THE ADVANTAGES OF MICROELECTRODES IN THE STUDY OF ELECTROCHEMISTRY * M.I. Montenegro

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Microelectrodes have recently been applied in several areas of electrochemistry. Some of their most relevant properties will be described and an overview of the most important applications during the last few years till be given. These include kinetic studies under steady state and non-steady state conditions, electrochemical studies without supporting electrolyte and in highly resistive media and electrochemical nucleation studies.

INTRODUCTION

Microelectrodes were first developed for use <u>in vivo</u> electrochemical studies, especially for measuring concentrations of chemicals inside biological cells¹⁻³. Their very small size, ranging from 0.1 to 100 μ m make them particularly suited for such studies. For sometime now, <u>in vivo</u> potentiometric measurements have successfully been made with metallic microelectrodes but only recently Wightman and coworkers demonstrated that <u>in vivo</u>⁴⁻⁶ voltammetric studies, e.g. of neurotransmitter molecules, were also possible. For such experiments, a small electrode is, of course, an essential prerequisite to enable the precise positioning and also to limit the magnitude of the current thereby minimizing the depletion of electroactive species.

There are, however, additional properties of very small electrodes which can be exploited in other areas of electrochemistry 3 .

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Perhaps the most important are:

- (a) high rates of steady state diffusion can be obtained and hence fast electron transfer reactions and coupled chemistry can be studied without recourse to transient techniques on a short timescale,
- (b) it is possible to obtain high quality data in highly resistive media; since the currents flowing through the cell are low, IR drops are negligible,
- (c) charging currents are much reduced and the ratio of faradaic to non-faradaic current is greatly enhanced,
- (d) it is possible to study the deposition of single nuclei of a phase onto an inert electrode and also catalysis of such single centres.

For a spherical electrode, there is both a transient and a steady state contribution to the diffusion flux and if the electrode is made small enough the steady state term becomes large and dominates except at very short times. This property can be useful in many electrode kinetic studies^{7,8}.

Another interesting feature of microelectrodes is: the IR drop should decrease with electrode radius and also should the RC time constant of the cell. The former property allows studies to be made in highly resistive media and in the absence of supporting electrolyte⁹ and the second enables transient faradaic measurements to be made at shorter times than is possible with conventional methods^{10,11}, thus enabling faster reactions to be studied. It is also possible to to study fast coupled chemical reactions¹². McCreery and coworkers^{10,11} obtained meaningful spectrochemical measurements at short times (\sim 5 µs) through employing microelectrodes and a highly aligned laser source.

The small area of a microelectrode makes possible the growth of a single nucleus of a metal and some work has already been reported concerning phenomena associated with nucleation^{13,14}. Moreover, the ability to design systems with single growing nuclei can offer attractive possibilities in the study of catalysis. Attempts have already been made to study the hydrogen evolution reaction on palladium deposited onto a carbon fibre microelectrode¹⁵. Some recent studies on microelectrodes will be presented here but, first, some of their most important properties will be described.

DIFFUSION TO A MICROELECTRODE

Let us consider the simple electron transfer reaction

$$0 + ne \rightleftharpoons R$$
 (1)

and assume that the reaction is diffusion controlled. In the simplest case of a large planar electrode, the mass transport is by semi-infinite linear diffusion and is described by equations

$$\frac{\partial c_0(x,t)}{\partial t} = D_0 \frac{\partial^2 c_0(x,t)}{\partial x^2}$$

$$\frac{\partial c_R(x,t)}{\partial t} = D_R \frac{\partial^2 c_R(x,t)}{\partial x^2}$$
(2)

with appropriate boundary conditions. $c_0(x,t)$ and $c_R(x,t)$ are the concentrations of species O and R at a distance x from the electrode at time t and D_0 and D_r are the diffusion coefficients of species O and R. The current-time transient in response to a potential step is given by the Cottrell equation¹⁶,

$$I = \frac{nFAD_0^2 c_0}{(\pi t)^{\frac{3}{2}}}$$
(3)

where A is the electrode area.

In the case of a spherical electrode, mass transport occurs in a spherical diffusion field and the current/time profile for a potential step is $^{17}\,$

$$i = \frac{nFD^{\frac{1}{2}}c_{0}}{(\pi t)^{\frac{1}{2}}} + \frac{nFDc_{0}}{r}$$

(4)

The current at a spherical electrode of area $4\pi r_0^2$ is therefore given by

$$I_{g} = \frac{4\pi r_{o}^{2} n F D^{\frac{1}{2}} c_{o}}{(\pi t)^{\frac{1}{2}}} + 4\pi n F D c_{o} r_{o}$$
(5)

This equation has two limiting forms. At short times:

$$\frac{nFAD^{\frac{1}{2}}c_{\Omega}}{(\pi t)^{\frac{1}{2}}} >> 4\pi nFDc_{O}r_{O}$$
(6)

and the current is equivalent to that at a planar electrode of the same area. Conversely, at long times

$$\frac{\mathrm{nFAD}^{\frac{1}{2}}\mathrm{c}_{0}}{(\pi \mathrm{t})^{\frac{1}{2}}} << 4\pi \mathrm{nFDc}_{0}\mathrm{r}_{0}$$
(6a)

and the current is now determined by the steady state term

$$I_{c} = 4\pi n FDc_{o}r_{o}$$
(7)

Contrary to the linear diffusion case, where for long times the current tends to zero, here, at long times a steady state current is observed.

Let us now consider the case of a single disc microelectrode lying on an infinite planar insulator⁷. This problem is more complex than the case of an infinite planar electrode. Due to the finite dimensions of the electrode, some perturbations known as edge effects occur. These edge effects (which also do not occur at a spherical electrode) correspond to a supplementary cylindrical contribution. Figure 1 shows diffusion for different electrode geometries. For large electrode areas, at short times, the edge



FIGURE 1 Diffusion for different electrode geometries.

effects are small and the Cottrell equation fits experimental data satisfactorily. For small electrode areas, or longer times, these perturbations become important and the Cottrell equation is no longer an adequate approximation. The determination of the current-time behaviour of the disc electrode requires the solution of the following partial differential equation,

$$\frac{\partial \mathbf{c}}{\partial \mathbf{t}} = \mathbf{D} \left(\frac{\partial^2 \mathbf{c}}{\partial \mathbf{r}^2} + \frac{1}{\mathbf{r}} \frac{\partial \mathbf{c}}{\partial \mathbf{r}} + \frac{\partial^2 \mathbf{c}}{\partial \mathbf{z}^2} \right)$$
(8)

where r is the distance from the centre of the electrode in the plane of its surface and z is the perpendicular distance from the electrode surface. The first two terms describe a cylindrical diffusion field whilst the third term describes a superimposed linear one. No analytical solution exists for this separation so simulation or numerical methods must be used to obtain an approximate solution¹⁸⁻¹⁹. Several solutions have been proposed and all seem to be in fair agreement. It turns out that the time dependence of the current at a microdisc electrode is very complex. However, at long times the current at a microdisc electrode will reach a steady state term similar to the case of a spherical electrode given by²⁰

$$I_{m} = 4nFDc_{0}r_{0}$$
(9)

which corresponds to a current density of

$$i_{m} = \frac{4nFDc_{0}}{\pi r_{0}}$$
(10)

Typically, taking $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $r_o = 10^{-4} \text{ cm}$ and $c_0 = 2 \text{ mM}$, this steady state current will be reached in less than ls.

It is interesting to note the similarity with the steady state current obtained at a microdisc electrode. In fact, it is identical to that obtained at a hemisphere of radius $\pi r_0/2$. Whilst this similarity exists, an important distinction between the two cases should be noted. The current density over a polarized hemispherical electrode is uniform, but at an inlaid electrode there is extreme heterogeneity in the current density.

For most cases it has been shown⁷ that microelectrode data can be treated using the approximation of a spherical diffusion field.

Current-voltage curves at a microelectrode

Let us consider cyclic voltammetry at a microelectrode carried out at a relatively fast scan rate (> 10 V/s). At these rapid time scales the majority of the diffusion is perpendicular to the electrode surface and the voltammogram obtained is peak shaped as it would be at an electrode of conventional size (radius \approx 1 mm).

At lower scan rates radial diffusion to the edges of the surface becomes important and a steady current arises because the electrolysis rate is approximately equal to the rate of diffusion of molecules to the electrode surface. Figure 2 shows cyclic voltammograms of anthracene at a microelectrode at 0.1 V/s and 1000 V/s. At an electrode of larger size, this type of effect is difficult to observe because the scan rate must be very slow for the radial diffusion to contribute appreciably to the current.

The small hysteresis observed in the steady state experiment is explained in terms of protonation of the anion radical product through contamination of the electrolyte solution. It can therefore be seen that the time scale of the measurement and the radius of the electrode affect the type of voltammogram that one obtains in stationary solutions. At fast time scales or at electrodes of large radius, pesk shaped voltammograms are obtained, whereas with small radius or with long time scales of measurements, steady-state voltammograms are obtained.



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FIGURE 2 Cyclic voltammograms for the reduction of anthracene in DMF/Bu_4NBF_4 at a carbon fibre microelectrode of 8 µm diameter. (a) c = 5 x 10⁻³M; scan rate = 0.1 V s⁻¹; (b) c = 1.5 x 10⁻²M; scan rate = 1000 V s⁻¹.

Electrodes of intermediate size (or measurements at intermediate scan rates), of course, give intermediate results: time-dependent and time-independent currents are superimposed.

OTHER FEATURES OF MICROELECTRODES

Microelectrodes show great potential for very fast measurements since double-layer charging currents are proportional to the electrode area. The charging current, in fact, determines the shortest time at which meaningful measurements of faradaic current can be made. For a potential pulse the charging current, I_{c} , is

$$I_{c} = \frac{\Delta E}{R} \ell^{-t/RC}$$
(11)

where ΔE is the amplitude of the pulse, R is the resistance of the electrochemical cell, C is the double layer capacitance and t is the time measured from the application of the pulse.

The double layer charging current decreases exponentially with a decrease of area, while the time-dependent faradaic current decreases linearly with area. Thus, the faradaic/non-faradaic current ratio is increased at a microvoltammetric electrode. For example, for a disc electrode of 4 μ m radius, the double layer should be 99% charged within 3 μ s, even assuming a 100 μ F cm⁻² double layer capacitance and a cell resistance of 10 KC. With this response, very rapid timedependent measurements of chemical events can be made. However, when carbon fibre microelectrodes are used, large non-faradaic currents are observed that restrict faradaic measurements to the millisecond time domain. This is probably due to microcracks in the carbon formed during the process of fabrication, or surface oxides on carbon³.

The internal resistance of microelectrodes may be approximated to the resistance of a conductor of uniform right cylindrical geometry by the equation

$$R_{\rm m} = \frac{\ell}{\sigma A} \Omega \tag{12}$$

where ℓ is the length of the conductor (cm), A is the cross-sectional area (cm²) and σ is the conductivity (mhos cm⁻¹). Thus for a platinum fibre microelectrode of length 2 cm and conductivity 9.4 x 10⁴ mhos cm⁻¹, the following internal resistances are obtained:

Radius	(µm)	Resistance	(Ω
1		675	
5		30	
10		7	
25		1	
50		0.3	

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In addition to the internal resistance of microelectrodes, the resistance between the electrode tip and an external electrode must also be considered. For a spherical electrode, this resistance is given by²¹,

$$R_{s} = \left(\frac{\rho}{4\pi}\right) \left(\frac{1}{r_{1}} - \frac{1}{r_{2}}\right)$$
(13)

where ρ is the specific resistance of the solution, r_1 is the radius of the microelectrode and r_2 the distance of the external electrode from the microelectrode.

In aqueous 1M KCl solutions with $r_1 = 10^{-4}$ cm, $r_2 = 1$ cm and $\rho = 8.98 \ \Omega$, the value of R_g is 7.15 x $10^3 \ \Omega$. Similarly, in DMF solutions containing tetrabutylammonium iodide (0.2M) with the same values of r_1 and r_2 and with $\rho \approx 100 \ \Omega$ cm, R_g is now approximately $8 \ x 10^4 \ \Omega$. Clearly this resistance exceeds that for the internal resistance of small microelectrodes. Nevertheless, the total voltage drop - IR drop - attributable to a microelectrode will remain less than a millivolt for measured currents < 10^{-8} A corresponding to current densities < 0.5 A cm⁻². This low IR drop value justifies the use of a two electrode cell for microelectrode experiments. Moreover, the use of microelectrodes of radius < 1 µm provides applications in fields such as monitoring of electrochemical reactions in organic solvents in the absence of supporting electrolyte.

Another important feature of microelectrode techniques is that they do not require any forced convective stirring or measurements to be made at short times, which greatly simplifies the experiments. Furthermore, the concentration is perturbed by electrolysis only a very small distance from the microelectrode (approximately six times the radius under totally steady-state conditions). Therefore, microelectrodes are not greatly affected by movements in solution. In fact, steady-state current density observed at microelectrodes of 4 μ m radius is equivalent to that observed at a rotating disc electrode operated at 500 r.p.s.

It is also important to note that because the currents at these electrodes are extremely small, they are virtually non-destructive of the species being electrolysed. Obviously, small electrodes are necessary when used as sensors of changes in chemical concentrations of neurotransmitters in the mammalian brain, so that the brain region is not destroyed in the measurements³. Surprisingly it has been suggested³ that microelectrodes might also have applications in synthesis. It is necessary to design a structure with many microelectrodes, far enough apart that each retains the special properties of a microelectrode. Then it is possible to see in principle how one could carry out synthesis in poorly conducting media or to carry out le reduction of a substrate normally undergoing an ECE reaction at a macroelectrode.

ELECTRODE CONSTRUCTION AND ELECTRONIC EQUIPMENT

Microelectrodes can be constructed by several techniques²² from different materials; here, only the methods to build platinum and carbon microelectrodes used in voltammetric experiments, will be described.

Platinum microelectrodes are made out of platinum wire coated with a layer of silver²³. A 1 cm length of this wire is silver soldered to one end of a fine helical spring while the other end of the spring is soldered to the central core of a low noise coaxial cable. The assembly is then placed inside a glass capillary until the platinum wire protrudes through the end of the capillary. About 0.5 cm of this wire is immersed in HNO_3 to remove the silver layer and carefully pushed back into the glass capillary and the metal tip can be sealed into glass under vacuum (figure 3(a)). The function of the helical spring is to adsorb any tension between the fixed coaxial cable and the wire. The final task is to expose the extreme tip of the metal through careful polishing of the glass tip using, in succession, very fine emery paper followed by 6 μ m and 1 μ m diamond paste as a suspension in an oil base lubricating fluid on a special polishing cloth; alumina powder in an aqueous suspension is also used to polish the electrode surface. The diameters available to construct these electrodes are 2, 5, 10, 25 and 50 μ m.

Carbon microelectrodes are constructed from carbon fibres with diameters in the range 6-12 μ m. Approximately 1 cm of the fibre is sealed into a glass capillary under vacuum and the external contact is made by melting Pb pellets inside the glass tube and inserting a copper or nickel wire in the melt; when the melt cools down a good contact is obtained (figure 3(b). The polishing of the exposed area is carried out in a similar way as described for a platinum microelectrode.

Due to the low currents in microelectrode experiments, a potentiostatic control with a three electrode cell is not necessary. Moreover, the reference electrode can serve also as a counter electrode and the potential can be directly applied by means of a waveform generator. The currents are measured by a high gain picoameter connected in series with the cell. The output current is then recorded either directly on an X-Y recorder or on an oscilloscope. A



FIGURE 3 Microelectrode assemblies for (a) platinum microelectrode and (b) carbon fibre microelectrode.



FIGURE 4 Circuit diagram for two cell operation

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schematic diagram of the circuit is shown in figure 4.

KINETIC DETERMINATIONS ON MICROELECTRODES UNDER STEADY STATE CONDITIONS

The large steady state mass transport coefficient that can be achieved at a microelectrode permits kinetic determinations to be made from steady state experiments (c.f. rapidly rotated disc electrodes). An example of this is the work by Fleischmann and co-workers²⁴ where the kinetics of Hg/Hg_2^{2+} system was studied. In this investigation, an ensemble of approximately 10^6 mercury droplets of radii ~ 10 nm, electrodeposited on vitreous carbon was used as the electrode and values of k^{Φ} and α were obtained from quasi steady state current-voltage measurements. Hills and co-workers²⁵ made similar studies on this reaction using a multiple pulse technique. Fleischmann et al⁷ have extensively studied the rate of electron transfer at small electrodes and find it to be comparable to that of electrodes of conventional size. However, because the effect of diffusion on the electrochemical signal is less pronounced, faster heterogeneous rate constants can be measured at microelectrodes.

The reduction of tert-nitrobutane in DMF/Bu₄NI (0.2M) was studied using tungsten and platinum microelectrodes.²³ A linear sweep for this reduction is shown in figure 5.

For an irreversible reaction at a spherical electrode

$$\frac{i_{g}}{i_{d} - i_{s} \left[1 + \exp \frac{nFE}{RT}\right]} = \frac{nFK_{o}c^{\infty}}{i_{d}} \exp - \frac{\alpha nFE}{RT}$$
(14)

where id is the diffusion controlled limiting current density and i



FIGURE 5 (a) Cyclic voltammogram for the reduction of tertnitrobutane (12 mM) at a platinum microelectrode (5.8 μm) in DMF/Bu₄NI, scan rate = 8.33 mV/s; (b) Tafel plot according to equation (15).

is the spherical diffusion current. The value of i_d could be calculated from the observed limiting current by assuming an electrode of circular cross section of area πr^2 .

Taking logarithms of equation (14) one gets

$$ln = \frac{i_g}{i_d - i_g \left[1 + \exp\frac{nFE}{RT}\right]} = ln \frac{nFK_o c^{\infty}}{i_d} - \frac{cnFE}{RT}$$
(15)

A plot of the left hand side of equation (15) against E should produce a straight line with,

slope =
$$\frac{\alpha nF}{RT}$$

intercept = $\ln \frac{nFK_{o}c^{o}}{i_{d}}$

from which values of α and K_o can be obtained. The data obtained for tert-nitrobutane was analysed in this manner and is presented in figure 5(b) showing in fact a slight curvature of the Tafel plot as a function of the applied potential. Values of $K_o = 3.6 \times 10^{-3} \text{ cm s}^{-1}$ and $\alpha = 0.6$ were obtained and they compare well with those obtained by Saveant and co-workers²⁶.

The high diffusive flux at a microelectrode also serves to mask the presence of coupled homogeneous chemical reactions and subsequent electron transfers that follow the initial electron transfer. The chemical processes that follow the initial electron transfer and are of moderate rate will have much less of an effect on the current at microelectrodes than at larger electrodes. To illustrate this fact let us consider the reaction

$$0 \xrightarrow{\text{ne}} R \xrightarrow{k_{c}} 0 + Y$$
(16)

which is a catalytic reaction. At a large electrode the regenerated species 0 will return to the electrode surface, resulting in an increased current. However, at a microelectrode with moderate values of k_c very little enhanced current is observed. In fact, the average distance into solution that R diffuses before reacting to form 0, given by $(D\tau)^{\frac{1}{2}}$, where τ is the half life of the reaction and D the diffusion coefficient, is larger than the radius of the microelectrode. Thus, a large part of the regenerated oxidant is removed from the vicinity of the electrode surface and a minimal catalytic contribution is observed. Wightman et al⁵ have demonstrated this in the case of a catalytic EC reaction, the electro-oxidation of dopamine in the presence of ascorbic acid, at a carbon fibre disc electrode, conditions at which catalytic reaction is known to occur. This reaction is of

importance in the measurement of dopamine in the brain since ascorbic acid is present in large concentrations in extracellular fluid and thus could distort measurements of extracellular dopamine. The reaction mechanism can be represented by

$$DA \xrightarrow{-2e} DQ \qquad (17)$$

$$\uparrow \xrightarrow{-2H^{+}} DQ \qquad (17)$$

$$\downarrow \xrightarrow{k_{c}} DA + DHA \qquad (18)$$

where DOQ and DHA represent oxidized forms of DA (dopamine) and AA (ascorbic acid). The catalytic rate (k_c) for this reaction is sufficiently fast that the faradaic current is equal to the sum of the diffusion controlled currents for DA and AA. Because of the small area of microelectrodes, only a small portion of the catalytically regenerated DA can return to the electrode and, thus, these electrodes are essentially blind to this interference.

Fleischmann et al⁷ determined the kinetics of fast first order or pseudo first order homogeneous chemical reactions coupled to heterogeneous electron transfer reactions, using platinum microelectrodes of radii in the range 0.3 - 25 μ m.

One of the reactions studied was the electroreduction of acetic acid. This reaction is known to proceed via the following reaction sequence (CE mechanism)

$$HA \underset{k_{2}}{\overset{k_{1}}{\underset{k_{2}}{\overset{k_{1}}{\underset{k_{2}}{\overset{k_{1}}{\underset{k_{2}}{\overset{k_{1}}{\underset{k_{2}}{\overset{k_{1}}{\underset{k_{2}}{\underset{k_{2}}{\overset{k_{1}}{\underset{k_{2}}{\atopk_{2}}{\underset{k_{2}}{\atopk_{2}}{\underset{k_{2}}{\underset{k_{2}}{\underset{k_{2}}{\underset{k_{2}}{\atopk_{2}}{\underset{k_{2}}{\atopk_{2}}{\underset{k_{2}}{\atopk_{2}}{\underset{k_{2}}{\atopk_{2}}{\underset{k_{2}}{\atopk_{2}}{\underset{k_{2}}{\atopk_{2}}{k$$

$$H^+ + e \rightleftharpoons \frac{1}{2} H_2$$
 (20)

where k_1 and k_2 are related to one another by the known equilibrium

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constant for the acid dissociation.

A solution for the steady state current density in a spherical diffusion field was obtained for a microdisk electrode expressed by equation

$$\frac{1}{i_{m}} = \frac{\left(k_{2}C_{A}^{\infty}\right)^{\frac{1}{2}}}{nF(D_{H})^{\frac{1}{2}}k_{1}c_{HA}^{\infty}} + \frac{\pi r_{m}}{4nFD_{HA}c_{HA}^{\infty}}$$
(21)

where r is the radius of the microelectrode.

A good linear relationship was obtained between i_m^{-1} and r_m and kinetic data was obtained from the slope and the intercept. Such a plot is presented in figure 6. From the slope the value of $c_{u_A}^{\infty}$ is



FIGURE 6 A plot of the inverse of the limiting current density as a function of electrode radius for the reduction of acetic acid in sodium acetate (1M). Acetic acid concentrations (a) 40 mM and (b) 70 mM.

found; then, from the intercept and assuming that

$$k_1 c_{HA}^{\infty} = k_2 c_H^{\infty} c_A^{\infty}$$

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the value of k_2 was calculated and found to be $4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ which agrees reasonably well with reported values²⁷.

The application of steady state current measurements at microelectrodes has been extended to ECE and DISP 1 reactions⁸. As a test ECE system, the oxidation of anthracene in acetonitrile was investigated and a test DISP 1 system was the oxidation of hexamethyl benzene. For these cases no analytical solution is obtainable and, therefore, simulation techniques were used to try to determine the rate constant. It was also concluded that the use of microelectrodes does not permit differentiation between ECE and DISP1 mechanisms.

The examples described so far clearly demonstrate the usefulness of microelectrode techniques for the determination of reasonably fast electrode kinetics. At this point it will be useful to consider what range of homogeneous and heterogeneous rate constants are accessible through steady state measurements. With a 1 μ m electrode, the upper limit of heterogeneous rate constant measurable is of the order 0.1 cm s⁻¹ while the corresponding limit for a microelectrode of radius 0.1 μ m increases to about 1 cm s⁻¹. Above these values, the current voltage curves become indistinguishable from the reversible wave and equation (14) cannot be applied²³.

A technique based on a micro-ring electrode in turbulent pipe flow conditions has recently demonstrated the ability to measure the rates of electron transfer processes with a claimed upper limit of 5 cm s⁻¹ 28.

When studying homogeneous rate constants, the following boundaries for k can be determined assuming $D = 2 \times 10^{-5}$ cm s⁻¹: using an electrode of 0.5 μ m radius the maximum limit is k = 1.5 x 10⁵ s⁻¹ (with ± 25% error) and with 0.1 μ m radius electrodes a value of k = 10⁶ s⁻¹ can be reached²⁹.

ELECTROCHEMICAL STUDIES WITHOUT SUPPORTING ELECTROLYTE AND IN HIGHLY RESISTIVE MEDIA

Electrochemical experiments are traditionally carried out in the presence of high concentrations of supporting electrolyte in order to lower the solution resistance which is particularly high in many organic solvents, and to suppress the migration current whenever charged species are under study. Unfortunately it happens very often that the use of an electrolyte complicates the voltammetric studies as it alters the kinetic and thermodynamic properties and ionic strength of the system. In fact, a wide range of co-ordinately unsaturated compounds have not been studied because of reactions with solvent and/ or supporting electrolyte³⁰. Spectroscopic measurements have no equivalent requirement, thus, electrochemical techniques are disadvantageous in this respect. However, recent developments in microelectrode design and instrumentation offer the possibility of using voltammetric methods without a supporting electrolyte³.

In fact, because of the spherical nature of the diffusion layer, microelectrodes are superior to planar electrodes with respect to minimization of resistance effects. Although the resistance between the microelectrode and the external electrode increases as the radius of the microelectrode is made smaller, the resistances per unit area of electroactive surface are low and become lower with decreasing radius of the microelectrode. This aspect was examined experimentally for the oxidation of ferrocene in acetonitrile without supporting electrolyte⁹. At conventional platinum electrodes in acetonitrile (0.1M Et_4NC10_4), the oxidation corresponds to a chemically reversible process to produce ferricinium cation

$$Fc \rightleftharpoons Fc^+ + e$$
 (23)

With a 25 μ m Pt electrode, a sigmoidal-shaped voltammogram is obtained, even when moderately fast scan rates of potential are used. Figure 7(a) shows such a cyclic voltammogram at a 25 μ m Pt electrode in the presence of 0.1M Et₄NClO₄ and 7(b) shows a cyclic voltammogram in the absence of electrolyte. The limiting current is almost the same as



FIGURE 7 Voltammogram for the oxidation of 10^{-3} M ferrocene in acetonitrile at 18° C using a 25 µm radius Pt microelectrode in (a) presence and (b) absence of 0.1M Et_ANC10_A. Scan rate = 5 mV s⁻¹.

that in the presence of supporting electrolyte. However, the absence of electrolyte produces a drawn-out curve consistent with significant ohmic drop. Figure 8 shows the log $\{(i_d^{-i})/i\}$ vs E plot with and without electrolyte and demonstrates how the shape is influenced by the concentration of electrolyte. $E_{\frac{1}{2}}$ becomes correspondingly more positive as the electrolyte concentration is increased. When using a 25 µm



FIGURE 8 Plot of log $\{(i_d-i)/i\}$ vs E for oxidation of 10^{-3} M ferrocene in acetonitrile at 18° C with (a) 0.1M Et₄NClO₄, (b) 0.01M Et₄NClO₄ and (c) no added electrolyte. 25 µm radius Pt microelectrode. Scan rate = 5 mV s⁻¹.

electrode, addition of small concentrations of electrolyte to a 10^{-3} M solution of ferrocene suggests that an electrolyte concentration only slightly in excess of that of the ferrocene is required to produce high quality data. By contrast, voltammetric curves shown in figure 9 demonstrate that with a much smaller 0.5 µm electrode, data in the absence of electrolyte are very similar to those obtained in the presence of electrolyte.

It was, then, concluded that microelectrodes of radius < 1 μm enable important electrochemical measurements to be made on uncharged



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FIGURE 9 Effect of addition of electrolyte to acetonitrile when using a Pt microelectrode of 0.5 μ m radius (a) without electrolyte and (b) with 10^{-3} M Et_aNClO₄.

compounds in a range of organic solvents in the absence of supporting electrolyte. Limitations apply to studies on charged species where migration currents are present but, fortunately, the great majority of compounds studied in organic solvents are uncharged species.

Some studies have also been done using platinum microelectrodes of radius less than 1 µm at temperatures down to the freezing point of the solvent (eutectic mixtures) in solvents such as acetonitrile and acetone³¹. The use of low temperature electrochemistry can be advantageous for studying the influence of chemical reactions accompanying charge transfer and in understanding mechanistic aspects of electron transfer. However, at low temperatures IR drop problems become severe because electrolytes are frequently insoluble. Fleischmann et al³¹ explored the use of platinum microelectrodes in non-aquecus solvents down to the temperature of the solution-solid eutectic temperature and in "glasses" at even lower temperatures. At low temperatures, even though R increases, substantially decreased diffusion coefficients will lead to a further significant decrease in the currents providing a compensating effect. Thus, if the currents are not too low to be measured, this strategy can be applied to eutectic mixtures and glasses, media which are generally considered unsuitable for electrochemical measurements. Again, the system ferrocene/ferricinium ion was studied in acetonitrile over the temperature range $25^{\circ}C$ to $-50^{\circ}C$ (approximate temperature of the eutectic) in the presence of 0.05M Et_A NClO_A.

Figure 10 shows a series of curves obtained for the oxidation process on lowering the temperature from $15^{\circ}C$ to the eutectic temperature. The limiting current decreases with temperature and 11s can be attributed to a change in diffusion coefficient.



FIGURE 10 Steady state voltammogram obtained for oxidation of 10^{-3} M ferrocene in acetonitrile (0.05 Et₄NCIO₄) at variable temperature with a platinum microelectrode of radius 25 µm. Scan rate = 5 mV s⁻¹.

Figure 11 shows a plot of log $\left(\frac{i_d-i}{i}\right)$ vs E. The slope increases with temperature and Nernst equation is obeyed in all conditions. For example at the eutectic temperature (^-.-50°C) the slope is -43 mV which can be compared with the Nernst 2.303 $\frac{RT}{nF}$ value of -43 mV. On lowering the temperature below the eutectic temperature

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FIGURE 11 Plot of $\log \left(\frac{id^{-1}}{i}\right)$ vs E for oxidation of 10^{-3} M ferrocene in acetonitrile (0.05M Et₄NClO₄) at variable temperature with a platinum microelectrode of radius 25 µm. Scan rate = 5 mV s⁻¹.

to generate a glass, electrochemical experiments had to be modified, and an acetone Ag/AgCl (saturated LiCl) reference electrode was built. A temperature of -78° C was obtained using a dry ice (acetone) slush bath to generate the glass; at this temperature the reference electrode is still in the solution phase since the freezing point of acetone is well below it.

It was observed that the oxidation of ferrocene in the presence

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of 0.05M $\operatorname{Et}_4\operatorname{NClO}_4$ gave rise to current-voltage curves which were irreproducible and erratic. The performance improved, however, as the concentration of supporting electrolyte decreased. This fact may be attributed to the lack of uniformity in "glass" generation when high concentrations are present.

The best results were obtained with electrodes of radius < 1 µm and in the complete absence of electrolyte. Clearly, conventional platinum electrodes would not work in these media.

The success of the measurements is due to the very low IR drops using electrodes of very small radius.

High quality data was also obtained when studying the electrodeposition and dissolution of lithium metal at copper microelectrodes using solvents of high dielectric constant in the presence of LiAsF₆³². Figure 12 shows a current-voltage curve for Li⁺ deposition | I/ μ A



in THF with a limiting current due to mass transport including some

contribution from migration. A range of experiments were also carried out in THF/diethyl ether mixtures with results similar to those obtained in THF. Pure diethyl ether gave curves of the same shape but the deposition currents were low. However, with the addition of only 10% THF the results compare well with those obtained with pure THF. Single potentiostatic transients recorded for lithium deposition are shown in figure 13. A series of double pulse experiments were also



FIGURE 13 Current-time responses to potential steps from 0 mV to the potential shown (vs the Li/Li⁺ reference electrode). THF/LiAsF₆. Cu microelectrode (area = $5 \times 10^{-5} \text{ cm}^2$).

carried out where the first pulse was used to form a layer of lithium on the copper microelectrode and then the rate of growth at the lower negative overpotential can be observed. In such experiments the lithium was found to grow at a steady state over at least 50 s. Also the anodic dissolution of lithium metal was studied by a series of double pulse experiments. A set of such transients is shown in figure 14. Over a wide potential range (+ 20 mV to + 175 mV), the



FIGURE 14 Current-time responses for the oxidation of freshly deposited lithium metal. THF/LiAsF₆. Cu microelectrode (area = $5 \times 10^{-5} \text{ cm}^2$).

lithium metal oxidises at an approximately uniform rate at each potential. Figure 15 shows plots of steady state current vs overpotential for both the deposition and dissolution of lithium. The log I-E plot obtained from figure 14 is clearly that for a rapid electron transfer couple. This study has shown that using microelectrodes, meaningful and reproducible data can be obtained in solvents commonly used in rechargeable lithium batteries.

The influence of temperature on the kinetics of the Li/Li⁺ couple in 90% diethyl ether/10% THF was also investigated and it was shown that temperature has a strong influence on the nucleation potential, the rate of mass transport and the kinetics of the Li/Li⁺ couple.



FIGURE 15 Plots of steady state current vs potential for the deposition of lithium and its dissolution. x Data from plateau currents of figure 12; o Data from the plateau currents of figure 13; • Data from double pulse experiments.

ELECTROCHEMICAL NUCLEATION STUDIES

Another specific application of microelectrodes is in the area of nucleation studies. In view of the small electrode area it is possible under certain conditions to study the nucleation and growth of a single nucleus¹³. A technique was developed to initiate and grow a single nucleus of mercury on C and Pt microelectrodes under diverse conditions of overpotential and of concentration of electrolyte. Figure 16 shows a cyclic voltammogram for the deposition of mercury on a carbon microelectrode. A large cross-over of the cathodic current is observed which is a result of the continued expansion of the electroactive mercury surface as the nucleus grows.



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FIGURE 16 Cyclic voltammogram for the deposition of mercury on a carbon fibre from a 5 x 10^{-3} M solution of Hg₂(NO₃)₂ in aqueous potassium nitrate. Sweep rate: 50 mV s⁻¹



FIGURE 17 Potentiostatic transient for the growth of a mercury nucleus on carbon fibre from 0.1M solution of $Hg_2(NO_3)_2$ in ENO_3 (aq) at -200 mV. Figure 17 shows a potentiostatic current transient. A long induction period (which varies from experiment to experiment) is observed before the birth of a nucleus on the electrode. This induction period is a direct consequence of the need of clusters of adatoms to grow to a critical size required for the onset of a new phase.

The growth of the mercury nuclei was found to be controlled by spherical diffusion and the results agree well with the predictions of the theory³³ and also with data obtained by computer simulation³⁴.

Assuming that the mercury nucleus formed in this experiment described by figure 17 is growing under mass transfer control, then its radius 1 ms after the birth of the nucleus is

$$r = \left[\frac{2DcMt}{\rho}\right]^{\frac{1}{2}} = 5.4 \times 10^{-6} \text{ cm}$$
(24)

and the current density at its interface is of the order of 50 A cm⁻². This is a very high limit for the mass transfer flux and attempts have been made to use this fact as a basis of an alternative method of electrode kinetics³⁵.

Since the formation of a small nucleus will proceed from the aggregation of one or more clusters of molecular dimensions, the nucleation step is a stochastic process. Thus, individual transients will show large fluctuations from the mean of an ensemble.

The rate constant for the electrochemical formation of single metallic nuclei is simply the inverse of the mean value of the induction time which precedes the birth of each growing crystallite. The mean values of the induction time and its standard variance were determined for the reduction of Hg_2^{2+} and the resultant distribution of induction times is shown in figure 18.



FIGURE 18 Temporal distribution of nucleation induction times observed at different overpotentials.

ELECTROCHEMICAL STUDIES UNDER NON-STEADY STATE CONDITIONS

The fact that the faradaic/non-faradaic current ratio increases at microelectrodes enables the measurement of fast transients³⁶. This feature of very small electrodes has recently enabled the determination of the standard oxidation potentials of aromatic hydrocarbons and their π -complexes with metals¹².

The oxidation of most aromatic compounds exhibits chemically irreversible behaviour at sweep rates < 100 V s⁻¹. This is shown by the absence of the cathodic component on the return potential sweep, largely owing to competition from fast follow-up reactions of the metastable arene cation radicals. As a result, the E⁰ values of the common benzene derivatives are absent in the literature.

For instance, at a conventional platinum electrode, the oxidation of mesitylene in trifluoroacetic acid required a scan rate of 20 V s⁻¹ before the cathodic wave could be observed on the return potential sweep. However, at these high scan rates, problems associated with uncompensated ohmic drop and capacitance effects became severe. Some microvoltammetric studies were then performed using a 13 μ m gold disc and cyclic voltammograms were recorded for sweep rates in the range 200 to 5000 V s⁻¹. Even over this extensive span of scan rates, the charging current represented less than 25% of the total peak current and the cyclic voltammogram peaks were broadened only slightly. Some representative examples are shown in figure 19.



FIGURE 19 Typical cyclic voltammograms of various polyalkylbenzenes $(\sim 10^{-3} \text{M})$ in trifluoroacetic acid at a gold microelectrode.

The standard oxidation potentials, $E_{\rm Ar}^0$, were obtained from the reversible cyclic voltammograms obtained at fast scan rates.

Similar experiments have been applied to the cathodic cleavage of tosyl esters and tosyl amides 37 which follows an ECE mechanism of the type

$$Tos-X + e \rightleftharpoons [Tos-X]^{-}$$
(25)
$$\begin{bmatrix} Tos-X \end{bmatrix}^{-} \stackrel{k}{\longrightarrow} Tos^{-} + X^{-}$$
(26)
$$X^{+} + e \implies X^{-}$$
(27)

(27)

where Tos = $p-CH_3C_6H_4SO_2$ and X = OR or NR₂.

The rate constant for the cleavage reaction is very high $(10^5 - 10^7 s^{-1})$ and was determined by means of the homogeneous redox catalysis 38.

Attempts have now been made to study the kinetics of the homogeneous chemical reaction by using microelectrodes and very high sweep rates. Figure 20 shows cyclic voltammograms for Tos $NHC_{g}H_{11}$ at a 10 µm radius platinum microelectrode. Sweep rates as high as



FIGURE 20 Cyclic voltammograms for the reduction of $2 \times 10^{-2} M$ Tos NHC6H, in DMF/BuANBF, (0.1M) at a 10 µm radius platinum microelectrode at different sweep rates as indicated.

 8000 V s^{-1} were used but no reverse peak was observed. Undoubtedly in the case of such large rate constants, much higher sweep rates will have to be used and further work is required in order to find the appropriate experimental conditions.

CONCLUSIONS

It can be seen from the above that microelectrodes have applications in quite diverse areas of electrochemistry. To the present, however, the literature is dominated by a few active groups. I would like to emphasise the simplicity of the instrumentation required for experiments with microelectrodes and the ease of carrying out such experiments. Moreover, the experimental data is highly reproducible. I therefore believe that microelectrodes are one of the truly significant innovations of recent years and that their uses will become universal in the future.

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