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CLAY-MODIFIED ELECTRODES: A REVIEW

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Abstract—Clay-modified electrode research indicates that adsorbed complexes are electroactive if the adsorption sites are clay edges. Interlayer adsorbed complexes may be electroactive if a charge shuttle is added or if interlayer swelling is large. Conductivity of the film towards anionic species depends upon the swelling of the clay, which depends on the electrolyte concentration and speciation. The diffusion coefficients measured by electrochemical experiments agree well with alternative measurements.

Key Words—Adsorption, Clay-modified electrode, Conductivity, Diffusion, Electrochemistry.

INTRODUCTION

Modified electrodes have been extensively used in the last decade by electrochemists attempting to control the direction and extent of electrode reactions. A variety of electrochemical techniques have been developed for the purpose of elucidating the formal potential of the electroactive substance and the diffusion coefficients of the reactants and products within the film. Clay-modified electrodes have attracted the attention of many electrochemists because of the ion exchange properties of the clay and because of the unique layered structure of the material. No review of the clay-modified electrode field has been published in the clay literature. A summary of the types of experiments performed to date and the information obtained from those experiments may stimulate further input from the clay community into the field of modified electrode electrochemistry.

DESCRIPTION OF MODIFIED ELECTRODES

By placing a film at an electrode surface and studying the redox reactions of a series of probe molecules, the effect of the film on the transport of the probe to the electrode surface can be studied. A typical experiment might consist of a modified electrode placed in a solution containing an electroactive probe ion, as diagrammed in Figure 1. The electrode (e.g., Pt, pyrolytic graphite, optically transparent SnO_2) is encased in a nonconducting support (e.g., glass, Teflon, inert glue such as Torr Seal) so that a single surface is exposed. A modifying layer is attached chemically or by dispersion forces to the entire surface of the electrode plus inert shield. The dimensions of the modifying layer must be large enough to exceed the area of the entire electrode base. The thickness, w, of the modifying layer ranges from submicrometer to a few micrometers. A typical clay-modified electrode was prepared in the author's laboratory by drying a small amount of clay on Pt. Sample SWy-1 was obtained from the Source Clays Repository of The Clay Minerals Society and prepared by stirring 10 g of clay in 200 ml of distilled water for 48 hr, centrifuging the suspension at 500 rpm for 1 hr, and collecting and freeze drying the supernatant. The freeze-dried clay was suspended (typically 5 g clay/liter) in deionized, distilled water and held in suspension for a period of months. A drop of the clay suspension (1 μl of the 5 g/liter solution) was dried on the surface of a Pt electrode for 10 min at 100°C.

Typically, the entire electrode is next bathed in an electrolyte solution for 5 min and then transferred to a solution containing the probe ion. On exposure to the bulk solution, the electroactive probe partitions between the bulk solution and the film, thereby creating a layer near the electrode surface, which is perturbed in concentration compared with the bulk bathing solution. For a cation-exchange modified electrode, such as montmorillonite-modified Pt, the cation concentration is enhanced in the vicinity of the substrate Pt (Figure 1). Current is observed if the probe is either reduced or oxidized at the electrode surface. This occurs if the concentration of the probe is pinned to zero at the electrode surface via an applied potential (Figure 1). The magnitude of the current depends on the rate-limiting step in the overall electrode reaction. In Figure 2, five possible (out of a multitude) rate-limiting steps are diagrammed. The steps diagrammed are those that might occur as the electroactive probe makes its way to the electrode surface in response to the potential step. Any one of the diagrammed reaction steps can be rate limiting. For example, a compound, Z, may first be converted to its product, A (reaction 1), followed by fast diffusion to the electrode (reaction 2), fast electron transfer to form the reduced species, A (reaction 3), and fast diffusion away of the reduced species (reaction 4) and/or conversion of the reduced A to a final product, B. Any one of the above steps may be rate limiting, giving a characteristic signature to the electrode reaction. For many cases, the rate and equilibrium constants for reactions 1 and/or 5 may be determined, as well as the equilibrium constants. Even

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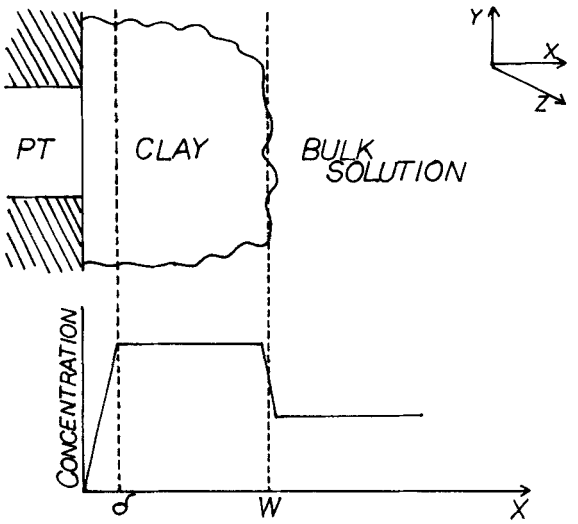


Figure 1. Diagram of a clay-modified electrode. Underlying Pt electrode is encased in an insulating material (cross hatched area) and covered with clay. Concentration of cationic species in solution ($x \rightarrow \infty$) is enhanced within the clay film ($x < w$) due to the negative charge of the clay and is depleted within the diffusion layer ($x < d$) at the surface of the electrode via a reduction/oxidation reaction at the electrode. Diffusion occurs primarily perpendicular to electrode surface in the x direction compared with y and z directions parallel to the electrode surface.

in the simplest diffusion-reaction mechanism (reactions 2 and 4 are rate limiting) information can be obtained from the electrochemical experiment, which is directly related to the presence and chemistry of the modifying film. Current is limited either by diffusion of the redox couple or associated counterions within the film.

ELECTROCHEMICAL EXPERIMENTATION

The current in an electrochemical experiment depends, in some explicit fashion, on three parameters: the diffusion coefficient, D; the accessible area of the underlying electrode; and the concentration of the species within the film. For example, in cyclic voltametry, the potential at the surface of the underlying electrode is swept in a linear fashion from some initial potential, E_i, negative to some switching potential, E_s, and back again to the E_i (Figure 3). If a species is present whose formal potential for reduction, E°, lies between E_i and E_s, a current corresponding to the reduction of the species will be observed in the negative sweep, and a current corresponding to the oxidation of the reduced material will be observed in the positive sweep. The current, plotted against potential, will have a peak shape if linear (perpendicular to the electrode surface) diffusion to the electrode surface occurs. The peak current can be described by:

$$i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}\nu^{1/2}C_0^*, \quad (1)$$

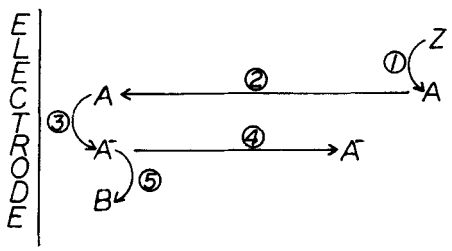


Figure 2. Possible rate-limiting steps in an electrochemical reaction. (1) An electroinactive species, Z, converts to A. (2) A diffuses to the electrode surface. (3) A is reduced (or oxidized) to its product A^-. (4) A^- diffuses away from the electrode surface. (5) A^- is converted to another chemical species, B.

where i_p is the peak current observed in amperes, n is the number of electrons involved in the reduction process, A is the area of the electrode in cm^2, D is the diffusion coefficient for the oxidized species in cm^2/s, ν is the rate at which the potential is swept (V/s), and C_0^* is the concentration of the oxidized species before the electrochemical perturbation is applied, in mole/cm^3 (Bard and Faulkner, 1980). For linear diffusion, E° is midway between the reduction and oxidation peaks.

If the electrochemical experiment is carried out at a modifying layer, the same relationships hold, except that the area of the conductive channel can now play an important role in defining the type of diffusion behavior observed (Amatore *et al.*, 1983a, 1983b; Sabatani and Rubinstein, 1987). Furthermore, if the distance δ sampled by the electrochemical experiment is much smaller than the layer modifying the electrode, w (Figure 1), the experiment can be considered to be

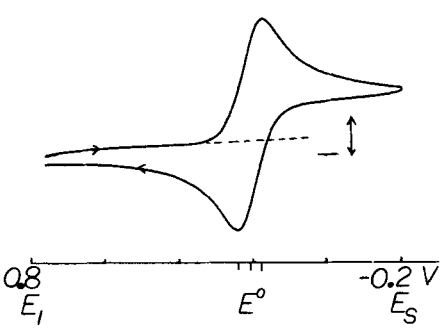


Figure 3. Cyclic voltametric experiment for the reduction of $Fe(CN)_6^{3-}$ (4 mM) at a bare Pt electrode in 0.7 M NaCl. In the forward potential sweep past E° (from E_i to E_s) a reduction peak is observed. In the reverse potential sweep past E° (from E_s to E_i) an oxidation peak is observed. The bar defines 0.1 μA of current. The peak height, measured from the extrapolated baseline, is dependent on scan rate, diffusion coefficient, and concentration of the complex. The formal potential for the reduction is determined from the midpoint between the two current peaks.

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a normal electrochemical experiment within a new medium. Here, D, C_0^*, and E° will be determined by the chemistry of the modifying layer.

All of the parameters accessible to the electrochemist depend upon the competitive exchange reaction as shown for a trivalent/monovalent exchange reaction:

$$A^{3+} + 3\,NaX = A^{3+}X_3 + 3\,Na^+, \quad (2)$$

where A^{3+} is an exchanging trivalent species, NaX is a single clay site containing a Na^+ counterion, and $A^{3+}X_3$ is the clay exchanged with the trivalent species. The selectivity coefficient for the exchange is:

$$K_{III} = [Na^+]^3[A^{3+}X_3]/[A^{3+}][NaX]^3. \quad (3)$$

The magnitude of D is directly dependent on the distance, d, between equilibrium sites, and exponentially dependent on $-E/RT$, where E is the activation energy necessary to leave the equilibrium site, R is the natural gas constant, and T is the temperature (Jost, 1952). E is related to K_{III}, or analogously, to K_{II}, for a divalent species. As the energy of interaction between a site and an intercalated molecule increases, the diffusion coefficient diminishes. Also, as the number of sites increases, the distance between sites decreases, so that the distance traveled in any one "hop" is small, and the observed diffusion coefficient decreases. Experimentally, if A and C_0^* are known, D can be obtained from a plot of i_p vs. $\nu^{1/2}$.

The magnitudes of C_0^* and E° for any bathing solution are also determined by the value of the selectivity coefficient. If the species sampled is A^{3+}, then C_0^* in Eq. (1) is equal to $[A^{3+}]$, and the measured current will depend upon the magnitude of K_{III}, [NaX], and $[Na^+]$. Concentrations of and, hence, currents for A^{3+} should be suppressed in the presence of large concentrations of Na^+. Experimentally, C_0^* can be determined by ultraviolet-visible (UV-VIS) absorption measurements at an optically transparent electrode (Ege *et al.*, 1985) by operating under conditions where the exchange reaction (2) is forced to completion, or by a coulometric measurement of the total charge, Q, within the film. The charge can be related to the total number of moles in the film through the simple relationship:

$$Q = nFN, \quad (4)$$

where F is the Faraday constant and n is the number of electrons involved in the reduction (or oxidation) process. N is the number of moles of electroactive species present and can be converted to a concentration if the volume of the film is known. This conversion is usually accomplished by combining the measurable area of the film with a value for the clay film thickness, as estimated in a variety of ways (White and Bard, 1986; Carter and Bard, 1987; Fitch *et al.*, 1988; Itaya *et al.*, 1987; Liu and Anson, 1985; Inoue *et al.*, 1988). For details on estimating the film thickness, these references should be consulted. Once C_0^* is known, the value of D can be determined from Eq. (1).

A second method for determining D is available. If the current at the electrode is governed not only by linear diffusion along the x dimension (perpendicular to the electrode), but in the y and z directions (parallel to the electrode surface) (Figure 1), as would occur for an electrode whose area is small with respect to the diffusion layer, δ, the current transient observed if the electrode potential is stepped from some potential positive of the formal potential (no observed current) to some potential well negative of the formal potential is:

$$it^{1/2} = nFAD^{1/2}C_0^*/\Pi^{1/2} + bC_0^*nFADt^{1/2}/\Pi^{1/2}R. \quad (5)$$

In Eq. (5), n is the number of electrons involved in the redox reaction, F is the Faraday constant, b is a constant whose value is about 2, R is the radius of the electrode (usually about 10 μm), and A, D, and C_0^* are defined as for Eq. (1) (Yap and Doane, 1982; Heinze, 1981; Aoki and Osteryoung, 1984). A plot of $it^{1/2}$ vs. $t^{1/2}$ yields a slope, S, and an intercept, I, which can be combined to give:

$$S/I = bD^{1/2}/R, \quad (6)$$

from which D can be determined in the absence of concrete knowledge of the film concentration.

Finally, combining expressions for divalent and trivalent exchange with the Nernst equation yields an expression for the shift (ΔE) in the observed formal potential in the film (E°_{app}) with respect to the solution formal potential (E°_{soln}) of the couple (Fitch, 1990):

$$\begin{aligned}\Delta E &= E^\circ_{app} - E^\circ_{soln} \\ &= (RT/nF)\ln(K_{II}/K_{III}[NaCl] \\ &\quad + (RT/nF)\ln C_{Na}. \end{aligned} \quad (7)$$

In Eq. (7), [NaC] is the number of exchange sites occupied by Na^+, and C_{Na} is the analytical concentration of Na^+, which approximates the equilibrium concentration of Na^+ if the bulk solution volume is large with respect to the volume of the film on the surface of the electrode. If a clay-modified electrode is exposed to a solution containing only the Na^+ electrolyte and a trivalent exchanging complex, the potential shifts positive as a function of the analytical concentration of the trivalent complex, C_{AIII}, and the total number of exchange sites, C_X, if C_{Na} is constant, as shown in Figure 4. The shift in potential is a function of the magnitude of the trivalent/Na^+ exchange constant. Naegeli *et al.* (1986) showed that the potential shift in Nafion (a cation-exchange polymer)-modified electrode should shift by 59 mV per decade in the electrolyte concentration. This shift is shown as line AB in Figure 4.

Experimentally, a clay-modified electrode is placed in an electrolyte solution containing the test ion of interest. The uptake of this ion can be monitored by performing multisweep-cyclic voltametry and observing the increase in the reduction and oxidation peaks with time. When a steady state voltamogram has been

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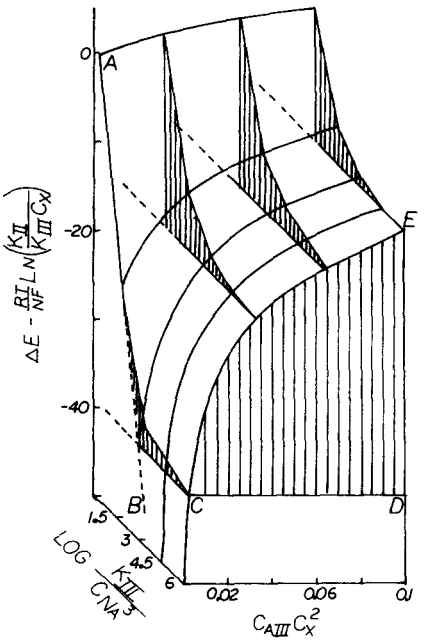


Figure 4. Plot of difference between apparent formal potential for the reduction of A^{3+} within the clay film and formal potential at a bare electrode (ΔE) as a function of the divalent and trivalent exchange constants, K_{II} and K_{III}, the total number of exchange sites present, C_x, and the bathing solution concentrations of A^{3+}, C_{AIII}, and Na^+, C_{Na}. ΔE is offset by a constant related to the exchange constants and C_x. In all cases, potential shifts positive with bathing solution concentration of A^{3+}, C_{AIII}. The 59 mV/decade change in potential with $[Na^+]$ (line AB) was predicted by Naegeli *et al.* (1986).

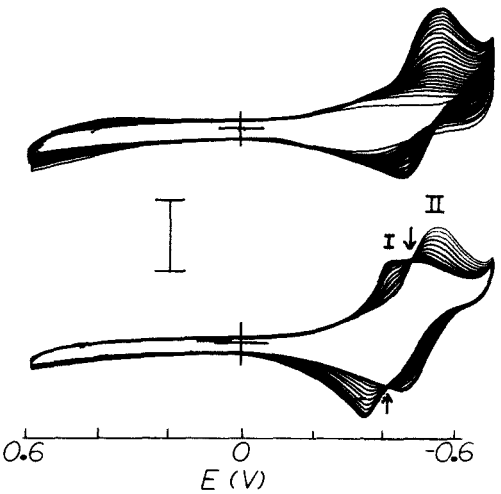


Figure 5. Uptake of 0.1 mM $Cr(bpy)_3^{3+}$ in 0.01 M Na_2SO_4 by SWy-1 montmorillonite-modified Pt electrode as measured by increases in current with time (bar marks 0.5 μA). Peak II first increases (upper) and then decreases as peak I increases (lower). Arrows mark location of isopotential points. Isopotential points can aid in the analysis of the rate of conversion of the electroactive species associated with peak II to the electroactive species associated with peak I. From Fitch *et al.* (1988).

reached, the electrode is transferred to a solution containing the electrolyte only, allowing freely diffusing substrate to be washed from the open pores. Following transfer, the scan rate, ν, is varied in the cyclic voltametric experiment to determine if the peak current varies with $\nu^{1/2}$ as predicted (Eq.(1)). If the concentration within the film is independently determined, the diffusion coefficient can be deduced, as described above.

In some experiments, the clay-modified electrode is soaked for an extended period of time in the electrolyte solution containing the substrate. A cyclic voltamogram corresponding to presumably, the steady-state concentration of the substrate within the film is then obtained. Two difficulties arise from this method. As noted below, film reorientation can occur during extended soaking. Additionally, the method results in some loss of information. For example, Fitch *et al.* (1988), in tracing the uptake of $Cr(bpy)_3^{3+}$ into an aerogel SWy-1 smectite clay-modified Pt electrode (Figure 5), observed two discrete reducible species. The species reduced at the more positive potential was clearly the product of some reaction involving the first appearing species in the clay. By observing the entire time-dependent process, the rate of conversion between the two species was determined.

CONDUCTIVITY OF CLAY-MODIFIED ELECTRODES

Current observed at a clay-modified electrode depends on both the porosity of the clay film and on the nature and number of sites responsible for the partitioning of the complex into the film. The porosity can be affected by the initial preparation of the film and the bathing solution. Ghosh and Bard (1983) obtained swollen (porous) films by drying clay in the presence of polyvinyl alcohol (PVA). The presence of PVA was thought to force the clay into a swollen configuration suitable for charge transport through the film. Liu and Anson (1985) and Ege *et al.* (1985), however, indicated that conductive films could be obtained without the addition of PVA.

The electrolyte and solvent can play a role in the conductivity of the film. (Electrolyte, in an electrochemical experiment, is always present to complete the current circuit between the clay-modified "working" electrode and the "counter" electrode.) Itaya and Bard (1985) compared the currents obtained for $Fe(bpy)_3^{2+}$ at pillared and nonpillared clay-modified electrodes in aqueous and nonaqueous media. In nonpillared clay-modified electrodes, currents for $Fe(bpy)_3^{2+}$ were suppressed in aqueous solutions of Li^+, K^+, and tetraethylammonium cation (TEA^+). In nonaqueous solutions, currents were reduced in the presence of $NaClO_4$ in

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ethanol and methanol, but not in dimethylformamide. If the clay was pillared, all currents were diminished, presumably by loss of cation-exchange sites. The differences observed between solvents for the nonpillared clay, however, were eliminated on pillaring, suggesting that solvation of the electrolyte is important in conductivity. The pillared clay, having an interlayer distance of about 7 Å, excluded the anion, $Fe(CN)_6^{3-}$.

Lee and Fitch (1990) examined SWy-1 montmorillonite-modified electrodes for a variety of film preparation and electrolyte conditions in order to elucidate the role of swelling. Inasmuch as the arrival of the anion, $Fe(CN)_6^{3-}$, at the electrode is constrained primarily by the available pore space, it was chosen as a marker of film structure effects. A clay film formed from spinning of the electrode showed a single well-defined X-ray powder diffraction (XRD) peak at 11 Å, whereas a clay film formed by oven or air drying showed a diffuse XRD peak centered at about 18 Å plus peaks at 11 and 3.1 Å. The single diffraction peak observed for the spin-coated electrode was attributed to the formation of a well-ordered film. The multiple XRD peaks observed for the air- and oven-dried electrodes were attributed to the presence of random orientations of the clay platelets that resulted in edge-to-face crosslinking of the film. These initial structural differences were observed in the conductivity of the films. A spin-coated electrode exposed to 0.02 M NaCl gave a time-invariant value for $Fe(CN)_6^{3-}$ reduction currents immediately upon exposure to the electrolyte. In contrast, an oven-dried electrode exposed to 0.02 M NaCl showed a reduction current for 0.4 mM $Fe(CN)_6^{3-}$ that was initially lower than that obtained for the spin-coated electrode and approached that of the spin-coated electrode over a 30-min time period. This was interpreted as the inhibition of swelling of the air- or oven-dried electrode by the presence of edge-to-face crosslinking bonds. In the presence of a larger electrolyte concentration the oven-dried film showed a faster increase in the reduction current for 0.4 mM $Fe(CN)_6^{3-}$.

The maximum reduction current for 0.4 mM $Fe(CN)_6^{3-}$ was a function of the nature of the cation of the supporting electrolyte. In the presence of CsCl and KCl, no current for $Fe(CN)_6^{3-}$ reduction was observed, whereas in the presence of LiCl, NaCl, and Na_2SO_4, the current was dependent upon the concentration of the cation. The electrolyte concentration dependent reduction of $Fe(CN)_6^{3-}$ was interpreted as resulting from the change in the face-to-face interlayer distance due to known differences in hydration of the electrolyte cation (Norrish, 1954; Sposito and Prost, 1982; Suquet *et al.*, 1975; Méring, 1946).

Inoue *et al.* (1988) attempted to determine the effect of edge vs. interlayer sites in the conductivity of an aerogel clay film with respect to $Ru(bpy)_3^{2+}$ and $Fe(CN)_6^{3-}$ while working at a glassy carbon electrode. They concluded that edge adsorption sites were important in charge conduction. No attempt, however, was made to control the total electrolyte concentration (pH was varied by addition of NaOH and HCl); hence, the swelling changes discussed above might have affected the results. Furthermore, pH can affect the adherence of the film to the electrode surface if a graphite electrode is used. Lee and Fitch (1990) found that reduction currents for $Fe(CN)_6^{3-}$ were affected by the pH changes if a pyrolytic graphic electrode was used but not if a Pt electrode was used. pH can change the amount of fixed charge at the electrode surface, arising from an oxide layer or deprotonated hydroxyl groups. Reduction currents for $Fe(CN)_6^{3-}$ were not affected by the applied electrode potential.

Charge transport for clay-adsorbed electroactive species depends not only on the hydration driven porosity of the film, but also on the number and activity of the reactive sites. Ideally, all cations adsorbed by the clay film will participate in the electrode reaction. In practice, only a few contribute to the observed current. Rudzinski and Bard (1986) found that only 15–30% of $Ru(bpy)_3^{2+}$ adsorbed at SWy-1 montmorillonite and pillared SHCa-1 hectorite-modified electrodes were electroactive. Inasmuch as the external surface area of SHCa-1 (measured by N_2 BET) was only 13% of the total surface area, the authors concluded that the interlayer adsorbed species did not contribute significantly to charge transport in pillared-clay electrodes. These results are consistent with those of Ege *et al.* (1985), who found that about 18% of the adsorbed $Ru(bpy)_3^{2+}$ at SWy-1 and SHCa-1 electrodes was electroactive.

King *et al.* (1987) found that complexes in clay films formed from suspensions of SWy-1 exchanged with $M(bpy)_3^{2+}$ (M = Fe, Os, Ru), $Fe(phen)3^{2+}$, and N,N′-dimethyl-4,4′-bypyridinium (methyl viologen, MV^{2+}) showed no electroactivity. On immersion of the exchanged film into a bulk solution containing additional complex in the presence of Na_2SO_4, electroactivity was observed that was consistent only with the additional complex. Added $Fe(bpy)_3^{2+}$ did not shuttle charge to the $Os(bpy)_3^{2+}$ adsorbed to the clay surface at ion exchange sites, as might be postulated from reactions (8) and (9):

$$\left.\begin{array}{l} Fe(bpy)_3^{2+} \rightleftharpoons e^- + Fe(bpy)_3^{3+} \qquad (8) \\ Fe(bpy)_3^{3+} + Os(bpy)_3^{2+}(Clay^-)_2 + \tfrac{1}{2}SO_4^{2-} \\ \quad \rightleftharpoons Fe(bpy)_3^{2+} + Os(bpy)_3^{3+}(Clay^-)_2(\tfrac{1}{2}SO_4^{2-}) \qquad (9) \end{array}\right\}$$

King *et al.* (1987)

The oxidation mechanism shown in Eq. (9) was one of several discussed by King *et al.* (1987). It is consistent with the fact that bipyridyl complexes are strongly adsorbed by clay surfaces and not likely to be desorbed. The change in Os complex charge on oxidation must be accommodated by anion adsorption, which the au-

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thors suggested is unlikely due to surface-anion charge repulsion. As a consequence, they concluded that all complexes adsorbed in amounts less than the CEC are electroinactive, even in the presence of a charge shuttle. The observed electroactivity, they suggest, must arise from ion-pair adsorption in excess of the CEC and can be correlated with the number of edge sites present, as confirmed by increased magnitude and rate of development of the reduction peak associated with the uptake of the complex from solution into a clay-modified electrodes in the order laponite > montmorillonite > fluorohectorite. This series corresponds to changes in the edge site for an approximately constant total basal area. Similar results were observed for methyl viologen. Fitch *et al.* (1988) also found that $Cr(bpy)_3^{3+}$ in clay films formed from $Cr(bpy)_3^{3+}$-exchanged SWy-1 suspensions were electroinactive; however, if a Na-exchanged SWy-1-modified electrode was placed in $Cr(bpy)_3^{3+}$, extensive electroactivity was observed. They suggested that the method of film preparation plays an important role in access to the adsorbed complex.

Unlike King *et al.* (1987), White and Bard (1986) found that adsorbed methyl viologen (MV) at STx-1-modified electrodes was electroactive. The complex could be reduced easily but could not be reoxidized. In conjunction with electron spin resonance and spectroelectrochemistry, they concluded that a MV^{2+} dimer was formed in an initial reduction step. The dimer was strongly adsorbed to face or planar surfaces of the clay, rendering it immobile and, hence, electroinactive. Unlike the trisbipyridine complexes, the methyl viologen adsorbed on the planar surfaces was found to be electroactive if a charge shuttle, $Fe(CN)_6^{3-}$, was added to the solution:

$$\ulcorner\ Fe(CN)_6^{4-} \leftrightharpoons Fe(CN)_6^{3-} + e^- \quad (10)$$
$$Fe(CN)_6^{3-} + \tfrac{1}{2}(MV^+)_2 \leftrightharpoons MV^{2+} + Fe(CN)_6^{4-} \quad (11)\ \lrcorner$$

Castro-Acuna *et al.* (1987), working with MV^{2+}/STx-1 modified electrodes, found that the addition of polypyrrole resulted in electronically conductive films, whose capacitance was large in the presence of MV^{2+}. The MV^{2+}/polypyrrole clay films showed evidence of greater clay organization (narrower XRD peaks, smaller interlayer spacings) than pure polypyrrole clay films. These effects were observed electrochemically by the presence of symmetrically shaped oxidation and reduction peaks.

Carter and Bard (1987) investigated currents associated with tetrathiafulvalene (TTF) at STx-1 modified electrodes. Two types of adsorbed complexes were observed electrochemically. Type I was associated with a two-electron transfer involving 10% of the ion-exchange sites. Its peak was lost on exposure of the electrode to electrolyte, but was recoverable. No potential shifts associated with the electrolyte were observed. Type-II adsorbed complex gradually replaced type-I adsorbed complex. Its peak was lost on exposure to electrolyte and was not recoverable. An extremely sharp reduction peak for type-II adsorbates was attributed to attractive interactions between adsorbates leading to dimerization. The potential of the type-II adsorbate peak was strongly dependent on halide concentration. The authors concluded that type-II adsorbate involved ion pair adsorption in regions of film disorder.

Similar behavior was noted by Brahimi *et al.* (1989). A Laponite-modified electrode in which electroactive (ferrocenylmethyl)dodecyldimethylammonium ($FDDA^+$) was adsorbed in amounts less than or equivalent to the CEC showed no electroactivity. Only $FDDA^+$ adsorbed, via van der Waals forces or an ion-pairing mechanism, in excess of the CEC resulted in an electroactive clay-modified electrode. Maximum adsorption of the complex was at 3.2 CEC for $FDDA^+$, as for the surfactant cetyltrimethylammonium (CTA^+). The adsorption of CTA^+ resulted in a positively charged clay surface, as evidenced by uptake of $Fe(CN)_6^{3-}$ and exclusion of methyl viologen (MV^{2+}). Neutral ferrecenium was postulated to partition into the CTA^+ bilayer.

In summary, electroactivity of cationic species in clay-modified electrodes is variable. Complexes adsorbed at face surfaces in amounts less than or equal to the CEC are not directly electroactive. A charge shuttle is required to access these nondesorbable species. Even in the presence of a charge shuttle, electroactivity may not be observed. Adsorbed $Os(bpy)_3^{2+}$ was not oxidized in the presence of mobile $Fe(bpy)_3^{3+}$ (King *et al.*, 1987), whereas adsorbed MV^{2+} was accessible via $Fe(CN)_6^{3-}$ (White and Bard, 1986). Access to these strongly adsorbed sites appears to depend on the method of film preparation, which affects porosity of the film (Fitch *et al.*, 1988). In addition to these strongly adsorbed sites, complexes can be adsorbed in excess of the CEC via ion-pairing mechanisms. These complexes may be localized at edge sites and give rise to much of the electroactivity observed at clay-modified electrodes.

DESCRIPTIVE RESULTS OF ELECTROCHEMICAL EXPERIMENTS

One of the attractive features of clays for use in electrode modification is the high reactivity of the clay surface with organics. This feature can be exploited to localize an organic substrate in close proximity to the electrode to enhance an electrochemical process. Inoue and Yoneyama (1987) capitalized on this feature by causing the electropolymerization of aniline supported in the clay. Aniline was concentrated near the surface of the electrode by adsorption into the clay film due to soaking of the clay-modified electrode in the aniline solution. Following concentration, a steady current was passed through the film to cause an oxidation. After

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electrolysis, the polyaniline product was observed by cyclic voltametry. Interestingly, major growth of the polyaniline reduction peak was observed over the next 12 hr. The authors suggested that the original electrolysis did not involve difficult-to-reach (interlayer) aniline, which was, however, observed in subsequent cyclic voltametry.

Following the same rationale, Rusling *et al.* (1988) attempted to combine the adsorption of organics with the CEC of clays to enhance the electroreduction of the aryl halogen, dibromobenzene (DBB). The reduction of the nonpolar DBB is difficult to achieve in an aqueous medium. Addition of an organic capable of forming a micelle, cetyltrimethyl ammonium bromide (CTAB), resulted in the formation of an organic layer near the electrode surface if the electrode potential was sufficiently negative (−0.9 V). The organic layer produced an environment favorable for the localization of DBB near the electrode surface, even in the presence of an aqueous environment. The authors hoped that the presence of a clay layer at the electrode surface would stabilize the formation of the CTAB micelle at less negative potentials and, hence, aid in the localization and reaction of DBB near the electrode, at the expense of less applied potential. To provide a charge shuttle to the DBB-containing CTAB micelle, the authors reduced $Co(bpy)_3^{2+}$ in the presence of bipyridine to $Co(bpy)_2^{-}$. The oxidized form of the charge shuttle should have been maintained in the clay film by exploitation of the cation-exchange properties of the clay. The reduced cobalt species diffused to the micelle and reacted with the localized DBB to reform the oxidized cobalt species, resulting in the catalytic reduction of $Co(bpy)_3^{2+}$. Although the reaction was carried out in the clay layer modifying the electrode, no decrease in the applied potential was observed; however, a slight increase in the catalytic current, indicating a slight increase in the reaction, was observed.

The clay-modified electrode has been used to support RuO_2 near the electrode surface (Ghosh *et al.*, 1984). In this application, a catalytic current for the reduction of $Ru(bpy)_2[bpy(CO_2)_2]$ was observed in which $Ru(bpy)_2[bpy(CO_2)]$ shuttled charge to a substrate, thought to be RuO_2. The authors suggested that RuO_2 was involved in the oxidation of H_2O.

Clay-modified electrodes may find use in photoreactions. The photocatalytic system may be described by the general equations:

$$M + h\nu = M^*, \quad (12)$$
$$M^* \rightarrow M, \quad (13a)$$
$$M^* + D = M^- + D^+, \quad (13b)$$
$$M^- \rightarrow M^-_{(x=0)}, \text{ and} \quad (14a)$$
$$M^-_{(x=0)} = M + e^-, \quad (14b)$$

where M is a photosensitive species, the subscript ($x = 0$) refers to the electrode surface, $h\nu$ is a photon, M* is the photoexcited state, and D is some solution electron donor. A photon excites M (Eq. (12)), which is reduced by some donor present (Eq. (13b)). The reduced form diffuses to the electrode and is oxidized (Eq. (14)). The goal is to harvest the electron in Eq. (14b), while reducing the effect of any quenching reactions (Eq. (13a)). Another advantage of supporting this reaction in clay at the electrode surface is an increased rate of excitation (Eq. (12)). The rate of excitation is increased due to large concentrations of M in the clay as a result of an ion-exchange reaction. Also, diffusion to the electrode surface (Eq. (14a)) is increased due to localization of the material at the electrode surface.

Kamat (1984) prepared Na-montmorillonite (Crook County, Wyoming)/colloidal Pt-modified SnO_2 electrodes. These electrodes were dipped into a solution of thionine for 15 min and then transferred to a 0.1 M H_2SO_4 solution. Reversible cyclic voltametry was obtained corresponding to a fraction of the total thionine adsorbed. A photovoltage maximum was observed at 600 nm corresponding to the S_0–S_1 transition in solution. Kamat (1984) concluded that trapped free dye molecules within the clay generated the photovoltage effect.

Further utilization of clay lies in its potential to impart chiral selectivity to the reaction. Yamagishi and Aramata (1984) found that a clay-modified electrode exposed to D-$Ru(phen)_3^{2+}$ showed no increase in currents (a measure of the concentration) on exposure to additional solutions of D-$Ru(phen)_3^{2+}$, but that it showed an increase in current on exposure to L-$Ru(phen)_3^{2+}$. (For a comparison of D and L enantiomers, see Figure 6.) Their conclusion was that the primed (D-$Ru(phen)_3^{2+}$) clay accommodated the L form of the complex via stereoselective packing. In a similar fashion, Fitch *et al.* (1988) observed larger reduction currents from a racemic vs. an enantiomeric solution of $Cr(bpy)_3^{3+}$. They concluded that the racemic solution allowed for more efficient packing of the complex on the clay surface.

Potentially of more interest to the clay chemist was the finding by Oyama and Anson (1986) that clay itself can participate in the redox reaction. Neither a pyrolytic graphite or a clay-modified pyrolytic graphite electrode showed a measurable reduction current for H_2O_2. Addition of a charge shuttle, $Ru(NH_3)_6^{3+}$, resulted in the catalytic reduction of the shuttle. The reaction mechanism suggested is shown in Figure 7. The active site for H_2O_2 reduction was suggested to be Fe in the clay structure.

For weakly adsorbed species, analytical enhancements may occur. Wielgos and Fitch (1990) demonstrated the analytic use of the CEC of the clay to enhance the concentration of a $Ru(NH_3)_6^{3+}$ near the electrode surface. They found that optimal concentration enhancements (two orders of magnitude) occurred

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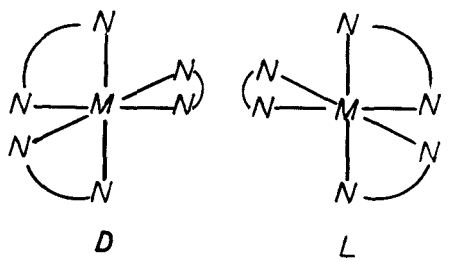


Figure 6. Spatially unique trisdiimine metal complexes (enantiomers) of the form ML_3 in which L is a ligand containing two N groups, such as phenanthroline or bipyridine. D is the mirror image of L. The two enantiomers can be resolved by their optical polarization.

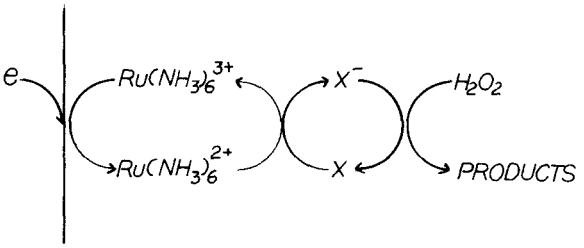


Figure 7. A charge shuttle, $Ru(NH_3)_6^{3+}$, carries an electron from electrode surface to a fixed electroactive site within the clay, X, which catalyzes the reduction of H_2O_2. Reaction mechanism proposed by Oyama and Anson (1986).

in the most dilute electrolyte solution that was able to support the electrochemical reaction.

QUANTITATIVE DATA

As indicated above, quantitative data are accessible from the electrochemical experiment from the value of the formal potential of the intercalated complex and from the measured diffusion coefficient. Unfortunately, the fact that the value of formal potential depends not only on the competitive exchange reaction, but also on the concentration of the competitive ion and the total number of occupied exchange sites (Figure 4) has only recently been recognized. As a consequence, early reports of formal potentials are of little physical significance. The situation with respect to the diffusion coefficient is better, even though data can be improved via better estimation of the accessible concentration of the electroactive substrate, as discussed above. The electrochemically derived diffusion coefficients of several

Table 1. Electrochemically derived diffusion coefficients within clays.

Clay	Electrode	Electrolyte	Species	D (cm^2/s)	Reference
		Metal complexes			
Na-mont[1] + PVA[2]	SnO_2	0.1 M Na_2SO_4	$Ru(bpy)_3^{2+}$ [3]	1×10^{-11}	Ghosh and Bard (1983)
SWy-1	SnO_2	0.1 M Na_2SO_4	$Os(bpy)_3^{3+}$	1.2×10^{-12}	Ege *et al.* (1985)
SWy-1	SnO_2	0.1 M Na_2SO_4	$Fe(bpy)_3^{2+}$	1.2×10^{-12}	Ege *et al.* (1985)
Na-mont	graphite	0.2 M CH_3COONa (pH 5.5)	$Os(bpy)_3^{3+}$	3.5×10^{-11}	Liu and Anson (1985)
Na-mont	graphite	0.2 m CH_3COONa (pH 5.5)	$Co(tpy)_2^{2+}$ [4]	1.8×10^{-11}	Liu and Anson (1985)
Na-mont (Fe pillared)	SnO_2	0.1 M Na_2SO_4	$Fe(bpy)_3^{2+}$	1×10^{-12}	Itaya and Bard (1985)
SWy-1	Pt	0.01 M Na_2SO_4	$Cr(bpy)_3^{3+}$	7×10^{-12}	Fitch *et al.* (1988)
Hydrotalcite	SnO_2	0.1 M Na_2SO_4	$Mo(CN)_8^{4-}$	8×10^{-12}	Itaya *et al.* (1987)
Hydrotalcite	SnO_2	0.1 M Na_2SO_4	$Fe(CN)_6^{3-}$	8×10^{-12}	Itaya *et al.* (1987)
Hydrotalcite	SnO_2	0.1 M Na_2SO_4	$Ir(Cl)_6^{2-}$	8×10^{-12}	Itaya *et al.* (1987)
		Organic species			
STx-1	SnO_2	0.05 M NaCl	MV^+ [5]	9×10^{-12}	White and Bard (1986)
STx-1	Pt	1 M Na_2SO_4	TTF^+ [6]	3.7×10^{-8}	Carter and Bard (1987)
STx-1	Pt	1 M Na_2SO_4	$(TTF)_2$ [7]	4.8×10^{-10}	Carter and Bard (1987)
Laponite	glassy carbon	0.05 M Na_2SO_4	$FDDA^+$ [8]	9.1×10^{-11}	Brahimi *et al.* (1989)
Laponite + CTA^+ [9]	glassy carbon	0.05 M Na_2SO_4	Fc[10]	2.9×10^{-10}	Brahimi *et al.* (1989)

[1] mont = montmorillonite.
[2] PVA = polyvinylalcohol.
[3] bpy = bipyridine.
[4] typ = terpyridine.
[5] MV = methyl viologen.
[6] TTF = tetrathiafulvalene. Monomeric TTF is suggested to reside outside of the interlayer giving rise to a large value for D.
[7] $(TTF)_2$ = tetrathiafulvalene dimer.
[8] $FDDA^+$ = (ferrocenylmethyl)dodecyldimethylammonium.
[9] CTA^+ = cetyltrimethylammonium.
[10] Fc = ferrocene.

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species are given in Table 1. Electrochemical estimates of the diffusion coefficient for $Ru(bpy)_3^{2+}$ in a hydrated clay compare well with those obtained from alternative measurements (10^{-8} to 10^{-10} cm^2/s (Habti *et al.,* 1984)). The small diffusion coefficients (typical solution value = 10^{-5} cm^2/s) correspond well with what is known about the interaction of these species with clay surfaces. Strong interactions of TTF^+ (Van Damme *et al.,* 1984), MV (Raupach *et al.,* 1979; Hang and Brindley, 1970), and the trisdiimine species (Krenske *et al.,* 1980; Schoonheydt *et al.,* 1978; Velghe *et al.,* 1977; Farmer and Mortland, 1965, 1966; Berkheiser and Mortland, 1977; Abdo *et al.,* 1981; Ghosh and Bard, 1984; DellaGuardia and Thomas, 1983) with the surface oxide layer have been observed by UV-VIS, nuclear magnetic resonance, and electron spin resonance techniques. These small values indicate that the activation energy required to jump from site to site is quite large.

SUMMARY

Clay-modified electrodes are useful in certain electrochemical applications. Diffusion coefficients of electroactive species can be estimated from the electrochemical data. Quantitative information about the nature of the exchange reaction via electrochemical data remains untapped, as yet. This is unfortunate because the magnitude of K_{III}, K_{II}, and various associated rate constants should be accessible from the electrochemical experiment. Future work needs to focus more specifically on more accurate determination of C_0^* and D. This will require a better measurement of the thickness of the clay layer or determination of C_0^* and D under conditions of nonlinear diffusion. Furthermore, an understanding of the mechanisms of charge transport, control of the pore dimensions to enhance transport properties, and complete elucidation of the role of the electrolyte in ion-exchange reactions and charge conduction are required. As these factors are mapped out, the technique will become more generally applicable in the determination of ion-exchange selectivity coefficients and diffusion coefficients for clay chemists.

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