Electrocatalysis of the Reduction of O2 to H2O by Tetraruthenated Cobalt *meso*-Tetrakis(4-pyridyl)porphyrin Adsorbed on Graphite Electrodes

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Coordination of $Ru(NH_3)_5$ groups to the four pyridine sites in cobalt *meso*-tetrakis(4-pyridyl)porphyrin adsorbed on pyrolytic graphite electrodes produces the tetraruthenated complex which acts as a catalyst for the four-electron reduction of O_2 to H_2O. The adsorbed catalyst, prepared by this heterogeneous coordination reaction, yields higher catalytic reduction rates than those obtained previously when the same catalyst was prepared within Nafion coatings on electrodes.[1] The coordination chemistry used in the preparation of the adsorbed catalyst and its behavior as an electrocatalyst are described.

In a recent report we described experiments in which the coordination of four $Ru(NH_3)_5{}^{2+}$ cations to the four pyridine groups of cobalt *meso*-tetrakis(4-pyridyl)porphyrin $(CoP(py)_4)$ converted the cobalt porphyrin from a two-electron catalyst for the reduction of O_2 to a four-electron catalyst.[1] The mechanism by which the tetraruthenated porphyrin functions as a four-electron catalyst was shown to involve rapid, intramolecular transfer of electrons from the $Ru(NH_3)_5{}^{2+}$ centers coordinated to the pyridine groups to O_2 molecules coordinated to the Co(II) center. The difficulties encountered in attempting to synthesize the active $CoP(pyRu(NH_3)_5)_4{}^{8+}$ complex in solution forced us to prepare it within coatings of the polyelectrolyte Nafion[2] on graphite electrodes.[1] Most of the electroreduction of O_2 at such coatings proceeded along a four-electron pathway leading to H_2O. However, the maximum rate with which the O_2 could be reduced was limited by the rate at which electrons could be transferred from the electrode to the immobile catalyst molecules located within the Nafion coatings. Some improvement in rate was achieved by decreasing the thickness of the coatings or by adding carbon powder to the coatings to decrease the distances that electrons had to travel to reach the catalyst molecules.[3] However, the maximum currents obtainable continued to be limited by electronic conduction through the coatings.

To eliminate electronic conduction through coatings as a current-limiting factor, we attempted to prepare the catalyst by adsorbing $CoP(py)_4$ directly on the surface of pyrolytic graphite electrodes and reacting the adsorbed porphyrin with $Ru(NH_3)_5$-$OH_2{}^{2+}$. In our previous study,[1] we were unsuccessful in coordinating four $Ru(NH_3)_5{}^{2+}$ groups to $CoP(py)_4$ molecules adsorbed on graphite surfaces. In the present study, higher concentrations of $Ru(NH_3)_5OH_2{}^{2+}$ and longer reaction times were employed, which resulted in essentially complete ruthenation of the pyridine groups of the adsorbed porphyrin. The resulting complex exhibited good electrocatalytic activity for the four-electron reduction of O_2 and the rates were higher than were available when the catalyst was confined within Nafion coatings. In addition, the electroreduction commences at somewhat more positive potentials. The coordination chemistry employed in the successful preparation of the adsorbed catalyst and its behavior as an electrocatalyst are described in this report.

Experimental Section

Materials. Cobalt *meso*-tetrakis(4-pyridyl)porphyrin $(CoP(py)_4)$ was prepared by reaction of *meso*-tetrakis(4-pyridyl)porphine (Strem Chem-

ical Co.) with cobalt acetate according to a literature procedure.[4] $[Ru(NH_3)_5Cl]Cl_2$ was prepared from $[Ru(NH_3)_6]Cl_3$ (Matthey-Bishop) by the standard procedure.[5] Solutions of 0.025 M $Ru(NH_3)_5OH_2{}^{2+}$ were prepared by mixing $[Ru(NH_3)_5Cl]Cl_2$ and zinc amalgam in 3 mL of 0.05 M NH_4PF_6 under argon. As the reduction and aquation proceeded, the $[Ru(NH_3)_5Cl]Cl_2$ gradually dissolved (ca. 30 min). The resulting solution was stored under argon. To coordinate $Ru(NH_3)_5{}^{2+}$ groups to the pyridine sites of $CoP(py)_4$ adsorbed on pyrolytic graphite electrodes, the electrodes were immersed in the solution of $Ru(NH_3)_5OH_2{}^{2+}$ for extended periods.

Other chemicals were analytical grade and were used as received. Laboratory distilled water was further purified by passage through a purification train (Sybron-Barnsted Nanopure). Pyrolytic graphite rods (Union Carbide Co.) with the edge of the graphite planes exposed were mounted to stainless steel shafts with heat-shrinkable polyolefin tubing to construct rotating disk electrodes. The electrodes were polished on 600 grit SiC paper followed by sonication in purified water.

Apparatus and Procedure. Cyclic, rotating disk, and rotating ring-disk voltammetries were carried out with a Model RDE 3 potentiostat (Pine Instrument Co.) using an ASR2 rotator (Pine Instruments) and an X-Y-Y' recorder (Kipp and Zonen). The rotating graphite disk-platinum ring electrode employed (Model AFDT 139, Pine Instrument Co.) had a large gap (0.125 cm) between the disk ring electrodes which facilitated the transfer of aliquots of solutions of $CoP(py)_4$ to the graphite disk electrode without contaminating the platinum ring electrode. A thick ring electrode (0.125 cm) was employed to obtain a reasonable collection efficiency of 0.39 despite the relatively large disk-ring gap.

A conventional two-compartment electrochemical cell was employed with a platinum wire counter electrode and a saturated calomel reference electrode against which all potentials are quoted.

To adsorb $CoP(py)_4$ on the graphite electrodes, 5-μL aliquots of 0.4 mM solutions of the porphyrin in 0.1 M aqueous CF_3COOH were transferred to the surface of the electrode (0.32 cm^2), the liquid was pushed across the surface to obtain full wetting, and the solvent was allowed to evaporate at room temperature. The quantities of $CoP(py)_4$ which remained adsorbed on the electrode after it was transferred to test solutions were estimated from coulometric assays conducted in dimethylformamide as described in the Results and Discussion section.

Results and Discussion

Estimation of Quantities of $CoP(py)_4$ Irreversibly Adsorbed on Graphite Electrodes. The goal of our experiments was to achieve the coordination of $Ru(NH_3)_5{}^{2+}$ groups to the four pyridine sites of molecules of $CoP(py)_4$ which were irreversibly adsorbed on the surface of pyrolytic graphite electrodes. The irreversible adsorption of $CoP(py)_4$ on graphite is known to occur,[6] but the voltammetric response from the Co(III)/Co(II) couple of the

[†] Contribution No. 8656.
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(2) Nafion is a registered trademark of E.I. du Pont de Nemours and Co.
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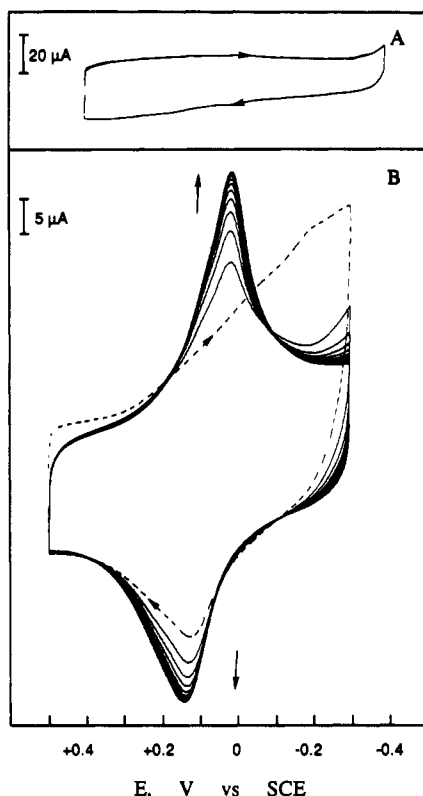
Figure 1. Cyclic voltammetry of CoP(py)$_4$ adsorbed on pyrolytic graphite electrodes. (A) 1.6×10^{-9} mol cm^{-2} of adsorbed porphyrin. Supporting electrolyte: 0.5 M NH$_4$PF$_6$–0.5 M HClO$_4$ in H$_2$O. Initial potential = 0.4 V. Scan rate = 50 mV s^{-1}. (B) 2.7×10^{-9} mol cm^{-2} of adsorbed porphyrin. Supporting electrolyte: 0.1 M NH$_4$PF$_6$ in DMF. Initial potential = 0.5 V. The dashed curve shows the first scan. The solid curves are the subsequent scans which were recorded without interruption at a scan rate of 50 mV s^{-1}.

adsorbed complex is not sufficiently well-defined in aqueous media to be useful in coulometric estimates of the quantities of CoP-(py)$_4$ adsorbed (Figure 1A). Fortunately, the response of the adsorbed complex is much better defined in dimethylformamide, and this property was exploited to evaluate the quantities of CoP-(py)$_4$ present on electrode surfaces.

In Figure 1B are shown the cyclic voltammograms recorded in DMF with a pyrolytic graphite electrode on which CoP(py)$_4$ had been deposited. The potential scans were initiated from 0.5 V, where the cobalt center is present as Co(III). The first scan to more negative potentials, shown by the dashed line in Figure 1B, was featureless, but the first return scan and all subsequent scans revealed the presence of a reversible couple near 0.1 V. The peak currents increased during the first few scans until steady values were reached which were stable for several minutes. The response can be attributed to the Co(III)/Co(II) couple of the adsorbed CoP(py)$_4$ on the basis of a recent study of the electrochemistry of the corresponding 1-methylpyridinium derivative in DMF.[7] The absence of a peak in the first scan toward more negative potentials followed by a gradual growth of the peaks is probably associated with the coordination of DMF molecules as axial ligands of the Co(III) center. The electro-chemical reversibility of the Co(III)/Co(II) couple in cobalt porphyrins is known to be sensitive to the identity of axial ligands.[7]

The areas under voltammetric peaks such as those in Figure 1B were utilized to estimate the quantities of CoP(py)$_4$ adsorbed on graphite electrode surfaces. This measurement procedure showed that CoP(py)$_4$ could be deposited on electrode surfaces reproducibly. However, transfer of the coated electrode from the DMF solution to aqueous solutions often caused a significant

quantity of the porphyrin to be desorbed from the surface. To avoid this difficulty, pairs of identical electrodes were usually coated with CoP(py)$_4$. One electrode was used to perform a coulometric assay in DMF to measure the quantity of CoP(py)$_4$ adsorbed on the surface. The second electrode was not exposed to DMF and was used in subsequent experiments in aqueous media.

Coordination of Ru(NH$_3$)$_5$$^{2+}$ to CoP(py)$_4$ Adsorbed on Graphite Electrodes. Electrodes coated with CoP(py)$_4$ were exposed to solutions of Ru(NH$_3$)$_5$OH$_2$$^{2+}$ in order to attach Ru(NH$_3$)$_5$$^{2+}$ centers to the four pyridine ligands of the adsorbed porphyrin. As the coordination of the ruthenium centers proceeded, the resulting adsorbed complex was gradually lost from the surface in aqueous media unless supporting electrolytes with suitable anions were present in the solutions. Hexafluorophosphate proved particularly effective in preventing the dissolution of the adsorbed complex, probably because of the insolubility of the PF$_6$$^-$ salts of the ruthenated complexes of CoP(py)$_4$. For this reason, the solution of Ru(NH$_3$)$_5$OH$_2$$^{2+}$ used for the coordination reaction was made 0.05 M in NH$_4$PF$_6$.

The rate constant for the substitution of pyridine for the water ligand in Ru(NH$_3$)$_5$OH$_2$$^{2+}$ is 1.1×10^{-1} M^{-1} s^{-1} in homogeneous solutions of the two reactants.[8] The rate of the reaction between Ru(NH$_3$)$_5$OH$_2$$^{2+}$ and adsorbed CoP(py)$_4$ proceeded considerably more slowly than might be calculated from this rate constant. For example, with the 0.025 M solutions of Ru(NH$_3$)$_5$OH$_2$$^{2+}$ employed, the time for ruthenation of half of the pyridine sites of the adsorbed porphyrin calculated from this rate constant is a little over 4 min, while many hours were required in practice. This difference between the calculated and observed rates is a reflection of the slower rate of the heterogeneous reaction and the likelihood that the rate decreases as Ru(NH$_3$)$_5$$^{2+}$ centers are coordinated because of electrostatic repulsion between the multiply-charged adsorbed complex and incoming Ru(NH$_3$)$_5$$^{2+}$ groups.

The extent of the reaction between the adsorbed CoP(py)$_4$ and Ru(NH$_3$)$_5$OH$_2$$^{2+}$ was monitored by removing the electrode from the Ru(NH$_3$)$_5$OH$_2$$^{2+}$ solution at various times, transferring it to a pure supporting electrolyte solution consisting of 0.5 M NH$_4$-PF$_6$ and 0.5 M HClO$_4$ saturated with argon, and recording cyclic voltammograms. Before exposure to the solution of Ru(NH$_3$)$_5$-OH$_2$$^{2+}$, the adsorbed CoP(py)$_4$ (CoP(pyH)$_4$$^{4+}$ in the acidic supporting electrolytes) exhibited no clear voltammetric response (Figure 1A) because of the irreversibility of the Co(III)/Co(II) couple in the supporting electrolyte employed. After 1-h exposure of the coated electrode to the solution of Ru(NH$_3$)$_5$OH$_2$$^{2+}$, the voltammetric response shown in Figure 2A was obtained. The reversible couple appears at the potential expected for the Ru(NH$_3$)$_5$py$^{3+/2+}$ couple,[9] which demonstrates that the pyridine sites of the adsorbed porphyrin are accessible for reaction with Ru(NH$_3$)$_5$OH$_2$$^{2+}$ cations in solution. The magnitude of the response attained 90% of its final value within 15 h, but the reaction was allowed to proceed for 24–48 h to obtain the maximum extent of reaction (Figure 2B). The resulting adsorbed complex, CoP(pyRu(NH$_3$)$_5$)$_4$$^{8+}$, exhibited an undiminished voltammetric response for several days so long as the supporting electrolyte contained PF$_6$$^-$ anions at a concentration of 0.1 M or greater. If the electrode was transferred to solutions containing no PF$_6$$^-$, the magnitude of the response gradually decreased as the adsorbed complex dissolved in the solution.

The well-known photosensitivity of complexes of Ru(II) with pyridine[10] made the stability of the adsorbed complex in laboratory light a point of concern. An electrode coated with the CoP-(pyRu(NH$_3$)$_5$)$_4$$^{8+}$ complex was removed from solution and

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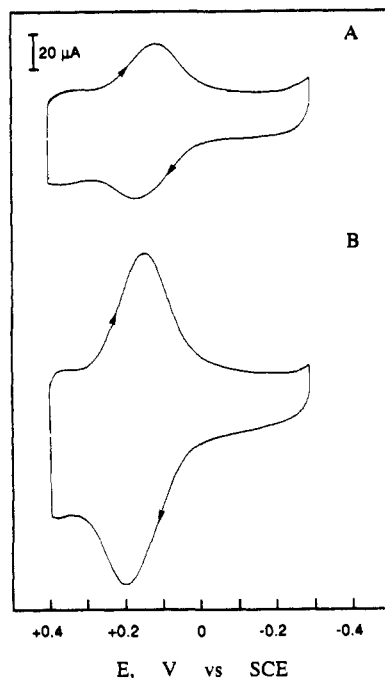**Figure 2.** Cyclic voltammograms for the coated electrode used to record Figure 1A after it had been exposed to a 0.025 M solution of $Ru(NH_3)_5$-OH_2^{2+} in 0.05 M NH_4PF_6 for (A) 1 h and (B) 48 h. Other conditions were as in Figure 1A.

Table I. Stoichiometric Ratio in the Reaction between Excess $Ru(NH_3)_5OH_2^{2+}$ and $CoP(py)_4$ Adsorbed on Graphite Electrodes

coating no.	$10^9\Gamma_{Co}$,[a] mol cm^{-2}	$10^9\Gamma_{Ru}$,[b] mol cm^{-2}	Γ_{Ru}/Γ_{Co}
1	0.79	3.2	4.1
2	1.53	5.8	3.8
3	2.7	11.3	4.2

[a] Quantity of $CoP(py)_4$ adsorbed on electrode as estimated from voltammograms like those in Figure 1B. [b] Quantity of $Ru(NH_3)_5^{3+/2+}$ groups coordinated to the adsorbed $CoP(py)_4$ as estimated from voltammograms like the one in Figure 2B.

irradiated in air with an ultraviolet lamp for 2 h. The irradiation produced no changes in the voltammetric response when the electrode was returned to solution. Both rapid quenching of the excited state by the electrode surface and likely oxidation of the ruthenium centers to the more stable Ru(III) state could account for the lack of photosensitivity of the adsorbed complex.

To determine the number of $Ru(NH_3)_5^{2+}$ centers coordinated to each molecule of $CoP(py)_4$ adsorbed on the electrodes, the quantity of $CoP(py)_4$ adsorbed was estimated from the area under the cathodic peak of the final steady voltammogram obtained in DMF (Figure 1B). The area under the cathodic peaks of voltammograms recorded in water after the coated electrodes were exposed to $Ru(NH_3)_5OH_2^{2+}$ for 24–48 h (Figure 2B) was used to estimate the total quantity of $Ru(NH_3)_5$ groups present on the electrode surface. The ratio of these two areas provided the ratio of Ru to Co in the adsorbed, ruthenated porphyrin. The results obtained with three coatings, summarized in Table I, show that with the reaction conditions employed all four of the pyridine sites of the adsorbed $CoP(py)_4$ are coordinated to $Ru(NH_3)_5$ groups.

The quantities of $CoP(py)_4$ stably adsorbed on the electrodes correspond to multiple monolayers based on the geometric area of the electrode. We believe the relatively large quantities adsorbed correspond to actual multilayers rather than monolayers adsorbed on electrodes with microscopic areas which are larger than their geometric areas because the quantities of porphyrin retained on the electrodes were not sensitive to the types of surface polishing employed. Surfaces polished with 0.05-μm alumina and with a variety of SiC papers behaved essentially similarly.

The intermolecular forces which hold the multilayered deposit on the electrode surfaces are evidently sufficiently strong to prevent the dissolution of the adsorbed porphyrin in aqueous NH_4PF_6 solutions while allowing $Ru(NH_3)_5OH_2^{2+}$ cations slowly to penetrate the coating to coordinate to the pyridine sites throughout the multilayers. Once formed, the $CoP(pyRu(NH_3)_5)_4^{8+/2+}$ complex is retained on the surface because of the insolubility of the PF_6^- salt.

Electrochemical Responses of the Adsorbed Complexes. It is noteworthy that the cyclic voltammetric response exhibited by the $CoP(pyRu(NH_3)_5)_4^{8+}$ complex adsorbed on the electrode (Figure 2B) contains only a single peak in the range of potentials near the formal potential of the $Ru(NH_3)_5py^{3+/2+}$ couple (9). This result shows that the four $Ru(NH_3)_5^{3+/2+}$ centers in the adsorbed complex do not interact with each other strongly enough to produce separated voltammetric peaks. (The behavior parallels that obtained when the same complex was examined in Nafion coatings on electrodes.[1]) The voltammetric response provides evidence of some intermolecular interactions in that the width of the peaks at half-height is 150 mV rather than the 90.6 mV expected for an adsorbed, ideally Nernstian couple and the peak potentials are separated by 40 mV instead of 0 mV. However, the interactions are too weak to produce multiple peaks in the response.

The voltammetric response for the Co^{III}/Co^{II} couple of adsorbed $CoP(py)_4$ recorded in DMF (Figure 1B) provides an interesting comparison with the response of the $Ru(NH_3)_5^{3+/2+}$ couple of the adsorbed $CoP(pyRu(NH_3)_5)_4^{12+/8+}$ complex (Figure 2B). The larger separation of the peak potentials in Figure 1B indicates that the electron-transfer rate of the cobalt-based couple (in DMF) is slower than that of the ruthenium-based couple (in H_2O), a result which has been noted in a previous study.[7] The narrower width of the peak due to the cobalt couple compared with that of the ruthenium couple (110 mV vs 150 mV fwhh), despite the larger separation of peak potentials for the cobalt couple, suggests strongly that the broader width of the peak in Figure 2B reflects the presence of some repulsive interactions among the $Ru(NH_3)_5$ centers of the adsorbed $CoP(pyRu(NH_3)_5)_4^{12+/8+}$ complex.

Electrocatalysis of the Reduction of O_2 by Adsorbed $CoP(pyRu-(NH_3)_5)_4^{8+}$. The adsorption of $CoP(py)_4$ on graphite electrode surfaces produces a large positive shift in the potential where O_2 is reduced (compare the solid curves in Figure 3A,B). The reduction at the electrode coated with $CoP(py)_4$ produces H_2O_2 quantitatively.[6] After the adsorbed $CoP(py)_4$ is converted to $CoP(pyRu(NH_3)_5)_4^{8+}$, the catalyzed reduction of O_2 proceeds near the potential where the $Ru(NH_3)_5py^{3+}$ centers of the adsorbed complex are reduced to $Ru(NH_3)_5py^{2+}$ and the cathodic current is significantly larger (Figure 3C). (By coincidence, the reduction of the $Ru(NH_3)_5py^{3+}$ centers happens to occur at potentials rather close to those where O_2 is reduced in the presenc· of adsorbed $CoP(py)_4$ (Figure 3B).) The anodic peak corresponding to the oxidation of the adsorbed catalyst in Figure 3C is not completely eliminated in the presence of O_2. The persistence of the peak suggests that some of the cobalt centers in the multilayers of catalyst present on the surface may not be accessible to O_2 molecules. The $Ru(NH_3)_5^{2+}$ centers coordinated to such inaccessible cobalt porphyrin molecules would not be oxidized by O_2 and remain to be electrooxidized during the scan to more positive potentials in Figure 3C. The larger catalytic reduction current at the electrode coated with $CoP(pyRu(NH_3)_5)_4^{8+}$ compared with $CoP(py)_4$ indicates that the reduction proceeds beyond the two-electron reduction to H_2O_2.

To examine the course of the catalyzed reaction more quantitatively, the $CoP(pyRu(NH_3)_5)_4^{8+}$ catalyst was prepared on the surface of a graphite disk which was subsequently employed as a rotating disk electrode. Current–potential curves for the reduction of O_2 are shown in Figure 4A, and the corresponding
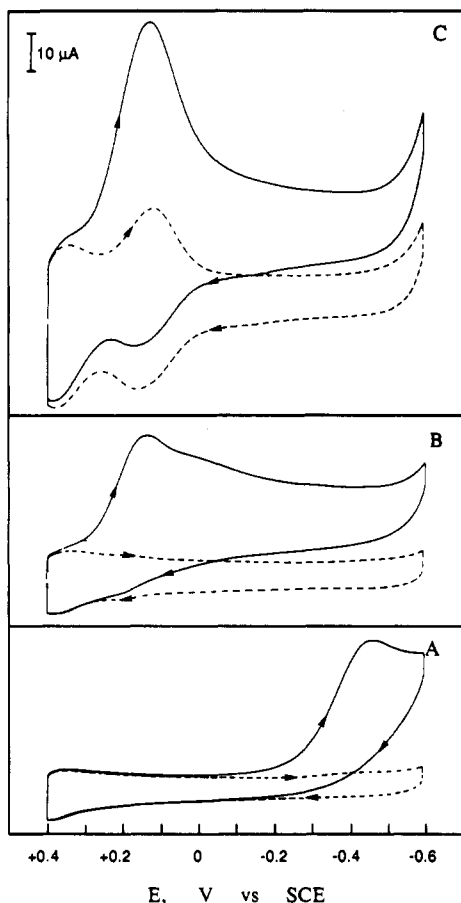
Figure 3. Cyclic voltammetric responses during the reduction of O_2 at bare pyrolytic graphite electrodes and after they are coated with CoP-(py)$_4$ or CoP(PyRu(NH$_3$)$_5$)$_4^{8+}$: (A) bare electrode; (B) electrode after 5.1×10^{-10} mol cm^{-2} of CoP(py)$_4$ was deposited on the surface; (C) electrode with 5.1×10^{-10} mol cm^{-2} of CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ on the surface. Dashed curves: in argon saturated solutions. Solid curves: in solutions saturated with air. Other conditions were as in Figure 1A.

Levich and Koutecky–Levich plots[11] are shown in Figure 4B,C. The slope of the Koutecky–Levich plot is very close to that calculated for the four-electron reduction of O_2 to H_2O (dashed line in Figure 4C). The nonlinear Levich plot (Figure 4B) and the positive intercept of the line in Figure 4C show that, as the electrode rotation rate increases, the plateau current is increasingly limited by a potential-independent chemical step preceding the electron transfer. The association of the O_2 molecules with the Co center of the adsorbed catalyst is usually assumed to be this current-limiting step.[1]

To measure the quantity of O_2 that was reduced to H_2O_2 instead of H_2O, a rotating graphite disk–platinum ring electrode was utilized. The disk was coated with CoP(py)$_4$ or CoP(pyRu-(NH$_3$)$_5$)$_4^{8+}$, and the ring was maintained at 1.0 V, where any H_2O_2 reaching it was oxidized to O_2. The resulting current–potential responses are shown in Figure 5. The ratio of the ring to the disk current obtained with adsorbed CoP(py)$_4$ as the catalyst (Figure 5A) shows that O_2 is reduced to H_2O_2 essentially quantitatively. When the catalyst was changed to CoP(py(Ru-(NH$_3$)$_5$)$_4^{8+}$, only a small amount of H_2O_2 was detected by the ring electrode during the reduction of O_2 at the disk (Figure 5B). The ratio of the disk to the ring current showed that ca. 85% of the disk current resulted from the reduction of O_2. The anodic ring current in Figure 5B increases throughout the range of disk potentials where the disk current rises. This behavior indicates
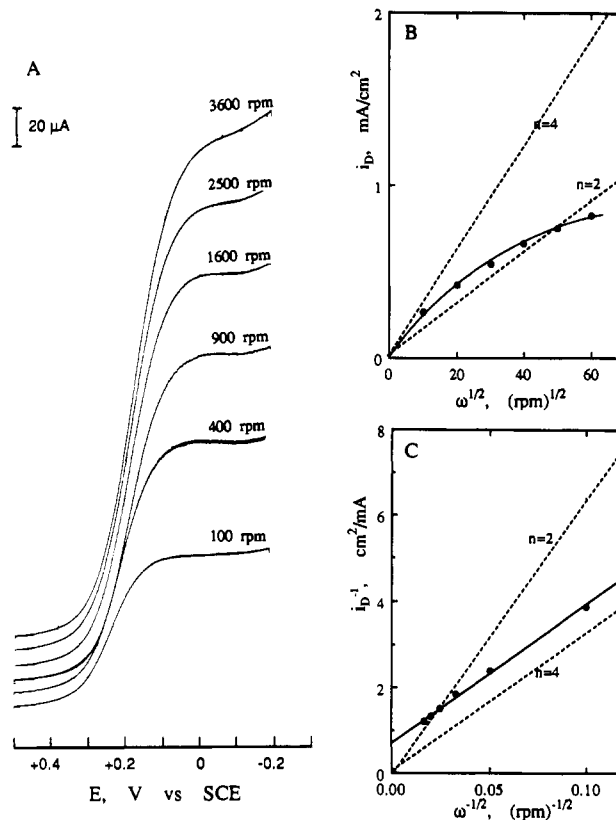
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Figure 4. Reduction of O_2 at a rotating graphite disk electrode coated with 1.6×10^{-9} mol cm^{-2} of CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$. (A) Current–potential curves in air-saturated 0.5 M NH$_4$PF$_6$–0.5 M HClO$_4$. Electrode rotation rates were as indicated. Scan rate = 2 mV s^{-1}. (B) Levich plot of plateau current vs (rotation rate)$^{1/2}$ for the curves in (A). (C) Koutecky–Levich plot of (plateau current)$^{-1}$ vs (rotation rate)$^{-1/2}$ for the curves in (A). The dashed lines in (B) and (C) were calculated for the diffusion-convection-controlled reduction of O_2 by two ($n = 2$) or four ($n = 4$) electrons.
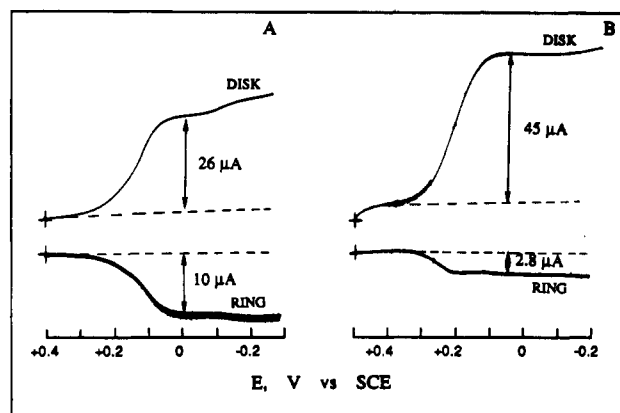

Figure 5. Current–potential curves for the reduction of O_2 at a rotating platinum ring–graphite disk electrode with 1.6×10^{-9} mol cm^{-2} of (A) CoP(py)$_4$ or (B) CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ adsorbed on the disk electrode. The platinum ring was maintained at 1.0 V. The collection efficiency of the ring–disk electrode was measured as 0.39 using the Fe(CN)$_6^{3-/4-}$ couple. Electrode rotation rate = 100 rpm. Scan rate = 2 mV s^{-1}. Supporting electrolyte was as in Figure 4.

that the side reaction leading to H_2O_2 has the same potential dependence as the primary reaction which leads to H_2O. The pattern is consistent with the presence of a small quantity of incompletely ruthenated catalyst which has been shown[12] to yield H_2O_2 instead of H_2O during the catalyzed reduction of O_2.

The deposition of the CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ catalyst directly on the electrode surface allows larger currents for the reduction

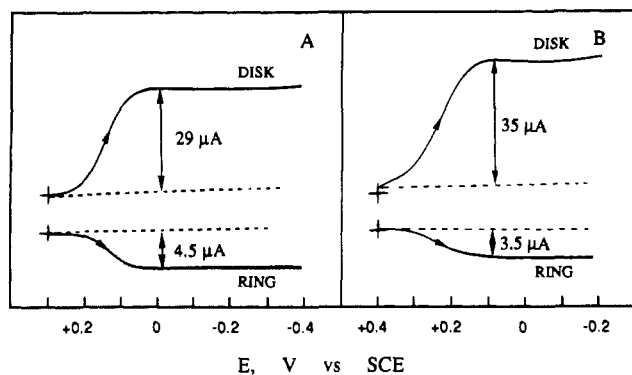(12) Steiger, B.; Shi, C.; Anson, F. C. Experiments to be published.

Figure 6. Comparison of rotating ring–disk electrode responses during the reduction of O_2 catalyzed by 7.0×10^{-10} mol cm^{-2} of CoP(pyRu-(NH$_3$)$_4$)$_4^{8+}$ incorporated in a Nafion coating (A) or adsorbed directly on the disk electrode surface (B). Supporting electrolyte: (A) 0.5 M CF$_3$COOH; (B) 0.5 M HClO$_4$–0.5 M NH$_4$PF$_6$. Other conditions were as in Figure 5.
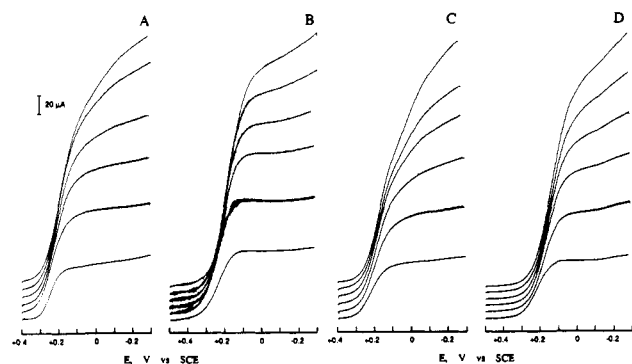

Figure 7. Supporting electrolyte effects on current–potential curves for the reduction of O_2 at a rotating graphite disk electrode coated with 1.6 $\times 10^{-9}$ mol cm^{-2} of CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$. Electrode rotation rates were 100, 400, 900, 1600, 2500, and 3600 rpm. Scan rate = 2 mV s^{-1}. Supporting electrolyte: (A) 0.1 M NH$_4$PF$_6$–0.1 M HClO$_4$; (B) 0.5 M NH$_4$PF$_6$–0.5 M HClO$_4$; (C) 0.5 M NH$_4$PF$_6$–0.1 M HClO$_4$; (D) 0.1 M NH$_4$PF$_6$–0.5 M HClO$_4$.

of O_2 to be realized than is possible when the catalyst is immobilized in Nafion coatings on electrodes, as in our previous study.[1] In Figure 6 is shown a comparison of the responses obtained at rotating ring–disk electrodes for the two cases. The absence of impediments to the rapid delivery of electrons to the catalyst sites when the catalyst is adsorbed on the electrode surface makes this mode of operation more attractive than incorporating the catalyst in Nafion coatings.

Supporting Electrolyte Effects. The need to employ PF$_6^-$ salts in the supporting electrolyte to decrease the solubility of the adsorbed CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ complex to increase its stability on the electrode surface was described earlier. Other factors which affect the response obtained during the catalyzed reduction of O_2 are the total supporting electrolyte concentration and the proton concentration. In Figure 7 four sets of current–potential curves are shown corresponding to different supporting electrolyte compositions. The best wave shapes resulted with the 0.5 M NH$_4$PF$_6$–0.5 M HClO$_4$ electrolyte. The reasons for the differences in the responses are doubtless complex, but the importance of high acidity in promoting the four-electron electroreduction of O_2 has been noted before[13] and the superior performance obtained with the higher total concentrations of electrolyte may reflect the need for adequate counterions to be present as the catalyst complex is cycled between oxidation states which are highly charged, +8 and +12. In any case, the best performance

was obtained under conditions that would prevail in typical fuel cell applications where high acidity and ionic strengths are commonly employed.

Mechanistic Speculations. In the previous experiments with the CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ catalyst incorporated in Nafion coatings of electrodes, it was demonstrated that electrons were transferred from the underlying electrode to the catalyst molecules by means of successive electron transfers between Ru(NH$_3$)$_5^{3+/2+}$ sites on adjacent molecules.[1] Thus, the only route available for the electrons to reach the O_2 molecule, which is assumed to be associated with the Co(II) center of the porphyrin when it is reduced, was via the Ru(NH$_3$)$_5$ groups coordinated to the porphyrin ring. It was, therefore, not difficult to imagine how the attachment of four such electron-donating groups to each catalyst molecule could lead to the catalysis of the four-electron reduction of O_2.[1]

By contrast, in the present experiments, the CoP(py)$_4$ molecules adsorbed directly on the graphite surface are readily accessible to electrons from the electrode whether or not Ru(NH$_3$)$_5$ groups are coordinated to the pyridine sites. Adsorbed CoP(py)$_4$ catalyzes the reduction of O_2 to H_2O_2 by accepting electrons directly from the electrode, and this reaction can presumably continue after Ru(NH$_3$)$_5$ groups are added to the adsorbed porphyrin. The reduction of both O_2 and the Ru(NH$_3$)$_5$py^{3+} groups can occur simultaneously because the potentials where the two processes occur are nearly coincident. CoP(pyRu-(NH$_3$)$_5$)$_4^{8+}$ does not catalyze the reduction of H_2O_2,[1] yet the conversion of adsorbed CoP(py)$_4$ to CoP(pyRu(NH$_3$)$_5$)$_4^{8+}$ causes most of the O_2 molecules reaching the electrode surface to be reduced to H_2O instead of H_2O_2 (Figure 5B). One possible explanation for these features of the results involves the assumption that the orbitals of the partially reduced dioxygen, e.g., O_2^{2-}, which is coordinated to the Co center are in a better position (in terms of donor–acceptor orbital interactions) to accept additional electrons from the Ru(NH$_3$)$_5$py^{2+} sites of the porphyrin than from the electrode surface. As a result, further reduction can occur before the dissociation–protonation of the partially reduced dioxygen species produces H_2O_2 toward which the catalyst is inactive. This explanation would lead one to expect that the coordination of only two Ru(NH$_3$)$_5$ groups to the adsorbed CoP-(py)$_4$ might suffice to accomplish the four-electron reduction of O_2. In fact, recent experiments have shown that a porphyrin containing just two Ru(NH$_3$)$_5$py groups catalyzes only the two-electron reduction of O_2.[12] Thus, the coordinated Ru(NH$_3$)$_5^{2+}$ groups may serve as more than mere electron donors in altering the course of the reduction of O_2. Additional mechanistic experiments in progress are designed to test this speculation.

Conclusions

The previous experiments demonstrating that coordination of four Ru(NH$_3$)$_5$ groups to the pyridine sites in CoP(py)$_4$ converts this porphyrin from a two-electron to a four-electron catalyst for the reduction of O_2 required that the catalyst be prepared within Nafion coatings on electrodes.[1] The present experiments have shown how the same catalyst can be prepared in an adsorbed state directly on graphite electrode surfaces. The resulting advantages include higher catalytic reduction rates both because electron transfer to the catalyst molecules can be much more rapid than when they are immobilized in insulating Nafion coatings and because larger quantities of catalyst can be deposited on the electrode surface than was possible with the Nafion coatings, which accepted only limited quantities of the porphyrin. Although rather lengthy reaction times are involved, the preparation of the catalyst by the heterogeneous reaction between CoP(py)$_4$ adsorbed on an electrode surface and Ru(NH$_3$)$_5$OH$_2^{2+}$ in solution is an intrinsically simpler procedure than that required for the preparation of the catalyst within Nafion coatings.[1]

The stability of the catalyst on the electrode surface is somewhat better when it is incorporated in Nafion than when it is merely

(13) (a) Collman, J. P.; Denisevich, P.; Konai, Y.; Marrocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027. (b) Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710.

irreversibly adsorbed, but the higher currents that can be obtained from the adsorbed catalyst make this method of immobilization more attractive. Methods for increasing the stability of the adsorbed catalyst layers, for example by overlayering them with thin polyelectrolyte coatings, are the objects of continuing studies.