). Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.

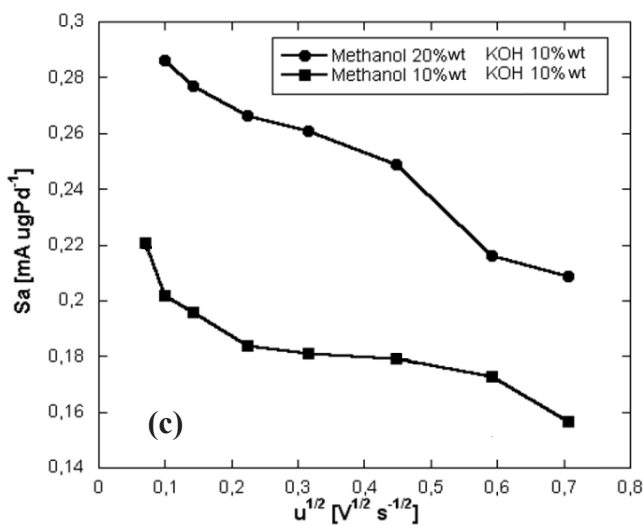
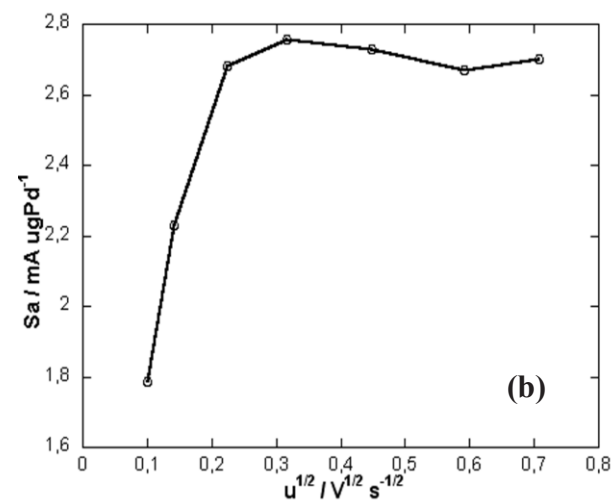


Figure 14. Continuation

CO bonding to the active sites and difficult product desorption (*vide infra*). In contrast, the peak current density of methanol oxidation decreases with the scan rate (Fig. 14c), even by increasing the concentration of MeOH from 10 to 20 wt%, in an attempt of magnifying the diffusion effects. Apparently, the diffusion of MeOH across the MWCNT support is very fast but the electrocatalyst is not sufficiently active and the peak current density decreases by increasing the scan rate.

As an indirect confirmation of the role of the carbon support in controlling the substrate diffusion, the same authors reported that the oxidation of methanol on an electrode catalyzed by nanostructured Pd particles supported on Vulcan XC-72 (same metal loading as in Pd/MWCNT) is diffusion-controlled in the scan-rate range from 50 to 500 mV s⁻¹.^{29,36}

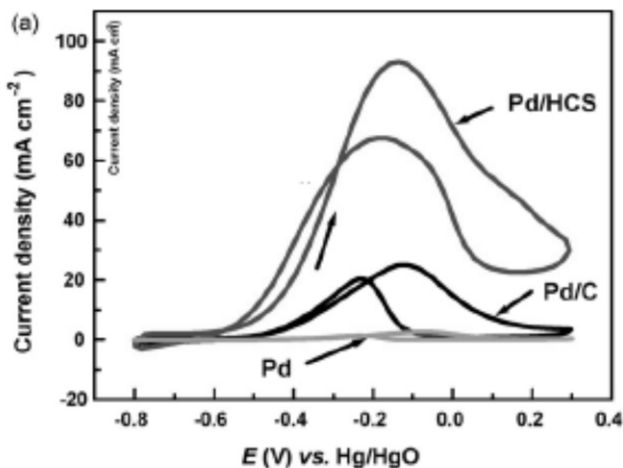


Figure 15. Cyclic voltammograms of ethanol oxidation on Pd/C and Pd/HCS in 1 M KOH/1 M ethanol solution at 303 K, scan rate: 50 mVs⁻¹. Pd loading 300 $\mu\text{g cm}^{-2}$. Reprinted from Feng Ping Hu, Zhenyou Wang, Yongliang Li, Changming Li, Xin Zhang and Pei Kang Shen, "Improved performance of Pd electrocatalyst supported on ultrahigh surface area hollow carbon spheres for direct alcohol fuel cells," *Journal of Power Sources*, 177 (2008) 61-66, Copyright (2008), with permission from Elsevier.

The capacity of the support material to allow for the fast diffusion of the substrate has been invoked to explain the excellent behavior of the Pd/HCS electrode for the oxidation of ethanol (Fig. 15).²⁶ Indeed, the HCS support exhibits a very high surface area (up to $1249 \text{ m}^2 \text{ g}^{-1}$ using the surfactant P123) as well as a much higher electrochemical active surface area ($10.718 \text{ mC cm}^{-2}$) as compared to Pd/C or Pd metal (1.913 and 0.287 mC cm^{-2} , respectively).

Simple experiments such as plotting the scan rate against the ratio between the integrated charge of the anodic peak at different scan rates (Q_v) and the maximum charge ($Q_{\max}$) (Fig. 16) or plotting the peak current density against the square root of the scan rate (inset of Fig. 16) show unequivocally that the mass transfer

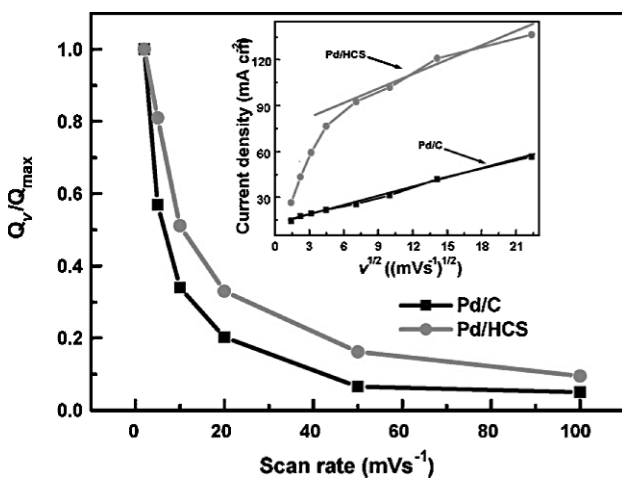


Figure 16. Plot of normalized charge of anodic peak of ethanol oxidation on Pd/C and Pd/HCS electrodes against the scan rate. Inset presents the plots of the peak current density against the square root of the scan rate for both electrodes. Reprinted from Feng Ping Hu, Zhenyou Wang, Yongliang Li, Changming Li, Xin Zhang and Pei Kang Shen, "Improved performance of Pd electrocatalyst supported on ultrahigh surface area hollow carbon spheres for direct alcohol fuel cells," *Journal of Power Sources*, 177 (2008) 61-66, Copyright (2008), with permission from Elsevier.

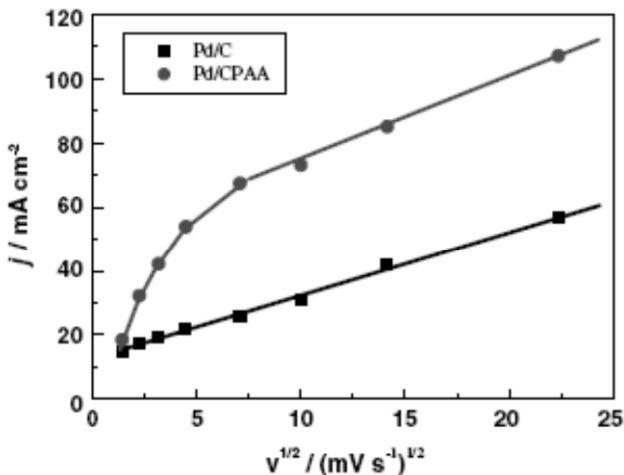


Figure 17. Plots of the peak current density against the square root of the scan rate for the ethanol oxidation in 1 M ethanol/1 M KOH solution on Pd/C and Pd/CPAA electrodes. Reprinted from Zhenyou Wang, Feng-ping Hu and Pei Kang Shen, "Carbonized porous anodic alumina as electrocatalyst support for alcohol oxidation," *Electrochemistry Communications*, 8 (2006) 1764-68, Copyright (2006), with permission from Elsevier.

across the Pd/HCS electrode is much faster than that across the Pd/C electrode so that the oxidation of ethanol on the former electrode is controlled by the activation polarization at low scan rates.

A similar beneficial effect of the support material on the substrate diffusion has been observed for the oxidation of various alcohols (methanol, ethanol, ethylene glycol and glycerol) on Pd electrocatalysts where Vulcan XC-72 is replaced by either CPAA²⁷ or carbonized TiO₂ nanotubes (TiO₂C) (Fig. 17).²⁸

As shown in Fig. 18, the Pd/CPAA electrode is quite active for the oxidation of all the alcohols investigated. The better performance of the Pd/CPAA electrode as compared to the Pd/C electrode has been attributed to the improved mass transport of the alcohols across the micropores and mesopores bimodal structure of the material supporting the Pd catalyst on the former electrode.²⁷ This effect is actually highlighted by the parabolic shape of the

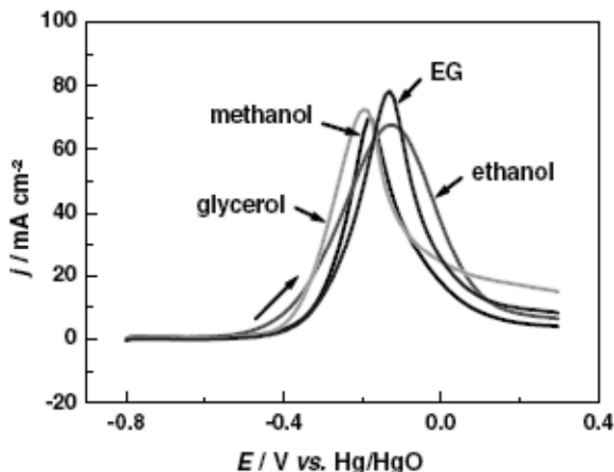


Figure 18. Linear potential sweep curves of the oxidation of methanol, ethanol, glycerol and ethylene glycol on the as-prepared three-dimensional Pd/CPAA electrode in 1 M alcohol/1 M KOH solution at 25 °C; Pd loading 300 $\mu\text{g cm}^{-2}$; scan rate: 50 mV s^{-1} . Reprinted from Feng Ping Hu, Zhenyou Wang, Yongliang Li, Changming Li, Xin Zhang and Pei Kang Shen, “Improved performance of Pd electrocatalyst supported on ultrahigh surface area hollow carbon spheres for direct alcohol fuel cells,” *Journal of Power Sources*, **177** (2008) 61-66, Copyright (2008), with permission from Elsevier.

$J_p/(V^{1/2} \text{ s}^{-1/2})$ plot for ethanol oxidation on Pd/CPAA at scan rates lower than 100 mV s^{-1} (Fig. 17).

Quite similar results, in terms of both electrochemical activity and stability have been reported for the ethanol oxidation on Pd/TiO₂C.²⁸

The combination of nanostructured Pd with other late transition metals or metal oxides has recently originated a distinctive class of electrocatalysts for DAFC applications.

The first report dealing with the synthesis and electrochemical characterization of Pd/C electrocatalysts promoted by nanocrystalline late transition metal oxides appeared in 2006 by P. K. Shen and C. Xu.²⁰ These authors demonstrated that the electroless reduction of PdCl₂ adsorbed onto oxide/C materials (oxide = CeO₂, Co₃O₄, Mn₃O₄, NiO) yields electrocatalysts for alcohol oxidation exhibiting much higher catalytic activity (onset oxidation potential

and peak current density) and electrochemical stability than any Pd/C or Pt/C catalyst under comparable experimental conditions.²⁰⁻

²² Figure 19a shows a comparative study of ethanol oxidation on different electrodes, while the much higher electrochemical stability of Pd/C promoted by nanocrystalline oxides is put in evidence by the chronopotentiometric experiments illustrated in Fig. 19b.

Various alcohols, including methanol, ethanol, glycerol and ethylene glycol, are effectively oxidized on Pd-oxide/C electrodes. Pd-Co₃O₄ (2:1, w:w)/C exhibits the highest activity for the electrooxidation of methanol, ethylene glycol and glycerol, while the most active catalyst for the ethanol electrooxidation is Pd-NiO (6:1, w:w)/C. On the other hand, Pd-Mn₃O₄/C shows significantly better performance stability than any other oxide-promoted Pd/C for the alcohol electrooxidation. It has been observed that the amount of metal oxide affects the catalytic activity as well as the electrode stability. In general, high contents of metal oxides reduce the electronic conductivity due to their semiconductor behavior, while, in some cases, the solubility of the metal oxides in alkaline solution can decrease the electrode stability, as is the case of the Pd-Co₃O₄/C electrocatalyst.²¹

It is worth noticing that, irrespective of the metal oxide, all Pd-based catalysts promote the selective conversion of ethanol to acetate ion.²⁰⁻²² No analytical data for the oxidation products of methanol, ethylene glycol and glycerol have been provided by K. P. Shen, yet one can surmise that the latter two substrates are mainly oxidized to carboxylic acid as found for other Pd-based electrocatalysts (*vide infra*).^{29,36}

The ethanol oxidation reaction on the catalysts Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C, obtained by the spontaneous deposition of Pd onto Vulcan XC-72-supported Ni-Zn or Ni-Zn-P alloys (*vide supra*), has been investigated by Bianchini and coworkers by CV.³⁶ Figure 20 shows the cyclic voltammograms acquired at very low Pd loading (22 $\mu\text{g cm}^{-2}$) in 2 M KOH solution.

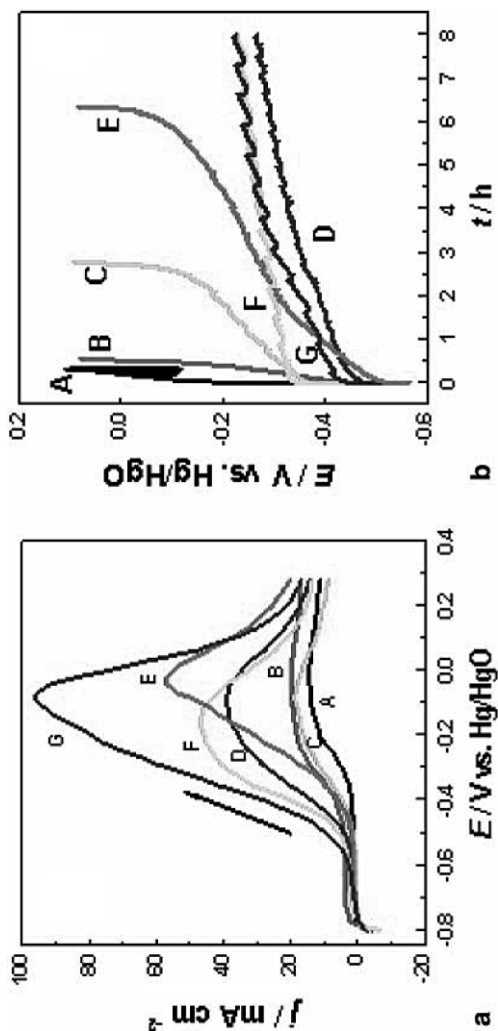


Figure 19. (a) Anodic oxidation curves of ethanol on different Pd-oxide/C catalysts in 1.0 M ethanol/1.0 M KOH solution at 50 mV s⁻¹. A, E-Tek Pt/C; B, E-Tek PtRu/C; C, Pd/C; D, Pd-CeO₂/C; E, Pd-Co₃O₄/C; F, Pd-Mn₃O₄/C and G, Pd-NiO/C. Pd loading: 300 μg cm⁻², 303 K. (b) Chronopotentiometric curves of ethanol oxidation at 3 mA cm⁻² on A, E-Tek Pt/C; B, E-Tek PtRu/C; C, Pd/C; D, Pd-CeO₂/C; E, Pd-Co₃O₄/C; F, Pd-Mn₃O₄/C and G, Pd-NiO/C in 1.0 M ethanol/1.0 M KOH solution, 303 K. Reprinted from Pei Kang Shen and Changwei Xu, "Alcohol oxidation on nanocrystalline oxide Pd/C promoted electrocatalysts," *Electrochemistry Communications*, **8** (2006) 184, Copyright (2006), with permission from Elsevier.

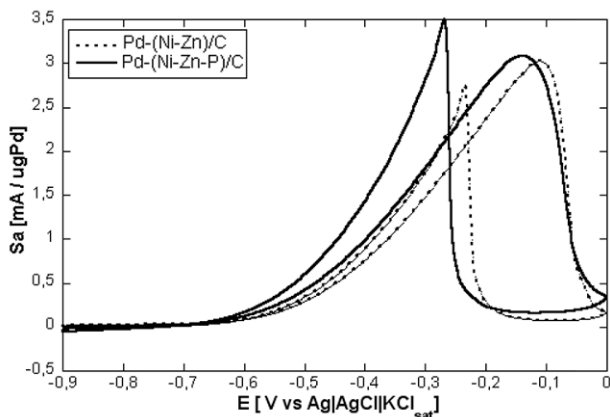


Figure 20. Cyclic voltammograms of ethanol oxidation on Pd-(Ni-Zn-P)/C and Pd-(Ni-Zn)/C electrodes in 2 M KOH and 10 wt% ethanol. Pd loading $22 \mu\text{g cm}^{-2}$. Scan rate: 50 mV s^{-1} . Room temperature.

From a perusal of the relevant literature one may readily realize that these catalysts outperform any known anode electrocatalyst for the ethanol oxidation in half cells, especially in terms of specific current densities which are higher than 3600 A gPd^{-1} .³⁶ Moreover, as shown in a forthcoming Section of this Chapter, anodes catalyzed with Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C exhibit unrivalled performance in both passive and active DAFCs equipped with anion-exchange polymeric membranes.

Electrodes coated with Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C are apparently stable for the oxidation of ethanol as shown by the chronopotentiometry experiments illustrated in Fig. 21. In fact, there is some potential oscillation in the first two-three hours of ethanol oxidation at a constant current density of 3.0 mA cm^{-2} , then no oscillation at all, as well as a potential increase by only a few tens of mV after 5.5 h. Both features suggest the absence of effective catalyst deterioration, for example by the formation of strongly adsorbed species on the catalysts surface.

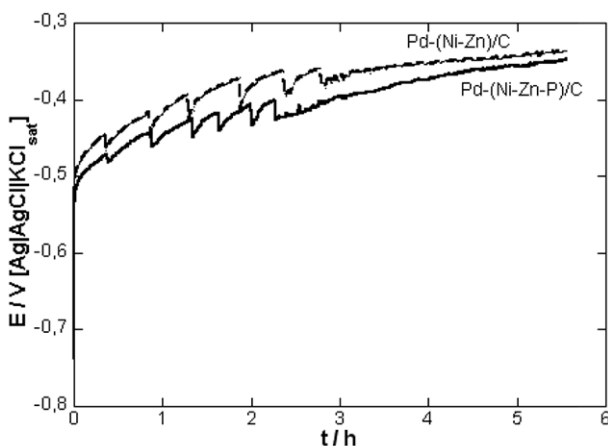


Figure 21. Chronopotentiometric traces of ethanol oxidation on Pd-(Ni-Zn-P)/C and Pd-(Ni-Zn)/C electrodes at 3.0 mA cm^{-2} in 2 M KOH and 10 wt% ethanol.³⁶

Catalyst poisoning along alcohol electrooxidation is generally related to strong adsorption of CO and CO-like species,^{3,5,7} and a specific study of ethanol oxidation on a Pd-NiO/C electrode has confirmed that also Pd is susceptible to CO poisoning, though to a much lesser extent than Pt.⁴² However, CO poisoning can be reasonably excluded as the factor responsible for the increase in the response potential exhibited by the Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C electrodes (Fig. 22). Indeed, like most of the Pd-based electrocatalysts examined here,^{20-22,29} also Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C are selective for the selective oxidation of ethanol to acetate in alkaline media. Accordingly, the observed overpotential may be due to other phenomena at the electrode interphase such as

- the increased viscosity of the solution, resulting in a slower diffusion rate of ethanol,
- the decreased concentration of OH^- anions, and
- the competitive adsorption of the acetate ion on the active metal sites.

Plotting the anodic specific peak current density for ethanol oxidation on Pd-(Ni-Zn-P)/C against the square-root of the scan

rate gives a linear relationship, typical of an electrochemical reaction under diffusion control, at scan rates lower than 100 mV s^{-1} (Fig. 22a). Above this scan rate, the slope decreases tending to a plateau. Apparently, at scan rates higher than 100 mV s^{-1} , the ethanol oxidation reaction on Pd-(Ni-Zn-P)/C is limited by other factors than substrate diffusion, for example the very low density of catalytic centers due to the very low Pd loading and/or the slow desorption of the oxidation product.

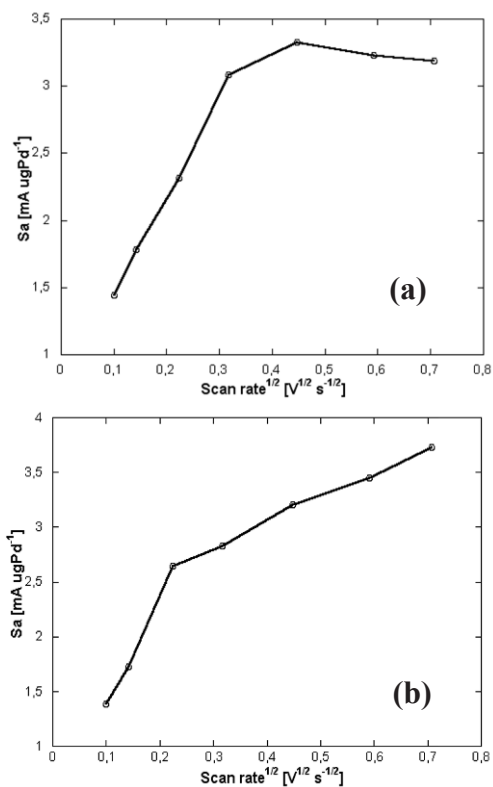


Figure 22. a) Plot of the anodic peak current density against the square-root of the scan rate for the Pd-(Ni-Zn-P)/C electrode. b) Plot of the anodic peak current density against the square-root of the scan rate for the Pd-(Ni-Zn)/C electrode. Reprinted from Ref. 36, Copyright (2009) with permission from Wiley-VCH.

The $S_{ap}/(V^{1/2} s^{-1/2})$ plot obtained for the Pd-(Ni-Zn)/C electrode is shown in Fig. 22b. A first linear correlation below the scan rate of 50 mV s^{-1} is followed by a second linear correlation. It has been suggested that the oxidation of ethanol on the Pd-(Ni-Zn)/C electrode is diffusion-controlled all over the range of scan rates investigated, yet with different impact on the reaction rate depending on the scan rate.³⁶ In other words, at scan rates higher than 50 mV s^{-1} , the reaction would be still diffusion-controlled, but not as effectively as occurs at lower scan rates. A similar behavior has been previously reported for the oxidation of ethanol on Pt electrodes in alkaline media and ascribed to the formation of a passive oxide layer during the early stage of the electron transfer.⁴¹ In the case of Pd-(Ni-Zn)/C, the CV and chronopotentiometric studies seem to exclude such a passivation path. As a possible explanation of the slope change exhibited by the $S_{ap}/(V^{1/2} s^{-1/2})$ plot reported in Fig. 22b, it has been suggested that the catalyst, being very active, would generate a high instantaneous concentration of acyl or acetate species on the catalyst surface from which the desorption might be too slow to allow for an effective substrate adsorption at high scan rates.

Unlike ethanol oxidation, chronopotentiometric experiments of methanol and glycerol oxidation on Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C electrodes show a remarkable increase of the overpotential with time, the oxygen discharge potential being attained after 2.5 and 1.5 h with methanol and glycerol, respectively.⁴³ In addition to decreasing the electrochemical stability of the electrodes, the oxidation of methanol and glycerol on Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C is also much slower than that of ethanol under comparable experimental conditions as shown by the CVs illustrated in Fig. 23.

The high dispersion of the Pd clusters and the presence of single Pd sites in Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C have been suggested to be important factors in boosting the electrocatalytic performance of these materials.³⁶ On the other hand, although independent CV experiments in KOH solution with Ni-Zn/C and Ni-Zn-P/C electrodes, prior and after alcohol addition, have excluded any direct role of the Ni support,^{36,43} the existence of a co-catalytic effect of Ni on the Pd-catalyzed oxidation reaction of alcohols cannot be disregarded. In fact, several researchers have reported that the co-presence of nickel or nickel oxide may have a

beneficial effect on the electro-oxidation of alcohols on transition metals in either acidic or alkaline media.^{20,22,46-49} A possible role of the Ni-based supports in enhancing the activity and stability of the Pd electrocatalysts for alcohol oxidation will be discussed in a forthcoming Section of this Chapter.

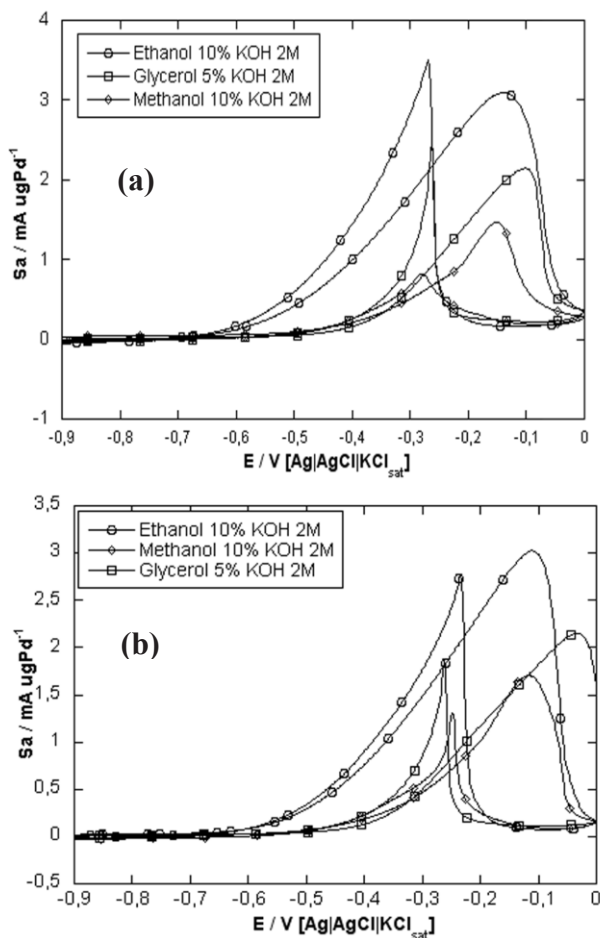


Figure 23. Cyclic voltammograms of methanol, ethanol and glycerol oxidation on Pd-(Ni-Zn)/C (a) and Pd-(Ni-Zn-P)/C (b) electrodes in 2 M KOH. Pd loading: $22 \mu\text{g cm}^{-2}$. Scan rate: 50 mV s^{-1} . Room temperature.^{36,43}

2. Direct Alcohol Fuel Cell: Passive Systems

To the best of our knowledge, the only examples of passive DAFCs equipped with an anion-exchange membrane are those realized independently by Bianchini^{29,36,43} and Coutanceau.^{16,17}

The membrane-electrode-assemblies (MEAs) described by Bianchini and coworkers comprise Fe-Co HypermecTM K-14 cathodes by ACTA SpA,⁴⁵ Tokuyama A-006 membrane and anodes coated with Pd/MWCNT, Pd-(Ni-Zn)/C or Pd-(Ni-Zn-P)/C electrocatalysts.^{29,36}

The polarization and power density curves obtained with methanol, ethanol and glycerol in 2 M KOH solutions at room temperature (20–22 °C) are reported in Fig. 24 for DAFCs where the cathode is exposed to either air or 1 bar oxygen and the fuel solution (13–15 mL) is introduced into a static compartment facing the anode.

From a perusal of Fig. 24, it is apparent that the Pd/MWCNT anode is particularly suitable for the oxidation of ethanol which shows the highest open circuit voltage (OCV, 0.74 V) and peak power density (18.4 mW cm⁻² at 0.2 V) out of the three fuels investigated.²⁹ Notably, the performance trend in the passive DAFC is different from that observed in the half cell where glycerol provides the highest peak current density (Fig. 13). On the other hand, the lower performance of both the *direct methanol fuel cell* (DMFC) and the *direct glycerol fuel cell* (DGFC) as compared to the DEFC is in line with the chronopotentiometric experiments illustrated in Fig. 13.

While no comparison can be made with other passive DGFCs for the lack of known examples, the power density provided by the DMFC (8 mW cm⁻²) at room temperature matches well the value reported by Coutanceau et al. for a *direct ethylene glycol fuel cell* (DEGFC) fuelled with 2 M ethylene glycol in 4 M NaOH¹⁷ and for a DMFC fuelled with MeOH in 1 M NaOH,¹⁶ both containing an ADP-type membrane from Solvay and anodes coated with 2 mg cm⁻² of Pt-Pd/C and Pt_{0.45}Pd_{0.45}Bi_{0.5}/C, respectively. Notably, Coutanceau has observed that palladium exhibits lower activity for ethylene glycol oxidation than platinum, especially in terms of onset oxidation potential, yet the addition of Pd to a Pt-Bi catalyst increases the current density without changing the onset potential. The beneficial effect of Pd has been attributed to the ability of this

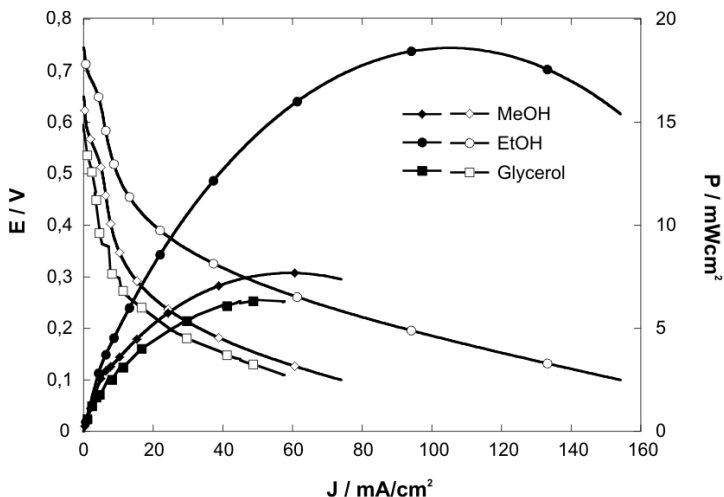


Figure 24. Polarization and power density curves provided by oxygen-breathing DAFCs fuelled with 2 M KOH solutions of methanol (10 wt%), ethanol (10 wt%) and glycerol (5 wt%) at 20–22 °C containing MEAs with Pd/MWCNT anodes, Hypermec™ K-14 Fe-Co cathodes and Tokuyama A006 membrane. Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.

metal to disfavor C-C bond breaking reactions (increased production of oxalate), thus reducing electrode poisoning by CO_{ads} .¹⁷

Much better performances, especially in terms of peak power densities, have been recently obtained with DEFCs containing anodes coated with the Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C electrocatalysts.^{36,43} As shown in Fig. 25, these catalysts are extremely active also at room temperature and at low Pd loading (1 mg cm^{-2}), providing up to 60 mW cm^{-2} at 0.3 V, which, to the best of our knowledge, is the highest value ever observed for a DEFC at room temperature. Just to better appreciate the result obtained with the DEFCs equipped with the Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C anodes, a peak power density of 27 mW cm^{-2} at 25 °C has been recently obtained with an *alkaline fuel cell* (AFC) containing a 3 M KOH solution as electrolyte and an anode coated with 1 mg cm^{-2} of Pt-black.⁵¹

For comparative purposes, Fig. 25 reports also the polarization and power density curves exhibited by a DEFC containing a Pd/C anode catalyst obtained by reduction with ethylene glycol of Vulcan XC-72-adsorbed PdCl_2 .^{36,43} Although providing good results, there is little doubt that the Pd/C catalyst is much less efficient, especially in terms of potential output and electrochemical stability, than the Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C catalysts, obtained by the spontaneous deposition procedure.

Galvanostatic experiments have been carried out at room temperature on DEFCs containing Pd/MWCNT, Pd-(Ni-Zn)/C, Pd-(Ni-Zn-P)/C or Pd/C anodes as well as on DMFCs and DGFCs containing a Pd/MWCNT anode. In all cases, the cathode was a Fe-Co Hypermec™ K-14 material and the solid electrolyte was a Tokuyama A-006 membrane.^{29,36,43,45} The anode compartments were filled with 28.3 mmol of EtOH, 40.7 mmol of MeOH or 6.8 mmol of glycerol. Accurate mass balance determinations were performed by means of both $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and ionic chromatography, using reference materials and calibration curves.

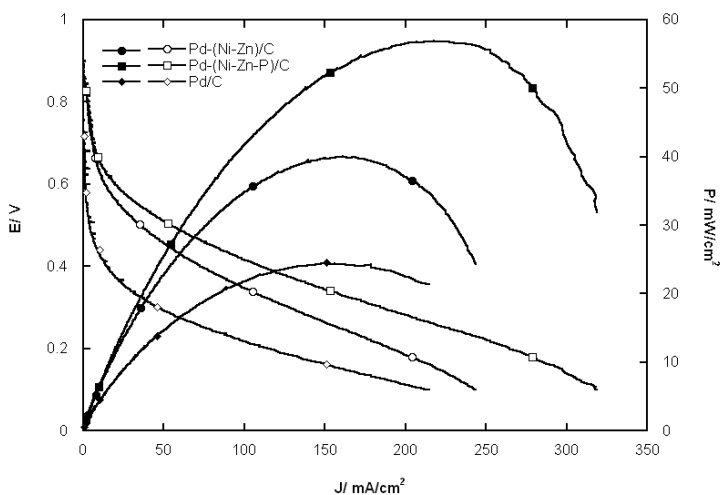


Figure 25. Polarization and power density curves provided by an oxygen-breathing DEFC fuelled with 2 M KOH solutions of ethanol (10 wt%) at 20–22 °C containing MEAs with Hypermec™ Fe-Co cathodes, Tokuyama A006 membrane and Pd-Ni-Zn)/C, Pd-(Ni-Zn-P)/C or Pd/C anodes. Pd loadings 1 mg cm^{-2} .⁴³

Irrespective of the Pd catalyst, the analysis of the DEFC exhausts was unequivocally consistent with the selective acetate formation (Eq. 1).



After a conditioning time of 1 h at the OCV, the circuit of the DEFC with the Pd/MWCNT anode was closed and a constant current of 102 mA was allowed to flow until zero voltage (Fig. 26). Under these conditions, the DEFC kept on providing 102 mA for 12.5 h to give 12 mmol of acetate (isolable as potassium acetate) with 12 mmol of unreacted ethanol.²⁹ The $^{13}\text{C}\{\text{H}\}$ NMR spectrum of the corresponding cell exhausts is shown in Fig. 27a.

In comparable experimental conditions, the DEFCs with the Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C anodes delivered 102 mA for 10.9 and 10.4 h, producing 10 and 9.6 mmol of acetate, respectively, at remarkably higher overpotentials than those provided by the Pd/MWCNT anode.^{43,45} According to the analytical data, ca. 4 mmol of EtOH were lost by evaporation irrespective of the anode catalyst. Since the anode compartments were accurately sealed during the experiments, the fuel losses have been attributed mostly to the evaporation of the cross-over ethanol from the cathode side.

Under comparable conditions, the DMFC with the Pd/MWCNT anode kept on working for 10.3 h yielding 3 mmol of formate and 7 mmol of carbonate (Eqs. 3 and 4) with 22 mmol of unreacted MeOH (Fig. 27b).²⁹ The loss of substrate was therefore ca. 8 mmol, in line with the lower boiling point of methanol and its easier permeation through the membrane as compared to ethanol.



The analysis of the DGFC exhausts of a passive cell equipped with a Pd/MWCNT anode showed the conversion of glycerol into various products (Scheme 1 and Fig. 28).²⁹

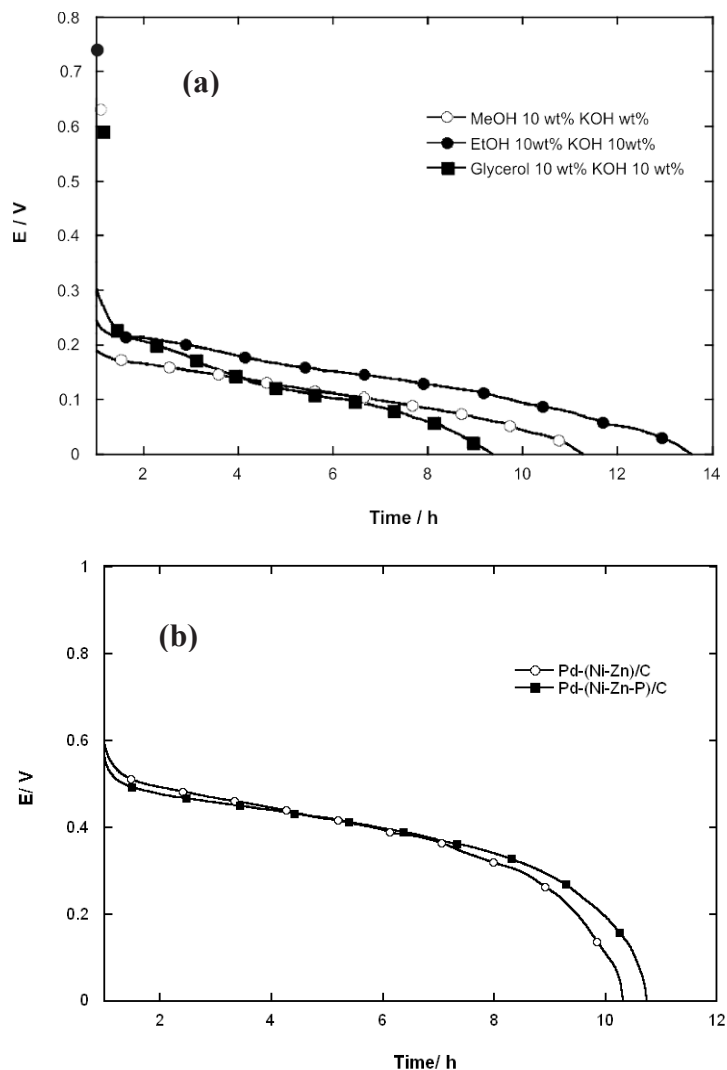


Figure 26. Galvanostatic traces at 102 mA of (a) DAFCs with Pd/MWCNT anode fuelled with methanol, ethanol or glycerol. Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier. (b) DEFC with Pd-(Ni-Zn)/C or Pd-(Ni-Zn-P)/C anode.⁴³

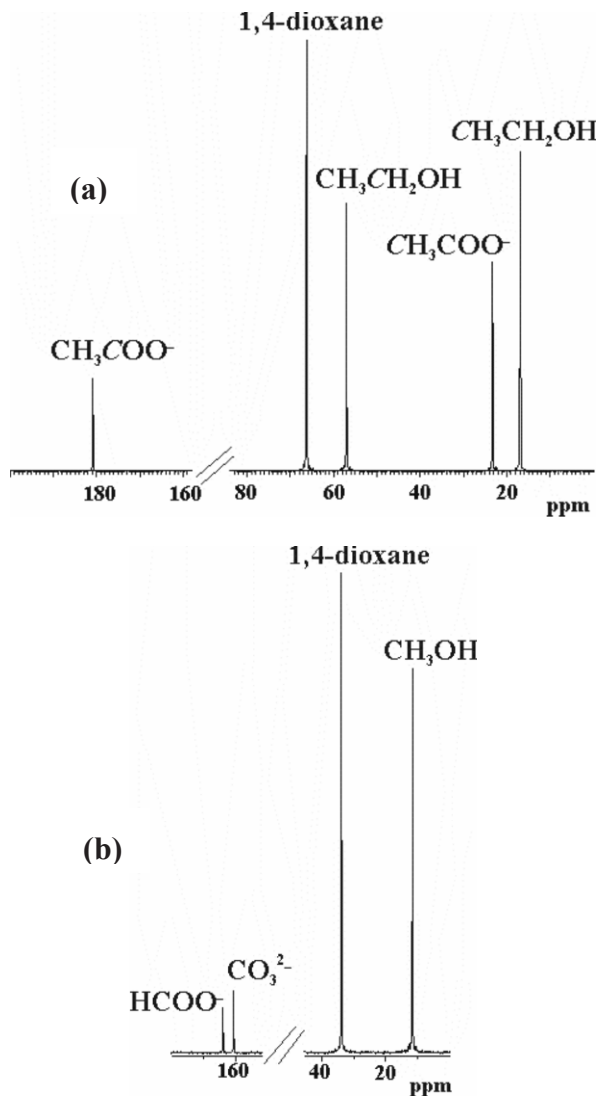
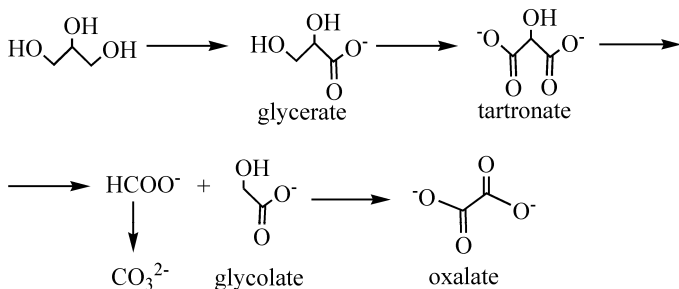


Figure 27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra at room temperature of the anode solution a) DEFC with a Pd/MWCNT anode supplying 102 mA for 12.5 h; b) DMFC with a Pd/MWCNT anode supplying 102 mA for 10.3 h. Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.



Scheme 1. Products obtained by the partial oxidation of glycerol on Pd/MWCNT anodes in a passive DGFC.²⁹

Overall, the DGFC provided current for 8.4 h producing 3070 coulomb and leaving 10 mmol of unreacted glycerol. About 4 mmol of glycerol were consumed to give glycolate (4%), glycerate (27%), tartrate (23%), oxalate (15%), formate (9%) and carbonate (22%). Consistent with the high boiling point and lower membrane permeability of glycerol, no appreciable loss of fuel was observed.

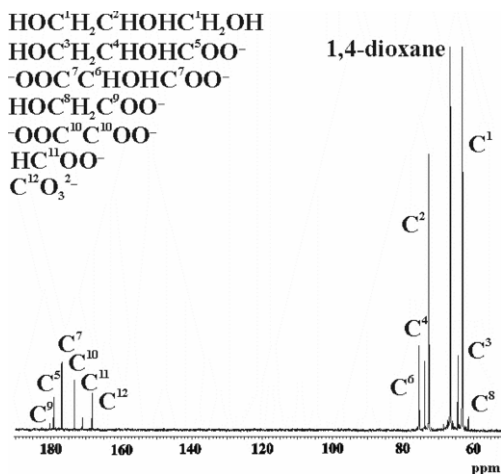


Figure 28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at room temperature of the anode solution of a DGFC with a Pd/MWCNT anode supplying 102 mA for 8.4 h. Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.

Most importantly, all the DAFCs described above are fully regenerated (same OCV and galvanostatic performance) upon replacement of the cell exhausts with fresh 2 M KOH solutions of methanol, ethanol or glycerol. This procedure was repeated several times with no apparent performance decay. In view of these results, Bianchini and coworkers ascribed the polarizations shown in Fig. 27 to other factors than catalyst or electrode poisoning, i. e. the increasing viscosity of the solutions, the decreased OH⁻ concentration and the competitive adsorption of substrate/partial oxidation product on the catalyst surface.

3. Direct Alcohol Fuel Cell: Active Systems

MEAs for active monoplanar DAFCs have been realized by Bianchini and coworkers with the same electrocatalysts and anion-exchange membrane used for the passive systems described above. Figures 29-31 show the polarization and power density curves of DAFCs containing a Pd/MWCNT anode (1 mg cm⁻² Pd), a Fe-Co Hypermec™ K-14 cathode and a Tokuyama A-006 membrane.²⁹ The fuel (2 M KOH solutions containing 10 wt% methanol, 10 wt% ethanol or 5 wt% glycerol) was delivered to the anode at 4 mL min⁻¹, while the oxygen flow was regulated at 200 mL min⁻¹. Each cell temperature was regulated at 25, 40, 60 or 80°C.

In the temperature interval from 25 to 40°C, the performance trend exhibited by the three DAFCs is analogous to that found for the passive cells, with the DEFC being superior to both the DMFC and the DGFC. Unexpectedly, however, increasing the cell temperature to 60°C leads to a reverse order of activity with the highest power density delivered by the DMFC (peak power density of 95 mW cm⁻² at 80°C) and the lowest peak power density supplied by the DEFC (73 mW cm⁻² at 80°C). In particular, the latter cell is clearly featured by a sudden drop of voltage after 300 mA cm⁻², which is consistent with a strong contribution of the concentration polarization to the overall cell polarization. Below 300 mA cm⁻² at 80°C, the DEFC is competitive with the other cells.

Bianchini and coworkers have suggested that the MWCNT support, rich of surface carboxylic acid groups,⁵² may be responsible for the observed activity trend of the cells with the Pd/MWCNT anode through a specific control of substrate dif-

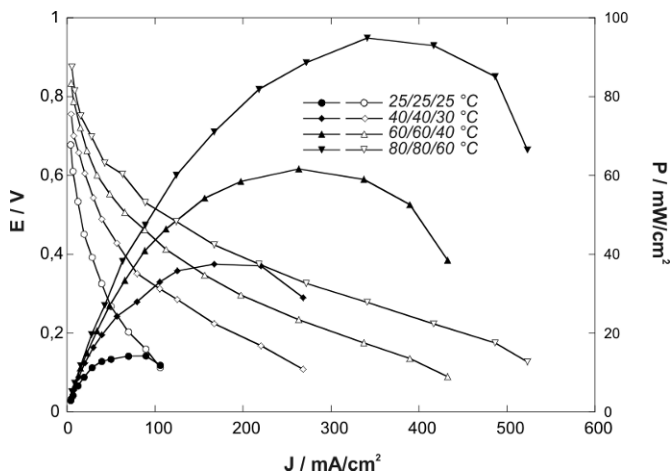


Figure 29. Polarization and power density curves at different temperatures of an active DMFC with a Pd/MWCNT anode (Pd loading 1 mg cm^{-2}), fuelled with an aqueous 2 M KOH solution of methanol (10 wt%). The inset reports the temperatures of fuel (left), cell (central), oxygen gas (right). Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.

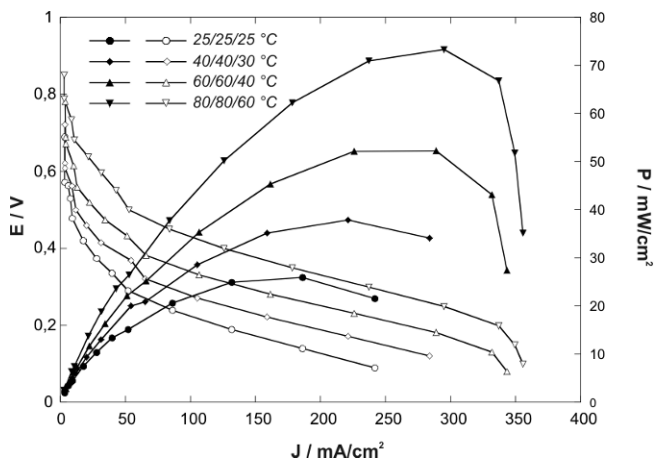


Figure 30. Polarization and power density curves at different temperatures of an active DEFC with a Pd/MWCNT anode (Pd loading 1 mg cm^{-2}), fuelled with an aqueous 2 M KOH solution of ethanol (10 wt%). The inset reports the temperatures of fuel (left), cell (central), oxygen gas (right). Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.

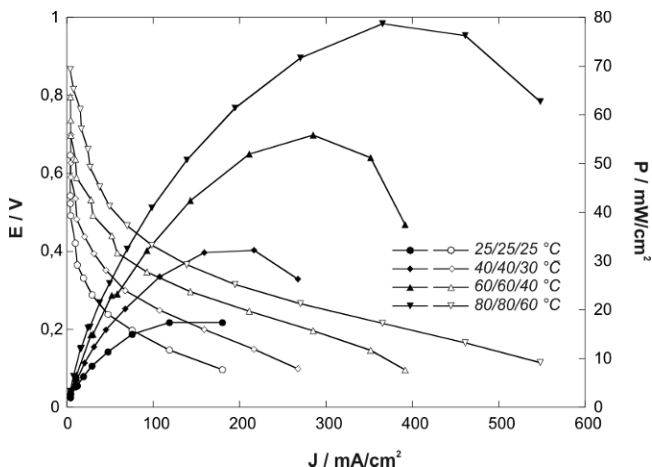


Figure 31. Polarization and power density curves at different temperatures of an active DGFC with a Pd/MWCNT anode (Pd loading 1 mg cm^{-2}), fuelled with an aqueous 2 M KOH solution of glycerol (5 wt%). The inset reports the temperatures of fuel (left), cell (central), oxygen gas (right). Reprinted from Ref. 29, Copyright (2009) with permission from Elsevier.

fusion/product desorption. Indeed, as already mentioned, among the partial oxidation products of glycerol there are hydroxy acids and bi-acids that can interact with the surface carboxylic acid groups on the MWCNT surface.

Indirect support to the role of the carbon support on the DAFC performance has been provided by following studies in the same laboratory showing that ethanol is a better fuel than methanol or glycerol at any temperature from 20 to 80°C in identical cells except for containing anodes coated with either Pd-(Ni-Zn) or Pd-(Ni-Zn-P) supported on Vulcan XC-72.^{36,43}

The polarization and power density curves of the DAFCs with Pd-(Ni-Zn)/C anodes are shown in Fig. 32. Only slightly inferior results have been obtained for DAFCs containing Pd-(Ni-Zn-P)/C anodes.⁴³

All peak power densities provided by these DAFCs, but especially those fed with ethanol, are extraordinarily high, up to 170 mW cm^{-2} at 80°C and 125 mW cm^{-2} at 60°C at 0.3 V (Fig. 32a). Galvanostatic experiments at 60°C lasting 20 h showed a

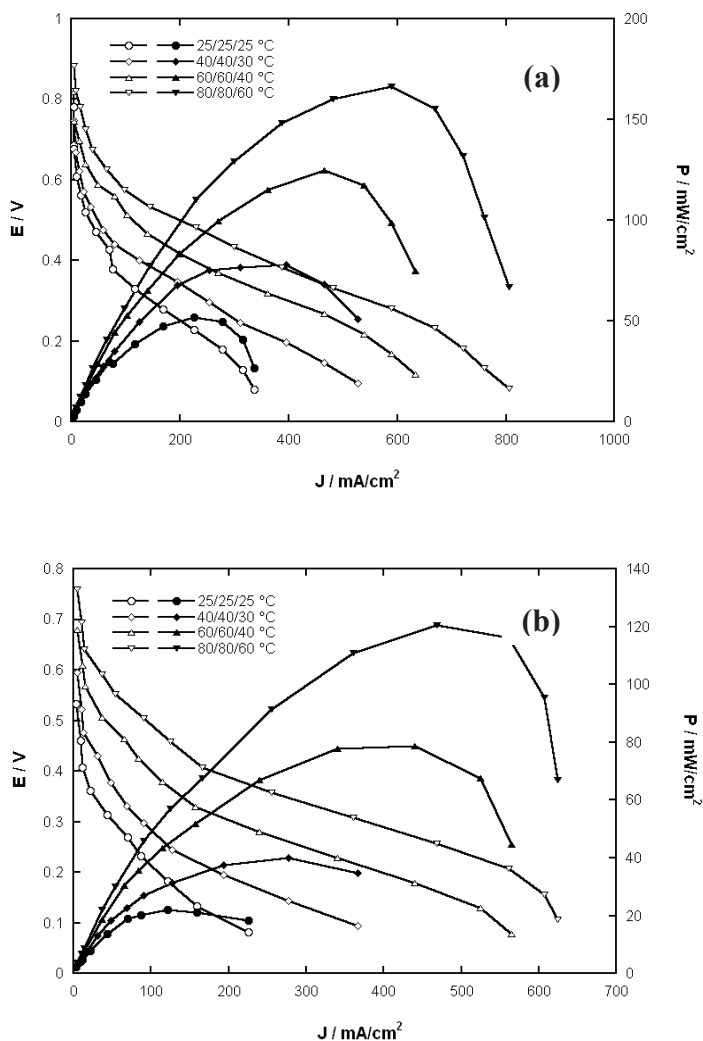


Figure 32. Polarization and power density curves at different temperatures of active DAFCs with Pd-(Ni-Zn)/C anodes fuelled with aqueous 2 M KOH solutions of ethanol (10 wt%) (a), methanol (10 wt%) (b) and glycerol (5 wt%) (c); Pd loading 1 mg cm⁻². The inset reports the temperatures of fuel (left), cell (central), oxygen gas (right).⁴³

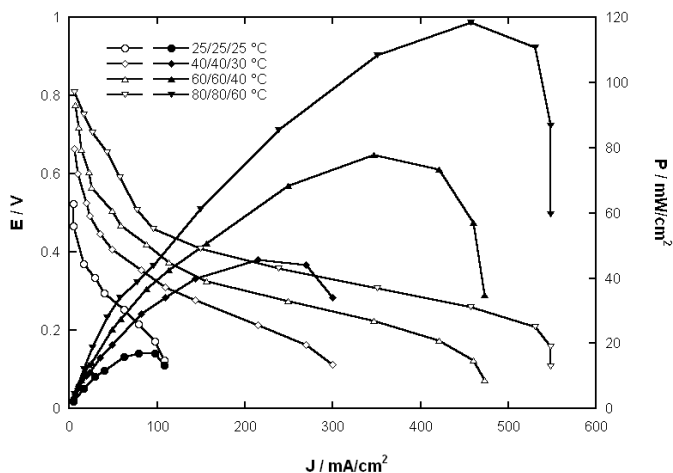


Figure 32. Continuation.

modest 3% decay of the cell performance. The power density values, combined with the good electrochemical stability of the MEAs, give a mark of excellence to the active DEFCs with the Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C anodes. In particular, Pd-(Ni-Zn)/C is more active than Pd-(Ni-Zn-P)/C, Pd/C and Pd/MWCNT and, as such, exhibits unrivalled activity as anode electrocatalyst for alcohol oxidation in alkaline media. Of course, the high quality of both the cathode catalyst and the membrane is not extraneous to the overall cell performance.

Some examples of active DAFCs with anion-exchange membranes and Pt-based anode electrocatalysts have been described in the literature. Ogumi et al. have reported on active DAFCs fed with 1 M KOH solutions of various alcohols and polyalcohols, including methanol and glycerol, but not ethanol.¹³

The anode and cathode catalyst were Pt-Ru/C (4 mg cm⁻²) and Pt/C (1 mg cm⁻²) (C = Vulcan XC-72) from E-TEK (USA), respectively, and the solid electrolyte was a Tokuyama AHA membrane. At 45°C, the peak power densities with methanol and glycerol were 8 mW cm⁻² at 28 mA cm⁻² and 6 mW cm⁻² at 27 mA cm⁻², respectively. Scott et al. have investigated the performance of an active DMFC using a Morgane[®]-ADP membrane from Solvay

using Pt-Ru/C (1 mg cm^{-2}) as anode catalyst and Pt/C as cathode catalyst (both from E-TEK).¹⁴ At 60°C using an oxygen flow, the highest power density was ca. 11 mW cm^{-2} at ca. 40 mA cm^{-2} . An active alkaline DEFC has been described by Hou et al. where the anode and cathode were catalyzed by commercial (Johnson-Matthey) Pt-Ru/C (2 mg cm^{-2}) and Pt/C (1 mg cm^{-2}) catalysts, respectively and the solid electrolyte was a polybenzylimidazole membrane doped with KOH, which is not a real anion-exchange membrane, however.¹⁵ At 75°C , a peak power density of 49 mW cm^{-2} was obtained that increased to 61 mW cm^{-2} by increasing the cell temperature to 90°C .

Finally, it is worth noticing that no known anode catalyst based on platinum, even at high metal loading, has demonstrated the capacity to produce acceptable power densities in an active DEFC in acidic environment, generally containing a Nafion[®] proton-exchange membrane. The best performances so far reported have been obtained in active cells at temperatures above 90°C with binary Pt-Sn and Pt-Ru anode catalysts in conjunction with platinum based cathodes and Nafion[®] proton-exchange membranes.³⁻⁶ However, the power densities never exceed $60\text{--}70 \text{ mW/cm}^2$ and the overall efficiency suffers the consequences of the partial oxidation of ethanol to mixtures of acetaldehyde, acetic acid and CO_2 , while severe overpotentials are originated by catalyst poisoning by CO.

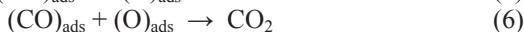
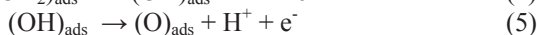
IV. MECHANISTIC STUDIES OF ALCOHOL OXIDATION ON Pd-ELECTRODES IN ALKALINE MEDIA

Innumerable mechanistic studies of alcohol oxidation on Pt-based electrocatalysts in acidic media have been published over the last few years. Methanol,⁵³⁻⁵⁶ ethanol^{5,57-60} and ethylene glycol⁶¹⁻⁶⁴ have been the most studied substrates and their oxidation paths on Pt or Pt alloys have been substantiated using a variety of *in situ*, *extra situ* and *operando* techniques as well as quantum mechanical calculations. The experimental techniques include reflection IR spectroscopy (IR),⁶⁴ surface enhanced IR absorption spectroscopy (SEIRAS),^{54,61} attenuated total reflection-IR absorption spectroscopy (ATR-IRAS),⁵⁵ differential electrochemical mass spectroscopy (DEMS),⁵⁷ single potential alteration IR spectroscopy

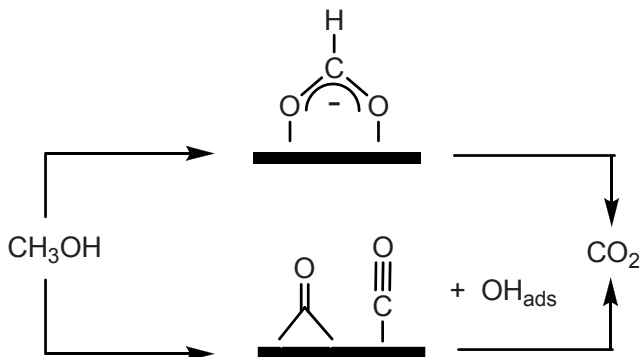
(SPAIRS),^{5,58,59} subtractively normalize interfacial Fourier transform IR spectroscopy (SNIFTIRS),^{5,58,59} high pressure liquid chromatography (HPLC),⁶⁰ ionic chromatography (IC),⁶² gas chromatography-mass spectroscopy (GC-MS),⁶³ ¹³C NMR spectroscopy.^{63,29}

It is generally agreed that all alcohols are oxidized in acidic media following two distinct reaction paths: the poisoning path, involving CO_{ads} intermediate, and the non-poisoning path where C-C bond breaking does not occur. Even for methanol with a single carbon atom, these two paths are possible (Scheme 2).^{53,54}

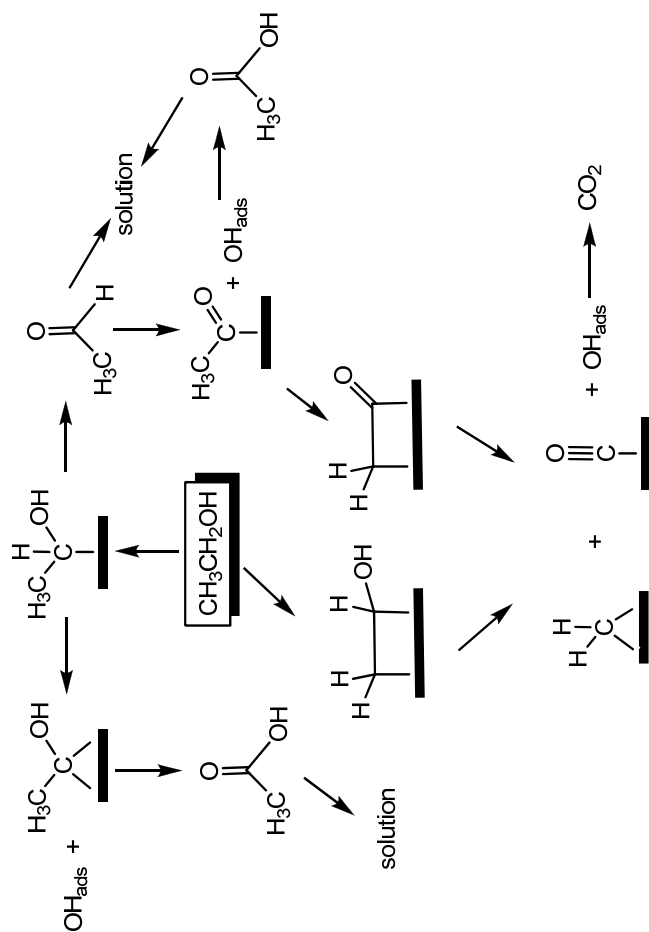
Prior to CO_{ads} formation, the following adsorbates have been spectroscopically detected along the oxidation of methanol in acidic media: CH_xOH_{ads}, -COH_{ads}, -HCO_{ads}, -COOH_{ads} and (HCOOH)_{2ads}.^{65,66,67} Water is required for the conversion of methanol to CO₂ (Eqs. 4-6).^{53,55}



A general scheme for ethanol oxidation on Pt-based catalysts in acidic media is shown in Scheme 3.^{5,59} The presence of two carbon atoms complicates remarkably the reaction mechanism that still involves a non-poisoning path (acetaldehyde and acetic acid formation) and a poisoning path (CO₂ formation). In either path, the activation of water again is mandatory for accomplishing the oxidation of ethanol.



Scheme 2. Reaction paths of methanol oxidation on Pt-based electrocatalysts.



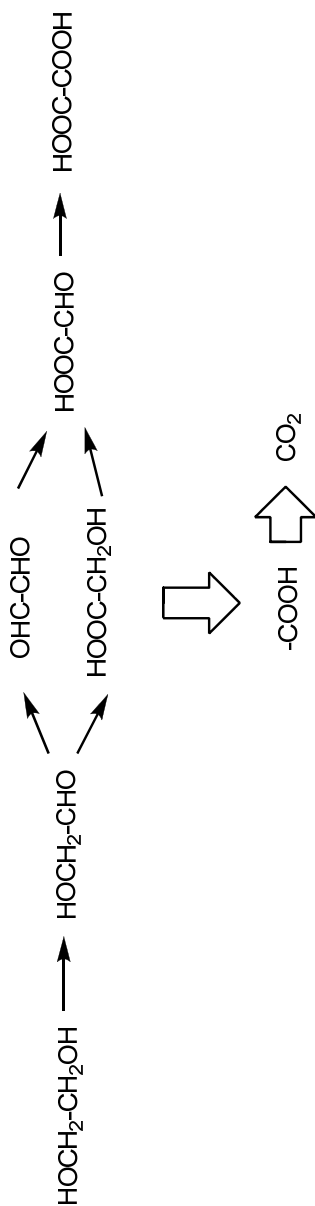
Scheme 3. General scheme for ethanol oxidation on Pt-based catalysts in acidic media.

To the best of our knowledge, no Pt-based catalyst is able to promote the selective oxidation of ethanol to either CO₂, acetic acid or acetaldehyde. However, the product composition can be modified by alloying Pt with other metals. For example, the addition of Sn to Pt increases the catalytic activity and also the production of acetic acid, while the addition of Ru improves the electrical performance without changing the product selectivity.^{5,60} Several authors have demonstrated that Ru and Sn are able to activate water at lower potential than pure Pt, thus boosting the formation of CO₂ and acetic acid, while Sn is particularly suited to reduce C-C bond breaking through a sort of “dilution” of adjacent Pt atoms.⁵

The oxidation of ethylene glycol on Pt-based catalysts is more complex than that of ethanol in accord with the presence of two hydroxyl groups (Scheme 4).

The large numbers of possible intermediates along both non-poisoning and poisoning paths has actually limited the use of in situ spectroscopic techniques and most of the mechanistic interpretations for ethylene glycol oxidation rely on product analysis by IC,⁶² DEMS,⁶¹ GCMS and ¹³C NMR methods.⁶³ A few IR studies are also available, showing CO_{ads} and CO_{2ads} species as well as several bands due to carboxylic acids such as glycolic, glyoxylic and oxalic acid, often difficult to distinguish from each other.^{62,64} According to some authors oxalate is not a primary product of ethylene glycol oxidation on Pt electrodes but it comes from further adsorption and oxidation of glycolates.^{17,61} This point, however, has not really clarified and further studies are needed to establish whether polyols are oxidized to polycarboxylic acids by either cascade or parallel reactions.

Unlike the relative abundance of mechanistic studies in acidic media, very few works dealing with alcohol electrooxidation on Pt-based systems in alkaline media have been published in the relevant literature,^{12,13,17,69} while studies involving Pd-based catalysts are virtually absent unless one considers some papers reporting the product analysis of alcohol oxidation^{16,29,36} or CO adsorption/oxidation on Pt/Pd electrodes.⁴² A theoretical rationalization of the excellent activity of Pd-based catalysts for ethanol oxidation in alkaline media but not in acidic media has been

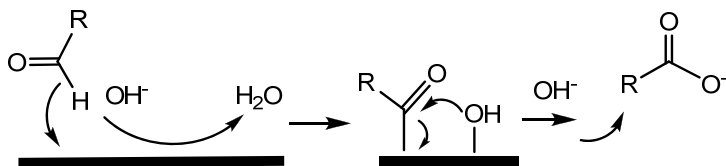


Scheme 4. General scheme for ethylene glycol oxidation on Pt-based catalysts in acidic media.

recently provided by P. K. Shen and Kowal.⁷⁰ DFT calculations show that, in acidic media, the hydrogen dissociated from H_3O^+ preferentially adsorbs on the Pd clusters, thus inhibiting the adsorption of ethanol, whereas, in alkaline media, ethanol can adsorb on Pd, leading to catalytic electrooxidation.

Increasing the pH from acidic to alkaline does not seem to affect the mechanism of methanol,^{13,68} ethanol¹² and ethylene glycol oxidation¹⁷ on Pt-based electrocatalysts, at least as far as the product selectivity is concerned. In contrast, Pd-based catalysts are much more selective in alkaline media by virtue of their aptitude to follow non-poisoning paths. As shown in previous Sections of this Chapter, ethanol is selectively converted to acetate on Pd-based catalysts on condition that they do not contain Pt, while glycerol or ethylene glycol are prevalently converted to carboxylates.^{16,20,29,36,45} The capacity of Pd to depress C-C bond cleavage, which results in lower overpotential and longer catalyst lifetime, has been clearly demonstrated by Coutanceau and coworkers by investigating the ethylene glycol oxidation on Pt-Pd, Pt-Pd-Bi and Pt-Bi catalysts in alkaline media.¹⁷

Finally, it is worth commenting the fact that the combination of Pd nanoparticles with either metal oxides (NiO , CeO_2 , Co_3O_4 , Mn_3O_4)²⁰⁻²² or nickel-zinc alloys³⁶ increases both the activity and stability of the corresponding electrocatalysts for alcohol oxidation in alkaline media. The beneficial effect of the added metal oxide or non-noble metal phase has been compared to that of Ru in Pt-Ru/C catalysts known as the *bifunctional mechanism*.⁵⁵ Within this context, metal oxides and non-noble metals would increase the concentration of OH_{ads} species on the catalyst surface, favoring the transformation of the aldehyde to the corresponding carboxylic acid via $\text{acyl}_{\text{ads}}\text{-OH}_{\text{ads}}$ coupling (Scheme 5).



Scheme 5. Selective conversion of aldehydes into carboxylates on Pd-based electrocatalysts in alkaline media.

V. CONCLUSIONS

If DAFCs fuelled with ethanol and higher alcohols have a commercial future, this seems to be indissolubly linked to Pd-based electrocatalysts and anion-exchange membranes. As shown in this Chapter, the known catalytic architectures for alcohol oxidation are extremely valid, yet they suffer the scarce ability to cleave C-C bond in a selective way as well as poisoning by CO_{ads}. Therefore increasing research efforts are required to design new catalysts with better performance and higher electrochemical stability.

Pd-based catalysts are particularly suitable for the oxidation of ethanol. Its partial oxidation to acetate might represent an obstacle to the use of Pd catalysts to fabricate stacks of DEFCs capable of delivering kilowatts. However, the good response observed at room temperature in passive single cells presages an effective application in the field of power generators for portable electronics and first aid devices. On the other hand, the selective oxidation of alcohols, in particular of ethanol and glycerol, to carboxylates, isolable as alkali metal salts, opens new perspectives to the use of DAFCs as reactors capable of supplying energy with concomitant production of chemicals from renewables.^{13,45,69,71,72}

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Structure and Reactivity of Transition Metal Chalcogenides toward the Molecular Oxygen Reduction Reaction

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I. INTRODUCTION AND SCOPE

Research in low temperature fuel cell reactions has mainly focused on the study of platinum, and/or platinum based materials.¹⁻²³ These studies have also been aimed at understanding the fundamentals of the electrode/electrolyte interfacial behavior, in order to optimize the catalytic properties of such materials.^{1,3,7,17,20,24-33} The reason why most of these studies have been devoted to platinum is evident: this material is the best catalyst, especially for processes occurring at the anode and cathode of low temperature fuel cells (FC).^{3,13,18,23,26,33-40} In the abundant literature, one can find reports going from studies on single crystals^{1-3,16-17,33,41-47} to highly dispersed powders (particle size 2-4 nm)^{22,39,48-65} in which interesting features towards multi-electron charge transfer reactions have been observed, such as the surface structure sensitivity.^{1,16-17,66-76} Other factors, less evident to detect, like the synergetic effects (local e-

lectronic modification)^{25,77-84} and distribution of active sites induced by the so-called ensemble effect⁸⁵⁻⁹⁰ can also be operating during electrocatalysis. All the studies put in evidence the fact that the gap between model systems (single crystals) and the understanding of phenomena occurring on the nanorange scale (dispersed catalysts), particularly on platinum, is becoming smaller. Therefore, highly dispersed systems can also be considered as models to understand processes in real working conditions in low temperature FC. In these systems (anode and cathode made of platinum) based on hydrogen (as a fuel) and oxygen (as the oxidant), the limiting factor is the slow kinetics of the reduction of the molecular oxygen at the cathode. This latter is two orders of magnitude slower than the hydrogen oxidation process. If the fuel is a liquid such as methanol (in a direct methanol fuel cell—DMFC), the slow kinetics of its oxidation at the anode is added to the electrical loss rendering it less efficient. Besides that, depolarization of the cathode occurs due to the permeability of the solid polymer electrolyte, reducing still more the electrical output of the system, further the Pt cathode suffers from oxidation, ion migration, loss of active surface area, and corrosion of the carbon support. Therefore, it is not only necessary to develop the anode to increase its reactivity towards methanol oxidation, but one also requires to develop cathodes with high selectivity or tolerant to the presence of methanol.

Tailoring novel materials, in fact, offers the opportunity of arranging individual transition metals to form cluster-like electrocatalysts. Therefore, the scope of the present chapter will be to trace the development and progress of novel materials based on chalcogenide using transition metal centers with the aim of understanding the complex interplay between materials synthesis, characterization and application as cathode materials for low temperature fuel cell.

II. TRANSITION METAL CHALCOGENIDES FOR ELECTROCATALYSIS

1. Metal Abundance, Economic Impact and Environmental Issues

The relationship between metal prices and relative abundance of the chemical elements in the Earth's upper continental crust is shown in Fig. 1. One can observe that Pt, being one of the rarest metals is the most expensive one. Its finite deposits are concentrated in just a few countries. Along the high and volatile price of this metal could be a potential showstopper for fuel cells in any truly mass market application such as transportation.⁹¹ Hence, in order to develop and commercialize fuel cells, it is necessary and challenging to partially reduce or completely replace Pt as the cathode electrocatalyst using non-precious metals such as cobalt, iron, molybdenum, tungsten, etc.

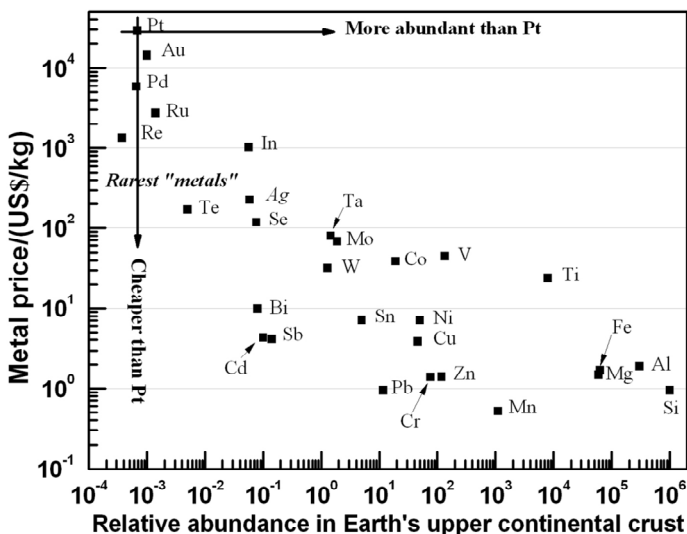


Figure 1. The price of some metal elements in relation to their abundance on the earth crust. Adapted from reference.⁹² Reproduced from Y. Feng, and N. Alonso-Vante. *Phys. Stat. Sol. (b)* **245** (2007) 1792, Copyright (2007) with permission from Wiley-VCH Verlag GmbH & Co KGaA.

2. Why Chalcogenides?

Partial or complete replacement of platinum for ORR has attracted a lot of interest in order to enhance electrocatalytic activity and reduce materials costs.⁹³⁻⁹⁶ Therefore, some non-platinum promising electrocatalysts for ORR have been developed, i.e., using carbides,⁹⁷⁻¹⁰² nitrides,¹⁰³⁻¹⁰⁶ macrocycle materials,^{12,104,107-114} and other precious metals, such as Pd¹¹⁵⁻¹¹⁹ or Ru-based materials,¹²⁰⁻¹³⁰ as well as non-precious metal chalcogenides.^{92,131-133}

Transition metal chalcogenides represent a family of chemical compounds with a large variety of physical, as well as chemical properties aiming at sustaining an electrocatalytic process in a selective way. In this sense, a survey of publications regarding the three kinds of material families, i.e., chalcogenide-, macrocycle- and platinum-based materials was made using the SciFinder data base (July 13, 2009). [Figure 2](#) shows the evolution of publications related to these materials with regard to the oxygen reduction reaction. One observes that, in spite of its low abundance and high price, platinum based materials constitute the hot topic in the laboratories of the world devoted to electrocatalysis, since the number of publications raised by a factor of 4.5 when comparing the two last decades. Publications on other type of materials are still rising. In this respect, the chalcogenides increased by a factor of ca. 2 in the last two decades.

This is an important and significant evolution considering that in the decade of the 80's the number of publications was rather insignificant. It is worth to recall that in the decade of the 80's the work performed on cluster chalcogenides of the Chevrel phase family can be considered as pioneering in the use of such materials as ORR electrocatalysts.¹³⁴ A detailed account of such type of materials was given in 2003 by the author.¹³⁵ [Figure 2](#) clearly shows that chalcogenides as well as macrocycle compounds are promising catalysts for the replacement of platinum in the future. Results obtained by Bashyam et al.¹³⁶ and Lefevre et al.¹³⁷ point out the feasibility of this strategy.

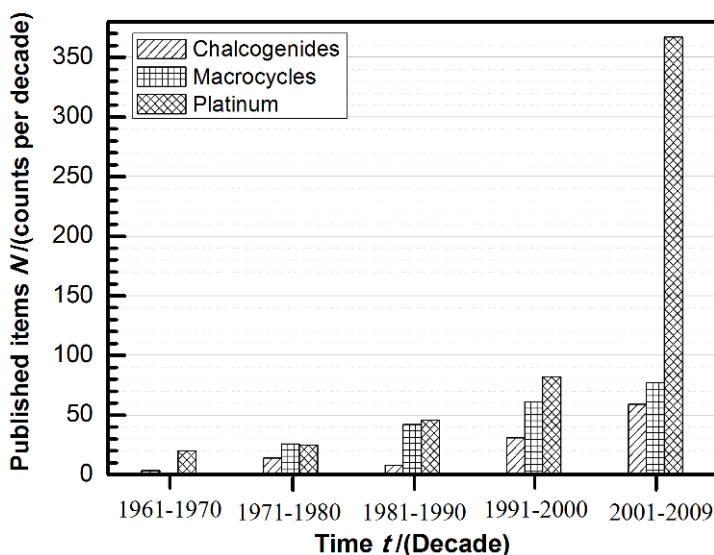


Figure 2. Number of publications devoted to the oxygen reduction reaction on chalcogenides, macrocycles and platinum materials between 1961 and July 13, 2009 based on SciFinder database using *oxygen reduction* as the keyword. Reproduced from Y. Feng, and N. Alonso-Vante *Phys. Stat. Sol. (b)* **245** (2007) 1792, Copyright (2007) with permission from Wiley-VCH Verlag GmbH & Co, KGaA.

3. Chemistry: Formation of High Nuclearity Complexes

The generation of metal nanoparticles is based on the use of M-CO complexes. This approach has been successfully used in generating ruthenium cluster-like, as well as platinum cluster-like compounds. The chemistry seems simple, since it is like a pyrolysis process made in a solvent in mild conditions. This latter can be aqueous or a partially aqueous one. The reaction can be summarized as follows:

- for ruthenium centers:



where, X = S, Se, Te,

- for platinum centers:



where, M = Sn, Ni, Cr, Co, Ru..., and X = Cl[−].

The high nuclearity complex is, actually, found in the intermediate species “[M-X-CO]” formed during the reaction process. This latter is considered as the materials chemistry engineering to tailor novel nanomaterials. Several examples found in the literature are briefly discussed below, as well as the data generated in our group.

4. The Design of Molecular Complexes

One of the strategies to design nanodivided electrocatalyst is the use of chemical precursors, which can react under mild conditions.^{13,39,138} This kind of chemical route led to the generation of transition-metal complexes. The base structure of such complexes can be the basis to obtain the so-called metallic cluster-like materials. In this way, for example, chemical precursors were furnished by the complex developed by Adams et al.¹³⁹ Indeed, these authors reported that Pt₂Ru₄(CO)₁₈ (see Fig. 3) was obtained by reacting Ru(CO)₅ and Pt(cyclo-octadiene)₂. The evolution of Pt₂Ru₄(CO)₁₈ and the carbide: PtRu₅C(CO)₁₆ to generate a bimetallic catalyst (Pt–Ru) supported onto carbon substrate was later published by Nuzzo et al.¹⁴⁰⁻¹⁴¹

One can imagine that the Pt₂Ru₄(CO)₁₈ cluster compound is the intermediate in the reaction (2). The reaction can be further made via chemical decomposition of the compound to generate the bimetallic nanocatalyst. Indeed, Nuzzo et al. demonstrated that mixed Pt–Ru nanoparticles, with an extremely narrow size distribution (particle size 1.4 nm), were obtained. The Pt–Pt, Pt–Ru, and Ru–Ru coordination distances in the precursor (2.66, 2.64, and 2.84 Å)¹³⁹ changed to 2.73, 2.70, and 2.66 Å, respectively, on the mixed-metal nanoparticles supported onto carbon black, with an enhanced crystalline disorder, as revealed by X-ray absorption fine structure (XAFS) spectroscopy. However, this example, using a controlled pyrolysis onto a designed molecular cluster, succeeds

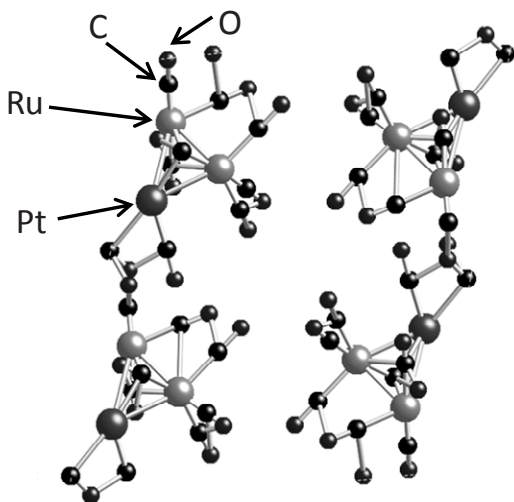


Figure 3. $\text{Pt}_2\text{Ru}_4(\text{CO})_{18}$ cluster compound unit cell. Figure generated from XRD data of Ref. 139.

the process developed in our group using the non-aqueous solvents route.

5. Genesis of a Catalyst: Ru_xSe_y

In order to understand the growth of metal clusters in solution, one should start from a metal complex precursor, such as $[\text{M}_y(\text{CO})_x]$, according to Eq. (1). The precursor can be generated in situ. The protocol synthesis of such a chemical precursor is represented by the flow-chart; see Fig. 4 for the case of ruthenium-selenide. This flow chart summarizes the synthesis initially reported in 1991,¹⁴² and it will be taken as the template for similar compounds. A careful follow-up of the reaction was made by means of the C^{13}NMR .¹⁴³ Indeed, following the synthesis without carbon, i.e., after step 3, a heteronuclear chemical precursor was identified: $\text{Ru}_4\text{Se}_2(\text{CO})_3(\text{CO})_8$.¹²⁹ The ongoing reaction under the boiling point of the solvent for 20 hours led to a complete pyrolysis of the heteronuclear molecular cluster compound to nanopowders of

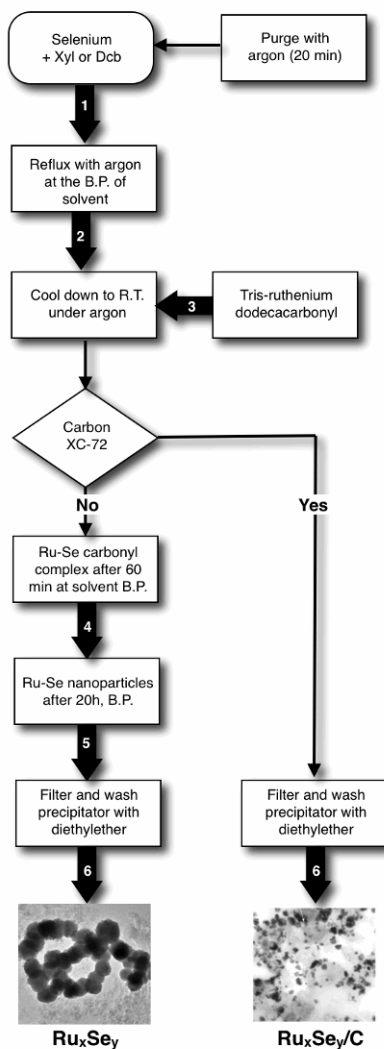


Figure 4. Flow-chart indicating the various steps of the ruthenium-selenide Ru_xSe_y cluster-like material synthesis either non-supported or carbon supported. Bottom: TEM pictures of the corresponding end-products.

Ru_xSe_y . Supporting on carbon was also easily done by adding the carbon Vulcan type readily after step 3. Such synthesis, either in xylene or 1,2-dichlorobenzene solvents produced nanomaterials as revealed by transmission electron microscopy (TEM) and wide angle X ray spectroscopy (WAXS) studies (cf. Figs. 4, 6 and 7). In order to take into account the dynamics of the heteronuclear carbonyl cluster compound (Fig. 5) to obtain the final catalyst material during the annealing process, this cluster was selectively synthesized in 1,2-dichlorobenzene after only 60 min of reaction of selenium with tris-ruthenium dodecacarbonyl.¹²⁹ In Fig. 6 the structural XRD pattern of the molecular cluster compound is depicted, according to the ICSD data collection—see the structure factors as vertical bars. A systematic in situ study by WAXS in a special beryllium-cell attached to a goniometer was carefully conducted,¹⁴⁴ so that structural changes as a function of the temperature could be studied. This was done by fixing two Bragg windows as indicated by the boxes in Fig. 6. The controlled pyrolysis of the molecular complex shows that the intensity of the diffraction peak (112), placed at $8.6^\circ/\theta$ ($0.2 \text{ \AA}^{-1}$), breaks down at ca. 220°C , with a concomitant increase of the peak at $21.4^\circ/\theta$ ($0.47 \text{ \AA}^{-1}$).

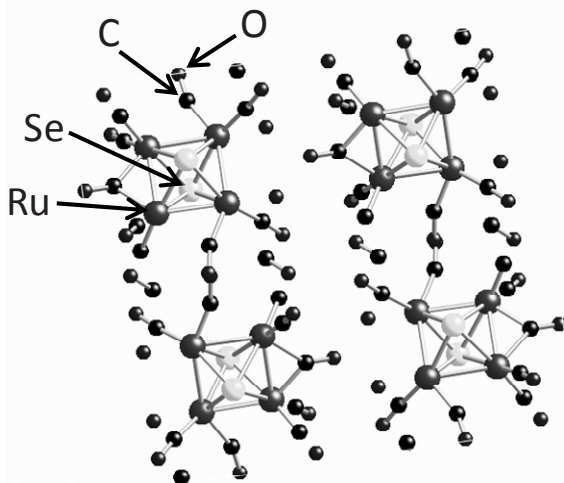


Figure 5. $\text{Ru}_4\text{Se}_2(\text{CO})_3(\text{CO})_8$ molecular cluster compound unit cell.

This later position corresponds to the ruthenium maximum diffraction peak as shown by the XRD pattern in Fig. 7. We observed that, on the one hand, an interesting fact is that this pyrolysis in gas phase resembles the XRD results published years before for Ru_xSe_y nanopowders synthesized after 20 h in a non-aqueous solvent, i.e., xylene or 1,2-dichlorobenzene.¹⁴⁵

On the other hand, the agglomeration of particles is not favored, thus leading to an average size of 1.9 nm, as indicated in the inset of Fig. 7. Finally, the pattern shown in Fig. 7 looks like the pattern of pure nanodivided ruthenium particles.¹⁴⁶ Thus, the question was: what is the fate of selenium? A pertinent answer is: the scattering power of Se is about 60% that of Ru. A total of 30% of the total intensity should be related to selenium. Hence, the total diffracted intensity after pyrolysis is quantitatively ascribed to a single phase of *hcp*-type nanoparticles. This is the reason why selenium should be coordinated with ruthenium surface atoms (Se-Ru). The existence of this bond was proven by means of EXAFS.¹³⁸

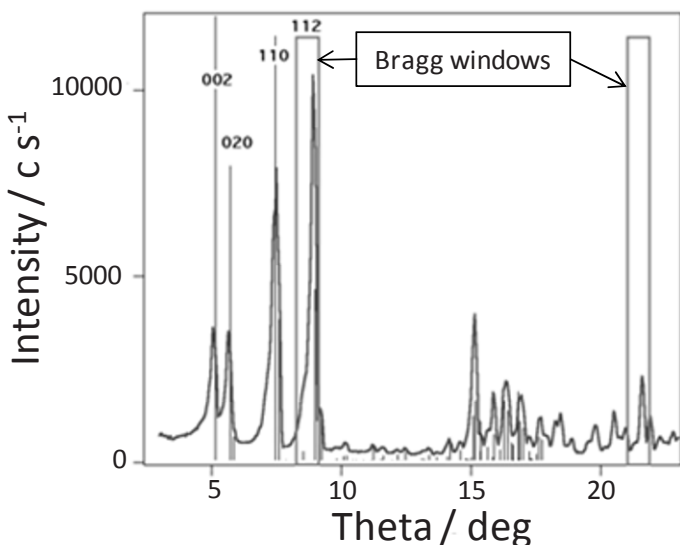


Figure 6. XRD pattern of $\text{Ru}_4\text{Se}_2(\text{CO})_3(\text{CO})_8$ together with the structural factors of the carbonyl complex. Adapted with permission from Ref. 144, Copyright (2007) American Chemical Society.

Since pyrolysis only favors the elimination of the CO ligands, the main core must be constituted by Ru_4Se_2 or Ru_2Se . This simple deduction ascribes the nanodivided materials of 1.7 nm in the *hcp*-symmetry as constituted of 153 atoms; of which 96 atoms of ruthenium and selenium are present at surface. Since selenium must be coordinated at the nanoparticles' surface, there are 42 ruthenium (or 44%) atoms available for the oxygen reduction reaction. Indeed, simple cyclic voltammetry experiments in nitrogen-saturated electrolyte to estimate the physical-chemical capacitance performed on reduced ruthenium Ru_x and Ru_xSe_y nanoparticles verified that the capacitance of the latter is 47% that of the former.¹⁴³

It is worth to discuss the passage from the state represented by the Fig. 6 to the state represented by the Fig. 7. Since no direct evidence exists as to intermediate species detection, one can imagine that during the process of pyrolysis in the temperature interval between 200°C and 220°C a structural change takes place that generates the driving force necessary to agglomerate the ruthenium atoms forming a metallic core.

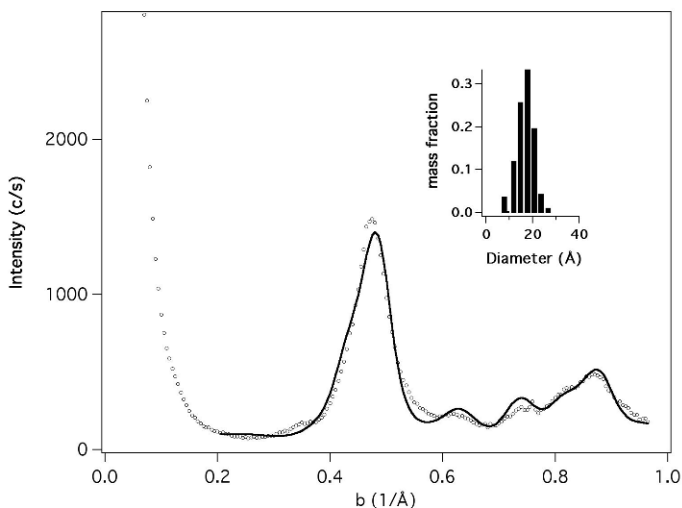


Figure 7. Diffraction pattern of a Ru_xSe_y sample after pyrolysis at 220 °C of $\text{Ru}_4\text{Se}_2(\text{CO})_{11}$. The full line is the Debye function analysis simulation. Adapted with permission from Ref. 144, Copyright (2007) American Chemical Society.

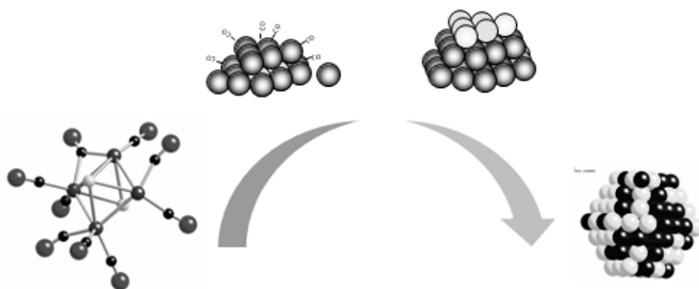


Figure 8. Schematics of the pyrolysis process leading to the formation of the ruthenium-selenide cluster-like compound. The *hcp*-symmetry of the 153 atoms cluster-like particle (see right) fits the experimental points in Figure 7 (continuous line).

This has the consequence of placing the selenium atoms at the surface in a decorated-like form, as schematized in Fig. 8.

The size of the particle is very certainly determined by the energetic equilibrium between Ru-Se. This is probably the reason why such nanomaterials are very stable against coalescence even at a temperature higher than 300°C (cf. Fig. 17).¹⁴⁵

6. New Trends in Materials Research

The investigations with respect to the synthesis reported above gave clear evidence that the Ru_xSe_y cluster-like material is basically constituted by a ruthenium core, which surface atoms are coordinated with selenium atoms, cf. Figs. 7 and 8. Coordinating selenium atoms onto nanodivided ruthenium can be attained using alternative chemical routes using chemical precursors in organic or water as solvents. In this sense, eliminating the box related to the heteronuclear molecular cluster (Fig. 4) represents actually a reaction template for chalcogenides supported on carbon using an aqueous solvent as depicted in Fig. 9. Here it is clear that a metallic salt (e.g., RuCl_3) can be used to generate Ru/C^{147} or the salt added at the same time with SeO_2 reduced by NaBH_4 to obtain $\text{Ru}_x\text{Se}_y/\text{C}$.¹⁴⁸ As an alternative to this, ruthenium black can be employed since it can be further selenized in xylene¹⁴⁹ or in water.¹⁴⁷ With the aim at reducing the precious metal content, cf. Fig. 1, effort has been devoted to dilute, e.g., the ruthenium in the Ru_xSe_y

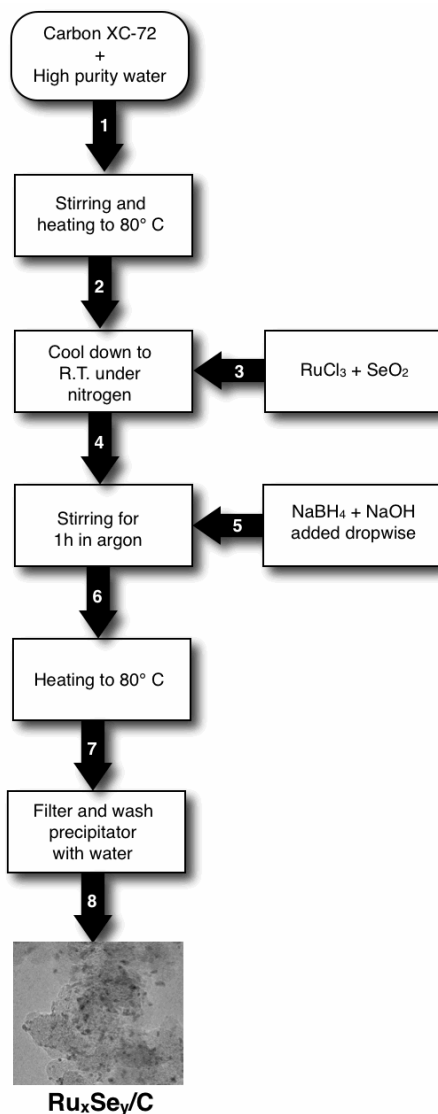


Figure 9. The use of the template in Fig. 4 led to another chemical route of ruthenium-selenide synthesis using water as a solvent. Bottom: TEM picture of the corresponding product.

material. This was done in such a way as to introduce Fe or Co to obtain $\text{Ru}_x\text{Fe}_y\text{Se}_z$ and $\text{Ru}_x\text{Co}_y\text{Se}_z$. It appears that Ru could be replaced by 50 at.% of Fe.^{13,150} However, such a structure can be stable if Fe constitutes the core of the electrocatalyst, forming a core-shell structure. Although no major changes toward the oxygen reduction reaction were observed, the desired structure is not yet confirmed, since via XPS a partial removal of iron was detected.

Other non-precious metal chalcogenides centers containing cobalt have been also synthesized following the template depicted in Fig. 9.¹⁵¹ In this work, the in situ free-surfactant method for carbon supported Co_xX_y ($\text{X} = \text{S}, \text{Se}$) based on the decomposition of cobalt carbonyls was obtained. To control the growth of the metal nanoparticles and to prevent agglomeration, the use of stabilizers, e.g., donor ligands, polymers and surfactants, i.e., oleic acid (OA), trioctylphosphine oxide (TOPO), trioctyl-phosphine (TOP) and triphenylphosphine (TPP) are necessary.¹⁵²⁻¹⁵⁶

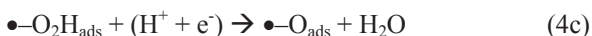
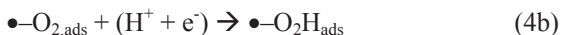
With the use of surfactants, the particle size of 1 to 3 nm is well controlled, however, they are difficult to be completely removed without causing agglomeration effects, which may affect the electrochemical properties of the material. One way to circumvent this problem was the use of carbon as support. Besides serving as a support, the carbonaceous material worked as a dispersing agent. However, the problem of controlling the particle size remains open. Up to now, the use of microwave heating allowed to obtain particles of the order of 36 nm in comparison to 52 nm obtained by conventional heating.¹⁵¹ Summing up, the template depicted in Fig. 4 served as a basis to tailor nanomaterials from molecular cluster complexes, such as the carbonyl of transition metals. This constitutes the bottom up approach for M_xX_y ($\text{M} = \text{Ru}, \text{Co}; \text{X} = \text{Se}, \text{S}, \text{Te}$) compounds synthesis. Furthermore, other chemical routes such as the solvothermal methods able to produce chalcogenide nanostructured materials containing metal centers such as: Co, Cd, Zn, and Cu under mild conditions have been reported in the literature and recently reviewed.¹⁵⁷

III. THE OXYGEN REDUCTION REACTION (ORR)

The ORR is one important reaction at the cathode of a fuel cell system, and the overall reaction is generally written as:



This multi-electron charge transfer reaction (1.23 V/SHE) depends on the electrolyte nature and the catalysts in form of a well defined surface or faceting nanoparticles, and represents a substantial cathodic overpotential loss of ca. 300 mV on the best catalyst, Pt.¹⁵⁸ This means that its four-electron ORR kinetics is slow with an exchange current density between 10^{-3} to 10^{-7} mA cm^{-2} depending on the nature of the exposed surface and electrolyte. The consequence is the generation of intermediate species of the overall reaction (3) that can be depicted by a series of reactions, namely:



where any catalytic site is represented by “ $\bullet$ ”. The proposed mechanism involves the production of hydrogen peroxide, Eq. (4c). And the key question for all tailored novel catalyst is to measure the amount of such an intermediate species. It is believed that the best catalyst for the ORR, i.e., platinum, promotes the reaction to water with a reaction yield of more than 95%. In the series of Eqs. (4) the ORR proceeds in an associative process. Since most catalytic centers developed up to now produce hydrogen peroxide, see Eq. (4c), we believe that the rate determining step is represented by the hydrogenation of O_2 , (Eq. 4b). This mechanism was proposed by Nørskov et al.¹⁵⁹ However, these authors discuss the fact that such a mechanism is mainly present on the right part of the volcano curve, see Fig 10.

Although this *simple* picture predicts activities of solely metal centers towards the ORR, thermodynamically speaking, it is clear

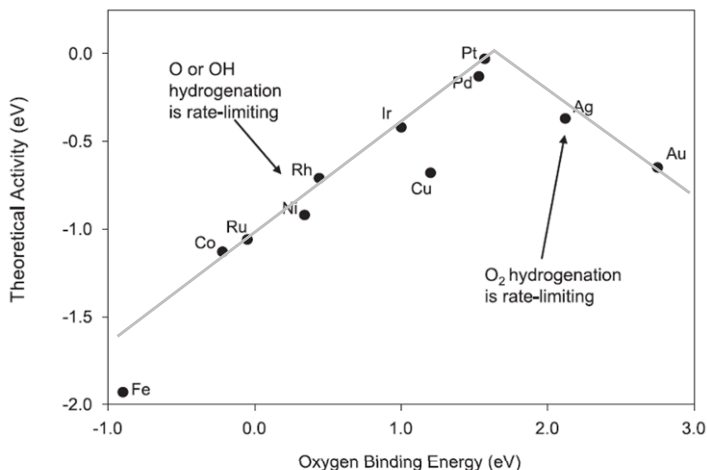


Figure 10. The ORR activity as a function of the oxygen binding energy. Adapted with permission from Ref. 159, Copyright (2004) American Chemical Society.

that no such centers are stable in acid environments. All non-precious metals (Ni, Cu, Co, Fe) corrode at potentials lower than 0.3 V/SHE. Precious ones oxidize at higher potentials (Ru, 0.68 V; Pt, 1.18 V; Ir, 1.156 V; Ag, 0.799 V; Pd, 0.915 V; Rh, 0.76 V; Au, 1.83 V/SHE).¹⁶⁰ Since one major concern is to tailor non-precious metal center catalysts, it is of paramount importance to stabilize chemically and thermally such centers against corrosion via coordinating ligands. This is actually one of the functions of chalcogen atoms (see point 3 below).

1. The ORR Activity on Selected Cases

The electrocatalytic activity of ORR on chalcogenides has been performed under hydrodynamic and temperature conditions using the rotating disk electrode (RDE) technique. We recall that dispersed catalysts either as non-supported or as supported on carbon have been prior prepared in form of inks, which are aliquoted onto a well geometrically defined substrate, such as glassy carbon¹⁶¹ and/or gold disks.^{149,162}

The electrocatalytic activity of 20 wt% CoSe₂/C nanoparticles in acid medium was recently reported.^{92,151} An open circuit voltage

(OCV) of about 0.7 V/RHE with a Tafel slope of -125 mVdec^{-1} . Figure 11 compares the ORR activity of various metal centers, namely: CoSe_2/C , Ru/C , $\text{Ru}_x\text{Se}_y/\text{C}$ and Pt/C . The figure of merit to compare these catalysts is the half-wave potential, $E_{1/2}$. This parameter of each system corresponds to 0.52 V/RHE for CoSe_2 and Ru; 0.73 V and 0.88 V/RHE for Ru_xSe_y and Pt, respectively. A closer inspection of the theoretical activity curve, Fig. 10, shows us that the trend towards high activity exists on ligand-stabilized metal centers such as cobalt- and ruthenium-selenide. This trend is not followed on cobalt and ruthenium metals, due to their affinity to oxygen to form oxide-like species. This was demonstrated with ruthenium by combining electrochemistry and X-ray Photoelectron Spectroscopy (XPS).¹⁶² The activities of CoSe_2 and Ru are similar and $j(E)$ curves are 0.36 V more negative than those for Pt. Despite the low activity towards ORR, the development of CoSe_2 material is worthwhile not only because it is cheaper than Ru-based material, but because like Ru_xSe_y it is also a methanol-tolerant catalyst.

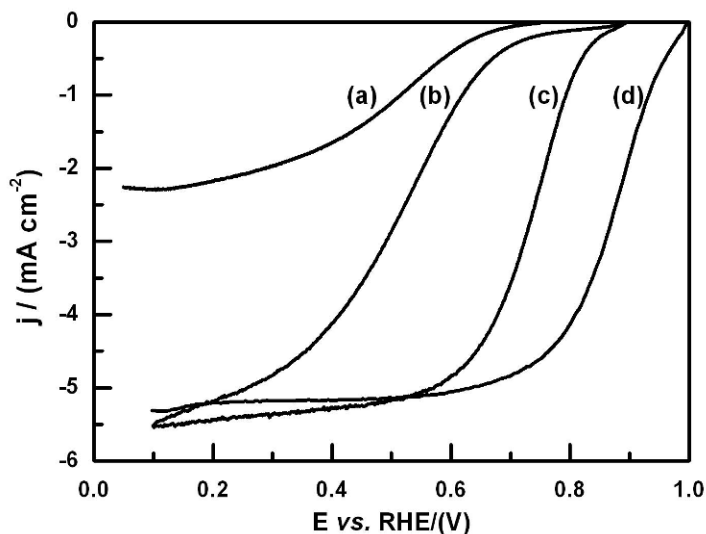


Figure 11. ORR current–potential curves obtained on RDE in O_2 saturated acid solution at 1600 rpm. (a) CoSe_2/C (50 wt %; 28 mg cm^{-2} ; $0.5\text{M H}_2\text{SO}_4$) (b) Ru/C (20 wt %; 56 mg cm^{-2} ; $0.1\text{M H}_2\text{SO}_4$) (c) $\text{Ru}_x\text{Se}_y/\text{C}$ (20 wt %; 56 mg cm^{-2} ; $0.1\text{M H}_2\text{SO}_4$) (d) Pt/C (10 wt %; 56 mg cm^{-2} ; $0.1\text{M H}_2\text{SO}_4$). Scan rate of 5mVs^{-1} .

Lee et al.¹⁶³ obtained similar results with Ir_xSe_y chalcogenides. The synthesized compound, Ir_4Se , has a high electrocatalytic activity towards the ORR and a strong methanol-tolerance. However, the ORR was not complete, since 10% of H_2O_2 were detected by RRDE experiments. This reminds us that one intermediate species easy to detect using the rotating ring-disk electrode (RRDE) is the hydrogen peroxide, see Eq. (4c). By a simple observation of the current-potential curves in Fig. 11, the limiting diffusion current for Ru/C , $\text{Ru}_x\text{Se}_y/\text{C}$ and Pt/C systems is similar. According to the Levich equation: $j_d = 0.2nFD^{2/3}\nu^{-1/6}C_{\text{O}_2}\omega^{1/2}$, the diffusion current, j_d , corresponds to $n = 4$ -electron charge transfer to produce water.

In similar conditions the diffusion plateau for CoSe_2/C attains half the value, meaning that a main reaction path is the production of hydrogen peroxide. Moreover, the theoretical activity, cf. Fig. 10, indicates that this metal center would favor the dissociation of molecular oxygen,¹⁵⁹ thus water formation. This phenomenon can be rationalized by plotting the molar fraction of the hydrogen peroxide as a function of the mass catalyst loading per unit surface, see Fig. 12. The cobalt-selenide mass catalyst variation was done from a catalyst loading of 20 wt%. For ruthenium-selenide the data were obtained for a same catalyst/carbon ratio.¹⁶⁴ If we assume that the layer thickness produced by a consequent deposition of catalyst does not play an important role, we arrive to the conclusion that the increase in the number of catalytic sites (or mass surface density) is necessary to favor the reaction: $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$. This hypothesis is confirmed by the experiment of three different catalyst/carbon ratios of CoSe_2/C , see full symbols in Fig. 12. This dynamic release, into the electrolyte of H_2O_2 with the catalytic site density has to be taken into account for practical systems.¹⁶¹

As already shown above in point 2 of Section II (Fig. 2), studies regarding the ORR electrocatalytic activity on polycrystalline chalcogenides of Co, Ni, W, Mo, V, Ti and Cr, as well as those of bimetallic chalcogenides were already reported in the seventies.¹³¹ Co-S and Co-Ni-S compounds displayed the highest activity for ORR in 2M H_2SO_4 at 70°C. The results of fuel cell tests, however, indicated that the durability of all examined materials was insufficient as a cathodic catalyst for fuel cells with acid electrolytes. Behret et al. reported in 1975¹⁶⁵ that Co_3S_4 had the highest activity among $\text{Me(a)Me}_2(\text{b})\text{X}_4$ spinels in 1 M H_2SO_4 . However, in both

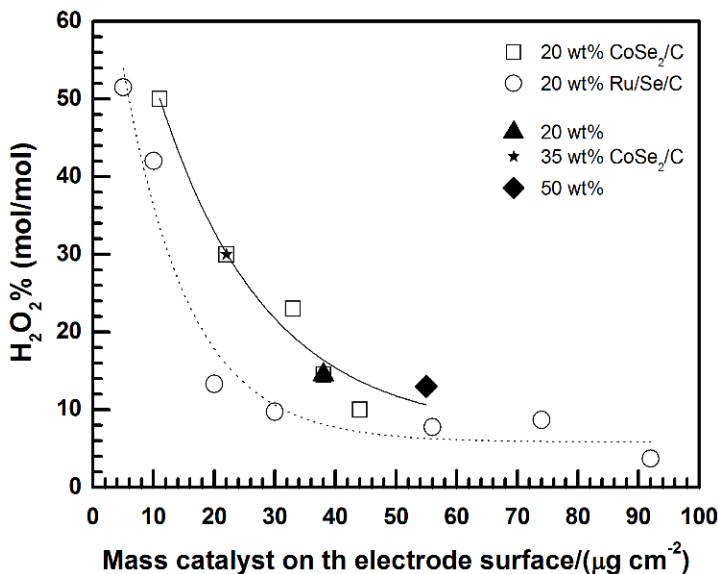


Figure 12. The H_2O_2 mol fraction evolution as a function of the mass catalyst per unit surface generated by the RRDE measurements. CoSe_2/C data from Ref. 161 RuSe/C data extracted from Ref. 164.

cases the electrocatalytic activity for the ORR decreases in the order $\text{S} > \text{Se} > \text{Te}$, possibly as the result of the geometric and electrostatic conditions in the spinel structure. Cobalt or Iron-based chalcogenides have attracted a lot of interest due to their low cost and abundance, although these materials have low chemical and electrochemical stabilities at high overpotentials in acid medium, as compared with Pt- or Ru-based cathode catalysts. Theoretical calculations predicting a reversible potential of about 0.74 V and 0.5 V/RHE for Co_9S_8 and Co_9Se_8 have been reported so far by Vayner et al.,¹⁶⁶ and Sidik et al.¹⁶⁷ These authors considered that the (202) surface of Co_9S_8 and Co_9Se_8 is active towards the ORR. Other non-precious metal catalysts for ORR in acid medium, in the form of thin films, such as $\text{Co}_{1-x}\text{Se}_x$,¹⁶⁸ FeS_2 and $(\text{Co,Fe})\text{S}_2$,¹⁶⁹ have been reported. Our investigations, however, led to the discovery that a different ORR activity exists between the orthorhombic and cubic phase structure of CoSe_2 . This change of phase takes place

by annealing at 430°C the as-prepared CoSe₂/C. The measured cathodic current at 0.50 V/RHE and 1600 rpm in 0.5 M H₂SO₄ (25°C) is of 1.58 mA cm⁻² and 2.92 mA cm⁻² for the orthorhombic and the cubic structure of 20 wt% catalyst, respectively. Thus, for the same loading the cubic structure appears to favor the production of water.

2. Why Tolerance is Required?

Tolerance on cathode materials is required with the aim at developing direct methanol fuel cell (DMFC) systems. As it is well known, in DMFCs the methanol crossover occurs through the solid electrolyte membrane from the anode to the cathode, where it is oxidized.¹⁷⁰⁻¹⁷¹ Simultaneous ORR and oxidation of methanol at the cathode leads to the drop in cathode potential, and hence reduction in the overall DMFC performance.¹⁷²⁻¹⁷⁴ Moreover, a methanol tolerant cathode catalyst is crucial in the mixed-reactant fuel cell design. Therefore, the search for methanol-tolerant cathode catalysts or other small organic species is a significant activity in DMFC, or generally in direct alcohol fuel cell (DAFC) research.

The tolerance of chalcogenide was reported a long time ago using the Chevrel Phase compound.¹⁷⁵ Some years later this property was documented with the cluster-like compounds of Ru_xSe_y comparing them with the platinum electrode performance coupling the mass spectrometry (DEMS) to the electrochemical cell.¹²¹

Experimental conditions were oxygen-saturated 0.5 M H₂SO₄ (solid line curves) and in the presence of 1 M CD₃OD (dashed line curves). The detected mass signal of oxygen (*m/e* = 32) is proportional to the concentration of oxygen at the working electrode surface. This concentration is given by the rate of incoming transport of oxygen to the electrode surface, its electrochemical consumption (reduction to water), and the amount of oxygen transferred into the vacuum system of the mass spectrometer. The rate of oxygen transport is sensitively influenced by the geometrical position of the oxygen bubbler near the working electrode. A shift of the mass signal with respect to the faradic current can be observed due to a high gas transport rate at the inlet system of the mass spectrometer, as clearly observed in the case of the chalcogenide: Ru_{1-x}Mo_xSeO_z system (Fig. 13, left). Here, with the electrocatalytic cathodic current of 2 mAcm⁻² no significant oxygen consumption

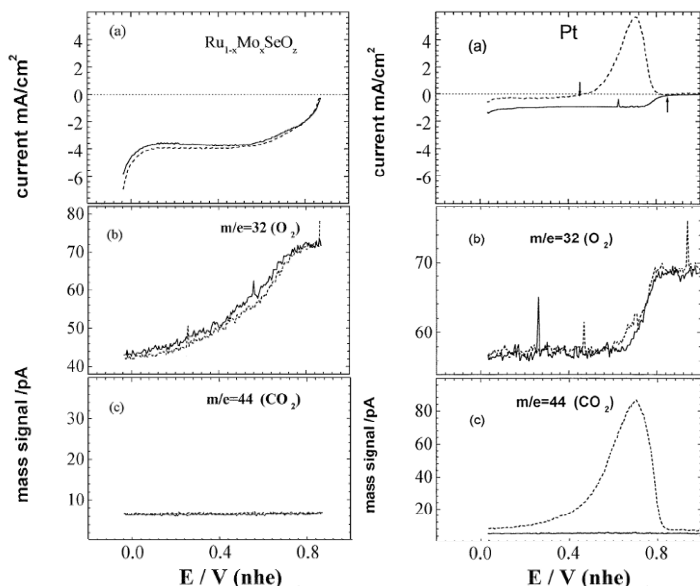


Figure 13. The upper panels show ORR current-potential curves in acid medium; the middle panels show the consumption of the molecular oxygen ($m/e = 32$) and the lower panels the reaction product of the methanol oxidation, i.e., carbon dioxide ($m/e = 44$) as a function of the electrode potential for ruthenium-chalcogenide (left) and platinum (right), respectively. Scanning was from positive to negative potentials at a rate of 5 mV/s. Reprinted from N. Alonso-Vante, P. Bogdanoff and H. Tributsch, On the Origin of the Selectivity of Oxygen Reduction of Ruthenium-Containing Electrocatalysts in Methanol-Containing Electrolyte, *Journal of Catalysis*, **190** (2000) 240, Copyright (2000) with permission from Elsevier.

difference in the mass signal exists, in an interval of 60 mV negative from the onset potential (0.86 V/NHE). The key question of tolerance is the reduction of molecular oxygen in the presence of methanol. The in situ confirmation is given by DEMS, since the presence of 1 M CD_3OD in 0.5 M H_2SO_4 perturbs neither the current-potential characteristics of the ruthenium chalcogenide nor the oxygen consumption mass signal. Within the experimental sensitivity of DEMS, the oxidation products of methanol, e.g., carbon dioxide ($m/e = 44$) in the explored potential range is absent. This result is contrasted to the well known behavior of platinum¹⁷⁶⁻¹⁷⁷ (cf. Fig. 13, right). It is worthwhile to notice that, in spite of the

methanol oxidation on platinum; its oxygen reduction path remains the same. This puts forth evidence for the possibility that this faradic process is occurring in parallel at different sites on the electrode surface. However, the overall electrochemical process, i.e., the oxygen reduction and methanol oxidation, leads to the formation of a mixed-electrode potential which has a negative consequence on the performance of the cell voltage or a 0.041 V shift negative from the onset potential. This is clearly observed in the upper right panel of Fig. 13.

The tolerance property of ruthenium-chalcogenide was put recently into advantage in a laminar flow fuel cell (LFFC).¹⁷⁸ Indeed, in the system depicted in Fig. 14, various concentrations of methanol in the anode stream were studied. A comparative study was performed with platinum black electrode using standard DMF as shown in the scheme represented in Fig. 14. The anode was Pt-Ru black. Methanol concentration was varied from 0.1 M to ca. 10 M. This allowed the observation that on Pt-cathode system the power peaks and drops due to the increasing crossover effect to the cathode. This crossover effect is schematized at the end length of the flow fuel cell in Fig. 14. The LFFC potential-current as well as the power-current characteristics are shown in Fig. 15. The maximum power obtained with 5 M CH_3OH was ca. 16 mWcm^{-2} . Although similar onset potentials are observed on Pt as well as on Ru_xSe_y cathode containing systems, the maximum power density of this latter is a factor 5 less than platinum.

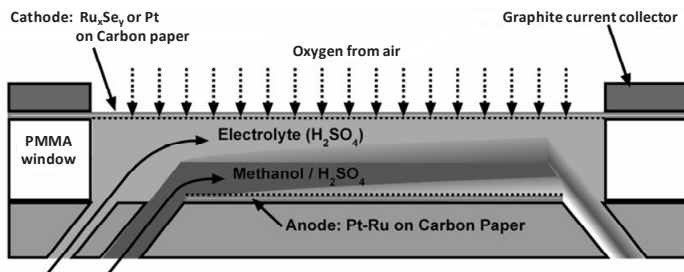


Figure 14. Design of an air-breathing laminar flow fuel cell (LFFC) showing the laminar flow profile of the anode side. Adapted with permission from Devin T. Whipple, Ranga S. Jayashree, Daniela Egas, Nicolas Alonso-Vante and Paul J.A. Kenis, Ruthenium cluster-like chalcogenide as a methanol tolerant cathode catalyst in air-breathing laminar flow fuel cells, *Electrochimica Acta* 54 (2009) 4382, Copyright (2009), with permission from Elsevier.

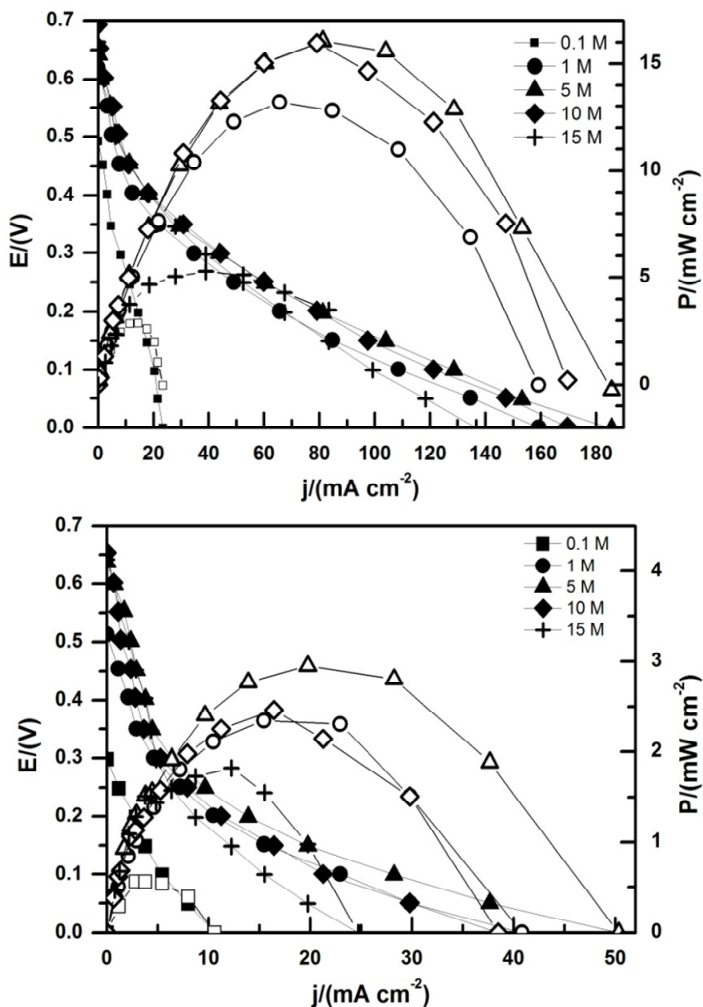


Figure 15. Polarization and power curves of an air-breathing laminar flow fuel cell (LFC) for Pt (left) and RuSey (right). Adapted from, Devin T. Whipple, Ranga S. Jayashree, Daniela Egas, Nicolas Alonso-Vante and Paul J.A. Kenis, Ruthenium cluster-like chalcogenide as a methanol tolerant cathode catalyst in air-breathing laminar flow fuel cells, *Electrochimica Acta* **54** (2009) 4384, Copyright (2009), with permission from Elsevier.

Another limiting factor to be mentioned is the slow kinetics of oxidation at the Pt-Ru anode. When in inflow of electrolyte in the flow cell system contains only methanol/sulfuric acid (mixed-reactant mode) the effect on Pt cathode in building a mixed-potential is dramatic, in contrast to Ru_xSe_y , see Fig. 16. This again is in agreement with the results generated by DEMS (cf. Fig. 13). The FFC voltage already breaks down to 0.33 V. This result confirms that Ru_xSe_y performs better when methanol concentration exceeds 2 M due to its tolerance.

The analysis of individual potentials showed that Ru_xSe_y improves its performance in the presence of methanol (1 to 7 M) by as much as 30 to 60% as compared to the absence of methanol.

The advantage of the chalcogenide with respect to platinum is the fact that a two streams laminar electrolyte can be eliminated, thus decreasing complexity in designing power systems.

3. The Chemical and Thermal Stability of Highly Selective Chalcogenide Materials

One of the paradigms of materials tailoring, out of fast charge transfer kinetics, high abundance, low cost, is the fact of developing stable compounds with respect to chemical and thermal environments. Here, we would like to demonstrate with the help of various techniques that the ruthenium-selenide cluster-like possess such ingredients, as far as the oxidation of selenide is not forced via the electrochemical potential oxidation, i.e., at a potential higher than 0.9 V/RHE, which is unfortunately one drawback to overcome the overpotential at the level of platinum. First, to demonstrate this, in-situ measurements at the interface with the gas phase were performed using the X-ray diffraction technique in the wide angle mode, so-called WAXS. The stability of Ru_xSe_y sample after some months of storage in air was confirmed by XRD, with however, a small signal identified at $16^\circ/\text{theta}$ (or $b = 0.38 \text{ \AA}^{-1}$), which is attributed to oxygen coordinated to some ruthenium sites. That was the reason why the stoichiometry of such compounds was formerly written as $\text{Ru}_x\text{Se}_y\text{O}_z$.¹⁷⁹ This small signal disappears under hydrogen treatment and the result is the pattern represented in Fig. 17 (left-upper panel). Ruthenium nanoparticles, on the other hand, ignite after some hours of exposure to air atmosphere,¹⁴⁵ so that to recover the nanoscale precursor a hydrogen treatment of up

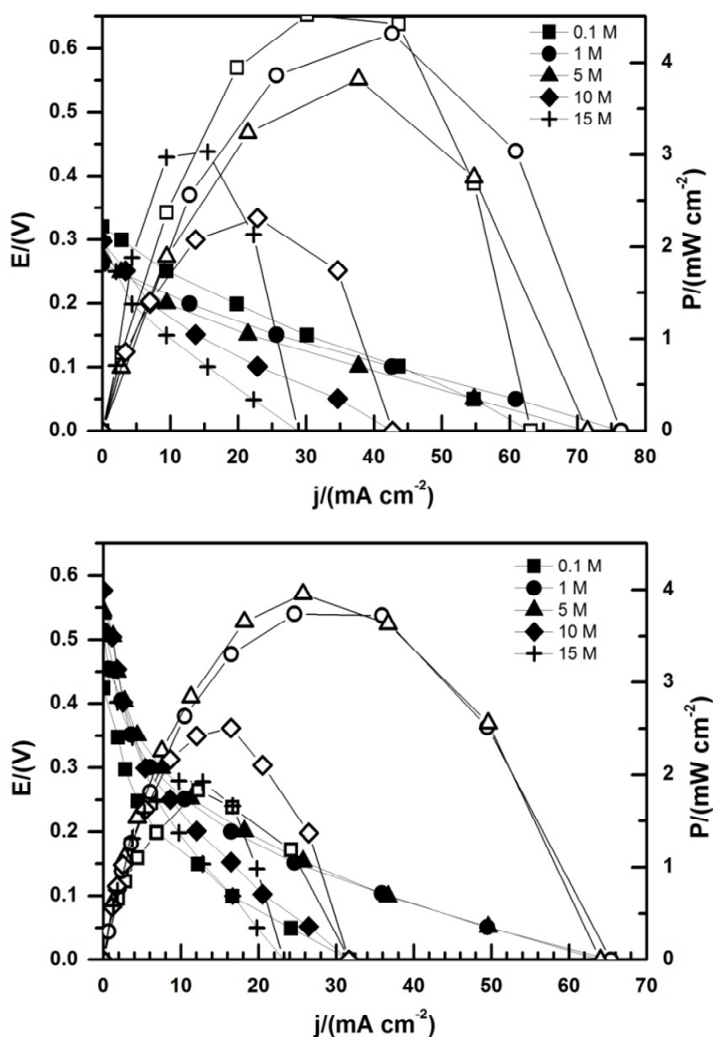


Figure 16. Polarization and power curves of an air-breathing laminar flow fuel cell (LFFC) for Pt (left) and RuSey (right). Adapted from Devin T. Whipple, Ranga S. Jayashree, Daniela Egas, Nicolas Alonso-Vante and Paul J.A. Kenis, Ruthenium cluster-like chalcogenide as a methanol tolerant cathode catalyst in air-breathing laminar flow fuel cells, *Electrochimica Acta* **54** (2009) 4384, Copyright (2009) with permission from Elsevier.

to 180°C was necessary. The pattern is depicted in Fig. 17 (right-upper panel). Thereafter both samples were submitted in situ to heat treatment under 1 bar of oxygen from RT to 320°C. Fig. 17 illustrates the evolution of the XRD pattern at 160° (middle panels) and after 320°C (bottom panels). This study put in evidence the remarkable thermal stability of the ruthenium-selenide nanoparticles with a resistance against particle agglomeration as deduced from the mass fraction distribution (see inset—left side, Fig. 17). Now, In comparison to Ru_x , which readily transforms to amorphous-like Ru_xO_y (right side, Fig. 17), and to a bulk oxide RuO_2 with rutile structure above $T \approx 250^\circ\text{C}$ and in which there is growth of particles, the question is raised: Where does this remarkable stability of Ru_xSe_y come from? Why does oxygen prefe-

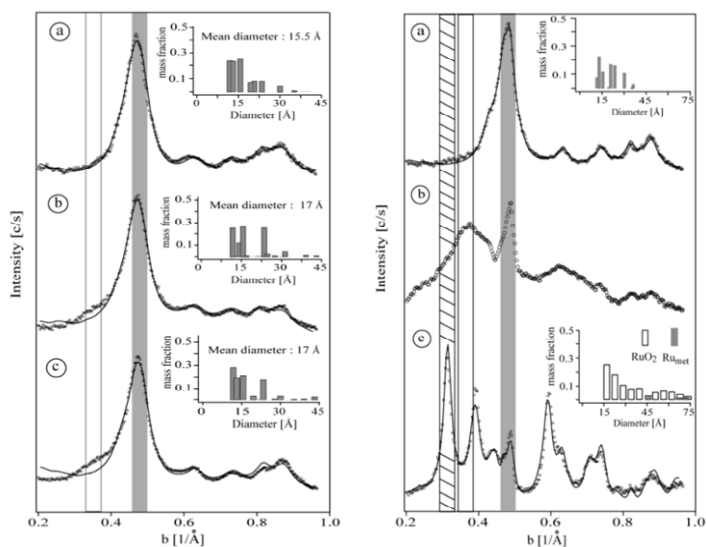


Figure 17. Upper panel: WAXS patterns (circles symbols) of hydrogen pre-reduced (1 bar of H_2 at 90°C) RuSe and Ru . Lower panels represent the treatment under 1 bar O_2 . Middle panels are the patterns after 160°C . Bottom panels are patterns after 320°C . The solid lines represent the DFA simulation of the diffraction pattern of the sample. The inserts show the mass fraction of the hcp model clusters Ru_xSe_y , Ru_x , versus their diameter used for the simulation. Adapted with permission from Ref. 145, Copyright (2002) American Chemical Society.

rentially coordinate to ruthenium despite the prominent presence of selenium atoms on the surface? The experimental answer to this question came six years later,¹⁸⁰ with the use of the electrochemical nuclear magnetic resonance (EC-NMR). A technique considered as a local surface and bulk nanoparticle probe.^{25,81-83} In short: besides the chemical or Knight shift; the spin-lattice relaxation time in the laboratory frame (T_1) and the spin-spin relaxation time (T_2) are the two major observables to be considered, since these parameters provide information on motions in a large time span going from 10^{-9} s to 10^2 s.

⁷⁷Se EC-NMR was performed on Ru_xSe_y , and Ru/Se, see Fig. 18. Both catalysts present similar shift centered at 1670 ppm. Ru/Se, whose synthesis was done by reacting Se onto Ru black nanoparticles,¹⁴⁹ shows a broader peak testifying for a high crystallographic disorder. ⁷⁷Se-NMR of the powder peaks at 857 ppm. The Se-NMR signals give account of the chemical state and/or strong interaction of this atom coordinated to ruthenium surface atoms, in such a way that the spin relaxation time (T_1) can be affected. The temperature dependence of the spin lattice relaxation rate (T_1^{-1}) is contrasted in Fig. 19, and from the slopes the Korringa constants (T_1T) deduced are 8.1 for Ru/Se and 8.5 sK for Ru_xSe_y . The values are, actually similar and reveal that selenium, being a semiconductor ($E_g = 1.99$ eV), becomes metallic by virtue of charge transfer from ruthenium atoms. In this way this latter becomes less labile to be oxidized, as demonstrated earlier by the WAXS in situ studies, Fig. 17.

4. The Interfacial Dynamics at the Cathode

The coordination distances for ruthenium-selenium and ruthenium-ruthenium are, respectively: $R_{(\text{Ru-Se})} = 2.43$ Å y $R_{(\text{Ru-Ru})} = 2.64$ Å. In in situ EXAFS measurements, ruthenium-selenide presented some distortion induced by the oxygen adsorption. This was discussed as being the precondition to break the O-O bond favoring thus the multi-electron charge transfer reaction.^{80,122,181-182} One example is depicted in Fig. 20.

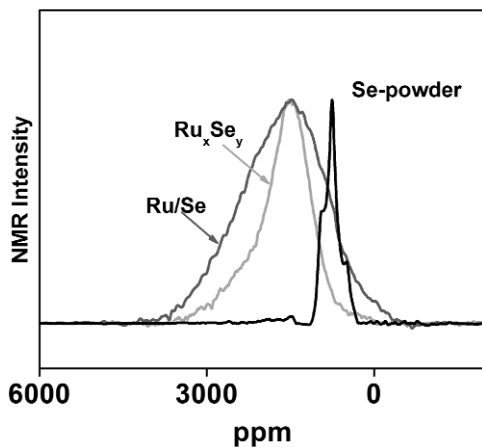


Figure 18. ^{77}Se NMR spectra of selenium powder, Ru_xSe_y and Ru/Se catalysts obtained at 8.45T and 80K. Adapted with permission from Ref. 180, Copyright (2007) American Chemical Society.

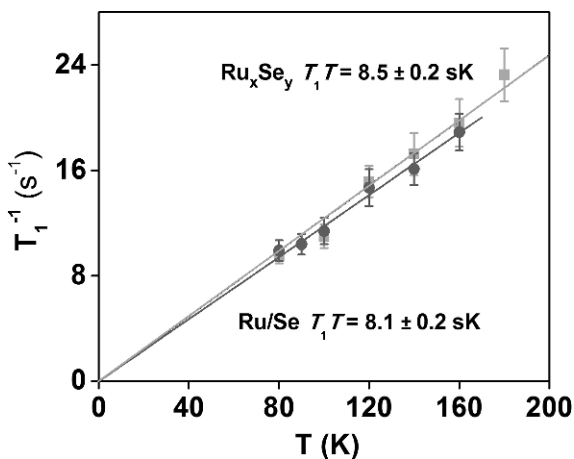


Figure 19. Temperature dependence of the spin-lattice relaxation rate on Ru_xSe_y and Ru/Se catalysts. Adapted with permission from Ref. 180, Copyright (2007) American Chemical Society.

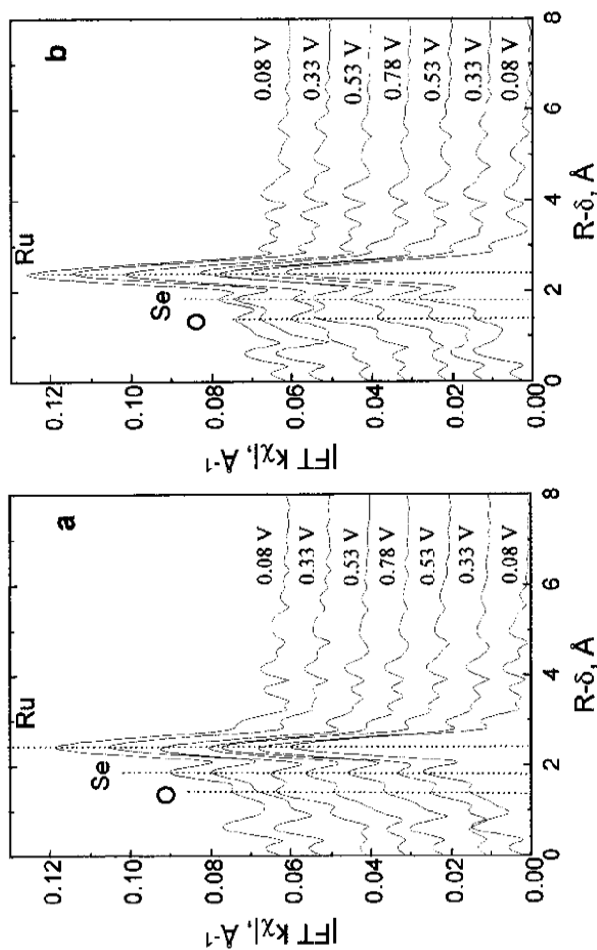


Figure 20. Fourier transform moduli (k_1 -weighted) for $\text{Mo}_x\text{Ru}_y\text{Se}_z$ catalyst as a function of the electrode potential in (a) Ar, and (b) oxygen atmospheres.¹⁸¹ Adapted with permission from Ref. 181, Copyright (2002) American Chemical Society.

The prominent peak at ca. 2.42 Å corresponds to the direct metal-metal bond (bond length 2.65 Å) in the core of the Ru cluster. Two longer Ru-Ru distances, at 3.7 and 4.6 Å, exceeding the possible length of the Ru-Ru chemical bond, are also present in the EXAFS spectra in the range from 0 to 5 Å. Observation of the latter allowed to conclude that the cluster size was not less than 6 Å. Se atoms establish binding of the Ru layers and give rise to a peak at $R-\delta$ 1.84 Å, corresponding to a Ru-Se distance of 2.41 Å. A peak at $R-\delta$ 1.4±0.1 Å is very much dependent on the potential and the presence of oxygen and corresponds apparently to the Ru-O distance at 2.02–2.17 Å. The variation of the applied electrode potential from 0.08 to 0.78 V/RHE in the presence of molecular oxygen produce an increase of the Ru–O apparent coordination number and a simultaneous decrease of the Ru–Ru ones in the first coordination shell of ruthenium. Reversible changes of the coordination distances were observed with the polarization, thus witnessing a distortion (dynamics) of the catalytic center upon oxygen adsorption. Using synchrotron X-ray fluorescence spectroscopy at the Se edge Inukai et al.¹⁸³ further confirmed the fact that coordinated selenium to ruthenium is highly disordered, and that the same ORR mechanism is acting on Ru/Se as previously described for Ru_xSe_y cluster compounds,^{80,181–182,184} and Fiechter et al.¹²⁸ using techniques such as thermogravimetry coupled with mass spectrometry (TGMS), extended X-ray absorption fine structure (EXAFS) analysis, and X-ray photoelectron spectroscopy (XPS) arrived at the conclusion that selenium is covalently bound at the cluster surface forming Se–Ru surface complex, which protects the ruthenium core against oxidation.

IV. THE ROLE OF CHALCOGENIDE IN PHOTOELECTROCATALYSIS

1. The Influence of Semiconducting Substrates on the Charge Transfer

Catalysts such as the cluster-like chalcogenide Ru_xSe_y can be deposited in thin layer form onto various substrates such as the tin-oxide ($SnO_2:F$),¹⁸⁵ titania (TiO_2)¹⁸⁶ or in powder form embedded in a polyaniline polymer matrix.¹⁸⁷ The nature of some semiconduct-

ing oxide substrate influences the current-potential characteristic (j - E) of the catalyst towards the ORR, as observed in curves (c) and (d), Fig. 21. If we consider the 0.8V/SHE as a reference potential for activation the activity on $\text{SnO}_2\text{:F}$ curve (c) and on nanostructured TiO_2 curve (d) is 0.9 and 2.8 orders of magnitude lower than that measured on typical carbon substrates, i.e., glassy carbon, see curves (a) and (b). The relatively enhanced catalytic current on SnO_2 ($E_g = 3.4$ eV) is due essentially to its increased majority charge carrier induced by doping with Fluor. F-doping levels bring the concentration of donor charge carrier at the level

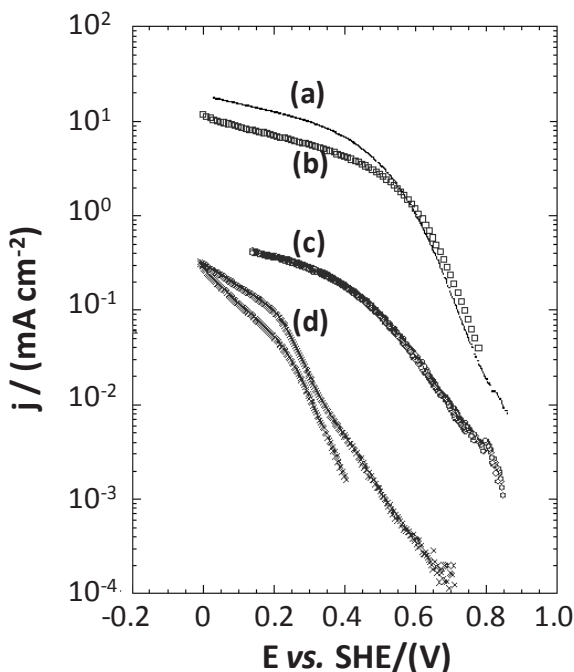


Figure 21. The ORR in 0.5M H_2SO_4 on Ru_xSe_y deposited on various substrates. (a) as a layer on glassy carbon; (b) as an ultra thin layer synthesized via colloidal solution on glassy carbon; (c) an ultra thin layer deposited via colloidal solution on $\text{SnO}_2\text{:F}$; and (d) an ultra thin layer deposited via colloidal solution on TiO_2 (anatase). The colloidal solution is described in Ref. 138.

of 10^{20} cm^{-3} . This is in contrast to undoped TiO_2 ($E_g = 3.2 \text{ eV}$, anatase) substrates, where the electrons start to be available at ca. 0.2V below the Fermi level.¹⁸⁶

In other words, the response depicted in curve (d) is an effective scavenging of conduction electrons via cluster-like nanoparticles of Ru_xSe_y leading directly to the formation of water. This process proceeds via surface states (dark process) and commences to be available from ca. 0.7 V/SHE (at a current density of 10^{-4} mA/cm^2). Some energetic considerations should be taken into account. The position of the flat band energy (E_{fb}) of anatase films corresponds, according to considerations of Rothenberg et al.,¹⁸⁸ to -0.18V/SHE (pH 0.3). The presence of cluster-like material modifying the titania (anatase) surfaces works as an effective electron scavenger relay (catalysts) of charges already available at ca. 0.88V below the Fermi level. These charges are conveyed to reduce the molecular oxygen via 4-electrons. This is necessary for the improvement of energetic efficiency in energy converter devices. The charges, although available (and/or stored), are not effectively conveyed to the oxygen molecules, in the absence of the cluster-like catalyst. The consequence of this phenomenon is that the presence of O_2 in the electrolyte favors the recombination process (e.g., lowering of photopotential) of nanostructured TiO_2 . If the cluster-like nanoparticles were able to accumulate electrons they would change their potential and in this way reduce oxygen or other oxidized species in solution. The accumulation of electrons in the chalcogenide nanoparticles can also be evidenced by photocatalytic experiments (see below).

2. Electrochemistry in Solution

The absorption of the chalcogenide colloidal solution was verified by its adsorption onto a thin film of TiO_2 as a function of time. A follow-up of this process was done by UV-VIS absorption. Figure 22 shows the evolution of the spectra. As expected, increasing the adsorption time of the colloids leads to an increase of the absorption in the whole visible region. It should be noted that the adsorption of the Ru_xSe_y nanoparticles is very fast, in fact, in 1 minute the adsorption is nearly the same as that measured after 51 minutes. The structureless spectra can be attributed to the fact that

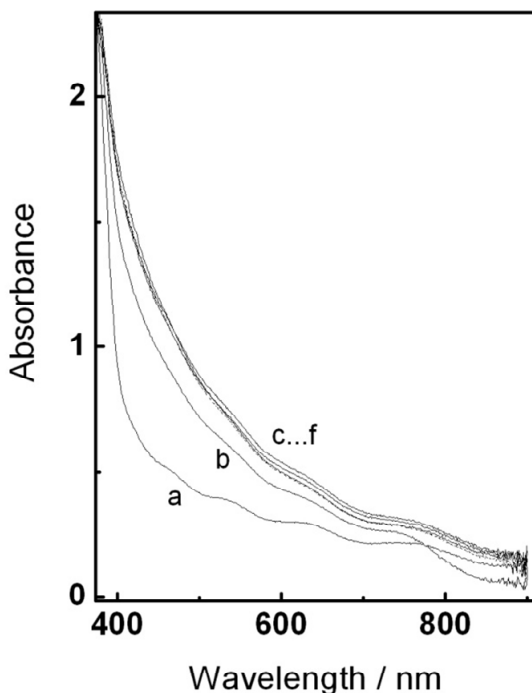


Figure 22. Absorption follow-up UV-Vis spectra for a thin film of TiO_2 after immersion in a colloidal Ru_xSe_y solution at different times. (a) before immersion; (b) after 5 seconds; (c) after 1 minute; (d) after 6 minutes; (e) after 16 minutes; (f) after 51 minutes. Quartz cuvette used with a 1 cm light path quartz.

chalcogenide nanoparticles are embedded in the semiconductor matrix. An aggregation processes which may induce a broadening of the spectrum was not expected because the nanoparticles were covered with an organic monolayer (1-octadecanethiol) as the stabilizer, which suppressed interparticle interactions.

To undertake electrochemistry in suspension at the interface $\text{TiO}_2/\text{Ru}_x\text{Se}_y$ under light, colloidal solutions of TiO_2 (10% solution in 2-propanol) as well as Ru_xSe_y (xylene) were prepared. Experiments were then performed in a mixture (50:50, v/v) of TiO_2 colloidal solution with xylene. Thereafter the composite $\text{TiO}_2/\text{Ru}_x\text{Se}_y$ was prepared by adding Ru_xSe_y solution without altering the ratio

xylene:ethanol. As electron acceptor a concentrated C_{60} solution (1 mM) in xylene was introduced directly into the TiO_2 or TiO_2/Ru_xSe_y suspensions previously illuminated.

For colloidal TiO_2 , a temporal evolution of the UV-Vis absorbance spectra is shown in Fig. 23. As observed, a relative broad peak centered at 650 nm grows as a function of increasing illumination time. Electron-hole pairs are generated by the band to band excitation using the UV light. The holes diffuse to the particle surface where they react with reduced dissolved species, such as ethanol, see upper scheme left. In contrast, the electrons remain in the particles, leading to a transitory charge. This negative charge induces recombination and accelerates the electron charge transfer to the solution. The accumulation of electrons in the TiO_2 colloidal solution can be detected by monitoring the increase of the absorbance in the visible region, i.e., the semiconductor particles become blue colored as earlier reported in the literature.¹⁸⁹ The electron accumulation is a function of the experimental conditions: whether the electrolyte is protic or aprotic.

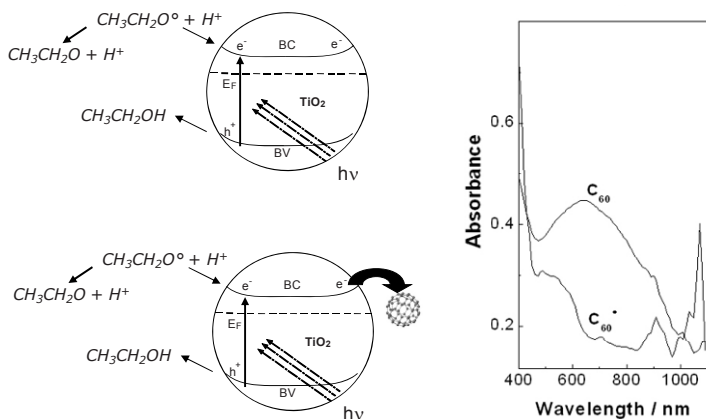


Figure 23. Absorption spectra evolution of TiO_2 (0.023 M solution purged with nitrogen), with thereafter addition of deaerated 1 mM C_{60} solution. Light was due to 150 W Xe lamp. The two pictures at the left schematize the photochemical process. Upper: accumulation of electrons. Bottom: transfer to C_{60} to produce the radical $C_{60}^\bullet$.

It is clear that presence of oxygen annihilates the accumulation of electrons. Instead, however, fullerene C_{60} can react with the electrons accumulated on the semiconductor surface as reported by Vinodgopal et al.¹⁹⁰ As reported by these authors, the electronic transfer between the TiO_2 particles and C_{60} takes place with a quantum efficiency of 24%. The reduction of C_{60} leads to the radical formation: $C_{60}^{\cdot -}$, with a characteristic peak centered at 1060 nm, see lower curve of the spectra, Fig. 23. Indicating that, in our experimental conditions, the reaction can proceed, after the scheme shown on the bottom left.

In order to verify that electron transfer from TiO_2 to Ru_xSe_y takes place, we have measured the UV-Vis spectra of the semiconductor colloidal solution purged with nitrogen after 20 minutes under illumination, with different amounts of the Ru_xSe_y colloidal solution distributed in various quartz cuvettes in a certain volume of the TiO_2 colloidal solution and illuminated each during 20 minutes. Thereafter, they were transferred into the spectrophotometer where different quantities of C_{60} were added. The absorbance at 1060 nm was monitored, see Fig. 24. From this figure it can be seen that as the number of chalcogenide nanoparticles increases from (b) to (c), the visible absorbance diminishes after 20 minutes under UV illumination. However, even if the absorbance is lower in the absence of C_{60} , the variation of the absorption at 1060 nm is higher in the presence of Ru_xSe_y nanoparticles.

As the composite system TiO_2/Ru_xSe_y is illuminated, electron-hole pairs are generated. The holes will diffuse to the semiconductor surface as mentioned above, where they will react with ethanol species present in solution. On the other side, the photogenerated electrons can be trapped at TiO_2 surface states or can move to the Ru_xSe_y nanoparticles, see scheme in Fig. 23. In this scheme the chalcogenide is embedded in a sheath of the chemical stabilizer: 1-octadecanthiol. Then, it seems that charge transfer takes place in the presence of these thiol chains, which adsorb by the thiol group leading the hydrocarbon chain in the external part. This configuration gives a certain hydrophobic character to the metal particles. Therefore, the colloidal Ru_xSe_y nanoparticles remain covered with a monolayer of octadecanthiol, even in the presence of TiO_2 . It can reasonably be assumed that the Fermi level of Ru_xSe_y nanoparticles must be placed below the conduction band of TiO_2 favoring the electrons to be transferred from the semiconductor to the chal-

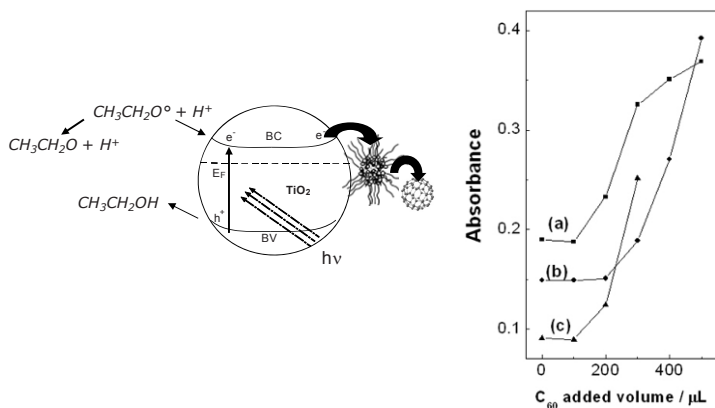


Figure 24. Absorption evolution at 1060 nm for different previously illuminated samples: (a) TiO_2 , (b) $\text{TiO}_2 + 20 \mu\text{L Ru}_x\text{Se}_y$; and (c) $\text{TiO}_2 + 40 \mu\text{L Ru}_x\text{Se}_y$ with the addition of C_{60} .

cogenide as shown experimentally. Once they are transferred, they are trapped. This process continues until a stationary state is attained. Thereafter, the photogenerated electrons and holes will recombine. When the C_{60} is added, it reacts with the accumulated electrons on the semiconductor via Ru_xSe_y . This is the reason why the change in the absorption at 1060 nm is higher in the presence of the chalcogenide: the electrons can accumulate in both materials.

3. Impact in Depollution of Water

The chemical/photochemical process above described for the $\text{TiO}_2/\text{Ru}_x\text{Se}_y$ composite^{186,191} served as a basis for its application in the treatment of waste water from the paper industry. Heterogeneous photocatalysis using TiO_2 (anatase), for the same purpose, has been devised by various workers.¹⁹²⁻¹⁹⁴ Here, the objective was to investigate the efficiency of the treatment of bleaching effluents with sequential processes, i.e., biological pre-treatment with *Trametes versicolor* immobilized on polyurethane foam followed by photocatalysis using Ru_xSe_y surface-modified nanostructured

TiO₂ thin films (composites).¹⁹⁵ All films were deposited onto aluminum foils.

Figure 25 depicts the percentage of decolorization and the chemical oxygen demand (COD) of the effluent previously treated with *Trametes versicolor*. The results were obtained under four different experimental conditions, namely: UV light; darkness and UV light on TiO₂ layers; and UV light on TiO₂/Ru_xSe_y. As observed, the oxide in the dark removed 13% of the color and reduced COD by 31%, probably due to the adsorption of some compounds onto the surface of the TiO₂. The decolorization achieved by treatment with UV irradiation on TiO₂ alone and TiO₂/Ru_xSe_y was low in comparison with that obtained in other studies.^{193,196} This behavior could be attributed to the oxidation of the aluminum foil when it was exposed to ultraviolet light. However, the experimental conditions are not comparable, since the effluent used in this study was more concentrated in color and COD than the effluent used in the studies done by Yeber et al.¹⁹³ Summing up the efficiency of the composite material is small due to the very complex composition of the residue (organic halide compounds, lignin, etc.). Nevertheless, this study showed that the total sequential treatment, i.e., biological followed by photocatalysis resulted in 92% color removal (CR), 97% chemical oxygen demand (COD) reduction and 99% chlorophenol removal in a period of 90 h.

V. CONCLUSIONS AND OUTLOOK

Clearly, the way to understand the tailoring of nanomaterials is the follow-up of the chemical process. This has been done with the ruthenium-chalcogenide materials. Thus using transition metal molecular cluster compounds paved to a certain extent, the bottom-up approach for chalcogenide catalysts in the nanoscale domain. We believe we have given a fairly comprehensive account of this chemical process. The use of the various clue techniques such as e.g., NMR, XPS, XRD, not all mentioned in this chapter, provided information as to the nature of the ruthenium-selenide material. Such information cannot be obtained if limited solely to pyrolysis, and to electrochemical techniques.

Driving forces regarding the scarcity, and low selectivity of the best ORR catalyst, Pt, have led to the development of non-

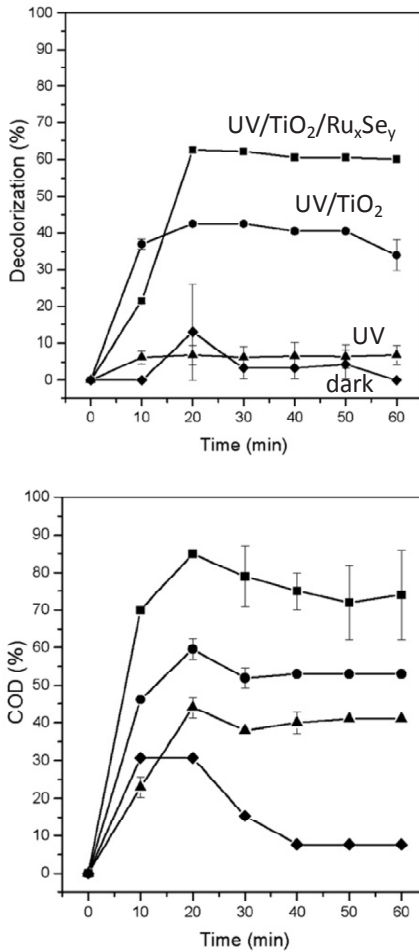


Figure 25. The sequential photocatalytic treatment of the effluent previously treated with *Trametes Versicolor*. The irradiation time used was 60 min. Reprinted from, Aura M. Pedroza, Rodolfo Mosqueda, Nicolas Alonso-Vante and Refugio Rodríguez-Vázquez, Sequential treatment via *Trametes versicolor* and UV/TiO₂/Ru_xSe_y to reduce contaminants in waste water resulting from the bleaching process during paper production, *Chemosphere* **67** (2007) 793, Copyright (2007), with permission from Elsevier.

precious metal center catalyst. The way to pave is still too long, since novel materials show, up to now, lower activity toward the ORR, although they show a higher tolerance. Interesting to note is the fact that such *cheap* metal centers should be stabilized by a ligand in order for them to keep activity and stability, either chemically or thermally. Among the various ligands, chalcogenide (e.g., selenium) appears as a good candidate. Other systems are based in the use of organic ligands such as macrocycles.

We found instructive to explore the possibility of novel materials as reservoirs of electrons, as shortly demonstrated in this contribution. Its combination with light energy, stored in semiconductor materials, such multi-electron charge transfer becomes feasible. Therefore, further development on novel catalytic centers, preferentially non-precious ones, is highly desired aiming at increasing selectivity and activity combining processes running under illumination (photocatalysis) as well as those running in darkness (electrocatalysis).

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Materials, Proton Conductivity and Electrocatalysis in High-Temperature PEM Fuel Cells

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I. INTRODUCTION: FUEL CELL TECHNOLOGIES

Fuel cells (FCs) are interesting alternatives to existing power conversion systems since they combine high efficiency with the usage of renewable fuels. Fuel cells can generate power from a fraction of a watt to hundreds of kilowatts and can be used in automotive, stationary or portable applications.^{1,2,3,4,5,6} A FC is an electrochemical device that converts in a continuous manner the free energy of a chemical reaction into electrical energy (via an electrical current). This galvanic cell consists of an electrolyte (liquid or solid) sandwiched between two porous electrodes. In order to reach de

sirable amounts of energy power, single cell assemblies can be mechanically compressed across electrically conductive separators to fabricate stacks.

The most common classification of fuel cells is by the type of electrolyte used as shown in Table 1 which summarizes the most commonly used fuel cell technologies and their applications. The operating temperature and useful life of a fuel cell dictate the physicochemical and thermomechanical properties of materials used in the cell components (i.e., electrodes, electrolyte, interconnect, current collector, etc.)

II. POLYMER ELECTROLYTE MEMBRANE FUEL CELLS (PEMFC)

1. Low-Temperature NAFION Based PEMFC

Among others, polymer electrolyte membrane fuel cell (PEMFC) have been identified as the most promising candidate and has been receiving increased attention due to the advantage of less corrosion, which arises from the all solid construction. PEM fuel cells are the most attractive type of fuel cell for many applications since they present mechanical simplicity, quick start-up, high efficiency, modularity and versatility⁷. The heart of a PEM fuel cell is composed of a polymeric membrane that presents specific capabilities. Particularly, the fuel cell membrane must exhibit relatively high proton conductivity, an adequate barrier to mixing of fuel and reactant gases and should finally be chemically and mechanically stable in the demanding fuel cell environment.

Typically, the membranes for low-temperature PEM fuel cells are made of perfluorocarbon-sulfonic acid ionomers (PFSA).⁸ The best material known is Nafion⁹ produced by DuPont, though similar materials have been developed for commercial or development purposes by other manufacturers such as Asahi Glass (Flemion) or Asahi Chemical (Aciplex). In the electrode part, the catalyst is generally dispersed as small particles on a conductive support (carbon powders). Despite many attempts to develop a non-noble-metal catalyst, platinum remains the best known electrocatalyst for ORR in PEM fuel cells. The most extensive limitations to large-scale commercial use of these materials arise from the fact that

Table 1
The Most Commonly Used Fuel Cell Technologies,² L. Carrette, K.A. Friedrich and U. Stimming, Fuel cells: Fundamentals and applications, *Fuel Cells*, 1 (2001) 5-39, Copyright (2001) Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

	AFC (Alkaline)	PEMFC (Polymer Electrolyte Membrane)	DMFC (Direct Methanol)	PAFC (Phosphoric Acid)	MCFC (Molten Carbonate)	SOFC (Solid Oxide)
<i>Operating temp. (°C)</i>	<100	60–120	60–120	160–220	600–800	800–1000 low temperature (500–600) possible
<i>Anode reaction</i>	$\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$	$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$
<i>Cathode reaction</i>	$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$	$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{3}{2} \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$	$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	$\frac{1}{2} \text{O}_2 + \text{CO}_3^{2-} + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$	$\frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$
<i>Applications</i>	Transportation Space Military Energy storage systems			Combined heat and power for decentralised stationary power systems	Combined heat and power for decentralised systems and for transportation (trains, boats, ...)	Combined heat and power for stationary decentralised systems and for transportation (trains, boats, ...)
<i>Realised Power</i>	Small plants 5–150kW modular	Small plants 5–250 kW modular	Small plants 5 kW	Small – medium sized plants 50kW – 11MW	Small power plants 100 kW– 2 MW	Small power plants 100–250kW
<i>Charge Carrier in the Electrolyte</i>	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}

they are proton-conductive only when they are hydrated, which results in a maximum operating temperature up to around 80°C under ambient pressure, susceptibility to chemical degradation at increased temperature and material cost.

Advanced features of the technology include high power density, environmentally friendly operation, all-solid construction and therefore little materials corrosion. Despite the significant progress and technological achievements, there are several challenges associated with this low temperature technology;^{10,11,12} high cost of the materials (electrolyte and noble metal catalyst), need of permanent humidification and careful management of the water balance due to the dual-phase water system arising from operation close to the boiling point, low cathode performance due to slow kinetics of oxygen reduction, reduced tolerance of the electrocatalyst to fuel impurities which makes essential the feed with high purity hydrogen,^{13,14,15,16} a complicated cooling system to maintain a thermal balance and little value of the heat for recovery resulting in low system efficiency.

2. High Temperature PEMFCs (HT-PEMFCs)

Most of the aforementioned shortcomings are associated with the low operating temperature, limited mainly due to the electrolyte used. A PEMFC technology operating above 100°C is desirable. First of all, the kinetics of both electrode reactions are enhanced and this can in principle lead to the use of lower amount of the expensive noble metal on the electrodes. More importantly, tolerance of the catalyst to fuel impurities (CO, sulphide) is dramatically enhanced, broadening the options for the feed gas. The CO poisoning effect is temperature dependent due to the weaker CO adsorption on the Pt surface.^{7,17} The CO tolerance has been found to increase from 10–20 ppm of CO at 80°C to 1000 ppm at 130°C and up to 30000ppm at 200°C.¹⁸ This can simplify the overall power system, reduce its cost and volume and improve the transient response capacity, reliability or maintenance-free operation of the system.¹⁹

A PEMFC operating at 80°C produces a large amount of low value heat that must be damped in order to maintain the operating temperature. In this respect the low temperature PEMFC is technologically difficult to be integrated in the combined heat and power

(CHP) systems. Higher working temperature could simplify the design of the cooling system due to the increased temperature gradient between the cell and the ambient temperature. Moreover, it is possible to recover a major part of the produced heat as e.g., steam which can be further used (direct heating, steam reforming), thus significantly increasing the overall efficiency of the system.

3. General Characteristics of a HT PEMFC

The research for new polymeric materials that fulfill all the prerequisites for applications in high temperature (140–200°) polymer electrolyte membrane fuel cells is of utmost importance due to the advantages that this operation offers over the conventional fuel cells operating at temperatures up to 80°C.^{20,21} High demands are put on the polymer electrolyte membrane because of the harsh chemical conditions existing under higher operating temperature. Thus, only few polymeric materials can efficiently withstand. The ideal polymer electrolyte for this type of cell should exhibit good mechanical properties and thermal and oxidative stability in order to be applicable in a HT PEMFC. The chemical environment in an operating fuel cell is harsh and the requirements for high chemical and especially oxidative stability of the polymeric materials are crucial.^{22,23} Chemical stability is critical for the lifetime of a HT PEMFC due to the in situ formation of H₂O₂ and hydroxy- or hydroperoxy- radicals. Due to their high oxidation potential, they can attack the polymer structure and disintegrate the membrane. This is presumed to be the principal degradation mechanism of common PEMFCs.

One of the most promising routes is the use of aromatic hydrocarbon polymers for polymer backbones,²⁴ which are thermally stable and cheaper than perfluorinated polymers. A very essential characteristic of the membranes must be their high proton conductivity, usually arising from its ability to be doped with a medium other than water, e.g., strong acids. Among the organic and inorganic acids, phosphoric acid is of special interest due to its thermal stability, very low vapor pressure and high proton conductivity, even in the anhydrous form and at high temperatures. The latter is a result of its amphoteric nature in the Brønsted sense, having proton donor and acceptor sites corresponding to a high degree of self-dissociation, high charge carrier concentration and formation

of dynamic extended intermolecular hydrogen bond networks promoting the proton conduction.²⁵ The main prerequisite for the acid polymer interaction is the existence of basic sides on the polymer chain. As discussed below, the imidazol and pyridine basic polar groups are used as part of the polymer chain so that the polymer membrane acquires basic character.

III. POLYMER ELECTROLYTES FOR HT PEMFCS

1. Polybenzimidazole Based High Temperature Polymer Electrolytes

(i) *Polybenzimidazole (PBI)*

The so far most prevalent polymer electrolytes for HTPMFCS are based on polybenzimidazole, PBI, and its derivatives. PBI based fuel cell systems seem most suited for stationary power applications based on natural gas reforming and combined heat and power generation.²⁶ In general, PBI materials are basic polymers ($pK_a = 5.23$ as protonated) containing benzimidazole units which bear both donor and acceptor hydrogen-bonding sites, as can be seen in Fig. 1. They can be synthesized by combining tetraamines and diacids. The proton acceptor sites of the imidazole ring react with H_3PO_4 or polyphosphoric acid as in a typical acid-base interaction. The basic polymer acts as a proton acceptor and an ion pair is formed.

Up to now mPBI, 2,2'-m-(phenylene)-5,5'-bibenzimidazole, the commercial product under the name Celazole[®], proposed by Aharoni and Litt²⁷ and investigated by Savinell and Wainright^{28,29} has been the state-of-the-art material that has been studied extensively doped with a strong acids^{30,31,32,33} or bases as a promising electrolyte for high temperature PEM fuel cells.

The most common and effective route for the lab scale synthesis of mPBI is the high temperature (170–200°C) polycondensation of tetraaminobiphenyl and isophthalic acid in polyphosphoric acid (PPA), Fig. 1.²¹ mPBI is a completely amorphous thermoplastic polymer with a glass transition temperature of around 420°C. Phosphoric acid doped mPBI exhibits high thermal stability,³⁴ low

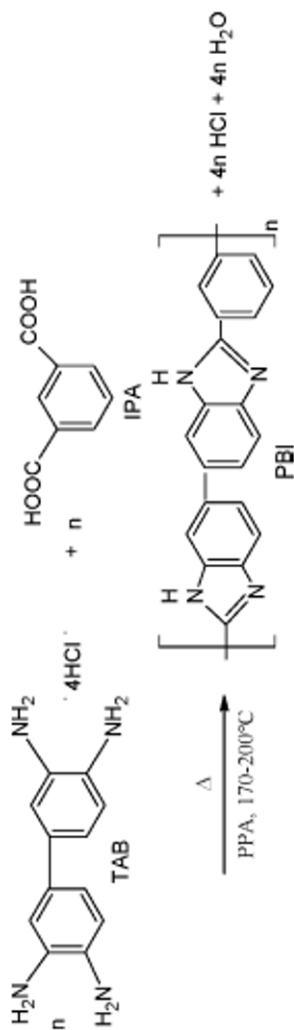


Figure 1. The PPA process for mPBI synthesis.

gas permeability, almost zero water electro-osmotic drag number^{35,36} and good mechanical flexibility at elevated temperatures.

Usually, the membranes are prepared by the solution casting method from their DMAc solutions and are doped with acid by immersing them in aqueous phosphoric acid solutions. When a PBI membrane is immersed in H_3PO_4 an equilibration time of up to 50 h is necessary at room temperature to reach saturation doping level. The saturation doping level of PBI membranes can reach values up to 15 mole H_3PO_4 per repeat unit of PBI depending on the concentration of the doping acid solution, as shown in Fig. 2.³⁷

Proton conductivity generally increases with acid-doping level. Two phosphoric acid molecules per repeat unit lead to complete protonation of mPBI as proven by infrared spectroscopic analysis.³⁰ Excess acid create acid rich regions of bound, (through hydrogen bonding), and unbound phosphoric acid molecules, H_3PO_4 and acid anion, H_2PO_4^- , as was observed using Raman and infrared spectroscopy³⁷ as well as ^1H and ^{31}P magic-angle spinning NMR.³⁸ The conductivity of these materials ranges typically between $0.04\text{--}0.08\text{ S cm}^{-1}$ at 150°C , and is dependent on acid doping level, humidity, temperature and pressure.^{20,26,29,30,39,40,41}

Alternatively, the direct fabrication of phosphoric acid doped PBI membranes from solutions in polyphosphoric acid (PPA) has been proposed.³⁹ In this method, PPA is used as the polycondensation agent, polymerization solvent and membrane casting solvent. After polymerization of the monomers as described in Fig. 1, casting of the PPA solutions and in-situ hydrolysis by moisture of PPA to phosphoric acid results in PBI- H_3PO_4 doped membranes. Under appropriate conditions, a sol-gel transition occurs and produces membranes with a combination of desirable physicochemical properties not obtainable from the conventional imbibing process. Moreover, acid doping levels as high as 20–40 mol phosphoric acid per repeat unit of PBI can be achieved which results in very high conductivity values.²⁶

Another promising modification of PBI is the introduction of immobilized polyvinylphosphonic acid (PVPA) in the PBI matrix.⁴² This approach is especially interesting since the acid is not likely to be washed out during operation, thus maintaining steady fuel cell performance. PEMEAS-BASF Fuel Cells has developed an MEA product, Celtec[®]-V, mainly for liquid feed DMFCs, based on this concept. Single-cell performance tests of CeltecV and Na

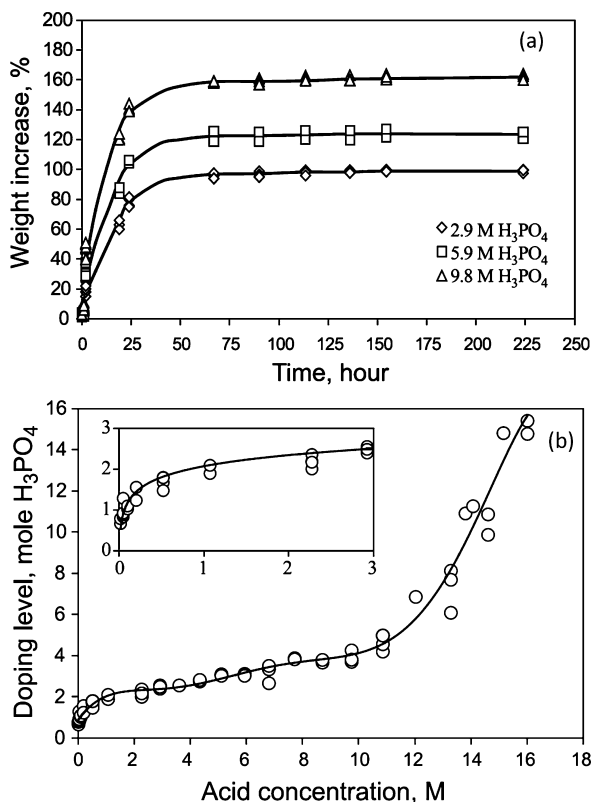


Figure 2. (a) Weight increases of PBI membranes after being immersed in phosphoric acid of different concentrations at room temperature, (b) Acid doping level of PBI membranes as a function of the acid concentration at room temperature. Reprinted from Q. Li, R. He, R. W. Berg, H. A. Hjuler, N. J. Bjerrum, Water uptake and acid doping of polybenzimidazoles as electrolyte membranes for fuel cells, *Solid State Ionics*, **168** (2004) 177-185, Copyright (2004) with permission from Elsevier.

fion 117 were carried out and compared. It was found that CeltecV MEAs showed 50% lower methanol crossover than Nafion.

In general, PBI based systems have shown very good cell performance.^{18,19,35,43,44} Figure 3 shows polarization curves of a PBI-

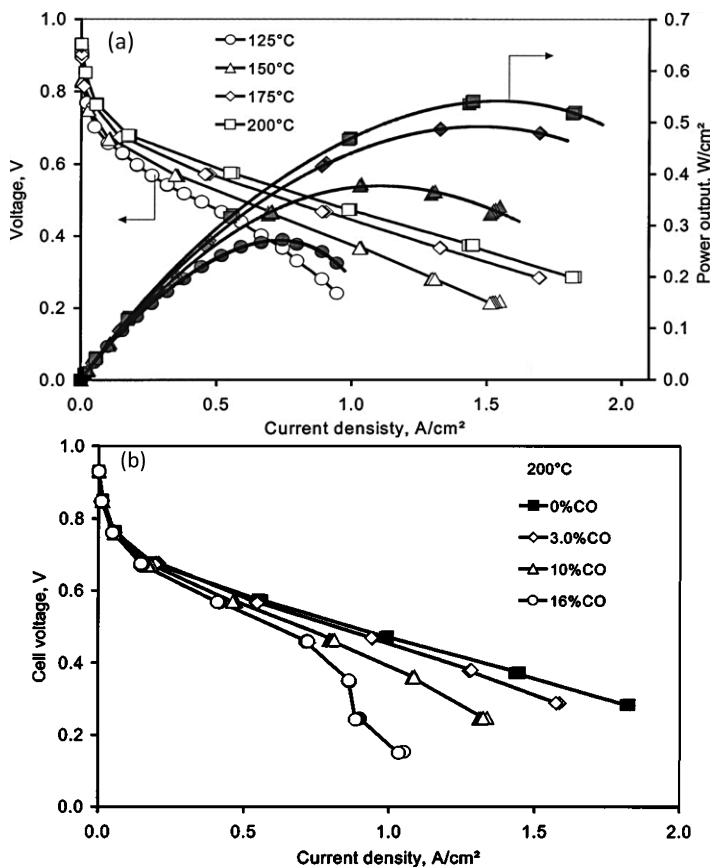


Figure 3. a) Polarization curves of a PBI-based PEMFCs at different temperatures. b) Polarization curves of a PBI-based PEMFC with pure hydrogen and hydrogen containing CO at 200°C. The CO concentrations are indicated in the figure. The working area of the electrodes was 10 cm². The PBI membrane was doped with 5.3 mol H₃PO₄ per repeat unit of the polymer. Oxygen and hydrogen were under atmospheric pressure. Hydrogen flow rate 27 mL min⁻¹ cm⁻². Both anode and cathode were made of carbon-supported platinum catalysts (20% Pt/C) with a platinum loading of 0.5 mg Pt/cm². Reproduced from Ref. 18, Copyright (2003) by permission of The Electrochemical Society.

based PEMFC at several temperatures with hydrogen and hydrogen-CO mixtures.

The challenge for the use of PBI membranes in HTPEMFCs is their long term stability. This is related to various factors^{15,21,45} comprising low molecular weights, mechanical integrity, chemical stability and phosphoric acid retention. In particular the incorporation of high amount of phosphoric acid in order to achieve high conductivity values, results in a highly plasticized membrane with T_g values even below 200°C. Improvements in the aforementioned properties are the focus of much research. Cross-linking of PBI material appears to be a promising method to overcome these issues.^{46,47} In addition the PBI polymer chains are vulnerable to oxidizing species (peroxide radicals), which are formed during fuel cell operation. Experimentally, the ex-situ generation of radicals can be achieved by the Fe^{2+} catalyzed decomposition of H_2O_2 , the so called Fenton test, which can simulate the environment of an operating fuel cell. Under the Fenton test conditions PBI membranes disintegrate chemically thus losing their membrane hypothesis.^{21,46,48} The initial stages of oxidative attack occur preferentially on the amine moieties, the aromatic rings bearing the nitrogen function.⁴⁹

Figure 4 shows a set of durability tests of PBI cells operating under hydrogen and oxygen feeds at ambient pressure.²¹ At temperatures up to 150°C a lifetime of 5000 h has been achieved at a constant cell voltage of 0.5 V. At temperatures above 180°C, the lifetime is very limited. Polymer oxidative degradation (attack by H_2O_2 and hydroxy and/or hydroperoxy radicals) is likely the principal reason of the failure. Therefore, PBI presents serious drawbacks such as moderate mechanical properties and low oxidative stability.

When the feed gas is air, degradation seems to be less pronounced. Acceptable degradation rates in the range of 5–6 μVh^{-1} have been reported with PBI based MEAs^{50,51} under steady-state or dynamic conditions.

In addition, as discussed below, several other factors such as catalyst dissolution and/ or agglomeration^{52,53,54} as well as carbon support corrosion are directly related to the loss of electrocatalytic activity of the electrochemical interface. Zhai et al.⁵⁵ observed that, after a constant current operation for over 500h, the mean particle size of Pt increased from 4.02 to 8.88 nm, indicating that this

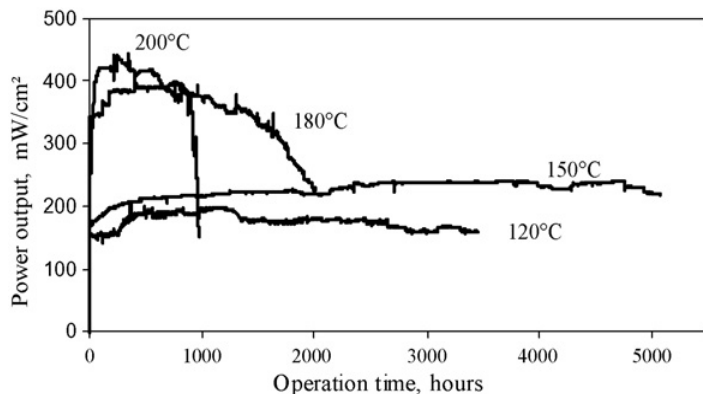


Figure 4. Lifetime test of a PBI cell under continuous operation at a constant voltage 0.5V and different temperatures with hydrogen and oxygen at ambient pressure. The membrane was fabricated from linear polymer with an average molecular weight of about $25,000 \text{ g mol}^{-1}$. Reprinted from Q. Li, J. O. Jensen, R. F. Savinell and N. J. Bjerrum, High temperature proton exchange membranes based on polybenzimidazoles for fuel cells, *Progress in Polymer Science*, **34** (2009) 449-477. Copyright (2009) with permission from Elsevier.

might be the main reason for the early performance loss in PBI cells.⁴⁸ Also Qi and Buelte⁵⁶ found that the cathodic platinum particle size increased by a factor of five under OCV at 180°C after 224 h.

(ii) AB-PBI

There is much work in the literature which is devoted to modifications made on the main chain of PBI.^{50,57,58,59} The properties of the different membranes and most importantly the acid doping level and in consequence the proton conductivity differ with the basicity of the polymer, the amount of imidazole groups, as well as their interspacing in the polymer backbone.

Poly(2,5-benzimidazole) or ABPBI, is another polybenzimidazole derivative that has been investigated as an alternative fuel cell membrane material. ABPBI can result from the polymerization of a single monomer (3,4-diaminobenzoic acid, DABA) in polyphosphoric acid^{60,61} (Fig. 5) or in P_2O_5 -MSA mixture.⁶² The

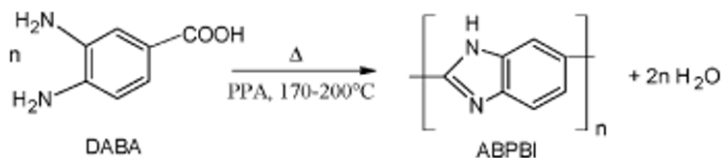


Figure 5. Synthesis of AB-PBI.

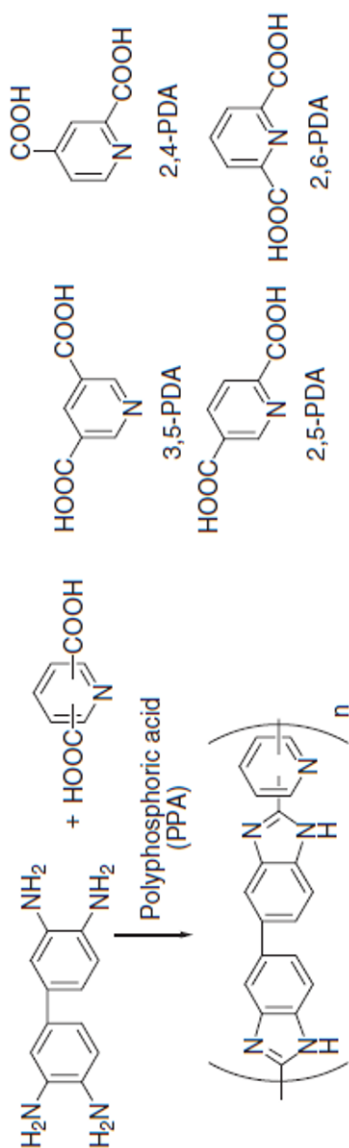
use of only one monomer makes the synthesis less demanding for the purity of the monomers.

Its structure is simpler than mPBI without the connecting phenyl rings and therefore ABPBI has a higher concentration of imidazol rings and consequently of basic sites leading to higher acid uptake.⁶⁰ ABPBI doped with phosphoric acid remained thermally stable at temperatures well above those needed for PEM fuel cells.⁶³ However, a high degradation rate of 20–25 μVh^{-1} under constant load has been reported for MEA incorporating acid doped ABPBI.⁶⁴

(iii) Pyridine-Based Polybenzimidazoles (PPBI)

In order to modify the state-of-the-art PBI structure and consequently its properties, significant effort has been focused on the synthesis of pyridine-based polybenzimidazoles.^{26,39,43,57} A systematic synthesis with different structures was initiated to study the effect of the polymer molecular structure on the final film properties. The substitution of pyridine dicarboxylic acids (PDA) for the iso-/terephthalic acids is particularly interesting, because it increases the number of basic groups in the polymer backbones. The general structure of the series of pyridine-based polybenzimidazole (PPBI) homopolymers from 3,3'-4,4'-tetraaminobiphenyl (TAB) and 2,4-, 2,6-, 2,5- or 3,5-pyridine dicarboxylic acids using the PPA synthetic process is shown in Fig. 6. Monomer purity and accurate stoichiometry are crucial to obtain high molecular weight polymers.

Different diacid monomers give different substitution patterns on the pyridine ring. The incorporation of the extra nitrogen in the polymer backbone significantly improves the solubility of the po-

Figure 6. Synthesis of PPBI homopolymers.²⁶

lymer in PPA and, thus, enhances the polymer processability.²⁶

As expected, the thermal stability of all PPBIs was found to be high ($T_d = 420^\circ\text{C}$ in air). For the preparation of the phosphoric acid doped membranes, a casting procedure from the PPA solution was followed. It is interesting that the PPA membrane properties depend very much on the polymer structures and molecular weight. 2,5-PPBI exhibits the best results giving mechanically strong membranes even at an acid level of 25 mol H_3PO_4 per repeat unit. An example of the ionic conductivity values of 2,5-PPBI is depicted in Fig. 7a. 2,5-PPBI membrane with the high acid doping level of 20.4 exhibited a conductivity of 0.018 S cm^{-1} at room temperature and approximately 0.2 S cm^{-1} at $160\text{--}200^\circ\text{C}$. It was concluded that polymer structure exerted a strong influence on membrane's processing, PA doping levels, and final membrane properties. In Fig. 7b, preliminary fuel cell evaluations are presented.

(iv) *PBI Polymer Blends*

In order to improve the mechanical properties of the mPBI membranes polymer blends of mPBI with other polymers and copolymers were prepared. The polymer mixture combines the properties of the components thus resulting in polymer membranes with tailor made properties regarding their T_g values, mechanical parameters and chemical stability.

(v) *PBI/SPSF Blends*

Blends of PBI with sulfonated polysulfone (SPSF) with different sulfonation degrees have been studied regarding their miscibility, mechanical properties⁶⁵ and doping behaviour.⁶⁶ PBI/SPSF show conductivities higher than acid doped PBI⁶⁷ while they have been tested in fuel cell showing high performance with both pure hydrogen and hydrogen-carbon monoxide⁶⁸ mixtures as depicted in Fig. 8.

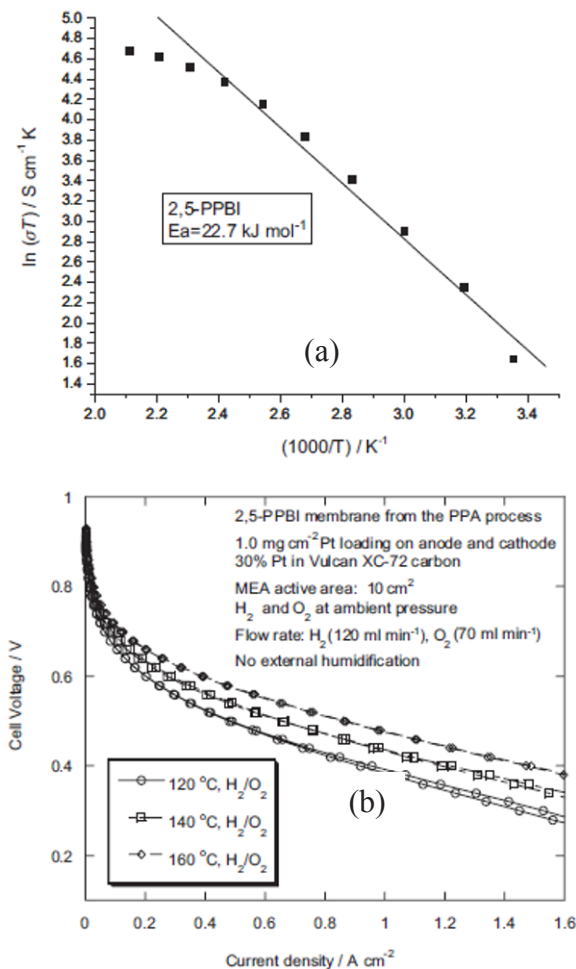


Figure 7. (a) Arrhenius plots and (b) Cell performance of 2,5-PPBI with doping level 20 mol H₃PO₄ per repeat unit. L. Xiao, H. Zhang, T. Jana, E. Scanlon, R. Chen, E.-W. Choe, L. S. Ramamathan, S. Yu, and B. C. Benicewicz: Synthesis and characterization of pyridine-based polybenzimidazoles for high temperature polymer electrolyte membrane fuel cell applications, *Fuel Cells* 5 (2005) 287-295. Copyright (2005) Wiley-VCH Verlag GmbH & Co. KGaA, reproduced with permission.

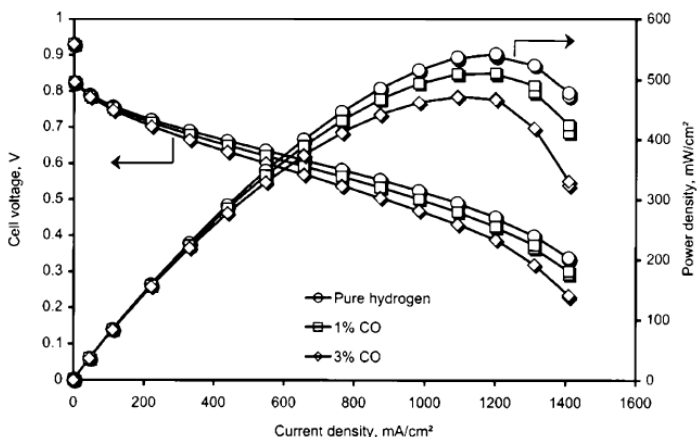


Figure 8. Cell voltage and power density vs. current density of the HT-PEMFC using PBI/SPSF 75/25 doped with 520 mol% H_3PO_4 as the electrolyte under atmospheric pressure at 200°C . Platinum loading on the electrodes 0.45 mg cm^{-2} . Reprinted from Ref. 68, Copyright (2002) by permission of The Electrochemical Society.

(vi) *PBI/PPy(x)coPSF Blends*

In recent years a series of polysulfone copolymers bearing pyridine units in the main chain have been prepared and studied. These copolymers will be described in the following section and their chemical structure can be seen in Fig. 10. Blends of the copolymer I_{50} (Fig. 10), which hereafter will be called PPy(50)coPSF (bearing 50% pyridine), with mPBI have been prepared and studied thoroughly with respect to their miscibility behavior, mechanical properties, their doping ability with phosphoric acid and conductivity values, as well as their thermal and oxidative stability.^{69,70,71}

The mPBI/PPy(50)coPSF 50/50 blend was found to be miscible, with excellent film forming properties and thermal stability ($T_d > 450^\circ\text{C}$), high glass transition temperature value ($T_g > 240^\circ\text{C}$) and high ionic conductivity after doping with phosphoric acid ($> 5 \times 10^{-2} \text{ S/cm}$ at $T > 120^\circ\text{C}$).⁶⁹ The electrolyte has been tested in a *home made* single cell ($2 \times 2 \text{ m}^2$) at temperatures between 140 – 170°C , as depicted in Fig. 9.

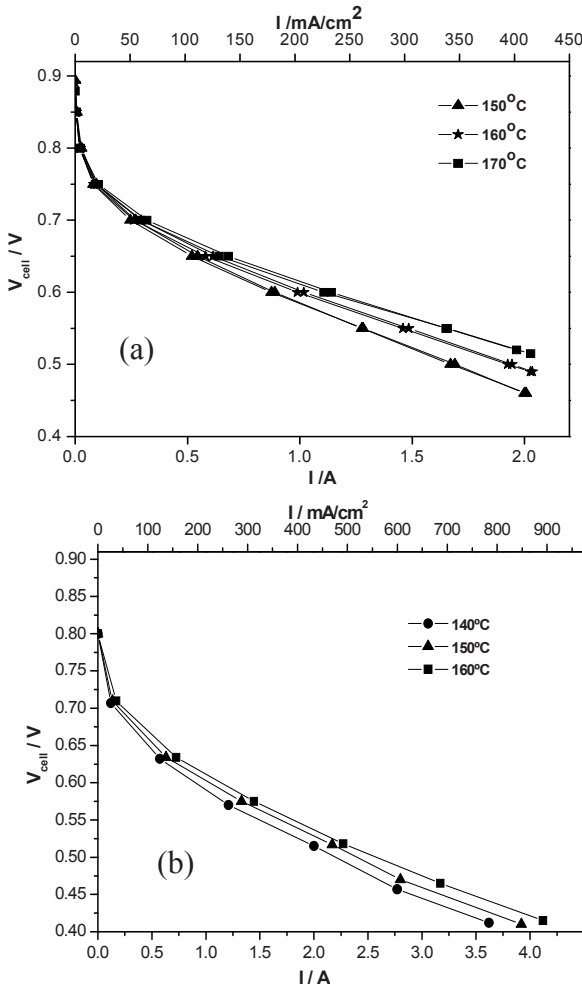


Figure 9. I-V plots at 140–170°C of PBI/PPy(50)coPSPF 50/50. Pt loading on the electrodes 1 mg/cm². Feed: H₂/O₂ 1 bar/1 bar. Electrolyte thickness 70 μ m and acid doping level 180%wt. (a) 1st day, (b) 42nd day of continuous operation.

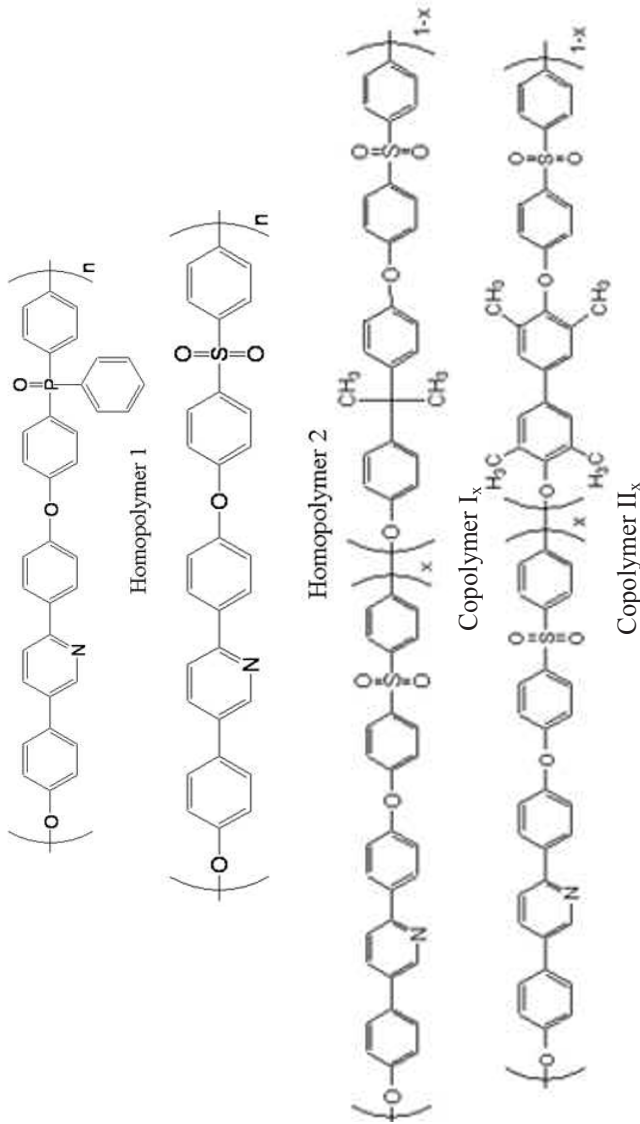


Figure 10. Various chemical structures of aromatic polyethers bearing main chain pyridine units.

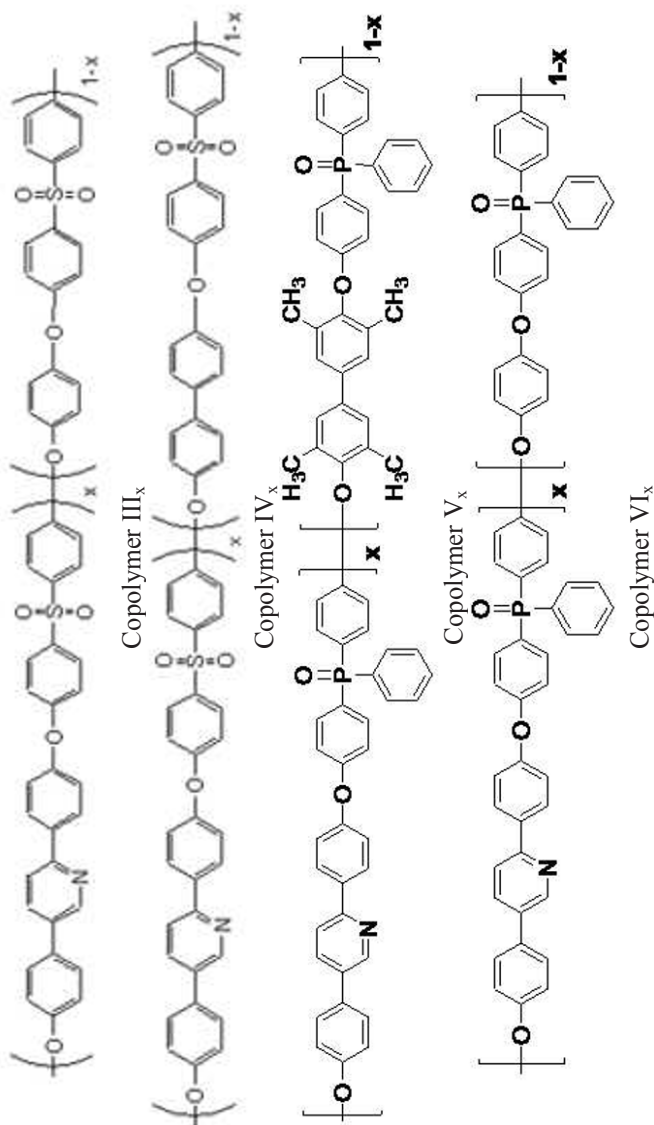


Figure 10. Continuation.

The interesting feature of this new polymer blend is that, in contrast to pure PBI and PBI/SPSF, the miscible PBI/PPy(50) coPSF polymer blends are chemically stable under the highly oxidative Fenton test conditions. In this respect it can be considered as chemically stable under the aggressive oxidative conditions (peroxide species formation at the cathode) under fuel cell operation.

2. Pyridine-Based Aromatic Polyethers

(i) *Synthesis and Characterization*

Pyridine based aromatic polyethers are novel polymer structures that contain polar pyridine groups as main chain linkage in aromatic copolymers.^{69,72,73,74} These polymer structures were designed and synthesized in order to provide functionalities such as high thermal and oxidative stability, mechanical integrity and the ability to form ionically conductive membranes after doping with phosphoric acid. The latter prerequisite is fulfilled by the introduction of the polar pyridine moieties in the main chain that are able to be protonated and moreover to form complexes with strong acids. All the other functionalities can be met by the proper selection of the aromatic polyether structure of the copolymers.

The introduction of polar-pyridine moieties was achieved by the use of the appropriate monomer diol and more specifically 2,5-bis(4-hydroxyphenyl) pyridine,⁷² which combines the rigid oligophenyl main chain structure with the presence of polar pyridine groups. The monomer can be prepared using palladium-mediated cross coupling⁷⁵ of 2,5- dibromopyridine with a properly protected boronic acid.⁷⁶

2,5-bis(4-hydroxyphenyl) pyridine was polymerized using conventional high temperature polycondensation methods while special attention was paid to the polymer solubility and high molecular weight. The diol was combined with either bis(4-fluorophenyl) sulfone or bis(fluorophenyl)phenyl phosphin oxide. It is well known that phosphorus compounds are excellent candidates for thermally stable materials and that is why phosphin oxide groups along with pyridine moieties were selected. The presence of the phosphorus compound plays an important role in the high

performance of thermally stable materials due to its ability to inhibit ignition and promote char formation.⁷⁷ On the other hand, the ability of the phosphin oxide group to interact with phosphoric acid makes these polymers promising candidates for use in high temperature PEM fuel cells. The phosphorus-containing polymers have been synthesized and characterized extensively in order to investigate the improvement of thermal properties and ionic conductivity.^{78,79}

Following this approach, new aromatic polyether materials have been synthesized by nucleophilic polycondensation polymerization.^{72,80} The chemical structures are depicted in Fig. 10. Homopolymer 2 was insoluble in all common solvents giving only oligomers. On the other hand, Homopolymer 1 was soluble, depending on the molecular weight. Film forming polymers with high glass transition temperatures up to 260°C were obtained with high thermal stability and initial decomposition temperatures higher than 450°C.⁷² However, in some cases insolubility problems were encountered mainly in cases where the molecular weights exceeded a certain value.⁸¹

To resolve this problem copolymerization of 2,5-bis(4-hydroxyphenyl) pyridine with various other diols bearing either aliphatic substituents^{69,73} or kinked structures⁸¹ were used. Solubility of the final material depends on the rigid pyridine diol content in the copolymers and its combination with various diols containing side alkyl groups. Consequently, the maximum pyridine percentage reached for each structure differs, with respect to its good solubility and high molecular weights. For lower pyridine content very soluble high molecular weight copolymers were obtained in all cases with excellent film forming properties. The maximum pyridine percentage reached for each structure can be seen in Table 2, where also the physicochemical properties of the synthesized copolymers are depicted.

As it is shown in Table 2, high molecular weight polymers with high glass transition temperatures in the range of 180–280°C and high decomposition temperatures (400–500°C) were obtained. An example of the analysis that took place (DMA and TGA) for Copolymer III, where the percentage of pyridine groups in the main chain was 50% and $M_n = 89000$, is presented in Fig. 11.

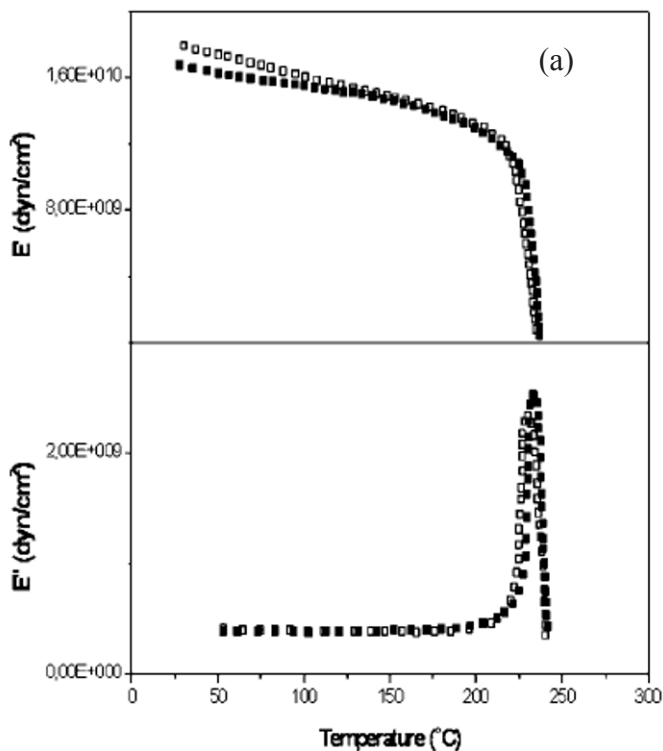


Figure 11. (a) Temperature dependence of the storage (E') and loss (E'') modulus and (b) Thermogravimetric analysis for Copolymer III₅₀ ($M_n=89000$) before (■) and after (□) the Fenton test. Reprinted with permission from M. Geormezi, V. Deimede, N. Gourdoupi, N. Triantafyllopoulos, S. Neophytides and J. K. Kallitsis, *Macromolecules* **41** (2008), 9051-9056. Copyright (2008) American Chemical Society.

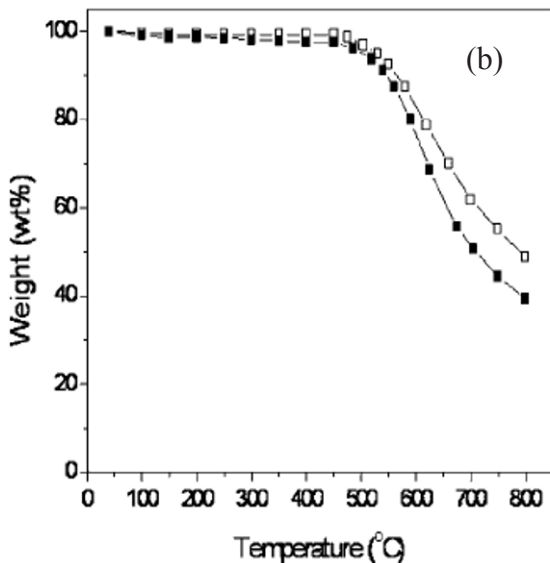


Figure 11. Continuation.

Table 2
Maximum Pyridine Percentage Achieved, Physicochemical Properties, and Maximum Doping Level Reached at Doping Temperature 100–120°C for Copolymers I–VI.

Copolymer	Max Py (%) ^a	Mn ^b	T _g (°C)	Oxidative stability ^c	T _d (°C)
I ⁶⁹	60	90000–130000	180–210	✓	450
II ⁷³	70	60000–70000	280	✓	400
III ⁷⁴	75	60000–115000	230	✓	470
IV ⁷⁴	60	27000–41000	245	✓	470
V ⁸²	80	70000–80000	260–270	✓	460
VI ⁸²	90	41000–47000	260	✓	500

^a Maximum pyridine percentage achieved while keeping the high molecular weights and good solubility in organic solvents.

^b from SEC using CHCl₃ as eluent, UV detector and PS standards.

^c As tested through the Fenton test.

^d Maximum doping level reached at doping temperature 100–120°C while keeping the excellent mechanical integrity of the membrane.

At the same time, the oxidative stability of the membranes is exceptionally good in all cases. Fenton test was performed in order to test the oxidative stability of these new materials, given the aggressive environment of an operating fuel cell.^{23,83} To ensure long term stability of the new membranes, study of the possible degradation mechanism caused by radicals such as $\text{HO}\cdot$ and $\text{HO}_2\cdot$ must be performed. Generation of oxygen containing radicals, in order to test the membrane stability towards these species, can be achieved by the degradation of H_2O_2 catalysed by Fe^{+2} . Though it is very difficult to relate ex situ tests to the real in situ conditions in an operating fuel cell, such an evaluation is important for screening purposes of the properties of the membrane. All membrane samples treated with hydrogen peroxide remained unchanged with respect to their structure and molecular weights^{80,82} as was proven with ^1H -NMR, Raman and SEC.

Figure 12 shows the ^1H -NMR spectra for Copolymer V, where $x = 0.6$, before and after the treatment with hydrogen peroxide in the presence of ferrous ions. SEC did not reveal any decrease in the molecular weight after the treatment even for Copolymer V with relatively low molecular weight, $M_n = 38000$, intentionally chosen for this study, as is depicted in the inlet of Fig. 12. Moreover, as is also evident from Fig. 11, the mechanical and thermal properties,^{69,73,74,80,81,82} tested by means of DMA and TGA respectively, remained unaffected proving their high resistance against oxidation under the harsh oxidative environment of the Fenton test.

(ii) *Impregnation with Phosphoric Acid*

In order to assure high ionic conductivity, copolymers must be able to be doped with strong acids like H_3PO_4 to a certain extent. The pyridine ring can react and be protonated by H_3PO_4 . This was demonstrated by means of FT-IR and FT-Raman spectroscopy. In particular, a blue shift from 1593 cm^{-1} to 1608 cm^{-1} of the absorption peak of the pyridine group in the Raman spectrum was observed upon doping with H_3PO_4 ⁷² and a new peak appears at 1630 cm^{-1} which is attributed to the $(\text{C}=\text{N})$ vibration of the protonated pyridine ring of the polymer.

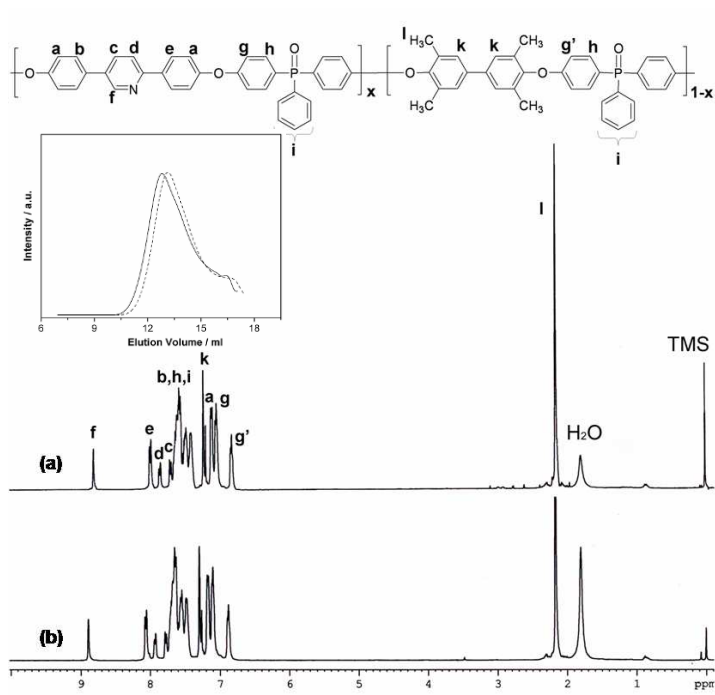


Figure 12. ^1H NMR of Copolymer V_{60} ($M_n = 38000$) with the assignment of the respective peaks in CDCl_3 (a) before and (b) after the Fenton test. Inlet: size exclusion chromatography for Copolymer V using CDCl_3 as eluent before (solid line) and after the Fenton test.⁸²

The doping behavior of these copolymers after immersion in 85 wt.% phosphoric acid at various doping temperatures was also studied. In Table 3, the number of polar groups per repeat unit and the maximum doping level reached for each copolymer are presented. Doping level depends on the doping time and temperature. The maximum doping levels discussed here are those reached for high doping temperatures (100–120°C). Depending on the structure, different doping times are needed in order to reach these values. Some of the materials studied (i.e., Copolymer V) could be further doped. Table 3 shows the doping levels achieved while maintaining morphological stability and mechanical integrity.

The acid uptake leading to full protonation of the pyridine groups is expected to be directly proportional to the amount of the polar groups and as shown in Table 3 is significantly less than the final doping level of the polymer films. Certainly this low doping level is not sufficient to lead to high proton conduction values. The high proton conductivity is further on facilitated by the excess amount of acid beyond the primary protonation, which through hydrogen bonding forms a continuous network for the proton conductivity. The retention of the excess phosphoric acid can be significantly affected by the content of pyridine groups and the chemical structure of the macromolecules.^{69,72,80,81}

As shown in Table 3 higher doping level is generally achieved with increasing pyridine content in the polymer chain. The existence of other groups interacting with phosphoric acid like phosphin oxide groups, as well as the organization of the acid-rich domains and the morphology formed upon doping can influence the final acid doping level of the materials. Moreover, other influencing factors can be the rigidity of the structure and the intermolecular bonds. The SEM images of Fig. 13 show the morphology of the doped and undoped membrane of copolymer II of Fig. 10. The doped membrane is composed of nanoclusters of 100nm rather indicating phase separation during the doping procedure.

Table 3
Number of Pyridine Groups per Repeat Unit and Maximum Doping Level Reached at Doping Temperature 100-120°C for Copolymers I-VI.

Copolymer I _x	No Py/ru	DLmax (%wt) ^a		$n_{H_3PO_4}/p.u$ ^b
I ₅₀ ⁶⁹	0.5	125	106	10
I ₆₃ ⁶⁹	0.63	180	153	11.5
II ₆₀ ⁷³	0.6	220	187	14.9
III ₅₀ ⁷⁴	0.5	240	204	16.6
III ₆₀ ⁷⁴	0.6	265	225	15.9
IV ₅₀ ⁷⁴	0.5	220	187	16.7
V ₈₀ ⁸²	0.8	350	297	19.7
VI ₈₀ ⁸²	0.8	240	204	13.2
VI ₉₀ ⁸²	0.9	260	221	13.1

^a First column corresponds to 85% H₃PO₄ and the second to pure H₃PO₄ content.

^b mol H₃PO₄ per polar-pyridine group for the maximum doping level.

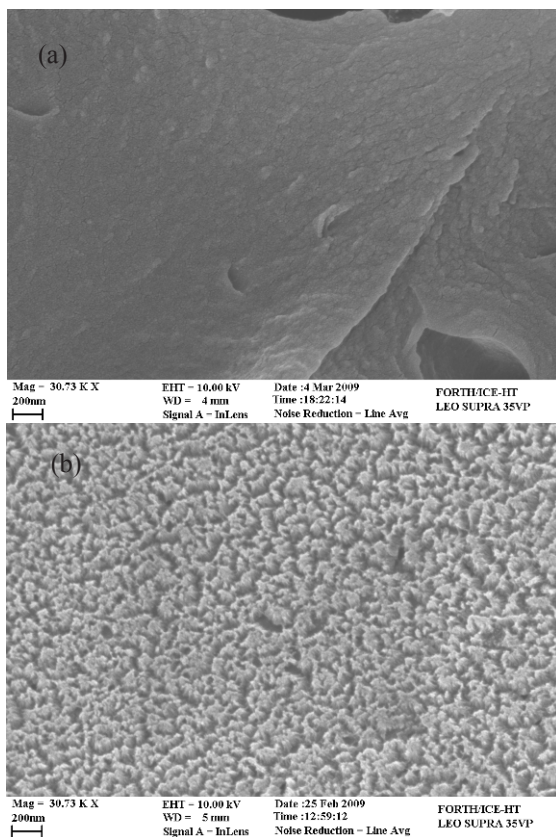


Figure 13. SEM images of (a) undoped and (b) H₃PO₄ doped co-polymer II₆₀ of Fig. 10.

It is important to note that for each polymer membrane there is an optimum range of acid uptake combining high conductivity values and good mechanical properties in order to be used in PEMFCs. This is also the case for acid doped mpBI prepared with the conventional way, doping of the membrane by immersion in phosphoric acid solutions. Qingfeng et al.⁴⁴ reported an optimum range of doping levels around 3.5 to 7.5 mol/r.u (112–280 %wt H₃PO₄ 85%).

The measurement of the ionic conductivity of the acid-doped membranes was carried out by means of four-probe current interruption technique.⁶⁶ As will be also discussed later in general proton conduction is strongly enhanced by humidity, temperature and acid doping level. The latter is presented in Fig. 14a, where conductivity values of Copolymer III₅₀ doped at different levels at room temperature are depicted. This is a characteristic behavior for all Copolymers. The interesting feature is that ionic conductivity of the imbibed membranes depends not only on the doping ability of the polymeric material but also on the physicochemical properties of the polymer matrix, such as chemical structure and most probably chain conformation and film morphology.^{80,82} An example is presented in Fig. 14b, where the temperature dependent conductivity measurements for several materials, Copolymers II₆₀, V₈₀ and VI₉₀ with doping levels 190, 200 and 270 wt.% respectively, are depicted.

All Copolymer showed very good behavior above 140°C, possessing values in the range of 10^{-2} S/cm. Copolymer V depicted higher conductivity values throughout the whole range of acid uptakes and temperatures compared to copolymer VI, indicating the significance of the structure and after doping conformation of the material on the proton conduction mechanism. The two materials differed, not only on the conductivity values, but also on the conductivity dependence on temperature.

The main difference in the chemical structure of copolymers V and VI is the introduction of methyl groups in the tetramethyl biphenol moiety in polymer V (Fig. 10). As it is shown in Fig. 14b the introduction of the methyl groups seems to affect significantly the proton conductivity. It is worth noticing that copolymer V in Fig. 10 bearing the methyl groups is in general more soluble.^{74,82} The positive effect on conductivity can be rather realized through an intense phase separation, thus enabling the creation of more efficient proton conducting pathways in the doped membrane. This can be attributed to the hydrophobic nature of the methyl group in combination to the polar pyridine groups that have high affinity for the phosphoric acid.

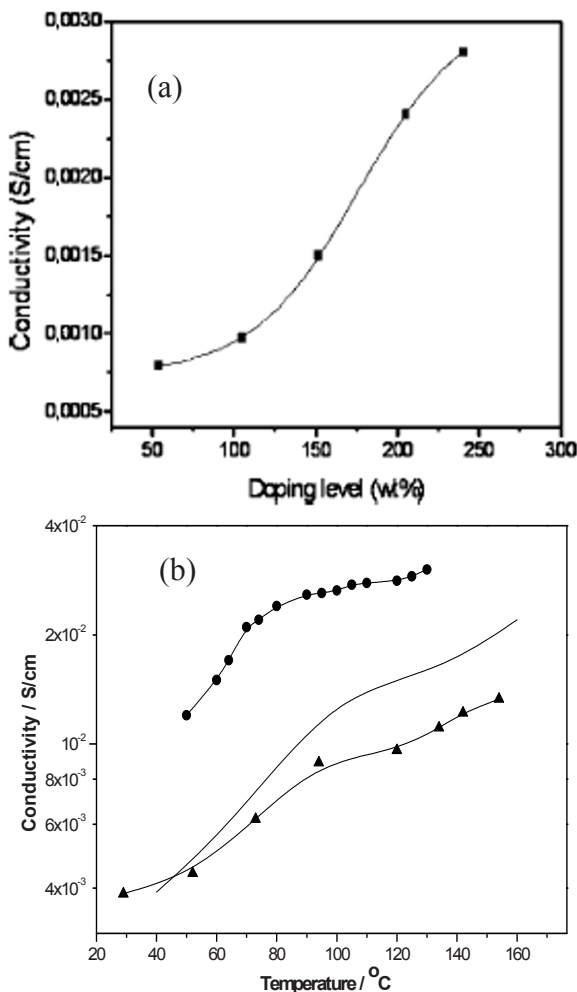


Figure 14. (a) Doping level dependence of ionic conductivity of copolymer III₅₀ at room temperature.⁷⁴ (b) Temperature dependence of ionic conductivity of acid doped Copolymers II₆₀ (-▲-) (acid doping level 190 wt.%), V₈₀ (-●-) (acid doping level 200 wt.%), and VI₉₀ (-■-) (acid doping level 270 wt.%). Anhydrous conditions.^{73,82} Copolymers are shown in Fig. 10.

(iii) *Fuel Cell Performance with Pyridine Containing Aromatic Polyethers*

The aforementioned polymeric electrolytes have been effectively used in polymer electrolyte fuel cells operating up to 200°C.^{74,80,84} In order to study the single cell performance and apart from the high ionic conductivity of the membrane, several parameters regarding the MEA construction must be taken into account in order to have optimum performance of the cell. Some of these parameters are the amount of the catalyst⁸⁵, the ionomer-binder used at the electrodes⁸⁶ and its percentage,³⁵ electrode surface and the preparation method,^{87,88,89} pressure and the temperature of the MEA assembling and design and construction parameters of the cell.^{90,91}

An example of the cell performance obtained for this category of polymer electrolytes is given in Fig. 15, where the polarization curve of a fuel cell operating at 180°C using hydrogen and air dry gases with stoichiometric flow rates at anode and cathode is depicted. Copolymer II_x (x = 60, Fig. 10) was formulated into MEAs.

IV. THE EFFECT OF STEAM ON THE PHYSICOCHEMICAL AND ELECTROCHEMICAL PROPERTIES OF THE MEMBRANES

1. Gas and Water Permeability

One of the frequently advertised advantages of the phosphoric acid imbibed polybenzimidazole systems is their zero water drag coefficient and their possibility to operate with dry hydrogen and oxygen. However, a vast literature has been devoted to the study of the proton conduction and the effect of relative humidity on the conductivity of the PBI-phosphoric acid system.^{20,29,92,93} The promoting effect and the physicochemical interactions of water vapors with the polymer electrolyte and on the fuel cell performance have been explicitly shown for the PBI/PPy(50)coPSF 50/50 polymer blend imbibed with phosphoric acid under fuel cell conditions.⁹⁴

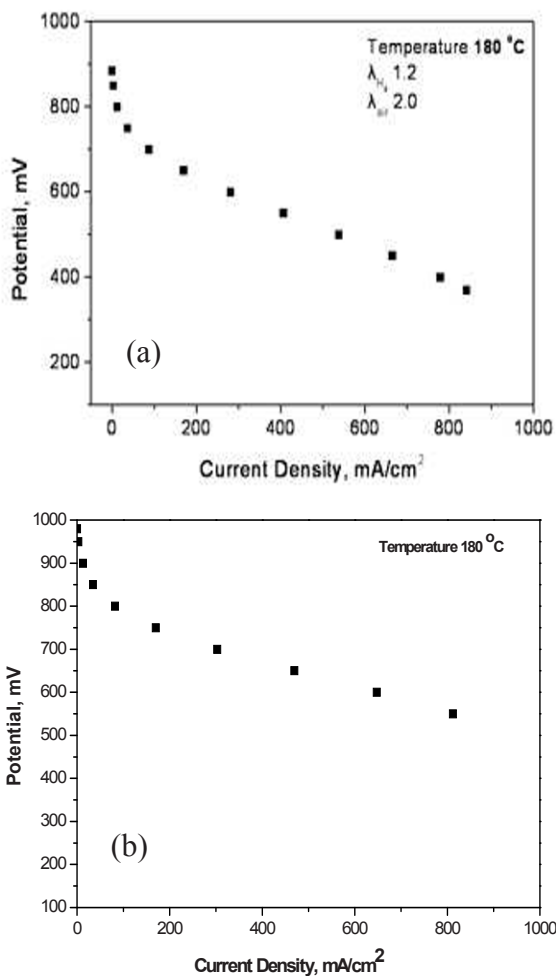


Figure 15. I-V curves of MEA based on copolymer II (Fig. 10) at 180°C with (a) H₂ and air feeds (λ_{H_2} : 1.2, λ_{air} : 2.0) and (b) H₂ and O₂ feeds at ambient pressure (λ_{H_2} : 1.2, λ_{O_2} : 1.5). The doping level and thickness of the imbibed membrane is 180 wt% and 80 μ m respectively. The active surface area of the electrode was 25 cm² and Pt loading 0.9 mg/cm².

The main emphasis was given on the understanding of the proton conduction mechanism and the effect of water vapor on the fuel cell performance. Though, it is generally accepted that the proton transfer mechanism is similar to that of concentrated phosphoric acid, however as has already been stated, the polymer matrix plays a significant role in the imbibed polymer electrolyte. The deeper insight on the proton conduction mechanism will allow for the optimum adjustment of the operating conditions and the modification or design of new materials towards the improvement of their properties and increase of the high temperature PEM fuel cell performance.

2. Steam Permeability through the Polymer Electrolyte: Hydration of the PBI/PPy(50)coPSF Membrane

One of the main role of a polymer electrolyte membrane is the efficient separation of the reacting (H_2 and O_2) gases. The membrane should possess the lowest possible permeability of gases. Figure 16 depicts a gas permeability experiment under fuel cell conditions at atmospheric pressure and $150^\circ C$ for the PBI/PPy(50)coPSF 50/50 polymer blend imbibed with phosphoric acid.⁹⁴ At a certain time as indicated in Fig. 16 different gases (H_2 , O_2 , He, H_2O) were introduced in the one compartment of the fuel cell with flow rate 80cc/min e.g., anode, while their QMS signal was monitored at the outlet of the other compartment (e.g., cathode) where 10 cc/min Ar, molar flow rate $F_{Ar} = 7.4 \times 10^{-6}$ mol/s was flowing. In this respect the permeated gases, from the anode to the cathode chamber, through the PBI/PPy(50)coPSF 50/50 membrane, could be detected at the outlet of the cathode chamber of the cell.

Within the sensitivity limits ($< 2 \times 10^{-16}$ mol cm cm⁻² s⁻¹ Pa⁻¹) of the instrument used in the study of Ref.94, the reacting gases permeability of the acid doped PBI/PPy(50)coPSF 50/50 membrane was not detectable, even for H_2 , in the temperature range of 130–170°C. It is also well known that oxygen solubility is very low in phosphoric acid systems (0.5×10^{-11} mol cm⁻³ Pa⁻¹)^{95,96} and below the detection limits of the present technique.

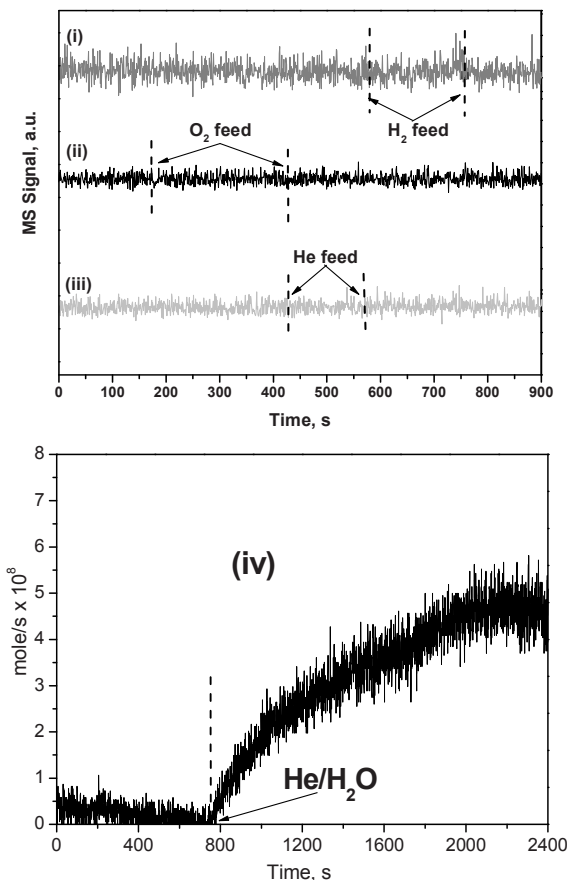


Figure 16. Gas permeability experiment for the PBI/PPy(50)coPSF 50/50-H₃PO₄ electrolyte at 150°C. Acid doping level: 200%wt. Membrane thickness: 70 μ m. (i) H₂, (ii) O₂, (iii) He and (iv) H₂O signals recorded by the mass spectrometer connected to the outlet of the one compartment of the cell. The dash lines show the time intervals during which the respective gases were fed through the other compartment of the cell. The partial pressures of the fed gases to the cell are: P_{H_2} =100kPa, P_{O_2} =100kPa, P_{He} =100kPa and P_{H_2O} =4.3kPa. Reprinted from M. K. Daletou, J. K. Kallitsis, G. Voyiatzis and S. G. Neophytides, The interaction of water vapors with H₃PO₄ imbibed electrolyte on PBI/polysulfone copolymer blends, *Journal of Membrane Science*, **326** (2009) 76-83, Copyright (2009), with permission from Elsevier.

There are many reports on the permeability of hydrogen and/or oxygen gases through pristine PBI,^{97,98} liquid phosphoric acid⁹⁹ as well as through acid doped PBI membranes.^{97,100} The non detected permeability of the reacting gases in the aforementioned⁹⁴ work is in contrast to other reported observations, where hydrogen permeability values as high as $3.0 \times 10^{-15} \text{ mol cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ were reported for the case of acid doped PBI membranes.⁹⁷ However large differences in oxygen permeability have been reported by He et al.⁹⁷ and Liu et al.¹⁰⁰ who used the two chamber cell and the micro-band electrode cell techniques, respectively. In the case of Ref. 97 oxygen permeability values as high as $8.0 \times 10^{-16} \text{ mol cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ were reported, while a value two orders of magnitude lower ($9.6 \times 10^{-18} \text{ mol cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) was reported by the authors of Ref. 100 for PBI doped with 6 moles of phosphoric acid per repeat unit at 150°C. The lower values reported by Liu et al. are comparable with the corresponding values reported for 95 wt% phosphoric acid and they concluded that the oxygen diffusivity, solubility and consequently permeability are related to the amorphous (non bounded) phosphoric acid in the polymer matrix. This essential difference can be rather attributed to the experimental technique used to carry out the permeability measurements.

As can be seen in Fig. 16, only water permeates through the membrane though the size of the water molecule is bigger than that of the other gases. This fact strongly indicates that the void volume of the polymer membrane is negligible, thus not permitting the crossover of the smaller gases. Therefore, the crossover mechanism of water cannot be interpreted by considering a diffusion process through the void volume of the polymer membrane.

The acid doped polymer absorbs and retains varying amounts of water at different temperatures. The effect of temperature as well as water partial pressures is explicitly shown by the TGA experiment depicted in Fig. 17. Initially the membrane was stabilized in all cases at 95°C under dry Ar flow, so that the free water was evaporated. Hereafter the temperature was raised and was maintained constant as several H₂O/Ar mixtures were fed over the membrane. The mole fraction of water in the feed gas increased gradually and remained constant at certain values for short periods, while the change in membrane weight was simultaneously recorded.

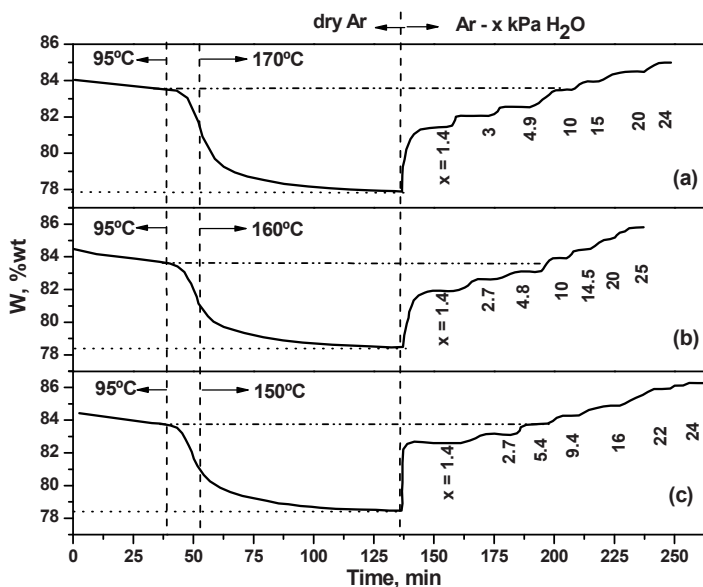


Figure 17. Thermogravimetric analysis of PBI/PPy(50)coPSF 50/50-H₃PO₄ with initial doping level DL = 180%wt under dry Ar and Ar-H₂O atmospheres at varying water partial pressures P_{H_2O} . (a) 170°C, (b) 160°C, and (c) 150°C. Reprinted from M. K. Daletou, J. K. Kallitsis, G. Voyiatzis and S. G. Neophytides, The interaction of water vapors with H₃PO₄ imbibed electrolyte on PBI/polysulfone copolymer blends, *Journal of Membrane Science*, **326** (2009) 76-83, Copyright (2009) with permission from Elsevier.

In accordance to Wainright et al.²⁹ the loss of weight at temperatures exceeding 120°C under dry conditions can be attributed to the dehydration of H₃PO₄ and the formation of H₄P₂O₇ according to reaction (1):



As shown in Fig. 17 by exposing the membrane to water vapors the material gradually absorbed water and the initial membrane weight at 95°C was recovered. Thus it is concluded that the dimerization of phosphoric acid is a fully reversible process. At higher temperature the initial weight of the membrane was recov-

ered at higher water partial pressure. At even higher water partial pressures excess water was being absorbed.

Steam can penetrate through the electrolyte and be retained in the membrane at different levels depending on temperature and humidity due to the high solubility of water in phosphoric acid and its chemical interaction with pyrophosphoric acid according to reaction (1). These two processes can be observed in Fig. 18 where the weight variation of the phosphoric acid doped membrane is plotted as a function of water partial pressure based on the results of the TGA experiment depicted in Fig. 17. Two regions (I and II) can be distinguished in Fig. 18. At lower water partial pressure (region I) a large amount and non linear water uptake is observed denoting the reformation of phosphoric acid by the reverse reac-

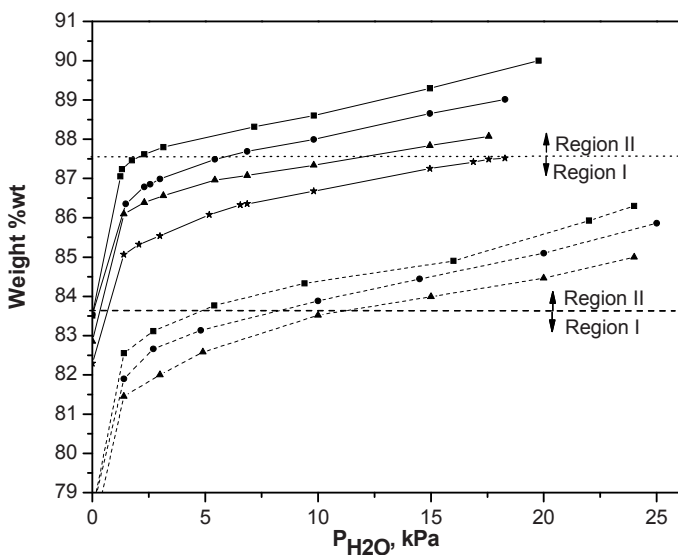
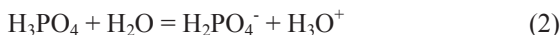


Figure 18. The effect of water vapor partial pressure (P_{H_2O}) on the weight of PBI/PPy(50)coPSF 50/50-H₃PO₄⁹⁴ with initial doping level DL = 180%wt at (---■---) 150°C, (---●---) 160°C and (---▲---) 170°C and Copolymer II₆₀ (Fig. 9) with initial doping level DL = 230%wt at (---■---) 150°C, (---●---) 160°C, (---▲---) 170°C and (---★---) 180°C. The dash and dotted lines corresponds to the weight of the doped blend membranes at 95°C (see Fig. 17) imbibed with 100% H₃PO₄.

tion of water with pyrophosphoric acid, reaction (1). Further increase in P_{H_2O} (region II) results in water uptake above the recovered weight of the membrane, which varies linearly with P_{H_2O} and can be attributed to the solubility of water in phosphoric acid:



The same experiment was carried out for Copolymer II_x ($x = 60$, Fig. 10) in order to investigate the effect of the polymer matrix of the acid doped samples on the hydration of the content phosphoric acid and the retention of water under specified conditions. In this case also, the two regions are distinguished as can be seen in Fig. 18. Above the border line in regions II the hydration level of the system can be defined as:

$$HL = (\text{mol } H_2O \text{ absorbed}) / (\text{mol } H_3PO_4 \text{ in the membrane})$$

In Fig. 19 the HL is plotted against P_{H_2O} for both H_3PO_4 doped PBI/PPy(50)coPSF blend and Copolymer II₆₀.

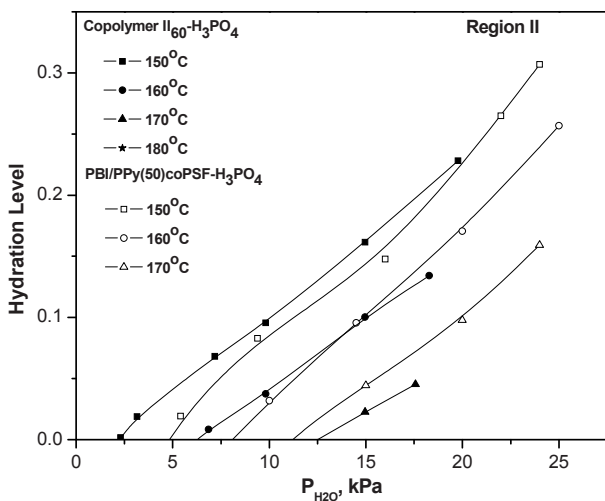


Figure 19. Region II (Fig. 18) presented in terms of hydration level defined as 'mol H_2O /mol H_3PO_4 .'

The enthalpy of hydration can be determined from the slope of $\ln(1/P_{\text{H}_2\text{O}})$ versus $1/T$ plots at constant weight (Fig. 18) or at constant hydration level Fig. 19. The various $P_{\text{H}_2\text{O}}$ values were extracted from Fig. 18 at 100% H_3PO_4 i.e., at the border line between regions I and II of Fig. 18. For the sake of comparison, corresponding values of liquid phosphoric acid are shown based on gravimetric experiments from Ref. 101.

The $\ln(1/P_{\text{H}_2\text{O}})$ versus $1/T$ is plotted in Fig. 20 for acid concentration around 100% and for all three acid doped PBI/PPy(50)co PSF 50/50, Copolymer II₆₀ and for liquid phosphoric acid.¹⁰¹ The resulting hydration enthalpies are shown in Table 4. The hydration enthalpy depends significantly on the chemical structure of the polymer matrix and differs from that of pure phosphoric acid. The H_3PO_4 doped Copolymer II₆₀ shows the highest hydration enthalpy values compared to the other two systems showing strong interaction with the water molecules.

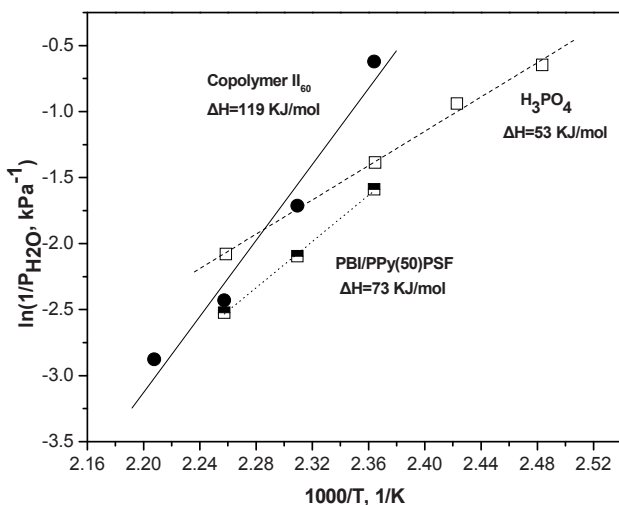


Figure 20. Van't Hoff diagrams, $\ln(1/P_{\text{H}_2\text{O}})$ versus $1/T$, at various hydration levels derived from Fig. 19. Phosphoric acid data are from Ref. 101. All data correspond to 100% H_3PO_4 concentration both in the membrane and in free H_3PO_4 solution of Ref. 101. Solid symbols for Copolymer II₆₀, open symbols for liquid H_3PO_4 and crossed open symbols for PBI/PPy(50)PSF.

Table 4
Hydration Enthalpies of Acid Doped Membranes and Liquid Phosphoric Acid at 100% H₃PO₄.

CH ₃ PO ₄ wt. %	Hydration level mol H ₂ O/mol H ₃ PO ₄	Enthalpy of hydration $-\Delta H$ kJ/mol		
		Copolymer II ₆₀	PBI/PPy(50)coPSF	H ₃ PO ₄
100	0	119	72.7	53

In all cases, the values of hydration enthalpy of the acid doped polymers reported in Table 4 are many times higher than those reported for phosphoric acid in other references.^{102,103,104,105} This fact strongly suggests the positive effect of the polymer matrix on the ability of the membrane/ phosphoric acid system to absorb and retain water.

The latter argument strongly implies the positive role of the polymer matrix on the strong interaction of water with the H₃PO₄. This strong interaction, as will be discussed below plays a major role in the proton conductivity of the H₃PO₄/membrane polymer electrolyte.

3. Steam Effect on Cell Performance

The experiment depicted in Fig. 21 represents real fuel cell operating conditions and shows how the water formed at the cathode contributes to the improvement of the performance of the cell. The transient evolution of the anode gases concentration was recorded upon cell potential application of -500 mV. As expected, on fuel cell operation ($t = 1570$ s) hydrogen is progressively consumed approaching steady state. Interestingly, the residual water signal is observed to increase approaching a constant value. In accordance to the permeability experiment of Fig. 16 the water increase at the anode compartment during fuel cell operation originates from the water produced at the cathode. It can penetrate through the polymer electrolyte and evolve at the anode compartment. In addition, the transient evolution of the water signal is followed by the corresponding increase in hydrogen conversion and cell current, thus indicating the direct effect of water transport through the membrane on the fuel cell performance.

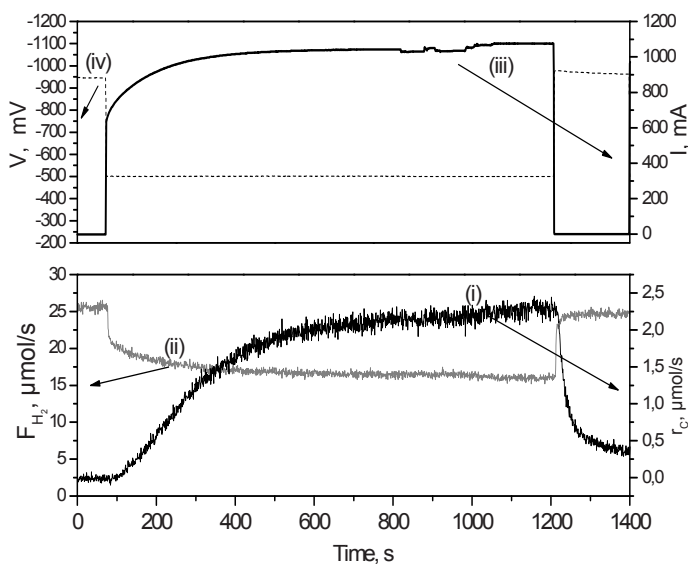


Figure 21. The transient evolution of (i) H_2O and (ii) H_2 flow rates at the anode outlet and (iii) current I upon (iv) voltage application of $V_{\text{cell}} = -0.5\text{V}$. Electrolyte: PBI/PPy(50)coPSF 50/50. Doping level: 200%wt. Membrane thickness: $70\mu\text{m}$. The anode/cathode feed gas composition was dry H_2 30%-Ar/ O_2 . Reprinted from M. K. Daletou, J. K. Kallitsis, G. Voyiatzis and S. G. Neophytides, The interaction of water vapors with H_3PO_4 imbibed electrolyte on PBI/polysulfone copolymer blends, *Journal of Membrane Science* **326** (2009) 76-83, Copyright (2009) with permission from Elsevier.

The positive effect of water on the fuel cell performance was further proven by introducing several $\text{H}_2\text{O}/\text{H}_2$ mixtures into the anode compartment. I-V curves were recorded for each water vapor partial pressure as shown in Fig. 22.⁹⁴ I-V curves were recorded fast, within a time interval less than 30 s, so that the water produced at the cathode would not equilibrate with the membrane. It is evident in Fig. 22 that by increasing the water partial pressure a threefold increase of the cell performance is observed, thus proving the vital importance of steam for the efficient operation of the phosphoric acid imbibed high temperature MEA.

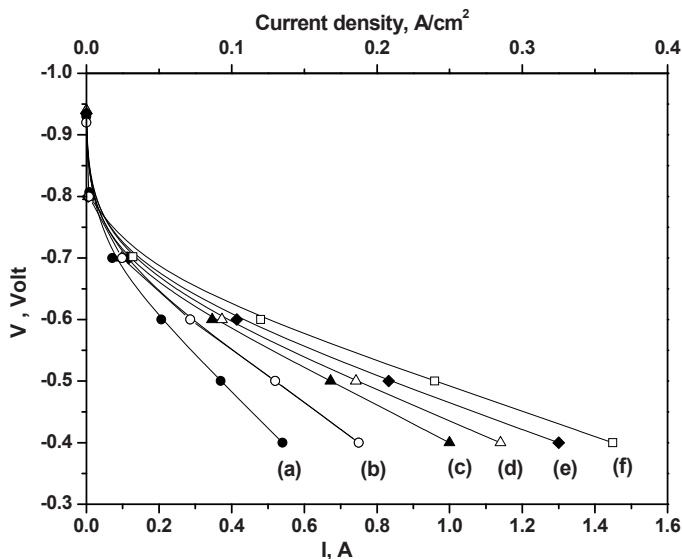


Figure 22. I-V curves at 150 °C under (●-) 0.14, (○-) 0.23, (▲-) 1.3, (△-) 2.15, (◆-) 4.52, (□-) 8.12 kPa P_{H_2O} at the anode feed gas. Electrolyte: PBI/PPy(50)coPSF 50/50. Doping level: 200%wt. Membrane thickness 140 μ m. Anode fed with H_2 /He/ H_2O ; Cathode fed with O_2 ; total pressure in both compartments 1 bar. Reprinted from M. K. Daletou, J. K. Kallitsis, G. Voyiatzis and S. G. Neophytides, The interaction of water vapors with H_3PO_4 imbibed electrolyte on PBI/polysulfone copolymer blends, *Journal of Membrane Science*, **326** (2009) 76-83, Copyright (2009) with permission from Elsevier.

Though water vapor plays a significant role in the fuel cell performance, the humidification of H_2 and O_2 is not necessary under fuel cell operating conditions. The water vapors produced at the cathode compartment are enough for the humidification of the membrane by the back-transport process from the cathode to the anode compartment of the cell (Fig. 21), thus affecting the ionic conductivity of the membrane electrolyte and, as shown below, on the polarization of the electrode/electrolyte interfaces.

4. Steam Effect on Conductivity

The proton conductivity of the H_3PO_4 imbibed PBI systems has been investigated by several groups. Steam presence was shown to have a positive effect on proton conductivity. Examples of the proton conductivity values recorded at different temperatures and relative humidity can be seen in Fig. 23.^{20,92} The proposed conductivity mechanism is proton migration from an imide site assisted by the counter anion and through the acid network based on the Grotthuss mechanism.^{20,30,106}

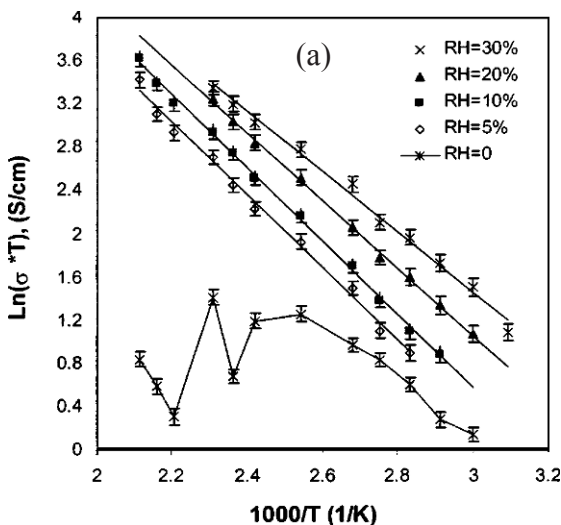


Figure 23. a) Temperature dependence of ionic conductivity of acid-doped PBI with doping level 6 moles $\text{H}_3\text{PO}_4/\text{ru}$. Reproduced from Ref. 20 by permission of The Electrochemical Society. b) Conductivity vs. Relative Humidity for Nafion® 117 and acid doped PBI membranes at a H_3PO_4 doping level of 5.6 moles $\text{H}_3\text{PO}_4/\text{ru}$. (a) Nafion® 117, 50°C; (b) PBI, 80°C; (c) PBI, 140°C; (d) PBI, 200°C. Reprinted from R. He, Q. Li, G. Xiao and N. J. Bjerrum, Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic proton conductors, *Journal of Membrane Science*, **226** (2003) 169-184. Copyright (2003) with permission from Elsevier.

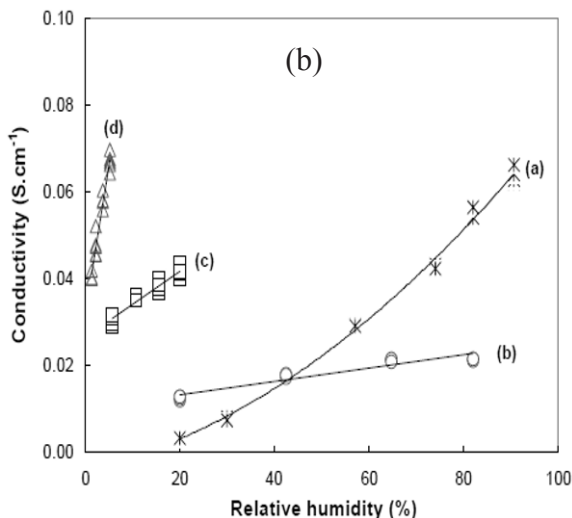


Figure 23. Continuation.

AC impedance spectroscopy was used to measure the ionic conductivity of the membrane and polarization resistance of the electrodes in a through plane configuration. The measurements were carried out in the 4-probe mode so that the connecting wires contact resistances were not included in the ionic resistance of the electrolyte. In general the ionic resistance of the electrolyte, R_{el} , was determined by the high frequency intersection of the Nyquist plot with the real axis, while the polarization resistance of the electrodes, R_p , was calculated using the segment on the real axis between the high and low frequency intersections. Both sides of the MEA were exposed to the same flowing H_2 -He- H_2O gas mixture.

Figure 24 shows a typical set of AC impedance spectra. The water content varied from 0–12 kPa. Both the resistance of the electrolyte and the polarization resistance of the electrodes/electrolyte interfaces decrease with increasing water partial pressure. This improvement is in accordance with the positive effect of water vapor content in the fuel cell performance depicted in Fig. 22 and with the increase of the ionic conductivity of PBI/

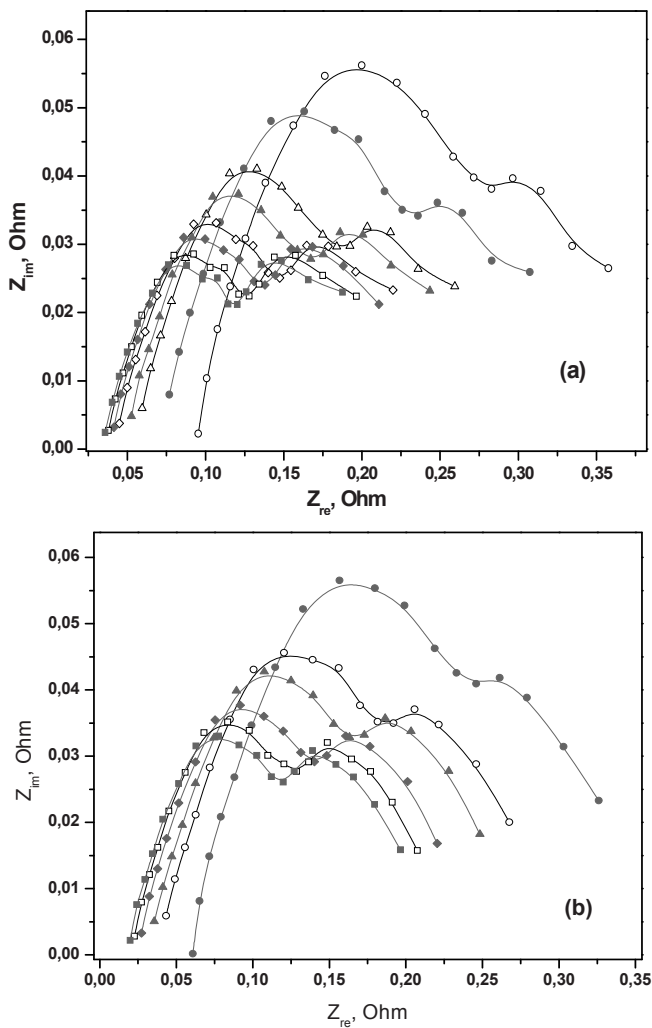


Figure 24. Nyquist plots at various P_{H_2O} values at (a) 140°C for (—○—) 0.55 kPa, (—●—) 0.96 kPa, (—△—) 1.9 kPa, (—▲—) 2.9 kPa, (—◇—) 4.9 kPa, (—◆—) 6.6 kPa, (—□—) 9.4 kPa and (—■—) 14 kPa water partial pressure. (b) 170°C for (—●—) 1 kPa, (—○—) 2 kPa, (—▲—) 3 kPa, (—◆—) 4.9 kPa, (—□—) 6.9 kPa and (—■—) 10 kPa water partial pressure. Electrolyte: PBI/PPy(50)coPSF 50/50, total pressure = 1 bar. Both electrodes were exposed to the same $H_2/H_2O/He$ mixture, $P_{H_2} = 4$ kPa.

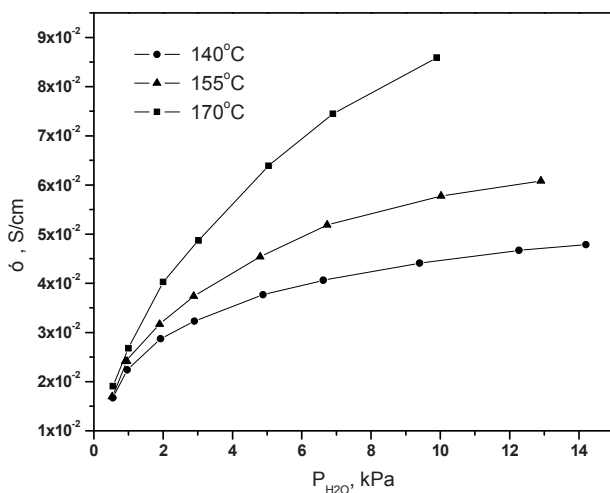


Figure 25. Water vapor partial pressure dependence on the electrolyte conductivity at various temperatures. Conditions as in Fig. 24.

H_3PO_4 recorded by several other research groups with increasing relative humidity.^{20,29,92,93}

The ionic conductivity of the PBI/PPy(50)coPSF membrane is depicted in Fig. 25 with respect to water partial pressure at various temperatures. The conductivity increases even by an order of magnitude with increasing steam partial pressure, especially at the higher temperature. At lower temperatures the conductivity is approaching asymptotically its maximum value already at P_{H_2O} values of 10 kPa, while at 170°C the conductivity increases with a large slope even for P_{H_2O} values above 10 kPa.

Arrhenius plots of conductivity at various P_{H_2O} values are depicted in Fig. 26. By fitting the data of Fig. 26 by Eq. (3) we can obtain the apparent activation energy E_a and the preexponential factor A which is directly related to the charge ionic capacity of the electrolyte:

$$\sigma(T) = A \exp\left(-\frac{E_{\text{ap}}}{RT}\right) \quad (3)$$

Interestingly E_{ap} increases with increasing $P_{\text{H}_2\text{O}}$, denoting an increase in the apparent activation energy for proton conduction which varies from 13–24 kJ/mol. Nevertheless the increase in proton conductivity is due to the increase in the preexponential factor A , which must be directly related to the increase of the ionic charge carriers concentration in the membrane.

It must be stressed that it is plausible that the observed increase of the activation energy is phenomenological. As described before, increasing temperature causes the dimerization of phosphoric acid according to reaction (1) and the shift of the equilibrium ionization reaction (2) to the left. Both factors contribute to the decrease of the ionic charge carriers thus resulting in the decrease of the ionic conductivity at elevated temperatures. The predominant effect of

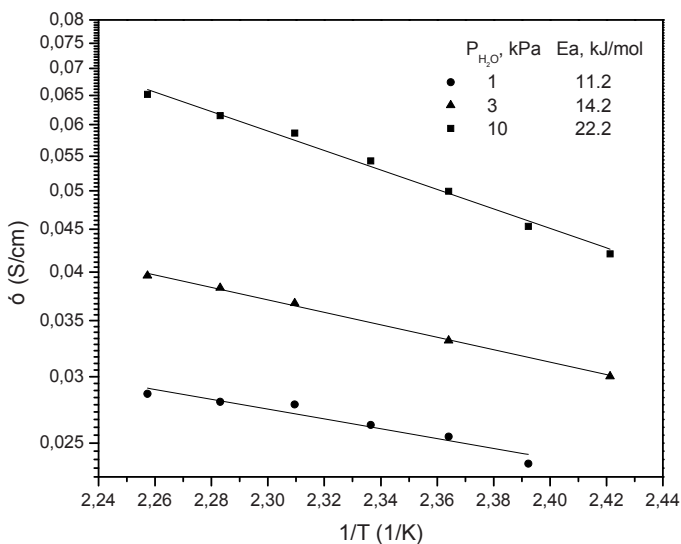


Figure 26. Temperature dependence of the electrolyte conductivity at various water partial pressures. Conditions as in Fig. 24

temperature on proton conduction does not allow the negative effect of dehydration to prevail but still the latter is negatively affecting the slope and respectively the apparent activation energy observed from these measurements.

5. Proton Conduction

The significant effect of water vapor on the proton conductivity strongly indicates that the proton conduction mechanism is similar to that of the water containing systems. Theoretical calculations by Stilingier et al.¹⁰⁷ showed that the solvated water in the phosphoric/pyrophosphoric acid acts as a base accepting protons from the phosphoric acid. It is also worth noticing that the values of the estimated apparent activation energies from Fig. 26 are close to the activation energy 16.4 kJ/mol reported for proton conduction in aqueous electrolytes.^{108,109}

The conduction mechanism is substantiated through the proton transfer/hopping between a proton donor and a proton acceptor in combination to the ability of the proton carrier (positive ion) to rotate and move so that it will transfer the proton to a negative ion according to reaction (2). As reported by Ma et al.,²⁰ the immobilization of phosphoric acid molecules in the frame of the polymer membrane chains results in proton conductivity values one order of magnitude below the corresponding proton conductivity of pure phosphoric acid.

Water interacts with the H_3PO_4 imbibed membranes either by reacting with the pyrophosphoric acid or by hydrating H_3PO_4 according to reactions (1) and (2) respectively. Both reactions can be considered as the main contributing processes for the proton conductivity. In this respect the significance of equilibrium reactions (1) and (2) for the improvement of the membrane proton conductivity and performance is critical. This can be attributed to the increase in the ionic capacity of the electrolyte either by maintaining H_3PO_4 at high concentrations through the reverse of reaction (1) or by the use of water as proton carrier according to the dissociation reaction (2). Its interaction and solubility with the H_3PO_4 / polymeric matrix will determine the degree of ionization of reaction (2). In this respect by the increase of the proton carrier concentration (H_3O^+) the proton conductivity is expected to increase. This is

reflected by the significant increase in the preexponential factor of the proton conductivity as depicted in Fig. 26.

It can also be stated that equilibrium reaction (2) is directly related to the solubility of water in the phosphoric acid. Water molecule can play the role of proton carrier since it can be more flexible because of its smaller size in comparison to the positive H_4PO_4^+ resulting from the self ionization of the H_3PO_4 . In addition and according to calculations of the H...O bond distances, the hydrogen bond between water and phosphoric acid molecules was calculated to have the longest distance (2.39 Å) in comparison to the hydrogen bonds of the other species (2.2 Å).²⁰ The longer H...O distance implies weaker hydrogen bonds, thus allowing higher degree of mobility/rotation of the H_3O^+ species.

The proposed proton conduction mechanism is based on proton transport between aligned hydronium-water molecules,^{108,110} which is referred to as structural proton transport or Grotthuss mechanism. According to this mechanism in aqueous electrolytes, there are two processes that must cooperate for a successful proton transfer. The one is the reorientation of water molecules so that the oxygen orbitals being able to receive a proton are aligned to the hydronium ion from which the proton will be transferred.¹¹¹ The second is the proton transfer itself which, according to the vast literature, can take place through proton hopping from the hydronium ion to the aligned water molecule depending on the oxygen separation distance.¹⁰⁸ Proton tunneling has been proposed in the past in order to explain the high ion mobility of H_3O^+ .^{110,111,112} It has been well established that the rate determining step in proton transfer is the water reorientation. This is due to the hydrogen bond of water with other water molecules. Its reorientation involves the torsional stretching and breaking of the hydrogen bond. Conway, Bockris and Lynton introduced the *field induced reorientation* mechanism of the water molecules, which is substantiated through the ion-dipole interaction.^{110,111}

However the concerted ion diffusion in parallel to the aforementioned structural proton transport (Grotthuss mechanism) cannot be excluded. Recent studies have shown that in diluted aqueous solutions and elevated temperatures the molecular diffusion for proton transport plays an equally significant role in parallel to structural diffusion.^{109,113,114} This is especially obvious if one considers the proton conductivity through Nafion polymer electrolyte

where water is transferred across the membrane upon current application.¹¹⁵

Nevertheless in the case of H_3PO_4 doped polymer electrolytes polymer electrolyte, though water was permeable through the membranes, the water transport rate remained unaffected with applying current. This strongly indicates that the diffusional proton transfer is negligible through the H_3PO_4 acid imbibed electrolytes (zero electroosmotic water drag). Assuming that the rate determining step for the structural proton transport is the field induced alignment of hydronium-water molecules,¹¹⁰ the increase of water concentration in the polymer electrolyte/ H_3PO_4 matrix is reasonably expected to result in the increase of the carriers and the hydrogen bonds–*proton paths*, either between water molecules or between water and H_3PO_4 due to the decrease of O/O separation within a hydrogen bond.¹⁰⁸ This will consequently result in the increase of tortional stretching and breaking of the hydrogen bond that will allow the alignment of the hydronium and water molecule, so that the proton transfer will be facilitated.

Based on the aforementioned considerations, it is possible to understand qualitatively the asymptotic behavior of the conductivity with respect to $P_{\text{H}_2\text{O}}$ as this is depicted in Fig. 25. Beyond the contribution of water vapors in maintaining the equilibrium of reaction (1), toward the formation of the H_3PO_4 , two competing factors determine the proton conductivity in the H_3PO_4 imbibed polymer electrolytes. These are

- the increase of the ionic concentration of the proton carrier species, reaction (2), which is contributing in the increase of the proton conductivity and as already mentioned,
- the reorientation of the hydronium-water molecules so that the proton transfer is facilitated.

The equilibration at higher $P_{\text{H}_2\text{O}}$ of these opposite acting processes stabilizes the proton conductivity to an asymptotically maximum value. It must be noted that the significantly higher enthalpy of hydration estimated for the case of the H_3PO_4 imbibed membranes (Table 4, Fig. 20) suggests the establishment of stronger hydrogen bonds between the water molecules and the H_3PO_4 network within the imbibed polymer matrix. This shows the strong influence of

the polymer matrix on the water affinity of the system and thus on its proton conductivity.

V. THE ELECTROCHEMICAL INTERFACE

1. Electrocatalytic Performance

In addition to the proton conductivity of the electrolyte, the performance of a fuel cell is largely dependent on the electrocatalytic activity of the anodic and cathodic interface. This depends both on the structure of the gas-electrocatalyst-electrolyte three phase boundaries and on the electrocatalytic activity of the charge transfer reaction that takes place along the electrochemical interface. The former case determines the extent of the electrochemical surface area (ESA), while the latter is directly related to the physico-chemical properties of the Pt based catalyst and the extent to which its catalytic properties are affected by its contact /interaction with the polymer electrolyte.

The structure of the electrochemical interface depends on the particle size, the loading and the active surface area of the carbon supported Pt particles. In addition for the case of HT PEMFCs the amount of H_3PO_4 plays a predominant role on the performance by affecting both the structure and the catalytic properties of the electrochemical interface.

In the first case the degree of wetting of the catalytic layer by the H_3PO_4 determines the extent of the electrochemical surface area. This hypothesis is further confirmed by the observation that MEAs with higher H_3PO_4 content in cathode have a higher double-layer charging current, which is determined by the value of background current in the double layer charging area of a cyclic voltammogram. Because double-layer charging arises from the surface interaction between the electrolyte (H_3PO_4) and the electrode (catalyst and supporting carbon), the level of double-layer charging current is an index of the area of contact between the catalyst and the H_3PO_4 .¹¹⁶

Too much phosphoric acid within the catalytic layer structure induces a flooding effect over the Pt particles thus resulting in the inhibition of reacting gases and especially O_2 to reach the catalyst surface, given the low permeability of oxygen in phosphoric ac-

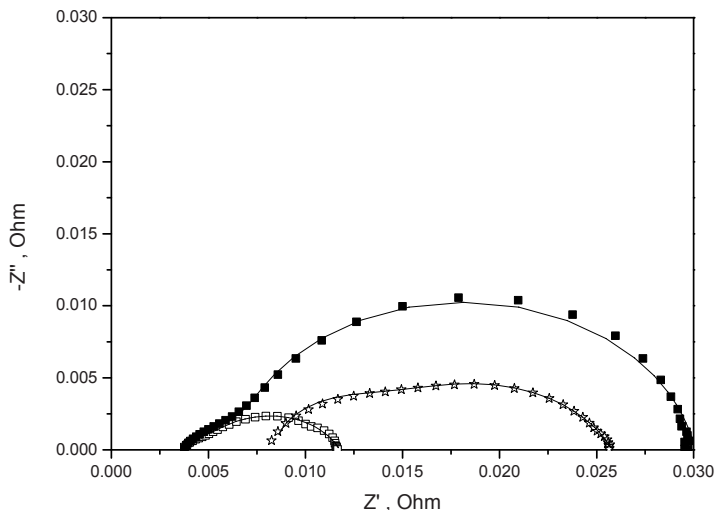


Figure 27. Nyquist plots depicting the effect of H_3PO_4 doping level within the electrochemical interface. The amount of phosphoric acid is expressed as wt% $\text{H}_3\text{PO}_4/\text{gr Pt}$. The spectra were recorded under load at 500 mV. ($\star$) 0.8 g $\text{H}_3\text{PO}_4/\text{g Pt}$, ($\square$) 3.2 g $\text{H}_3\text{PO}_4/\text{g Pt}$ and ($\blacksquare$) 13.2 g $\text{H}_3\text{PO}_4/\text{g Pt}$. MEA with copolymer II_{60} (Fig. 10) and active area $5 \times 5 \text{ cm}^2$, $F_{\text{air}} = 1 \text{ lt/min}$, $F_{\text{H}_2} = 1 \text{ lt/min}$, $T = 180^\circ\text{C}$.

id.¹¹⁷ On the contrary, the stripping of the interface from H_3PO_4 results in a poor conduct between the electrolyte membrane and the catalytic layer. This is shown clearly in the Nyquist plots of Fig. 27 where the AC impedance spectra of three MEAs with varying amount of H_3PO_4 on the electrodes are presented.

The AC spectra were recorded under load at cell potential 500mV. A certain amount of H_3PO_4 was sprayed onto the catalytic layer prior to the MEA assembly. It is evident that by increasing the amount of H_3PO_4 at the interface both the ohmic/ionic resistance of the MEA and the polarization resistance of the electrochemical interface are being improved. Further increase of the amount of H_3PO_4 keeps the ohmic/ionic resistance unaffected, while a significant negative effect is observed on the polarization resistance of the electrochemical interface. The improvement of the ohmic/ionic resistance of the MEA is due to the increase of the interface (ionic conduct) between the electrolyte and the Pt/C elec-

trocatalytic layer. Thus H_3PO_4 acts as an ionic link between the polymer electrolyte and the catalytic layer. Similarly the polarization resistance is improved due to the electrochemical utilization of higher Pt surface area, thus causing an increase in the electrochemical surface area. Further on, the overdoping of the interface with phosphoric acid results as already mentioned in flooding of the Pt/C particles with H_3PO_4 thus resulting in inhibiting the access of the reacting gases and especially O_2 to the Pt surface.

In general the Nyquist plots of Fig. 27 can be simulated by two semicycles which rather correspond to the anodic (high frequencies arc) and cathodic (low frequencies arc) electrocatalytic processes (Table 5).^{118,119,120} The anodic H_2 oxidation reaction being faster than the cathodic O_2 reduction reaction appears at higher frequencies and with lower polarization resistance.

It is quite interesting to notice that with increasing H_3PO_4 doping of the electrochemical interface both arcs decrease thus implying an improvement of the activity of the electrocatalytic processes both at the anode and cathode, which reasonably reflects on the increase of the electrochemically active surface area both at the anode and cathode. In the case of the spectrum of Fig. 27, which corresponds to the high doping level of the phosphoric acid at the interface, only the low frequency arc is affected thus manifesting a poisoning effect of the phosphoric acid at the cathodic oxygen reduction reaction (ORR). This can be attributed either to the poisoning effect of the phosphoric acid anions on Pt for the ORR or to

Table 5
The Ionic Resistance of the Electrolyte R_{el} and the Polarization Resistances R_1 and R_2 Based on the Fitting of the Niquist Plots of Fig. 30.

	R_{el} , electrolyte Ohm	R_1 , anodic (high freq) Ohm	R_2 , cathodic (low freq) Ohm
(Open stars) 0.8g H_3PO_4 /g Pt	0.00846	0.00643	0.0109
(Open square) 3.2g H_3PO_4 /g Pt	0.00385	0.00147	0.00644
(Closed square) 13.2g H_3PO_4 /g Pt	0.00391	0.00235	0.0243

the low diffusivity of oxygen through the phosphoric acid layer that drenches the Pt particles.^{121,122}

Based on the aforementioned considerations the structure of the electrochemical interface can be the most important step for the efficient performance of phosphoric acid doped high temperature MEAs. The introduction of species and moieties in the catalytic layer that can be evenly distributed within the catalytic layer and interact (bind) with H_3PO_4 is an interesting concept for the increase of the electrochemically active surface area.¹²³ This can be accomplished by the use of modified carbon nanotubes where pyridine based organic molecules have been attached to the side walls of the carbon nanotubes. The modified system can be used as the support of Pt nanoparticles and it is expected that the interaction of the H_3PO_4 with the pyridine polar groups will result in an optimized distribution of the phosphoric acid throughout the catalytic layer.¹²³

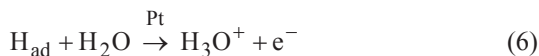
2. The Effect of Water Vapors on the Structure of the Electrochemical Interface

Kwon et al.,¹¹⁶ by the use of cyclic voltammetry following the H_2 oxidation, noticed that the electrochemical surface area (ESA) decreases significantly when it was measured immediately after the cell operation and after being at open circuit and under dry N_2 flow for a longer time. The latter was attributed to the dehydration of the electrochemical interface, thus affecting the wetting of the electrocatalyst by the phosphoric acid.

As is evident from the spectra of Fig. 24 the polarization resistance, R_p , is also significantly decreased with increasing $P_{\text{H}_2\text{O}}$. This eventually corresponds to the enhancement of the electrocatalytic activity of the electrode/electrolyte electrochemical interface. This can be quantitatively rationalized through the exchange current density of the electrochemical interface, I_o , as this is described by the Battler-Volmer eletrokinetic equation:¹²⁴

$$I = I_o \left(\exp\left(-\frac{a_a \eta}{RT}\right) - \exp\left(-\frac{a_c \eta}{RT}\right) \right) \quad (5)$$

Equation (5) shows that the electrocatalytic rate expressed in terms of current density I is a linear function of I_0 at constant overvoltage η . In general I_0 is a linear function of the ionic species concentration $C_{H_3O^+}$ and the kinetic constant k of the electrocatalytic reaction which in the present case is described by the proton discharge or adsorbed H_{ad} oxidation on either electrode according to the general reaction:



In this respect it is expected that the polarization conductivity, being the reciprocal of R_p , should be linearly related to the proton conductivity of the membrane, if the ionic concentration $C_{H_3O^+}$ is the main reason that affects I_0 and consequently R_p . Indeed, as shown in Fig. 28, where conductivity is plotted against $1/R_p$ for

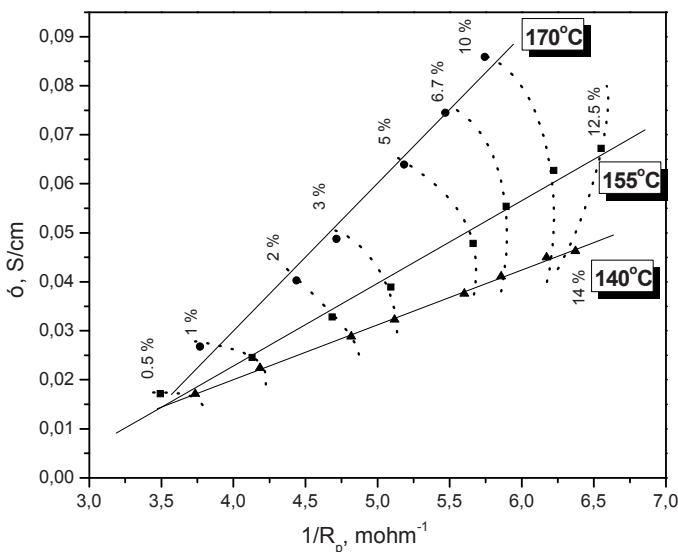


Figure 28. Conductivity of the PBI/Ppy(50)coPSF 50/50 electrolyte versus $1/R_p$ for different partial pressures of water at temperatures 140, 155 and 170°C. Conditions as in Fig. 24

three temperatures, a linear relationship is obtained thus corroborating the aforementioned considerations.

However it is worth noticing in Fig. 28 that, for constant or near-constant H_2O vapor pressures the polarization resistance increases with increasing temperature especially at the higher temperature. This is certainly a non expected behavior leading to a negative apparent activation energy while at the same time the proton conductivity of the membrane increases significantly with temperature, Fig. 25.

This interesting behaviour can be rationalized by considering the combination of proton transfer and water molecules reorientation. It has been shown that the hydration degree of the membrane and consequently of the H_3PO_4 decreases with increasing temperature (Figs. 17 and 18). Regardless of this the conductivity increases, which can be attributed to the faster relaxation/reorientation of the water molecules due to the weakening of the hydrogen bonds. However in the case of polarization resistance the concentration of the charge carriers $\text{C}_{\text{H}_3\text{O}^+}$ at the vicinity of the interface plays the most significant role for the determination of the I_o and consequently of the polarization resistance. Therefore partial dehydration of the membrane will result in a detrimental decrease of the electrocatalytic activity of the interface.

3. Effect of Water Vapor on the Promotion of the H_2 Oxidation Reaction (HOR)

It has been recently found that water vapor affects the shape of the hydrogen oxidation and reduction regions¹¹⁶ of cyclic voltammograms carried out at 150°C for high temperature H_3PO_4 proton exchange membranes. Under humidified N_2 flow H_2 oxidation peaks are well resolved in contrary to the dry N_2 flow. The improvement of the resolution of the H_2 oxidation peaks implies that the presence of steam affects the electrocatalytic interaction of H_2 with the Pt sites. This is also clearly shown in Fig. 29 where cyclic voltammograms of the H_2 adsorption/oxidation region under dried and humidified conditions are depicted. The working electrode is fed with N_2 or $\text{N}_2/\text{H}_2\text{O}$ mixtures while the counter electrode is fed with 200cc/min H_2 . N_2 is humidified by passing the N_2 flow through a saturator at room temperature. The redox peaks of H_2 , located around 0.22 V under dry conditions, are shifted towards

lower cell potential (0.16 V) under humidified conditions. This shows that under humidified conditions H_2 oxidation is enhanced while shift of underpotential deposition of H_2 (UPD) to lower cell voltage generally shows weaker bonding of H on the Pt surface. The total H_2 oxidation peak areas of the two voltammograms is 0.48Cb and 0.56 Cb for the humidified and dry experiment respectively, thus showing a slightly lower coverage under humidified conditions.

This experiment shows the role of H_2O as proton carrier not only in the proton conductivity through the electrolyte membrane but also as a promoter for the electrocatalytic oxidation of H_2 through reaction (6). Certainly reaction (6) is well established in aqueous systems, however in the present case it has been possible to discriminate between humidified and dry conditions. Based on the cyclic voltammogram of Fig. 29 the estimated H_2 uptake corresponds to a surface area of $10.6 \text{ m}^2/\text{gr}$. This value was estimated

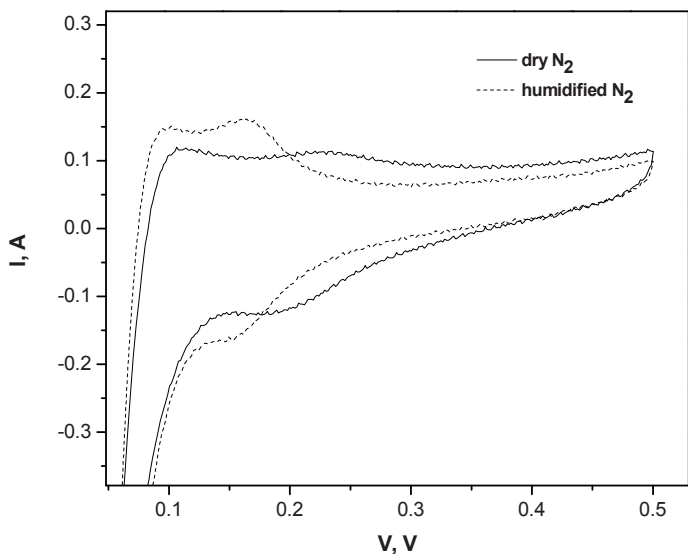


Figure 29. Cyclic voltammograms of the H_2 redox region under dry and humidified (N_2 saturated at room temperature, $P_{\text{H}_2\text{O}} = 4 \text{ kPa}$) conditions. A 5% mole H_2/Ar mixture was fed at the counter electrode. MEA with copolymer II_{60} (Fig. 10) and active area of 25 cm^2 . Scan rate 50 mV/s , $T = 140^\circ\text{C}$.

by considering $210 \mu\text{C}/\text{cm}^2$ for polycrystalline Pt.¹²⁵ This corresponds to almost 10 times lower catalytic surface area measured by H_2 chemisorption and to the ca. 11% of the corresponding surface area measured for the same catalyst by the use of rotating disc in aqueous solution of 0.1 M HClO_4 . This very low value of catalyst utilization may not reflect to the real electrochemical surface due to the uncertainty of a monolayer formation during the cyclic voltammograms of Fig. 29.

4. The Electrokinetics of the Oxygen Reduction Reaction

The oxygen reduction reaction (ORR) is one of the key reactions in electrochemical energy conversion devices like fuel cells. Despite many attempts to develop a non-Pt catalyst, platinum remains the best known electrocatalyst for ORR in acid fuel cells and numerous studies have been reported on the kinetics in acid electrolytes.^{126,127,128,129,130} In concentrated phosphoric acid medium the factor limiting the efficiency is the high overpotential for oxygen reduction. The decrease in the OR reaction rate as acid concentration increases can be attributed to lower oxygen solubility and proton activity, increased specific adsorption of anions and a thicker double layer.¹²² Consequently, oxygen reduction in phosphoric acid has been often studied.^{131,132} ORR on Pt is a structure sensitive reaction, mainly due to the structural sensitivity of the adsorption of spectator species like anions from the supporting aqueous electrolyte. Adsorption of phosphoric acid anion inhibits oxygen reduction by blocking initial adsorption of oxygen molecule. In this respect the amount of phosphoric acid at the cathodic electrochemical interface is one of the most critical issues for the kinetics of the ORR as this affects both the access of O_2 to the electrochemical interface and the activity of the Pt surface. This is shown in Figs. 30 and 31 where the cell's performance is depicted for various partial pressures of oxygen and two different phosphoric doping levels at the interface.

The measurements were carried out under differential conditions so that a uniform composition of the reacting gases was maintained along the MEA. This was achieved by controlling the inlet flowrate so as to maintain the oxygen conversion below 15%. Figure 30 shows I-V curves at varying partial pressures of O_2 and the corresponding AC spectra recorded under load at $200 \text{ mA}/\text{cm}^2$.

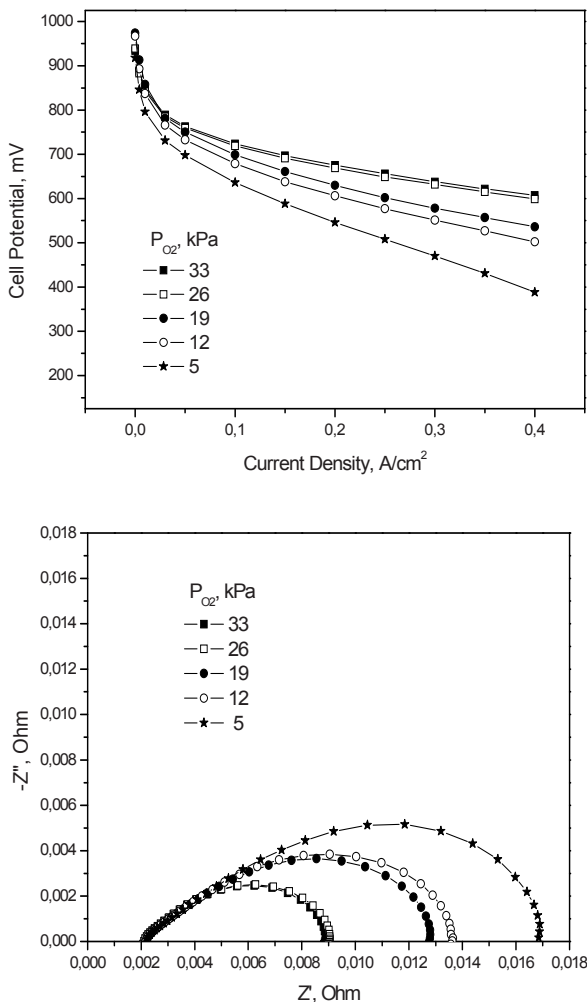


Figure 30. I-V curves and AC impedance measurements at various partial pressures of O₂ (P_{O₂}) and P_{H₂O} = 12 kPa. The AC spectra were recorded at 200 mA/cm². A 5% mole H₂/Ar mixture was fed at the counter electrode. MEA with copolymer II₆₀ (Fig.10) and active area of 25 cm². F_{anode} = 1 lt/min, F_{cathode} = 3 lt/min.

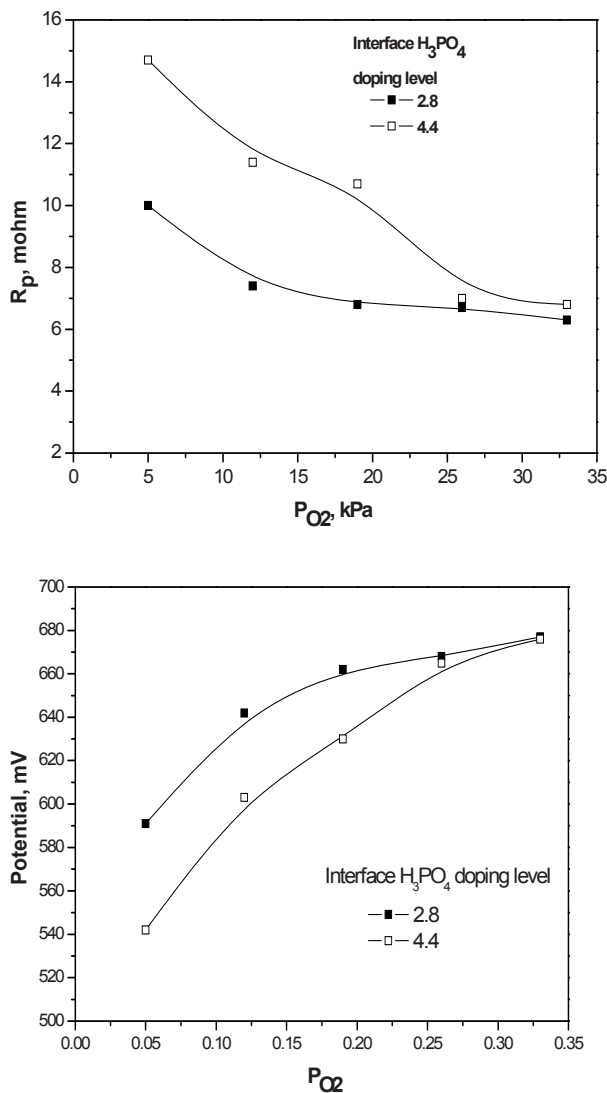


Figure 31. Effect of Partial pressure of O_2 P_{O_2} on the polarization resistance R_p and cell potential. The H_3PO_4 doping level at the interface is defined as g H_3PO_4 /g Pt. Conditions as in Fig. 30.

As it can be clearly observed significant decrease in fuel cell performance was observed at $P_{O_2} = 5$ kPa.

A more clear view can be seen in Fig. 31 where the polarization resistance and cell voltage at $200\text{mA}/\text{cm}^2$ is plotted against P_{O_2} for two different phosphoric acid doping levels at the electrochemical interface.

Though at lower P_{O_2} values the ORR activity is lower for the case of the high doping level phosphoric acid, exhibiting high polarization resistance and low Cell voltage (V_{cell}), the performance of both doping levels converges to the same electrocatalytic activity at high P_{O_2} values. In addition the performance of the cathodes with the low doping level approaches a plateau in its ORR activity from P_{O_2} value as low as 10 kPa. Based on these observations it can be concluded that the most significant reason for the observed differences on the electrocatalytic activity of the ORR reactions is directly related to the dilution and diffusivity of oxygen through the phosphoric acid layer and the extent of screening of the Pt particle surface by the phosphoric acid. Certainly the effect of poisoning of the phosphoric acid cannot be excluded however the observed differences in Fig. 31 cannot be attributed to the varying degree of poisoning due to the variation of the doping level of phosphoric acid at the interface, as for both doping levels the electrokinetic parameters at high P_{O_2} values are the same.

The significant effect of O_2 solubility in the PBI- H_3PO_4 system is supported by the work of Liu et al. who studied ORR at Pt interfaced with phosphoric acid doped PBI. They concluded that the H_3PO_4 doping level and the water content of the electrolyte affect the ORR exchange current density, oxygen diffusion and the oxygen solubility in PBI- H_3PO_4 membranes. However oxygen solubility in PBI- H_3PO_4 system is higher than in H_3PO_4 alone.¹⁰⁰

5. Degradation Issues of the Electrocatalytic Layer^{52,53,54}

Pt so far was proved to be the most active electrocatalytic material for both H_2 oxidation and O_2 reduction reactions being at the same time the most resistive to corrosion in both alkaline and acidic media. However even Pt has been shown to corrode at the cathode of PEMFC especially at operating voltages above 0.7 V with respect to a reference hydrogen electrode (RHE). Polymer electro-

lyte membrane fuel cell (PEMFC) performance loss under steady-state and cycling conditions has been attributed in part to a loss of electrochemically active surface area (ECSA) of the high-surface-area carbon supported platinum electrocatalyst.¹⁵ There is growing evidence that platinum dissolution plays a major role in the ECSA loss, especially of the cathode catalyst, where high potentials are encountered. This dissolved platinum can thereafter either deposit on existing platinum particles to form larger particles or diffuse into electrochemically inaccessible portions of the membrane-electrode assembly (i.e., sites not fulfilling the requirements of gas, electron, and proton access).

Much of the knowledge in Pt/C durability derives from the experience with phosphoric acid fuel cells (PAFCs) at operating temperatures of about 200°C. Catalyst degradation is witnessed as an apparent loss of platinum electrochemical surface area over time,^{133,134} associated with platinum crystal growth. These changes are ascribed to different processes which include

- (i) platinum dissolution and redeposition known as Ostwald ripening,
- (ii) coalescence of platinum nanoparticles via platinum nanocrystallite migration on the carbon support, and
- (iii) platinum particle agglomeration triggered by corrosion of carbon support and leaching of Pt and alloyed metals.¹³⁵

The third process can be circumvented by using more corrosion-resistant graphitized carbon supports. Other critical aspect is catalyst sensitivity to the dynamic behavior of the fuel cell, e.g., during the fuel cell ignition or extinction.

The long term stability of high temperature PEM fuel cells is largely dependent on the stability of the electrochemical interface which comprises both phosphoric acid stability and distribution throughout the interface and the stability of the Pt/C electrocatalyst against corrosion and agglomeration.

IV. CONCLUSIONS

The phosphoric acid-doped polymeric membranes are the most successful system so far as high temperature polymer electrolytes preferable for operation under ambient pressure. The most thor-

oughly studied high temperature polymer electrolytes are based on imidazole containing polymers comprising PBI, ABPBI and PBI blends. Among the various synthetic procedures of these materials the Acid-doped polybenzimidazoles prepared by a sol-gel seems to be the most promising route giving membranes with high doping levels, good mechanical properties and enhanced proton conductivities.

The second highly potential state of the art high temperature polymer electrolytes are based on recently synthesized aromatic polyethers containing pyridine groups. Based on this chemical structure a group of materials has been developed that posses all the prerequisites for high temperature operation. Materials with excellent mechanical, thermal and oxidative properties along with high ionic conductivity values and good cell performance ranks theses polymer electrolytes among the most promising technologies for the successful implementation of fuel cells.

The molecular structure significantly affects both the physico-chemical and electrochemical properties of the high temperature polymer electrolytes. It has been shown that water vapor strongly interact with the phosphoric acid imbibed polymer electrolytes and plays a major role in facilitating the proton conduction through the polymer matrix. Nevertheless the produced water from the electrochemical reaction at the cathode is capable of hydrating the polymeric material and promoting the cell performance, without the need for gases humidification.

The presence of water affects in a positive way both the proton conductivity of the H_3PO_4 electrolyte, the polarization resistance of the electrodes. The latter refers either on the enhancement of the ionic capacity of the interface or on the promotion of electrocatalysis regarding oxygen reduction reaction as well as the bonding strength of adsorbed H_{ad} on the Pt surface.

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