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Modified Electrodes: Chemically Modified Electrodes for Electrocatalysis [and Discussion]

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MODIFIED ELECTRODES

Chemically modified electrodes for electrocatalysis

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At a modified electrode, electrocatalysis is accomplished by an immobilized redox substance acting as an electron transfer mediator between the electrode and a reaction substrate. Such mediated electrocatalysis is possible with monomolecular and multimolecular layers of the redox substance. The electron transfer mediation can assume several special forms; these are identified and experimental examples are given. The differences between electrocatalytic behaviour of monomolecular and multimolecular layers are discussed; electrocatalysis in the latter circumstance can include reaction rate elements of electrochemical charge and substrate migration through the multilayer in addition to the chemical rate. Theoretical ideas are presented that interconnect these three rate elements, to show that either all of the multilayer sites can participate in the electrocatalytic reaction, or only about the equivalent of a monolayer, depending on the relative rates of the electrochemical charge transport, the diffusion of substrate, and the chemical reaction rate.

1. Introduction

Surface synthetic procedures have been developed over recent years for immobilizing monomolecular and multimolecular layers of electrochemically reactive substances on electrode surfaces (Murray 1980*a*). Monomolecular layers can be chemically bonded to or chemisorbed on the electrode. An example of (monomolecular) chemical bonding is shown in figure 1, where tetra(*p*-aminophenyl)porphyrin (Lennox & Murray 1978; Rocklin & Murray 1979) is amide-coupled to the carboxylic acid functions of an oxidized carbon surface, and metallated with cobalt. This modified electrode is designated $C|\sim Co(NH_2)_4TPP$. Multimolecular layers of redox substances have been primarily formed from polymeric materials, which can be chemically bound (Wrighton 1978) to the electrode or simply be applied as insoluble adherant films (Van De Mark & Miller 1978) permeable to supporting electrolyte ions and solvent. The redox substance can be affixed to (Itaya & Bard 1978) or be part of the polymeric matrix; examples of such redox polymers are films of polyvinylferrocene (Merz & Bard 1978) and an electropolymerized (Abruña *et al.* 1980) form of $[Ru^{II}$(4-methyl-4′-vinyl-2,2′-bipyridine)$_3](ClO_4)_2$ (figure 1). Alternatively, the redox substance can be an ionic substance (Oyama & Anson 1980*a*) partitioned into a polymer matrix containing fixed charged sites by ion exchange action. The latter is exemplified by $(C_2H_5O)_3\,Si(CH_2)_3NH(CH_2)_2NH_2$, *en* silane (Lenhard & Murray 1977; Murray 1980*b*), which can be filmed onto a superficially oxidized Pt surface, both bonding to that surface and forming an alkylaminesiloxane polymer film. In aqueous acid (protonating the amine sites), this anion exchanger film (K. Kuo, unpublished) strongly absorbs ferrocyanide, retaining this highly charged ion for a considerable time even when the electrode is placed in an electrolyte solution devoid of ferrocyanide. This surface will be designated Pt/poly(*en* silane)H^+, $Fe(CN)_6^{4-}$.

The redox sites in monomolecular and multimolecular layers such as the above can be oxidized and reduced by the electrode. Trying to understand and exploit electron transfer and chemical reactions in the special circumstances of surface-confined reactants is an interesting topic (Murray 1980*a*). Electrochemical reactions corresponding to the C| ~ $Co^{II/I}(NH_2)_4TPP$, Pt/poly($Ru^{III/II}(vinylbpy)_3)^{3+/2+}$, and Pt/poly(*en* silane)H^+, $Fe(CN)_6^{3-/4-}$ redox couples of these immobilized sites are illustrated by the cyclic voltammetric surface waves shown in figures 2*c*, 2*d*, 3*a* and 4*a*, respectively. The formal potentials of these surface waves are near those of the analogous, unattached chemicals (Lenhard *et al.* 1978).

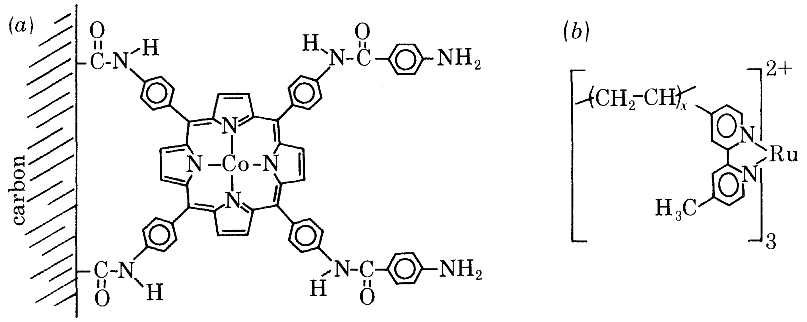
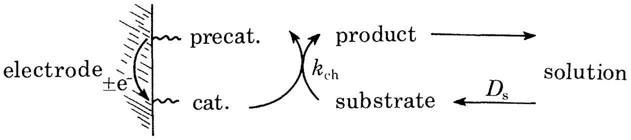
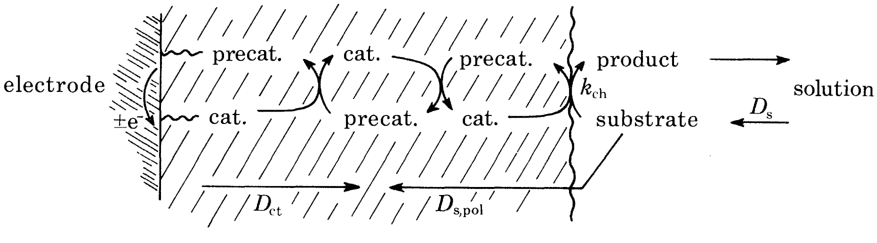


FIGURE 1. Exemplary electrocatalytic layers on chemically modified electrodes: (*a*) C | ~ $Co(NH_2)_4TPP$; (*b*) poly($Ru(vinylbpy)_3^{2+}$).

The use of the electrochemical and chemical reactivities of immobilized redox substances as a means of electrocatalysing electrode reactions of other substances is a particular focus of research interest and, many believe, potential technological utility. Such electrocatalysis is accomplished by the immobilized substance acting as an electron transfer mediator, cycling between its reactive (catalyst) and oxidized or reduced (precatalyst) states, as illustrated in the following schemes for electrocatalysis, by a monolayer (scheme 1) and by a multimolecular (scheme 2) layer film. These schemes point out two potential differences between electrocatalysis by monomolecular and by multimolecular layers: (i) the quantity of mediator or catalyst sites, and by inference the electrocatalytic rate, can be much greater for multilayers, but (ii) in multilayers the electrocatalytic rate is potentially moderated by the rate at which catalyst sites migrate through the polymer film (D_{ct}) and the rate at which substrate diffuses through the polymer



SCHEME 1



SCHEME 2

film ($D_{\mathrm{s,pol}}$). Theory relating these several processes, D_{ct}, $D_{\mathrm{s,pol}}$, and the chemical step, k_{ch}, i given later in this paper. First, however, it will be useful to categorize the different special form that modified electrode electrocatalysis can assume. Some examples will be cited from recen experimental work at the University of North Carolina, full details of which are given elsewher (Abruña *et al.* 1980; R. Leidner & P. Denisevich, unpublished; K. Kuo, unpublished; Rockli & Murray 1981).

2. Forms of modified electrode electrocatalysis

(*a*) *Substrate undergoes outer sphere electron transfer at naked electrode*

Andrieux & Saveant (1978) considered theory for the case where the substrate is reduced or oxidized by a naked electrode at rates predicted from the Marcus relations, to see if substituting mediated outer sphere electron exchange with immobilized Nernstian catalyst could enhance such rates. They concluded, unsurprisingly, that with monomolecular layers, e.g. as in scheme 1, such electrocatalysis was ineffective, but that electrocatalysis with 100 molecular layers, e.g. as in scheme 2, could be very effective.

(*b*) *Substrate reacts slowly at naked electrode*

This is the most interesting situation, practically speaking. The substrate reacts slowly (sub-Marcusian rates) at a naked electrode but more rapidly (rate k_{ch}) with catalyst sites on the electrode, either by simple outer sphere pathways or by more involved chemical pathways, including transient surface adducts between catalyst and substrate. Several successes in electrocatalysis of slow substrates have been reported (Tse & Kuwana 1978; Bettelheim *et al.* 1980; Collman *et al.* 1980; Oyama & Anson 1980*b*; Murray 1980*a*; Rocklin & Murray 1981); and there has been some imaginative design of the chemical nature of the catalyst sites to yield rapid or selective reactions with the substrate. Progress in 'slow substrate' electrocatalysis with modified

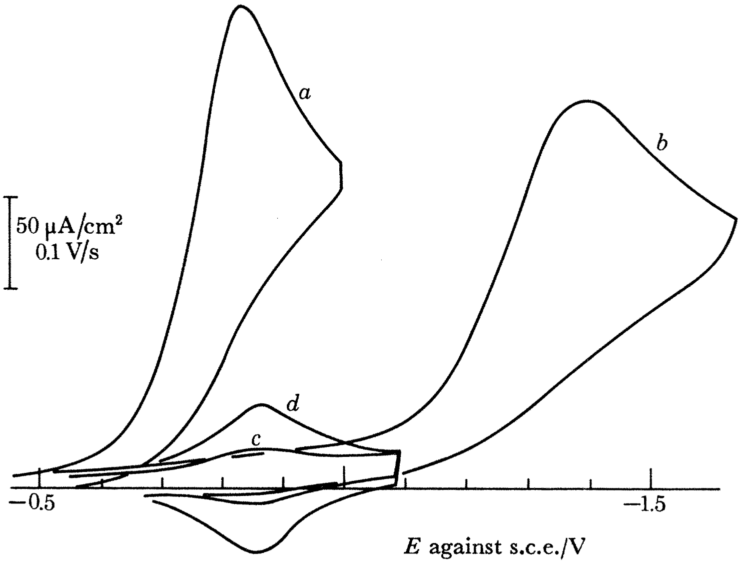


Figure 2. Electrocatalysis of PhCHBrCH$_2$Br by a C | ~ Co(NH$_2$)$_4$TPP surface (*a*) and at naked carbon (*b*) in 0.1 M Et$_4$NClO$_4$/DMSO; (*c*) and (*d*), as (*a*) but without PhCHBrCH$_2$Br. Γ_t values: (*a*, *c*) 5×10^{-11}, (*d*) 4×10^{-10} mol/cm^2.

electrodes will principally be controlled by success in designing the catalyst–substrate chemical interaction rather than by the ability to immobilize the catalyst on the electrode surface.

'Slow substrate' electrocatalysis is illustrated in figure 2, where the substrate, $PhCHBrCH_2Br$, is slowly reduced to styrene by a naked carbon electrode (curve *b*) but is rapidly reduced on a $C|\sim Co(NH_2)_4TPP$ electrode (nearly diffusion controlled, curve *a*), at a potential about 0.6 V less negative than on the naked electrode and where $C|\sim (Co^{I})(NH_2)_4TPP$ sites are generated electrochemically on the electrode surface. This strong electrocatalysis involves less than a monolayer coverage of $Co(NH_2)_4TPP$ sites (curves *c* and *d* are cyclic voltammograms in the absence of $PhCHBrCH_2Br$). This emphasizes the difference between theory based on outer sphere (Andrieux & Saveant 1978) (§ *a* above) and 'slow substrate' electrocatalysis as in scheme 1. When the cobalt porphyrin is immobilized on Pt by using organosilane chemistry (Rocklin & Murray 1981), the reaction rates are similar and k_{ch} was measured as $10^3 k_{ch} = 10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at sub-monomolecular layer coverages.

(*c*) *Substrate denied access to the electrode*

Polymer film coatings on electrodes can restrict access or permeability of otherwise electrochemically reactive substances into the electrode, i.e. the product $PD_{S,\,pol}$ is very small, P being the partition coefficient of substrate from the solution into the film. In such instances, redox constituents of the film can be employed as electron transfer mediators between electrode and the excluded substance. There are three known versions of this kind of electrocatalysis.

(i) *Electrode – redox polymer film – solution of electroactive substance*

A solution of the complex $Fe^{II}(bpy)_2(CN)_2$, where bpy = 2,2′-bipyridine, gives a diffusion-controlled, reversible wave at a naked rotating disc Pt electrode for oxidation of the complex to $Fe^{III}(bpy)_2(CN)_2^+$ (figure 3, curve *b*). However, if the rotating disc is first coated with a film

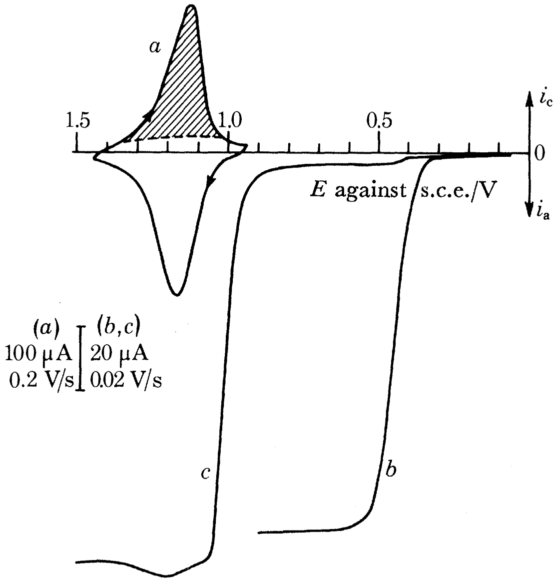


FIGURE 3. Cyclic voltammetry of $Pt/poly(Ru(vinylbpy)_3^{2+})$ electrode (*a*), 1 mM $Fe(bpy)_2(CN)_2$ at naked Pt rotating disc (*b*) and at $Pt/poly(Ru(vinylbpy)_3^{2+})$ rotating disc (*c*), all in 0.1 M Et_4NClO_4/CH_3CN. (*a*, *c*) $\Gamma_{Ru} = 6 \times 10^{-9}\ \mathrm{mol/cm^2}$.

of poly(Ru(vinylbpy)$_3^{2+}$) containing *ca.* 6×10^{-9} mol/cm^2 of monomer sites, the Fe(bpy)$_2$(CN)$_2$ normal oxidation wave is reduced to a small percentage of its original limiting current (curve *c*). The main part of the wave is shifted to a potential oxidixing a few Ru^{II} sites in the poly(Ru(vinylbpy)$_3^{2+}$) film. The Fe(bpy)$_2$(CN)$_2$ is now being electrocatalytically oxidized by Ru^{III} sites presumably located near the polymer film – solution interface. The low permeability of Fe(bpy)$_2$(CN)$_2$ (low $PD_{s,\,pol}$) into the poly(Ru(vinylbpy)$_3^{2+}$) film is thought to be a combination of its bulkiness and the cross-linked nature of the polymer film. Cations (such as methyl viologen) are also excluded from the poly(Ru(vinylbpy)$_3^{2+}$), but anions (such as Fe(CN)$_6^{4-}$) are not.

This type of electrocatalysis can be viewed as 'negative catalysis', since the potential for electrolysis of the substrate is shifted to higher values, rather than an overpotential being reduced. It can be a useful experimental strategy in several ways, however, such as for study of polymer film permeability ($PD_{s,\,pol}$) and for the measurement of electron exchange rates (k_{ch}) between one-electron, nominally outer sphere redox couples, one couple being the catalyst in the film and the other being the excluded substrate (Oyama & Anson 1980*b*).

(ii) *Electrode – redox polymer film*

During oxidation of *ca.* 60 monomolecular layers of Ru^{II} sites in the Pt/poly(Ru(vinylbpy)$_3^{2+}$) film in figure 2, curve *a*, it is not realistic to expect that the Pt electrode experiences direct contact with more than the innermost several layers of Ru^{II} sites. The other, outermost sites in the film are oxidized, as shown in scheme 2, by successive exchanges of electrons between neighbouring poly(Ru(vinylbpy)$_3^{2+}$) and poly(Ru(vinylbpy)$_3^{3+}$) sites, the latter being generated at the electrode–polymer interface. This kind of self-electrocatalysis is probably a general mechanism for electrochemical reactions of multimolecular layer redox polymer films (Daum *et al.* 1980, 1981; Kaufman & Engler 1979; Nowak *et al.* 1980). A flow of anions (and associated solvent) is necessary to provide counterions for the increasingly positively charged fixed sites, and there will be polymer lattice motions accommodating the counterion and solvent flow and the motions of neighbouring sites towards one another, so that the overall process is actually somewhat complex. It is termed electrochemical charge transport. The energetics of rate control in charge transport are not yet firmly established, but its effective rate is measurable as a diffusion constant, D_{ct}. P. Denisevich (unpublished), for example, has measured $D_{ct} \approx 4 \times 10^{-10}$ cm^2/s in the poly(Ru(vinylbpy)$_3^{2+}$) film.

Self-catalysis undoubtedly also plays a role in electrochemical charge transport in ion-exchange polymer films containing electrostatically trapped redox ions (Oyama & Anson 1980*a*). K. Kuo (unpublished) has recently measured charge transport rates (i.e. D_{ct}) in a Pt/poly(*en* silane)H$^+$, Fe(CN)$_6^{4-}$ film (by potential step chronoamperometry at times where the 'diffusion layer' of charge transport of redox sites remained less than the film thickness (Nowak *et al.* 1980; Daum *et al.* 1980)). The Pt/poly(*en* silane)H$^+$ film had a constant thickness (d), and a succession of quantities Γ_t of Fe(CN)$_6^{4-}$ were incorporated into the film, D_{ct} being measured in each case. The results, obtained as $D_{ct}^{\frac{1}{2}}C$ products, where C is the concentration of Fe(CN)$_6^{4-}$ sites in the film, are plotted against Γ_t in figure 4*b*. The plot, which has slope $D_{ct}^{\frac{1}{2}}/d$, is clearly not linear at high Fe(CN)$_6^{4-}$ loadings but approaches linearity at low loadings. The decrease in slope (i.e. $D_{ct}^{\frac{1}{2}}/d$) at high loadings may reflect electrostatic cross-linking of the film by the highly charged Fe(CN)$_6^{4-}$ ions, this increased film rigidity slowing the charge transport process. An alternative explanation involves slowing of Fe(CN)$_6^{4-}$, Fe(CN)$_6^{3-}$ electron self exchange rate at high anion concentration. At the smallest Fe(CN)$_6^{4-}$ loading, where $C \approx 2 \times 10^{-4}$ mol/cm^3,

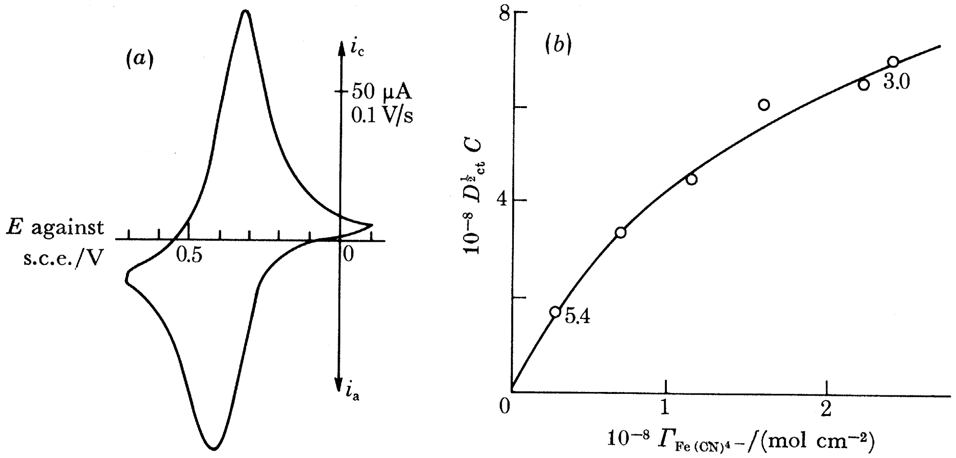


FIGURE 4. (*a*) Cyclic voltammetry of $Fe(CN)_6^{4-}$ electrostatically trapped in a Pt/poly(*en* silane)H$^+$ film, 0.5 M KCl, pH 3.2 (glycine); $\Gamma_t = 1.1 \times 10^{-8}$ mol/cm^2. (*b*) Charge transport rate through *ca.* 160 nm Pt/poly(*en* silane)H$^+$, $Fe(CN)_6^{4-}$ film containing various amounts of trapped $Fe(CN)_6^{4-}$; $D_{ct} = 2$–7×10^{-9} cm^2/s. Numbers on the curve are values of $D_{ct}^{\frac{1}{2}}/d$.

the site–site separation of $Fe(CN)_6^{4-}$ units averages a very considerable 2.5 nm, yet no special decrease in $D_{ct}^{\frac{1}{2}}/d$ appears. The most reasonable of several possible interpretations of the latter result is that charge transport by electron exchange between neighbouring $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ sites involves significant motion of these sites towards one another before the actual electron hopping event.

(iii) *Electrode – redox polymer film A – redox polymer film* B

If one redox polymer film is layered on another, a special situation occurs where the interface between the two redox polymer films is a current-rectifying barrier (Abruña *et al.* 1980), although no semiconductor materials or space charge effects are at work. This property is derived from the fact that, as described above in §*c*(ii), electrons are transported across redox polymer films by electron self-exchange, which amounts to a narrow-band conductor with insulating gaps at other potentials. Figure 5 shows an example of a bilayer of redox polymers, in which the outer layer of poly(vinylferrocene) is isolated from the electrode by an inner layer

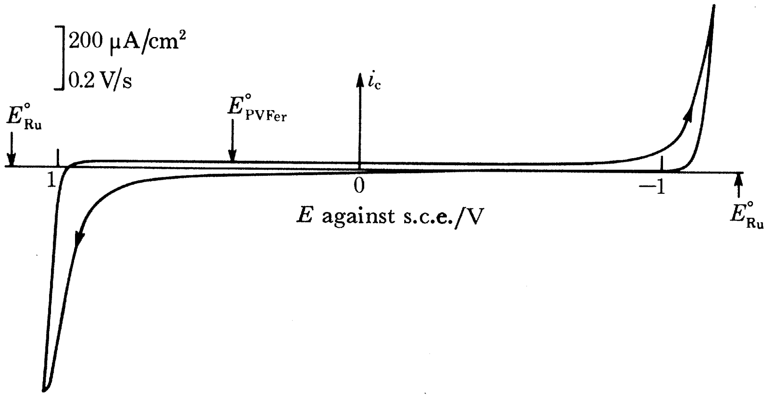


FIGURE 5. Diode-like cyclic voltammogram of redox polymer bilayer Pt/poly(Ru(vinylbpy)$_3^{2+}$)/PVFer in 0.1 M Et_4NClO_4/CH_3CN. Upper part of curve, addition of electrons to polymer; lower part, removal of electrons.

of poly(Ru(vinylbpy)$_3^{2+}$) so that the potential at which poly(vinylferrocene) is oxidized and re-reduced is where electron transfer-mediating Ru^{III} and Ru^{I} sites are electrogenerated within the inner film, respectively, rather than at the normal ferrocene potential. Our laboratory has prepared a number of bilayer assemblies and the phenomenon appears to be a general one. Note that figure 5 has the general appearance of a diode response, and indeed bilayer electrodes have promise of mimicking solid state electronic functions and even possibly of creating new electronic response functions.

(*d*) *Redox polymer films on semiconductor electrodes*

Films of redox polymers can be oxidized or reduced by absorption of light within the depletion layers of n-type and p-type semiconductor electrodes, respectively, at potentials where no electrochemical reactions of the film, or of solution substrates, should occur in the dark. This phenomenon has been employed to protect small band-gap semiconductor materials such as n-Si^0 from photoanodic lattice dissolution, the ferrocene-containing redox polymer film employed becoming (by favourable kinetics) oxidized instead. To regenerate the reduced form of the ferrocene polymer film, substances are added to the solution which are (ideally) rapidly oxidized by the ferricenium sites in the film. This amounts to a photocatalytic oxidation of the dissolved substance. This form of modified electrode electrocatalysis has been developed by Wrighton and coworkers (Lewis *et al.* 1980; Wrighton 1979).

The above discussion shows that electrocatalysis at modified electrodes assumes diverse forms, and diverse uses will probably result. The theory for each form of electrocatalysis will differ to some extent. The theoretical discussion that follows is appropriate to §§ *b* and *c* (i) above.

3. THEORY OF ELECTROCATALYSIS AT ROTATING DISC ELECTRODES

When a 'slow substrate' (§ 2*b*) is electrocatalytically reduced by a sub-monomolecular or monomolecular layer of catalyst sites on a rotating disc electrode, as in scheme 1, where the catalyst sites are reversibly regenerated by reduction of precatalyst by the electrode, the limiting electrocatalytic current at the rotating disc is given by

$$\frac{nFA}{i_{\max}} = \frac{1}{k_{\mathrm{ch}}\,\Gamma C_{\mathrm{s}}} + \frac{1}{0.62\nu^{-\frac{1}{6}}D_{\mathrm{s}}^{\frac{2}{3}}\omega^{\frac{1}{2}}C_{\mathrm{s}}}, \tag{1}$$

where Γ is the coverage of chemically active catalyst sites, C_{s} is solution substrate concentration, D_{s} is its diffusion constant in the solution, and k_{ch} is the rate constant for the catalyst–substrate reaction according to the rate law $-\mathrm{d}\Gamma/\mathrm{d}t = k_{\mathrm{ch}}\,\Gamma C_{\mathrm{s}}$. This equation assumes, reasonably for a monomolecular layer, that substrate should have relatively unrestrained permeability into the monolayer film and access to all catalyst sites, i.e. $\Gamma = \Gamma_{\mathrm{t}}$, where Γ_{t} is the total coverage of catalyst sites. The electrocatalysis portrayed in figure 2 is thought to correspond to this situation. With sub-monomolecular coverages of Co$(NH_2)_4$TPP immobilized on Pt (by using organosilane chemistry) (Rocklin & Murray 1980), plots of (1) ($1/i_{\max}$ against $1/\omega^{\frac{1}{2}}$) were linear, and k_{ch} obtained from the $1/\omega^{\frac{1}{2}} = 0$ intercept was $10^5\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and independent of the value of Γ_{t}. This is as yet the only quantitative kinetic information available for sub-monomolecular coverages in 'slow substrate' electrocatalysis, although numerous qualitative reports of this type of electrocatalysis exist.

Equation (1) contains two electrocatalytic rate elements, the rate of the chemical reaction between catalyst and substrate, and the rate of hydrodynamic mass transport of substrate from the solution to the catalyst surface (the right-hand, Levich term). When the electrode is covered by multimolecular layers of catalyst sites in a polymer film, as in scheme 2, two additional rate elements can appear. These are (i) the rate at which catalyst sites migrate (charge transport) from the electrode–polymer interface outward toward the polymer–solution interface, described by the diffusion constant D_{ct}, and (ii) the product of the rate at which substrate diffuses ($D_{\mathrm{s,\,pol}}$) into the polymer film from the polymer–solution interface and the partition coefficient P with which substrate crosses that interface from the solution, i.e. $PD_{\mathrm{s,pol}}$, the permeability. Depending on the relative values of k_{ch}, D_{ct} and $PD_{\mathrm{s,\,pol}}$, these two new factors can seriously affect the overall catalytic rate, as I shall show. The charge transport and substrate permeability factors appear as modifications to the $1/\omega^{\frac{1}{2}}$ intercept term in (1) (Rocklin & Murray 1981).

An interesting property of polymeric multimolecular layer films is the possibility that electrocatalytic rates can be greatly enhanced, since the quantity of catalyst (as measured by Γ_{t}) can be as much as 10^3 times the typical monomolecular layer value. In current studies (Oyama & Anson 1980*b*; Legrand & Miller 1980; Rocklin & Murray 1981) of electrocatalysis by redox polymer and by ion exchange polymer-trapped redox ion films, however, qualitative and quantitative rate measurements show that the electrocatalytic rate does not increase linearly with Γ_{t}, and in fact can be independent of Γ_{t}. Such results are not expected from the early theoretical analyses of modified electrode electrocatalysis (Andrieux & Saveant 1978; Anson 1980), but neither of these analyses encompassed all the rate elements pointed out above. It is possible (Daum & Murray 1981; Rocklin & Murray 1981) to deal with the complexities of two additional rate elements D_{ct} and $PD_{\mathrm{s,\,pol}}$, and our treatment will be expanded upon here with emphasis especially on understanding how electrocatalysis can be so unresponsive to Γ_{t}. For simplicity, the treatment will be confined to the rotating disc electrode experiment, and will also assume that mass transport of substrate from the solution is fast.

The rates of the three kinetic elements, the chemical reaction, charge transport and substrate diffusion, are conveniently expressed as flux values whose *nominal* values *in* the polymer film (i.e. without regard to effects of one flux on another) are given by the relations

$$f_{\mathrm{chem,\,nom}} = k_{\mathrm{ch}}\,\Gamma_{\mathrm{t}}\,C_{\mathrm{s}}, \tag{2}$$

$$f_{\mathrm{ct,\,nom}} = D_{\mathrm{ct}}\,C_{\mathrm{cat}}/d = D_{\mathrm{ct}}\,\Gamma_{\mathrm{t}}/d^2, \tag{3}$$

and

$$f_{\mathrm{subs,\,nom}} = PD_{\mathrm{s,\,pol}}\,C_{\mathrm{s}}/d, \tag{4}$$

respectively. The *actual* flux values are, however, not independent of one another. The electrode current is controlled by f_{ct}, since that directly represents the generation of catalyst sites, and at steady state the consumption of catalyst sites by the chemical reaction means that f_{ct} and f_{chem} must be equated. Finally, the flux of substrate inside the polymer must equal the chemical flux of substrate consumed, which is f_{chem}. So the three *actual* flux values must equal one another and this means, among other things, that the distances over which significant charge transport and substrate diffusion gradients exist may be less than the total film thickness, d. The actual fluxes for these are

$$f_{\mathrm{ct,\,act}} = D_{\mathrm{ct}}(C_{\mathrm{cat}(x=0)} - C_{\mathrm{cat}(x=p)})/p, \quad \text{monolayer} < p \leqslant d; \tag{5}$$

$$f_{\mathrm{subs,\,act}} = PD_{\mathrm{s,\,pol}}(C_{\mathrm{s}(x=d)} - C_{\mathrm{s}(x=q)})/(d-q), \quad \text{monolayer} < d-q \leqslant d; \tag{6}$$

where restriction is imposed on p and $d-q$ because a flux profile over less than a monomolecular layer thickness interval would not be physically sensible.

Finally, it is evident that the flux of one of the three rate elements can be so small that it limits the flux of the others. An overall flux limited by the rate of the chemical reaction step would be expressed as

$$f_{\mathrm{chem,\,lim}} = k_{\mathrm{ch}}\,\Gamma C_{\mathrm{s}}, \tag{7}$$

where Γ is the quantity of chemically reacting catalyst sites and $\Gamma \leqslant \Gamma_{\mathrm{t}}$. An overall flux limited by the rate of charge transport would be

$$f_{\mathrm{ct,\,lim}} = D_{\mathrm{ct}}C_{\mathrm{cat}}/d. \tag{8}$$

Flux limitation by substrate diffusion has a special quality in that it is physically reasonable to assume that substrate always has access to the outermost catalyst sites in the polymer film (approximately a monolayer). Under this presumption, f_{subs} does not become limiting even if $PD_{\mathrm{s,\,pol}} \sim 0$.

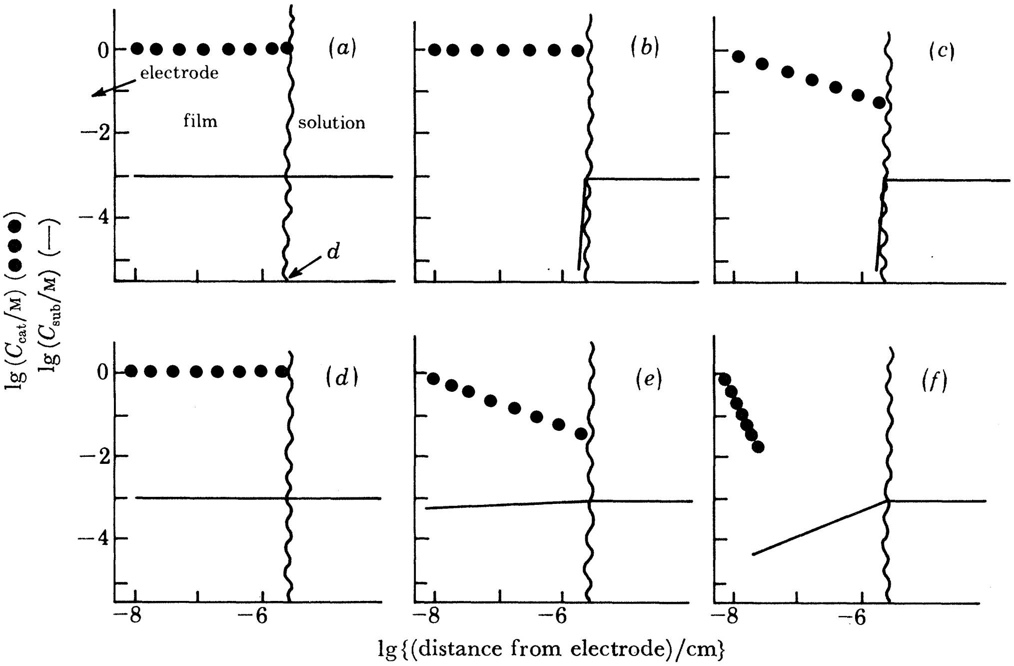


FIGURE 6. Estimated catalyst and diffusing substrate concentration–distance profiles within polymer film on electrode, assuming a fast supply of substrate from solution to film surface, for specified orderings of nominal fluxes, and $\Gamma_{\mathrm{t}} = 2\times10^{-9}$ mol/cm², $d = 2\times10^{-6}$ cm and $C_{\mathrm{cat}} = 1$ M. (*a*) $f_{\mathrm{ct}} > f_{\mathrm{subs}} > f^{*}_{\mathrm{chem}}$; (*b*) $f_{\mathrm{ct}} > f^{*}_{\mathrm{chem}} > f_{\mathrm{subs}}$; (*c*) $f_{\mathrm{chem}} > f^{*}_{\mathrm{ct}} > f_{\mathrm{subs}}$; (*d*) $f_{\mathrm{subs}} > f_{\mathrm{ct}} > f^{*}_{\mathrm{chem}}$; (*e*) $f_{\mathrm{subs}} > f_{\mathrm{chem}} > f^{*}_{\mathrm{ct}}$; (*f*) $f_{\mathrm{chem}} > f^{*}_{\mathrm{subs}} > f^{*}_{\mathrm{ct}}$. Asterisks denote the limiting flux; actual fluxes are shown in the table below.

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
$PD_{\mathrm{s,\,pol}}/(\mathrm{cm^2\,s^{-1}})$	2×10^{-8}	2×10^{-8}	2×10^{-8}	10^{-6}	10^{-6}	10^{-6}
$D_{\mathrm{ct}}/(\mathrm{cm^2\,s^{-1}})$	2×10^{-9}	2×10^{-9}	2×10^{-9}	10^{-11}	10^{-11}	10^{-11}
$10^3\,k_{\mathrm{ch}}/(\mathrm{M^{-1}\,s^{-1}})$	10^2	10^6	10^8	10^2	5×10^4	5×10^8
$f_{\mathrm{act}}/(\mathrm{mol\,cm^{-2}\,s^{-1}})$	2×10^{-10}	10^{-7}	10^{-6}	2×10^{-10}	5×10^{-9}	5×10^{-7}

Thus, given a set of nominal f_{ct}, f_{chem} and f_{subs} values, by choice of k_{ch}, D_{ct} and $PD_{\mathrm{s,\,pol}}$, the smaller limiting flux can be identified and the actual flux values of the others equated to it. Then, using the above equations (keeping the caveat about limiting f_{subs} in mind) and calculating p, q, $C_{\mathrm{cat}(x=p)}$ and $C_{\mathrm{s}(x=q)}$, one can produce a set of concentration–distance profiles of catalyst and substrate within the polymer film. This has been done in figure 6, by using a representative and realistic range of choices for k_{ch}, D_{ct} and $PD_{s,\,pol}$. Values of $10^3 k_{ch}$ employed range from a moderately slow $10^2\,\text{M}^{-1}\,\text{s}^{-1}$ upward to a (nearly diffusion limited) value of $5 \times 10^8\,\text{M}^{-1}\,\text{s}^{-1}$. Experimental values of D_{ct} are scarce, but those available fall into the range used, 10^{-11} to $10^{-8}\,\text{cm}^2/\text{s}$. Finally, $PD_{s,\,pol}$ data are not available at all, but the range 10^{-6} to $10^{-8}\,\text{cm}^2/\text{s}$ is chosen because $PD_{s,\,pol}$ cannot reasonably exceed D_s (*ca.* $10^{-6}\,\text{cm}^2/\text{s}$) at steady state, and the electrocatalytic example in figure 2 showed that $PD_{s,\,pol}$ could be one hundredth of this, or less. $C_{cat} = 1\,\text{M}$ is typical for a redox polymer, as is $C_s = 1\,\text{mM}$ for the substrate.

Figure 6 shows that choosing $f_{ct,nom}$ and $f_{subs,nom}$ and allowing f_{chem} to have smaller, intermediate and greater values (curves *a–c*) has three important consequences: (i) rate control shifts from control by the chemical reaction (in curves *a* and *b*) to control by charge transport (curve *c*), but (ii) owing to our (reasonable) outermost layer access assumption about substrate, rate control does not pass to f_{subs}, and (iii) the gradient for substrate extends in curves *b* and *c* over a monolayer-thick interval so that the quantity of catalyst sites active in the chemical reaction is only that on the outermost boundary of the film, which in the limit is only a monomolecular layer value, $1–5 \times 10^{-10}\,\text{mol/cm}^2$. In fact, curve *b* offers an explanation for experimental results where the electrocatalytic rate is proportional to C_s (a criterion for chemical rate control) but not proportional to or independent of Γ_t, as in the experimental results cited above. Rocklin & Murray (1981) proposed the conditions of curve *b* as an explanation for electrocatalytic results on immobilized $Co(NH_2)_4TPP$ and $PhCHBrCH_2Br$ substrate. Profiles such as those in curves *a–c* may well prove to be common once further experimental studies are completed.

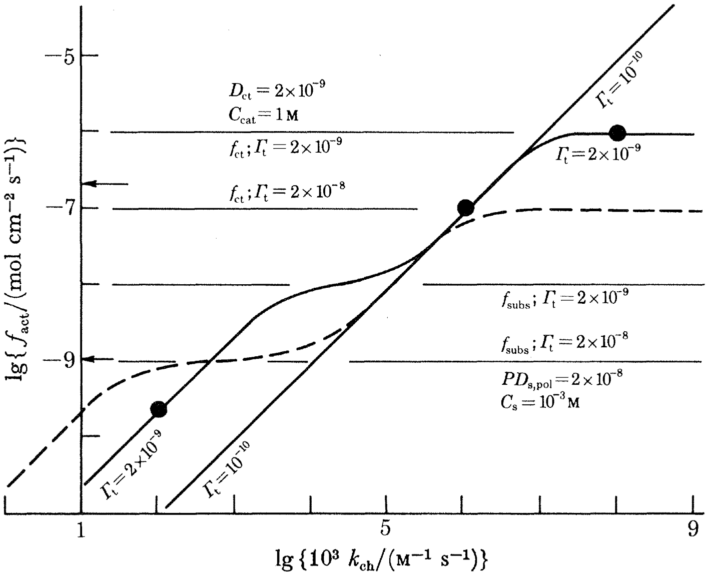


FIGURE 7. Estimated limiting electrocatalysis flux for redox polymer with $\Gamma_t = 10^{-10}$ (——), 2×10^{-9} (——) and 2×10^{-8} (– – – –) mol/cm², plotted against chemical rate. Heavy dots represent conditions of figure 6*a–c*. Arrows represent approximate maximum and minimum electrocatalytic fluxes practically measurable with a rotating disc electrode. Light horizontal lines are nominal fluxes for charge transport and substrate diffusion.

A different representation of the profiles of curves *a–c* in figure 6 is given in figure 7. This portrays more directly the limiting flux values obtained over a range of k_{ch} for the situation, where $f_{ct,\,nom} > f_{subs,nom}$. The conditions of curves *a–c* in figure 6 are the heavy dots on figure 7.

At low chemical rate constants, the advantages of large Γ_t are retained (e.g. faster reaction flux), but once the chemical reaction and substrate diffusion fluxes become similar (at larger k_{ch}), this advantage is lost (the profile becomes that in curve *b* in figure 6) and the thicker redox polymer film exerts no greater electrocatalytic rate than would a monomolecular layer. The thicker polymer film also enters the régime of charge transport rate control (curve *c* in figure 6) at a lower chemical rate k_{ch} than with the thinner polymer film, owing to the proportionality of *d* to Γ_t. These results assert, then, that for the 'slow substrate' kind of electrocatalytic reaction, a very thin film of catalyst sites can yield the faster electrocatalytic conversions when the chemical rate constant k_{ch} is large. This is the opposite of the prediction by Andrieux & Saveant (1978), who did not consider the important charge transport rate element.

In curves *d–f* in figure 6 an analogous set of profile calculations has been done for the condition that $f_{subs} > f_{ct}$. Curve *d* is identical to curve *a*; again for slow chemical rates, the reactive catalyst sites correspond to Γ_t. Curve *e* is a more complex situation in which it is difficult to quantitatively formulate the number of active catalyst sites but they are less than Γ_t. Curve *f* is analogous to curve *c* in that the catalyst–substrate reaction zone collapses to a monolayer-like thickness of catalyst sites but this thickness interval now occurs in the depths of the polymer film. The catalyst and substrate fluxes are co-limiting in this instance.

Finally, to summarize the lessons learned from the above computations relevant to designing redox polymer film catalysts: (i) when the chemical reaction rate constant is small, the catalyst film can profitably be large, since most or all catalyst sites will participate in the reaction; (ii) when the chemical reaction rate constant is large but not as large as one wishes it to be, then the catalyst film should be as thin as is practicable to increase f_{ct}, and probably the film should not be highly cross-linked since this may decrease f_{subs}. At first glance the latter properties would seem to be antagonistic to a goal of stable polymer films. Important practical limitations and constraints on some kinds of electrocatalytic chemistry and films will, of course, arise from stability requirements of operating electrocatalysis. The extent of these is not yet evident and it remains for continued development of electrocatalytic reactions for this to become satisfactorily appreciated. An important step will be the design of readily regenerable catalyst films.

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REFERENCES (Murray)

Abruña, H. D., Denisevich, P., Umaña, M., Meyer, T. J. & Murray, R. W. 1981 *J. Am. chem. Soc.* **103**, 1.
Andrieux, C. P. & Saveant, J. M. 1978 *J. electroanalyt. Chem.* **93**, 163.
Anson, F. C. 1980 *J. phys. Chem.* **84**, 3336.
Bettelheim, A., Chan, R. J. H. & Kuwana, T. 1980 *J. electroanalyt. Chem.* **110**, 93.
Collman, J. P. *et al.* 1980 *J. Am. chem. Soc.* **102**, 6027.
Daum, P. & Murray, R. W. 1981 *J. phys. Chem.* **85**, 389.
Daum, P., Lenhard, J. R., Rolison, D. R. & Murray, R. W. 1980 *J. Am. chem. Soc.* **102**, 4649.
Degrand, C. & Miller, L. L. 1980 *J. Am. chem. Soc.* **102**, 5728.
Itaya, K. & Bard, A. J. 1978 *Analyt. Chem.* **50**, 1487.
Kaufman, F. B. & Engler, E. M. 1979 *J. Am. chem. Soc.* **101**, 547.

Lenhard, J. R. & Murray, R. W. 1977 *J. electroanalyt. Chem.* **78**, 195.
Lenhard, J. R. *et al.* 1978 *J. Am. chem. Soc.* **100**, 5213.
Lennox, J. C. & Murray, R. W. 1978 *J. Am. chem. Soc.* **100**, 3710.
Lewis, N., Bocarsly, A. B. & Wrighton, M. S. 1980 *J. phys. Chem.* **84**, 2033.
Merz, A. & Bard, A. J. 1978 *J. Am. chem. Soc.* **100**, 3222.
Murray, R. W. 1980*a* *Acct. chem. Res.* **13**, 135.
Murray, R. W. 1980*b* In *Silylated surfaces* (ed. D. E. Leyden & W. T. Collins), pp. 125–137. Gordon & Breach.
Nowak, R. J. *et al.* 1980 *Analyt. Chem.* **52**, 315.
Oyama, N. & Anson, F. C. 1980*a* *J. electrochem. Soc.* **127**, 247, 249.
Oyama, N. & Anson, F. C. 1980*b* *Analyt. Chem.* **52**, 1192.
Rocklin, R. D. & Murray, R. W. 1979 *J. electroanalyt. Chem.* **100**, 271.
Rocklin, R. D. & Murray, R. W. 1981 *J. phys. Chem.* **85**. (In the press.)
Tse, D. C. S. & Kuwana, T. 1978 *Analyt. Chem.* **50**, 1315.
Van De Mark, M. R. & Miller, L. L. 1978 *J. Am. chem. Soc.* **100**, 3223.
Wrighton, M. S. 1979 *Acct. chem. Res.* **12**, 303.
Wrighton, M. S. *et al.* 1978 *J. electroanalyt. Chem.* **87**, 429.

Discussion

J. B. GOODENOUGH (*Inorganic Chemistry Laboratory, South Parks Road, Oxford, U.K.*). Could Professor Murray tell us from his experience whether electrodes normally unstable under operating conditions can be stabilized by molecular attachments to the surface? For example, could molecular attachments to the surface of a sulphide semiconductor transform it from an unstable, inefficient oxygen-evolution electrode to a stable, efficient one?

R. MURRAY. Yes, as discussed in my written presentation, the M.I.T. group under Wrighton has stabilized Si^0 toward photoanodic corrosion by using ferrocene polymer films. Ferricenium sites are produced by electron vacancies at the Si^0 surface and consumed by a sacrificial reductant, more rapidly than such electron vacancies corrode the surface. If the important rate determinants are electron and perhaps proton percolation through the polymer film, not pre-emptive bonding–deactivation of surface semiconductor atoms by –OSi–, then simply coating (not bonding) other redox polymers on other semiconductors could be a generally protective measure. I believe that this is a topic deserving further research.

W. J. ALBERY (*Department of Chemistry, Imperial College, London, U.K.*). It is interesting to speculate whether D, the 'diffusion coefficient' for the change of charge in the modified layer, describes an electron hopping mechanism or the movement of counter-ions. In the thionine-coated electrode, if the low value for D of $5 \times 10^{-13}\ \mathrm{cm^2\ s^{-1}}$ described the electron hopping process, the maximum current that would be passed in the steady state would be about 1 mA $\mathrm{cm^{-2}}$. Since we have observed currents greater than 10 mA $\mathrm{cm^{-2}}$, it seems more probable that D describes the movement of counter ions. If that is so, the change of charge in the modified layer is controlled by the slow movement of counter-ions. In the steady state when the ions are in position, larger currents than those predicted from D can be passed by the more efficient electron hopping rate.

R. MURRAY. Whether the charge transport D_{ct} represents counter-ion or solvent motion, electron self-exchange between neighbouring redox sites, segmental motions of polymer chains antecedent to these, or something else, is not simply answered. Consider the diverse ideas in the literature of diffusion in polymers, and that the electrochemical situation includes chemical transformation of the polymer, as realistic measures of the magnitude of the problem. Also, what controls D_{ct} may well change from polymer to polymer, from redox site to redox site, from solvent to solvent, or from counter-ion to counter-ion. I propose that the most believable answers will come from observing how D_{ct} depends on systematic, definable changes in polymer structure or redox site chemistry, and by analysis of the activation and pre-exponential factors for D_{ct}.