New Strategies for Electrocatalysis at Polymer-Coated Electrodes. Reduction of Dioxygen by Cobalt Porphyrins Immobilized in Nafion Coatings on Graphite Electrodes

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Abstract: A new method for introducing porphyrin molecules into Nafion coatings on electrodes is described. The incorporated porphyrins are exceptionally stable and can readily be metallated while remaining in the coating. Coatings containing cobalt tetraphenylporphyrin (CoTPP) were prepared to exemplify the method, which is applicable to a variety of macrocyclic ligands possessing basic sites. The CoTPP in the Nafion coatings retained its ability to catalyze the electroreduction of dioxygen when the electrons were carried from the electrode to the almost immobile catalyst sites by $Ru(NH_3)_6^{2+}$ ions also incorporated in the coating. The resulting separation of the catalytic and electron transport functions within such coatings is argued to have general virtues that may be exploited to extend the range of applicability of polymer-coated electrodes in electrocatalysis and to diagnose the mechanisms by which they operate.

Much of the current interest in polymeric coatings on electrode surfaces originated in the hope that catalytically active molecules incorporated in the polymers could be used as electrocatalysts. Although the number of successful electrocatalytic applications of polymer-coated electrodes is still rather small,[1-6] there has been significant recent progress in delineating and analyzing the various factors that may limit the current in electrocatalytic systems.[1,3b,4,6-9] There is now general consensus that there are four potential current-limiting processes: (i) transport of the substrate in the solution to the electrode surface; (ii) transport of the substrate within the electrode coating to the catalyst sites; (iii) transport of the charge (electronic and ionic) required to reduce or oxidize the catalyst between the electrode surface and the catalytic sites within the coating; (iv) the rate of the electron cross-reaction between substrate and catalyst when they encounter each other within the coating. To optimize the electrocatalytic efficiency of electrodes coated with polymers in which catalysts are incorporated, it is essential that the first three of these processes be faster than the fourth. Thus, one must seek electrocatalysts for incorporation in polymeric coatings that are both highly reactive toward the substrate of interest and capable of sustaining high rates of charge transport within the coating. The latter property can sometimes be realized by employing high concentrations of catalysts that diffuse rapidly within the polymer coating or exhibit large effective diffusion coefficients because high rates of electron self-exchange produce efficient electron hopping between oxidized and reduced forms of the catalyst.[3,4c,10-16] However, rapid physical diffusion of a catalyst can lead to its continuous loss from the coating with a corresponding degradation in the catalytic efficiency of the electrode. In addition, it is undesirably restrictive to demand that a catalyst provide both high reactivity toward the substrate and large electron exchange rates with itself. For example, the recently developed cofacial dicobalt porphyrin electrocatalysts for dioxygen reduction[17-19] are not likely to exhibit rapid electron self-exchange [between cobalt(II) and cobalt(III)] or high rates of physical diffusion in polymeric coatings. There is, nevertheless, considerable incentive for devising ways to bind such catalysts to electrode surfaces within polymeric coatings in order to diminish the rate with which they are lost from graphite electrode surfaces when bound only by "irreversible" adsorption.[17]

The approach described in this study utilizes an auxiliary, rapidly diffusing redox reagent, $Ru(NH_3)_6^{2+}$, to carry electrons from the underlying electrode to much more slowly diffusing cobalt porphyrin molecules that are bound permanently within coatings of Nafion on graphite electrode surfaces. The strategy shares some common features with that employed recently by Fukui et al.,[20] who utilized a redox mediator dissolved in solution to increase the fraction of a quinoid polymer coating that could be electroreduced. In the present instance the molecules of cobalt tetraphenylporphyrin in the coating are shown to retain their ability to catalyze the reduction of dioxygen with the electrons delivered by the $Ru(NH_3)_6^{3+/2+}$ couple that is attracted into the polyanionic coating where it serves as an electron-transfer mediator. The kinetic behavior of the coating can be accounted for, at least qualitatively, on the basis of a model developed by Andrieux et al. for two-component coatings.[9] This three-component coating (polymer, catalyst, mediator) seems likely to represent only the

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first example of a new class of polymer coated electrodes in which the combinations of catalysts and polymeric coating materials that may be utilized in electrocatalytic applications encompass a significantly broader range.

Experimental Section

Materials. Aliquots of a 0.52 wt % stock solution of Nafion were applied to graphite electrodes to prepare electrode coatings. The stock solution was prepared by diluting a 5.2% solution (provided by E. I. du Pont de Nemours Co. a number of years ago) 10-fold with 2-propanol. Sections of a Nafion 1200 membrane (supplied as a sample by E. I. du Pont de Nemours Co.) were used to make spectral measurements on *meso*-tetraphenylporphyrin (H_2TPP) and its cobalt derivative incorporated in Nafion. $Ru(NH_3)_6Cl_3$ (Matthey Bishop, Inc.), H_2TPP (Strem Chemicals, Inc.), and other reagent-grade chemicals were used as received. Solutions were prepared from deionized water that was also passed through a Barnstead Nanopure purification train. Basal plane-pyrolytic graphite electrodes (Union Carbide Co.) were cut and mounted as previously described[21] to expose an area of 0.174 cm^2. The calomel reference electrode was saturated with sodium chloride and all potentials are quoted with respect to this electrode (SSCE). Standard two-compartment cells were used for both cyclic voltammetric and rotating disk electrode experiments.

Instrumentation. Cyclic voltammetry and coulometry were performed with appropriate PAR instruments (E, G and G Industries). For rotating disk voltammetry a Pine Instrument Co. RDE3 potentiostat, ASR2 rotator and ASR speed control were employed. Spectra were recorded with Hewlett-Packard Model 8450A spectrophotometer.

Procedures. The Nafion membrane was cleaned before use by soaking in 2-propanol for several hours, which removed most of a yellow-brown color initially present. To incorporate porphyrin into the membrane it was soaked for several days in a 9 M H_2SO_4 solution saturated with *meso*-tetraphenylporphyrin. Under these conditions the porphyrin is doubly protonated, H_4TPP^{2+}, and the solution is bright green. Cobalt(II) was subsequently introduced into the incorporated porphyrin by washing the membrane with dilute buffer to remove residual acid and then immersing it for 2 h in a 0.1 M solution of $Co(NO_3)_2$ at 80 °C. Excess Co^{2+} was then removed by stirring the membrane in 0.25 M NaCl. For spectral measurements the loaded membranes were clamped between two microscope slides.

Nafion coatings were prepared by pipeting a few microliters of the 0.52% stock solution onto the electrode surface and allowing the solvent to evaporate. The thickness of the resulting films was estimated to be 0.1–0.3 μm on the basis of measurements with a Dektak Profilimeter of films formed from the same quantities of the Nafion stock solution on more highly polished substrates such as glassy carbon or platinum.

Because of the long soaking times required for incorporation of porphyrin into the Nafion coatings (typically 2–3 days), special care was required in sealing the electrodes: After an electrode was cleaved to expose a fresh surface of graphite by cutting with a razor blade through the electrode and its surrounding shroud of heat-shrinkable tubing, the fresh electrode was heated with a heat gun just enough to cause the polyolefin tubing to soften, thereby forming a tight seal around the freshly exposed surface. Failure to include this step often resulted in unusually large background currents that were presumably the result of the 9 M solution of acid creeping between the electrode and the insulating tubing.

The porphyrin was incorporated into Nafion coatings by the same method used with Nafion membranes. The coatings developed much more intense lime green colors than did the much thicker Nafion membrane. This indicates that the coatings incorporate larger quantities of the porphyrin than the membrane, presumably because of the more open structure of the coatings.[3b,16] After metallation of the incorporated porphyrin by the same procedure used with the membranes, the electrode surface acquired a brown-purple color characteristic of CoTPP; no remnants of the bright green H_4TPP^{2+} could be detected when the film was exposed to acid, indicating that cobalt had been introduced into all of the incorporated porphyrin. The quantities of CoTPP introduced into Nafion films in this way were estimated as described under Results.

Results

Spectra and Stability of the Porphyrin in Nafion Membranes. A procedure for incorporation of the green, diprotonated form of *meso*-tetraphenylporphyrin, H_4TPP^{2+}, into Nafion membranes from 9 M H_2SO_4 solutions was described under Experimental Section. The resulting green membranes were converted to the brown-purple color characteristic of unprotonated porphyrin, H_2TPP, by soaking for a few minutes in a borate buffer (pH 10). These color changes were quite reversible and could be repeated many times by soaking the membranes alternatively in 0.5 M acid or pH 10 buffer.

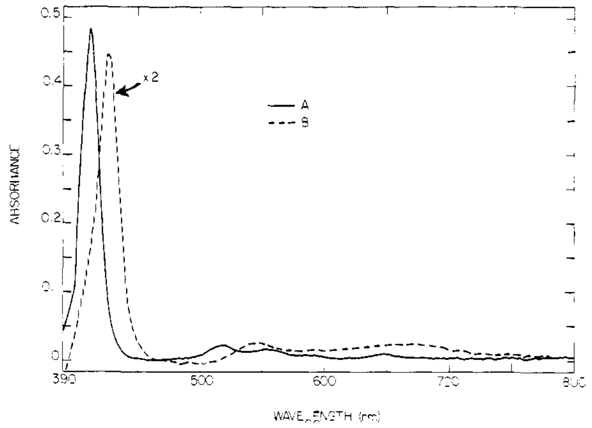

Figure 1. Absorption spectra of *meso*-tetraphenylporphyrin incorporated in a Nafion membrane. (A) The neutral metal-free porphyrin; (B) after metallation with Co^{2+}. See the text for details.

A spectrum of the neutral porphyrin in Nafion is shown in Figure 1. The relative positions of the Soret (412 nm) and Q (515, 553, 592, and 650 nm) bands match those obtained in solution in nonaqueous solvents,[22] showing that the incorporated porphyrin molecules remain intact. (The broad, weak absorption centered at 650 nm varied from membrane to membrane and is believed to result from an impurity.) The original spectrum in Figure 1 was changed to that traced by the dashed line by treating the membrane with $Co(NO_3)_2$ as described under Experimental Section. The decreased intensity and red shifts of the Soret and Q bands correspond to those expected for conversion of H_2TPP to $Co^{II}TPP$.[23] The intensities of the Soret bands in the two spectra in Figure 1 are in about the same ratio as those for H_2TPP and CoTPP dissolved in dichloromethane.[22,23] Assuming that the extinction coefficients are approximately equal in Nafion and dichloromethane, this observation implies that essentially all of the H_2TPP incorporated in the Nafion remains in the membrane and is converted to CoTPP during the reaction with $Co(NO_3)_2$.

H_4TPP^{2+}, H_2TPP, and CoTPP were all quite stable in the Nafion membrane. No detectable loss was noted even after several day's soaking in supporting electrolytes (0.5 M H_2SO_4 for H_4TPP^{2+}; 0.5 M Na_2SO_4 for H_2TPP and CoTPP). However, when a membrane loaded with CoTPP was soaked for 2 days in 0.5 M H_2SO_4, it began to turn the green color characteristic of H_4TPP^{2+}. The color change resulted from the loss of Co^{2+} from the porphyrin ring because subsequent treatment of the membrane with $Co(NO_3)_2$ followed by reexposure to 0.5 M H_2SO_4 produced no trace of the green color. A similar acid-promoted demetallation of $Co^{II}TPP$ incorporated in Nafion coatings on electrodes was also observed and could be reversed by repetition of the treatment with $Co(NO_3)_2$.

Electrochemical Response of CoTPP in Nafion Coatings. Curves A and B in Figure 2 are cyclic voltammograms for H_2TPP and CoTPP, respectively, incorporated in a Nafion coating on a graphite electrode. Except for the small decrease in background current, introduction of Co(II) produces no change in the response. That is, there is no evidence of electrochemical oxidation of $Co^{II}TPP$ or reduction of $Co^{III}TPP$. For comparison, curve C gives the voltammetric response obtained from ca. 10^{-8} mol cm^{-2} of CoTPP adsorbed directly on a bare graphite electrode under the same conditions. The reversible couple evident at 0.35 V corresponds to the $Co^{III}TPP/Co^{II}TPP$ couple. It seems clear from the difference between curves B and C that incorporation of $Co^{II}TPP$ in the Nafion coating essentially eliminates its electrochemical

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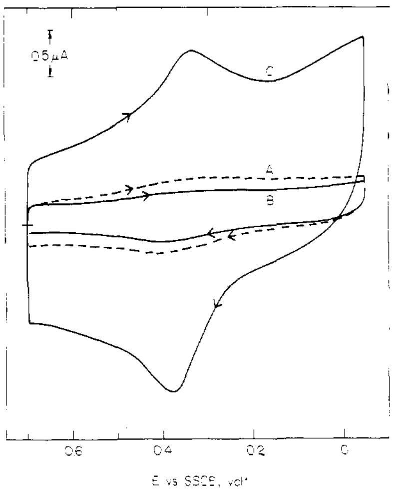

Figure 2. Cyclic voltammograms of H_2TPP and CoTPP at basal plane pyrolytic graphite electrodes. (A) Electrode coated with 3.7×10^{-8} mol cm^{-2} Nafion in which H_2TPP was incorporated. (B) Repeat of A after the incorporated porphyrin was converted to CoTPP. (C) Bare graphite electrode on which ca. 10^{-8} mol cm^{-2} CoTPP had been adsorbed. Supporting electrolyte: 0.5 M H_2SO_4 saturated with argon. Scan rate: 50 mV s^{-1}.

response. We believe this loss of detectable voltammetric activity is the result of the extremely small mobility of the metalloporphyrin within the Nafion coating. Very small diffusion rates of porphyrin in Nafion are also consistent with the days of immersion time required to obtain incorporation equilibrium when the coatings are exposed to solutions of H_4TPP^{2+} as well as the remarkable stability of the porphyrins in the coating once they have been incorporated.

Estimation of Quantities of $Co^{II}TPP$ Incorporated in Nafion Coatings. The very low mobility of $Co^{II}TPP$ in Nafion coatings complicates the usual coulometric method for determining the quantities of complex in the coating[24] because excessively long times are required for all of the complex to diffuse to the electrode and contribute to the measured faradaic charge.

To circumvent this difficulty an indirect procedure was developed for the coulometric assay of the $Co^{II}TPP$ in Nafion coatings. First, the coating, loaded with $Co^{II}TPP$, was allowed to stand for 2 days in 0.5 M Na_2SO_4 saturated with air, which resulted in the oxidation of the $Co^{II}TPP$ to $Co^{III}TPP$. The oxidized coating was then transferred to a 0.5 M H_2SO_4 solution also containing 1×10^{-8} M $Ru(NH_3)_6^{3+}$, which is relatively rapidly incorporated by the coating even at this low concentration because of electrostatic binding to the sulfonate groups as previously described.[15] The incorporation of $Ru(NH_3)_6^{3+}$ does not displace the CoTPP already present in the coating because the interactions that bind the porphyrin to the coating are predominantly hydrophobic rather than electrostatic ($Co^{II}TPP$ is neutral) and the low mobility of CoTPP within the coating also impedes its displacement. After the incorporation was complete the solution was thoroughly purged with argon to remove dioxygen and the cyclic voltammogram shown in Figure 3 was recorded by using a scan rate low enough (5 mV s^{-1}) to ensure that all of the rapidly diffusing $Ru(NH_3)_6^{3+}$ ions were able to reach the electrode to be reduced.[25] The area under the cathodic portion of the voltammogram is a measure of the sum of the reducible $Ru(NH_3)_6^{3+}$ and $Co^{III}TPP$ in the coating because the $Ru(NH_3)_6^{2+}$ generated at the electrode diffuses throughout the coating and reduces all of the accessible $Co^{III}TPP$. The resulting $Ru(NH_3)_6^{3+}$ is subsequently reduced again to $Ru(NH_3)_6^{2+}$ at the electrode surface.

The very low concentration of $Ru(NH_3)_6^{3+}$ in the bulk of the solution (10^{-8} M) assured that the contribution to the cathodic area from this source was insignificant. The smaller area under the anodic portion of the voltammogram measures only the quantity of $Ru(NH_3)_6^{2+}$ in the coating because there is no efficient pathway for direct or indirect oxidation of $Co^{II}TPP$. There is no significant loss of $Ru(NH_3)_6^{2+}$ from the coating during the time required to record the voltammogram so that the difference between the areas of the cathodic and anodic portions corresponds to the $Co^{III}TPP$ in the coating. The cathodic and anodic faradaic charges were also measured by potential step techniques but cyclic voltammetry with low potential scan rates was preferable because visual correction for the relatively large background currents was more straightforward.

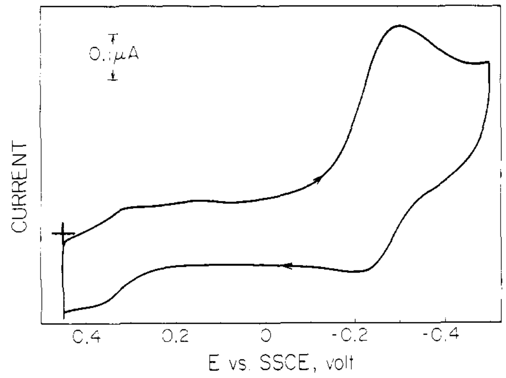

Figure 3. Cyclic voltammogram for $Ru(NH_3)_6^{3+}$ incorporated in a Nafion coating (2.4×10^{-7} mol cm^{-2}) also containing CoTPP. Supporting electrolyte: 0.5 M H_2SO_4 plus 1×10^{-8} M $Ru(NH_3)_6^{3+}$. Scan rate: 5 mV s^{-1}.

This procedure was applied to several Nafion coatings that contained 3.7×10^{-7} mol cm^{-2} of sulfonate groups. The values obtained for the amount of incorporated CoTPP varied from 2×10^{-10} to 10×10^{-10} mol cm^{-2} even though the same incorporation procedure was employed in each case. This rather wide variation in the quantity of CoTPP incorporated results from difficulties in controlling the quantity of H_4TPP^{2+} that is incorporated by the coatings from 9 M H_2SO_4.

Catalysis of the Reduction of Dioxygen by CoTPP in Nafion Coatings. Rotating graphite disk electrodes coated with Nafion in which CoTPP is incorporated do not yield sustained dioxygen reduction currents at potentials where rapid reduction of dioxygen proceeds when CoTPP is adsorbed on the electrode surface in the absence of Nafion. The lack of the catalyzed reduction of dioxygen with the Nafion–CoTPP coating seemed clearly to result from the lack of an efficient means to transport electrons from the electrode surface to the catalytically active CoTPP sites. (Penetration of the Nafion coating by O_2 molecules was shown to be rapid by observing their uncatalyzed reduction at more negative potentials.)

To provide a mechanism for electrons to reach the essentially immobile CoTPP sites, $Ru(NH_3)_6^{3+}$ was added to the solutions of dioxygen at concentrations in the micromolar range. The tripositive cation was readily incorporated by the polyanionic Nafion coating where it could be reduced to $Ru(NH_3)_6^{2+}$ to produce an efficient shuttle for ferrying electrons between the electrode and CoTPP molecules throughout the coating in the same way it does during the coulometric assays of the coating (vide supra).

In Figure 4 a series of rotating disk current potential curves is shown for experiments in which this strategy was employed. The dashed line in Figure 4A is the background response obtained for a coating containing H_4TPP^{2+} before metallation with Co^{2+}. The response from the 1.3 μM $Ru(NH_3)_6^{3+}$ in the solution is too small to see at this low concentration (in the steady state there is, of course, no response from the larger concentration of $Ru(NH_3)_6^{3+}$ present in the coating) and the dioxygen present is not reduced by $Ru(NH_3)_6^{2+}$ in the absence of CoTPP at a rate high enough to produce a significant response.

The solid curves in Figure 4 are the responses obtained when CoTPP is present in the coatings. Two features of the sets of curves merit attention: (i) The waves corresponding to the cat-

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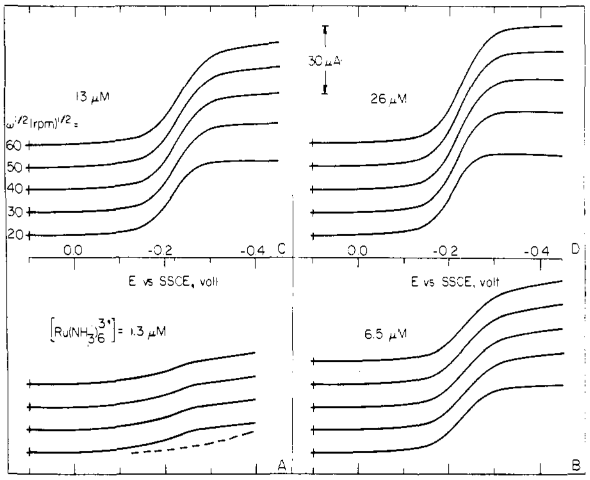

Figure 4. Current–potential curves for reduction of dioxygen at a rotating graphite disk electrode coated with 2.5×10^{-7} mol $\mathrm{cm^{-2}}$ Nafion in which ca. 5×10^{-10} mol $\mathrm{cm^{-2}}$ CoTPP was incorporated. Supporting electrolyte: 0.5 M H_2SO_4 saturated with air and also containing $\mathrm{Ru(NH_3)_6^{3+}}$ at concentrations of (A) 1.3, (B) 6.5, (C) 13, and (D) 26 μM. Potential scan rate: 2 mV $\mathrm{s^{-1}}$. Electrode rotation rates are as indicated in (C) except that the curve for $\omega^{1/2} = 60$ is omitted from (A). The dashed curve in (A) was recorded before the incorporated porphyrin was metallated with Co(II).

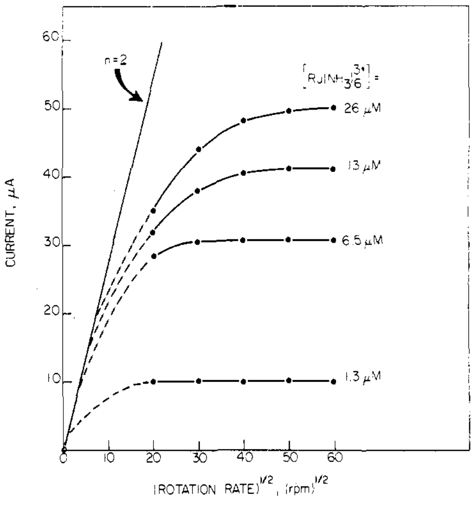

Figure 5. Levich plots (i vs. $\omega^{1/2}$) of the limiting currents for the curves in Figure 3. The unbroken line is the calculated response for the two-electron reduction of dioxygen at a bare electrode.

alyzed reduction of dioxygen appear at the potential where $\mathrm{Ru(NH_3)_6^{3+}}$ is reduced to $\mathrm{Ru(NH_3)_6^{2+}}$ *not* at the more positive potential where CoTPP adsorbed directly on graphite electrode surfaces catalyzes the reduction of dioxygen.[26] This is the expected result if the $\mathrm{Ru(NH_3)_6^{3+/2+}}$ couple is serving as a mediator for the catalyzed reduction reaction. (ii) The limiting reduction currents are essentially independent of the rate of rotation of the electrode at the lowest concentration of $\mathrm{Ru(NH_3)_6^{3+}}$ but show an increasing dependence on rotation rate as the concentration of the $\mathrm{Ru(NH_3)_6^{3+}}$ mediator is increased. At any fixed rotation rate the magnitude of the limiting catalytic current increases with the mediator concentration. Even at 26 μM the reduction of $\mathrm{Ru(NH_3)_6^{3+}}$ contributes no more than 10% to the observed limiting currents.

The rotation rate dependence of the limiting currents is made clearer in the Levich plots[27] shown in Figure 5. The straight line through the origin in Figure 5 is the calculated response for the direct two-electron reduction of dioxygen in the absence of kinetic complications, and it is clear that the measured currents lie well below the Levich currents. Kinetic analysis of such data is often facilitated by examining them in the form of Koutecky–Levich plots of i^{-1} vs. $\omega^{-1/2}$.[28] This is done for the same data in Figure 6.

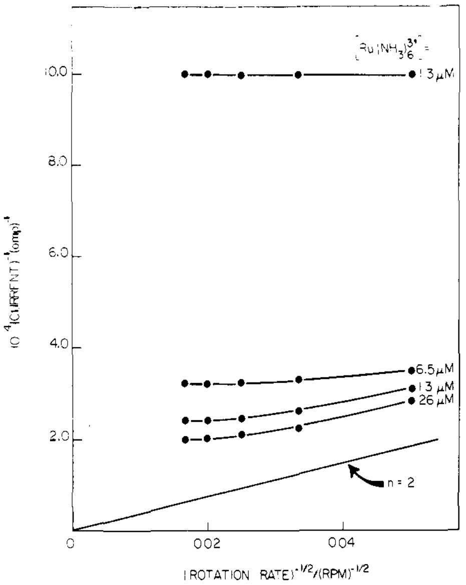

Figure 6. Koutecky–Levich plots (i^{-1} vs. $\omega^{-1/2}$) of the data from Figure 5.

The absence of a rotation rate dependence at low concentrations of the $\mathrm{Ru(NH_3)_6^{3+}}$ mediator indicates that the kinetic process limiting the current does not decrease significantly the concentration of dioxygen at the coating/solution interface. At higher mediator concentrations the dependence of the currents on rotation rate shows that the dioxygen concentration at the interface is being depleted. At the lowest rotation rates the Koutecky–Levich plot for the 26 μM solution of $\mathrm{Ru(NH_3)_6^{3+}}$ exhibits a slope that matches that of the line calculated for the mass-transfer limited two-electron reduction of dioxygen. This is strong evidence that hydrogen peroxide is the product of the electroreduction of dioxygen under these conditions.

The Current-Limiting Processes. It is instructive to consider the possible current-limiting processes in the reduction of dioxygen at Nafion–CoTPP coatings in terms of the theoretical analyses of Saveant and co-workers.[9] They describe the catalyzed reactions of substrates at rotated disk electrodes coated with polymers containing redox couples that act as catalysts in terms of four characteristic currents.[9b] These four currents measure the magnitudes of the four possible processes enumerated in the introduction that may impose limits on the currents that can be obtained at such electrodes. The magnitude of the currents measured at coated, rotated disk electrodes is determined by the relative rates of these four processes.[9]

The rate of supply of substrate to the coating/electrolyte interface was evaluated by reducing dioxygen at an uncoated rotating graphite disk electrode. The rate of diffusion of dioxygen through the coating was obtained from similar measurements at an electrode with a Nafion coating in which no CoTPP was incorporated. The currents at both electrodes were essentially equal at all rotation rates and 2–15 times larger than the observed catalytic currents under the same conditions. (The absence of significant pin holes in the Nafion coatings was indicated by their ability to block the reduction of small anionic reactants such as ferricyanide.) Thus, the supply of dioxygen to both the surface and the interior of the Nafion coatings was adequate to eliminate these processes as current-limiting factors.

With the lowest amounts of incorporated $\mathrm{Ru(NH_3)_6^{3+}}$ mediator, where the disk currents are essentially independent of rotation rate, there are two possible processes that may limit the current.

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One is the diffusion of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ through the coating, which serves to transport charge to the catalyst sites. The other is the reaction between $Ru(NH_3)_6^{2+}$ and the CoTPP–O_2 adduct that is almost certainly the species responsible for the activation of the O_2 toward reduction.[26,29] Depending on their relative rates, one or both of these two processes could limit the observed current.

The rate of the charge transport process was determined from potential-step chronocoulometric measurements with the coatings containing $Ru(NH_3)_6^{3+}$ but in the absence of dioxygen.[30] The charge-time transients obtained were used to calculate transport rates across the entire coating[31] that were much smaller than the measured limiting currents in Figure 5. For example, the 1.3 μM solution of $Ru(NH_3)_6^{3+}$ of Figure 5 produced a chronocoulometric slope corresponding to a steady-state limiting current for pure charge transport of 0.2 μA cm^{-2} while the observed limiting current is almost 60 μA cm^{-2}. The large difference between the calculated and measured currents indicates that the $Ru(NH_3)_6^{3+/2+}$ couple may shuttle electrons across a "reaction layer" that encompasses only a small portion of the coating next to the electrode surface. The thickness of such a reaction layer would be determined by the competition between the diffusional transport of electrons to the catalyst sites by $Ru(NH_3)_6^{2+}$ and the rate of its oxidation to $Ru(NH_3)_6^{3+}$ by the CoTPP–O_2 adduct. The situation would then resemble that labeled "ER" in the terminology of ref 9a. As long as the net rate of reduction of the CoTPP–O_2 adduct remained small enough to produce little or no decrease in the concentration of dioxygen at the coating/electrolyte interface, the disk currents would show no rotation rate dependence, as is the case.

When the concentration of $Ru(NH_3)_6^{3+}$ in the coating is increased, larger catalytic currents result, which also show increasing dependences on the electrode rotation rate (Figure 5). Koutecky–Levich plots under these conditions are nonlinear (Figure 6), but they approach linearity with a slope that matches that for the two-electron reduction of dioxygen for low rotation rates at the highest concentration of $Ru(NH_3)_6^{3+}$ examined (Figure 6). This is the expected behavior if the increase in mediator concentration causes the rate of formation of the CoTPP–O_2 adduct to assume increasing importance in limiting the current until, with a sufficient quantity of mediator in the coating, the current becomes independent of further increases in mediator concentration and depends only on the concentrations of CoTPP and O_2. We did not quite reach this limiting situation before the contribution to the catalytic current from the $Ru(NH_3)_6^{3+}$ ions in the bulk of the solution became too large to neglect but the data in Figure 6 seem clearly to be heading toward that limit.

Discussion

The good stability of the CoTPP catalyst within Nafion coatings and the relative ease with which the metal-free porphyrin molecule can be incorporated into the coatings are both highly encouraging results. The approach we have described for introducing porphyrin molecules into Nafion coatings by extraction from strongly acidic solutions followed by metallation to produce an active catalyst should be generally applicable to many types of macrocyclic ligands bearing basic sites. It seems likely that coatings prepared from other polymers could also be loaded with catalysts in a similar fashion. It is noteworthy that the solubility of the ligand to be incorporated in the acidic loading solution may be quite low (as was true of tetraphenylporphyrin) because the equilibria governing the extraction of the ligand into the coating will often feature hydrophobic interactions between the polymer chains and the ligand as well as ion-exchange forces when polyelectrolyte coatings are involved.[17,32] The procedure for metallation of the porphyrin after it is incorporated in the polymer coating also has the advantage of allowing common water-soluble metal salts to be employed instead of the less readily available lipophilic salts often required for such reactions.[33]

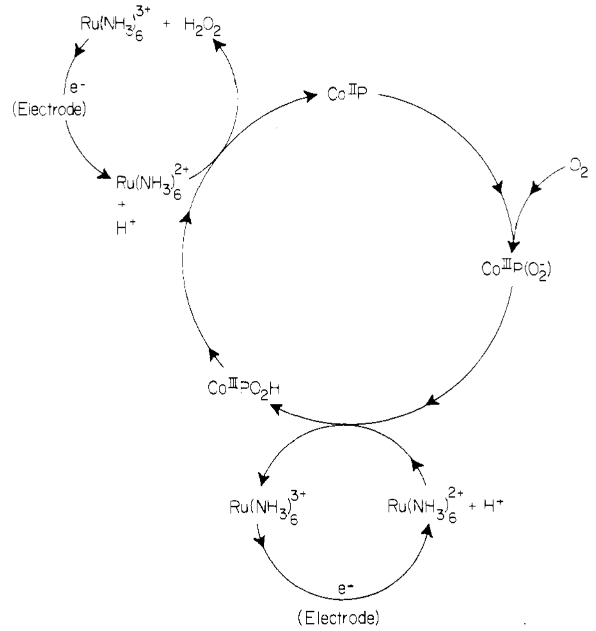

Figure 7. Schematic depiction of the catalytic cycle operating in the Nafion coating. "CoP" represents cobalt tetraphenylporphyrin.

The use of a redox mediator such as the $Ru(NH_3)_6^{3+/2+}$ couple to carry electrons to and from catalyst molecules in electrode coatings is a strategy with several attributes. It allows catalysts to be selected because of their intrinsic reactivities toward the substrate without regard for their ability to shuttle electrons to the underlying electrode. Indeed, potential catalysts that move slowly within the coatings are often particularly attractive because of the increased lifetimes that low mobility provides. The longevity of the CoTPP catalyst in Nafion coatings certainly depends upon this factor.

A final point worth stressing is that the selection of experimental conditions for optimizing the efficiencies of polymer- and polyelectrolyte-coated electrodes in electrocatalytic applications should be simplified considerably when the catalytic and charge propagation functions can be assigned to different reactants incorporated in the coatings. This dual reactant approach permits the flux of reducing (or oxidizing) species within the coating to be varied *without changing the quantity of catalyst present in the coating*. This can be a valuable feature in diagnosing the rate determining processes in such coatings. A full theoretical analysis of coatings containing separate catalyst and mediator species is under way[34] but the existing analyses for coatings with a single catalyst–mediator species[9] were adequate to allow us to conclude that increases in the mediator concentration at fixed catalyst loading shifts kinetic control from the mediator–catalyst reaction to the catalyst–substrate reaction. It is important that the latter situation, labeled "R" by Saveant et al.,[9a] can be reached with polymer-coated electrodes because it is only under this condition that the intrinsic reactivity of the catalyst toward the substrate can be fully exploited.

Figure 7 provides a schematic depiction of the catalytic cycle that proceeds within the Nafion coatings on the electrodes we have described. Note that the electrode itself plays no role in the cycle except to supply electrons to the $Ru(NH_3)_6^{3+}$ form of the mediator couple. The same reduction of dioxygen by $Ru(NH_3)_6^{2+}$ as catalyzed by cobalt porphyrins can be examined in homogeneous solution in the absence of electrodes and the catalytic efficiency compared with that available with the coated electrode. Such experiments are currently in progress.

Finally, it may be noted that the catalytic cycle depicted in Figure 7 resembles those by which some biological catalysts

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(29) Durand, R. R., Jr.; Anson, F. C. *J. Electroanal. Chem.* **1982**, *134*, 273–289.

(30) Buttry, D. A. Ph.D. Thesis, California Institute of Technology, 1983.

(31) Anson, F. C.; Saveant, J. M.; Shigehara, K. *J. Am. Chem. Soc.* **1983**, *105*, 1096–1106.

(32) Martin, C. R.; Dollard, K. A., preprint.

(33) See ref 21, p 174.

(34) Saveant, J. M.; Anson, F. C., work in progress.

function in that electrons are delivered to a preformed catalyst–substrate complex by a transition metal redox couple that cycles between oxidation states. That polymer coatings on electrodes might be used to mimic such systems and that the biological catalysts themselves could be incorporated in the coatings to produce catalyzed conversions of substrates by mechanisms such as that shown in Figure 7 are possibilities that deserve continued experimental testing.

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Registry No. $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(NH_3)_6^{3+}$, 18943-33-4; CoTPP, 14172-90-8; H_4TPP^{2+}, 50849-35-9; H_2TPP, 917-23-7; O_2, 7782-44-7; Nafion 1200, 87901-14-2; graphite, 7782-42-5.

Free Radical Decay in Adamantane

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Abstract: Kinetic electron paramagnetic resonance (EPR) techniques have been used to characterize the decay behavior of the "stable" free radical 2-cyclohexanonyl in the plastic crystal phase of an adamantane matrix over the temperature range 257–313 K. Typical plots of the EPR signal intensity as a function of time are biexponential in nature, suggesting the existence of at least two channels for free radical decay. The activation parameters for both processes have been measured in both protonated and deuterated samples. A comparison of these results with those in other systems suggests that the host does, as expected, considerably reduce the preexponential factors for decay of the radical by bimolecular processes but has relatively little influence on the corresponding activation energies.

Adamantane (tricyclo[3.3.1.1]decane, $C_{10}H_{16}$) has been widely employed as a matrix for studies of free radicals by electron paramagnetic resonance (EPR) and optical spectroscopy.[1] Radicals generated by ultraviolet or X-ray irradiation of suitable precursors in this host are randomly distributed and apparently isolated from one another. As "substitutional" impurities, they exist in cavities within the matrix which are of sufficient size that radicals no larger than the molecules they replace can rotate freely, at least in the plastic phase of adamantane. This means that sharp, "isotropic" EPR spectra whose line shapes do not change with time are obtained over a wide temperature range. Further, as adamantane is transparent to visible and near-UV light, the medium can also be used for a variety of optical experiments.

It occurred to us that the adamantane matrix technique might also prove useful for kinetic studies of free radicals. Thus, radical rearrangements, isomerizations, and other unimolecular processes, normally obscured in gas phase or solution experiments by more rapid recombination reactions, might be detectable in an adamantane matrix where the rates of diffusion-controlled bimolecular reactions could be reduced considerably.[2] In this report, we describe some preliminary experiments which were designed to test these ideas. Specifically, we have incorporated the relatively stable free radical 2-cyclohexanonyl in adamantane, made measurements of its decay behavior at different temperatures with EPR methods, and used these data to establish the kinetic and thermodynamic parameters governing radical decay in this system. Both protonated and deuterated guest and host molecules have been employed.

Experimental

A detailed description of our experimental procedures has been given earlier.[3] Briefly, samples were prepared by recrystallizing adamantane from cyclohexanone and irradiating them, in air and at room temperature, with use of an XRD-1 X-ray generator with a Cu-target tube. EPR spectra were obtained with a Varian E4 spectrometer and E257 variable temperature accessory. Temperatures are believed accurate to ±2 K. Decay measurements were performed by tuning the field into resonance with a strong line in the spectrum and monitoring its intensity as a function of time following temperature equilibration of the sample. Kinetic data were determined by constructing semilog plots of intensity vs. time; fitting by least squares the linear long lifetime component; subtracting this component from the total, normally biexponential, decay; and fitting by least squares the linear short lifetime component. Fits characterized by correlation coefficients less than 0.999 were rejected.

Results

Figure 1 shows the EPR spectra, recorded at 135 K, of the 2-cyclohexanonyl (A) and 2-cyclohexanonyl-*1,3,3'*-d_3 (B) radicals in a $C_{10}D_{16}$ host matrix. The former, having a single α proton (a_1^H = 18.0 G) and two magnetically inequivalent β protons (a_6^H = 23.5, $a_6^{H'}$ = 43.7 (G), exhibits an eight-line spectrum at this temperature. Weak lines attributable to the 2-cyclohexanonyl-*1*-d_1 radical, produced by exchange between the guest and host, are also observed. The spectrum of the 2-cyclohexanonyl-*1,3,3'*-d_3 radical is similar except that the α-proton hyperfine splitting (hfs) is replaced by hfs due to the α deuteron (a_1^D = 6.4 G). A small **g** tensor anisotropy is detectable in the spectra of Figure 1. At higher temperatures, the increased reorientational mobility of the radical leads to a more nearly symmetrical spectrum. In addition, increasing the temperature produces an alternating line width effect owing to ring interconversion.[4] However, neither the widths nor the positions of the wing lines in these spectra are significantly

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[1] See, for example: D. E. Wood, and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970); D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Am. Chem. Soc.*, **92**, 4115 (1970); R. V. Lloyd and D. E. Wood, *Mol. Phys.*, **20**, 735 (1971); D. W. Pratt, J. J. Dillon, R. V. Lloyd, and D. E. Wood, *J. Phys. Chem.*, **75**, 3438 (1971); D. E. Wood, R. V. Lloyd, and W. A. Lathan, *J. Am. Chem. Soc.*, **93**, 4145 (1971); R. V. Lloyd and D. E. Wood, *ibid*, **96**, 659 (1974); R. V. Lloyd and D. E. Wood, *J. Chem. Phys.*, **60**, 2684 (1974); J. E. Jordan, D. W. Pratt, and D. E. Wood, *J. Am. Chem. Soc.*, **96**, 5588 (1974); R. V. Lloyd and D. E. Wood, *ibid.*, **97**, 5986 (1975); M. B. Yim and D. E. Wood, *ibid.* **98**, 2053 (1976); D. L. Winters and A. C. Ling, *Can. J. Chem.*, **54**, 1971 (1976); M. B. Yim, S. DiGregorio, and D. E. Wood, *J. Am. Chem. Soc.* **99**, 4260 (1977); R. V. Lloyd and D. E. Wood, *ibid.*, **99**, 8269 (1977); and references contained therein.

[2] Some work along these lines has been reported. See: R. Sustmann and F. Lübbe, *J. Am. Chem. Soc.*, **98**, 6037 (1976).

[3] D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Am. Chem. Soc.*, **95**, 7978 (1973).

[4] D. M. Camaioni and D. W. Pratt, *J. Am. Chem. Soc.*, **94**, 9258 (1972).

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