Chemically Modified Electrodes

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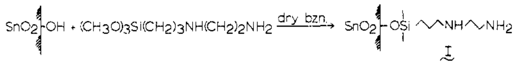
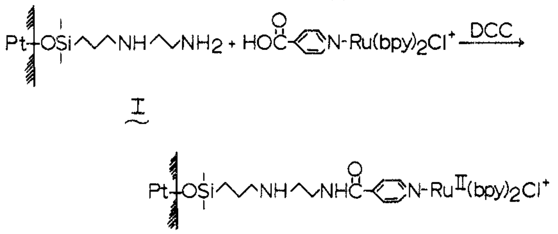
My colleagues[1] and I ventured into surface synthesis in the spring of 1974. Using X-ray photoelectron spectroscopy (XPS), we demonstrated[2] reaction 1. The



(1)

SnO_2 electrode surface was thus functionalized, or "chemically modified", with amine groups and, from a synthetic perspective, can be considered an "amine surface". This was in important step because now one can rationally plan coupling reactions with the "amine surface" to attach other interesting molecules to it.

Electrochemically reactive molecules are the most interesting candidates to attach to a functionalized electrode surface. For example, ruthenium complexes with peripheral carboxylic acid groups can be amide coupled[3] to an alkylamine-silanized Pt oxide[4] surface (eq 2). By applying a potential to the Pt electrode II immersed in an electrolyte/solvent medium, the immobilized Ru(II) complex can be made to undergo the same oxidation and reduction reactions it would exhibit if dissolved in solutions of electron acceptor or donor reagents. Thus, sweeping the potential linearly as in cyclic voltammetry, II becomes oxidized in an anodic current peak at +0.79 V (Figure 1). The Ru(III) complex product remains attached to the Pt, and is reducible in a reverse potential sweep, giving a cathodic current peak. The cathodic and anodic peaks occur at nearly the same potential, which means[5] that electrons are transferred between the ruthenium complexes and Pt much more rapidly than the experimental time scale. The immobilized complexes can be exhaustively oxidized and reduced many times, and the quantity of attached complex, or coverage, Γ_{Ru}, is approximately monolayer (1.1×10^{-10} mol/cm^2, 6.6×10^{13} molecules/cm^2, 151 Å^2/molecule). These observations are typical of a number of reports of redox species immobilized on electrodes.

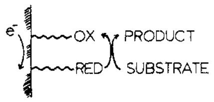


(2)

II

Why is it of interest to attach electrochemically reactive molecules to electrodes? First, such molecules should have special characteristics favoring study of intramolecular and electrochemical electron transfers. For example, it is interesting to view the surface "molecule" (Pt lattice)–OSi⁓Ru(II) in terms of an intramolecular electron exchange in which one end (the Pt) of the "molecule" has a continuously adjustable chemical potential. In semiconductor electrodes, "surface states" are energy levels in the semiconductor band gap whose chemical nature is generally unknown. Deliberate surface attachments offer a means of introducing[6] surface states of known energy and molecular nature into the band gap. Another feature, with electrochemical kinetic implications, is that no conventional mass transfer of reactant and product to and from the electrode is required for the reaction in Figure 1, since the ruthenium complexes already reside near the plane of space next to the Pt lattice where electron transfer occurs.

Secondly, there are a number of interesting ways to exploit the chemical and optical as well as electrochemical properties of attached molecules. Thus, electrochemically reactive molecules attached to electrodes can be applied in electrocatalysis. In electrocatalysis, the attached molecule acts as a fast electron transfer mediator[7] for a substrate dissolved in the contacting solution and only slowly reduced directly by a naked electrode (eq 3). Conceptually, the mediation reaction can be either inner or outer sphere. On a semiconductor electrode such electrocatalytic reactions can be incorporated into more complicated photosensitization[8] and anti(photoanodic) corrosion[9] schemes.



(3)

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The optical properties of multimolecular layers of redox substances immobilized on transparent electrodes like SnO_2 can also be exploited to devise potential-switchable colored electrodes.[10]

It is evident that a major virtue of the ability to synthetically manipulate the molecular composition of an electrode surface is that schemes of behavior like the above can be anticipated and then experimentally sought. This is a sharp departure from the traditional Edisonian surface treatment approach used by electrochemists in the course of seeking useful electrochemical behavior of solid electrodes toward reactants dissolved in the contacting solvent. Chemical modification yields a new degree of freedom in electrochemical science. It follows then that an important aspect of modified electrodes is to what extent, if any, the chemical behavior(s) of molecules is *un*predictably altered by immobilization.

How To Make Modified Electrodes

Procedures for immobilizing reagents on electrodes have been devised at a steady pace and now include several types of covalent bonding between reagent and electrode, coating the electrode with an insoluble variant of the reagent, and chemisorption. Covalent immobilization is tolerant of exposure to different solvents and can be effected on metal oxide and carbon electrodes.

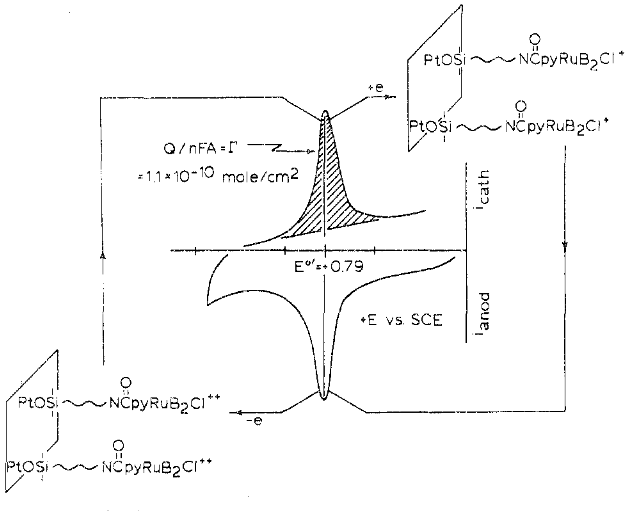

Figure 1. Cyclic voltammetry (0.2 V/s triangular potential sweep) of (isonicotinic acid)bis(2,2′-bipyridine)ruthenium(II)(1+) chloride attached to Pt/PtO surface as in reaction 2 (CH_3CN/Et_4NClO_4).

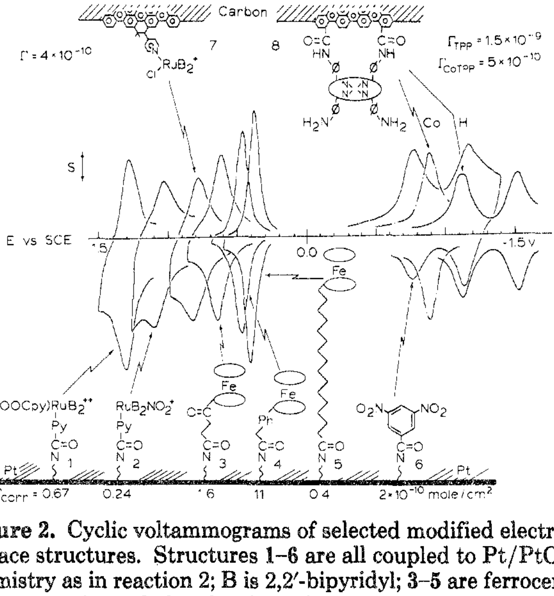

Figure 2. Cyclic voltammograms of selected modified electrode surface structures. Structures **1**–**6** are all coupled to Pt/PtO by chemistry as in reaction 2; B is 2,2′-bipyridyl; **3**–**5** are ferrocenes. Structure **7** is made by abrading glassy carbon in the presence of vinylpyridine followed by reaction with a solution of RuB_2(dimethoxyethane)$^{2+}$ containing chloride. Structure **8** is the α,β surface isomer for tetrakis(*p*-aminophenyl)porphyrin reacted as in reaction 4 and metalated with a solution of $CoCl_2$. Cyclic voltammograms at positive E are in CH_3CN (except **2** which is −80 °C butyronitrile), those at negative E are in Me_2SO. Structure, current sensitivity (S), scan rates are: **1**, 6 $\mu A\ cm^{-2}$, 0.2 V/s; **2**, 3 $\mu A\ cm^{-2}$, 0.2 V/s; **3**, 11 $\mu A\ cm^{-2}$, 0.2 V/s; **4**, 70 $\mu A\ cm^{-2}$, 0.2 V/s; **5**, 3 $\mu A\ cm^{-2}$, 0.2 V/s; **6**, 12 $\mu A\ cm^{-2}$, 0.2 V/s; **7**, 16 $\mu A\ cm^{-2}$, 0.2 V/s; **8** (unmetalated), 55 $\mu A\ cm^{-2}$ 0.1 V/s; **8** (cobalt), 14 $\mu A\ cm^{-2}$, 0.1 V/s.

Metal Oxide Surfaces. SnO_2,[2,11] RuO_2,[11c,d,12] TiO_2,[6,11a,c,13] Pt/PtO,[3,4,6,11c–e,12b,14] Au/Au(oxide),[14b,d] Si/Si(oxide),[15] and Ge[16] electrodes[17] can be functionalized with a variety of organosilanes, including alkylamine (I, III), acid chloride (IV), and pyridine (V) silanes. These surfaces can be coupled variously as amides[4,11d,w,12a] and sulfonamides,[11e] quaternized,[11a] and coordinated to metals.[3] Thus, silanization is a versatile

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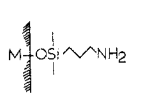

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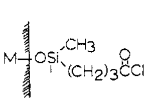

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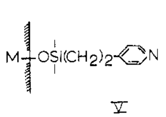
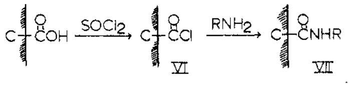


V

covalent immobilization strategy. Figure 2 illustrates the cyclic voltammetry of molecules (structures 1–6) we have immobilized as amides of I on Pt/PtO;[18] note that the silanization chemistry accommodates a wide span of potentials (ca. 2.5 V) of surface redox structures.

Oxidized Sites on Carbon Surfaces. The carboxylic acid functions on edge planes[19] of graphitic carbon generated by thermal[20] or O_2 plasma oxidation[21] can be coupled with amines or alcohols after activation with thionyl chloride[20] or acetyl chloride.[7c] Reaction 4 has



VI VII (4)

been used to prepare a chiral electrode surface[20] and to immobilize tetrakis(aminophenyl)porphyrin[22,23] and a pyridine ligand.[24] The immobilized porphyrin (Figure 2, structure 8) can be metalated[7c,22] with Co, Mn, Cu, Ni, Zn or Fe. Carbon surface hydroxyl groups can be activated for coupling reactions with[25] cyanuric chloride; this promises to have a useful range of reactivity. Carbon surface quinone reacts with nitrophenylhydrazine to form a phenylhydrazone.[26]

Oxide-Free Carbon. Mazur,[27] reasoning that vacuum pyrolysis of carbon surface oxides should create usefully reactive surfaces, demonstrated coupling of olefins to "oxide-free" carbon. Improved coupling yields of reagents with "oxide-free" carbon were subsequently demonstrated with Ar plasma[28] and mechanical abrasion[29] procedures for removing the oxides. Vinylpyridine, subsequently coordinated to ruthenium,[30a] is represented in Figure 2 (structure 7) as a cycloaddition product of the abrasion approach, although the true chemical nature of "oxide-free" carbon surface coupling products remains to be adequately illuminated.

Chemisorption. Chemisorption (or "irreversible" adsorption) is a less controlled approach. Nonetheless, interesting immobilization chemistry is accessible, as shown by Hubbard[5] in a pioneering study of functionalized olefin chemisorption on Pt and later work with π-system reagents on Pt,[31] basal plane pyrolytic graphite,[7f,g,j,32] and Pt/PtO.[14a] The π-system–graphite chemisorption tends to be impermanent when the immobilized reagent is soluble in the contacting solvent.

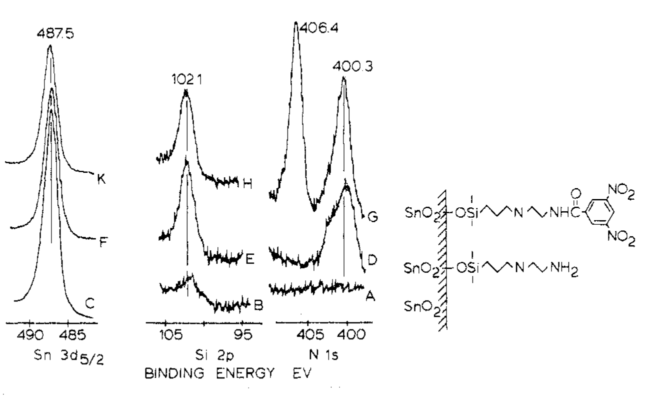


Figure 3. X-ray photoelectron spectroscopy of a native film of SnO_2 on glass (curves A–C), after silanization with (en)silane (curves D–F), and after further amide coupling with 2,4-dinitrobenzoyl chloride (curves G–K).

Redox Polymers. If the reagent of interest is incorporated into a polymeric matrix, the equivalent of many monolayers (10–1000) of reagent can be immobilized. The polymer adheres to the electrode surface by some combination of adsorption and low solubility in the contacting solvent or by covalent bonding. Polymers have been coated on electrodes by dip[7e,33] and spin coating,[6,10,34] organosilane bonding,[11f,w,14a,c] electrochemical precipitation[35] and polymerization,[30b,36] adsorption from solutions,[37] and plasma discharge polymerization.[29,38,39] Poly(vinylferrocene), poly(vinylpyridine)/ruthenium complex, and poly(nitrostyrene) are examples of these redox polymers.

Polymer coatings have been appealing on several accounts. First, immobilization experiments are technically less demanding than working with monolayers. Secondly, electrochemical responses are larger (since multiple layers of redox sites react). Thirdly, it has been supposed that improved stability results from incorporating reagents into polymers. A polymer framework may, however, be highly stable while an electrochemically reactive moiety attached to it is no more stable than when immobilized as a nonpolymer monolayer. Finally, a theoretical model[40] for electrocatalysis at modified electrodes has suggested that

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(18) Silanized Pt/PtO is advantageous because of its superior electrical properties, wide potential window, and relative reproducibility, and since microscopic surface roughness determination[14a] permits measurement of true coverage, Γ_{cor}.

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(23) Reaction 4 aptly illustrates one of the several technical eccentricities of surface synthesis: a too thorough wash of VI to remove excess $SOCl_2$ leads to its hydrolysis by trace moisture, and the preparation of VII fails.

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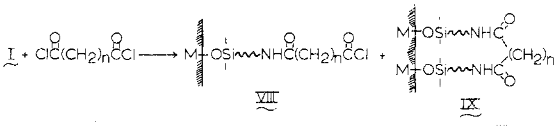
multilayers are best. The assumptions in this model are not adequately tested. These questions are being addressed in several laboratories and doubtless will soon be answered.

The business of immobilizing molecules on electrodes, while not a mature science, is well advanced. It clearly is possible to rationally select target molecules for electrode immobilization which is important in designed applications of modified electrodes. Emphasis in the field is gradually shifting to applications.

Analysis of Surface Population and Structure

Since immobilization of a reagent tends to fix the microenvironment of its electron-transfer reactions, we have stressed analytical characterization of bonded layers. For example, in reactions 1 and 2, we should determine yields of these surface reactions and should assess structural, spatial, and dynamic relationships of I and II to the -MOSi- plane and to their neighbors. These are not easy tasks.

X-ray photoelectron spectroscopy (XPS) has been informative in tracking surface reactions. Figure 3 illustrates how XPS follows reaction I and a subsequent amidization building up an electrochemically active surface.[4,12a] Appearance of surface elements is a simple qualitative diagnostic, and from relative peak intensities the layer thickness[2,41] and N/Si surface atom ratio can be measured.[11c] The amidization reaction yield, obtained from the N 1s peaks in curve G, demonstrated that the γ-amine site on I has low reactivity while the terminal amine reacts readily. XPS also allows probing[11h] of amine site spacing using the bifunctional coupling reaction (eq 5). Relative populations of VIII and IX assayed as a function of n show that bifunctional coupling (IX) is possible if n is such that the reagent can accommodate to an amine N–N spacing of 4–8 Å.



(5)

XPS has also been useful to study reaction 4 and establish a connection between graphitic edges and reactive carboxylic acid sites.[42] XPS shows that tetrakis(p-aminophenyl)porphyrin in reaction 4 forms,[22b] on the average, two surface amide bonds; the more probable (α,β) of the two possible surface isomers is shown in Figure 2. The α,δ isomer would have a "face-to-face" electrode–ring cavity.

Coverages of electroactive silane-bonded reagents (Figure 2), determined by cyclic voltammetry, are most commonly 0.8 to 4×10^{-10} mol/cm^2 and, in comparisons to expected molecular sizes, approximate noncompacted monolayers. The 0.4×10^{-10} mol/cm^2 coverage of structure 5, for example, is much less than the value for a (Langmuir trough) oriented monolayer of the carboxylic acid of this substance. Coverages by the ruthenium complex[3] II are closer to monolayer models. The coverage data, in general, suggest loosely organized monomolecular surface structures with consequent thermal motional freedom and interfacial fluidity, supporting our "floppy molecule" model for electron transfer discussed below.

In occasional samples and under certain reaction conditions (structure 4), and especially with chlorosilanes, larger coverages are obtained in silane bonding reactions, suggesting siloxane polymer formation. Coverages usually amount to only ca. 3–6 monolayers, although thicker layers have been observed.[11f,14c,d] Such results suggest that even for samples with average coverage in the monolayer range, some dimer, trimer, etc., sites probably are scattered among the monomer monolayer (I) population. Siloxane polymer globule formation[43] is on the other hand avoidable with proper reaction conditions.

Numerous analytical challenges remain, for silane bonding as well as for other modification schemes. In addition to more detailed surface structure evidence, the surface dynamic inferences obtained from electrochemical measurements (see below) need verification from other methods. Polymer-coated electrodes pose special analytical problems, ranging from physical topology of thickly coated surfaces[10] to spatial uniformity of subsequently metalated ones[37a] to the detailed chemical nature of plasma generated films.[38,39]

Immobilized Electron-Transfer Couples Swapping Electrons with the Electrode

The report by Moses[11a] of an electrochemically reactive silane-immobilized compound, methylpyridinium, was quickly followed by additional[26] and more reversibly stable examples on carbon,[22a] RuO$_2$,[12a] and Pt/PtO.[4] Today electrochemistry of many immobilized electron-transfer couples has been described, including nitro aromatics,[4,6,7e,11f,12a] iron–sulfur clusters,[11u] pyrazolines,[10,11p,q] ferrocenes,[11d,w,14,15,25a,29,31,35,36b,39] ruthenium complexes,[3,7i,24,28,32a,37] tetrathiafulvalene,[12c] viologens,[25d] porphyrins,[7c,i,j,l,22] quinones,[7b,g,27,32b] and o-tolidine.[25c] The emphasis has been on simple and stable oxidized and reduced forms, and the electron-transfer chemistry is thus mostly one-electron outer sphere.

We have shown[12b] that the formal potential, $E^{\circ\prime}_{\mathrm{surf}}$, of an immobilized electron-transfer couple (Figure 1) is nearly the same as that of its unattached, structural analogue, $E^{\circ\prime}_{\mathrm{soln}}$, and not perceptibly sensitive to electrode material or immobilization chemistry. One readily calculates that 2×10^{-10} mol/cm^2 of a molecule tethered by a 10-Å chain corresponds to a 2 M "volume concentration", large enough to depress the concentration of interfacial solvent and to potentiate substantial activity effects. The data indicate that the net effects on the free-energy difference between oxidized and reduced forms are fairly small for the cases studied.

Surface activities do manifest themselves in the broadness (E_{fwhm}) of cyclic voltammetric peaks.[32b] E_{fwhm} = 90.6 mV for surface activity proportional to coverage,[5] but an exponential relation with "repulsive" activity parameters[32b,44] predicts broadened surface peaks. E_{fwhm} >90.6 mV is an almost universal effect observed to date.[45] Surface structural heterogeneity may also

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(41) D. F. Untereker, J. C. Lennox, L. M. Wier, P. R. Moses, and R. W. Murray, *J. Electroanal. Chem.*, 81, 309 (1977).

(42) B. E. Firth, L. L. Miller, M. Mitani, T. Rogers, J. Lennox, and R. W. Murray, *J. Am. Chem. Soc.*, 98, 8271 (1976).

(43) I. Haller, *J. Am. Chem. Soc.*, 100, 8050 (1978).

(44) (a) B. E. Conway, E. Gileadi, and M. Dzieciuch, *Electrochim. Acta*, 8, 143 (1963); (b) H. Angerstein-Kozlowska, J. Klinger, and B. E. Conway, *J. Electroanal. Chem.*, 75, 45 (1977); (c) E. Laviron, *ibid.*, 52, 395 (1974).

(45) Ferrocene 5 (E_{fwhm} = 85 mV) and high coverages of ferrocene 4,[14a] Figure 2, are interesting exceptions.

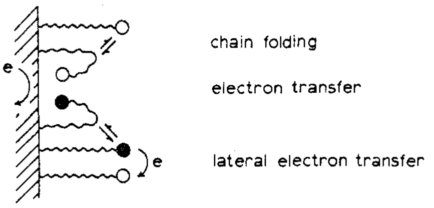

Figure 4. Schematic view of electron transfer reactions of oxidized (○) and reduced (●) moieties on monolayer electrode surfaces.

contribute to peak broadening,[11d,22b] complicating analysis of the problem.

A crucial observation is that electron-transfer couples exhibit electrochemical reactivity irrespective of how they are immobilized: electronically insulating connecting chains[11a] as in the organosilanes or carefully chosen conjugated connections[25a,32a] or in polymeric multilayers.[7e,14b,c] For π-system molecules chemisorbed on pyrolytic graphite,[7f] close contact makes the electron-transfer process easy to visualize, and the collision number (frequency factor) for electron transfer is conceivably as large as kT/h (ca. 6×10^{12} s^{-1}). Anson[46] has reasoned that, given equal electron-transfer energy barriers for attached and unattached reagents, this frequency term could provoke larger electron-transfer rates for the former. Indeed, except where a proton-transfer step intervened, electron-transfer rates for graphite-adsorbed reactants proved immeasurably fast, and only a lower limit (ca. 10^4 s^{-1}) could be placed on the rate constant.

When the electron-transfer couple is immobilized via some connecting molecular bridge or is distributed throughout a polymer lattice, short-range motions of the redox site may become important. In this view, recognizing the combination of connecting chain flexibility and coverage-suggested layer noncompactness in organosilane-bound monolayers, we proposed[11a,c] that "floppy" chain folding of the surface structures would be associated with electron transfer, as illustrated in Figure 4. The average distance for electron transfer is unknown and possibly more separated from the conducting electrode material than for an unattached reactant. The time-average electrode–reactant separation depends on the distribution of structural conformations as influenced by Coulombic terms (e.g., electrode vs. reactant charge) from the electrode side[47] and solvation effects[14a] (e.g., relative solvation of reactant, connecting chain, and electrode) from the solution side. In some instances the average conformation might be folded and floppiness unnecessary for electron transfer; in others lateral electron-transfer events (Figure 4) could be an important accessory mode of reaction.[11c]

The collision frequency of a reactant tethered to an electrode by a chain of length d can be approximated as $A = 4D'/d^2$ s^{-1} where D' is a transport parameter. If chain-folding energy barriers are comparable to barriers for molecules diffusing in solutions, D' is comparable to a diffusion coefficient. For ferrocenes 3 and 5 in Figure 2, assuming $D' \sim 10^{-6}$ cm^2/s, $A = 2 \times 10^8$ and 2×10^7 s^{-1}. These are much smaller collision frequencies than estimated by Anson,[46] but as mass transport factors remain too fast to be limiting even during fast (ca. 10^{-2} s) voltammetric scans.[48]

The transport of electrochemical charge through multilayers of electron-transfer sites, as in redox polymers, is more complex than the monolayer situation, but is slower and more amenable to study. Polymer-coated electrodes bear large coverages of immobilized electron transfer couples, 10^{-9}–10^{-6} mol/cm,^{2} and often exhibit cyclic voltammetric wave shapes[7e,10,11w,14c,d,29,35,39] indicative of slow electrolysis of the surface film. Conceptually, it seems likely that electron hopping between adjacent localized oxidation states will be a mechanism for the migration of charge through a fixed-site polymer matrix. That migration of charge in redox polymers can obey Fick's laws has been observed.[39] What controls the rate of the migration, whether site–site collision,[10a] counterion mobility,[10b,37b] solvent swelling,[39c] or polymer chain deformations,[39b] for any given redox polymer, or if any one factor will be general, is at present an unsettled matter. These issues must be understood over a range of redox polymers before systematic application can be made to electrocatalysis, photoelectrocatalysis, and analysis.

Chemical Reactions of Attached Reagents

Assuming that the initially immobilized (resting) oxidation state of an electron-transfer couple is stable, we are particularly interested in any chemical reactivity (or stability) incited by electrochemical change of oxidation state, since this determines usefulness in applications. Instability as reflected in decay of the electrochemical response of an immobilized electron-transfer couple can arise by reaction of the nonresting oxidation state, by reaction attendent to electron transfer itself, or by potential-dependent phenomena such as electrode corrosion and reactions of the immobilizing bonds. For organosilane-based immobilization it has been established in several cases[4,12a,21a] that stability is dictated by reactivity of the electron-transfer couple, not the silane–electrode bonding. Specifically, decay of the wave for ferrocene 4 in Figure 2 is associated with the time the electrode spends in the ferricenium state, not the number of electrochemical turnovers between states. This is an important distinction for electrocatalytic applications and illustrates the inadequacy of characterizing electrode stability by stating a number of usable cycles as is common in the literature.

Whether reactivity is promoted or diminished by immobilization varies. As compared to unattached molecular analogues and to polymeric multilayers,[6,7e] nitroaromatic radical anions are less stable as immobilized monolayers.[4,12a,49] A dependence on electrode material suggests some specific interaction with the electrode. Decreased stability, as compared to solution analogues, of monolayers of monocyclic pyrazoline radical cations[11p] and of (polypyridine)ruthenium(I) complexes[3] has also been reported. The rate of nitrile ligand substitution in the Ru(III) state of II is enhanced,[3] whereas in an attached Ru(III)–EDTA complex, ligand substitution is slowed[50] by ca. 10^3. The substantial photola-

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(46) A. P. Brown and F. C. Anson, *J. Electroanal. Chem.*, **92**, 133 (1978).

(47) Hubbard has presented a model for this: R. F. Lane and A. T. Hubbard, *J. Phys. Chem.*, **77**, 1411 (1973).

(48) Coulostatic relaxation (ca. 50 μs) was not successful in measuring the electron-transfer rate constant for ferrocenes 4 and 5: P. Daum and J. R. Lenhard, University of North Carolina, unpublished results, 1978.

(49) L. M. Wier, Ph.D. Thesis, University of North Carolina, 1977.

bility of II is quenched by its immobilization on Pt, presumably because of proximity to the metal.[3]

Considering the concentrated nature of bonded monolayers and redox polymers, evidence of intermolecular surface reactions is of interest since collisional frequencies and cross sections may differ from those in freely diffusing fluids. Detected reactions between monolayer sites include dimerization of a pyrazoline cation radical[11r] and disproportionation[7i] of the Ru(III)–NO_2 complex of 2 of Figure 2. Both reactions were *slower* than for the unattached versions. Figure 2 illustrates the usefulness of low temperatures to "freeze" disproportionation of attached Ru(III)–NO_2; at the temperature used (–80 °C in butyronitrile) the Ru(III) reduction wave persists for many minutes whereas for an unattached complex it is undetectable at room temperature. In a quantitative kinetic study, Lenhard[14a] showed that ferrocene 4 (Figure 2) decays by a rate law second order in ferricenium, with a rate constant of $(7 \pm 3) \times 10^5$ $cm^2/(mol{\cdot}s)$. Although the reaction could be followed over several half-lives, the eventual breakdown of the second-order rate law anticipated if ferricenium–ferricenium collisions are involved was not reached.

Electrocatalytic reactions (reaction 3) are an important designed application of modified electrodes. Examples of electrocatalysis so far reported include ascorbic acid oxidation by attached benzidine,[7a] $NADH^+$ oxidation by 3,4-dihydroxybenzylamine,[7b] and O_2 reduction by [tetrakis(*p*-aminophenyl)porphyrin]iron,[7a] all amide coupled to carbon as in reaction 4, ascorbic acid[7a] and $NADH^+$[7d] oxidation by carbon surface oxides, CCl_4 and O_2 reduction by poly(*p*-nitrostyrene) dip coated on Pt,[7e] O_2 reduction by (protoporphyrin IX)iron,[7f] (tetrasulfonatophthalocyanine)cobalt,[7g] and a cofacial dicobalt porphyrin dimer,[7h] all chemisorbed on basal plane pyrolytic graphite, O_2 reduction by (tetrapyridylporphyrin)cobalt adsorbed on glassy carbon,[7j] and tris(chlorophenyl)phosphine oxidation[7i] by Ru(III)–NO_2 complex 2 of Figure 2. The detail in mechanistic and product identification known for these examples varies substantially, as does the turnover stability of the surface couple. In no case has an adequate quantitative kinetic analysis been developed. In qualitative terms, the most spectacularly successful modified electrode electrocatalysis has been the four-electron, mass-transfer-controlled reduction of O_2 to H_2O without significant H_2O_2 production.[7h] This elegant electrocatalytic reaction is based on the concept of dual binding and electron transfer to O_2 from the faces of a porphyrin dimer, the spacing between which is critical.

Noncatalytic forms of reactivity of the electron-transfer reagent where the product remains electroactive and attached to the electrode include reversible proton[7f] and ligand[22b,51] transfer closely associated with electron transfer, and certain protonations[7c,i] and ligand substitutions.[3] Such reactions are of interest by probing immobilized reagent chemistry for comparison to familiar solution events.

Photoinitiated reactivity of immobilized molecules is also of interest. On illuminated (n-type) semiconductor electrodes, the immobilized chromophore acts in photosensitization[8,11i,j,m,52,53] as an excited-state reductant, irreversibly injecting an electron into the conduction band, and in bandgap absorption as a ground-state reactant, neutralizing a valence band hole (antiphotocorrosion[9]). Both schemes depend on efficient reduction of the resulting oxidized surface reagent by some consumable solution substrate in a cycle analogous to reaction 3, which is central to both electrocatalytic and photoelectrochemical applications.

Electrochemistry of Unattached Reactants at Modified Electrodes

Electron-transfer reactions of unattached substances (typically stable one-electron types) at nonmediating monolayer and multilayer modified surfaces are useful probes of interfacial structure. Silane bonded[2,4,11c,q] and chemisorbed[7f,47] monolayers on electrodes in most cases retard the reaction rate of dissolved reactants, although exceptions exist.[2,7f,11q,47] The expected effects are (i) enhancement of current *density* at accessible surface sites (sites of bonding being considered inaccessible), (ii) steric barriers to such access, and (iii) (for charged attached molecules) changes in the interfacial potential distribution altering the potential experienced by the solution reactant at its distance of closest approach (ϕ_2 effect).[54] The ϕ_2 factor for bonded cationic molecules retards the electron-transfer rate of cationic solution reactants and enhances that of anionic reactants. Such effects have been observed for both silane bonded[2] and chemisorbed[47] cationic layers, and an elegant theoretical analysis was carried out for the latter. The enhancement of current density effect applies to any solution reactant and will be most noticeable for reactants with slow electron transfers (at naked electrodes). Sterically impeded access of solution reactants (by the bonded reagent) to open sites is, strictly speaking, a mass transport effect, but over monolayer distances such kinetics become incorporated with those of electron transfer. Attempts to demonstrate steric effects by study of a given solution reactant at a series of surfaces with successively more bulky bonded organosilanes[11q] are unfortunately compromised by uncertainty whether organosilane coverage remains constant in the series.

Coatings of nonmediating multilayers (polymers) on electrodes pose a greater likelihood of access limitations on unattached reactants, which may not be able to cross (dissolve in) the polymer film. Since the distances are greater, access kinetics are more readily associated with mass transport. This point has relevance to electrocatalysis theory[40] where a questionable assumption of uniform access to all polymer sites was made. Although investigations have only recently begun, examples of retardation of electrochemical rates have been encountered[7e,11c,14e,33,38,39] and exceptions.[11c,11w,39] Important factors can be expected to include reactant size and charge, solvent swelling, and counterion penetration (degree and rate) into the film and pinholes and channels. Solvent swelling, normally greater for polymers bearing fixed charged sites, is important in permitting access of electrolyte into the film, without which either

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(50) N. Oyama and F. C. Anson, *J. Am. Chem. Soc.*, 101, 1634 (1979).

(51) C. P. Jester, M.A. Thesis, University of North Carolina, 1979.

(52) M. Fujihira, T. Osa, D. Hursh, and T. Kuwana, *J. Electroanal. Chem.*, 88, 285 (1978).

(53) T. Miyasaka, T. Watanabe, A. Fujishima, and K. Honda, *J. Am. Chem. Soc.*, 100, 6657 (1978).

(54) P. Delahay, "Double Layer and Electrode Kinetics", Interscience, New York, 1965.

a large uncompensatable resistance effect is experienced[7e] or by adequate "dry" electronic conductivity the film becomes an extension of the electrode material with electron transfer occurring at its solution interface.[34a,38] With charged polymer films, penetration of neutral reactants or reactants of opposite charge to the fixed sites is much more facile than penetration of reactants of like charge, due to Donnan exclusion, as observed with a siloxane polymer version of I under conditions protonating the amine sites.[11c] The role of solvent swelling is illustrated[39c] with plasma polymerized vinylferrocene films, which in CH_3CN (swells the film) permit reactant access but in water (nonswelling) act as a barrier.

The Near Future

Given the many excellent research programs attracted by the tailormade appeal of chemically modified surfaces, the chemical diversity and applications of decorated electrodes are likely to grow for some time. In particular, electrocatalytic, photoeffect, and electrochromic phenomena at modified electrodes will be intensely scrutinized applications, some of which will translate into far future technology. Selective analysis is a hardly broached but pregnant applications area. An enormous potential remains for using modified surfaces as fundamental probes of transient interfacial charge-transfer and transport events. The depth of our achievable insights into such events is fettered by ignorance about details of attached molecules' spatial distribution and dynamics, and more useful probes of these and of the potential distribution at the electrode need invention. Finally, study of polymer-coated electrodes is likely to lead to significant contributions to the physical chemistry of polymers.

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