

# Nanometre electrodes—a new tool for electrochemical studies

V. Lakshminarayan and S. R. Rajagopalan

The advent of ultramicroelectrodes in recent times is an exciting development in electrochemistry and has provided a powerful tool for electrochemical studies<sup>1</sup>. These electrodes, fabricated from ultra-thin fibres (< 10  $\mu\text{m}$ ) 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  $\text{cm s}^{-1}$ . 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  $\mu\text{m}$ —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 electrochemists<sup>2</sup>. 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  $\mu\text{m}$  and 10% were in the range of 10 to 100  $\text{\AA}$  (1 to 10 nm). Scanning electron micrographs of the electrodes reveal that when the electrode radius is  $\geq 0.5 \mu\text{m}$ , 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

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

where  $n$  is the number of electrons transferred,  $F$  the Faraday constant,  $D$  the diffusion coefficient,  $C^*$  the bulk concentration, and  $\gamma_{\text{app}}$  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  $m_0 (= D/\gamma_{\text{app}})$  arising out of the extremely small  $\gamma_{\text{app}}$  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  $\gamma \gg D/k_{\text{het}}$ , mass-trans-

port behaviour was observed, and no quantitative kinetic information can be obtained. However, when electrode radius is comparable to  $D/k_{\text{het}}$ , the mass transport is so rapid that  $k_{\text{het}}$  can be calculated easily. In fact, nanodes with  $\gamma_{\text{app}} \sim 10 \text{\AA}$  are capable of measuring  $k_{\text{het}}$  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  $k_{\text{het}}$  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  $k_{\text{het}}$  and transfer coefficient  $\alpha$  from a kinetic voltammogram was derived by Oldham and Zoski<sup>3</sup>. 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  $k_{\text{het}}$  cannot be determined by conventional techniques<sup>4</sup>. In contrast,  $k_{\text{het}}$  determined using platinum nanodes of  $\gamma_{\text{app}} = 10$  to 20  $\text{\AA}$  was  $79 \pm 44 \text{ cm s}^{-1}$ . Similarly, from microelectrodes of  $\gamma = 0.3 \mu\text{m}$ , Bond *et al.*<sup>5</sup> measured  $k_{\text{het}}$  for the ferrocene/ferrocenium system to be  $> 6 \text{ cm s}^{-1}$ . When the same system was studied using platinum nanodes with  $\gamma_{\text{app}} = 15$  to 20  $\text{\AA}$ , a  $k_{\text{het}}$  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  $\gamma_{\text{app}} \approx 20 \text{\AA}$ . 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. Marcus<sup>6</sup> 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 ( $10^{11} \text{ m}^{-1} \text{ s}^{-1}$ ) 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 neurophysiology<sup>7</sup>, lithography<sup>8</sup>, chemical analysis<sup>9</sup> and scanning tunnelling microscopy<sup>10</sup>, where ultramicroelectrodes have already established their place.

1. Fleischmann, M., Pons, S., Rolison, D. R. and Schmidt, P. P, *Ultramicroelectrodes*, Datatech Systems, Morgantown, 1989, chapter 3.
2. Penner, R. G., Heben, M. J., Longin, T. L. and Lewis, N. S., *Science*, 1990, **250**, 1118.
3. Oldham, K. B. and Zoski, C. G., *J. Electroanal. Chem.*, 1988, **256**, 11.
4. Gennett, T. and Weaver, M. J., *Anal. Chem.*, 1984, **56**, 1444.

5. Bond, A. M. *et al.*, *Anal. Chem.*, 1988, **60**, 1878.
6. Marcus, R. A., *J. Phys. Chem.*, 1963, **67**, 853.
7. Mamoon, A. M., Schlapfer, W. T., Fahwiler, B. H. and Tobias, C. A., *Adv. Biol. Med. Phys.*, 1977, **16**, 1.
8. Lin, C. W., Fan, F. R. and Bard, A. J., *J. Electrochem. Soc.*, 1987, **134**, 1308.
9. Nuwer, M. J. and Osteryoung, J., *Anal. Chem.*, 1989, **61**, 1954.
10. Lustenberger, P., Rohrer, H., Christoph, R. and Siegenthaler, H., *J. Electroanal. Chem.*, 1988, **243**, 225.

V. Lakshminarayan is in the Raman Research Institute, Bangalore 560 080, and S. R. Rajagopalan is in the Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017.