

Nanometre electrodes—a new tool for electrochemical studies

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The advent of ultramicroelectrodes in recent times is an exciting development in electrochemistry and has provided a powerful tool for electrochemical studies¹. These electrodes, fabricated from ultrathin fibres (< 10 μm) of platinum, gold, carbon, etc. embedded in insulating matrix, are exposed to the electrolyte under study to generate their current-voltage behaviour. The measured current is generally separated into the faradaic component containing all the useful kinetic information and the capacitive component arising from the electrical double layer. When electrochemical reaction constants are to be determined using conventional macroelectrodes, very fast transient or high-frequency AC perturbation must be applied to the system. This has the disadvantage of producing a large charging current, which masks the more useful faradaic-current component. This limits the maximum measurable heterogeneous rate constant using macroelectrodes to less than 0.1 cm s⁻¹. To overcome this limitation ultramicroelectrodes are increasingly being used in kinetic studies. The advantage arises because the ratio of faradaic to charging current is in inverse proportion to electrode radius, and ultramicroelectrodes—with extremely small tip diameter of less than 10 μm—have a large i_F/i_C ratio. However, there is a price to be paid by way of instrumentation, as high-speed potentiostats (> megahertz) capable of handling sweep rates of the order of a million volts per sec must be used.

The recent reports of further miniaturization of ultramicroelectrodes to nanometre size have caused excitement among electrochemists². These electrodes, christened nanodes, have remarkably extended the range of measurable heterogeneous rate constants by as much as two orders of magnitude. Further, the requirement for fast-rise potentiostat and associated instrumentation is dispensed with. For the first time, it is now recognized that the area of the electrode has a crucial role in the kinetic measurements.

The nanodes are fabricated by an ingenious two-step procedure. A sharpened 0.5-mm-diameter platinum or platinum-iridium wire is electrochemically etched by AC. By means of controlled translational motion the wire is introduced into a molten glass bead to coat the wire with glass. The temperature of the molten glass and the translational velocity determine electrode radius. Using this procedure, it was found, out of 200 samples, 50% had a radius < 0.1 μm and 10% were in the range of 10 to 100 Å (1 to 10 nm). Scanning electron micrographs of the electrodes reveal that when the electrode radius is ≥ 0.5 μm, it is in agreement with electrochemically determined electrode radius. The smaller-aperture nanodes, however, appear to be completely covered with glass even at the highest magnification of 50,000. These electrodes still exhibited conventional steady-state microelectrode behaviour, showing that they are not totally insulating.

The measurement of electrode radius is carried out using electrochemical techniques. This involves measurement of mass-transport current i_L from the plateau region of the sigmoidal voltammogram. Radius is measured from the expression

$$i_L = 2\pi n F D C^* \gamma_{app}$$

where n is the number of electrons transferred, F the Faraday constant, D the diffusion coefficient, C^* the bulk concentration, and γ_{app} the apparent electrode radius. The radius of any particular electrode is measured in two separate experiments using different redox couples.

How does the small electrode radius help in measuring the fast electrode reactions? This is due to a large mass-transport velocity $m_0 (= D/\gamma_{app})$ arising out of the extremely small γ_{app} that nanodes have. This effectively transforms the nature of the reaction from mass-transfer-limited Nernstian behaviour to a charge-transfer-limited one. Further, when $\gamma \gg D/k_{het}$, mass-trans-

port behaviour was observed, and no quantitative kinetic information can be obtained. However, when electrode radius is comparable to D/k_{het} , the mass transport is so rapid that k_{het} can be calculated easily. In fact, nanodes with $\gamma_{app} \sim 10 \text{ \AA}$ are capable of measuring k_{het} that are within a factor of 6 of the values attainable by a hypothetical single platinum atom ($\gamma = 1.53 \text{ \AA}$) as electrode! It is owing to this ability to obtain k_{het} by merely changing electrode radius that nanodes occupy a unique position among electrochemical tools available for kinetic studies. This characteristic of nanodes leads to what is known as a 'kinetic voltammogram', which depends on electrode radius, as distinct from the 'Nernstian voltammogram' obtained using conventional electrodes.

The exact equation for calculating k_{het} and transfer coefficient α from a kinetic voltammogram was derived by Oldham and Zoski³. The magnitude of the potential shift from Nernstian voltammogram and its position on the potential axis were used to evaluate these kinetic parameters.

Measurement of kinetic parameters for $\text{Ru}(\text{NH}_3)_6^{3+}/\text{Ru}(\text{NH}_3)_6^{2+}$ in 0.5 M KCl is a case in point. In this system, the heterogeneous state constant k_{het} cannot be determined by conventional techniques⁴. In contrast, k_{het} determined using platinum nanodes of $\gamma_{app} = 10$ to 20 Å was $79 \pm 44 \text{ cm s}^{-1}$. Similarly, from microelectrodes of $\gamma = 0.3 \text{ \mu m}$, Bond *et al.*⁵ measured k_{het} for the ferrocene/ferrocenium system to be $> 6 \text{ cm sec}^{-1}$. When the same system was studied using platinum nanodes with $\gamma_{app} = 15$ to 20 Å, a k_{het} value of $220 \pm 120 \text{ cm s}^{-1}$ was obtained in $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NClO}_4$ electrolyte. However, the system of methyl viologen $\text{MV}^{2+}/\text{MV}^{+}$ and 1,1'-dicarbomethoxycobaltocene ($\text{CP}_2\text{Co}^{+/0}$) exhibited Nernstian behaviour even at nanodes with $\gamma_{app} \approx 20 \text{ \AA}$. The rate constants for the $\text{MV}^{2+}/\text{MV}^{+}$ and $\text{CP}_2\text{Co}^{+/0}$ system are $170 \pm 90 \text{ cm s}^{-1}$ and $130 \pm 70 \text{ cm s}^{-1}$ respectively. These examples illustrate

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. Marcus⁶ has proposed the electron transfer theory, where he has derived a relation between homogeneous self-exchange rate constant (k_{ex}) and k_{het} :

$$k_{het} = Z_{het} (k_{ex}/Z_{bi})^{\ddagger},$$

where Z_{bi} is the bimolecular collision frequency ($10^{11} \text{ m}^{-1} \text{ s}^{-1}$) 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 neurophysiology⁷, lithography⁸, chemical analysis⁹ and scanning tunnelling microscopy¹⁰, where ultramicroelectrodes have already established their place.

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Surface electrochemistry — going deep into interfaces

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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 Forschungsgemeinschaft (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. Plath (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.