

Faraday Discussions 140

The need to develop cleaner and greener methods of energy production and chemical synthesis has been driving renewed interest in electrocatalysis.

Experimental advances in the application of spectroscopic methods are providing a wealth of data that enable structure/property relationships in electrocatalysis to be investigated. Similarly, developments in theoretical methods are providing new insights regarding old catalysts, and promise to provide direction in the search for new catalysts. The advent of high throughput catalyst preparation methods means that many more electrocatalyst formulations are being screened for an ever-wider variety of reactions. Directing this effort requires the combined efforts of theoretical models and the development of new experimental techniques.

This volume brings surface scientists and electrochemists together to foster the development of both in situ spectroscopic methods in electrochemistry and the study of single crystal electrode surfaces.

Work is presented in the following areas:

- Structure in electrocatalysis: from single crystals to nanoparticles
- Structural effects in electrocatalysis and fuel cells
- Hydrogen reactions and novel electrocatalysts
- Biological electrocatalysis and alcohols as fuels

Faraday Discussions

Vol 140

Faraday Discussions documents a long-established series of Faraday Discussion meetings which provide a unique international forum for the exchange of views and newly acquired results in developing areas of physical chemistry, biophysical chemistry and chemical physics.

The papers presented are published in the Faraday Discussion volume together with a record of the discussion contributions made at the meeting. Faraday Discussions therefore provide an important record of current international knowledge and views in the field concerned.

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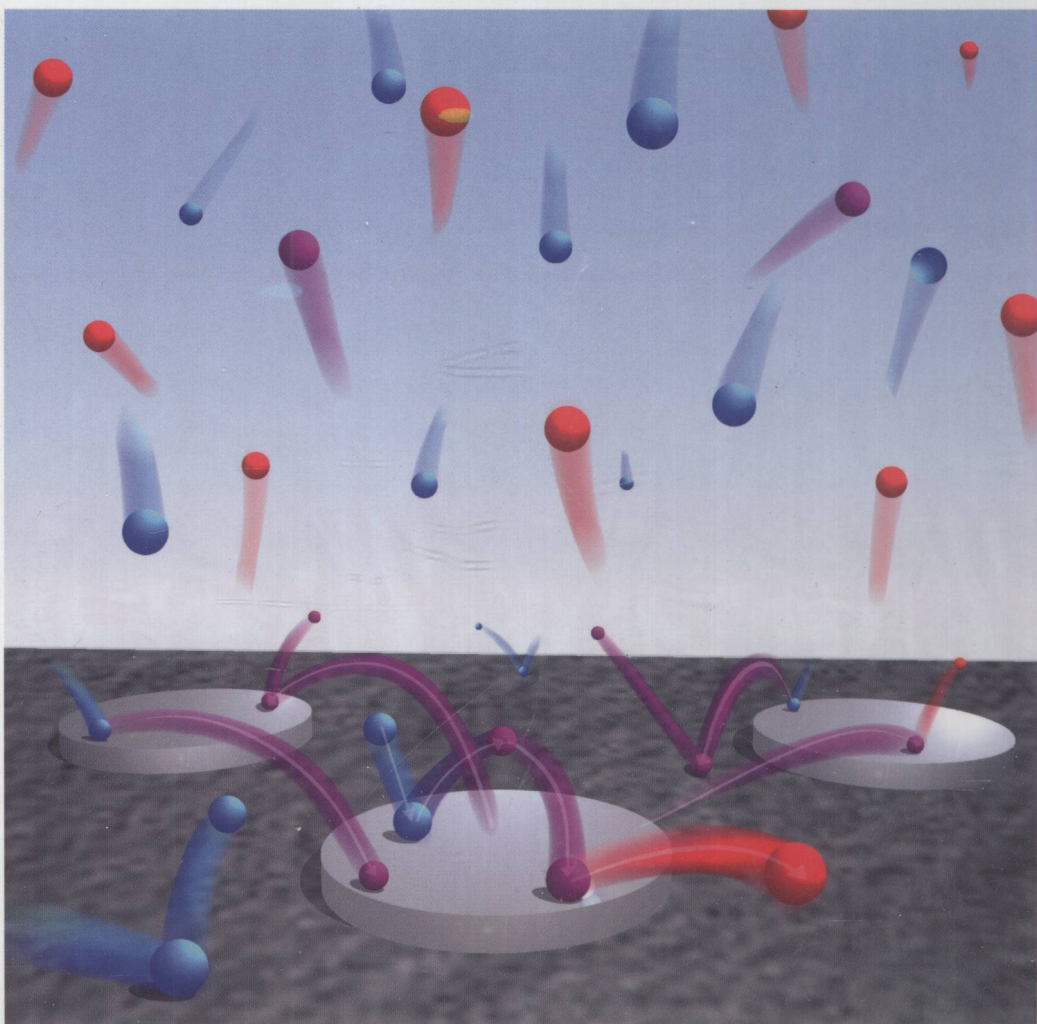


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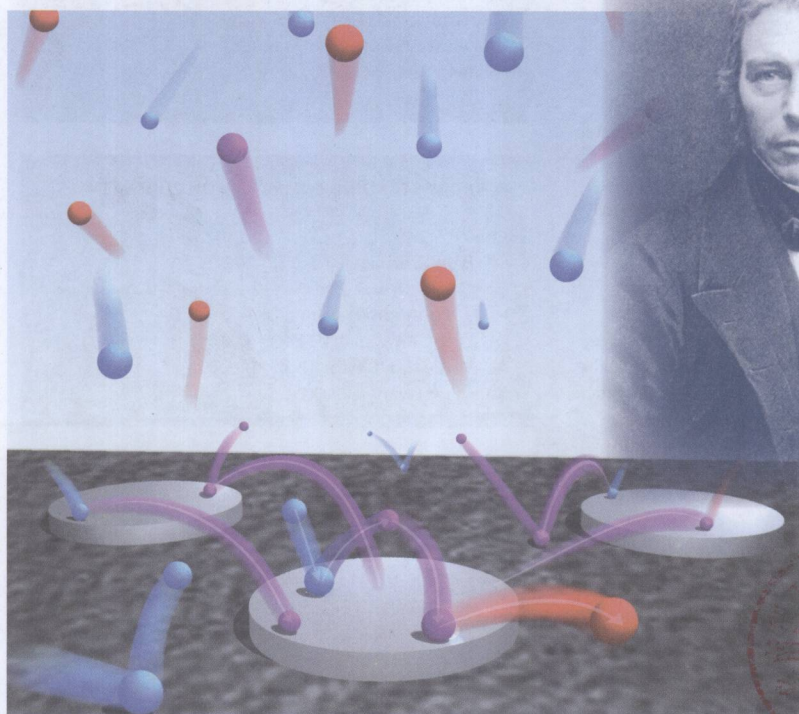
Electrocatalysis: theory and experiment at the interface



Electrocatalysis - Theory and Experiment at the Interface

University of Southampton, UK

07–09 July 2008



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Electrocatalysis- Theory and Experiment at the Interface

Faraday Discussions

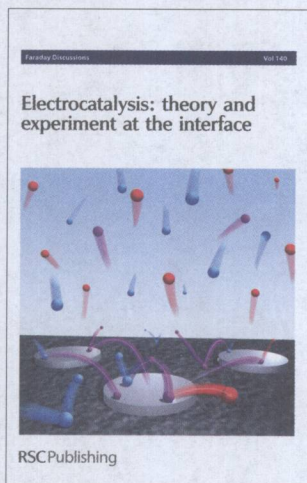
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See Y. E. Seidel, A. Schneider, Z. Jusys, B. Wickman, B. Kasemo and R. J. Behm, *Faraday Discuss.*, 2008, **140**, 167–184. Transport processes in an electrocatalytic reaction on an electrode surface with active metal structures (grey) on an inert substrate (black): with arriving reactants (blue), reactive intermediates (purple) desorbing into the diffusion layer, which can re-adsorb and react further, and final products (red) leaving into the bulk electrolyte.

Image reproduced by permission of Professor R. J. Behm, from *Faraday Discuss.*, 2008, **140**, 167.

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Preface

Andrea E. Russell*

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The need to develop cleaner/greener methods of both energy production and chemical synthesis has been driving renewed interest in electrocatalysis. Experimental advances in the application of spectroscopic methods, such as IR, INS, NMR, and XAS, and structural probes such as STM, AFM, high resolution TEM, and XRD are providing a wealth of data that enable structure/property relationships in electrocatalysis to be investigated. Similarly, developments in theoretical methods (MD simulations, DFT calculations, and Monte Carlo simulations combined with *ab initio* methodologies) are providing new insights regarding old catalysts and promise to provide direction in the search for new catalysts. The advent of high throughput catalyst preparation methods means that many more electrocatalyst formulations are being screened for an ever-wider variety of reactions. Directing this effort will require the combined efforts of theoretical models and the development of new experimental techniques. Such was the motivation behind the proposal for Faraday Discussion 140, which was originally proposed by David Schiffrin of the University of Liverpool whilst attending a workshop on Computational Electrochemistry in Santorini, Greece in September 2004. It was a bit of a surprise to me to find that I had been selected to put the proposal together and to chair the meeting, given that I wasn't attending the workshop. However, David can be very persuasive and it has been my privilege to organise the Discussion described in this text.

The organisation began properly at a second workshop meeting hosted by Marc Koper of Leiden University in Leiden, the Lorentz Workshop on Fuel Cell Electrocatalysis, in Oct 2006. There Elisabeth Ahlberg (University of Göteborg), Carol Korzeniewski (Texas Tech University), and Elena Savinova (then dividing her time between the Borskov Institute of Catalysis, Novosibirsk and the University of Strasbourg) and I met over dinner with Marc to draw up a plan of whom we'd like to have as invited speakers and to discuss the various themes we would want to feature in the meeting. Of particular importance to us were papers from theoreticians that would reach out to experimentalists, experimental/spectroscopy papers that were pushing the boundaries of the techniques to provide new information, discussion of the state-of-the-art catalysts for both the hydrogen and oxygen reactions, and a desire to see that electrocatalysis is more than just fuel cells. To our delight all of the speakers we approached on our most wanted list accepted the invitation and, more importantly for a Faraday Discussion, they all produced their manuscripts for discussion at the meeting and inclusion in the volume. Together with the contributed papers, where there were four times as many abstracts submitted than we could accept as full papers in the meeting, I believe that the meeting lived up to our aims.

To address the problem of demand for a contributed paper at the meeting, I organised a special issue of *Physical Chemistry Chemical Physics*, which the editorial and production teams of the RSC managed to deliver on time to be handed out to each participant at the meeting. This special issue, also entitled "*Electrocatalysis: Theory and Experiment at the Interface*" is available as volume 10, issue 25, of *Physical Chemistry Chemical Physics*. It contains 22 further papers that I wholeheartedly recommend to readers of this Discussion.

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The meeting itself was comprised of four sessions, intended to represent those aims that Elisabeth, Carol, Elena and I discussed over dinner almost two years previously. Marc Koper gave an excellent opening lecture, setting this Discussion in the context of previous Faraday Discussions on electrochemistry related topics and then going on to highlight the power of combining theoretical and experimental methods in exploring the structure and properties of electrocatalysts. His talk enthused and energised the delegates, who went on to vigorously discuss the other papers presented for the meeting. The concluding remarks were expertly presented by David Schiffrin, who did an excellent job of both summarising the meeting and pointing out where we should be thinking of going next.

The meeting also included a packed poster session with 37 posters, which were also enthusiastically discussed. I do not believe that any student or postdoc attending the meeting ever felt that their poster was ignored and many were able to present and discuss their work at the highest level. The Organising Committee awarded the Skinner prize (for best student poster) to M. J. T. C. van der Niet (Leiden University) for her work on “Interactions between H₂O and preadsorbed H or O on Pt(533)”.

On behalf of the Organising Committee, I would like to thank all those who participated in Faraday Discussion 140. I am sure that those unable to attend who will read this volume will absorb some of the excitement that was generated at the meeting, and I hope that many of the points continue to be vigorously discussed when we meet again or in the literature. We would also like to thank the RSC staff who made the organisation so much easier than I (Andrea) anticipated. In particular, we would like to thank Morwenna Gilbert and Nicola Nugent for all of their hard work and emails. We would like to thank all of those whose papers appear in this volume, for meeting the deadlines (well, almost) and keeping to the 5 minutes allowed for presentation. Finally we thank Piotr Kleszyk, Gaël Chouchelamane, Jon Speed and Rob Johnson, from my group, for their excellent skills in keeping delegates to time, managing the University's data projector systems, and otherwise keeping me calm. Finally, we acknowledge the International Society of Electrochemistry and the Electrochemical Society for their co-sponsorship of the meeting, and the University of Southampton and the Army Research Office for their generous financial support of the meeting.



Andrea E. Russell (*Chair, Editor*)

Introductory Lecture

Electrocatalysis: theory and experiment at the interface

Marc T. M. Koper

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Introduction

Browsing through the history of Faraday Discussions typically serves as a good indicator of the development of concepts and challenges in physical chemistry. The first Royal Society Discussion Meeting held under the name “Faraday Discussions”, at the University of Manchester in 1947, was on the topic of “Electrode Processes”. Among the list of contributors were illustrious names such as Randles, Levich, Frumkin, Bockris, Butler, Eley, and Heyrovsky†. This was the time that electrochemical measuring techniques, such as electrochemical impedance spectroscopy, were developed, and electrochemists were still very much in the dark about the molecular nature and theoretical description of electrode reactions, in particular hydrogen evolution, which was a prominent discussion topic. One remarkable statement was that made by Eley,¹ who seriously questioned whether it would ever be possible to measure on a clean platinum surface in an electrolyte solution.

By 1968, at a Faraday Discussion on “Electrode Reactions of Organic Compounds” at the University of Newcastle-upon-Tyne, some remarkable leaps in development had taken place. Most prominently, there was by then a theory of electron transfer reactions, introduced at the meeting by Marcus. The contributions by Parsons and Conway were essentially concerned with the kinetic modeling of electrocatalytic reactions, whereas Hush used semi-empirical quantum-chemical calculations (!) to study bond breaking. Breiter had a contribution on methanol oxidation at platinum, and there was an interesting paper by Brummer and Cahill on the interaction between adsorbates, such as chemisorbed hydrogen and carbon monoxide. The relation with some of the relevant issues still raised at this meeting is remarkable. However, there was the nagging problem of specific adsorption, as put forward by Parsons²: “The greatest uncertainty in the adsorption behaviour arises from the lack of knowledge about the way the relative adsorption of different species depends on the nature of the metal.” Thirsk, in his concluding remarks, also mentioned the “resistance to theoretical attack” of adsorption as one of the main problems of electrochemical science.

Five years later, at a meeting at Oxford University called “Intermediates in Electrochemical Reactions”, one of the founding fathers of electrochemical surface science, Heinz Gerischer, was quite optimistic about the possibilities of new

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† At the meeting it was pointed out by Professor Roger Parsons, who was also present at the Faraday Discussion 1 in 1947 as a graduate student of Professor Bockris, that the contributors from the Soviet Union and Eastern Europe (Frumkin, Levich, Ershler, Heyrovsky) were not able to be present at the meeting at Manchester. This severely limited discussion of their important work and significantly delayed the impact of their contributions. This clearly illustrates the importance of discussion in person which characterises the Faraday Discussions.

surface-sensitive techniques to probe intermediates in electrode reactions.³ Indeed, this was the meeting where the field witnessed the introduction of new non-electrochemical methods, such as reflectance spectroscopy (Kolb and MacIntyre) and online mass spectrometry (Bruckenstein). However, only few participants of that meeting would have foreseen the explosion of new techniques that was going to transform interfacial electrochemistry in the next 10–20 years. In fact, Randles, in his closing address, seemed rather reserved about the future of electrochemistry.⁴ He felt that, somehow, “chemistry has lost its glamour”, though “electrochemistry still has vitality and a potential for continuing usefulness”. However, “we should refrain from barren mathematising, we should use the techniques we have where they are most appropriate and think actively about possible new ones”.

The lesson to be learnt? Just browse through the next Faraday Discussion volume 94 on electrochemistry “The Liquid/Solid Interface at High Resolution”, held in Newcastle-upon-Tyne in 1992. There is no lack of glamour in the papers that were contributed to that meeting! Scanning tunneling microscopy and other scanning probe techniques had revolutionized the field of surface science and electrochemists such as Kolb, Itaya, and Bard, amongst many others, were actively studying the unprecedented potential of these new techniques. Also spectroscopic techniques such as infrared spectroscopy, Raman spectroscopy and non-linear methods, such as second harmonic generation, had become part of the modern electrochemist’s toolbox. In the flood of STM papers, theory remained somewhat underexposed (apart from one isolated theory paper by Nagy, Heinzinger and Spohr on the modeling of water at platinum⁵).

The most recent Faraday Discussion meeting on electrochemistry was in 2002 in Berlin, entitled “The Dynamic Electrode Surface”. 2007 Nobel Laureate Gerhard Ertl, Heinz Gerischer’s successor at the Fritz-Haber-Institute at Berlin, pointed out in his Introductory Lecture the importance of looking at surface reactions at different time- and length scales, and the different experimental and theoretical tools needed for their proper description.⁶ Theory and computational chemistry, in particular quantum-chemical calculations based on density functional theory (DFT) and (kinetic) Monte Carlo simulations of surface reactions, were beginning to play an important role in the interpretation of experimental results, as exemplified in the papers by Rikvold,⁷ Weaver,⁸ and myself.⁹ In the electrocatalysis talks, the role of surface diffusion, especially Pt-bonded CO, was a matter of intense debate.

Since 2002, theory and computational chemistry have played an increasingly important role in fundamental electrocatalysis work. Reactions such as hydrogen oxidation and evolution, oxygen reduction, methanol oxidation and carbon monoxide oxidation have all been studied using modern computational techniques, such as first-principles DFT calculations and Monte Carlo simulations, which both complement and give input for the more widespread kinetic modeling approaches. The interaction with experiment has been become very fruitful, and it is this synergy that provided the motivation for the present Faraday Discussion.

My aim in this paper is to illustrate the ideas and concepts on which I believe this interaction or “interface” of theory and experiment should be based, and then to illustrate this on two topics of my own current research focus. Since I am primarily interested in moving electrocatalysis forward as a science, as opposed to “technology”, I will only discuss the general fundamental challenges that we face, as opposed to the specific challenges related to *e.g.* fuel cell catalysis and the development of better and more efficient low-temperature fuel cells (which is undoubtedly one of the main drivers of the field).

Theoretical and computational electrochemistry

A famous statement made by Dirac in 1929¹⁰ claims that “all of chemistry” follows from the laws of quantum mechanics, and the main difficulty lies in the fact that the equations are “too complex to be solved”. However, in his statement Dirac did

not foresee (or did not include) the invention of the computer, ultimately made possible by the development of quantum mechanics itself. Much of modern theoretical chemistry is concerned with developing clever ways of using the computing power of computers to solve the complex equations. The success of theoretical chemistry has been immense, as illustrated by the award of the 1999 Nobel Prize to Pople and Kohn, two founding fathers of modern computational quantum chemistry. However, modern quantum chemistry still suffers—to some extent—from Dirac's demon: the number of atoms that can be included in a full-blown “first principles” computation, especially when coupled to dynamics, is limited to at best a few hundred. The impressive work of Neurock and coworkers, as exemplified by their paper in this volume, is a good example of what is currently achievable. The extrapolation to real sizes and realistic time scales is by no means trivial, and involves approximation schemes, the accuracy of which is often unclear and difficult to assess. The accuracy and/or reliability of model calculations (and therefore of the inherent approximations) may be evaluated on the basis on a comparison to experimental data, but this is a practice which, at least in the author's opinion, should be carried out with great care, no matter how successful and gratifying such a comparison may often appear.

So what would be an ideal but still practical way to model an electrocatalytic system? In other words: how to go from quantum mechanics to, say, a real voltammogram? First of all, it is imperative that the atomic structure of the electrode surface is known accurately. Experimentally, this implies working with well-defined single crystals, and knowing how the exact structure of the single-crystalline or nanoparticulate surface and possible defects influence reactivity. This aspect becomes less important if one, for instance, compares the activity of a series of metals for a certain reaction, but at the expense of losing quite a bit of detail. Next, one has to set up a hierarchy of calculations that will finally lead to the prediction of the experimental outcome, where typically one level of calculation delivers the input for the next level. For instance, one may carry out a series of first-principles DFT calculations to estimate interaction energies between adsorbates on an electrode surface, and rate constants for reactions between adsorbates (based on transition state theory). These numbers may be input for a lattice-gas kinetic Monte Carlo (KMC) simulation of an extended surface, say 1000×1000 lattice points. The KMC simulation may directly give the desired macroscopic variable, such as for instance the electric current, as well as much more, such as the time-dependent distribution of adsorbates on the surface. Essentially, the KMC simulation serves as a way to estimate the system's partition function, *i.e.* as a simulation method to sample the long-time statistics of the system in a way that would be impossible by quantum chemistry alone. On the other hand, one often approximates the statistics of the system by assuming a perfect mixing, also known as the “mean-field approximation”, which is the basis of most kinetic modeling approaches and of, for instance, the well-known Frumkin isotherm.¹¹ In this case, a KMC simulation should in principle still be carried out in order to confirm the validity of the mean-field approximation. Note, however, that the complexity of the system often forces one to make many more (implicit) assumptions: the lattice-gas approximation, the assumption of the additivity of interaction potentials (sometimes three-particle interactions may be included but even this is an approximation), entropic or other solvent effects are often neglected as first-principles free energy calculations are extremely expensive, assumptions about the exact structure of the surface and role of defects, assumptions about which reactions to include and which not, assumptions about the reaction mechanism (sometimes reactions may be included the rates of which are difficult to calculate and therefore they are estimated or guessed), *etc.* Although there may be examples where many of these approximations may be (or may appear to be) reasonable for the particular system under consideration, it will still be necessary to compare carefully to experimental data as well as to more accurate simulation data to finally assess the reasonableness of a model.

A key challenge in first-principles simulations of electrode systems is the introduction of the electrode potential. Since all existing quantum chemistry codes work with

a fixed number of electrons in the simulation box, rather than with a fixed electrochemical potential of the electrons, applying an electrode potential to the simulation of a half cell is usually approximated by adjusting the charge distribution within the simulation cell. This can be achieved by applying an electric field to the cell,^{8,12,13} adding or removing electrons to the metal slab representing the electrode,^{14,15} or adding electron-drawing or withdrawing adsorbates to the metal surface.¹⁶ The first two methods should also screen the electrostatic field or charge by an artificial background. The corresponding electrode potential is determined at the end of the fully converged calculation, typically by referring the Fermi level of the metal electrons to a field-free reference somewhere in the simulation cell, in combination with the known relation between the vacuum scale of the metal work function and the normal hydrogen electrode.^{14–16} Practically all current first-principles calculations including the effect of the electrode potential are carried out in this fashion. The fundamental limitation of these methods is that they are essentially *coulostatic* methods, and cannot readily be applied to mapping out the reaction path of a charge transfer reaction, as most electrode reactions are. During a charge transfer reaction under coulostatic conditions, the electrode potential will change during the reaction. The preferred way to circumvent this problem is to switch to a grand-canonical simulation method,¹⁷ in which the electrochemical potential of the electrons in the half cell is held fixed rather than their number. The computational limitation of this method is that it requires an additional iterative loop in the already very time-consuming simulation, such that in practice the method is still hardly used.

An interesting approach that allows a rapid assessment of the influence of the electrode potential was suggested by Nørskov *et al.*,¹⁸ and is based on the very simple assumption that the only effect of the electrode potential is to change the energy of the electrons. For the adsorption reaction of hydrogen:



the reaction energy is written as:

$$\Delta G_{\text{reaction}}(E) = \Delta G_{\text{ads}}(\text{H}_{\text{ads}}; E) - \Delta G_{\text{ads}}(\text{H}^+ + \text{e}^-; E) \quad (2)$$

Nørskov *et al.* make the assumption that the first term on the right-hand side of eqn (2) does not depend on potential E , whereas the second term is simply equal to $e_0 E$, with the potential referred to the NHE (normal hydrogen electrode), as the energy of $[\text{H}^+ + \text{e}^-]$ is 0 at the potential of the NHE by convention. In mathematical terms, the first assumption implies that

$$\text{d}\Delta G_{\text{ads}}(\text{H}_{\text{ads}})/\text{d}E = 0 \quad (3)$$

In so far as the electrode potential is proportional to the interfacial field F , this is equivalent to stating that the adsorbate (in this case H_{ads}) forms an apolar bond with the surface, or, more accurately, that its static surface dipole moment is zero. As a result, the quantity $(1/e_0)\text{d}\Delta G_{\text{reaction}}(E)/\text{d}E$, which is known as the electrosorption valency,¹⁹ is equal to the (integer) number of electrons transferred in the adsorption reaction. Though this assumption seems reasonable for reaction (1), it remains to be seen how valid it is in general, and it should certainly be tested for every adsorbate considered. Note that the relationship between the electrosorption valency and the surface dipole moment is not a trivial one, and depends on the structure of the double layer.²⁰

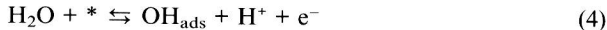
Electrocatalytic oxidation of carbon monoxide

The oxidation of carbon monoxide is not only one of the favorite model reactions in electrocatalysis, but it is also a hugely important reaction in the development of

more efficient low-temperature fuel cells. We have studied the CO electro-oxidation on various stepped single crystals of platinum and rhodium,^{21–24} and have demonstrated the importance of low-coordination step and defect sites in the oxidation mechanism. However, there remain quite a few fundamental issues that I believe are not yet fully understood. One of them is the importance of CO_{ads} surface mobility in the oxidative stripping of pre-adsorbed CO, an issue that was quite intensely debated 6 years ago at the Faraday Discussion in Berlin. The other is the nature of the oxygen-donating species. I will discuss these two issues in this and in the next session.

From the DFT point-of-view, CO seems to be a somewhat problematic molecule, as DFT has difficulty in correctly predicting the preferred adsorption site on a Pt(111) surface. Whereas experimentally CO prefers atop coordination on Pt(111) (in UHV at low CO coverage),²⁵ most DFT calculations predict the three-fold hollow site to be most stable.²⁶ This is typically explained by the tendency of DFT to overestimate bonding interactions, which are stronger for higher coordination. Olsen, Philipsen and Baerends²⁷ have recently shown that using a localized basis set and taking care of achieving full convergence of the DFT calculations, the atop site is found to be the preferred site on Pt(111). Nevertheless, their binding energies seem somewhat low compared to experiment. These observations clearly underpin the statement by Feibelman *et al.*²⁶ that “DFT calculations cannot be used as black-box simulation tool.” Typically, qualitative or relative predictions are more reliable than quantitative or absolute predictions, having error bars of *ca.* 0.1 and 0.3–0.5 eV, respectively. At any rate, these calculations suggest the *qualitative* conclusion that the corrugation potential for CO on Pt(111) should be rather flat, in agreement with the experimental observation that CO mobility on Pt(111) is high.

The oxidation of carbon monoxide, under electrochemical conditions, is believed to follow the Langmuir–Hinshelwood-type mechanism originally suggested by Gilman:²⁸



The second step in this mechanism, the CO + OH combination reaction, is believed to be rate-determining, primarily because the Tafel slope observed for CO monolayer oxidation is *ca.* 70–80 mV dec^{–1},^{29,30} close to the theoretical value of 60 mV dec^{–1} expected for an EC mechanism. DFT calculations indeed show that there is sizeable barrier for the CO + OH reaction: Shubina *et al.*³¹ report *ca.* 0.6 eV on Pt(111) in the absence of water, whereas Janik and Neurock³² have obtained values of 0.5–0.3 eV in the presence of water, depending on whether the surface was charged or not. Note that these values apply to *T* = 0 K, hence these are not free activation energies.

By carrying out extensive chronoamperometry measurements on a series on stepped Pt surfaces in sulfuric acid, we have shown that the rate for CO monolayer stripping is proportional to the step density, and that there is no evidence for CO slowly reaching the active step sites. This strongly suggests that OH_{ads} formation takes place preferentially on the step sites, and the CO diffusion on the terrace is rapid, in agreement with the flat corrugation potential predicted by DFT.

More recently, we have performed a similar series of experiments, but in alkaline media.³³ Alkaline media typically show higher catalytic activities than acidic media, even if the potential scale is converted to the reversible hydrogen electrode to correct for trivial pH effects.^{34,35} I believe that these observations are not well understood, and cannot be explained simply by referring to the higher affinity of OH for step sites in alkaline media, as this effect must have been accounted for by the RHE scale.

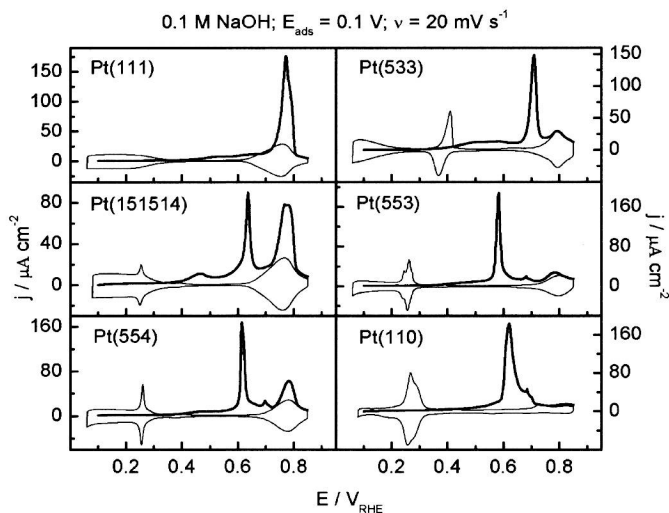


Fig. 1 CO stripping (thick solid line) and the subsequent cyclic voltammogram (thin solid line) for Pt(111), Pt(15 15 14), Pt(554), Pt(533), Pt(553) and Pt(110) in 0.1 M NaOH, sweep rate 20 mV s^{-1} , CO adsorbed at a potential of 0.1 V, no CO in solution during stripping. Reproduced with permission from ref. 33.

Fig. 1 shows the CO stripping voltammetry on a number Pt single crystals surfaces in 0.1 M NaOH. The remarkable observation here is that the CO voltammetry exhibits as many as 4 features. We can take the CO stripping voltammetry on Pt(554) as an example. By comparing to Pt(111), Pt(15 15 14), and Pt(553), we can conclude that the high-potential stripping peak between 0.72 and 0.80 V is due to the oxidation of CO on (111) terraces. Inspection of the surfaces with (110) and (100) step sites, we conclude that the stripping peak at around 0.6 V is CO oxidation at (110) sites, and that peak at *ca.* 0.70 V is due to CO oxidation at (100) sites. Note the small feature at 0.7 V in the stripping curve for Pt(554) (and Pt(553) and Pt(110) as well), which we ascribe to CO oxidation at a small amount of defects of (100) orientation. Finally, a broad low-potential potential feature, which can start at a potential as low as 0.35 V, is observed on all surfaces. This feature was also observed by Spendelow and Wieckowski³⁶ in their studies of CO adlayer oxidation on lightly disordered Pt(111) in alkaline media. By combining voltammetry with scanning tunneling microscopy, they suggested that this feature is due to CO oxidation on small monoatomically high islands on the Pt(111) surface, which present low-coordination sites (essentially kink sites) that are particularly active for CO oxidation. Following their assignment, we suggest that this low-potential feature is CO oxidation on “kink”-type sites, or defects in the steps. This leads to the remarkable observation that a single voltammogram such as that shown for Pt(554) reveals as many as 4 different active oxidation sites for CO: kink sites, (110) step sites, (100) sites, and (111) terrace sites, in decreasing order of activity. Such an observation is only possible if the mobility of CO on the surface is low, as in the case of high CO mobility most if not all CO would oxidize at the most active oxidation sites.

A simple way to probe the role of low CO mobility is to study the scan rate dependence of the CO stripping voltammetry, as shown in Fig. 2 for Pt(554). It is observed that at high scan rates (500 mV s^{-1}) there is a significant amount of CO oxidizing on the terraces. However, as the scan is lowered, the charge corresponding to CO oxidizing at the terraces decreases until finally at 5 mV s^{-1} it is almost negligible. This clearly suggests that at low scan rates, CO has more time to diffuse to the