*Coordination Chemistry Reviews*, 86 (1988) 135–189
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# COORDINATION CHEMISTRY IN TWO DIMENSIONS: CHEMICALLY MODIFIED ELECTRODES

HECTOR D. ABRUÑA

*Department of Chemistry, Cornell University, Ithaca, New York 14853 (U.S.A.)*

(Received 30 March 1987)

CONTENTS

## A. INTRODUCTION

One of the primary objectives of electrochemists is the deliberate control of reactivity at the electrode/solution interface. Such control, if possible, would have profound effects on the areas of electrocatalysis, corrosion, analysis, electrochromics and many others. The one variable that has always

0010-8545/88/$19.25

been available to electrochemists is the applied potential. By controlling it, one can dictate the energetics of the interface; however, this affords only modest variations and generally poor selectivity. Thus, investigators have pursued the deliberate modification of the electrode surface as a means of dictating and controlling its properties. Through the deliberate design of the modification process, it is hoped that the physicochemical properties of the modifier will be transferred to the electrode surface, thus giving it the range of reactivity and selectivity available in homogeneous chemical systems. In addition, and perhaps more importantly, due to the physical constraints that such modification would necessarily impose, new reactivities and structured interfaces could in principle be achieved.

The field of chemically modified electrodes (in its various forms) thus seeks to dictate and control the properties of the interface through its deliberate modification.

The intent of this review is to present this area of electrochemical research from the perspective of coordination chemistry. The outline to be followed will be as shown below.

(1) Brief historical perspective.
(2) Basic electrochemical concepts and techniques as applied to chemically modified electrodes.
(3) Survey of procedures employed in the modification of electrode surfaces, especially those involving transition metal complexes.
(4) Selected examples and applications.

The intent is not to give a comprehensive review of the literature but rather present an introduction with emphasis on coordination chemistry and point to some of the new frontiers that await this most interesting and promising area of research.

There have been a number of reviews of this field [1–7] that have emphasized various aspects, in addition to the comprehensive and authoritative review by Murray [1] which covers the literature to about 1982.

## B. HISTORICAL PERSPECTIVE

The origins of the field of chemically modified electrodes can be traced to the areas of adsorption, chemisorption and electrodeposition (electroplating). The literature of these areas is vast, and will not be addressed in any detail in this review. In the early days of these fields, the approaches taken were strictly Edisonian and as a result, there was little in the way of a coherent framework that could bridge experiment with theoretical prediction. A significant step in trying to unravel some of these processes, especially those related to adsorption at electrode surfaces, was provided by the work of Fred Anson (at the California Institute of Technology) in the 1960s and

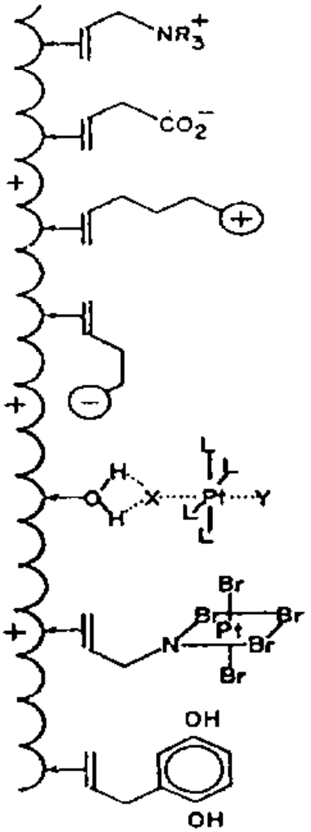

Fig. 1. Structure of functionalized olefins adsorbed on to a platinum electrode. (From ref. 9 with the permission of the American Chemical Society.)

early 1970s. From his work emerged a framework for the rational and systematic understanding of the chemical and structural principles underlying adsorption [8]. Of particular importance was the fact that many of his studies involved coordination compounds and from these studies Anson derived some relatively simple rules that described the adsorption properties of a wide range of materials.

The first example of the deliberate modification of an electrode surface by exploiting concepts of chemisorption was by Lane and Hubbard [9,10] who chemisorbed a variety of olefin-bearing species on to platinum electrodes, thus exploiting the well-known propensity of olefins to chemisorb on to platinum. Both electroactive and non-electroactive (Fig. 1) species were incorporated, including various hydroquinones with an olefin-bearing side-chain, pentahaloplatinates ($Br^-$, $Cl^-$) with coordinated allylamine, 3-allylsalicylic acid and others. There were a number of interesting observations made. One of the more significant, within the scope of coordination chemistry, was the potential dependence of the ability of adsorbed 3-allylsalicyclic acid to coordinate iron from solution, with binding taking place at potentials negative of 0.0 V, but not at potentials positive of +0.2 V. This was interpreted in terms of the potential of zero charge ($E_{pzc}$) of platinum being about 0.1 V in the medium involved. (Note that the potential of zero charge represents a condition where the electrode and the solution potentials are the same so that there is no net charge at the electrode.) This was an especially notable observation since it demonstrated the ability of a surface confined group to coordinate a metal ion and the ability to modulate the coordination via the applied potential.

These early observations generated much enthusiasm and stimulated further investigations. In 1975, L. Miller and co-workers reported the preparation of a "chiral electrode" [11] via the immobilization of an asymmetric reagent (*S*(−)phenylalanine methyl ester). When used in the electrolysis of 4-acetylpyridine, optically active products (albeit with small enantiomeric excesses) could be obtained. This was a clear indication that by suitable modification of the surface, reactions could be made to proceed via a predetermined pathway.

Also in 1975 Murray and co-workers, in their now classic paper [12], demonstrated for the first time how a designed synthetic sequence could be employed for the deliberate modification of an electrode surface. To the author's knowledge, this was also the first time that the term Chemically Modified Electrode appeared in the literature. In this work, Murray and co-workers made use of the reactivity of organosilanes, commonly employed in the preparation of bonded phases for chromatographic applications, and applied them to the modification of tin dioxide electrodes since these were known to have reactive surface hydroxy groups. They immobilized a number of species and were able to follow the course of the synthetic steps by employing ESCA (electron spectroscopy for chemical analysis). A significant advance was made when they found that superficially oxidized metal electrodes (e.g. Pt, Au and others) had similar surface hydroxy groups and as such were also amenable to surface modification [13]. The use of silane-based chemistry was then extended to the incorporation of numerous redox couples [14]. Most of these procedures gave rise to electrodes modified with amounts that were in the monolayer (ca. $1 \times 10^{-10}$ mol cm$^{-2}$) regime. However, these modified interfaces had limitations with regards to stability. Nonetheless, Murray's early work clearly demonstrated the feasibility of modifying the surface of an electrode in a rational and deliberate fashion.

A versatile extension of this silane chemistry by the Wrighton group at MIT was to incorporate a redox center on a hydrolytically unstable silane reagent so that upon reaction with surface hydroxy groups the surface would be rendered modified with the specific reagent. The initial materials contained a ferrocene unit [15,16], but Wrighton's group has prepared a broad repertoire of molecules that incorporate a variety of redox groups. These materials were notable because they gave rise to surfaces modified with large amounts of material (coverages as high as $10^{-6}$ mol $cm^{-2}$) and in addition, these coatings were very stable to repeated cycling between oxidation states. The original intent was to use these reagents for the modification of small bandgap semiconductors (e.g. Si), employed in photoelectrochemical cells, in order to stabilize them against photoanodic corrosion. In fact, these reagents proved to be quite effective for this purpose [17].

Oyama and Anson [18] made a very significant observation when they reported that electrodes coated with protonated films of poly-4-vinylpyridine (pvp) could incorporate large amounts of electroactive anions such as $[Fe(CN)_6]^{4-}$. This technique of electrostatic binding opened a new venue for research in chemically modified electrodes since by virtue of its simplicity, it allowed for numerous systems to be prepared and studied. This approach was extended to the use of polyanionic materials, most notably Nafion [19] (a perfluoro sulfonate membrane produced by DuPont) and polystyrene sulfonate [20]. This period marked the transition from electrodes modified with monolayers (or a few monolayers) to what would be called polymer modified electrodes [21].

In 1981, Abruña, Murray, Meyer and co-workers [22] reported that vinylpyridine and vinylbipyridine complexes of ruthenium and iron could be readily electropolymerized to give rise to very adherent and electrochemically active polymeric films of the parent monomer. The reaction proved to be quite general and a large number of electropolymerizable metal complexes were prepared and many applications explored. Of these, the so-called bilayer-electrode [22,23] represented an especially interesting device in that it could exhibit rectifying behavior without the use of any semiconductor material.

The utility of structured electrochemical interfaces was further demonstrated by the groups of Wrighton [24] and Murray [25] who were able to prepare electronic devices through the use of spatially well-defined layers of polymers.

These areas continue to grow at a very rapid rate, fueled by the belief that virtually any redox material can be incorporated. Thus, new strategies and new applications continue to appear.

Concurrent with these developments were investigations on electronically conducting polymers such as polyacetylene, polypyrrole, polythiophene, polyaniline and many others. This is an area that has also experienced an explosive growth in terms of new materials and applications [26]. However, it is largely beyond the scope of this review and as such will not be covered to any extent.

## C. BASIC ELECTROCHEMICAL CONCEPTS

### *(i) Cyclic voltammetric responses for freely diffusing species and surface immobilized monolayers*

Although the major emphasis of this review is on coordination chemistry at modified electrodes, I believe that it is worthwhile to consider briefly some of the aspects related to the electrochemical response of redox centers immobilized on an electrode surface (i.e. a modified electrode) vs. that obtained for a freely diffusing species in solution. The discussion will center around cyclic voltammetry since it is the technique that has most often been employed in these studies. The readers who are well versed in electrochemistry may feel justified in going over to the next section.

In a cyclic voltammetric experiment [27] one has an unstirred solution containing supporting electrolyte and a redox species (in solution or on the surface). The experiment consists of applying a triangular wave form (rates typically varying from a few millivolts to a few volts per second) to an electrode with the concurrent measurement of current. A plot of current vs. potential is termed a voltammogram.

Consider having a solution of a species Ox which can be reduced to Red with a characteristic potential $E^{0\prime}$ for the process. We begin by applying a potential $E_{\mathrm{init}}$ (A in Fig. 2) that is sufficiently removed from $E^{0\prime}$ so that essentially no current flows. We will initiate a scan in the negative direction. As the applied potential approaches $E^{0\prime}$ the current begins to increase (B) and continues to do so (C) until a peak (D) is reached. Upon continued

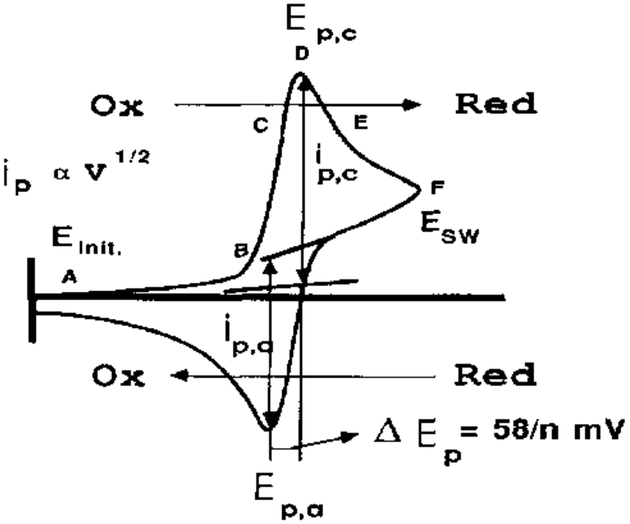

Fig. 2. Cyclic voltammogram for a freely diffusing species.

scanning, the current decays in a characteristic "tailing" fashion (E). At point (F) ($E_{sw}$) the direction of the sweep is changed and the reverse sweep will be analogous to the forward sweep (as long as $E_{sw}$ is $> 35/n$ mV ($n$ = number of electrons transferred) past the peak). Qualitatively we can describe the shape of this voltammogram by considering that early on the applied potential is so far removed from $E^{0\prime}$ that no current flows. In the vicinity of $E^{0\prime}$ we begin to reduce (Ox to Red) the material that is closest to the electrode surface and at point (D) we essentially exhaust it so that the surface concentration of Ox is zero. Any further material to be electrolyzed needs to diffuse to the electrode surface from the solution and this gives rise to the tailing decrease in the current (often referred to as diffusional tails). The reverse sweep can be understood in analogous terms except that the process now is the re-oxidation of the reduced material that was generated in the forward sweep. In a cyclic voltammogram the parameters of importance are the peak potential ($E_{p,c}$; $E_{p,a}$) (c = cathodic, a = anodic) and current ($I_{p,c}$; $I_{p,a}$) values as well as the difference in peak potential values $\Delta E_p$. For a chemically reversible system, (that is, when Ox and Red are both chemically stable species), the ratio of peak currents will be unity at all sweep rates. For an electrochemically reversible system, (that is one that is always at nernstian equilibrium), the difference in peak potential values will be $58/n$ mV (at 25 ° C). Deviations from these indicate complications; either kinetic or chemical (see Bard and Faulkner [27] for an authoritative treatment of these). The average of the peak potentials is taken as the formal potential ($E^{0\prime}$) for the redox couple. The peak current (in amp) is given by the Randles–Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C^b v^{1/2}$$

where $n$ is the number of electrons transferred, $A$ is the electrode area (cm$^2$), $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), $C^b$ is the bulk concentration (mol cm$^{-3}$) and $v$ is the sweep rate (V s$^{-1}$). Thus $i_p$ is proportional to $v^{1/2}$, $C^b$, and $n^{3/2}$.

The response obtained at an electrode coated with a monolayer of an electroactive material is shown in Fig. 3 and it is immediately apparent that the response (often referred to as a surface wave) is quite different from that previously described. We can go through an analogous analysis. Again, at potentials far removed from $E^{0\prime}$ (A) no current flows. The current increases as we scan negatively (B), (C) and again a current peak (D) is observed. However, in this case the current decay (E) is just as rapid as was the increase, giving rise to a symmetrical response. The reverse scan is a mirror image of the forward scan. These differences arise from the fact that in this case there is no diffusion of electroactive material to the electrode since it is all at the electrode itself. The voltammogram shown is again for a chemically

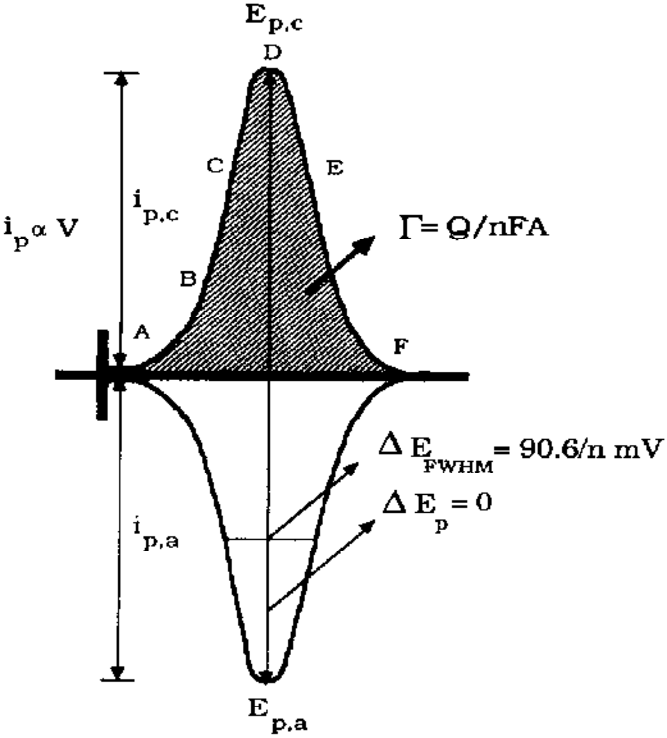

Fig. 3. Cyclic voltammogram for a surface immobilized redox couple at monolayer coverage.

and electrochemically reversible system. As for the diffusion case, a chemically reversible system will exhibit a ratio of peak currents of 1. However, for an electrochemically reversible system the $\Delta E_p$ value will be zero with larger values (which increase with sweep rate) indicating some sluggishness in the electron transfer event. According to the theory for surface immobilized redox centers [9,28] if surface concentration and activity are equated, the current/potential behavior in a cyclic voltammetric experiment for a nernstian process is given by

$$i = \left( \frac{n^2 F^2 \Gamma v}{RT} \right) \left( \frac{\chi}{(1+\chi)^2} \right)$$

or

$$i = \frac{4 i_p \chi}{(1+\chi)^2}$$

where $\chi = \exp[(nF/RT)(E - E^0)]$, $\Gamma$ = total amount of reactant initially present on the electrode surface, $v$ = potential sweep rate. The peak current is given by

$$i_p = \frac{n^2F^2\Gamma v}{4RT}$$

From this it follows that the peak current will be linearly dependent on the rate of potential sweep. This is important to note because it means that the signal to noise ratio will not degrade with increasing sweep rate as is the case for solution species. This is because the double layer charging current also grows linearly with sweep rate.

There are in addition other properties of surface waves that have no equivalent in the cyclic voltammetric response for diffusing species. The first one has to do with the fact that the oxidation or reduction of the surface layer represents a coulometric experiment. Thus by integrating the area under the voltammetric wave (i.e. obtaining the charge $Q$) one can determine the surface coverage ($\Gamma$)

$$\Gamma = \frac{Q}{nFA}$$

(Note that for most of the materials to be considered in this review, a monolayer will represent approximately $1 \times 10^{-10}$ mol cm$^{-2}$.)

Finally, for the case of non-interacting neighbors within a film, the full width at half-maximum (FWHM) for a surface wave should be $90.6/n$ mV. Values larger than this reflect repulsive interactions whereas smaller values indicate attractive or stabilizing interactions [29–32]. The limit of extremely sharp peaks usually indicates a phase transition.

In general, many immobilized redox couples exhibit symmetrical waveshapes as well as the linear dependence of peak current with rate of potential sweep. The $\Delta E_p$ values are typically small ($< 30$ mV) but seldom zero and generally do not increase with increasing sweep rate, indicating that there are no kinetic limitations. However, the true origin of this effect is not at present clear.

Also, although many of the reported voltammograms are symmetrical, values of FWHM are typically larger than expected. One interpretation [29b,32,33] for this effect is based on the assumption that in a layer of immobilized redox centers, there might be (and more than likely there are) subtle variations in structure, solvation, environment, etc. that give rise to a range of closely spaced $E^{0\prime}$ values (rather than a single one) and that this is responsible, at least in part, for the observed broadening.

Alternatively, this has been interpreted in terms of surface activity coefficients that are dependent on surface coverage. This approach, proposed by Brown and Anson [31] and later modified by Murray and co-workers [32], introduces the concept of an interaction parameter $r_i$ whose properties (positive values indicate attractive interactions with narrowed peaks whereas negative values indicate repulsive interactions with broadened waves) dictate the width of the wave. This leads to a modified version of the wave equation

$$i = \frac{-4 i_p \exp(P)}{(1 + \exp(P))^2 - (r_{Ox} + r_{Red}) \exp(P)}$$

where $P = (nF/RT)(E - E^0) + (r_{Ox} + r_{Red})\ \Gamma_{Ox} - r_{Red}\Gamma_{Tot}$ and where it is generally assumed that $r_{Ox} = r_{Red} = 2r$.

### *(ii) Polymer films*

In the case of polymeric films on electrode surfaces a wide range of voltammetric waveshapes have been reported [34–51]. Reactions at these interfaces are much more complex than those at electrodes covered with monolayers because there are numerous aspects to be considered. Some of these include the mechanisms for electron transfer and transport through the film, especially to sites that are physically remote from the electrode surface. Also of importance are the movement of polymer chains in order to accommodate the movement of species through the film, including charge compensating ions as well as solvent molecules. The exact voltammetric waveshape is then dictated by the interplay of all of these factors.

Kaufman et al. [38] proposed a model for the transport of charge through polymer films where charge propagation takes place via electron-self exchange reactions between oxidized and reduced neighbors within the film. However, although this may represent the mechanism for the process, as we mentioned previously, the overall rate (and therefore the waveshape) will be dictated by the combination of effects mentioned above.

An approach that has been quite successful in the treatment of this problem is based on the fact that transport rates through these films appear to obey the laws of diffusion [52–80]. Thus, the measurement of diffusion coefficients (variously termed $D_{ct}$ (charge transport diffusion coefficient) $D_{app}$ (apparent diffusion coefficient) $D_{eff}$ (effective diffusion coefficient)) has provided some very useful insights into these processes. This is usually expressed in terms of the parameter $D_{ct}\ \tau/d^2$ where $\tau$ is the time scale of the experiment (dictated by the rate of potential sweep in a cyclic voltammogram) and $d$ is the polymer film thickness. When $D_{ct}\ \tau/d^2$ is $\gg 1$ the voltammetric waveshape is that of a monolayer in nernstian equilibrium with the electrode (Fig. 3). When $D_{ct}\ \tau/d^2 \ll 1$ the response is that for a species in solution (Fig. 2). In this case the voltammogram loses its symmetrical shape and the peak current is proportional to $v^{1/2}$.

In addition, one can describe these processes in terms of $D_{ct}^{1/2}C$ ($C$ is the concentration of redox centers in the film), where $D_{ct}^{1/2}$ is obtained from a potential step experiment and the Cottrell equation

$$i = \frac{nFAD_{ct}^{1/2}C}{(\pi t)^{1/2}}$$

For systems with large values of $D_{ct}$, for low sweep rates or for sufficiently thin films, the voltammetric response will again be that of a monolayer film with symmetrical waveshapes and peak currents proportional to the rate of potential sweep. For the opposite case of small $D_{ct}$, thick films or short experimental times, the response will revert back to that exhibited by a solution species with the characteristic diffusional tails.

In many cases one can observe the transition from a surfacewave response to a diffusional wave response by simply changing the rate of potential sweep. The literature of polymer modified electrodes is replete with examples of this.

In some instances the anodic and cathodic waveshapes can be significantly different and this is particularly prevalent in systems where one of the oxidation states of the polymer is electrically neutral. In addition, solvent effects can be dramatic in such instances.

Perhaps the most thorough study of waveshapes and their changes was by Peerce and Bard [41] who studied and simulated the electrochemical response for electrodes modified with polyvinylferrocene.

In the limit of strong interaction between near neighbors, extremely sharp waveshapes, indicative of a phase transition type of behavior can be observed. One of the more illustrative examples of this was the study by Bard and Henning [81,82] on TTF in Nafion (Fig. 4) (notice the expanded potential scale).

There have also been some attempts at trying to factor out the various contributions to measured values of $D_{ct}$. For example, Majda and Faulkner [83] employed a luminescence quenching technique in order to measure the apparent diffusion coefficient of $[Ru(bpy)_3]^{2+}$ in polystyrene sulfonate in the absence of counterion motion. The measured value was larger than that obtained by potential step methods (which necessitates counterion movement) indicating that the latter process is rate determining in the transport of charge.

Buttry and Anson [66] measured the apparent diffusion coefficients for $[Co(bpy)_3]^{3+/2+}$ and $[Co(bpy)_3]^{2+/+}$ electrostatically bound to Nafion. Due to the very large difference in the electron self-exchange rates for these two processes (with the latter being larger by a factor of more than $10^7$) they were able to separate the contribution of electron self exchange from the apparent diffusion coefficient. This is dramatically demonstrated in Fig. 5

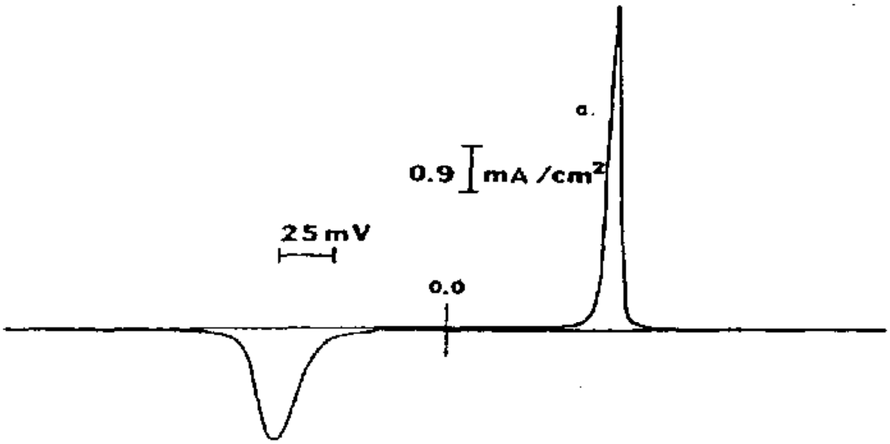

Fig. 4. Cyclic voltammogram of TTF-Br in Nafion (notice expanded voltage scale). (From ref. 81a with permission of the American Chemical Society.)

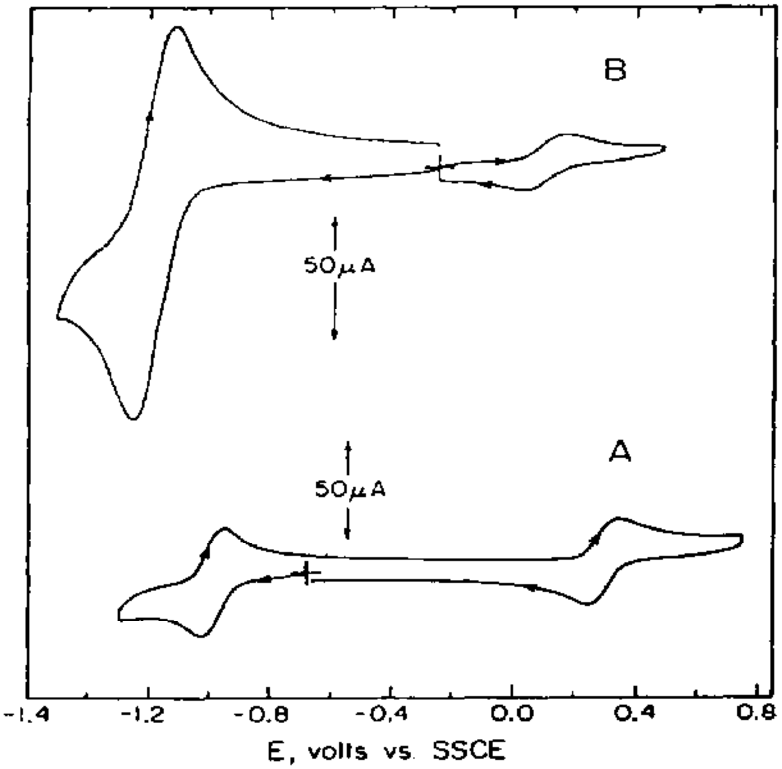

Fig. 5. Cyclic voltammograms for $[Co(bpy)_3]^{3+/2+}$ and $[Co(bpy)_3]^{2+/1+}$ in solution (A) and incorporated into Nafion (B). (From ref. 66 with permission of the American Chemical Society.)

which shows a cyclic voltammogram for both processes in solution and in Nafion. The very large difference in peak currents in the latter case is a manifestation of the contribution of the electron self-exchange process to the $[Co(bpy)_3]^{2+/1+}$ process but not to that of $[Co(bpy)_3]^{3+/2+}$. These observations were in good agreement with the theoretical treatments of Dahms and Ruff [84].

## D. METHODS FOR MODIFYING THE SURFACE OF AN ELECTRODE WITH REDOX ACTIVE COMPONENTS

A variety of methods can and have been employed in incorporating a redox component on an electrode surface. The methods to be discussed include: (i) adsorption; (ii) covalent bonding; (iii) polymer films; (iv) others.

### *(i) Adsorption*

Adsorption (or more appropriately in this case; chemisorption) represents the oldest and simplest technique for anchoring redox centers to electrode surfaces. Although there is a vast literature of materials that adsorb to various electrode surfaces, I will take as a point of departure the early experiments of Lane and Hubbard, Anson and others on the adsorption of monomeric species. As mentioned previously Lane and Hubbard [9,10] exploited the chemisorptive bond between olefins and platinum to incorporate a number of redox species (Fig. 1). Of these the most interesting case was that of the adsorbed 3-allylsalicylic acid and the potential dependence of its ability to coordinate iron from solution.

Although these early studies were on platinum surfaces, the majority of adsorption studies have been performed on pyrolytic graphite and glassy (vitreous) carbon. A particularly strong and effective interaction that has been heavily exploited is that between the basal planes of pyrolytic graphite and molecules having extended $\pi$-electron systems. Examples of these are found in the early work of Anson and co-workers who adsorbed phenanthrene quinone, *o*-dianisidine, a $Ru(NH_3)_5Py$ (Py = pyridine) moiety bound to phenanthrene (Fig. 6) and others [31,85].

The vast majority of adsorption studies carried out on carbon surfaces have been directed at electrocatalytic applications, especially the reduction of molecular oxygen employing a wide range of substituted porphyrins and phthalocyanines. Of these, the most thorough and successful series of investigations have been by Anson and Collman [86–94]. Of particular note is the now classic example of $O_2$ reduction employing face-to-face porphyrins (vide infra) [86,87,91].

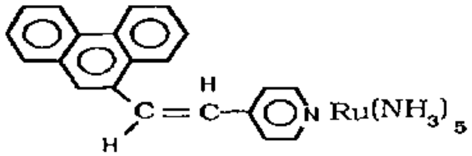

Fig. 6. Structure of anthracene derivative of [Ru$(NH_3)_5$Py] employed as an adsorbed layer on pyrolytic graphite.

There have also been other studies based on the adsorption of electroactive species. Price and Baldwin [95] attached a ferrocene unit by the condensation of ferrocene carboxaldehyde to a previously adsorbed layer of allylamine on a platinum electrode. Cox and Majda [96] adsorbed adenosine monophosphate on a platinum electrode with the subsequent incorporation of iron from solution. Yeager and co-workers [97] adsorbed cobalt and iron tetrasulfonated phthalocyanines on to gold and platinum electrodes and were able to obtain reflectance spectra of the same.

In a related area, there has been a recent surge in the use of Langmuir–Blodgett films for the modification of electrode surfaces. A variety of redox couples has been incorporated in this way including ferrocenes [98a–c], bipyridine complexes of ruthenium and osmium [98d,e], viologens [98b,c] and others [98f].

### *(ii) Covalent bonding*

#### *(a) Silane-based modification*

Although adsorption represents the simplest way of modifying the surface of an electrode, it suffers from the fact that it is an equilibrium process. Thus, inevitably, the material will desorb from the electrode surface, giving rise to electrodes with limited lifetime. In addition, adsorption rarely gives rise to coverages in excess of a monolayer, thus limiting the amount of material that can be incorporated.

These limitations prompted the investigation of alternative means of modifying electrode surfaces. It was Murray's group who first articulated a general strategy for the covalent attachment of redox centers on to electrode surfaces. The approach was based on the use of silane reagents that had been employed by chromatographers in the derivatization of silica surfaces for the preparation of bonded phases. Such reagents could be reacted with the surface hydroxy groups found on metal oxide electrodes to give rise to covalently attached species via siloxane bonds. The original work centered on tin oxide [12,99] because of its similarity with silica. However, they then discovered that when oxidized in acidic media, most metal electrodes are

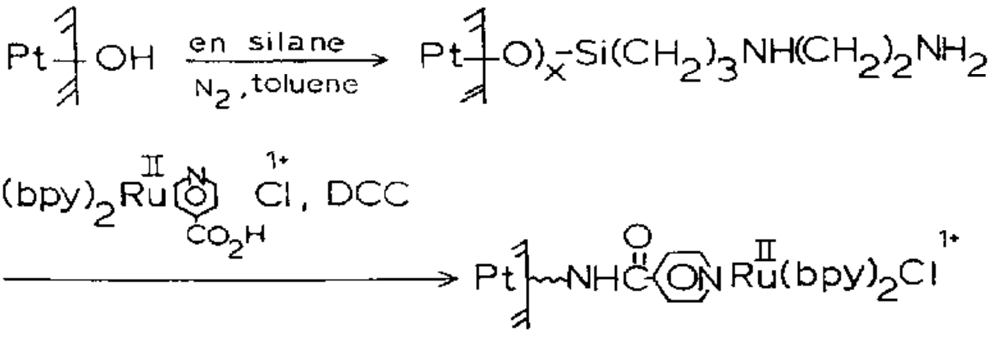

Fig. 7. Synthetic sequence for the modification of a superficially oxidized platinum electrode (DCC is dicyclohexyl carbodiimide).

coated with a thin oxide layer which is also quite reactive towards silane reagents [13]. Thus, platinum and gold surfaces could be easily modified by these techniques. This generated much enthusiasm and a wide range of redox active centers were immobilized via this approach [14,99–104]. One of the most versatile reagents for this application was the so-called ethylenediamine silane (3(2-aminoethylamino)propyltrimethoxysilane) whose primary amino end-group could be employed to attach a wide range of species containing either a carboxylic acid or an acid chloride group. A typical reaction sequence for $[Ru(bpy)_2(isonic)Cl]^+$ (isonic is isonicotinic acid) is shown in Fig. 7. In these early days, a great deal of emphasis was placed on establishing the surface chemistry. Thus, ESCA [99–111] was extensively employed to follow the course of such reactions (Fig. 8).

Another approach based on silane chemistry was to attach a silane that contained a coordinating group and subsequently react this "surface ligand" with a metal complex with a weakly bound and easily displaced ligand. Figure 9 shows an example for a surface bound pyridine group. Such ligand substitution reactions were also carried out with immobilized nitrile and thio ligands [112].

In 1978 Wrighton and co-workers prepared a series of hydrolytically unstable ferrocene derivatives [15,16] (Fig. 10) which could polymerize to give rise to coatings with coverages as high as $10^{-6}$ mol $cm^{-2}$. These proved to be quite durable and were employed in the effective suppression of photoanodic corrosion of a number of small bandgap semiconductor electrodes [16,113–118]. Wrighton's group has, over the years, developed an extensive series of redox reagents which can be immobilized via this approach including viologens [119–128], quinones [129], tetramethyl-*p*-phenylenediamine [130], and these have been employed in various applications including the photoassisted evolution of hydrogen, electrocatalytic reduction of oxygen to hydrogen peroxide and others [131].

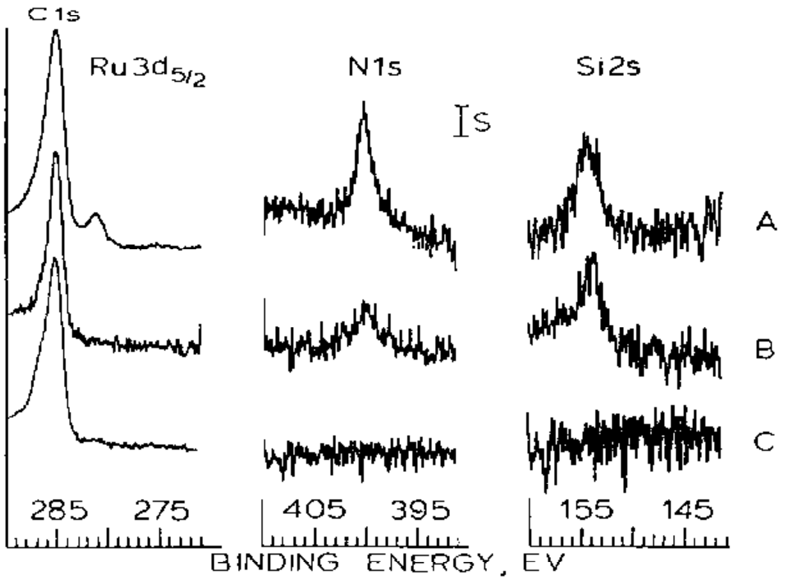

Fig. 8. C, Ru, N and Si ESCA spectra for a platinum electrode at different stages of modification. (C) prior to modification, (B) after modification with ethylene diamine silane, (A) after modification with silane and the ruthenium complex shown in Fig. 7. (From ref. 104 with permission of the American Chemical Society.)

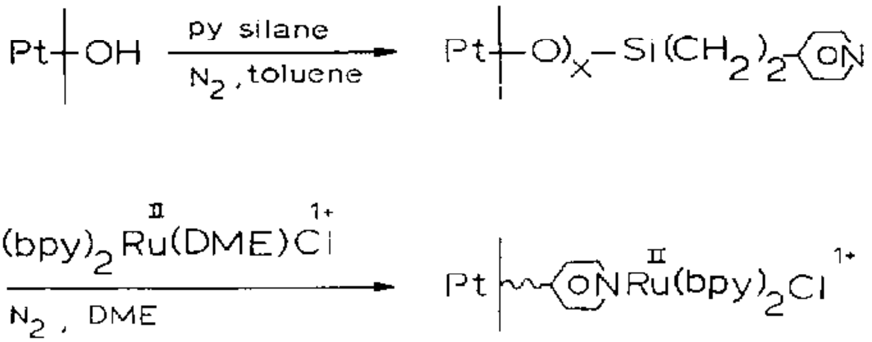

Fig. 9. Synthetic sequence for the modification of a platinum electrode with a ruthenium complex by reaction with a surface immobilized pyridine ligand (DME is dimethoxy ethane).

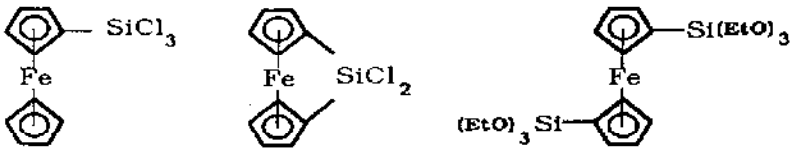

Fig. 10. Hydrolytically unstable ferrocenyl silanes employed by Wrighton and co-workers.

Reagents immobilized via silane chemistry include $[Ru(bpy)_2bpy\text{-}Si]^{2+}$ [132] (where bpy-Si is 4-ethyltrichlorosilyl, 4′-methyl-2,2′-bypyridine) among others [133]. Murray's review [1] contains an extensive listing of materials immobilized via silane chemistry.

In most of these examples, the electrochemical responses follow those anticipated for immobilized redox reagents, although the waves are generally broader than expected and the $\Delta E_p$ values, although small, are not zero. In addition, the formal potentials for the immobilized species follow closely those of the dissolved analogs. This indicates that immobilization does not significantly alter electronic differences between the oxidized and reduced forms, which dictates the formal potential. This also has the important consequence of bringing an element of predictability which can be (and has been) exploited in electrocatalytic applications.

The stability of these electrodes is important, especially with regards to electrocatalytic applications. Stability can be dictated by a number of aspects including the inherent stability (instability) of the oxidized and reduced forms of the couple, stability of the surface linkage and others. In the case of immobilized ferrocenes it is found that such electrodes can be stored indefinitely in air or solvents. However, the electrochemical response decays when the electrode is cycled between oxidation states (ferrocene/ferricenium).

Lenhard and Murray [102] performed a very extensive study and determined that the instability of the ferricenium was responsible for the decay and that, analogous to solution studies, it followed second order kinetics. In addition, this asserted the stability of the surface bond. For immobilized bipyridine complexes of ruthenium [104] and nitroaromatics, it was found that their stability in the reduced state was largely decreased, relative to their behavior in solution.

Analogous behavior was obtained by Wrighton for electrodes modified with his series of hydrolytically unstable silanes.

### *(b) Modification of carbon electrodes*

Given the immense literature of organic synthesis, the modification of carbon surfaces represents a most logical step. Although carbon is available in a wide range of forms, most electrode modification studies have focused on pyrolytic graphite and glassy carbon, with carbon paste electrodes receiving some attention. In order to understand reactivity patterns at carbon electrodes, one must first of all recognize the differences between the edge and basal planes. The basal planes of carbon represent the infinite sheets that we tend to associate with graphite. Such a continuous surface has a very low density (in principle none) of ionic sites and a high $\pi$-electron density. Thus molecules with large aromatic sections can interact very strongly and give rise to the strong chemisorptive bonding that was discussed previously.

Termination of the lattice dictates that dangling bonds (or surface states) will be present. These are chemical states and are generally thought to be oxygenated functionalities such as alcohols (phenols), carboxylic acids, ketones (quinones) and anhydrides. At this surface, termed the edge plane, all of the chemical reactivity is focused. Thus, the modification of carbon electrodes has been largely based on the manipulation of these surface groups. In addition, many "activation" procedures have been employed (e.g. heating at 500 ° C) in order to increase the density of such sites.

Comparisons are very difficult due to the lack of reproducibility as well as the very rough nature of these surfaces and so these are generally qualitative (semiquantitative at best). Recently, Kuwana and co-workers [134] have expended a great deal of effort in unraveling some of these complexities.

A number of approaches have been employed in the modification of carbon surfaces by exploiting the known chemistry of the groups that are known to be present on the edge plane. One of the most successful has been the generation of acid chloride groups by reaction of the electrode with thionyl chloride. Subsequent treatment with an aminosubstituted species gives rise to covalent bonding via amide bond formation. The first example of this was Miller's chiral electrode [11]. In addition, a wide range of metalloporphyrins based on tetra-(4-amino phenyl)porphyrin (Fig. 11) have been immobilized in this fashion. These include the free base as well as the Fe, Co, Cu, Zn, Ni and Mg metalloderivatives [135–138]. Various ferrocenes [139] and ruthenium complexes ($[NH_2\text{-py-Ru}(NH_3)_5]^{2+}$ [140] and

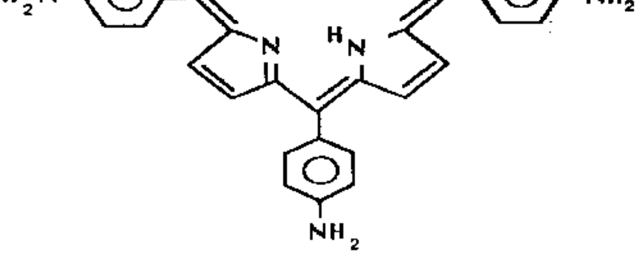

Fig. 11. Structure of tetra(4-aminophenyl)-porphyrin employed in the modification of carbon electrodes activated with thionyl chloride.

-PyRu(EDTA) [141]) have also been incorporated. In general, however, coverages obtained were low (monolayer or less).

Kuwana [142–145] introduced an approach based on the reactivity of cyanuric chloride (Fig. 12) with surface hydroxy groups. With this approach he was able to incorporate hydroxymethyl ferrocene [142,143], a viologen (methyl, aminopropyl viologen [144]) as well as a phenylene diamine [145]. Fox employed this procedure for the incorporation of quinones [146] and Yacynych for immobilizing glucose oxidase [147]. Although this is clearly a very versatile reagent, its use has not been as widespread as one would have anticipated.

Mazur et al. [148] introduced the concept of employing "oxide free" carbon (generated by plasma etching) to exploit the reactivity of the freshly exposed surface. This procedure was later modified by Anson and co-workers [149] who reacted the surface with various amines and subsequently attached various redox couples via amide bond formation.

An intriguing way of modifying carbon was discovered by Umaña [150] who termed it the "abrasion experiment" where a glassy carbon electrode is abraded on emery paper in a pool of a reactant containing a vinyl group (e.g. vinylpyridine and vinylferrocene). This operation is carried out inside a dry box, and gives rise to modification of the surface, presumably via free-radical polymerization.

Carbon paste electrodes present a rather different medium for modification [151–159]. In this case, the material of interest is often mixed with the pasting material, so that the use of the term immobilization is not always applicable. There are, however, well documented cases of true immobilization. The biggest advantage of this approach is the ready regeneration of the electrode. A number of applications of this approach have appeared including electrocatalysis [155a,156] and electroanalysis [155b,157–159] (vide infra). It is my belief that the use of carbon paste modified electrodes will, in the future, find widespread analytical use.

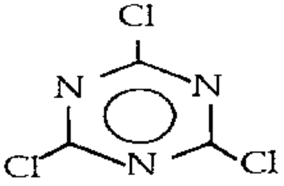

Fig. 12. Structure of cyanuric chloride employed in the modification of carbon surfaces by reaction with surface –OH groups.

### *(iii) Modification with polymer films*

Although the early work on chemically modified electrodes centered on materials at about monolayer coverages, most of the recent effort has been centered on polymers. This is partly due to the fact that the signals obtained at electrodes modified with polymer films are greatly amplified over those at monolayer coverages, thus making their measurement much easier. For catalytic applications polymer films are expected to exhibit higher stability. In addition there were theoretical predictions [160] that pointed to the advantages of polymer films (vs. monolayers) in electrocatalytic applications. In addition their use opened the way for the preparation of deliberately structured interfaces. Furthermore, many of the methods employed in the modification step can be very simple and include dip coating, spin coating, electropolymerization and others.

Many approaches to the preparation of electroactive polymer films have appeared. These can be subdivided into two main categories depending on how the redox active species is immobilized. If the redox center is part of the polymer backbone it is termed a redox polymer. The second group is termed ion-exchange polymers and in this case the redox active component is a counterion to a poly-ionic (anionic or cationic) film.

Because of the typically larger coverages involved, the electrochemical response of polymer films can be greatly complicated by the interplay of charge transfer and transport, polymer film motions, solvent swelling and others. As a result, the voltammetric responses obtained are much more difficult to interpret and in fact, a great deal of effort has been focused on the unraveling of these processes [34–83].

The preparation of electrodes modified with redox polymers can be achieved in a number of ways. One can employ a pre-formed polymer containing the redox center, or the redox center can be coupled to a previously prepared polymer (e.g. by ligand substitution). They can also be generated in situ by the electroinitiated polymerization of redox active monomers.

Ion exchange polymers depend on the incorporation of redox species by serving as charge compensating ions. These materials can be prepared by placing an electrode modified with the polymeric ion-exchange material in a solution of the redox ion whereby the polymer extracts the redox ions from solution. Alternatively, the ion-exchange polymer can be deposited with the charge compensating redox ion already incorporated. Experiments by Anson [161] have demonstrated that the latter approach gives rise to better behaved films.

### (a) Redox polymers

*Adsorbed films.* The preparation of redox polymers is by no means a new area. For example Cassidy's book [162] (published in 1965) entitled "Oxidation-Reduction Polymers (Redox Polymers)" clearly expresses the existence of such materials. However, these were largely based on organic redox species such as quinones in addition to ferrocenes. This early work focused on the synthesis and characterization of redox polymers, but they were not employed as materials with which to modify the surface of an electrode.

The first reports of electrodes modified with redox polymers were by Miller's group [43,163] who prepared polymers containing aromatic nitro groups, quinones and other redox active components. All of these were bulk polymers and were therefore purified and characterized prior to use. They were generally deposited on to graphite electrodes either by adsorption or droplet evaporation. In some cases the stability of the films was enhanced by a brief thermal treatment that apparently increased the degree of crosslinking. The redox behavior of these polymers was obtained and a wide range of responses (depending on coverage, crosslinking, etc.) were obtained. Since the emphasis of this review is on coordination compounds, these materials will not be discussed to any greater extent. However, they are mentioned because they were the first family of well-characterized redox polymers.

Perhaps the first electrochemical study of a redox polymer containing a transition metal was by Oyama and Anson [164a] who employed pyrolytic graphite electrodes coated with polyvinylpyridine or polyacrylonitrile and

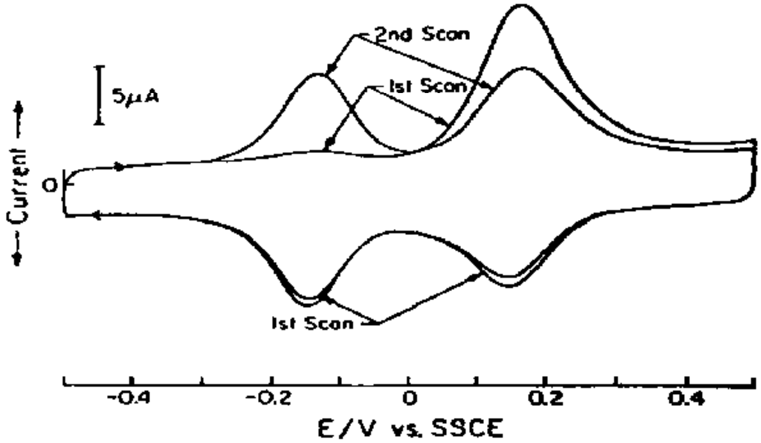

Fig. 13. Cyclic voltammograms for a pvp electrode containing $[(Py)_2Ru(EDTA)^{II}]$ depicting the loss of one coordinated pyridine. (From ref. 164b with permission of the American Chemical Society.)
]

made use of the coordinative properties of the pyridine and nitrile groups to incorporate ~PyRu(EDTA), ~CNRu(EDTA), ~PyRu$(NH_3)_5$ and ~CNRu$(NH_3)_5$ (~Py and ~CN refer to polymer bound pyridine and nitrile groups, respectively). After the initial observation that such ligand exchange reactions could be performed, they carried out a series of experiments where the coordination chemistry of the immobilized complexes was probed [164b]. Particular emphasis was placed on the Ru(EDTA) complex coordinated to a pvp modified electrode. First of all, the observed electrochemical response was a function of the oxidation state of the ruthenium present in solution from which incorporation took place. Using [Ru(III)(EDTA)], a well developed wave for ~PyRu(III)EDTA could be observed at an $E^{0\prime}$ value of ca. −0.15 V. However, when the solution contained Ru(II)EDTA, waves for both ~PyRu(EDTA) and ~$Py_2$Ru(EDTA) could be observed. The fact that at $Ru^{II}$ two pyridines whereas at $Ru^{III}$ only one could coordinate, is in excellent concurrence with the higher degree of $\pi$-backbonding present in Ru(II). More dramatic was the ability to take an electrode modified with ~$Py_2$Ru(EDTA) and observe the loss (reversible) of a coordinated pyridine upon oxidation to $Ru^{III}$ (Fig. 13). Spectroelectrochemical experiments were also performed in order to follow the dissociation kinetics [165].

Anson's group was also able to prepare electrodes where two different redox centers are coordinated to the same surface ligand and where the same complex is coordinated to two surface ligands [164b]. More recently his group prepared a copolymer containing pyrrolidone and iron porphyrin groups and applied the same to the reduction of $O_2$ [166]. The advantages of this system were that whereas the polymer was insoluble in aqueous solutions, the hydrophilic character of the pyrrolidone groups gave rise to good swelling characteristics. Although electrocatalytic activity was observed, it was not very long lived.

Meyer's group at North Carolina has applied its extensive synthetic expertise to the preparation of a wide range of polymeric materials containing complexes of Ru, Os, Re and other transition metals. The early work focused on complexes coordinated to pvp (polyvinylpyridine). An especially well characterized series of polymers was based on the reaction of $[Ru(terpy)(bpy)(H_2O)]^{2+}$ (terpy is 2,2′:6′2″-terpyridine) with pvp to give rise to $[Ru(terpy)(bpy)(py)]^{2+}$ where the total loading of metal was varied systematically [167]. At low loadings, the spectral features of the polymer were essentially identical to those of the monomer. However, at the higher loadings, significant changes were observed, indicating interactions between the chromophores along the polymer chain. They were also able to incorporate $[\sim PyRu(bpy)_2(H_2O)]^{2+}$ [168] and exploit its oxidative electrocatalytic activity. Although the stability of the system was not high, catalytic turnovers were clearly established. In addition they noted that at pH values below the $pK_b$ of the pyridine groups in pvp, the film's pH remained invariant with changes in the solution pH. This effect was termed pH encapsulation [168].

Meyer's group also developed an especially clever way of incorporating a redox site by electrochemically generating an open coordination site on a metal complex. If this is done in a non-coordinating solvent ($CH_2Cl_2$) at an electrode coated with pvp, then the metal complex can bind to a pyridine site. This was elegantly demonstrated by using a variety of Os and Re chloro complexes which upon reduction undergo chloride ion loss. The complex is coordinated by a surface pyridine group which in essence "captures" the metal complex [169] (Fig. 14).

Meyer and Ellis [170] devised a very general approach for the incorporation of metal complexes into pre-formed polymers based on the chemical reactivity of *p*-chlorosulfonated polystyrene [170] towards amino, hydroxy and carboxylate groups to give rise to sulfonamide, sulfonester and sulfonanhydride linkages, respectively. Thus, by employing metal complexes that bear one of the aforementioned substituents on the periphery of one of the ligands, a large number of metal complexes can be immobilized. Since

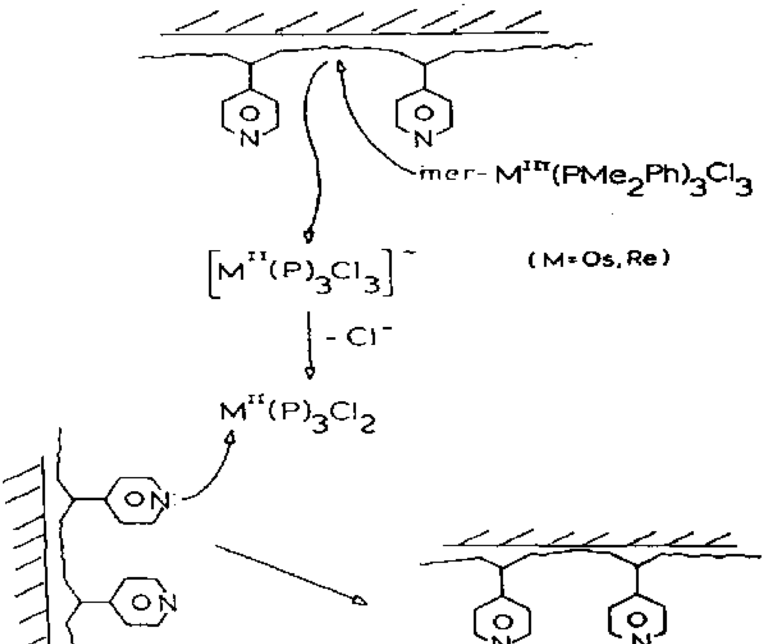

Fig. 14. Schematic depiction of coordination of transition metal complexes of Os and Re to a pvp coated electrode via electrochemically induced chloride loss. (From ref. 169 with permission of the American Chemical Society).

TABLE 1

Complexes immobilized by sulfonamide formation

| Redox couple | $E^{0\prime}$ soln (V) [a] | $E^{0\prime}$ surf (V) [a] |
|---|---|---|
| $(bpy)_2Ru(5\text{-}phenNH_2)^{2+}$ | +1.31 | +1.28 |
| $(bpy)Ru(5\text{-}phenNH_2)_2^{2+}$ | +1.39 | +1.37 |
| $Ru(5\text{-}phenNH_2)_3^{2+}$ | | +1.53 |
| $(bpy)_2Ru(4\text{-}pyNH_2)_2^{2+}$ | +0.99 | +1.14 |
| $(bpy)_2Ru(3\text{-}pyNH_2)_2^{2+}$ | +1.18 | +1.32 |
| $(bpy)_2Ru(4\text{-}pyOH)_2^{2+}$ | +1.18 | +1.20 |
| $(bpy)_2Ru(3\text{-}pyOH)_2^{2+}$ | +1.24 | +1.25 |
| $(bpy)_2Ru[4,4'\text{-}bpy(COOH)_2]^{2+}$ | +1.28 | +1.25 |
| $(bpy)_2Ru(4\text{-}pyCOOH)Cl^{+}$ | +0.75 | +0.74 |
| $(NH_3)_5Ru(4\text{-}pyNH_2)^{2+}$ | +0.12 | −0.18 |
| $Fe(5\text{-}phenNH_2)_3^{2+}$ | | +1.23 |
| $Fe(5\text{-}phenNH_2)_2(CN)_2$ | +0.40 | +0.32 |
| $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{-}4\text{-}C_6H_4NH_2)$ | +0.31 | +0.36 |
| $(5\text{-}phenNH_2)_2Os(dppm)^{2+}$ | | +1.37 |
| $[Ni\{(NH_2Ethi)_2Me_2[16]tetraeneN_4\}]^{2+}$ | +1.16 | +1.13 |
| $H_2N\text{-}4\text{-}C_6H_4N(CH_3)_2$(DMPD) | +0.78 | +0.55 |
| | +0.15 | |
| Nickel tetrakis(*o*-aminophenyl)porphyrin | −1.24 | −1.32 |
| | −1.74 | −1.83 |

[a] Volts vs. Ssce in 0.1 M $(E_t)_4NClO_4/CH_3CN$.

the sulfonamide linkage is the most stable, the incorporation of amino-bearing species has been emphasized. Redox centers incorporated include a wide range of polypyridine complexes of ruthenium, iron and osmium, aminoferrocene, nickeltetraaza macrocycles and others (Table 1). This approach has been employed in various applications including bilayer electrodes [170], photoactive assemblies [171], luminescent polymers [170] and others [172].

Vos and Haas [173–176] have prepared electrodes modified with $[\sim PyRu(bpy)_2Cl]^+$ [173–175] and $[\sim Im\text{-}Ru(bpy)_2Cl]^+$ [176] (~Im represents a polymer bound imidazole from poly n-vinyl imidazole). These electrodes showed very well behaved electrochemical responses but more important was their photochemical behavior. Upon irradiation, a photosubstitution would take place with the final product being strongly dependent on the solvent and the presence of other ligands (Fig. 15). The presence of isopotential points (these are the electrochemical equivalent of isosbestic points in spectroscopy) indicates a simple reaction sequence. Such reactivity is unusual in that one would anticipate rapid quenching of the excited state by the electrode. Perhaps most of the redox centers are sufficiently removed from the electrode so that the quenching is not effective. These results are in

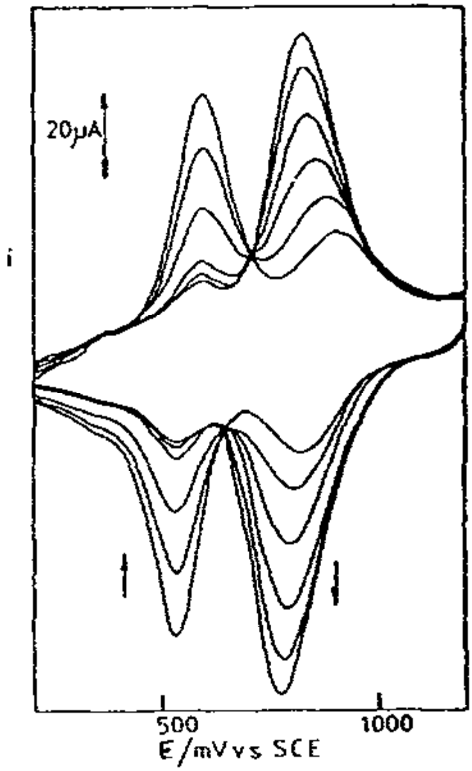

Fig. 15. Cyclic voltammograms for a $[\sim\text{ImRu(bpy)}_2\text{Cl}]^+$ modified electrode during photolysis in 1 M $HClO_4$. (From ref. 176, with permission.)

contrast to those of Abruña, Murray and Meyer on a similar system [104] where no photoactivity was noticed. However, in the latter case, the coverage was near monolayer so that quenching could have been much more effective. In addition to the systems mentioned here, there is a very extensive literature on polymer bound transition metal complexes for catalytic applications. Although many systems have been prepared and investigated, very few have been electrochemically characterized. This is clearly an area that awaits further study and development.

*Electropolymerization.* Electropolymerization of redox active monomers represents one of the most versatile ways to modify the surface of an electrode. The process is generally applicable to a broad range of electrode materials including metals, semiconductors, carbon, conducting metal oxides and others. In addition, the coverage can be exquisitely and reproducibly controlled through the polymerization conditions.

Perhaps the best characterized and most extensive family of compounds in this regard are the vinylpyridine, vinylbipyridine (and related compounds),

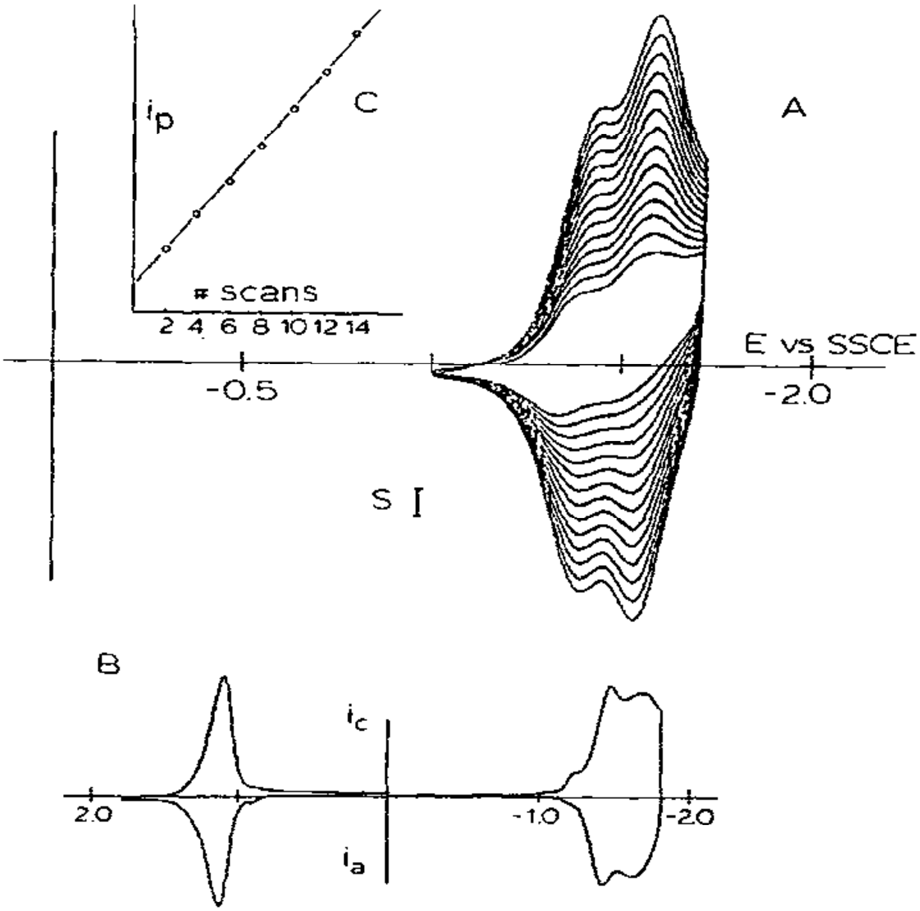

Fig. 16. Cyclic voltammograms for $[Ru(v\text{-}bpy)_3]^{2+}$ depicting electropolymerization (A). A cyclic voltammogram of the modified electrode in a solution of supporting electrolyte only (B) and the linear correlation between growth and number of scans (C). (From ref. 56 and with permission of the American Chemical Society.)

complexes of ruthenium, osmium and iron first reported by Abruña, Murray and Meyer [22]. These materials undergo electroreductively initiated polymerization to give rise to electrodes coated with extremely adherent, electrochemically active films of the parent monomer (Fig. 16). A wide variety of synthetic variations are possible and numerous monomers can be copolymerized to give rise to electrodes with multiple redox states.

The process was believed to be due, in part, to the fact that the reduction processes are ligand localized and in addition there is a significant degree of $\pi$-backbonding, thus localizing a significant amount of charge on the ligands. This charge redistribution was then believed to be responsible for the polymerization, especially in light of the fact that vinylpyridine undergoes anionic polymerization. However, extensive studies by Murray and Meyer [177] indicate that the dominant mechanism involves radical coupling through the ligands. Thus the picture that emerges from these studies is that the polymers are not metallated polyvinylpyridines, but rather ligand bridged extended structures.

Most recently Guarr and Anson [178] elegantly corroborated the importance of this pathway by examining the behavior of $[Ru(P)_2(v\text{-}bpy)]^{2+}$ (p = phenanthroline derivative) complexes. They found that although polymerization was initiated at the vinyl group, there was a very extensive degree of coupling through the 4 and 7 positions of the phenanthroline ligands. In fact, they were able to isolate an ESR-active species that was identified as a ligand based free radical.

A truly vast number of complexes have been synthesized and electropolymerized following this approach and these are presented in Table 2. As a rule, all of these materials give rise to exceptionally stable deposits with well behaved responses and very uniform coverage. Virtually pin-hole free films can be obtained for layers as thin as 20 Å [179].

Polymeric films of these complexes have been employed by Murray and co-workers to probe a wide range of processes including transport phenomena [180,183–185], electrocatalysis [181,182,186–189], redox conduction [25,187], photoactive interfaces [190] and others [191]. In addition, a number of interesting applications have also emerged including bilayer electrodes [22,23,192], electronic-type devices [188] and others. Calvert and co-workers also prepared numerous electropolymerizable complexes derived from pyridineacetylene [193].

Recently we were able to prepare and characterize a large series of vinylterpyridine complexes of ruthenium, iron and cobalt [194a]. Again, these materials undergo the predicted electropolymerization to give rise to well behaved films of the corresponding monomer. In the case of cobalt, novel chemical pathways (especially ligand substitution) not exhibited by the corresponding solution species were found [194b].

Ellis and Meyer [195] have found that aminophenanthroline complexes of a wide range of metal ions will undergo electrooxidatively initiated polymerization to give again electrochemically well behaved films. As with the previous approach, this method offers great latitude in terms of the synthetic variations. The polymerization is probably analogous to that of aniline. This approach was extended by Spiro and co-workers to a variety of aminoporphyrins [196,197].

Deronzier and co-workers [198] and Parker [199] prepared a series of complexes of pyrrole substituted pyridines and bipyridines. By taking advantage of the oxidative electropolymerization ability of the pyrrole residue, they were able to deposit a number of metal complexes. There have also

TABLE 2

Complexes immobilized by electropolymerization of vinyl containing ligands

| Complex | Soln [a] | | | Polymer films [a] | | |
|---|---|---|---|---|---|---|
| | $E^{0\prime}$ox | $E^{0\prime}$red(1) | $E^{0\prime}$red(2) | $E^{0\prime}$ox | $E^{0\prime}$red(1) | $E^{0\prime}$red(2) |
| $[\mathrm{Ru(bpy)_2(vpy)_2}]^{2+}$ | 1.24 | −1.35 | −1.55 | 1.22 | −1.36 | −1.52 |
| $[\mathrm{Ru(bpy)_2(vpy)Cl}]^{+}$ | 0.76 | −1.49 | −1.74 | 0.76 | −1.48 | – |
| $[\mathrm{Ru(bpy)_2(vpy)NO_2}]^{+}$ | 1.03 | −1.45 | −1.69 | 1.03 | | |
| $[\mathrm{Ru(bpy)_2(vpy)NO_3}]^{+}$ | 0.96 | – | – | 0.91 | – | – |
| $[\mathrm{Ru(bpy)_2(vpy)NO}]^{3+}$ | 0.53 | – | – | 0.47 | – | – |
| $[\mathrm{Ru(vbpy)_3}]^{2+}$ | 1.16 | −1.43 | −1.54 | 1.16 | −1.43 | −1.54 |
| $[\mathrm{Fe(vbpy)_3}]^{2+}$ | 0.93 | −1.42 | −1.58 | 0.93 | −1.44 | −1.57 |
| $[\mathrm{Ru(vbpy)_2Cl_2}]$ | 0.30 | – | – | 0.36 | – | – |
| $[\mathrm{Ru(vbpy)_2(MeCN)vpy}]^{2+}$ | 1.36 | – | – | 1.29 | – | – |
| $[\mathrm{Ru(vbpy)_2(MeCN)_2}]^{2+}$ | 1.41 | – | – | 1.35 | – | – |
| $[\mathrm{Ru(trpy)(bpy)(vpy)}]^{2+}$ | 1.21 | −1.26 | −1.59 | 1.20 | | |
| $[\mathrm{Ru(trpy)(bpy)(BPE)}]^{2+}$ | 1.21 | −1.26 | −1.58 | 1.20 | | |
| $[\mathrm{Ru(trpy)(bpy)(4'\text{-}Cl\text{-}stilb)}]^{2+}$ | 1.21 | −1.35 | −1.55 | 1.20 | | |
| $[\mathrm{Os(bpy)_2(vpy)Cl}]^{+}$ | 0.36 | −1.46 | | 1.35 | | |
| $[\mathrm{Os(bpy)_2(BPE)Cl}]^{+}$ | 0.33 | −1.50 | | 0.33 | | |
| $[\mathrm{Ru(bpy)_2(vpy)_2}]^{2+}$ | 1.25 | −1.36 | −1.54 | 1.22 | | |
| $[\mathrm{Os(bpy)_2(vpy)_2}]^{2+}$ | 0.77 | −1.33 | −1.53 | 1.74 | | |
| $[\mathrm{Ru(bpy)_2(BPE)_2}]^{2+}$ | 1.30 | −1.35 | −1.53 | 1.23 | | |
| $[\mathrm{Ru(bpy)_2(stilb)_2}]^{2+}$ | 1.23 | −1.36 | −1.54 | 1.22 | | |
| $[\mathrm{Ru(bpy)_2(4'\text{-}Cl\text{-}stilb)_2}]^{2+}$ | 1.22 | −1.38 | −1.54 | 1.24 | | |
| $[\mathrm{Ru(bpy)_2(4'\text{-}OMe\text{-}stilb)_2}]^{2+}$ | 1.19 | −1.39 | −1.59 | 1.25 | | |
| $[\mathrm{Ru(bpy)_2(4'\text{-}CN\text{-}stilb)_2}]^{2+}$ | 1.25 | −1.40 | −1.64 | 1.23 | | |
| $[\mathrm{Ru(bpy)_2(p\text{-}cinn)_2}]^{2+}$ | 1.19 | −1.39 | −1.70 | 1.20 | | |
| $[\mathrm{Os(bpy)_2(p\text{-}cinn)_2}]^{2+}$ | 0.74 | −1.36 | −1.65 | 0.72 | | |
| $[\mathrm{Ru(bpy)_2(m\text{-}cinn)}]^{2+}$ | 1.28 | −1.38 | −1.63 | 1.27 | | |
| $[\mathrm{Ru(bpy)_2(p\text{-}CH_2\text{-}cinn)_2}]^{2+}$ | 1.26 | −1.39 | −1.61 | | | |
| $[\mathrm{Ru(bpy)_2(p\text{-}fum)_2}]^{2+}$ | 1.22 | −1.40 | −1.71 | 1.20 | | |
| $[\mathrm{Ru(bpy)_2(\mathit{N}\text{-}Me\text{-}py)_2}]^{4+}$ | 1.22 | −1.39 | −1.65 | 1.19 | | |
| $[\mathrm{Ru(phen)_2(vpy)_2}]^{2+}$ | 1.25 | −1.37 | −1.51 | 1.24 | | |
| $[\mathrm{Ru(trpy)(stilb)_2Cl}]^{+}$ | 0.77 | −1.38 | −1.74 [b] | 0.78 | | |
| $[\mathrm{Ru(i\text{-}Pr\text{-}bpy)_2(p\text{-}cinn)_2}]^{2+}$ | 1.46 | −0.96 | −1.16 | | | |
| $[\mathrm{Ru(trpy)(vpy)_3}]^{2+}$ | 1.23 | −1.24 | −1.76 [b] | 1.22 | | |
| $[\mathrm{Ru(trpy)(BPE)_3}]^{2+}$ | 1.23 | −1.26 | −1.54 [b] | 1.30 | | |
| $[\mathrm{Ru(trpy)(stilb)_3}]^{2+}$ | 1.20 | −1.25 | −1.68 [b] | 1.23 | | |
| $[\mathrm{Ru(trpy)(4'\text{-}Cl\text{-}stilb)_3}]^{2+}$ | 1.20 | −1.25 | −1.60 [b] | 1.22 | | |
| $[\mathrm{Ru(HC(pz)_3(vpy)_3)}]^{2+}$ | 1.17 | −1.58 | | 1.16 | | |
| $[\mathrm{Ru(\overset{*}{py}\text{-}py\text{-}py)_2}]^{2+}$ | 1.25 | −1.22 | −1.44 | 1.22 | −1.24 | −1.47 |
| $[\mathrm{Ru(py\text{-}\overset{*}{py}\text{-}py)(tpy)}]^{2+}$ | 1.27 | −1.22 | −1.47 | 1.24 | −1.23 | −1.44 |
| $[\mathrm{Ru(py\text{-}\overset{*}{py}\text{-}py)_2}]^{2+}$ | 1.24 | −1.22 | −1.43 | 1.21 | −1.24 | −1.46 |
| $[\mathrm{Co(py\text{-}\overset{*}{py}\text{-}py)_2}]^{2+}$ | 0.27 | −0.75 | −1.60 | 0.20 | −0.80 | −1.64 |

[a] Values vs. Ssce in 0.1 M $(\mathrm{E_t})_4\mathrm{NClO_4/CH_3CN}$.

[b] Irreversible reduction, $E_{\mathrm{p,c}}$ value

Abbreviations: vpy = 4-vinylpyridine, vbpy = 4-vinyl-4′-methyl-2,2′-bipyridine, BPE = bis-pyridine-ethylene; stilb = stilbazole, p-cinn = pyridyl cinnamide; p-fum = pyridyl fummaride; * denotes location of vinyl group in vinylterpyridine.

been reports of other electropolymerization procedures including that of an acylnickel derivative [200], cobalt tetraazaannulenes [201], and Schiff base complexes [202].

### *(b) Ion exchange polymers*

*Cationic polymers.* As mentioned previously this method of electrode modification is based on the principles of ion exchange for the incorporation of redox species. This very versatile approach was introduced in 1980 by the now classic papers of Oyama and Anson [18] where they termed the procedure "electrostatic binding". It essentially involves the incorporation of redox active counterions to an electrode modified with a polyionic film. The early work was focused on the use of protonated polyvinylpyridine [18a] and deprotonated polyacrylic acid [18b]. In the former case, polyanionic redox couples such as $Fe(CN)_6^{3-/4-}$, $IrCl_6^{2-/3-}$ were incorporated up to coverages of ca. $10^{-7}$ mol $cm^{-2}$. It was noted early on, however, that factors other than charge control the degree of incorporation. For example, exposure of a pvp modified electrode to a 5 mM solution of $Fe(CN)_6^{3-}$ and $IrCl_6^{2-}$ results in greater binding of the latter [18a]. In addition, $Fe(CN)_6^{3-}$ exhibits a larger partition coefficient than the more highly charged $Fe(CN)_6^{4-}$. Thus, there are clearly numerous aspects involved in the partitioning process. In the case of deprotonated polyacrylic acid (a polyanion) $Ru(NH_3)_6^{3+/2+}$ was incorporated, again with high coverage [18b].

In the examples mentioned above, once the electrodes were modified, they could be placed in a solution containing only supporting electrolyte and a very persistent electrochemical response could be obtained. However, since the partitioning is a reversible process, the redox ions would slowly leach away. Nonetheless, a very persistent response could be obtained when very small (micromolar) concentrations of the redox ions were present, pointing to the large partition coefficients involved.

This approach to electrode modification was extremely attractive due to its simplicity and broad scope. After Anson's early reports, great emphasis was placed on this mode of immobilization. This was especially true for multi-anionically charged redox ions such as $Fe(CN)_6^{3-/4-}$, $IrCl_6^{2-/3-}$, $Mo(CN)_8^{3-/4-}$, $Ru(CN)_6^{3-/4-}$ and $Co(CN)_6^{3-/4-}$ which were incorporated into a variety of polycationic films including quaternized polyvinylpyridine [20,54,57,58,203,204,207], polymeric viologens [63,119,122,123,205] and others [206–208].

One of the problems that is commonly encountered with these materials is the small apparent diffusion coefficients. (Typically smaller than $10^{-10}$ $cm^2$ $s^{-1}$). This has been ascribed to various effects including poor swelling of the polymer film by the solvent, the crosslinking effect that multiply charged anions have and others.

Since electrocatalytic applications (which represent one of the biggest attractions of chemically modified electrode research) require rapid rates of charge propagation, investigators have focused on the development of polymers with open structures in order to accelerate charge transport. Perhaps the most successful of these has been the use of poly-l-lysine first reported by Anson [64]. This material exhibits exceptional swelling in aqueous media (by as much as a factor of 100) so as to give rise to a polymer with a very open structure and large pools of solvent. This material thus allows for the electrostatic binding of redox anions and allows very rapid rates of exchange. In fact, some of the largest reported values of apparent diffusion coefficients have been in poly-l-lysine. Anson and co-workers have carried out extensive studies on the transport properties of redox couples incorporated into this material [65,209].

Very recently Anson presented a very thorough study on the electrochemical response of $Fe(CN)_6^{4-/3-}$ incorporated into protonated random and block copolymers containing varying ratios of styrene and *p*-(diethylaminomethyl)styrene [210]. With ratios of styrene to *p*-(diethylaminomethyl)styrene groups of up to 2 : 1 the electrochemical responses observed for $Fe(CN)_6^{3-/4-}$ electrostatically bound to coatings prepared from random and block copolymers of the same composition are dramatically different. For block copolymers, large quantities of material can be incorporated, the electrochemical response is very well defined and the kinetics of charge transport appear to be significantly rapid. The random copolymers, on the other hand, could not incorporate nearly as many redox ions and in addition exhibited very low rates of charge propagation. This again points to the critical importance of the polymer structure.

In addition to the materials mentioned, there have been numerous other polycationic polymers employed. In general, the redox systems studied have been the multianionic species such as $Fe(CN)_6^{4-}$, $IrCl_6^{3-}$ and $Mo(CN)_8^{4-}$ and related materials [208,211].

*Anionic polymers.* In terms of anionically charged polymers, one of the earliest to be employed was polystyrene sulfonate. Numerous cationic redox species such as $[Ru(bpy)_3]^{2+}$, $[Co(bpy)_3]^{3+}$ and related materials have been studied [83,212]. Similarly, Meyer and co-workers have recently employed partially hydrolyzed *p*-chlorosulfonated polystyrene to incorporate a number of redox species, most of them involving polypyridine complexes of ruthenium and osmium [213,214]. They have employed such films in a number of electrocatalytic applications including water [213] and chloride oxidation [214].

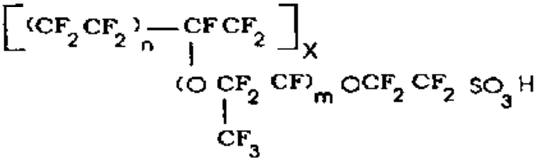

Fig. 17. Structure of Nafion.

Perhaps the most widely used anionic polymeric material for modifying electrode surfaces has been the perfluoro sulfonate material Nafion [215] (Fig. 17). By virtue of the sulfonate side chain, Nafion is a cation exchanger; however its properties are significantly different from those of conventional sulfonate resins (based on divinyl benzene/styrene sulfonate). In conventional sulfonate resins, the ion selectivity properties are dictated by the interrelated effects of ion exchange capacity, degree of crosslinking and water sorption. Nafion, however, has ostensibly no crosslinking, the density of exchange sites is significantly lower than that of typical sulfonate resins and the fluorocarbon backbone provides a highly hydrophobic environment. Its non-crosslinked nature makes its solvent swelling characteristics very dependent on the nature of the counterion present (and its solvation properties) and pretreatment. In addition, there is mounting evidence that Nafion exists in segregated phases or domains with hydrophobic (fluorocarbon) and hydrophilic (with clusters of sulfonate sites) domains being connected by an interfacial region [216]. Nafion also exhibits exceptional affinity for hydrophobic cations. Martin and co-workers [217] have performed extensive studies of selectivity coefficients and report values as large as $10^6$ (relative to sodium).

Although Nafion is available in a variety of forms, it is the soluble form that has found the most widespread use for electrode modification. Martin and co-workers have also reported on a procedure for preparing soluble Nafion from the solid membrane material [218].

Nafion has been extensively employed in numerous studies especially by the groups of Anson [61,66,219–227], Bard [19,68,69,81,82,228–233] and Martin [217,218,234–237]. A variety of redox cations have been incorporated into Nafion including $[Ru(bpy)_3]^{2+}$, $[Fe(bpy)_3]^{2+}$, $[Os(bpy)_3]^{2+}$, $[Ru(NH_3)_6]^{3+}$, methylviologen, $[Co(bpy)_3]^{2+}$, $[Co(terpy)_2]^{2+}$ and others. Many of the studies have been geared to understanding the details of the charge transport and propagation mechanisms. Anson has also employed these systems for the electrocatalysis of $O_2$ reduction [220–222]. Bard has focused on the study of charge transport mechanisms in Nafion [81,82,238]. He has also performed electrochemical/ESR studies of redox species in Nafion [231,232] in addition to using them for catalytic applications [229,230]. Martin and co-workers have carried out extensive studies aimed at the understanding of the ion selectivity properties of Nafion films as well as the micro-environments mentioned previously.

One of the problems with Nafion is that materials that are retained in the hydrophobic domains exhibit very sluggish transport rates. This can have very deleterious effects in an electrocatalytic cycle if the active component resides mainly in the hydrophobic domain. In order to remedy this situation, Buttry and Anson [221,222] have developed systems where an active catalyst is employed in conjunction with a material that will remain largely in the hydrophilic phase and thus serve as an electron shuttle between the electrocatalyst and the electrode. In addition, Redepenning and Anson [238] have recently reported on the effects of pH and electrolyte concentration on the formal potentials of species incorporated into Nafion layers due to Donnan potential effects.

Lewis and co-workers [239] have examined the kinetics and mechanisms of substitution reactions for $[Ru(NH_3)_5(OH_2)]^{2+}$ with various ligands when the complex is incorporated into a Nafion film. Significant differences in behavior were observed when compared to the behavior in solution (Section E).

### *(iv) Other methods of electrode modification*

There are a number of other methods that do not fit into any of the previously mentioned categories and these are considered here.

The first has to do with precipitated films of polynuclear transition metal cyanides of general formula $M_k^A[M^B(CN)_6]_l$ [240]. Of these, prussian blue (iron(III) hexacyanoferrate(II)) is the prototypical example. It is a highly insoluble polymeric inorganic material whose intense color has been known for 250 years. Prussian blue (PB) can be both oxidized and reduced to give Everitt's salt and Berlin green, respectively. The deposition of PB on to conducting substrates was first described by Neff [241] who in addition showed that such films could be electrochemically oxidized. A typical cyclic voltammogram for a gold wire coated with a PB film is shown in Fig. 18. The most extensive studies on PB have been by Itaya, Uchida and Neff [240] who in addition have studied ruthenium purple (ferric ruthenocyanide) and osmium purple (ferric osmocyanide).

Bocarsly and co-workers [242–248] introduced a very elegant method for preparing films of nickel hexacyanoferrate by the dissolution of nickel in the presence of ferricyanide ions. They have performed extensive studies of this system including electrochemical characterization and transport studies [242,243], reflectance studies [245], and others. In addition they have studied the dependence of growth on the crystallographic orientation [248]. There is a very interesting counterion (cation) effect in the redox response of these

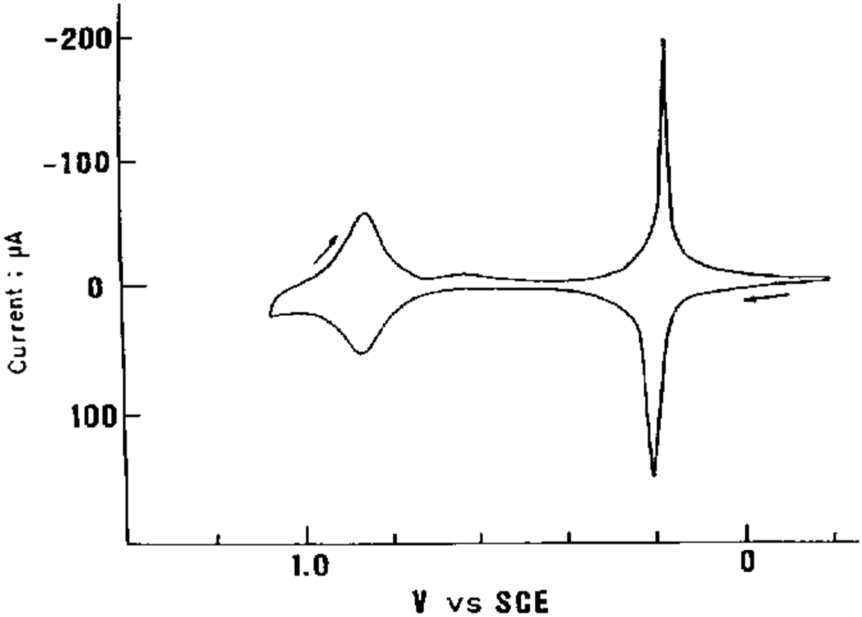

Fig. 18. Cyclic voltammogram for a Prussian blue modified gold electrode. (From ref. 240, with permission of the American Chemical Society.)

films which has been ascribed to the ease of penetration of the ions into the lattice as charge compensating counterions during redox transformation [243].

Finally there have been numerous applications of these films including display devices, electrocatalysis and others [249–255].

Majda [256–258] and co-workers have prepared porous alumina films of controlled porosity and have coated the inner walls with various polymers with the subsequent incorporation of redox couples. For example, they have employed protonated pvp and incorporated $[Fe(CN)_6]^{4-}$. In addition they have employed self assembling monolayers containing a redox active species (e.g. viologen). Their main interest is in the investigation of lateral electron transfer.

Clays and zeolites have also been employed as media for incorporating redox couples by taking advantage of their ion exchange properties. The first example on the use of clays was by Bard and Ghosh [259] who employed hectorite layers dispersed on polyvinyl alcohol (pva) (they later determined that the pva addition was unnecessary) and coated tin oxide electrodes with it. Subsequently they incorporated redox ions such as $[Ru(bpy)_3]^{2+}$, $[Fe(bpy)_3]^{2+}$, $[Ru(NH_3)_6]^{3+}$ and methyl viologen and characterized their electrochemical responses and in some cases obtained ESR spectra [260–264]. Except for $[Ru(NH_3)_6]^{3+}$, the cyclic voltammograms had a waveshape that was typical of a diffusion controlled process. For $[Ru(NH_3)_6]^{3+}$ the waveshape resembled that of a surface confined monolayer and this was attributed to the larger mobility of the redox ion due to its smaller size. These observations were in accord with measured diffusion coefficients. Other investigators have also employed clays for electrode modification [265].

In terms of zeolites, the first report on their use for electrode modification was by Rolison and co-workers [266]. The deposition procedure was rather peculiar in that crushed molecular sieves (3 or 4 Å) were placed in an electrochemical cell with an electroreducible species (e.g. 1,4-dinitrobenzene) and the potential was scanned while the electrode was rotated. This gave rise to deposited films which in some instances retained the redox behavior of the redox couple employed during the deposition.

## E. APPLICATIONS

### *(i) Electrocatalysis*

#### *(a) Description*

As with any catalytic process, electrocatalysis aims at reducing the energy of activation of a reaction (a redox transformation in this case) by providing low-energy pathways between reactants and products [267]. The ability to do this in a rational and predictable manner was and continues to be one of the main objectives of chemically modified electrode research.

In talking about electrocatalysis at modified electrodes we need to consider the cases of electrodes modified with sub or monolayer amounts of material and those modified with multimolecular layers. In addition we need to distinguish between simple charge transfer mediation, where the redox centers at an electrode surface serve merely as electron shuttles, from the case where there is a more intimate chemical interaction between catalyst and substrate. These are commonly referred to as redox catalysis and chemical catalysis, respectively.

For the case of redox catalysis at an electrode modified with a monolayer of a redox active component, Saveant [160] demonstrated that essentially no catalytic effect would be expected when compared to the case of a mediator in homogeneous solution. This was ascribed to a loss of dimensionality. It was also pointed out, however, (Fig. 19) that redox polymers with 100 monolayer equivalents could be very effective.

In the case of chemical catalysis, catalytic activity could be observed even at monolayer coverages. In addition the commonly mentioned advantages of use of small amounts of catalyst and ready separability of the catalyst from the reaction medium are clearly operational.

A second distinction that needs to be made when comparing reactions at electrodes modified with monolayers vs. multilayers is the fact that in the

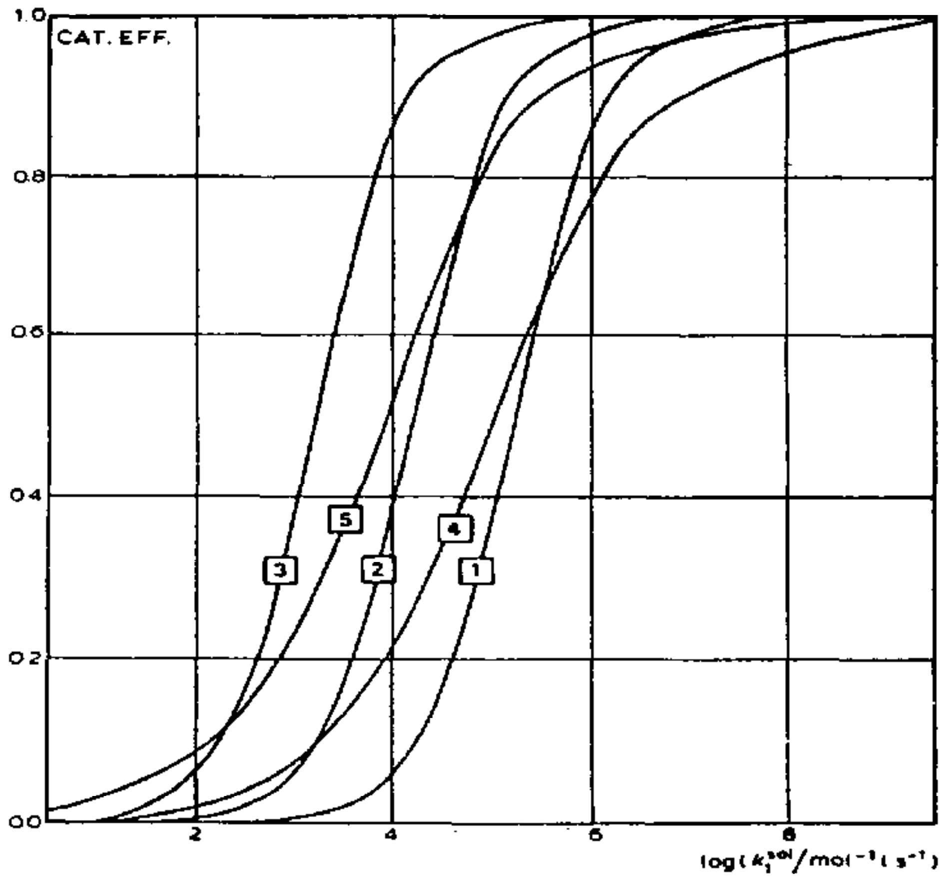

Fig. 19. Catalytic efficiency as a function of the rate constant of the catalytic step. Derivatized electrode at monolayer coverage (1); polymer electrode with 10 equivalent monolayers (2); 100 equivalent monolayers (3); homogeneous catalysis; $c_P^0 = 10^{-3}$ mol l$^{-1}$; $c_A^0 = 0.1$ mol l$^{-1}$ (4), 0.01 mol l$^{-1}$ (5). Sweep rate = 0.1 V s$^{-1}$. (From ref. 160, with permission.)

latter, the rate of charge propagation [268] and substrate permeability [269] can play very important roles, and in fact be rate determining.

Because of the well defined transport processes and steady state response, electrocatalytic reactions at chemically modified electrodes are often studied by rotated disk electrode techniques. For an electrode covered with a monolayer of material the limiting electrocatalytic current is given by

$$\left(\frac{1}{i_{\max}}\right) = \left(\frac{1}{nFAk_{\text{ch}}\Gamma C_{\text{s}}}\right) + \left(\frac{1}{0.62nFA\nu^{-1/6}D_{\text{s}}^{2/3}\omega^{1/2}C_{\text{s}}}\right)$$

where $\Gamma$ represents the surface coverage of catalyst sites, $C_s$ is the solution substrate concentration, $D_s$ is the substrate's diffusion coefficient in solution, $k_{ch}$ is the rate constant for the substrate/catalyst reaction, $\nu$ is the

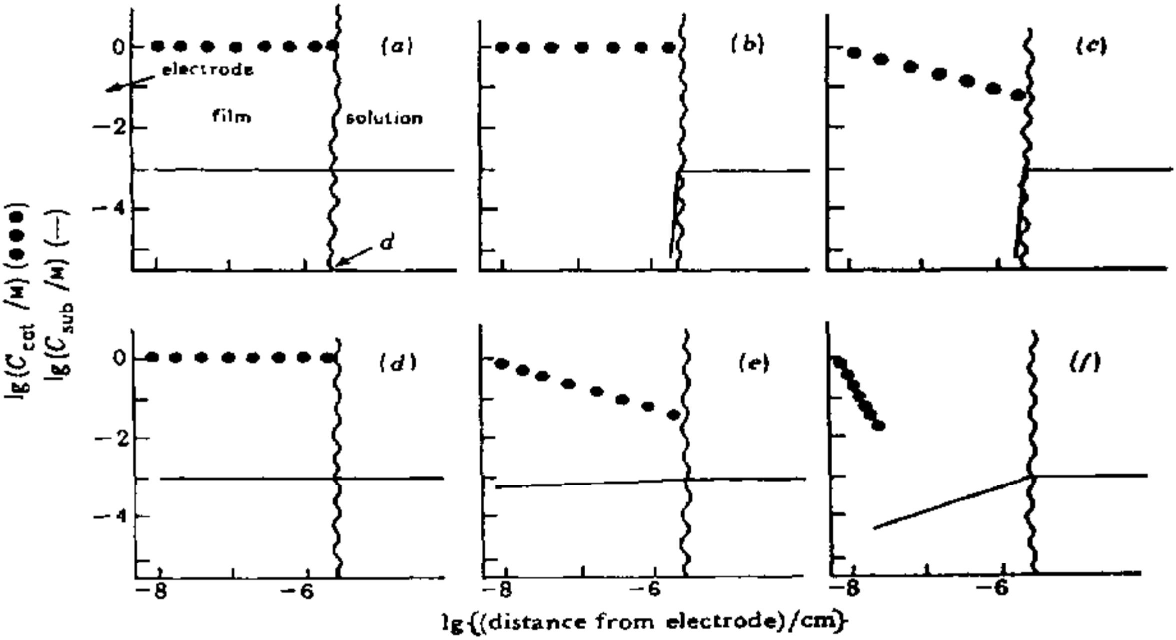

Fig. 20. Estimated catalyst and diffusing substrate concentration–distance profiles within polymer film on electrode, assuming a fast supply of substrate from solution to film surface, for specified orderings of nominal fluxes, and $\Gamma_1 = 2\times10^{-9}$ mol cm$^{-2}$, $d = 2\times10^{-6}$ cm and $C_{cat} = 1$ M. (a) $f_{ct} > f_{subs} > f_{chem}$; (b) $f_{ct} > f_{chem} > f_{subs}$; (c) $f_{chem} > f_{ct} > f_{subs}$; (d) $f_{subs} > f_{ct} > f_{chem}$; (e) $f_{subs} > f_{chem} > f_{ct}$; (f) $f_{chem} > f_{subs} > f_{ct}$. Asterisks denote the limiting flux; actual fluxes are shown in the table below. (From ref. 269 with permission.)

| | (a) | (b) | (c) | (d) | (e) | (f) |
|---|---|---|---|---|---|---|
| $PD_{s,pol}$ (cm$^2$s$^{-1}$) | $2\times10^{-8}$ | $2\times10^{-8}$ | $2\times10^{-8}$ | $10^{-6}$ | $10^{-6}$ | $10^{-6}$ |
| $D_{ct}$ (cm$^2$s$^{-1}$) | $2\times10^{-9}$ | $2\times10^{-9}$ | $2\times10^{-9}$ | $10^{-11}$ | $10^{-11}$ | $10^{-11}$ |
| $10^3k_{ch}$ (M$^{-1}$s$^{-1}$) | $10^2$ | $10^6$ | $10^8$ | $10^2$ | $5\times10^4$ | $5\times10^8$ |
| $f_{act}$ (mol cm$^{-2}$s$^{-1}$) | $2\times10^{-10}$ | $10^{-7}$ | $10^{-6}$ | $2\times10^{-10}$ | $2\times10^{-9}$ | $2\times10^{-7}$ |

kinematic viscosity and $\omega$ is the rate of rotation in rad s$^{-1}$. Plots of $1/i_{max}$ vs. $1/\omega^{1/2}$ (so called inverse Levich plots or Koutecky–Levich plots) should be linear and from the intercept, the value of $k_{ch}$ may be obtained.

When electrocatalytic reactions take place at polymer films, other factors need to be considered, including the rate of charge propagation through the film as well as the permeability of the substrate through the film. These factors have been considered in a model proposed by Murray [269] whose principal features are depicted in Fig. 20.

Cyclic voltammetry can also be employed for the study of electrocatalysis although it is more difficult to extract quantitative information. However, it is simple to establish a qualitative picture. For example, consider an electrode modified with a redox reagent Ox/Red and the reduction of a species

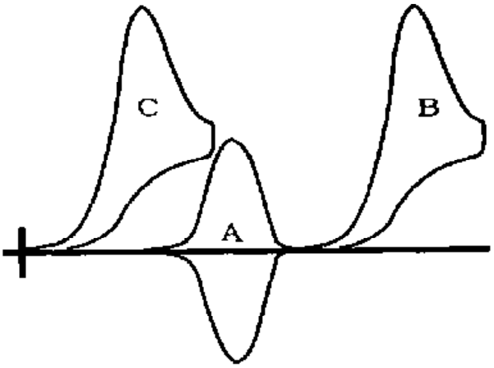

Fig. 21. Depiction of cyclic voltammetric responses for electrocatalysis at a chemically modified electrode. (A) Voltammogram for surface confined redox couple. (B) Direct reduction of Subs. (C) Reduction of Subs. at the modified electrode.

Subs. at the bare and modified electrode (Fig. 21). The modified electrode will exhibit a reversible response (curve A) whereas the direct reduction of Subs. takes place at a significant overpotential (that is, at a potential far removed from its reversible potential) (B). At the modified electrode, the reduction of Subs. (C) takes place at a potential that is lower than the direct reduction and that in addition can be displaced from the potential of the Ox/Red couple depending on the catalytic activity. If the return wave (anodic in this case) is absent and the peak current is proportional to $v^{1/2}$, the catalysis is rapid and is controlled by the diffusion of Subs. to the surface. Although this method gives a clear qualitative picture, obtaining quantitative measurements is somewhat involved.

### *(b) Examples*

*Reduction of $O_2$.* The $4e^-$ reduction of $O_2$ to water is a reaction of great technological relevance in terms of energy conversion via fuel cells. It is a process that is quite difficult since it is a four-electron process that is also coupled to proton transfers. In addition, competing reactions, such as peroxide formation can result in a significant voltage loss from the maximum value of 1.23 V

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad E^0 = +1.23 \text{ V vs. NHE}$$

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad E^0 = +0.68 \text{ V vs. NHE}$$

A number of approaches, including the modification of electrode surfaces have been employed in an effort to achieve this transformation. The now classic work of Anson and Collman [86–88,90,91] represents one of the most

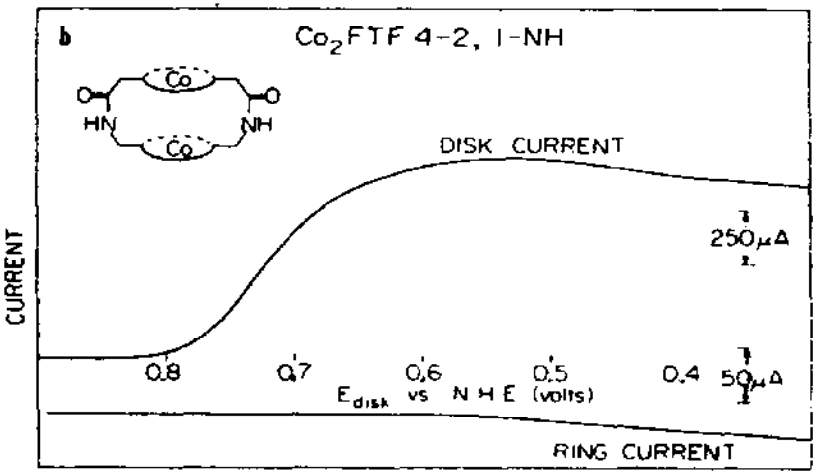

Fig. 22. Disk and ring currents vs. the potential of the graphite disk coated with the dimeric cobalt porphyrin shown. Platinum ring potential held at +1.4 V. (From ref. 87 with permission of the American Chemical Society.)

elegant examples of electrocatalysis at chemically modified electrodes. They employed a family of dicobalt face-to-face porphyrins where the length of the link between the two porphyrins was systematically varied. These were adsorbed on to pyrolytic graphite electrodes and their electrocatalytic activity assessed. In order to test for the generation of peroxide, they employed a rotated ring-disk electrode configuration [270] with a platinum ring and a graphite disk. Any peroxide generated at the disk would be detected at the ring as an oxidation current. Figure 22 shows a ring-disk voltammogram for a graphite electrode coated with the cofacial porphyrin shown in the inset. The onset of cathodic current is at about +0.8 V and very little peroxide is formed (notice differences in current scales). Although the system is not very long lived and the synthesis is difficult, it points to the feasibility of achieving very strong catalytic effects by the rational and deliberate modification of an electrode surface.

Anson and Chang [94] have also employed a different family of cofacial porphyrins with high electrocatalytic activity towards $O_2$ reduction. In this case, the synthesis is significantly simplified. Most recently, Collman [271] presented the first example of a monomeric Ir porphyrin capable of the four electron reduction of $O_2$.

*Reduction of $CO_2$.* Analogous to the reduction of $O_2$, the electrocatalytic reduction of $CO_2$ also presents a great challenge; again because of the need to have multi-electronic transformations while avoiding high energy intermediates. A number of transition metal complexes have been shown to effect some degree of catalysis in the reduction of $CO_2$. In addition some of these materials have been employed as modifiers of electrode surfaces.

Lieber and Lewis [272] employed carbon electrodes modified with cobalt phthalocyanine (deposited by droplet evaporation from THF) and electrolyzed aqueous solutions of various pH values under an atmosphere of $CO_2$. They report high turnover numbers $3.7 \times 10^5$ and high current efficiency (typically above 80%). The main products are CO and $H_2$. Much lower activity was obtained for the complex in solution, pointing to a favorable interaction of the surface with the active form of the catalyst. We [273] and others [189,274,275] have employed electrodes modified with a polymeric film of $[Re(CO)_3(v\text{-}bpy)Cl]$ for the electrocatalytic reduction of $CO_2$. The choice of this system originated from solution studies by Lehn and co-workers [276,277]. Although high catalytic activity was observed, the turnover numbers were modest (ca. 600) presumably due to a dimerization reaction of the catalyst which effectively competes with the electrocatalytic step.

### *(ii) Stabilization of small band gap semiconductors*

The use of semiconductor electrodes in photoelectrochemical cells represents an efficient and potentially important way of converting solar energy into either electricity or high energy redox products. One of the problems that has plagued this area is the inherent instability of many of these materials under irradiation, especially small band gap non-oxide n-type materials. This is because upon absorption of a photon (to generate an electron in the conduction band and a hole in the valence band) the photogenerated hole can react either with a redox system in solution (the desired reaction) or alternatively, it can oxidize the semiconductor itself. This process of photoanodic dissolution is especially severe for materials such as n-Si and n-GaAs which are potentially some of the most efficient materials for the conversion of solar energy. The problem, in its simplest form can be reduced to one of relative rates (i.e. rate of interfacial charge transfer to a redox system in solution vs. dissolution of the electrode) and many investigators have proposed and employed numerous approaches geared at achieving this, thereby stabilizing the semiconductor.

Early on, Wrighton and co-workers [15–17] proposed the modification of the surface of the semiconductor with a polymeric film containing a reversible, outer sphere redox couple envisioning that this would accelerate interfacial charge transfer and thereby stabilize the semiconductor. An added feature was the fact that the local concentration of redox sites would be of the order of 1 M, thereby further enhancing stability. With this purpose in mind Wrighton and co-workers developed a series of hydrolytically unstable ferrocenyl silanes (Fig. 10) that could be employed in the surface modifica-

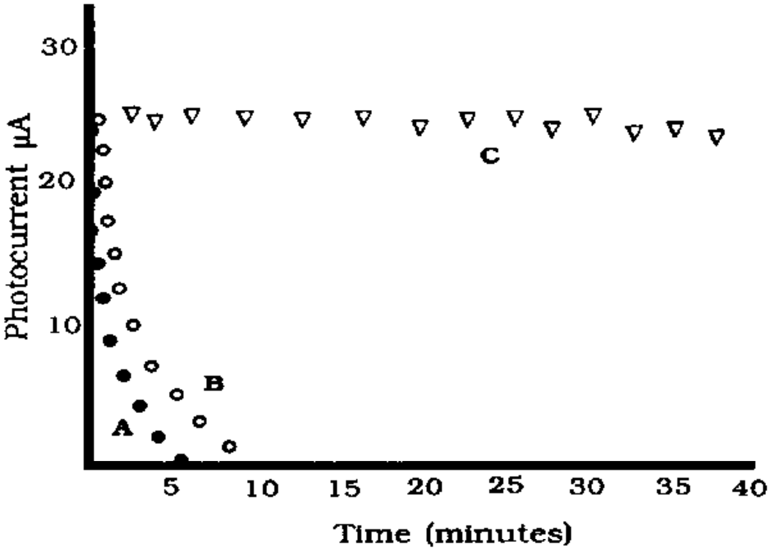

Fig. 23. Stabilization of n-Si in aqueous solution. Plots of photocurrent vs. time for (A) naked Si in contact with 0.1 M $NaClO_4$; (B) same as (A) but in the presence of 4 mM $Fe(CN)_6^{4-}$; (C) same as (B) but electrode modified with (1,1′-ferrocenediyl)dichlorosilane (adapted from ref. 114).

tion of these semiconductor surfaces. As shown in Fig. 23 the use of these materials had a dramatic effect in enhancing the long term stability of these electrodes under operation. These early findings of Wrighton prompted vigorous research by many investigators so that today many redox systems have been incorporated on to a wide variety of semiconductor materials [278–288].

### *(iii) Electroanalysis*

Modified electrodes are ideally suited for the development of analytical techniques, particularly for the determination of transition metal ions. This is due to the inherent sensitivity of the method (recall that a monolayer of metal complex represents about $1 \times 10^{-10}$ mol $cm^{-2}$) and the fact that the interface can be tailored to contain a wide range of reactants that can coordinate to a metal center. Thus, the approach is to perform the equivalent of stripping voltammetry where the preconcentration step is driven by coordination and not electrodeposition. This has the advantage of allowing for unprecedented levels of selectivity and sensitivity. The ability to perform this preconcentration was established conceptually by Lane and Hubbard on their study of adsorbed olefins on platinum [9,10]. Of particular relevance was the coordination of iron to an immobilized salicylate ligand. Although the analytical implications were not pursued, they were clearly established.

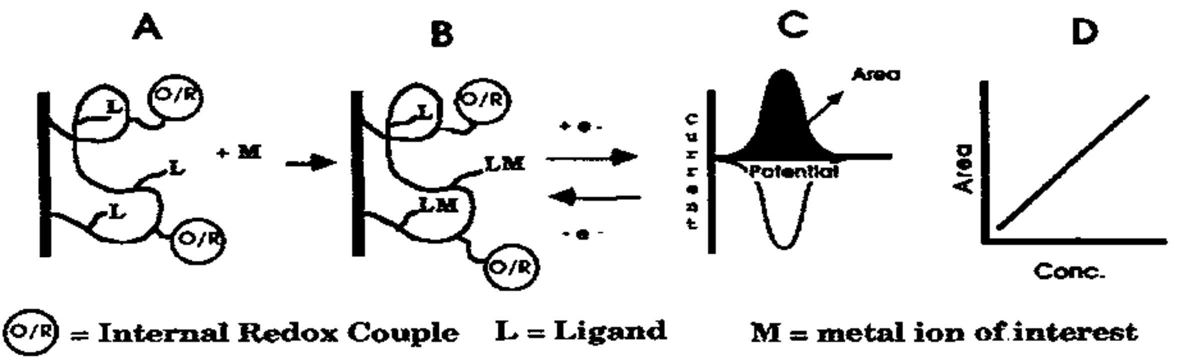

Fig. 24. Schematic representation of the use of chemically modified electrodes for electroanalysis of metal ions.

The author and co-workers recently proposed and demonstrated [289–291] an approach based on the use of functionalized polymer films that contained a ligand (chosen to exhibit high affinity and selectivity for a metal ion) as well as an additional redox couple which served as an internal standard.

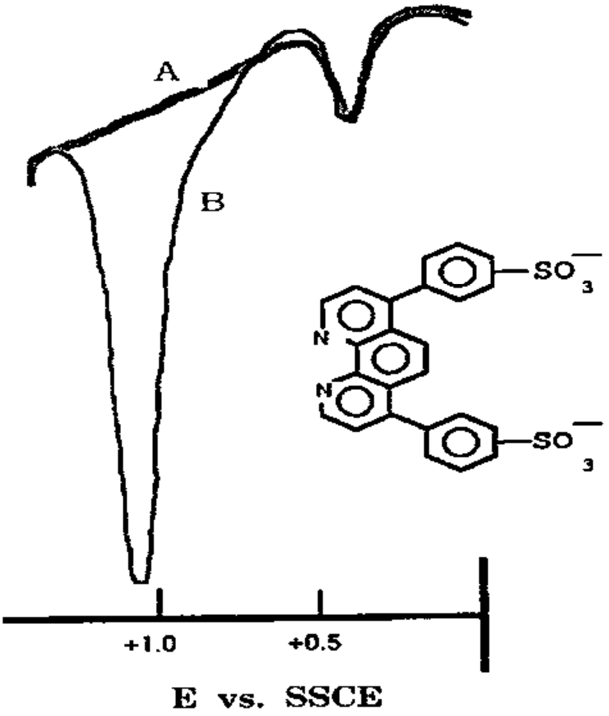

Fig. 25. Differential pulse voltammograms for an electrode coated with a layer of quaternized polyvinyl-pyridine vinyl/ferrocene copolymer with the ligand shown incorporated by ion exchange. (A) Prior to and (B) after contact with a $10^{-6}$ M solution of $Fe^{2+}$.

The technique depicted in Fig. 24 involves the modification of the electrode, exposure to the analysis solution and the subsequent electrochemical determination of the metal/ligand complex. From the electrochemical response and a calibration curve, the determination of the concentration of the metal ion in solution can be achieved.

An approach that we have employed for the ligand immobilization has been ion exchange, due to its simplicity. Figure 25 shows two voltammograms that depict the coordination of iron to an electrode modified with a quaternized vinyl pyridine vinyl ferrocene copolymer containing the ligand depicted in the inset incorporated by ion exchange. Voltammograms A and B were obtained prior to and after exposure of the electrode to a solution of iron at $10^{-6}$ M. (The wave at about $+0.5$ V is due to ferrocene centers in the polymer which serve as an internal standard.) This is an area that awaits further development which the author and others are currently pursuing [95,96,155,157,158,159,292–295].

### *(iv) Kinetics and mechanisms of reactions*

Although not generally recognized as such, the use of modified electrodes provides some distinct advantages in the investigation of the kinetics and mechanisms of redox reactions. Perhaps the biggest advantage is the enhanced time resolution obtained at modified electrodes when compared to solution redox processes. This derives from the fact that whereas in solution the faradaic component of the current grows as $v^{1/2}$, for a surface immobilized reagent, it grows linearly with sweep rate. This is of critical importance because the double layer charging current also grows linearly with sweep rate. Therefore, for solution redox processes there is a limitation as to the accessible sweep rates due to the degradation in signal to noise that accompanies increases in the rate of potential sweep. However, for a surface immobilized redox couple such limitations do not exist so that the accessible range of sweep rates is dramatically enhanced. Although rather evident, this advantage has not been exploited extensively.

In addition to the faster experimental time scales available, the use of modified electrodes for kinetic and mechanistic studies is aided by the small amounts of material required as well as the utility of isopotential points (when present).

An especially illustrative example of the utility of modified electrodes for kinetic and mechanistic studies was by Murray, Meyer and Abruña. The system under study was the oxidation of $[\mathrm{Ru(bpy)_2PyNO_2}]^+$. Such a redox transformation gives rise to a disproportionation reaction with $[\mathrm{Ru(bpy)PyNO_3}]^+$ and $[\mathrm{Ru(bpy)_2PyNO}]^{3+}$ as products [296]. In effect, the oxidized form (e.g. $[\mathrm{Ru(bpy)_2PyNO_2}]^{2+}$) serves as an oxygen atom transfer

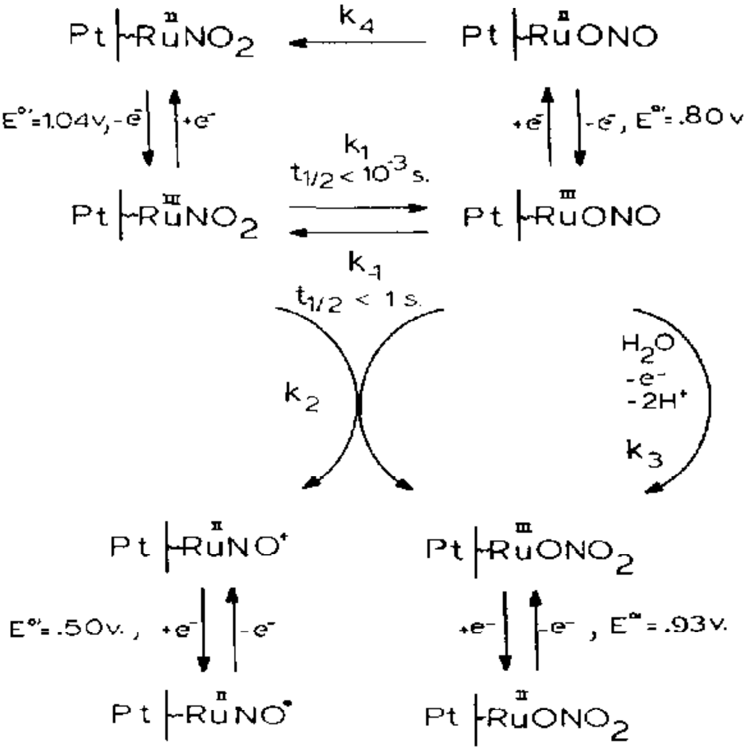

Fig. 26. Mechanism for the disproportionation reaction of $[Ru(bpy)_2PyNO_2]^{2+}$ immobilized at the surface of a platinum electrode. (From ref. 107, with permission.)

reagent. In the presence of a suitable substrate, the oxidized form of the complex can oxidize the substrate and under these conditions the nitrosyl complex is the only ruthenium-containing product. Since the nitro ligand is N bound, whereas the nitrate is necessarily O bound, the mechanism dictates the generation of an oxygen bound (nitrito) species as a precursor to the nitrate product. By employing an electrode modified with $[Ru(bpy)_2PyNO_2]^+$ (anchored via ethylene diamine silane) [106,107] the authors group were able to detect the presence of an intermediate ascribed to the nitrito bound complex. The presence of isopotential points and their position afforded clear evidence as to the nature of the intermediate. In addition, the potential for the intermediate species was consistent with the bonding characteristics of a nitrito (oxygen bound) ligand. Based on this study, a rather complex mechanism was unraveled (Fig. 26).

The effects of immobilization upon the kinetics of ligand substitution have also been investigated. Lewis and co-workers [239] recently reported a study on the kinetics of ligand substitution for $[Ru(NH_3)_5H_2O]^{2+}$ incorporated into Nafion films. They found that for a family of pyridine ligands the rates of substitution vary by about a factor of five whereas in homogeneous

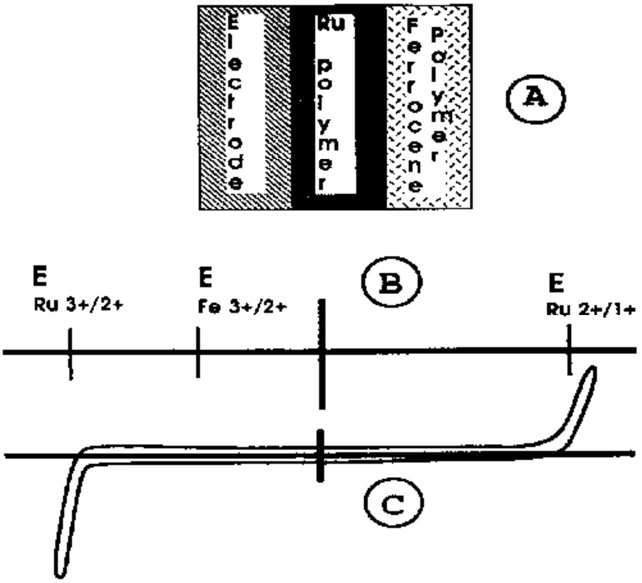

Fig. 27. (A) Schematic representation of a bilayer electrode; (B) redox levels of the polymer films; (C) current/voltage curve for a bilayer electrode depicting rectifying behavior.

solution the rates remain relatively constant. They ascribed these differences to a change in mechanism from dissociative in homogeneous solution to one having significant associative character in Nafion. These experiments point to novel chemical pathways that can be elicited upon immobilization of a redox reagent. They also point towards the tantalizing prospect of controlling and changing (in a predictable fashion) the mechanisms of reactions. This may have very significant effects in the design of catalytic systems.

### *(v) Novel devices*

Novel chemical devices can be prepared by the deposition of structurally segregated films of electroactive materials. The earliest example of this was the so-called bilayer electrode which exhibits bistable switching behavior [22,23,181,182,187,192]. To prepare such a device, an electrode is coated with two layers of redox active materials where the inner layer has two redox processes that straddle the redox process of the outer film. An example of this is presented in Fig. 27 where the inner film is a polymeric layer of $[Ru(v\text{-}bpy)_3]^{2+}$ (with redox potentials at about $+1.30$, $-1.35$, $-1.55$ and $-1.78$) and the outer film is a layer of polyvinyl ferrocene (redox potential at about $+0.5$ V). The operation of this device can be understood by considering what happens when the applied potential is varied. If we start with both the $[Ru(bpy)_3]^{2+}$ and ferrocene in their reduced form and sweep the potential in the positive direction, the direct oxidation of the ferrocene is not observed since the inner (ruthenium) film renders it inaccessible. When potentials for the oxidation of the ruthenium film are reached, both the ruthenium and ferrocene polymers become oxidized. Reversal of the potential in the positive direction reduces the inner ruthenium film back to the 2+ oxidation state. However, since this species is thermodynamically unable to reduce the ferricenium sites, the latter are trapped in their oxidized state. They can be released by scanning in the negative direction (towards the $Ru^{2+/+}$ redox couple). This species, however, can easily reduce the ferricenium sites and thus both inner and outer films are reduced at this potential. This device thus has rectifying properties (as depicted in Fig. 27(C)) even though no semiconducting material is employed.

In addition to bilayer electrodes, Murray has also developed a number of other arrangements based on the redox conduction ability of these films [188].

Another especially elegant example of the types of devices that can be prepared was produced by Wrighton and co-workers [24] who employed a microelectrode array (3 electrodes) coated with a polypyrrole film. By taking advantage of the large variation in conductivity of the polypyrrole film with applied potential they were able to prepare a molecular based transistor. Although the switching times were slow, it demonstrated the types of structures and effects that can be achieved by the control of the chemistry and spatial details. They have since explored numerous applications in this area [297–301].

## F. FUTURE DEVELOPMENTS

The field of chemically modified electrodes has experienced a period of great growth and maturity over the last decade. As a result, numerous strategies for the incorporation of redox active species have been developed. In addition, the theoretical descriptions have provided a framework for interpretation of the observed electrochemical responses and have pointed to those areas that require further development.

Many applications have been, and continue to be, explored, with emphasis on catalysis and although all of these systems are still limited to the confines of research laboratories, I am confident that large scale applications will emerge. The preparation of structured interfaces of well-defined and deliberately designed character offer some of the most promising future prospects, especially with regards to the development of chemical sensors.

In the process of development, the field has attracted numerous practitioners from other areas. As this trend continues new methods and applications will continue to emerge as we try to dictate the properties of electrochemical interfaces by deliberate modification.

## ACKNOWLEDGEMENTS

This work was generously supported by the National Science Foundation, Dow Chemical Co., C.S. Johnson & Son, Inc., Honeywell Inc., Eastman Kodak Co. and the Materials Science Center at Cornell University. The author thanks A.R. Guadalupe for valuable comments and for a critical reading of this manuscript.

## REFERENCES

1 R.W. Murray in A.J. Bard (Ed.), Electroanalytical Chemistry, Vol. 13, M. Dekker, New York, 1984, p. 191.
2 R.W. Murray, Acc. Chem. Res., 13 (1980) 135.
3 L.R. Faulkner, Chem. Eng. News, Feb 27 (1984) 28.
4 K.D. Snell and A.G. Keenan, Chem. Soc. Rev., 8 (1979) 259.
5 W.J. Albery and A.R. Hillman, Ann. Rev. C. R. Soc. Chem. Lond., (1981) 377.
6 M. Fujihira, Modified electrodes, in A.J. Fry and W.R. Britton (Eds.), Topics in Organic Electrochemistry, Plenum, New York, 1986, Chap. 6, p. 255.
7 J.S. Miller (Ed.), Chemically Modified Surfaces in Catalysis and Electrocatalysis. ACS Symp. Series No. 192, Am. Chem. Soc., Washington DC, 1982.
8 F.C. Anson, Acc. Chem. Res., 8 (1975) 400.
9 R.F. Lane and A.T. Hubbard, J. Phys. Chem., 77 (1973) 1401.
10 R.F. Lane and A.T. Hubbard, J. Phys. Chem., 77 (1973) 1411.
11 B.F. Watkins, J.R. Behling, E. Kariv and L.L. Miller, J. Am. Chem. Soc., 97 (1975) 3549.
12 P.R. Moses, L.M. Wier and R.W. Murray, Anal. Chem., 47 (1975) 1882.
13 J.R. Lenhard and R.W. Murray, J. Electroanal. Chem., 78 (1977) 195.
14 J.R. Lenhard, R. Rocklin, H. Abruña, K. Willman, K. Kuo, R. Nowak and R.W. Murray, J. Am. Chem. Soc., 100 (1978) 5213.
15 M.S. Wrighton, R.G. Austin, A.B. Bocarsly, J.M. Bolts, O. Haas, K.D. Legg, L. Nadjo and M.C. Palazzotto, J. Electroanal. Chem., 87 (1978) 429.
16 M.S. Wrighton, M.C. Palazzotto, A.B. Bocarsly, J.M. Bolts, A. Fischer and L. Nadjo, J. Am. Chem. Soc., 100 (1978) 7264.
17 (a) M.S. Wrighton, Acc. Chem. Res., 12 (1979) 303.
(b) K.A. Daube, D.J. Harrison, T.E. Mollouk, A.J. Ricco, S. Chao, M.S. Wrighton, W.A. Hendrickson and A.J. Drube, J. Photochem., 29 (1985) 71.
18 (a) N. Oyama and F.C. Anson, J. Electrochem. Soc., 127 (1980) 247.
(b) N. Oyama and F.C. Anson, J. Electrochem. Soc., 127 (1980) 249.
19 I. Rubinstein and A.J. Bard, J. Am. Chem. Soc., 102 (1980) 6641.
20 N. Oyama, T. Shimomura, K. Shigehara and F.C. Anson, J. Electroanal. Chem., 112 (1980) 271.
21 R.W. Murray, Annu. Rev. Mater. Sci., 14 (1984) 145.
22 H.D. Abruña, P. Denisevich, M. Umaña, T.J. Meyer and R.W. Murray, J. Am. Chem. Soc., 103 (1981) 1.
23 P. Denisevich, K.W. Willman and R.W. Murray, J. Am. Chem. Soc., 103 (1981) 4727.
24 H.S. White, G.P. Kittlesen and M.S. Wrighton, J. Am. Chem. Soc., 106 (1984) 5375.
25 P.G. Pickup and R.W. Murray, J. Electrochem. Soc., 131 (1984) 833.
26 T.A. Skotheim (Ed.), Handbook of Conducting Polymers, M. Dekker, New York, 1986.
27 A.J. Bard and L.R. Faulkner, Electrochemical Methods, John Wiley & Sons, Inc., New York, 1980, Chap. 6.

28 E. Laviron, J. Electroanal. Chem., 39 (1972) 1.
29 (a) E. Laviron, J. Electroanal. Chem., 52 (1974) 395.
   (b) E. Laviron, J. Electroanal. Chem., 100 (1979) 263.
   (c) E. Laviron, J. Electroanal. Chem., 105 (1979) 25.
   (d) E. Laviron, J. Electroanal. Chem., 105 (1979) 35.
30 B.E. Conway and H. Angerstein-Kozlowska, Acc. Chem. Res., 14 (1981) 154.
31 A.P. Brown and F.C. Anson, Anal. Chem., 49 (1977) 1589.
32 D.F. Smith, K. Willman, K. Kuo and R.W. Murray, J. Electroanal. Chem., 95 (1979) 217.
33 J.C. Lennox and R.W. Murray, J. Am. Chem. Soc., 100 (1978) 3710.
34 L.L. Miller and M.R. Van de Mark, J. Am. Chem. Soc., 100 (1978) 3223.
35 R. Nowak, F.A. Schultz, M. Umaña, H. Abruña and R.W. Murray, J. Electroanal. Chem., 94 (1978) 219.
36 A.H. Schroeder, F.B. Kaufman, V. Patel and E.M. Engler, J. Electroanal. Chem., 113 (1980) 193.
37 A. Merz and A.J. Bard, J. Am. Chem. Soc., 100 (1978) 3222.
38 F.B. Kaufman, A.H. Schroeder, E.M. Engler, S.R. Kramer and J.Q. Chambers, J. Am. Chem. Soc., 102 (1980) 483.
39 P. Daum and R.W. Murray, J. Electroanal. Chem., 85 (1981) 389.
40 S. Nakahama and R.W. Murray, J. Electroanal. Chem., 158 (1983) 303.
41 P.J. Peerce and A.J. Bard, J. Electroanal. Chem., 114 (1980) 89.
42 K.W. Willman, R.D. Rocklin, R. Nowak, K. Kuo, F.A. Schultz and R.W. Murray, J. Am. Chem. Soc., 102 (1980) 7629.
43 J.B. Kerr, L.L. Miller and M.R. Van de Mark, J. Am. Chem. Soc., 102 (1980) 3383.
44 P.J. Peerce and A.J. Bard, J. Electroanal. Chem., 112 (1980) 97.
45 K. Itaya and A.J. Bard, Anal. Chem., 50 (1978) 1487.
46 A.H. Schroeder and F.B. Kaufman, J. Electroanal. Chem., 113 (1980) 209.
47 G.J. Samuels and T.J. Meyer, J. Am. Chem. Soc., 103 (1981) 307.
48 J. Leddy, A.J. Bard, J.T. Maloy and J-M. Saveant, J. Electroanal. Chem., 187 (1985) 205.
49 P. Joo and J.Q. Chambers, J. Electrochem. Soc., 132 (1985) 1345.
50 J.Q. Chambers and G. Inzelt, Anal. Chem., 57 (1985) 1117.
51 G. Inzelt, J. Bacskai, J.Q. Chambers and R.W. Day, J. Electroanal. Chem., 201 (1986) 301.
52 P. Daum, J.R. Lenhard, D.R. Rolison and R.W. Murray, J. Am. Chem. Soc., 102 (1980) 4649.
53 R.J. Nowak, F.A. Schultz, M. Umaña, R. Lam and R.W. Murray, Anal. Chem., 52 (1980) 315.
54 N. Oyama and F.C. Anson, J. Electrochem. Soc., 127 (1980) 640.
55 P. Daum and R.W. Murray, J. Electroanal. Chem., 103 (1979) 289.
56 P. Denisevich, H.D. Abruña, C.R. Leidner, T.J. Meyer and R.W. Murray, Inorg. Chem., 21 (1982) 2153.
57 J. Facci and R.W. Murray, J. Phys. Chem., 86 (1981) 2870.
58 J. Facci and R.W. Murray, J. Electroanal. Chem., 124 (1981) 339.
59 E. Laviron, J. Electroanal. Chem., 112 (1980) 1.
60 D.A. Buttry and F.C. Anson, J. Electroanal. Chem., 130 (1981) 333.
61 D.A. Buttry and F.C. Anson, J. Am. Chem. Soc., 104 (1982) 4824.
62 N. Oyama, S. Yamaguchi, Y. Nishiki, K. Tokuda, H. Matsuda and F.C. Anson, J. Electroanal. Chem., 139 (1982) 371.
63 R.J. Mortimer and F.C. Anson, J. Electroanal. Chem., 138 (1982) 325.

64 F.C. Anson, J-M. Saveant and K. Shigehara, J. Am. Chem. Soc., 105 (1983) 1096.
65 T. Ohsaka and F.C. Anson, J. Phys. Chem., 87 (1983) 640.
66 D.A. Buttry and F.C. Anson, J. Am. Chem. Soc., 105 (1983) 685.
67 F.C. Anson, J-M. Saveant and K. Shigehara, J. Phys. Chem., 87 (1983) 214.
68 H.S. White, J. Leddy and A.J. Bard, J. Am. Chem. Soc., 104 (1982) 4811.
69 C.R. Martin, I. Rubinstein and A.J. Bard, J. Am. Chem. Soc., 104 (1982) 4817.
70 J. Leddy and A.J. Bard, J. Electroanal. Chem., 153 (1983) 223.
71 C.R. Martin and K.A. Dollard, J. Electroanal. Chem., 159 (1983) 127.
72 N.S. Lewis and M.S. Wrighton, J. Phys. Chem., 88 (1984) 2009.
73 T.J. Lewis, H.S. White and M.S. Wrighton, J. Am. Chem. Soc., 106 (1984) 6947.
74 R.E. Simon, T.E. Mallouk, K.A. Daube and M.S. Wrighton, Inorg. Chem., 24 (1985) 3119.
75 D.J. Harrison, K.A. Daube and M.S. Wrighton, J. Electroanal. Chem., 163 (1984) 93.
76 T. Ohsaka, T. Okajima and N. Oyama, J. Electroanal. Chem., 215 (1986) 191.
77 N. Oyama, T. Ohsaka and T. Ushirogouchi, J. Phys. Chem., 88 (1984) 5274.
78 N. Oyama, T. Ohsaka, H. Yamamoto and M. Kaneko, J. Phys. Chem., 90 (1986) 3850.
79 K. Aoki, K. Tokuda, H. Matsuda and N. Oyama, J. Electroanal. Chem., 176 (1984) 139.
80 T. Ohsaka, N. Oyama, K. Sato and H. Matsuda, J. Electrochem. Soc., 132 (1985) 1871.
81 (a) T.P. Henning, H.S. White and A.J. Bard, J. Am. Chem. Soc., 103 (1981) 3937.
(b) A.J. Bard, T.P. Henning and H.S. White, J. Am. Chem. Soc., 104 (1982) 5362.
82 T.P. Henning and A.J. Bard, J. Electrochem. Soc., 130 (1983) 613.
83 M. Majda and L.R. Faulkner, J. Electroanal. Chem., 169 (1984) 77, 97.
84 (a) H.J. Dahms, J. Phys. Chem., 72 (1968) 362.
(b) I. Ruff, Electrochim. Acta, 15 (1970) 1059.
(c) I. Ruff and I. Korosi-Odor, Inorg. Chem., 9 (1970) 186.
(d) I. Ruff and V. Friedrich, J. Phys. Chem., 75 (1971) 3297, 3303.
85 (a) A.P. Brown and F.C. Anson, J. Electroanal. Chem., 92 (1978) 133.
(b) A.P. Brown, C. Koval and F.C. Anson, J. Electroanal. Chem., 72 (1976) 379.
86 J.P. Collman, M. Marrocco, P. Denisevich, C. Koval and F.C. Anson, J. Electroanal. Chem., 101 (1979) 117.
87 J.P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval and F.C. Anson, J. Am. Chem. Soc., 102 (1980) 6027.
88 J.P. Collman, F.C. Anson, S. Bencosme, A. Chong, T. Collins, P. Denisevich, E. Evitt, T. Geiger, J. Ibers, G. Janeson, Y. Konai, C. Koval, M. Meier, R. Oakley, R. Pettman, E. Schmitlou and J. Sessler, in B.M. Trost and C.R. Hutchinson (Eds.), Organic Synthesis Today and Tomorrow, Pergamon Press, New York, 1981.
89 R.R. Durand, Jr. and F.C. Anson, J. Electroanal. Chem., 134 (1982) 273.
90 J.P. Collman, F.C. Anson, C.E. Barnes, C.E. Bencosme, T. Geiger, E.R. Evitt, R.P. Kreh, K. Meier and R.B. Pettman, J. Am. Chem. Soc., 105 (1983) 2694.
91 J.P. Collman, F.C. Anson, C.S. Bencosme, R.R. Durand, Jr. and R.P. Kreh, J. Am. Chem. Soc., 105 (1983) 2699.
92 R.R. Durand, Jr., C.S. Bencosme, J.P. Collman and F.C. Anson, J. Am. Chem. Soc., 105 (1983) 2710.
93 R.R. Durand, Jr., J.P. Collman and F.C. Anson, J. Electroanal. Chem., 151 (1983) 289.
94 H-Y. Liu, I. Abdalmuhdi, C.K. Chang and F.C. Anson, J. Phys. Chem., 89 (1985) 665.
95 J.F. Price and R.P. Baldwin, Anal. Chem., 52 (1980) 1940.
96 J.A. Cox and M. Majda, Anal. Chem., 52 (1980) 861.
97 (a) J. Zagal, R.K. Sen and E. Yeager, J. Electroanal. Chem., 83 (1977) 207.
(b) B.Z. Nicolic, R.R. Adzic and E.B. Yeager, J. Electroanal. Chem., 103 (1979) 281.

98 (a) J.S. Facci, P.A. Falcigno and J.M. Gold, Langmuir 2, (1986) 732.
(b) M. Fujihira and T. Araki, Bull. Chem. Soc. Jpn., 59 (1986) 2375.
(c) M. Fujihira and T. Araki, J. Electroanal. Chem., 205 (1986) 329.
(d) H. Daipuku, I. Yoshimura, I. Hirata, K. Aoki, K. Tokuda and H. Matsuda, J. Electroanal. Chem., 199 (1986) 47.
(e) H. Daipuku, K. Aoki, K. Tokuda and H. Matsuda, J. Electroanal. Chem., 183 (1985) 1.
(f) M. Fujihira and S. Poosittisak, J. Electroanal. Chem., 199 (1986) 481.
99 P.R. Moses and R.W. Murray, J. Am. Chem. Soc., 98 (1976) 7435.
100 D.F. Untereker, J.C. Lennox, L.M. Wier, P.R. Moses and R.W. Murray, J. Electroanal. Chem., 81 (1977) 309.
101 P.R. Moses and R.W. Murray, J. Electroanal. Chem., 77 (1977) 393.
102 J.R. Lenhard and R.W. Murray, J. Am. Chem. Soc., 100 (1978) 7870.
103 K. Kuo, P.R. Moses, J.R. Lenhard, D.C. Green and R.W. Murray, Anal Chem., 51 (1979) 745.
104 H. Abruña, T.J. Meyer and R.W. Murray, Inorg. Chem., 11 (1979) 3233.
105 H.O. Finklea, H. Abruña and R.W. Murray in M.S. Wrighton (Ed.), Interfacial Photoprocesses: Energy Conversion and Synthesis. Adv. Chem. Ser., 184, American Chemical Society, Washington, DC, 1980, p. 253.
106 H.D. Abruña, J.L. Walsh, T.J. Meyer and R.W. Murray, J. Am. Chem. Soc., 102 (1980) 3272.
107 H.D. Abruña, J.L. Walsh, T.J. Meyer and R.W. Murray, Inorg. Chem., 20 (1981) 1481.
108 P.R. Moses, L.M. Wier, J.C. Lennox, H.O. Finklea, J.R. Lenhard and R.W. Murray, Anal. Chem., 50 (1978) 576.
109 H.O. Finklea and R.W. Murray, J. Phys. Chem., 83 (1979) 353.
110 A.B. Fischer, M.S. Wrighton, M. Umaña and R.W. Murray, J. Am. Chem. Soc., 101 (1979) 3442.
111 K.W. Willman, E. Greer and R.W. Murray, Nouv. J. Chem., 3 (1979) 455.
112 (a) G.J. Leigh and C.J. Pickett, J. Chem. Soc. Dalton Trans., (1977) 1797.
(b) R.J. Burt, G.J. Leigh and C.J. Pickett, J. Chem. Soc. Chem. Commun., (1976) 940.
113 (a) M.S. Wrighton, R. Austin and A.B. Palazzotto, J. Am. Chem. Soc., 100 (1978) 1602.
(b) J.M. Bolts and M.S. Wrighton, J. Am. Chem. Soc., 100 (1978) 5257.
114 J.M. Bolts, A.B. Bocarsly, M.C. Palazzotto, E.G. Walton, N.S. Lewis and M.S. Wrighton, J. Am. Chem. Soc., 101 (1979) 1378.
115 J.M. Bolts and M.S. Wrighton, J. Am. Chem. Soc., 101 (1979) 6179.
116 A.B. Bocarsly, E.G. Walton, M.G. Bradley and M.S. Wrighton, J. Electroanal. Chem., 100 (1979) 283.
117 A.B. Bocarsly, E.G. Walton and M.S. Wrighton, J. Am. Chem. Soc., 102 (1980) 3390.
118 N.S. Lewis, A.B. Bocarsly and M.S. Wrighton, J. Phys. Chem., 84 (1980) 2033.
119 D.C. Bookbinder, J.A. Bruce, R.N. Dominey, N.S. Lewis and M.S. Wrighton, Proc. Natl. Acad. Sci. USA, 77 (1980) 6280.
120 D.C. Bookbinder and M.S. Wrighton, J. Am. Chem. Soc., 102 (1980) 5123.
121 N.S. Lewis and M.S. Wrighton, Science, 211 (1981) 944.
122 J.A. Bruce and M.S. Wrighton, J. Am. Chem. Soc., 104 (1982) 74.
123 R.N. Dominey, N.S. Lewis, J.A. Bruce, D.C. Bookbinder and M.S. Wrighton, J. Am. Chem. Soc., 104 (1982) 467.
124 R.N. Dominey, T.J. Lewis and M.S. Wrighton, J. Phys. Chem., 87 (1983) 5345.
125 D.C. Bookbinder and M.S. Wrighton, J. Electrochem. Soc., (1983) 1080.
126 D.J. Harrison and M.S. Wrighton, J. Phys. Chem., 88 (1984) 3932.

127 C.J. Stalder, S. Chao and M.S. Wrighton, J. Am. Chem. Soc., 106 (1984) 3673.
128 J-F. Andrée and M.S. Wrighton, Inorg. Chem., 24 (1985) 4288.
129 G.S. Calabrese, R.M. Buchanan and M.S. Wrighton, J. Am. Chem. Soc., 105 (1983) 5594.
130 R.M. Buchanan, G.S. Calabrese, T.J. Sobieralski and M.S. Wrighton, J. Electroanal. Chem., 153 (1983) 129.
131 R.A. Simon, T.E. Mallouk, K.A. Daube and M.S. Wrighton, Inorg. Chem., 24 (1985) 3119.
132 P.K. Ghosh and T.G. Spiro, J. Am. Chem. Soc., 102 (1980) 5543.
133 P.K. Ghosh and T.G. Spiro, J. Electrochem. Soc., 128 (1981) 1281.
134 (a) G.W. Hance and T. Kuwana, Anal. Chem., 59 (1987) 131.
(b) D.H. Karweik, I.F. Hu and T. Kuwana, ACS Symp. Series No. 288, American Chemical Society, Washington, DC, 1985, p. 582.
(c) D.T. Fagan, I.F. Hu and T. Kuwana, Anal. Chem., 57 (1985) 2759.
(d) I.F. Hu, D.H. Karweik and T. Kuwana, J. Electroanal. Chem., 188 (1985) 59.
(e) B. Kazee, D.E. Weisshaar and T. Kuwana, Anal. Chem., 57 (1985) 2736.
(f) D.E. Weisshaar and T. Kuwana, Anal. Chem., 57 (1985) 378.
(g) S. Dong and T. Kuwana, J. Electrochem. Soc., 131 (1984) 813.
135 (a) J.C. Lennox and R.W. Murray, J. Electroanal. Chem., 78 (1977) 395.
(b) J.C. Lennox and R.W. Murray, J. Am. Chem. Soc., 100 (1978) 3710.
136 R.D. Rocklin and R.W. Murray, J. Electroanal. Chem., 100 (1979) 271.
137 C.P. Jester, R.D. Rocklin and R.W. Murray, J. Electrochem. Soc., 127 (1980) 1979.
138 C.M. Elliott and C.A. Marresse, J. Electroanal. Chem., 119 (1981) 395.
139 N. Oyama, K.B. Yap and F.C. Anson, J. Electroanal. Chem., 100 (1979) 233.
140 C.A. Koval and F.C. Anson, Anal. Chem., 50 (1978) 223.
141 N. Oyama and F.C. Anson, J. Am. Chem. Soc., 101 (1979) 1634.
142 A.W.C. Lin, P. Yeh, A.M. Yacynych and T. Kuwana, J. Electroanal. Chem., 84 (1971) 411.
143 A.M. Yacynych and T. Kuwana, Anal. Chem., 50 (1978) 640.
144 D.C.S. Tse, T. Kuwana and G.P. Royer, J. Electroanal. Chem., 98 (1979) 345.
145 M.F. Dautartas, J.F. Evans and T. Kuwana, Anal. Chem., 51 (1979) 104.
146 M.A. Fox, F.J. Nobs and T.A. Voynick, J. Am. Chem. Soc., 102 (1980) 4029.
147 (a) R.M. Ianello and A.M. Yacynych, Anal. Chim. Acta, 131 (1981) 123.
(b) R.M. Ianello and A.M. Yacynych, Anal. Chem., 53 (1981) 2090.
148 S. Mazur, T. Matusinovic and K. Camman, J. Am. Chem. Soc., 99 (1977) 3888.
149 N. Oyama, A.P. Brown and F.C. Anson, J. Electroanal. Chem., 87 (1978) 435.
150 R. Nowak, F.A. Schultz, M. Umaña, H. Abruña and R.W. Murray, J. Electroanal. Chem., 94 (1978) 219.
151 T. Kuwana and W.G. French, Anal. Chem., 36 (1964) 241.
152 F.A. Schultz and T. Kuwana, J. Electroanal. Chem., 10 (1965) 95.
153 D. Baver and M.Ph. Gaillochet, Electrochim. Acta, 19 (1974) 592.
154 M. Lamanche and D. Bauer, J. Electroanal. Chem., 79 (1977) 359.
155 (a) R. Ravichandron and R.P. Baldwin, J. Electroanal. Chem., 126 (1981) 293.
(b) R. Ravichandron and R.P. Baldwin, Anal. Chem., 55 (1983) 1586.
156 (a) W. Kutner, T.J. Meyer and R.W. Murray, J. Electroanal. Chem., 195 (1985) 375.
(b) E.S. Takeuchi and R.W. Murray, J. Electroanal. Chem., 188 (1985) 49.
157 G.T. Cheek and R.F. Nelson, Anal. Lett. Sect. A, 11 (1978) 393.
158 T. Yao and S. Muscha, Anal. Chim. Acta, 110 (1979) 203.
159 R.P. Baldwin, J.C. Christensen and L. Kryger, Anal. Chem., 58 (1986) 1790.
160 C.P. Andrieux and J-M. Saveant, J. Electroanal. Chem., 93 (1978) 163.

161 K. Shigehara, N. Oyama and F.C. Anson, J. Am. Chem. Soc., 103 (1981) 2552.
162 H.G. Cassidy and K.A. Kun, Oxidation-Reduction Polymers (Redox-Polymers), Wiley Interscience, New York, 1965.
163 (a) L.L. Miller and M.R. Van de Mark, J. Am. Chem. Soc., 100 (1978) 3223.
  (b) L.L. Miller and M.R. Van de Mark, J. Am. Chem. Soc., 100 (1978) 639.
  (c) J.B. Kerr and L.L. Miller, J. Electroanal. Chem., 101 (1979) 263.
  (d) C. Degrand and L.L. Miller, J. Electroanal. Chem., 117 (1981) 267.
  (e) M. Fukui, C. Degrand and L.L. Miller, J. Am. Chem. Soc., 104 (1982) 28.
  (f) C. Degrand and L.L. Miller, J. Electroanal. Chem., 132 (1982) 163.
164 (a) N. Oyama and F.C. Anson, J. Am. Chem. Soc., 101 (1979) 739.
  (b) N. Oyama and F.C. Anson, J. Am. Chem. Soc., 101 (1979) 3450.
165 N.S. Scott, N. Oyama and F.C. Anson, J. Electroanal. Chem., 110 (1980) 303.
166 G-X. Wan, K. Shigehara, E. Tsuchida and F.C. Anson, J. Electroanal. Chem., 179 (1984) 239.
167 J.M. Calvert and T.J. Meyer, Inorg. Chem., 20 (1981) 27.
168 G.J. Samuels and T.J. Meyer, J. Am. Chem. Soc., 103 (1981) 307.
169 J.M. Calvert, B.P. Sullivan and T.J. Meyer, in J.S. Miller (Ed.), Chemical Modification of Surfaces, Adv. Chem. Ser. 192, American Chemical Society, Washington, DC, 1982, p. 159.
170 C.D. Ellis and T.J. Meyer, Inorg. Chem., 23 (1984) 1748.
171 (a) J.T. Hupp, J.P. Otruba, S.J. Paurs and T.J. Meyer, J. Electroanal. Chem., 190 (1985) 287.
  (b) T.D. Westmoreland, J.M. Calvert, R.W. Murray and T.J. Meyer, J. Chem. Soc. Chem. Commun., (1983) 65.
172 L.D. Margerum, R.W. Murray and T.J. Meyer, J. Phys. Chem., 90 (1986) 728.
173 O. Haas and J.G. Vos, J. Electroanal. Chem., 113 (1980) 139.
174 O. Haas, M. Kriens and J.G. Vos, J. Am. Chem Soc., 103 (1981) 1318.
175 (a) O. Haas, H.R. Zumbrunnen and J.G. Vos, Electrochim. Acta, 30 (1985) 1551.
  (b) C.P. Andrieux, O. Haas and J-M. Saveant, J. Am. Chem. Soc., 108 (1986) 8175.
176 S. Geraty and J.G. Vos, J. Electroanal. Chem., 176 (1984) 389.
177 J.M. Calvert, R.H. Schmehl, B.P. Sullivan, J.S. Facci, T.J. Meyer and R.W. Murray, Inorg. Chem., 22 (1983) 2151.
178 T.F. Guarr and F.C. Anson, J. Phys. Chem., 91 (1987) 4037.
179 T. Ikeda, R. Schmehl, P. Denisevich, K. Willman and R.W. Murray, J. Am. Chem. Soc., 104 (1982) 2683.
180 (a) T. Ikeda, C.R. Leidner and R.W. Murray, J. Am. Chem. Soc., 103 (1981) 7422.
  (b) T. Ikeda, C.R. Leidner and R.W. Murray, Rev. Polarog. Jpn., 27 (1981) 54.
181 P. Denisevich, H.D. Abruña, C.R. Leidner, T.J. Meyer and R.W. Murray, Inorg. Chem., 21 (1982) 2153.
182 K.W. Willman and R.W. Murray, J. Electroanal. Chem., 133 (1982) 211.
183 T. Ikeda, C.R. Leidner and R.W. Murray, J. Electroanal. Chem., 138 (1982) 343.
184 (a) C.R. Leidner and R.W. Murray, J. Am. Chem. Soc., 106 (1984) 1606.
  (b) C.R. Leidner and R.W. Murray, J. Am. Chem. Soc., 107 (1985) 551.
  (c) J.S. Facci, R.H. Schmehl and R.W. Murray, J. Am. Chem. Soc., 104 (1982) 4959.
185 B.J. Feldman, A.E. Ewing and R.W. Murray, J. Electroanal. Chem., 194 (1985) 63.
186 H.D. Abruña, J.M. Calvert, C.D. Ellis, T.J. Meyer, R.W. Murray, B.P. Sullivan and J.L. Walsh, in J.S. Miller (Ed.), Chemical Modification of Surfaces Adv. Chem. Ser., 192, American Chemical Society, Washington, DC, 1982, p. 133.
187 P.G. Pickup, W. Kutner, C.R. Leidner and R.W. Murray, J. Am. Chem. Soc., 106 (1984) 1991.

188 C.E.D. Chidsey and R.W. Murray, Science, 231 (1986) 25.

189 T.R. O'Toole, L.D. Margerum, T.D. Westmoreland, W.J. Vining, R.W. Murray and T.J. Meyer, J. Chem. Soc. Chem. Commun., (1985) 1416.

190 (a) S. Kanda and R.W. Murray, Bull. Chem. Soc. Jpn., 58 (1985) 3010.
(b) L.D. Margerum, T.J. Meyer and R.W. Murray, J. Electroanal. Chem., 149 (1983) 279.

191 W.J. Vining, N.A. Surridge and T.J. Meyer, J. Phys. Chem., 90 (1986) 2281.

192 (a) P.G. Pickup, C.R. Leidner, P. Denisevich and R.W. Murray, J. Electroanal. Chem., 164 (1984) 39.
(b) C.R. Leidner, P. Denisevich, K.W. Willman and R.W. Murray, J. Electroanal. Chem., 164 (1984) 63.

193 J.M. Calvert, D.L. Peebles and R.J. Nowak, Inorg. Chem., 24 (1985) 3111.

194 (a) K.T. Potts, D. Usifer, A. Guadalupe and H.D. Abruña, J. Am. Chem. Soc., 109 (1987) 3961.

195 C.D. Ellis, L.D. Margerum, R.W. Murray and T.J. Meyer, Inorg. Chem., 22 (1983) 1283.

196 (a) K.A. Macor and T.G. Spiro, J. Am. Chem. Soc., 105 (1983) 5601.
(b) K.A. Macor and T.G. Spiro, J. Electroanal. Chem., 163 (1984) 223.
(c) R.M. Kellet and T.G. Spiro, Inorg. Chem., 24 (1985) 2378.

197 B.A. White and R.W. Murray, J. Electroanal. Chem., 189 (1985) 345.

198 (a) G. Bidan, A. Deronzier and J-C. Moutet, J. Chem. Soc. Chem. Commun., (1984) 1185.
(b) S. Cosneir, A. Deronzier and J-C. Moutet, J. Electroanal. Chem., 193 (1985) 193.
(c) S. Cosnier, A. Deronzier and J-C. Moutet, J. Phys. Chem., 89 (1985) 4895.
(d) S. Cosnier, A. Deronzier and J-C. Moutet, J. Electroanal. Chem., 207 (1986) 315.

199 J.G. Eaves, H.S. Munro and D. Parker, J. Chem. Soc. Chem. Commun., (1985) 684.

200 G. Schiavon, G. Zotti and G. Bontempelli, J. Electroanal. Chem., 161 (1984) 323.

201 M. Yamana, R. Darby, H.P. Dhar and R.E. White, J. Electroanal. Chem., 152 (1983) 261.

202 J. Asseraf, F. Bedioui, O. Reges, Y. Robin, F. Devynck and C. Bed-Charreton, J. Electroanal. Chem., 170 (1983) 255.

203 N. Oyama and F.C. Anson, Anal. Chem., 52 (1980) 1192.

204 (a) N. Oyama, K. Sato and F.C. Anson, J. Electroanal. Chem., 115 (1980) 149.
(b) N. Oyama, T. Ohsaka and T. Ushirogouchi, J. Phys. Chem., 88 (1984) 5274.

205 N. Oyama, K. Sato and H. Matsuda, J. Electroanal. Chem., 115 (1980) 149.

206 H.R. Zumbrunnen and F.C. Anson, J. Electroanal. Chem., 152 (1983) 111.

207 (a) K. Doblhofer, H. Braun and W. Storck, J. Electrochem. Soc., 130 (1983) 807.
(b) H. Braun, F. Decker, K. Doblhofer and H. Sotobayashi, Ber. Bunsenges. Phys. Chem., 88 (1984) 345.
(c) K. Doblhofer, H. Braun and R. Lange, J. Electroanal. Chem., 206 (1986) 93.
(d) K. Niwa and K. Doblhofer, Electrochim. Acta, 31 (1986) 553.

208 E.S. De Castro, E.W. Huber, D. Villaroel, C. Galiatsatos, J.E. Mark, W.E. Heineman and P.T. Murray, Anal. Chem., 59 (1987) 134.

209 F.C. Anson, T. Ohsaka and J-M. Saveant, J. Am. Chem. Soc., 105 (1983) 4883.

210 K. Sumi and F.C. Anson, J. Phys. Chem., 90 (1986) 3845.

211 (a) T. Ohsaka, T. Okajima and N. Oyama, J. Electroanal. Chem., 215 (1986) 191.
(b) N. Oyama, T. Ohsaka and T. Okajima, Anal. Chem., 58 (1986) 981.

212 B.R. Shaw, G.P. Haight, Jr. and L.R. Faulkner, J. Electroanal. Chem., 140 (1982) 147.

213 W.J. Vining and T.J. Meyer, J. Electroanal. Chem., 195 (1985) 183.

214 W.J. Vining and T.J. Meyer, Inorg. Chem., 25 (1986) 2023.

215 Nafion is a trademark of E.I. DuPont de Nemours, Inc.

216 A. Eisenberg and H.L. Yeager (Eds.), Perfluoro Sulfonate Ionomer Membranes, A.C.S. Symposium Series 180, American Chemical Society, Washington, DC, 1982.
217 M.N. Szentirmay and C.R. Martin, Anal. Chem., 56 (1984) 1898.
218 (a) C.R. Martin, Anal. Chem., 54 (1982) 1639.
(b) R.B. Moore III and C.R. Martin, Anal. Chem., 58 (1986) 2569.
219 D.A. Buttry and F.C. Anson, J. Am. Chem. Soc., 104 (1982) 4824.
220 H.Y. Liu and F.C. Anson, J. Electroanal. Chem., 158 (1983) 181.
221 D.A. Buttry and F.C. Anson, J. Am. Chem. Soc., 106 (1984) 59.
222 D.A. Buttry, J-M. Saveant and F.C. Anson, J. Phys. Chem., 88 (1984) 3086.
223 R.C. McHatton and F.C. Anson, Inorg. Chem., 23 (1984) 3935.
224 K. Shigehara, E. Tsuchida and F.C. Anson, J. Electroanal. Chem., 175 (1984) 291.
225 F.C. Anson, J-M. Saveant and Y-M. Tsou, J. Electroanal. Chem., 178 (1984) 113.
226 F.C. Anson, C-L. Ni and J-M. Saveant, J. Am. Chem. Soc., 107 (1985) 3442.
227 Y-M. Tsou and F.C. Anson, J. Phys. Chem., 89 (1985) 3818.
228 I. Rubinstein and A.J. Bard, Anal. Chem., 53 (1981) 102.
229 M. Krishnan, J.R. White, M.A. Fox and A.J. Bard, J. Am. Chem. Soc., 105 (1983) 7002.
230 A. Mau, C.B. Huang, N. Kakuta, A. Campion, M.A. Fox, J.M. White, S.E. Webber and A.J. Bard, J. Am. Chem. Soc., 106 (1984) 6537.
231 J.G. Gaudiello, P.K. Ghosh and A.J. Bard, J. Am. Chem. Soc., 107 (1985) 3027.
232 A.E. Kaifer and A.J. Bard, J. Phys. Chem., 90 (1986) 868.
233 J. Leddy and A.J. Bard, J. Electroanal. Chem., 189 (1985) 203.
234 C.R. Martin and K.A. Dollard, J. Electroanal. Chem., 159 (1983) 127.
235 G. Nagy, G.A. Gerhardt, A.F. Oke, M.E. Rice, R.N. Adams, R.B. Moore III, M.N. Szentirmay and C.R. Martin, J. Electroanal. Chem., 188 (1985) 85.
236 C.R. Martin, J. Chem. Soc. Faraday Trans. 1, 82 (1986) 1051.
237 R.M. Penner and C.R. Martin, J. Electrochem. Soc., 132 (1985) 514.
238 J. Redepenning and F.C. Anson, J. Phys. Chem., 90 (1986) 6227.
239 (a) C.M. Lieber, M.H. Schmidt and N.S. Lewis, J. Am. Chem. Soc., 108 (1986) 6103.
(b) C.M. Lieber, M.H. Schmidt and N.S. Lewis, J. Phys. Chem., 90 (1986) 1002.
240 For a recent review see K. Itaya, I. Uchida and V.D. Neff, Acc. Chem. Res., 19 (1986) 162.
241 V.D. Neff, J. Electrochem. Soc., 125 (1978) 886.
242 A.B. Bocarsly and S. Sinha, J. Electroanal. Chem., 137 (1982) 157.
243 A.B. Bocarsly and S. Sinha, J. Electroanal. Chem., 140 (1982) 167.
244 A.B. Bocarsly, S.A. Galvin and S. Sinha, J. Electrochem. Soc., 130 (1983) 1319.
245 B.D. Humphrey, S. Sinha and A.B. Bocarsly, J. Phys. Chem., 88 (1984) 736.
246 S. Sinha, B.D. Humphrey, E. Fu and A.B. Bocarsly, J. Electroanal. Chem., 162 (1984) 351.
247 S. Sinha, B.D. Humphrey and A.B. Bocarsly, Inorg. Chem., 23 (1984) 203.
248 L.J. Amos, M.H. Schmidt, S. Sinha and A.B. Bocarsly, Langmuir, 2 (1986) 561.
249 D.W. DeBerry and A. Viehbeck, J. Electrochem. Soc., 130 (1983) 249.
250 (a) L.M. Siperko and T. Kuwana, J. Electrochem. Soc., 130 (1983) 396.
(b) L.M. Siperko and T. Kuwana, J. Electrochem. Soc., 133 (1986) 2440.
251 K. Itaya, N. Shoji and I. Uchida, J. Am. Chem. Soc., 106 (1984) 3423.
252 T. Ikeshoji, J. Electrochem. Soc., 133 (1986) 2108.
253 D. Shaojun and L. Fengbin, J. Electroanal. Chem., 210 (1986) 31.
254 R.J. Mortimer and D. Rosseinsky, J. Electroanal. Chem., 151 (1983) 133.
255 K. Ogura and M. Takagi, J. Electroanal. Chem., 206 (1986) 209.
256 C.J. Miller and M. Majda, J. Am. Chem. Soc., 107 (1985) 1419.

257 C.J. Miller and M. Majda, J. Electroanal. Chem., 207 (1986) 49.
258 C.J. Miller and M. Majda, J. Am. Chem. Soc., 108 (1986) 3118.
259 A.J. Bard and P.K. Ghosh, J. Am. Chem. Soc., 105 (1983) 5691.
260 P.K. Ghosh, A.W.-H. Mau and A.J. Bard, J. Electroanal. Chem., 169 (1984) 315.
261 D. Ege, P.K. Ghosh, J.R. White, J-F. Equey and A.J. Bard, J. Am. Chem. Soc., 107 (1985) 5644.
262 J.R. White and A.J. Bard, J. Electroanal. Chem., 197 (1986) 233.
263 K. Itaya and A.J. Bard, J. Phys. Chem., 89 (1985) 5565.
264 W.E. Rudzinski and A.J. Bard, J. Electroanal. Chem., 199 (1986) 323.
265 H.Y. Liu and F.C. Anson, J. Electroanal. Chem., 184 (1985) 411.
266 C.G. Murray, R.J. Nowak and D.R. Rolison, J. Electroanal. Chem., 164 (1984) 205.
267 T.J. Meyer, J. Electrochem. Soc., 131 (1984) 221C.
268 F.C. Anson, J. Phys. Chem., 84 (1980) 3336.
269 R.W. Murray, Philos. Trans. R. Soc. London Ser. A, 302 (1981) 253.
270 A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980, Chap. 8.
271 J.P. Collman and K. Kim, J. Am. Chem. Soc., 108 (1986) 7847.
272 C.M. Lieber and N.S. Lewis, J. Am. Chem. Soc., 106 (1984) 5033.
273 (a) C.R. Cabrera and H.D. Abruña, J. Electroanal. Chem., 209 (1986) 101.
(b) A.I. Breikss and H.D. Abruña, J. Electroanal. Chem., 201 (1986) 347.
274 (a) B.P. Sullivan and T.J. Meyer, J. Chem. Soc. Chem. Commun., (1984) 1244.
(b) B.P. Sullivan, C.M. Bolinger, D. Conrad, W.J. Vining, R.W. Murray and T.J. Meyer, J. Chem. Soc. Chem. Commun., (1985) 1416.
(c) T.R. O'Toole, L.D. Margerum, T.D. Westmoreland, W.J. Vining, R.W. Murray and T.J. Meyer, J. Chem. Soc. Chem. Commun., (1985) 1416.
275 S. Cosnier, A. Deronzier and J-C. Moutet, J. Electroanal. Chem., 207 (1986) 315.
276 (a) J. Hawecker, J-M. Lehn and R. Ziessel, J. Chem. Soc. Chem. Commun., (1983) 536.
(b) J. Hawecker, J-M. Lehn and R. Ziessel, J. Chem. Soc. Chem. Commun., (1984) 328.
(c) J. Hawecker, J-M. Lehn and R. Ziessel, J. Chem. Soc. Chem. Commun., (1985) 56.
277 J. Hawecker, J-M. Lehn and R. Ziessel, Helv. Chim. Acta, 69 (1986) 1990.
278 H.D. Abruña and A.J. Bard, J. Am. Chem. Soc., 103 (1981) 6898.
279 H.S. White, H.D. Abruña and A.J. Bard, J. Electrochem. Soc., 129 (1982) 265.
280 R. Noufi, J. Electrochem. Soc., 130 (1983) 2126.
281 D.L. Dubois and J.A. Turner, J. Am. Chem. Soc., 104 (1982) 4989.
282 H. Yoneyama, J. Shiota and H. Tamura, J. Electroanal. Chem., 159 (1983) 361.
283 R.E. Malpas, F.R. Mayers and A.G. Osborne, J. Electroanal. Chem., 153 (1983) 92.
284 R.E. Malpas and B. Rushby, J. Electroanal. Chem., 157 (1983) 382.
285 D.L. Dubois, Inorg. Chem., 23 (1984) 2047.
286 M.D. Rosenblum and N.S. Lewis, J. Phys. Chem., 88 (1984) 3103.
287 K. Rajeshwar, M. Kaneko, A. Yamada and R.N. Noufi, J. Phys. Chem., 89 (1985) 806.
288 K. Honda and A.J. Frank, J. Phys. Chem., 88 (1984) 5577.
289 A.R. Guadalupe and H.D. Abruña, Anal. Chem., 57 (1985) 142.
290 L.M. Wier, A.R. Guadalupe and H.D. Abruña, Anal. Chem., 57 (1985) 2009.
291 A.R. Guadalupe, L.M. Wier and H.D. Abruña, Am. Lab., 18(8) (1986) 102.
292 M-C. Pham, G. Tourillon, P-C. Lacaze and J.E. Dubois, J. Electroanal. Chem., 111 (1980) 385.
293 J.A. Cox and P.J. Kulesza, J. Electroanal. Chem., 159 (1983) 337.
294 K.H. Lubert, M. Schnurrbush and M. Thomas, Anal. Chim. Acta, 144 (1982) 123.
295 M.J. Gehron and A. Brajter-Toth, Anal. Chem., 58 (1986) 1488.

296 F.R. Keene, D.J. Salmon, J.L. Walsh, H.D. Abruña and T.J. Meyer, Inorg. Chem., 19 (1980) 1968.
297 (a) G.P. Kittlesen, H.S. White and M.S. Wrighton, J. Am. Chem. Soc., 106 (1984) 7389. (b) G.P. Kittlesen, H.S. White and M.S. Wrighton, J. Am. Chem. Soc., 107 (1985) 7373.
298 E.W. Paul, A.J. Ricco and M.S. Wrighton, J. Phys. Chem., 89 (1985) 1441.
299 J.W. Thackeray, H.S. White and M.S. Wrighton, J. Phys. Chem., 89 (1985) 5133.
300 M.J. Natan, T.E. Mallouk and M.S. Wrighton, J. Phys. Chem., 91 (1987) 648.
301 M.S. Wrighton, Science, 231 (1986) 32.