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Electrode kinetics

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An electrode is an ideal catalyst in that the potential difference at the electrode–solution interface controls both the thermodynamics and the kinetics of the electrochemical reactions. However, the kinetics of electrode processes are relatively unselective. Greater selectivity can be achieved by the use of modified electrodes in which a redox catalyst is attached to the electrode surface. The kinetics of charge transfer in the modified layer are discussed in this paper. Another major problem is that the reactant must find the electrode. High conversions can be achieved by using a packed bed electrode. Results are presented showing how the performance of this type of electrode can be improved by using a graded bed rather than a uniform bed.

There are three reasons why an electrode is an ideal catalyst for carrying out reductions and oxidations. First and most important the reactivity of the electrode can be controlled by changing the potential difference at the electrode–solution interface. For a one-electron transfer a change of 1 V alters the equilibrium constant of the reaction $O + e^- \rightleftharpoons R$ by 10^{18}. The electrode can be seen as a giant molecule with a wire sticking in its back which may make it as reducing as $Na^\cdot$ or as oxidizing as F_2. Turning to the kinetics of electrode processes, the rate of an electrochemical reaction is characterized by a rate constant k' which has the slightly unusual units of cm s^{-1}:

$$\frac{\text{rate}}{\text{mol cm}^{-2}\,\text{s}^{-1}} = \frac{k'}{\text{cm s}^{-1}} \times \frac{c}{\text{mol cm}^{-3}}. \tag{1}$$

The rate constant k' obeys the Tafel Law (1900), which states how the rate constant changes with electrode potential, E:

$$k'_{\mathrm{e}} = k'_{\mathrm{e},0} \exp\left(\pm \alpha EF/RT\right), \tag{2}$$

where α, the transfer coefficient, is usually about $\frac{1}{2}$. Because of the exponential form of the equation, k' is sensitive to changes in E. For a one-electron transfer a change of 1 V produces a change of 10^9 in k'. This ability to control both the thermodynamics and the kinetics of electrode processes is the first great advantage of electrochemistry. The second advantage is that by driving electrochemical reactions with the applied potential, electrical energy is directly converted into chemical energy. This conversion (and the reverse) is of course vital for energy storage in batteries. But in addition, if and when we rely more heavily on electrical energy produced by nuclear power as a primary energy source, then this direct conversion will become an attractive route for the synthesis of energy-rich chemical compounds. The third advantage is an obvious one. The electrode is a heterogeneous catalyst and so does not have to be separated from the reactants and products. It can be used in a flow system. Electrochemistry is really heterogeneous catalysis in solution, with the added advantage of being able to control the reactivity of the catalyst.

But if the electrode is so wonderful why are there so few electrochemical processes on an industrial scale? What are the problems with the ideal catalyst? First and foremost, the reactant has to find the electrode. Figure 1 shows a typical current–voltage curve at an electrode. The broken line shows the exponential behaviour predicted by (2). The solid line shows the observed behaviour where the current becomes limited (the 'limiting current') by the transport of the reactant to the electrode surface. This is shown in the concentration profiles in the insets. In the transport-limited region the electrode is so reactive that every molecule that reaches it is destroyed. The reaction can be regarded as a two-step process (Albery 1975):

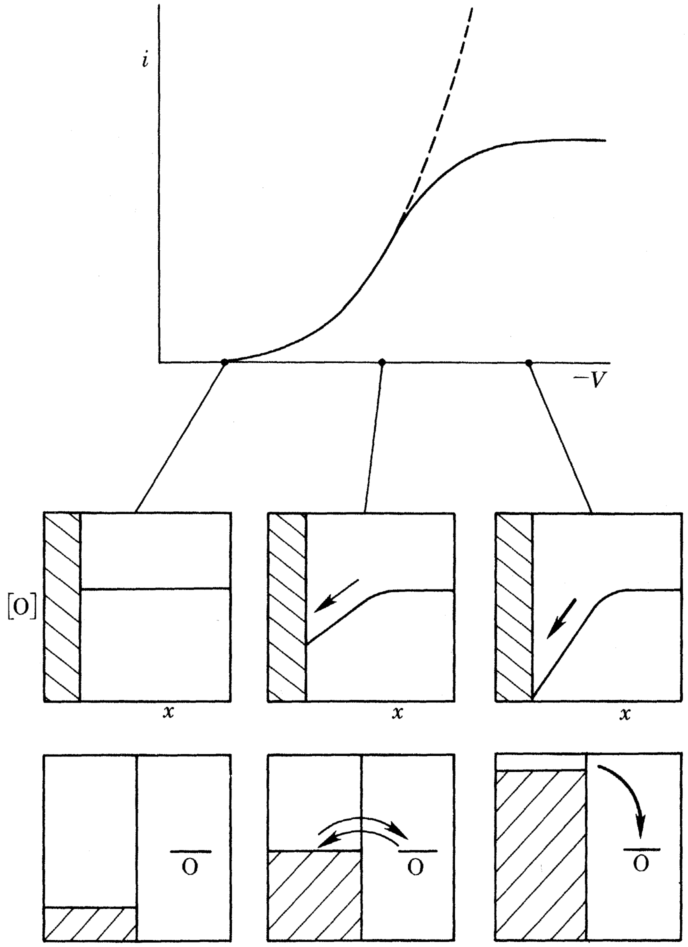


FIGURE 1. A typical current–voltage curve for the reduction $O + e^- \rightarrow R$. The broken line shows the exponential behaviour predicted by (2). The first row of insets shows concentration profiles near the electrode, and the second row of insets shows how the supply of electrons from the Fermi level of the electrode to the species O in solution is affected by the potential.

$$O_{\text{bulk}} \underset{k'_{\text{m}}}{\overset{k'_{\text{m}}}{\rightleftarrows}} O_0 \xrightarrow[e^-]{k'_{\text{e}}} \quad ,$$

where k'_{m} is a mass transfer rate constant (with dimensions of $\mathrm{cm\,s^{-1}}$) given by

$$k'_{\mathrm{m}} = D/\delta,$$

and δ is the thickness of the diffusion layer. For such a two-step process the observed rate constant is given by

$$\frac{1}{k'_{\mathrm{obs}}} = \frac{1}{k'_{\mathrm{e}}} + \frac{1}{k'_{\mathrm{m}}}. \tag{3}$$

By using the potential (10^9 for 1 V), k'_{e} can usually be made so large that it is negligible and hence the rate is limited by the mass transport to the electrode. This is desirable in many electroanalytical applications where, provided that δ is controlled, for instance either by forced hydrodynamics or by a membrane, the limiting current is then proportional to the concentration of the target species. Such amperometric methods are often preferable to potentiometric techniques, which require the establishment of equilibrium. However, as a catalyst the limitations from mass transport are serious.

Having emphasized that electrochemical rate constants are measured in units of $\mathrm{cm\,s^{-1}}$, it might be thought rather difficult to compare the electrochemical catalyst with a homogeneous catalyst. The kinetics for the latter would normally be measured by a second-order rate constant with units of $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. We shall now examine the connection between the electrochemical system and the homogeneous system by considering an efficient catalyst for which the rate of the reaction is diffusion controlled. Despite the apparent differences the diffusion-limited rate for a homogeneous molecular catalyst is exactly the same as that for a spherical electrode:

$$\frac{\text{rate}}{\mathrm{mol\,cm^{-3}\,s^{-1}}} = \underset{\text{(area)}}{(4\pi r^2)} \times \underset{\text{(transport)}}{(D/r)} \times \underset{\text{(number of spheres)}}{(c_{\mathrm{s}} L)} \times \underset{\text{(reactant concentration)}}{c_{\mathrm{r}}}.$$

For the homogeneous case we choose to write

$$\text{rate} = k_2 c_{\mathrm{s}} c_{\mathrm{R}},$$

so that

$$k_2/\mathrm{cm^3\,mol^{-1}\,s^{-1}} = 4\pi D r L. \tag{4}$$

While for the electrode we write

$$\text{rate} = A k'_{\mathrm{m}} c_{\mathrm{R}},$$

where

$$k'_{\mathrm{m}} = D/r, \tag{5}$$

and

$$c_1 L = 1.$$

Hence the difference in the units of the rate constants used in homogeneous and electrochemical kinetics arises from the choices described above. It is interesting that the diffusion-controlled second-order rate constant for an electrode of radius 1 cm is $7.5 \times 10^{21}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$; unfortunately its concentration is only *ca.* $10^{-23}\,\mathrm{mol\,cm^{-3}}$.

Comparison between the efficiency of different catalysts can most easily be made by considering the lifetime, τ_{R}, of the reactant R. We write

$$\text{rate} = c_{\mathrm{R}}/\tau_{\mathrm{R}}. \tag{6}$$

Then

$$\tau_{\mathrm{R}} = V_{\mathrm{s}}/4\pi r D,$$

where V_s is the volume occupied by one sphere. Now V_s must be significantly larger than the volume of the sphere itself, and so we find that

$$\tau_R \approx r^2/D, \tag{7}$$

which is the time required for a reactant molecule to diffuse to an individual sphere. Figure 2 shows a plot of this equation (for $D = 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$). It can be seen that for molecular catalysts for enzymes and for dispersed microelectrodes, τ_R is so small that the diffusion controlled rate for such a catalyst will never mar the ability of the catalyst to achieve a rapid turnover. However, when the size of the spheres reach that of macroelectrodes, then τ_R may become too long for the patience and profits of I.C.I. In developing a homogeneous catalyst the main problem is to make the reaction go faster. For the electrochemical catalyst the reaction can be driven, but a crucial problem is designing the system so that the reactant finds the catalyst.

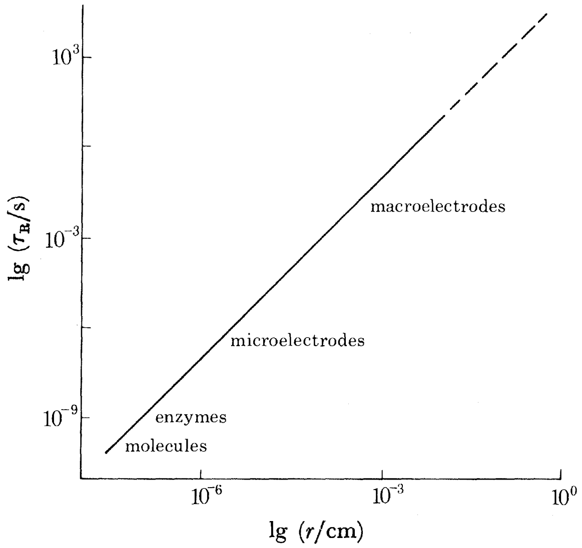


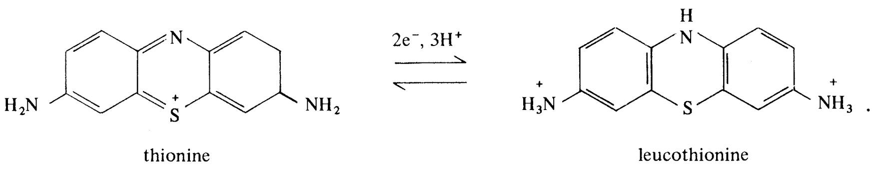
FIGURE 2. Plot of (7) to show how τ_R, the lifetime of a reactant R, varies with the radius, r, of a catalyst particle, assuming that the reaction is diffusion controlled and $D/\text{cm}^2\,\text{s}^{-1} = 10^{-5}$.

The second main problem with electrochemistry is poisoning of the electrode. This is particularly true for organic electrochemistry. It arises from the fact that by and large organic electrochemical reactions are two-electron changes. However, the electrode adds or subtracts the electrons one at a time. The intermediate radical species can dimerize, trimerize and indeed polymerize. Control therefore of the fate of the intermediate $R^\cdot$ is all-important. Unfortunately, since it is a reactive species it usually has a variety of possible reaction routes. I expect that one of the themes of this conference will be how to guide the reactive intermediates down the chosen desirable channel and to prevent such intermediates from literally gumming up the works.

The third problem is that an electrode can be relatively unselective between different reactants. For instance, for an oxidation all reactions with halfwave potentials less than that of the electrode potential will be switched on. It is true that outer sphere electron transfer reactions do involve the solvent reorganization (Libby 1952; Marcus 1963, 1964; Dononadze 1962) around the redox couple involved, but even so there are no specific interactions between the electrode and the reactant. It is rather passive and unselective encounter. The ideal catalyst should be more active and more selective, and that is why the development of modified electrodes (Moses *et al.* 1975; Snell 1979; Murray 1980) is one of the most exciting and challenging innovations in electrochemistry.

A modified electrode consists of a metal electrode coated with a polymer film. The film is thin enough to permit the transfer of electrons, but the rate of the desired reaction is enhanced by the properties of the film. One possibility is that the film binds the reactant, and more importantly the transition state for electron transfer, thereby lowering the free energy of activation for the reaction. This is the role of bipyridyl in the electron transfer to and from cytochrome *c*, which is discussed later in the symposium by Dr Hill (Eddowes *et al.* 1979). Here the modified electrode resembles an enzyme in its ability to select and bind the target reactant. A second possibility is that one can introduce into the layer a redox couple that acts as an electron-transfer agent to give a 'mediated electron transfer' between the electrode and the target reactant. Electrons are transferred from the metal to the redox centre, which then reacts with the species in solution. Such a reaction between two molecules is likely to be more specific than the transfer from a Fermi level.

Work in our laboratory has involved studies on the thionine-coated electrode (Albery *et al.* 1979, 1980*a*, *b*). We have shown that up to 20 layers of thionine can be coated onto an electrode by holding the electrode at 1.2 V (with respect to a saturated calomel electrode) for several minutes. Thionine can be easily reduced with two electrons to leucothionine:



This process can be followed for the molecules in the coat either by measuring the current required for the oxidation or reduction, or by observing the change in colour of the coat; thionine is a highly coloured purple dye ($\lambda_{max}/nm = 600$), whereas leucothionine is colourless. Typical results for these two types of experiment are shown in figures 3 and 4.

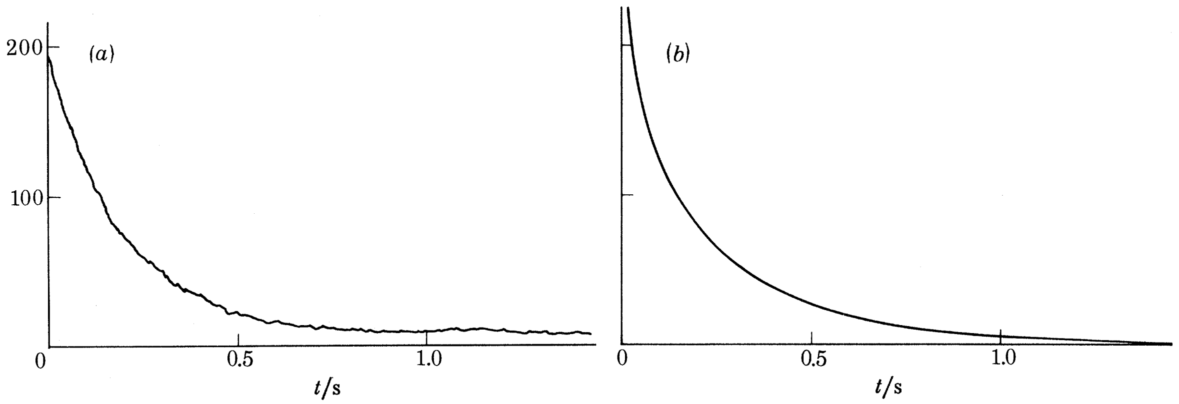


FIGURE 3. (*a*) A typical current–time transient for the reaction in the coat of the modified electrode, L → Th + 2e⁻. (*b*) A theoretical curve calculated from (8) with $D/\mathrm{cm^2\,s^{-1}} = 5 \times 10^{-13}$.

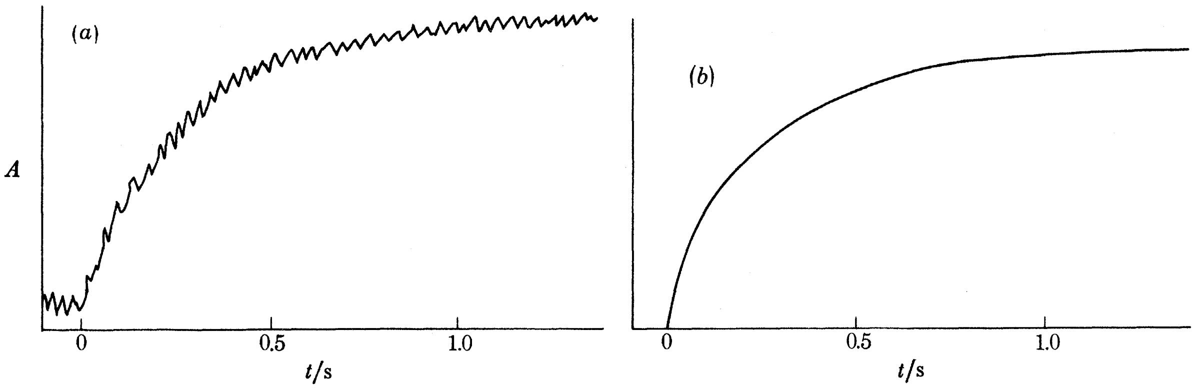


FIGURE 4. (*a*) A typical absorbance–time transient for the reaction in the coat, $L \rightarrow Th + 2e^-$. (*b*) The theoretical curve calculated from (9) with $D/\mathrm{cm^2\,s^{-1}} = 5 \times 10^{-13}$.

The kinetics of the charge transfer processes occurring in the coat can be described by a simple model in which the charge diffuses randomly among the different redox centres in the coat. The current is then given by (Oglesby *et al.* 1965)

$$\frac{i}{FA} = \frac{2D\Delta c}{(\pi\tau)^{\frac{1}{2}}}\left\{1 + 2\sum_{n=1}(-1)^n \exp\left(-\frac{n^2}{\tau}\right)\right\}, \tag{8}$$

where $\tau = Dt/l^2$, l is the thickness of the coat, A is the area of the electrode, and Δc is the change in concentration of the redox species in the coat.

Whereas the current measures the rate of change of the redox couple, for the optical density transients one has to integrate the number of thionine molecules in the whole coat. One then finds that

$$\frac{A}{A_\infty} = 2\left(\frac{\tau}{\pi}\right)^{\frac{1}{2}} + 2\sum_{n=1}(-1)^n\left\{2\left(\frac{\tau}{\pi}\right)^{\frac{1}{2}}\exp\left(-\frac{n^2}{\tau}\right) - 2n\,\mathrm{erfc}\left(\frac{n}{\tau^{\frac{1}{2}}}\right)\right\}, \tag{9}$$

where A is the absorbance of the coat.

Figures 3 and 4 show that good agreement between the experimental and theoretical curves is found with

$$D/\mathrm{cm^2\,s^{-1}} = 5 \times 10^{-13}. \tag{10}$$

A similar model has been found by Murray (Daum *et al.* 1980) to work for charge transport in polyvinyl ferrocene, although their values for D are somewhat larger than ours. Similar studies by Schroeder & Kaufman (1980) have found values for D that range from less than 10^{-14} to $10^{-9}\,\mathrm{cm^2\,s^{-1}}$.

It may be that D describes the kinetics of the electron transfers between adjacent redox centres (electron hopping). Following the Eyring model of diffusion, one could interpret D as a first-order rate constant k_1 of $500\,\mathrm{s^{-1}}$ and a jump distance *ca.* 0.3 mm. With a concentration of redox centres of $9\,\mathrm{mol\,dm^{-3}}$ the first-order rate constant corresponds to a second-order rate constant of only $50\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. This rate constant is several orders of magnitude slower than the rate constant for the conproportionation reaction in aqueous solution, $Th + L$, of $k_2 = 10^4\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ (Brokken-Zijp & De Groot 1981). Furthermore, from the value of D and the thickness of the coat we can calculate that the maximum steady-state current should be about $1.5\,\mathrm{mA\,cm^{-2}}$. We have observed currents that are more than 10 times this value. It is therefore probable that D does refer to the diffusion of ions. One possibility would be the diffusion of H^+, but we have shown that there is a negligible barrier to the diffusion of H^+ through the coat; the kinetics of the H^+ discharge reactions are virtually unaffected. Hence we conclude that D describes the diffusion of the counterions in the coat, which are necessary to balance the change in charge. Similar conclusions were reached by Schroeder and coworkers (Schroeder & Kaufman 1980; Schroeder *et al.* 1980) for their systems. It is important to emphasize that even if the transient behaviour is controlled by slow counterion diffusion, once a profile is established, the transfer of charge through the layer in the steady state may be limited by the faster electron hopping.

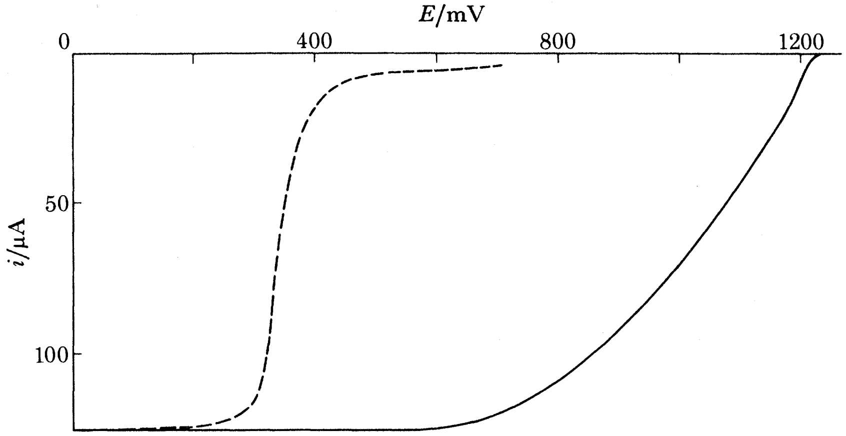


FIGURE 5. Current–voltage curves for the reduction of $\mathrm{Ce^{IV}}$ at a rotating disc electrode. The solid curve shows the reaction on a clean electrode and the broken curve the reaction on a thionine-coated electrode.

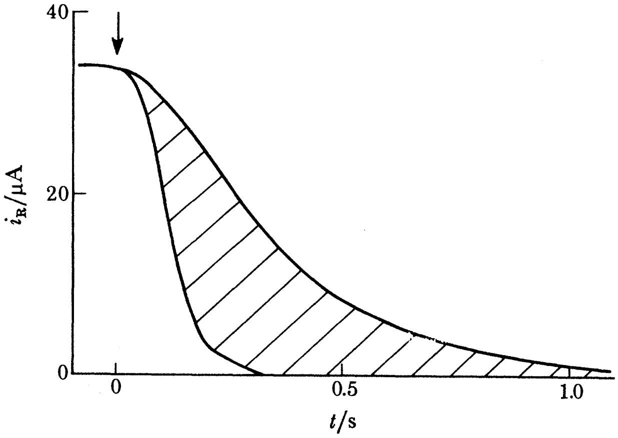


FIGURE 6. Ring current transients for the oxidation of $\mathrm{Fe(CN)_6^{4-}}$ produced on the disc electrode. The potential of the disc electrode is changed at $t = 0$. With the modified electrode the ring current persists for longer because of the reaction of $\mathrm{Fe(CN)_6^{3-}}$ with L on the outside of the coated disc electrode.

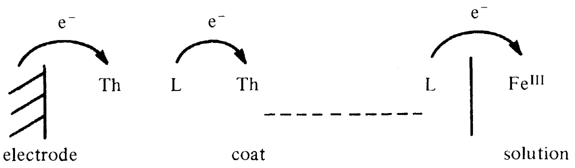
The selective kinetics of the thionine-coated electrode are remarkable in that the reactions of organic molecules such as quionones or thionine itself are hardly affected whereas the reduction of powerful oxidants such as $\mathrm{Ru(bpy)_3^{3+}}$ and $\mathrm{Ce^{IV}}$ are blocked for 0.5–0.6 V as shown in figure 5 (Albery *et al.* 1980*b*). In fact the reductions take place close to the $E^\ominus$ for the thionine–leucothionine couple. This is to be expected if the inorganic ion is reacting not with the metal but with the leucothionine on the outside of the coat.

This model has been confirmed by the following ring-disc electrode experiment:

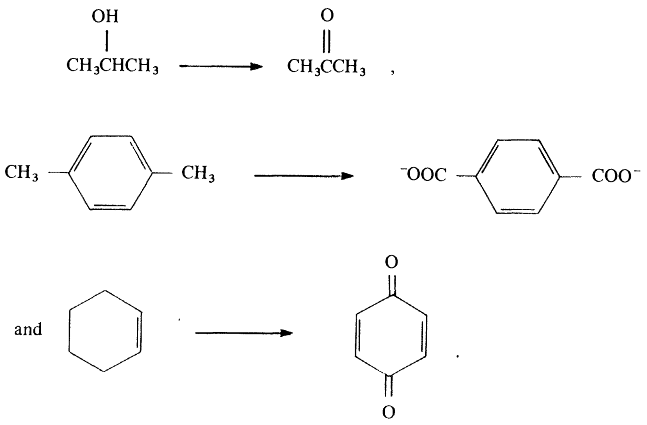
$$\text{disc electrode, } \mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Fe(CN)_6^{3-}} + \mathrm{e^-};$$

$$\text{ring electrode, } \mathrm{Fe(CN)_6^{3-}} + \mathrm{e^-} \rightarrow \mathrm{Fe(CN)_6^{4-}}.$$

The results are shown in figure 6. On the disc electrode the potential is jumped at $t = 0$ to a value where on a clean electrode the oxidation of $\mathrm{Fe(CN)_6^{4-}}$ no longer takes place. The downstream ring electrode monitors the product of the disc reaction ($\mathrm{Fe(CN)_6^{3-}}$). With a clean disc electrode the ring current is sustained for *ca.* 0.1 s by the $\mathrm{Fe(CN)_6^{3-}}$ that is already in transit between the two electrodes. Thereafter the ring current drops to zero. By contrast, with a modified disc electrode, the ring current is sustained for 1 s. This means that $\mathrm{Fe(CN)_6^{3-}}$ is still being produced on the modified disc after the potential jump. The timescale of the transient is similar to that in figures 3 and 4, and we conclude that $\mathrm{Fe(CN)_6^{4-}}$ is reacting directly with the leucothionine in the coat. Integration of the difference between the two curves shows that the amount of reaction corresponds to between one and two monolayers. Thus the reaction takes place on the outside of the coat.



The strategy of using such mediated electron transfer to effect the oxidation of organic substrates with a two-electron oxidant is an exciting prospect. Meyer (Moyer *et al.* 1980) has shown that bipyridine complexes of $\mathrm{Ru^{IV}}$ are useful oxidants, carrying out such reactions as



Work on the attachment of the $\mathrm{Ru^{IV}}$–$\mathrm{Ru^{II}}$ couple to an electrode using polyvinylpyridine is already under way; Murray (this symposium) describes the development of such modified electrodes.

Another ingenious method of obtaining increased kinetic selectivity is to use two-phase electrolysis. The electrochemical reaction is carried out in a thin film of organic solvent which 'wets' the electrode. This film is in contact with aqueous electrolyte. There are three advantages of this method. First, the right microenvironment for the electrochemical reaction is created.

Secondly, while the electrochemistry is carried out in a non-aqueous solvent, the bulk aqueous electrolyte ensures a low cell resistance. Thirdly, the organic products can be easily separated in the organic layer from ionic species, which remain in the aqueous layer. An example of this work is the cyanation of arromatic compounds pioneered by Eberson (1975, 1977). In association with I.C.I., current work at Southampton University under the direction of Professor Fleischmann and Dr Pletcher has improved the efficiency of the cyanation reaction, shown in figure 7, so that the yield is now more than 80 %. Furthermore, the cell voltage for the two-phase system is only 13 V, compared with 90 V if the reaction is carried out in CH_2Cl_2 by itself.

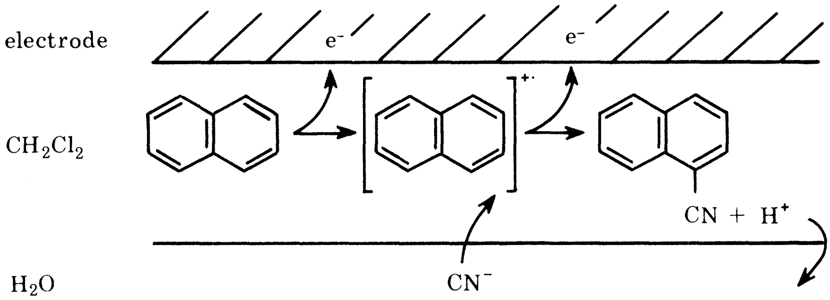


FIGURE 7. An example of two-phase electrolysis where the electrode is wetted with the organic solvent.

Having held out the prospect of electrochemical reactions of greater selectivity and efficiency, let me now return to a second main theme of this conference: the problem of achieving efficient mass transport. In the ideal process, after the solution has flowed past the electrode all of the reactant will have been converted to product. This is particularly important when electrochemical reactors are used to remove undesirable pollutants from effluent streams. It can also be desirable in electrosynthesis, for instance the following sequence of reactions leads to the formation of azobenzene from nitrobenzene:

electrode 1, $PhNO_2 + 4e^- + 4H^+ \rightarrow PhNHOH + H_2O$;
electrode 2, $\frac{1}{2}PhNHOH \rightarrow \frac{1}{2}PhNO + H^+ + e^-$;
homogeneous solution, $\frac{1}{2}PhNHOH + \frac{1}{2}PhNO \rightarrow \frac{1}{2}PhNONPh$;
electrode 3, $\frac{1}{2}PhNONPh + H^+ + e^- \rightarrow PhN{:}NPh + H_2O$.

In our work, the current on electrode 2 is controlled to be one-quarter of that on electrode 1, to optimize the homogeneous coupling reaction. The main problem with the route is that nitrobenzene forms a separate stable liquid phase with either azoxybenzene or azobenzene. It is therefore desirable that electrode 1 should convert nearly all the nitrobenzene to phenylhydroxylamine.

One of the simplest types of electrode for achieving high conversions is the packed-bed electrode shown in figure 8, in which the electrolyte solution flows through a bed of conducting particles, which can be made of cheap material such as graphite. Most theoretical treatments of these electrodes (Pickett 1979) have assumed plug flow of the electrolyte solution with a constant diffusion layer thickness perpendicular to the flow direction. In our model, the 'pore mix' model, we assume that in each layer of particles there is laminar flow through the 'pores' between

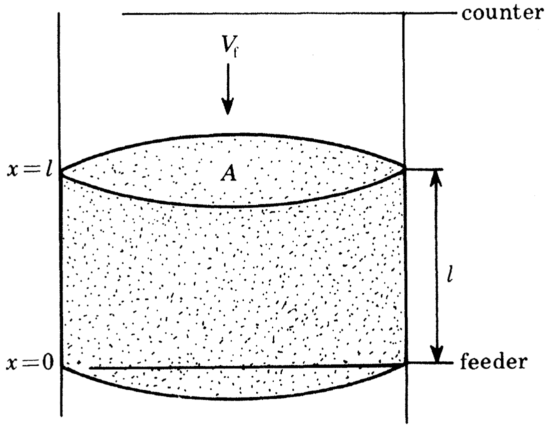


FIGURE 8. A packed bed electrode of area A and length l with volume flow rate V_f. The positions of the counter and feeder electrodes are indicated. In our electrode, up to 18 probe electrodes can be inserted, at various heights in the bed.

the particles, but that between the layers of particles there is perfect mixing of the solution before it proceeds to the next layer. We can then solve the convective diffusion equation for laminar flow in a pore of radius r_p to obtain the collection efficiency N for that layer:

$$N = \frac{\text{flux on electrode}}{\text{flux entering pore}} = \frac{6.5\,D^{\frac{2}{3}}}{r_p^{\frac{2}{3}}\,v_0^{\frac{2}{3}}}, \tag{11}$$

where v_0 is the velocity of flow at the centre of the pore.

For a uniform bed, where the potential is such that the current is everywhere mass transport controlled, the concentration falls exponentially through the bed:

$$c = c_0 \exp\left(-x/\lambda\right). \tag{12}$$

The collection efficiency of the whole bed is given by

$$N = 1 - \exp\left(-l/\lambda\right), \tag{13}$$

where l is the thickness of the bed.

Chu *et al.* (1974) have shown, for example, that (13) holds for the extraction of copper from dilute aqueous solution. Application of (11) gives

$$\lambda = a_1 (r_s)^{\frac{5}{3}} V_f^{\frac{2}{3}} / A^{\frac{2}{3}} D^{\frac{2}{3}}, \tag{14}$$

where r_s is the radius of the particles, V_f is the volume flow rate/$\text{cm}^3\,\text{min}^{-1}$, A is the area of the bed, and a_1 is a numerical constant, *ca.* 0.025, which depends on the geometry and voidage of the bed.

Figure 9 shows the results of λ plotted according to (14); the good straight line confirms the $V_f^{\frac{2}{3}}$ law, and a_1 is found to be 0.020.

Another example is the work of Alkire & Gracon (1975) on the reduction of Fe(CN)_6^{3-} on a packed-bed electrode; they measured the total current. From (13) and (14) we find

$$\begin{aligned} i &= Fc_0 V_f N \\ &= Fc_0 V_f \{1 - \exp\left(-a_2/V_f^{\frac{2}{3}}\right)\}. \end{aligned} \tag{15}$$

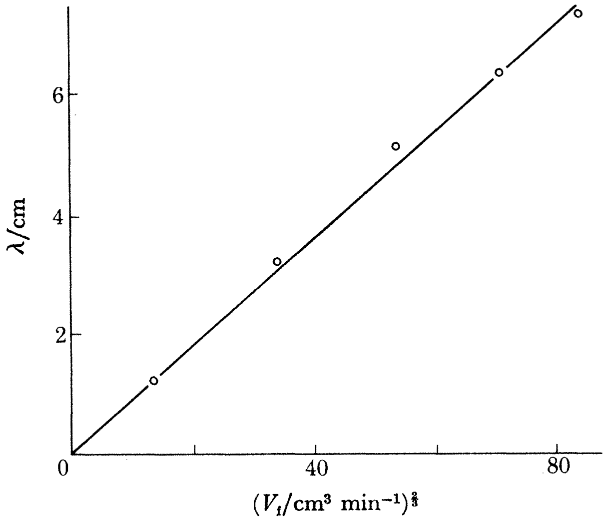


FIGURE 9. Plot of data for λ from Chu *et al.* (1974) against $V_f^{\frac{2}{3}}$ as required by (14).

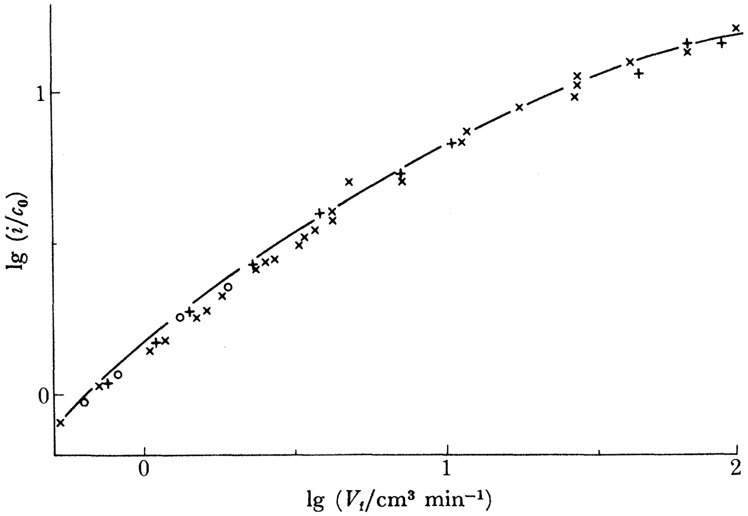


FIGURE 10. Plot of data for current from Alkire & Gracon (1975) according to (15). The data were obtained at three different concentrations: c_0/mmol dm^{-3} = 2 (×), 10 (+), or 50 (○).

Figure 10 shows that their data do indeed obey (15) with $a_2 = 2.38$.

One of the problems with the exponential decrease of concentration is that the current is unevenly distributed on the bed. With academic currents of a few milliamps this causes no problem, but in industrial processes much higher currents must be passed. Because of the resistance of both the bed and electrolyte these currents then generate substantial potential differences. This in turn means that the potential difference between the electrode and the solution is not constant. Instead of being able to use the potential difference to select the target reaction, the passage of the current causes such variations that part of the bed may be inactive while another part may be wasting energy by decomposing the solvent.

To overcome these problems, in collaboration with J. Bridgewater, we are developing a bed where the size of the particles is graded, to use the mass transport to achieve a better current distribution.

From (11), for the jth layer of particles,

$$\mathrm{d}\ln c/\mathrm{d}j = -N_j = -N_1(r_1/r_j)^{\frac{2}{3}}, \tag{16}$$

where N_1 refers to the first upstream layer of particles. Next we consider a bed of n layers graded so that

$$r_j/r_1 = (1-j/n)^{\frac{3}{2}p}, \tag{17}$$

where p describes our choice of grading. Substitution in (16) and integration gives the general equation

$$\ln\left(\frac{c_j}{c_0}\right) = \frac{N_1 n}{1-p}\{(1-j/n)^{1-p}-1\}. \tag{18}$$

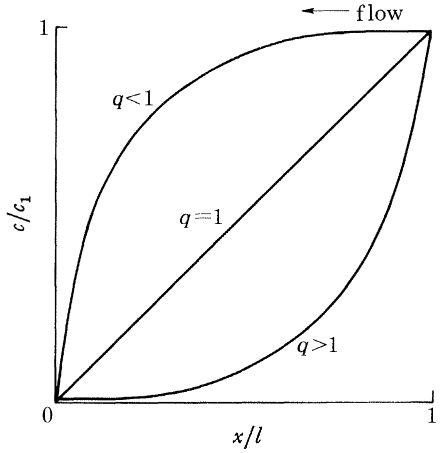


Figure 11. Typical concentration profiles on a graded bed, calculated from (20).

(A particular case of this equation is the uniform bed with $p = 0$.) In general because of the logarithmic term the equation will still give very unequal current distributions on the bed. The best choice of p is to put it equal to unity to obtain the special case with no exponential term, where

$$c_j/c_0 = (1-j/n)^{nN_1}. \tag{19}$$

For this case, integration of the varying widths of the layers with distance gives

$$1-j/n = (x/l)^{\frac{2}{5}}.$$

Substitution in (17) and (19) gives the equations for the concentration distribution and for the optimum grading to achieve this distribution:

$$c/c_0 = (x/l)^q, \tag{20}$$

where $$q = lN_1/2r_1$$

and $$r/r_1 = (x/l)^{0.60}. \tag{21}$$

Now N_1, and hence q, can be varied by changing the velocity of flow. Figure 11 shows some typical curves. At high flow rate (low q) more material reacts on the downstream end of the bed, while at low flow rate most of the material will react on the upstream end of the bed. The variation in the potential difference between electrode and solution is minimized if

$$q = R_s/R_b, \tag{22}$$

where R_s and R_b are the resistances of the solution and the bed respectively. For low q, corresponding to higher bed resistance, most of the reaction should take place close to the feeder electrode, while for high q the reaction should be carried out as close as possible to the counter-electrode.

Using probe electrodes (Goodridge & Ismail 1971; Goodridge *et al.* 1971 *a*, *b*) we have investigated the potential distribution both in the graded bed and in the electrolyte solution. Figure 12 shows how our bed was graded with distance. We have inserted some 18 electrodes of three kinds.

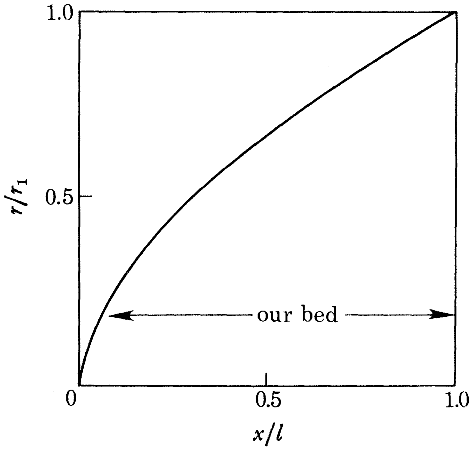


FIGURE 12. Variation of r with distance through the bed, according to (21) to achieve the optimum grading. In our bed the radius ratio changed by a factor of 5.

The first type were wires sealed onto small graphite particles to investigate the potential of the bed; the second type were Ag–AgCl electrodes to investigate the potential of the solution; the third type were Pt electrodes to measure the conversion of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$. Some typical results are shown in figure 13, were the lines are calculated from (20) with $q = 0.60$. The bed was achieving 80% conversion, and q is nearly matched to the relative resistances, as given by (22). This is shown by the fact that the potential differences at the top and bottom of the bed are almost the same. The degree of conversion of a uniform bed is also shown for comparison. Figure 14 shows the calculated behaviour of a uniform bed designed to achieve 80% conversion at the same flow rate. Because the bed has to be much longer and because the current is badly distributed, a much larger variation in the potential difference of about 1.3 V is found, compared with the acceptable variation of 0.3 V on the graded bed. Further improvement in the graded bed can be achieved by using layers of particles of varying resistance so as to make the variation of potential in the bed match that in the solution.

In this work we have seen how control of the mass transport can be used to improve the performance of packed bed electrodes. The papers on electrochemical engineering in this symposium enlarge on this theme and describe other ingenious cells designed to overcome the problem of getting the reactant to the electrochemical catalyst. In conclusion, the development of greater kinetic selectivity and of better mass transport are two of the main lines of research that must be pursued to improve the prospects for industrial electrochemistry.

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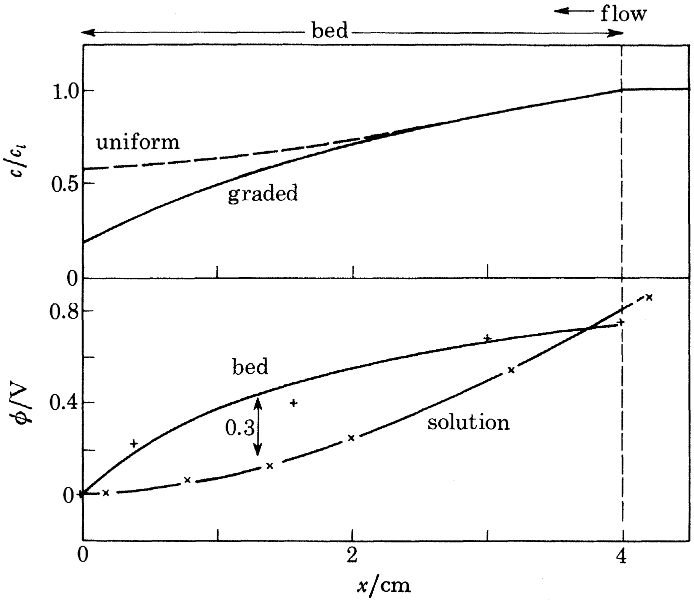

FIGURE 13. Variation of conversion (c/c_l) and of potential, ϕ, both in the bed and in the electrolyte solution for the graded bed. The points show the potentials measured by the probes; the curves are calculated for $q = 0.6$.

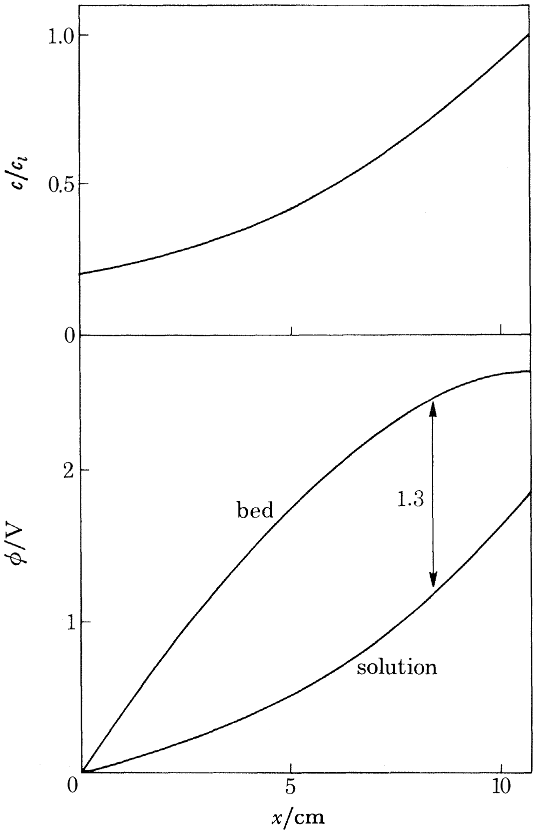

FIGURE 14. Variation of conversion (c/c_l) and of potential calculated for a uniform bed designed to achieve the same degree of conversion as the bed in figure 13. The uniform bed is over twice as long and the variation in the potential difference (1.3 V) is four times greater than for the graded bed (0.3 V).

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