the importance of nanodes in determination of rate constants in the previously inaccessible regions.

Since the values obtained for fast electrode reactions using nanodes cannot be cross-checked by any other electrochemical method, one must resort to theoretical estimates. Marcus[6] has proposed the electron transfer theory, where he has derived a relation between homogeneous self-exchange rate constant (k_{ex}) and k_{het}:

$$k_{het} = Z_{het}(k_{ex}/Z_{bi})^{\frac{1}{2}},$$

where Z_{bi} is the bimolecular collision frequency ($10^{11}\ m^{-1}\ s^{-1}$) and Z_{het} the unimolecular collision frequency into a surface. The k_{het} so calculated from k_{ex} is found to be in reasonable agreement with the values estimated using nanodes!

In addition to their use in kinetic studies, nanodes can be used more profitably in such diverse areas as neurophysiology[7], lithography[8], chemical analysis[9] and scanning tunnelling microscopy[10], where ultramicroelectrodes have already established their place.

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Surface electrochemistry — going deep into interfaces

S. K. Rangarajan

The frontiers of electrochemistry have always been at the interfaces. Considering that the interfaces themselves are continually changing, and being restructured and modified, it is no surprise that breakthroughs in materials technologies are driven by an ability to understand and design, observe and characterize such interfaces. It is this theme that formed the backdrop of a recent Indo-German meeting.

The Indo-German Seminar on Electrochemistry, sponsored by Deutsche Forschungs Gemeinschaft (DFG), Bonn, and the Indian National Science Academy (INSA), New Delhi, was organized by Central Electrochemical Research Institute, Karaikudi, in two phases —the first in Madras (Kalpakkam), 25–27 February 1991, and the second in Karaikudi, 1–3 March. The meeting in Madras focused on surface structure and surface modification, while the Karaikudi part discussed emerging concepts and technologies.

Not surprisingly, the emphasis was on the ability of modern optical *in situ* techniques for observing electrode–solution interfaces. W. Plieth (Berlin) demonstrated how *in situ* infrared spectroscopy, together with modulation reflection spectroscopy and Raman spectroscopy, helps in understanding the structure of adsorbed inhibitors on electrode surfaces, while L. Dunsch (Dresden) illustrated the power of *in situ* ESR spectroscopy for the study of both electrochemical reactions and electrode structures (typically polymer-modified electrodes and nafion-modified electrodes).

The lecture by H. Strehblow (Dusseldorf) highlighted the use of electron and ion spectroscopies working in ultrahigh vacuum (such as the surface-analytical techniques X-ray photoelectron spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS) and Rutherford backscattering (RBS), in obtaining detailed information on the processes occurring on electrode surfaces, besides chemical compositions and structure of a wide range of systems in which passive layer formation takes place (e.g. Fe, Cr, Ni, Cu and Fe/Cr and Fe/Ni alloys).

Scanning tunnelling microscopy (STM), the new powerful and versatile surface-analytical technique, has been demonstrated by D. M. Kolb (Ulm) to be yet another important *in situ* tool, with atomic-scale resolution, useful for electrochemists in the study of interfaces formed by two condensed phases. He reported studies on surface topography of gold single-crystal electrodes induced by specific anion adsorption, atomic structure of metal underpotential-deposit (UPD) adsorbates, and nucleation/growth processes of bulk metal deposition.

The importance of *ex situ* techniques for surface characterization was not forgotten, and their use in the context of passive films on corroding systems, as well as the use of spectroelectrochemical techniques in analysing films on copper and brass in different anions, were described by K. Balakrishnan (Karaikudi). A. S. Nigavekar (Pune) described the use of AES, electron microscopy, quadrupole mass spectroscopy and small-angle X-ray diffraction in understanding surface structure and surface changes with illustrative problem studies.

M. Stratmann (Dusseldorf) in his lecture stressed how the thin surfaces of materials during atmospheric and indoor corrosion conditions need special techniques.

Motivation for modifying electrode surfaces comes from different directions, but the thrust is usually to prepare electrocatalytic surfaces and protective surfaces against corrosion. Presentations by F. Beck (Duisburg), G. Prabhakara Rao (Karaikudi), K. Juttner (Frankfurt), U. K. Chatterjee (Kharagpur), K. Doblhofer (Berlin), A. Q. Contractor (Bombay) and D. C. Trivedi (Karaikudi) brought to focus different aspects like ingenuity in preparation and novelty in the systems proposed for modification and methodologies adopted for investigation.

W. Paatsch (Berlin) dealt with laser-induced copper and nickel deposition on p-type silicon single crystals. K. E. Heusler (Clausthal) described electrochemical uses of the quartz oscillator, especially to study *in situ* mass changes associated with electrochemical reactions.

Elegant ways of modelling stochastic aspects in interfacial growth (and aggregation), by S. K. Rangarajan (Karaikudi); novel transient techniques for studying corrosion, by S. R. Rajagopalan (Bangalore); kinetics of anodic film growth of nickel in chloride-containing electrolytes, by R. Narayanan (Madras); and a variety of electrochemical sensors, by C. K. Mathews (Kalpakkam), were the subjects of other notable presentations.

Emphasis on the use of single-crystal electrodes with well-defined surfaces and the role of *ex situ* low-energy electron diffraction (LEED) and RHEED techniques in characterizing electrode surface topography and adlayers on gold and platinum electrodes and their surface reconstruction were detailed by Kolb in his lecture at Karaikudi. Surface-analytical techniques figured in a number of other presentations; for example: (i) the study of structure and reactivity of modified electrodes using mercaptanes and silanes for obtaining corrosion-resistant nickel surfaces, by Stratmann (who also introduced the Langmuir–Blodgett-film technique for modifying electrode surfaces); (ii) examination of surface oxide layers on copper, by Strehblow; and (iii) investigations leading to the identification of intermediates, the kinetics and mechanism of photoelectrochemical etching of semiconductors (*in situ* Raman and IR spectroscopic studies), by Plieth. Nigavekar spoke on the role of surface-spectroscopic techniques in characterization of modified surfaces.

S. Ramakrishna (Bangalore) discussed the role of surface states in photoelectrochemistry. Models of adsorption and electron transfer at electrochemical interfaces were introduced by A. K. Mishra (Madras). A theoretical analysis for electron transport through modified electrodes modelled as a many-body problem was presented by M. V. Sangaranarayanan (Karaikudi). The emerging interest aroused by ultrasonics in the study of interfacial reactions was brought to focus by V. Yegnaraman (Karaikudi).

A novel concept of measurement of volta potential differences between an 'emersed' and a reference metal, leading to computation of the apparent work function of the emerged electrode, was presented by Doblhofer, who also pointed out its use in obtaining information on the surface dipole potentials that help in elucidation of properties of thin membrane films (e.g. of conducting polymers). An interesting account of measurement of intrinsic electrochemical noise, as distinct from external electrical noise, on passive iron in electrolyte systems and attempts to correlate the same with surface reactions (including pitting) formed the basis of a presentation by Heusler.

The role of electrochemistry in what is termed molecular engineering to produce new materials was highlighted by G. Bidan (Grenoble, France). The wealth of experimental data presented covered novel (electrochemically prepared) hybrids of conducting polymers and inorganic heteropolyanions/nafion membrane, and composites of conducting polymers and magnetic particles. All these new materials have prospective applications in Smart windows, electrocatalysis and sensors. Emergence of ultramicro- (nano-) structural materials and recent advances in the synthesis of cluster species of metallic and semiconducting nature were brought to focus by K. L. N. Phani (Karaikudi). Rajagopalan illustrated, with several examples, the preparation and applications of nanomaterials.

Some materials made up of fluorinated compounds exhibit extraordinary properties. M. Noel (Karaikudi) dealt with the preparation of such compounds, including electrochemical fluorination of graphite intercalation compounds (draining applications in the battery industry).

New materials arising out of carefully designed deposition of a mixture of underpotential deposits (UPDs) on suitable electrodes can offer advantages hitherto not realized. A report of mixed lead and thallium UPDs on silver electrode was described by Prabhakara Rao.

The technological opportunities for novel organic electrosynthesis in aqueous system were reviewed by Beck, while Juttner brought to fore the novel chemical and electrochemical routes being evolved for gas (sulphur dioxide and nitrous oxides typically) purification of relevance to pollution control.

New technologies for the production of nuclear materials were presented by Mathews. A state-of-the-art report of the emerging technologies for electrolytic production of aluminium and magnesium was presented by C. O. Augustin (Karaikudi), while secondary recovery of nonferrous metals was presented by K. V. Venkateswaran (Karaikudi). Paatsch described electroplating procedures for high-strength steel to avoid hydrogen embrittlement. Sodium sulphur batteries and studies on lithium surface state (of relevance to lithium batteries) were discussed by M. Kamaludin (Karaikudi) and P. V. S. S. Prabhu (Karaikudi) respectively for an appraisal of the problems faced in the respective areas.

An overview of corrosion science and technology was presented by Balakrishnan, while corrosion protection measures with state-of-the-art methodology were reviewed by S. P. Manoharam (Karaikudi). R. Narayan (Madras) dealt with electrochemical machining. K. S. V. Santhanam (Bombay) attempted to throw light on some aspects of electrobiology, including photobiology.

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