

The Dynamic Electrode Surface

REPORT OF THE BERLIN MEETING OF FARADAY DISCUSSION 121

Faraday Discussion 121, organised by the Royal Society of Chemistry, Faraday Division, was held at the Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany, from 15th to 17th April 2002. This event attracted 107 prominent electrochemists or surface scientists from research centres or universities from 17 countries. Less than five representatives from industry attended.

Faraday Discussions are international scientific conferences focusing on rapidly developing areas of physical chemistry. About 20 to 24 selected papers are distributed to delegates for review before the meeting. The main part of the conference then discusses the papers, giving participants the opportunity to join in the peer review of the article, which is then published, as are the original papers (by the Royal Society of Chemistry).

To open the Discussion Professor G. Ertl from the host institute presented the Spiers Memorial Lecture, entitled 'Dynamics of Surface Reactions'. Professor Ertl reviewed electrochemistry at quantum, atomic, mesoscopic and macroscopic levels. Many advances have been made, but there is still much to investigate to reach a better mechanistic understanding of the dynamic electrode interface.

After this, 24 papers were presented, passionately discussed and reviewed. There were also 38 poster contributions. Most of the papers were on single crystal metal electrodes, although semiconducting, particulate, polycrystalline and surface modified electrodes were covered. Electrochemical methods (cyclic voltammetry, chronoamperometry, chronocoulometry), an *ex situ* surface characterisation technique (X-ray photoelectron spectroscopy (XPS)), and a wide range of *in situ* structural imaging and spectroscopic techniques were described. This selective review focuses on the platinum metals and some important electrochemical issues.

Island and Step Dynamics

Professor E. Borguet (University of Pittsburgh, U.S.A.) described the effect of the local environment on nanoscale dynamics at electrochemical

interfaces. Using potential pulse perturbation time-resolved scanning tunnelling microscopy (STM) on gold single crystal, Au(111), in HClO₄ solution, experimental evidence supported the existence of an electrochemical Schwobel-Ehrlich barrier. This is an energy barrier to atoms crossing a step from one terrace to the next, either from above or below.

M. Giesen (Forschungszentrum Jülich, Germany) used electrochemical STM to study Au islands on Au(100) electrodes in sulfuric acid as a function of electrode potential. Theoretical models and experimental methods recently developed for ultra high vacuum experiments on metal islands were applicable to a liquid environment. Discussions included how the step free energy is a function of orientation and kink energy. How these quantities depend on electrode potential was also discussed.

Adlayers and Hydration Processes

Professor M. Ito (Keio University, Japan) discussed FTIR, STM and XPS to study the hydration process of electrolyte anions and cations on Pt(111), Ir(111), Ru(001) and Au(111) surfaces. The validity of the model used for carbon monoxide (CO) and water co-adsorption which predicted a more ordered structure at higher temperature was questioned. Professor J. W. Halley (University of Minnesota, U.S.A.) suggested that an intermediate stage, between *ab initio* calculation and Monte Carlo or classical molecular dynamics is required to predict electrochemical behaviour from first principles. Preliminary results on the structure and dynamics of water on the 110 face of rutile titanium dioxide were discussed.

Deposition and Dissolution

Professor P. N. Bartlett (University of Southampton, U.K.) described the first use of waveguide surface plasmon resonance to study surface reactions on Au electrodes. The results from this method attracted a lot of discussion. B. Pettinger (Fritz-Haber-Institut) described the

simultaneous use of *in situ* second harmonic generation (SHG) and cyclic voltammetry to elucidate the structural and electronic behaviour of Au(111) surfaces during camphor adsorption and desorption. More generally, R. J. Nichols (University of Liverpool, U.K.) described the use of *in situ* FTIR in the attenuated total reflectance mode to study the surface chemistry of Si(111) during etching in alkaline solution.

Catalysis

In the first of two sections on catalysis, Professor G. A. Attard (Cardiff University, U.K.) described the influence of anions and kink structure on the enantioselective electrooxidation of glucose. P. A. Christensen (Newcastle University, U.K.) presented *in situ* FTIR studies on the effect of temperature on the electrooxidation of formaldehyde, formic acid and methanol at Ru(0001) electrodes in perchloric acid solution. The results were compared with prior ones obtained from the adsorption of CO under similar conditions.

The three papers in the second set of catalysis papers had a common theme of electrochemical oxidation of CO adsorbed on Pt and Pt/Ru electrodes. Professor M. T. M. Koper (Eindhoven University of Technology, The Netherlands) studied the dynamics of CO at the solid/liquid interface by simulation of CO electrooxidation on Pt and PtRu electrodes. Professor D. A. Scherson (Case Western Reserve University, U.S.A.) described the use of *in situ* potential step SHG to study the electrochemical oxidation of adsorbed CO on Pt(111) in aqueous electrolytes.

The use of electrochemical NMR to study surface diffusion of chemisorbed CO (from methanol electrochemisorption) on Pt and Pt/Ru nanoparticles in the presence of supported electrolyte was described by Y. Y. Tong (Georgetown University, U.S.A.). The activation energy, deduced from temperature-dependent nuclear spin-spin and spin-lattice relaxation measurements, correlated with the steady state current for methanol electrooxidation. A simple two-dimensional collision theory model was proposed to explain the results. The paper suggested that in addition to the conventional bifunctional mechanism, surface dynamic

effects may play a more important role in enhancing CO tolerance in Pt/Ru fuel cell catalysts than has previously been suggested.

Adsorbed Layers and Films

In the final group of papers, Professor R. J. Forster (Dublin City University, Ireland) described the use of transient emission spectroscopy and cyclic voltammetry to investigate the ground and excited states of monolayers and trimers of novel osmium complexes in solution. Professor A. R. Hillman (University of Leicester, U.K.) reported the dynamics of regioregular conducting polymer electrodes in response to electrochemical stimuli.

Conclusions

Given the complicated nature of the electrode-electrolyte interface, many of the mechanisms are controversial. It is therefore not surprising that some conclusions attracted energetic debate. However, as Professor D. E. Williams (University College London, U.K.) stated in his concluding remarks, the event had great benefit and relevance.

The forum created a stimulating environment enabling specialists to suggest alternative explanations and propose further experiments. It was of major importance in reviewing the state of electrochemistry and shaping directions of future work on the electrode interface. With many advanced analytical tools available, the field is very exciting and still has many challenges to be overcome.

KIM CHANDLER

Kim Chandler is a Principal Chemist in Electrocatalyst Development, Johnson Matthey, Royston. Her current interests lie in developing precious metal catalysts and gas diffusion electrodes for the gas sensing and biosensing industries.

Platinum Coatings in Memory Capacitors

The production of a Pt film which has continuous smoothness and good step coverage, useful in capacitors, such as container capacitors for memory cells, is described in a patent by E. P. Marsh of Micron Technology Inc. (*U.S. Patent 6,387,802*). The Pt film is deposited by CVD from a Pt-based organic precursor in an inert carrier gas onto a substrate, such as TiN, which coats a silicon substrate. Ultraviolet light is used to decompose the precursor during or following the CVD. The film finally undergoes low-temperature annealing in oxygen to avoid metal silicide formation.