Surface Functionalization of Electrodes with Molecular Reagents

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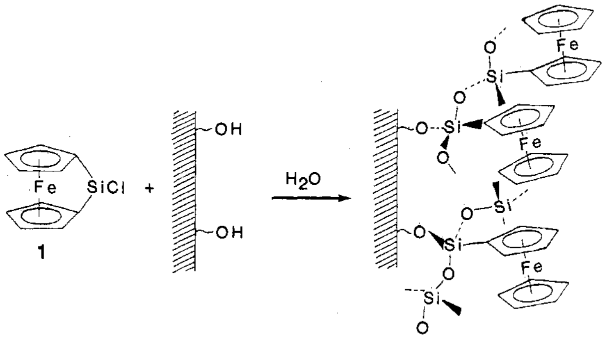
The use of molecular reagents to manipulate the properties of electrode surfaces has broad application in areas such as electrochemical synthesis, energy conversion and storage, displays, sensors, and new kinds of microelectronic devices. Surface modification of electrodes has contributed to a revival of interest in basic and applied research in electrochemistry and electrochemical devices. This article is focused on specific examples of systems modified electrodes where basic developments provide promising opportunities for applications stemming from the properties of molecules attached to an electrode surface.

CHANGES OF ELECTRODE SURFACE PROPERTIES CAN BE effected by the functionalization of such surfaces with molecular reagents (*1*). The aim of this article is to illustrate examples of recent basic research results that have potential practical applications in the future. Many of the areas discussed represent research projects in my laboratories, so that the coverage is not intended to be a critical assessment of the entire field. Applications in a variety of areas stem from the ability to prepare functionalized surfaces bearing molecule-based substances—monolayer and thick (~1 μm) polymeric layers—having specific properties. Modification of electrode surfaces by films of a metal or a metal oxide, or mixtures of these, can be useful, but my focus will be on systems where the properties of a molecule-based substance are crucial. In many areas of application, the central issue is whether surface modification can be useful to accelerate the rate of a desired electrode process (electrocatalysis). However, as will be developed below, other properties of surface-confined molecules can be exploited. In addition to electrocatalytic effects, properties such as color, charge, hydrophobicity, and conductivity, and the variation of these with electrode potential, underlie particular applications of synthetic surfaces and interfaces.

Corrosion Suppression of Semiconductors

It is now well appreciated (*2*) that semiconductor photoelectrodes provide a way of efficiently converting optical energy directly to electricity or stored chemical energy in the form of high-energy redox products (Fig. 1). Optimum efficiency for the conversion of solar energy can be obtained when the band gap (E_g) of the semiconductor is between 1.1 and 1.7 eV (*3*). A major difficulty has been that nonoxide (*n*-type) semiconductors undergo irreversible photoanodic decomposition competitively with desired oxidation processes. An approach (*4*) to suppressing photocorrosion is to modify the semiconductor surface with a redox polymer that can capture photogenerated oxidizing equivalents and transfer them to appropriate solution species. This approach was inspired by the discovery that $\mathrm{Fe}(\eta_5\text{-}\mathrm{C_5H_5})_2$, a fast, one-electron, outer-sphere reductant, could effectively capture oxidizing equivalents at illuminated *n*-type silicon anodes (E_g, 1.1 eV) (*5*). By attaching a polymerizable ferrocene-based reagent (**1**) to the surface of *n*-type silicon (Scheme 1), it is possible to photooxidize any species *B* oxidizable with the oxidized form of the polymer. Importantly, a species *B* that cannot be oxidized at the "naked" (nonderivatized) surface can be oxidized at the ferrocene-modified surface. It is especially significant that species *B* in aqueous electrolyte systems can be oxidized because the photooxidation of silicon in aqueous solution (Eq. 1) is highly competitive with desired reactions (*5*).

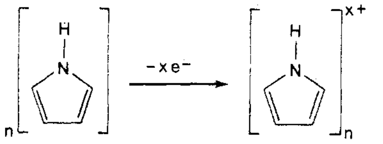


Scheme 1

$$\mathrm{Si} + 2\mathrm{H_2O} + 4h^+ \longrightarrow \mathrm{SiO_2} + 4\mathrm{H^+} \tag{1}$$

A dramatic effect can be realized from derivatization of *n*-type silicon with reagent **1**. For example, oxidation of $\mathrm{Fe(CN)_6^{4-}}$ to $\mathrm{Fe(CN)_6^{3-}}$ can be effected at the derivatized electrode but not at the naked electrode, where $\mathrm{SiO_2}$ grows (Eq. 1) so rapidly that the electrode is covered with an insulating layer of $\mathrm{SiO_2}$ that precludes current (*4*). Thus, surface modification with molecule-based materials can contribute to the improvement of the durability of semiconductor-based photochemical conversion devices.

The results with reagent **1** were followed quickly by work on the suppression of silicon photoanode corrosion with anodically grown



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polypyrrole (Eq. 2) as the surface reagent (*6*). In comparison to the polymer derived from reagent **1**, the polypyrrole has exceptional

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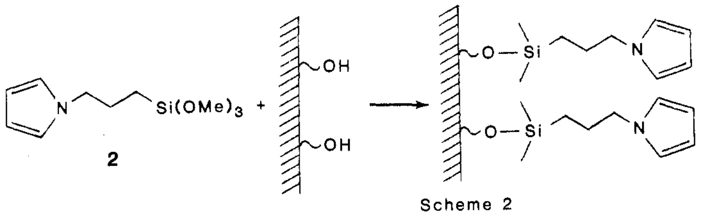
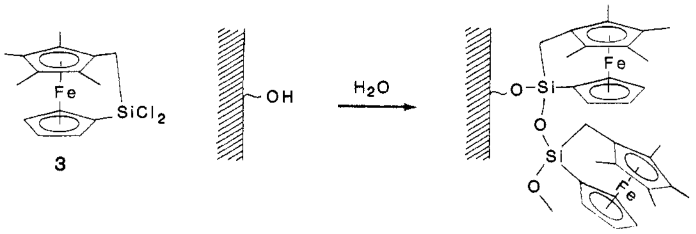
conductivity in its oxidized state (*7*). Thicker coatings of polypyrrole can be used without retarding photocurrent because the conductivity of the polypyrrole is high. The polypyrrole is, effectively, a metal with a very large internal surface area that can reduce the hole density. The use of oxidizing redox couples such as I_3^-/I^- and Fe^{3+}/Fe^{2+} in acid solution was demonstrated in cells for the conversion of light to electricity. Polypyrrole and other conducting polymers thus have the potential advantage of improving the rate of slow oxidation processes—by virtue of their very large, solvent-reagent accessible, internal surface areas—while suppressing corrosion. Further improvement in the polypyrrole system can be achieved with additional molecular-level surface chemistry. First functionalizing the surface with the pyrrole derivative **2** (Scheme 2) and then anodically growing the polypyrrole film leads to remarkable improvement of the adhesion of the polypyrrole film (*8*). This in turn leads to improvement in durability because the electrolyte solution cannot undermine the adhered polypyrrole (*8, 9*). The rationale for the improvement in the adhesion is that the covalently bound *N*-alkylpyrrole can be the site of initiation of polypyrrole chain growth, providing numerous points of covalent attachment to the electrode surface.



Scheme 2

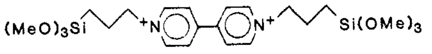
Electrocatalysis at Semiconductor Electrodes

An interesting extension of the results from functionalization of *n*-silicon with reagent **1** involves the use of the polyalkylated ferrocene-based reagent **3** to derivatize *n*-silicon (Scheme 3) (*10*). A serendipitous discovery was that the formal potential, $E°'$, of the surface polymer from reagent **3**, $PMFc^{+/0}$, is nearly the same as $E°'$ for horse heart ferri-/ferrocytochrome c [cyt $c_{(ox)}$/cyt $c_{(red)}$]. The polyalkylation shifts $E°'$ significantly more negative compared to the value for the polymer derived from reagent **1**. In addition, the polyalkylation makes the reagent more hydrophobic. This property, coupled with the covalent connection of the C_5 rings and the more sterically hindered iron center, gives rise to a surface polymer that is more durable in H_2O at high *p*H (such as *p*H 7) than is polymer from reagent **1**. All the properties of $PMFc^{+/0}$ contribute to the ability of the electrode to effect the visible light–driven oxidation of cyt $c_{(red)}$ in aqueous solution. $PMFc^{+/0}$ has several functions: (i) it suppresses corrosion; (ii) it alters the electrode surface properties in such a way that irreversible adsorption of the large biological reagent is minimized; and (iii) it can rapidly come into charge-transfer equilibrium with cyt $c_{(ox)}$/cyt $c_{(red)}$. The point is that even if *n*-silicon were durable it would not be an effective naked photoanode for the photooxidation of cyt $c_{(red)}$ because of poor kinetics or adsorption or a combination of these problems. Thus, reagent **3** is not merely a species for suppressing corrosion but also provides a method for bringing the solid surface of an electronic conductor into charge-transfer equilibrium with a biological redox reagent. The visible light–driven oxidation of cyt $c_{(red)}$ indicates that it may be possible to exploit redox enzymes as catalysts for multielectron transfer, fuel-forming reactions (*11*).



Scheme 3

Photocathodes, or *p*-type semiconductors, have also been modified with molecule-based materials to improve photoelectrochemical performance. A noteworthy example with respect to optical energy conversion concerns catalysis of H_2 evolution. Reagents **4** (*12*) or **5** (*13*) can be used to functionalize small band-gap *p*-type semiconductors with a polymeric redox material having $E°'$ near that for H_2O/H_2 at *p*H approximately 6. The redox polymer $(PQ^{2+/+})_n$ or $[Co(CpR)_2^{+/0}]_n$ from reagents **4** and **5**, respectively, provides a rapid path to remove the photogenerated reducing equivalents from the



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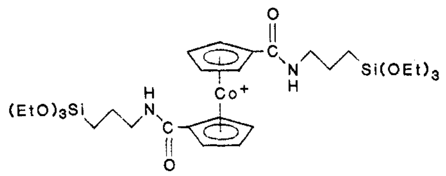

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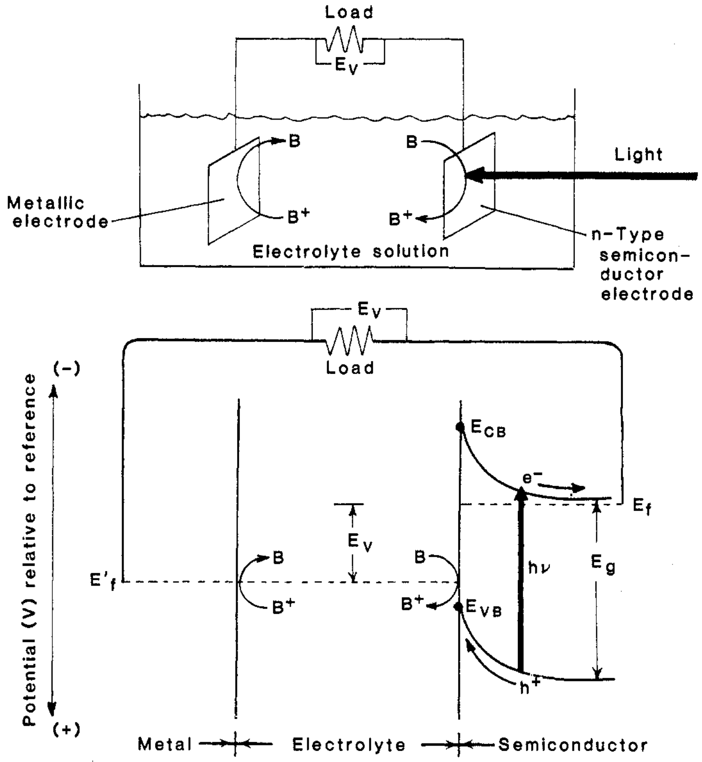


Fig. 1. An *n*-type semiconductor-based photoelectrochemical cell for the conversion of light to electricity. The top portion of the figure shows the cell and the bottom portion shows the energetics. The crucial feature is that the oxidation of *B* to B^+ occurs at an electrode potential (E_f) that is more negative (by the photovoltage, E_v) than the electrochemical potential of the solution (E_f'). When the photogenerated hole (h^+) comes to the semiconductor-electrolyte interface, oxidation of *B* to B^+ or oxidative corrosion of the semiconductor can occur. Redox polymers coated on the photoanode surface can suppress corrosion.

photocathode surface. However, these reagents alone do not catalyze H_2 evolution. The redox polymer consists of fast, one-electron, outer-sphere redox subunits that are incapable, kinetically, of liberating H_2 from H_2O. Accordingly, the materials derived from reagents **4** or **5** must be used in conjunction with noble metal catalysts, such as palladium, platinum, or rhodium, deposited onto the polymer to liberate H_2.

Figure 2 illustrates the improvement in performance of a thin-film (~1 μm) *a*-Si:H photocathode for H_2 evolution (*14*). The improvement in overall photoelectrolysis efficiency by this method is general, but the highest efficiencies for photoelectrochemical generation involve the direct deposition of the noble metal onto the photocathode surface (*15, 16*). The polymer system does have the advantage that the noble metal does not come into direct contact with the surface of the *p*-type semiconductor because of the intervening polymer layer. Typically, the contact between a *p*-type semiconductor and the noble metals would be expected to be an ohmic contact (*3*); this would lead to poor performance, as is often found in attempts to platinize *p*-WS_2 (*16*). However, for silicon, *a*-Si:H, and InP it is likely that ohmic contacts can be avoided without the redox polymers owing to thin intervening oxide layers. Thus, the use of redox polymers will probably only be an advantage in those cases where the large internal surface area of the polymer can be exploited or where the molecular-based material is required to achieve a desired reduction process, such as the reduction of a biological redox reagent that would not be reduced at naked or metallized photocathode surfaces. Viologen derivatives are known to be effective redox mediators in solution (*17*). Surfaces derivatized with **4** or **5** have been demonstrated to equilibrate with large biological redox reagents (*18*).

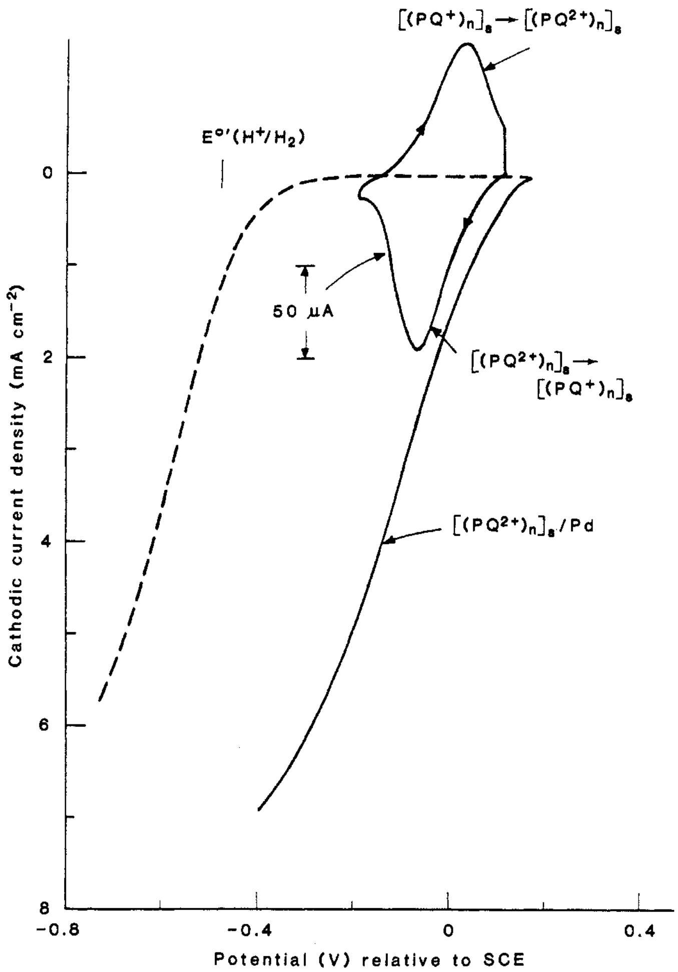


Fig. 2. Comparison of H_2 evolution photocurrent for "naked" (----) and derivatized *i*-*a*-Si:H photocathodes. The derivatized electrode is similar to that in Fig. 3, where the polymer is derived from reagent **4**, except that the noble metal palladium is restricted to the outermost region of the polymer. The crucial finding is that the catalytic electrodes give a large photocurrent at an electrode potential significantly positive of $E^{\circ\prime}(H^+/H_2)$, reflecting a large E_V. The photoelectrochemical response of the $(PQ^{2+/+})_n$ polymer without palladium on its surface indicates that the noble metal is required to effect a significant rate of H_2 evolution at electrode potentials positive of $E^{\circ\prime}(H^+/H_2)$ (*14*). [Reprinted with permission from *The Journal of Vacuum Science and Technology*]

The large internal surface area of the $(PQ^{2+/+})_n$ system confined to a planar electrode surface has been exploited to effect the reduction of an aqueous CO_2 equivalent as shown in Fig. 3, where the palladium, dispersed throughout the polymer, plays the crucial role of equilibrating the $(PQ^{2+/+})_n$ system with the CO_3H^-/HCO_2^- redox system (*19*). The formation of HCO_2^- can be effected with better than 80 percent current efficiency within 100 mV of $E^{\circ\prime}$ for the reaction. The dispersed systems based on large surface area palladium are the only known catalysts, other than enzymes (*20*), for the equilibrium at standard temperature and pressure represented by Eq. 3.

$$H_2 + CO_3H^-_{(aq)} \rightleftarrows HCO_2^- + H_2O \qquad (3)$$

For electrochemical and photoelectrochemical systems, the formation of C–H-containing molecules from CO_2 under mild conditions is an important objective. The performance of the catalytic cathode represented by Fig. 3 and quantitative data concerning the rate of interconversion represented by Eq. 3 establish that C–H bond formation can be facile under mild conditions (*19*).

Electrocatalysis of O_2 Reduction for Improved Fuel-Cell Performance

One elegant and potentially useful example of electrocatalysis by means of molecular derivatization of a surface is the catalysis of the $4e^-$ reduction of O_2 in acid solution (*21*). The technological connection here is again energy conversion. Fuel cells and batteries that employ O_2 in air as the oxidant suffer from poor electrode kinetics for the half-reaction to produce H_2O (Eq. 4) compared to the kinetics for the half-reaction to produce H_2O_2 (Eq. 5) (NHE, normal hydrogen electrode).

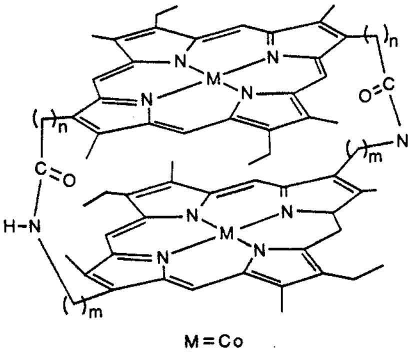
$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O, E^\circ = +1.23 \text{ V relative to NHE} \qquad (4)$$

$$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2, E^\circ = +0.68 \text{ V relative to NHE} \qquad (5)$$

The result is a significant voltage loss from the value (~1.23 V) expected for a H_2/O_2 fuel cell operated under standard conditions. Improved rates of O_2 reduction to H_2O near $E^\circ(O_2/H_2O)$ would have a large impact on the efficiency of fuel cells.

Anson and Collman (*21*) have collaborated to demonstrate that species **6** adsorbed onto graphite electrode surfaces will catalyze the $4e^-$ reduction of O_2 to H_2O in acid solution at an electrode potential positive of the O_2/H_2O_2 potential. Species **6** is the only synthetic material known to be a catalyst for the $4e^-$ reduction of O_2. Although the catalyst lifetime is not sufficiently long to be useful in fuel cells, and although the synthesis of species **6** is difficult, the results with **6** provide an especially noteworthy existence-proof for synthetic, molecular catalysts for complex, multielectron transfer reactions.

Catalysts such as species **6** may be useful in a less demanding application, such as an amperometric O_2 sensor. In such an application, the $4e^-$ reduction of O_2 would obviously give a larger current than a $2e^-$ process. Also, there would be practical value in being able to effect the O_2 reduction at a potential where the $2e^-$ process cannot occur thermodynamically, so that H_2O_2 will not be formed and the observed current will be more quantitatively related to O_2 concentration. The results with species **6** also spur speculation concerning the nature of the O_2 evolution catalyst in photosynthesis. A good O_2 evolution catalyst is needed for the visible light–driven oxidation of H_2O at small band-gap (especially nonoxide) semiconductor photoanodes. The results with species **6** may be the first crack in the barrier to finding a good, reversible catalyst for the O_2/H_2O couple. In this regard, it is worth noting that the photosynthesis O_2 site is believed to involve two manganese atoms (*22*) and that a molecular dinuclear ruthenium complex has been demonstrated to catalyze H_2O oxidation (*23*). Further progress in the catalysis of O_2/H_2O with molecular catalysts is a likely prospect.



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Electrochemical Synthesis of H_2O_2 via O_2 Reduction

The clean $2e^-$ reduction of O_2 could provide a new practical route to synthesis of H_2O_2. However, selective reduction of O_2 has several complications. First, there is the issue of whether the $4e^-$ reduction to H_2O would compete, since the driving force for the $4e^-$ process would be considerably more than that for the $2e^-$ process. Second, there is the prospect that, once formed, the H_2O_2 would be reduced because the half-reaction represented by Eq. 6 would have an even larger driving force than the $4e^-$ reduction of O_2.

$$H_2O_2 + 2e^- + 2H^+ \longrightarrow 2H_2O, E^\circ = +1.68 \text{ V relative to NHE} \qquad (6)$$

Finally, there is the problem of generating large amounts of H_2O_2 free of electrolyte. One industrial synthesis of H_2O_2 is via the two-step process represented by Eq. 7 (with heterogeneous catalyst) and Eq. 8, where AQ is a 9,10-anthraquinone derivative and AQH_2 is the reduced dihydroxy form (*24*).

$$H_2 + AQ \longrightarrow AQH_2 \qquad (7)$$

$$AQH_2 + O_2 \longrightarrow AQ + H_2O_2 \qquad (8)$$

$$H_2 + O_2 \longrightarrow H_2O_2 \qquad (9)$$

The net reaction is given by Eq. 9, with AQ being recycled. A practical problem is that AQ is irreversibly hydrogenated and is slowly drained from the system. In addition, the net reaction given by Eq. 9 is downhill by 1.36 eV per molecule of H_2O_2. It should be possible to exploit this large driving force to liberate electrical energy during the formation of H_2O_2 from the elements H_2 and O_2.

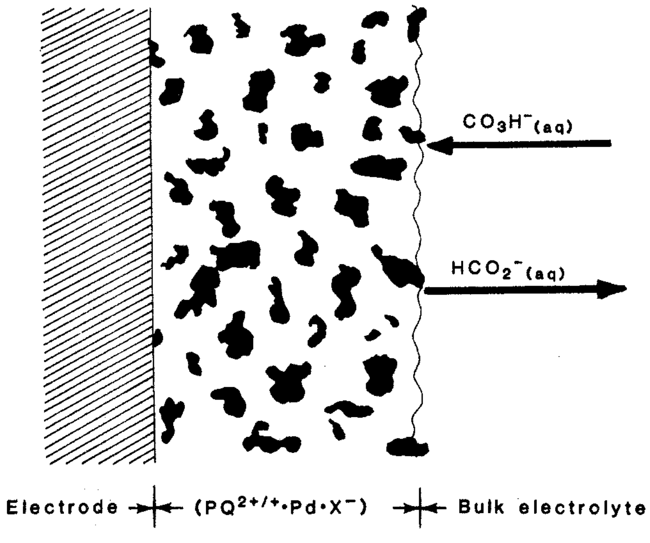
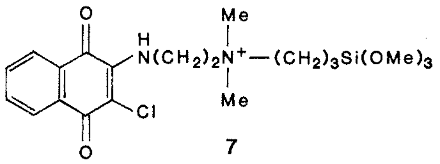


Fig. 3. Catalytic electrode for the reduction of an aqueous CO_2 equivalent, CO_3H^-. The charge compensating anion (or anions), X^-, are a mixture of CO_3H^- and HCO_2^- (*19*).

Modification of electrode surfaces with the quinone derivative **7** is effective in producing an electrode surface that is selective for the reduction of O_2 to H_2O_2 in aqueous solution (*25*). The $E^{\circ\prime}$ of the surface-bound quinone is about 400 mV more negative than that of O_2/H_2O_2, and the rate constant (k_{et}) for the process represented by Eq. 10 is more than $10^5 M^{-1}$ sec^{-1}.



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$$QH_2(\text{surface}) + O_2 \xrightarrow{k_{et}} Q(\text{surface}) + H_2O_2 \qquad (10)$$

It would be desirable to use a Q/QH_2 modifier that has an $E^{\circ\prime}$ closer to that of the O_2/H_2O_2 couple without sacrificing the good rate achieved with reagent **7**. Since the electrochemical reduction of the quinone does not proceed by the same mechanism as for catalytic hydrogenation (Eq. 7), the side reactions that drain AQ do not occur with the electrochemical procedure. The Q/QH_2 (surface)

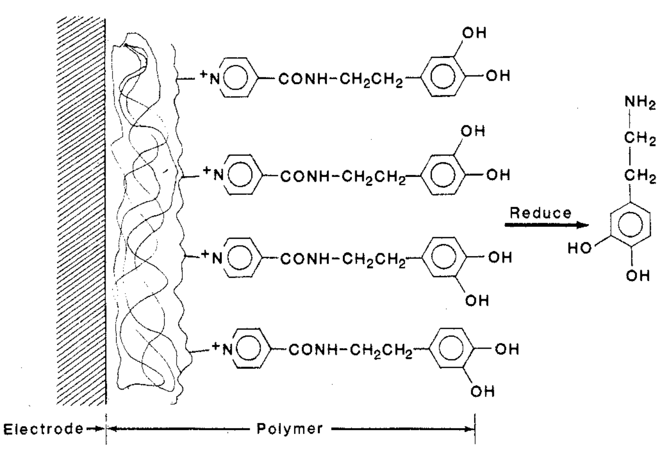

Fig. 4. A redox polymer electrode for the electrochemical release of the neurotransmitter dopamine (*26*).

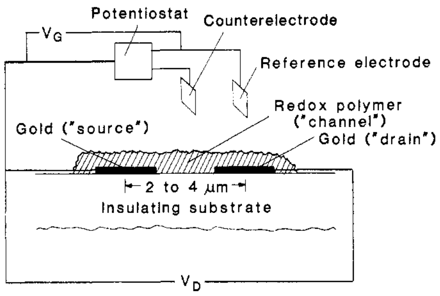

Fig. 5. A microelectrochemical transistor based on the large conductivity change in polymers such as polypyrrole, poly-3-methylthiophene, and polyaniline (*33, 39, 40*).

system derived from reagent **7** is selective and durable even in 0.1*M* H_2O_2, and the number of H_2O_2 molecules generated per Q entity on the surface has been demonstrated to exceed 10^6 (*25*).

The electrochemical reduction of O_2 with the Q/QH_2 (surface) system from reagent **7** was extended in a way that allows the generation of high H_2O_2 concentration in H_2O free of electrolyte (*25*). The electrochemical reduction of large surface area SiO_2 derivatized with reagent **7** in the cathode compartment of an electrochemical cell results in immobilized QH_2 that can be isolated by physical means, washed with H_2O, and exposed to aerated H_2O to generate H_2O_2 in an amount equal to the amount of QH_2 generated electrochemically. Large surface area SiO_2 derivatized with even a monolayer of reagent **7** is significantly quinone by mass, and up to 0.1*M* H_2O_2 can be prepared in a single cycle of the process. The electrochemical reduction of the powder enables pure H_2O_2 to be prepared and makes it possible to use a trivial separator in the electrochemical cell.

Controlled Release of Chemically Active Reagents

Work by Miller and colleagues (*26, 27*) has demonstrated that it is possible to exploit electrochemically labile linkages to release physiologically active reagents. The specific system for the release of neurotransmitters is illustrated in Fig. 4. The fundamental key is to find an electrochemical cleavage reaction that can release the desired reagent in its active form. Miller's work establishes an important principle that could be useful in the controlled, in situ delivery of drugs. At the present time there are questions concerning whether modified electrodes could have the "capacity" and other properties that would make them useful in applications, but the idea is one worth exploring.

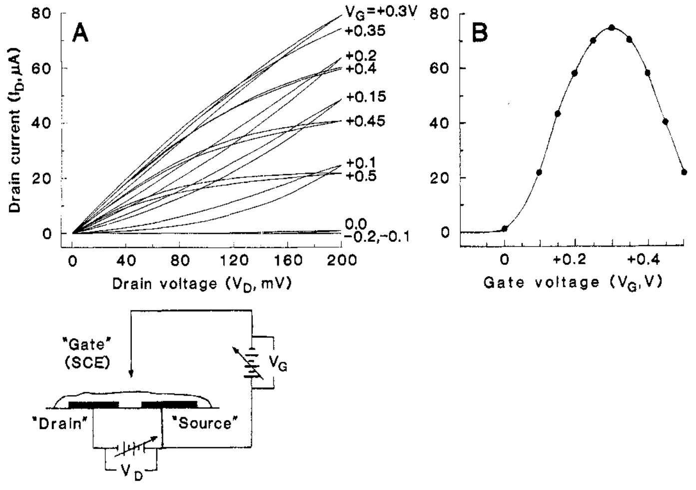

Fig. 6. Characteristic curves of a polyaniline-based transistor device represented by Fig. 5. The thickness of the polyaniline is approximately 5 μm. The plots of I_D versus V_D at fixed V_G were measured by varying V_D at 10 mV/sec^{-1} from 0 V to +0.2 V and back to 0 V. The plot of I_D versus V_G on the right curve is for V_D = 0.18 V (*40*). [Reprinted with permission from *The Journal of Physical Chemistry*. Copyright 1985, American Chemical Society]

The electrochemical release of reagents other than those important as physiological agents may have unforeseen practical applications. For example, controlled release of homogeneous catalysts may have value as a chemical amplification method and may be especially valuable if the catalyst can be resequestered. Such reversible systems may be based on the fact that redox polymers undergo a change in the state of charge upon oxidation or reduction and hence change their affinity for electrostatically bound reagents. As is the case for many surface-bound cationic polymers (*28*), the polymers derived from reagents **4** (*29*) and **5** (*13*) firmly bind transition metal anions such as $Fe(CN)_6^{4-}$. Upon reduction of $(PQ^{2+})_n$ or $[Co(CpR)_2^+]_n$, the positive charge of the polymer declines and the electrostatically bound anion can be released. The process can be reversed by reoxidizing the polymer to reintroduce a polycation that will bind the anion (Eq. 11).

$$[Co(CpR_2)^+ \cdot ¼\ Fe(CN)_6^{4-}]_n \underset{-ne^-}{\overset{+ne^-}{\rightleftharpoons}} [Co(CpR)_n^0] + ¼Fe(CN)_6^{4-} \tag{11}$$

Such systems promise greater reversibility than cleavage of covalent bonds, but it is not clear now that useful practical applications exist. However, the general area of controlled release of chemical reagents is significant, and the conceptual notion of chemical amplification of an electrode process by release of a catalyst brings to mind biological systems in which a small stimulus (electrical or chemical) can be amplified.

Electrochromic Surfaces

Surface-confined redox polymers can undergo large optical spectral changes upon oxidation and reduction. This may be useful in the development of new kinds of display devices. Molecule-based materials offer the ability to develop systems involving a wide range of colors—indeed full color—and colors that depend on potential. Molecules sometimes have several accessible redox states, each with a characteristic spectrum. The polymer system derived from reagent **4** illustrates some of the possibilities (*30*). Electrochromic displays can be based on the reductive deposition of *N,N'*-di-*n*-heptyl-4,4'-bipyridinium (HV^{2+}) to HV^+ onto a display element according to the process given by Eq. 12 (*31*).

$$\underset{\text{(Colorless)}}{n\text{HV}^{2+}\text{(solute)}} \underset{-ne^-}{\overset{+ne^-}{\rightleftharpoons}} \underset{\text{(Violet)}}{n\text{HV}^+(\downarrow)} \tag{12}$$

The properties of a molecule-based display such as that represented by the $HV^{2+/+}$ system are attractive in some respects. However, the viologen-based electrochromic polymer derived from reagent **4** and confined to an electrode surface offers certain advantages because the electrochromic material is permanently attached to the conducting surface. The advantages include providing a wider temperature range for useful operation and better chemical reversibility while giving the essential optical properties associated with the $HV^{2+/+}$ system.

With our present knowledge of molecular synthesis, it seems plausible that practical, molecular-based, electrochromic materials can be designed. The crucial properties are the color (or colors) involved, the change in absorptivity per unit charge passed to effect the color change, the speed of switching from one color to another, and the durability of the electrochromic material. For designing the best electrochromic materials, better methods must be developed to predict the properties of a polymer from what is known about the monomer. The switching speed and durability of an electrochromic polymer are properties that cannot be straightforwardly predicted by knowing the properties of the monomer. The polysiloxane derived from hydrolysis of reagent **4** does have good durability and switching speed, and both these properties are consistent with those of *N*,*N*′-dialkyl-4,4′-bipyridinium monomers. In addition, the color of the various redox states of the polymer and the efficiency of coloration are predictable from the properties of the monomer (*30*). For other electrochromic polymers, such as poly-3-methylthiophene (*32, 33*), none of the essential properties can be easily extrapolated from the properties of the monomer. For electrochromic polymers that are good electronic conductors in one redox level, such as poly-3-methylthiophene (*32, 33*), polypyrrole (*34*), or polyaniline (*35*), the switching speed may be superior to materials formed by polymerization of "conventional" redox reagents.

Microelectrochemical Devices

Basic research results in the area of electrode modification have led to opportunities for the development of new kinds of microelectronic devices involving molecular materials as the active elements. The work of Murray and co-workers (*36*), especially, has demonstrated the possibility of fabricating microelectrochemical diodes having characteristics (turn-on voltage and switching speed) that depend on the combination of molecular materials. Polymer-polymer bilayer assemblies that could function as diodes when immersed in an electrolytic solution have been demonstrated (*37*). Another important "device" demonstrated with macroscopic system is the ion-gate electrode, which is an electroactive membrane (*38*).

In another vein, the techniques of microfabrication used in the manufacture of solid-state electronic devices have been combined with electrode modification techniques to prepare analogs of solid-state transistors and diodes. Figure 5 illustrates the kind of transistor device that has been made by surface modification of a pair of closely spaced (~ 1 μm) gold microelectrodes (approximately 1 to 2 μm wide, 50 μm long, and 0.1 μm thick) (*33, 39, 40*). The key is that the redox polymer spanning the gap between the two microelectrodes has a conductivity that depends on its redox potential. The resistance between the electrodes called "source" and "drain" varies by more than six orders of magnitude upon a variation of about 0.5 V in the gate potential (V_G). Figure 6 illustrates the characteristic curve for drain current (I_D) versus V_G (at a fixed drain potential) for a polyaniline-based transistor (*40*). The characteristic curve is distinguished from that for a solid-state transistor in that the former shows a peak, which means that the device can be switched from off to on to off again by increasing V_G. A discrete solid-state device can be turned only from off to on (or vice versa) by increasing V_G. It is characteristics such as this one that may make the microelectrochemical device useful. Near-term applications are likely to be in the sensor field, where the molecular materials may present superior ways to detect and amplify specific chemical signals. For example, only redox reagents that will bring polyaniline to a potential of about +0.4 V relative to SCE (saturated calomel electrode) will turn on a polyaniline-based transistor to the maximum extent. By employing subsequent surface modification of the active polymer it should be possible to build in sensitivity to only specific redox signals. Work involving surface modification to improve the rate of heterogeneous redox reaction of biological redox reagents (enzymes and their substrates) should prove especially fruitful in combination with microfabrication techniques.

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