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Novel Chemical Pathways and Charge-Transport Dynamics of Electrodes Modified with Electropolymerized Layers of $[Co(v\text{-}terpy)_2]^{2+}$

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Abstract: Electropolymerized films of $[Co(v\text{-}terpy)_2]^{2+}$ (v-terpy is 4′-vinyl-2,2′:6′,2″-terpyridinyl) exhibit reactivity patterns, especially with regard to ligand exchange, that differ significantly from those exhibited by $[Co(terpy)_2]^{2+}$ in solution. These differences are attributed to the physically constrained environment present in the polymer film. The charge-transport properties follow the model of Dahms and Ruff and the predicted concentration dependence of the diffusion coefficient. These electropolymerized films are also active in the electrocatalytic reduction of carbon dioxide.

A main goal of research in the area of chemically modified electrodes[2] is the preparation of interfaces with very active catalytic properties. The advantages to be gained are severalfold and include control of the reaction rate by the applied potential, use of very small amounts of material, and ready separation of the catalyst (the modified electrode) from the reaction medium. In general, the approach followed has been to identify those materials that exhibit high catalytic efficiency in solution and then devise means of incorporating these materials on electrode surfaces with the expectation that the incorporated material will retain its high catalytic activity. A number of systems have been studied with this approach including nitro complexes of ruthenium for catalytic oxidations,[3] porphyrins and phthalocyanines[4] for the catalytic reduction of oxygen, and others.[5]

Although it has been generally found that catalytic systems incorporated in this fashion will exhibit some activity, in some instances very limited activity has been observed. In an elegant study, Anson and co-workers[6] established that, in these cases of limited activity, separation of function can be very effective. That is, inclusion of components with high catalytic activity as well as mediators that will serve in accelerating charge-transport rates has a very positive effect on the catalytic activity.

A potentially more profitable approach is the design of systems whose chemical activity on a surface is altered from that in solution due to the constraints imposed by immobilization of the system. The design and synthesis of such systems offer an appreciable challenge, both conceptually and practically, but very novel and interesting reactivity patterns should emerge.

We now present a study on vinylbipyridinyl and vinylterpyridinyl complexes of cobalt that illustrates very effectively the significant changes in reactivity that arise on generation of electropolymerized layers of the respective complexes. In addition, we present data on the electron-transport dynamics in such systems as well as some preliminary studies on the electrocatalytic reduction of carbon dioxide by the electropolymerized vinylterpyridinyl–cobalt complex.

Experimental Section

Synthesis of Ligands and Metal Complexes. Vinylbipyridinyl (v-bpy) is 4-vinyl-4′-methyl-2,2′-bipyridinyl, and vinylterpyridinyl (v-terpy) is 4′-vinyl-2,2′:6′,2″-terpyridinyl; the corresponding cobalt complexes were prepared as described previously.[7-9] 2,2′-Bipyridinyl and 2,2′:6′,2″-terpyridinyl (Aldrich) were used as received. All cobalt complexes were prepared according to published procedures.[9]

Reagents. Acetonitrile (Burdick and Jackson, distilled in glass) was dried over 4-Å molecular sieves. Tetra-*n*-butylammonium perchlorate (TBAP) (G. F. Smith) was recrystallized (ethyl acetate, 3×) and dried at 75 °C under vacuum for 72 h. All other materials were of reagent-grade quality and were used without further purification.

Instrumentation. Electrochemical experiments were performed on either a BAS 100 electrochemical analyzer or an IBM EC225 voltammetric analyzer. Data were recorded on a Soltec XY recorder. Chronocoulometric experiments for the determination of diffusion coefficients were performed on the BAS 100 system. Electrochemical cells were of conventional design, and platinum disk electrodes sealed in glass were used throughout. Prior to use, they were polished with 1-μm diamond paste (Buehler) and rinsed thoroughly with water, acetone, and methanol. Rotating-disk electrode experiments were carried out on a Pine Instruments Model MSR rotating-disk electrode assembly and controller. Spectral measurements utilized a Hewlett Packard Model 8451 spectrophotometer. The thickness of electropolymerized layers was determined with a Sloan Profilometer. All potentials are referenced to the sodium-saturated calomel electrode (SSCE) without regard for the liquid junction.

In order to determine the concentration of redox centers, we employed platinum films sputtered on float glass as electrodes. The protocol involves electropolymerization of $[Co(v\text{-}terpy)_2]^{2+}$ followed by a rinse with acetonitrile and the subsequent determination of the film's thickness with a Sloan Profilometer. From a knowledge of the coverage (from a voltammetric scan at slow sweep rate) and the film's thickness, the concen-

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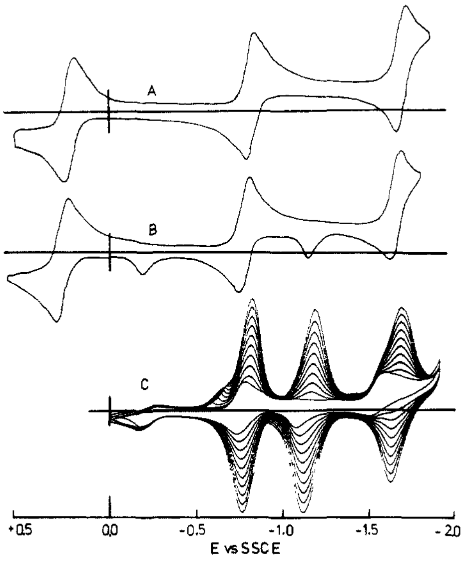

Figure 1. Cyclic voltammograms at 200 mV/s for a platinum electrode in contact with an acetonitrile/0.1 M TBAP solution containing (a) 1 mM [(Co(terpy)$_2$]$^{2+}$, (b) 1 mM [Co(v-terpy)$_2$]$^{2+}$ (first scan), and (c) same as b (10 consecutive scans).

tration of redox sites could be determined. These measurements were performed over a wide range of coverage, and from these data, a coverage/concentration calibration curve was constructed. Since the thickness measurements were performed on emersed electrodes, there is clearly some uncertainty in them. However, the time between emersion and measurement was typically short (less than 2 min).

Results and Discussion

(a) Electrochemical Characterization. The electrochemistry of [Co(bpy)$_3$]$^{2+}$ has been the subject of a number of studies,[10] and in acetonitrile solution, the complex underwent two one-electron reversible processes with formal potentials of +0.32 and -0.95 V. These correspond to cobalt(3+/2+) and cobalt(2+/1+) redox processes, respectively. There is an additional reduction at -1.55 V, which represents a two-electron reduction (i.e. cobalt^{1+} to cobalt^{1-}) with the concomitant loss of one bipyridine ligand to give rise to a four-coordinate, tetrahedral complex.

$$[\mathrm{Co(bpy)_3}]^+ + 2e^-, -\mathrm{bpy} \rightarrow [\mathrm{Co(bpy)_2}]^-$$

This has been established by the variations in the potentials of this wave as a function of the bipyridinyl concentration in solution.[10a]

Analogous to the bipyridinyl complex, [Co(terpy)$_2$]$^{2+}$ exhibited cobalt(3+/2+) and cobalt(2+/1+) couples at +0.27 and -0.77 V, respectively. There was an additional reduction at -1.65 V, but in this case, it is a one-electron, reversible process and we associate it with a ligand localized reduction. A typical cyclic voltammogram is presented in Figure 1A.

[Co(v-bpy)$_3$]$^{2+}$. Similar to [Co(bpy)$_3$]$^{2+}$, the vinylbipyridinyl complex showed redox processes corresponding to the cobalt(3+/2+) and cobalt(2+/1+) couples at +0.22 and -0.98 V, respectively. There is, in addition, a third irreversible reduction at a peak potential value of -1.57 V, again in close agreement with the results for [Co(bpy)$_3$]$^{2+}$. This behavior, however, is in marked contrast to the behavior of vinylbipyridinyl derivatives of metal ions such as iron, ruthenium, osmium, chromium, and rhenium, where, upon repeated cycling in the negative potential region, the complex underwent electropolymerization to give rise to an electroactive polymer film.[11] In the case of [Co(v-bpy)$_3$]$^{2+}$ very little, if any, deposition took place. The electropolymerization process requires reduction of the vinylbipyridinyl ligand.[11] However, in the case of the cobalt complex, the first two redox processes are metal localized (formally, cobalt(3+/2+) and cobalt(2+/1+)) and, as such, no polymerization is expected. In order to effect polymerization, the potential needs to be scanned past the third reduction wave. However, as demonstrated for [Co(bpy)$_3$]$^{2+}$, scanning past this wave resulted in the loss of one of the bipyridinyl ligands. Thus, although scanning past this wave should result in the electrodeposition of the complex, the fact that 33% of the coverage (i.e. one bipyridinyl ligand) is lost on the scan precludes any significant polymer deposition. It should be mentioned, however, that cycling past the cobalt(2+/1+) wave for long periods of time (e.g. over 1 h) gave rise to a small amount of deposited polymer.

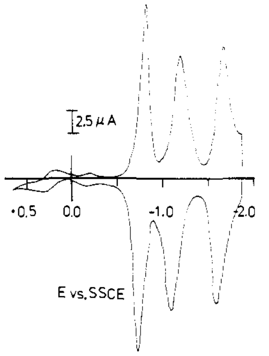

Figure 2. Cyclic voltammogram at 100 mV/s for a platinum electrode modified with a polymeric film of [Co(v-terpy)$_2$]$^{2+}$ in contact with an acetonitrile/0.1 M TBAP solution.

[Co(v-terpy)$_2$]$^{2+}$. This material exhibited the most interesting and complex series of reactions. On an initially negative-going scan (Figure 1B), two well-developed reversible reductions were observed at formal potentials of +0.26 and -0.79 V, and these correspond to the cobalt(3+/2+) and cobalt(2+/1+) redox processes, respectively. There was, in addition, a third reduction wave with a peak potential of -1.70 V. On a reverse sweep, however, the anodic counterpart of this wave was somewhat attenuated. There were, in addition, two new anodic waves at peak potentials of -1.18 and -0.20 V, respectively. Continued scanning (Figure 1C) showed these to be chemically reversible processes with formal potentials of -0.21 and -1.16 V. In addition, the growth of all five waves with continued scanning was indicative of electropolymerization occurring. It should be noted, however, that the waves centered at +0.25 and -0.21 V grew in magnitude only during the early stages of deposition and that they reached an apparent steady-state value while the other three continued to grow (see Figure 1C). If the electrode was removed, rinsed with acetone, and placed in acetonitrile/0.1 M TBAP, a voltammogram such as that shown in Figure 2 was obtained, with five redox couples present. This behavior is in marked contrast to that previously described for monomeric [Co(terpy)$_2$]$^{2+}$ itself.

We believe that upon polymerization the metal-ligand complexes find themselves in a much more rigid environment than that present in solution. When we scan past the wave at -1.70 V, there seems to be a significant change in bond lengths (dictated by the driving force to form a tetrahedral complex), which can be accommodated by the complex in solution. However, in the environment of the polymeric film these changes give rise to partial displacement of the coordinated terpyridinyl (resulting in two biscoordinated terpyridinyls or, alternatively, a triscoordinated terpyridinyl and a monocoordinated terpyridinyl) with concomitant coordination by acetonitrile. Thus, we believe the new redox processes centered at -0.21 and -1.19 V to be the cobalt(3+/2+) and the cobalt(2+/1+) processes of the terpyridinyl-acetonitrile complex of cobalt (see Scheme I). The changes in the redox potentials are consistent with the changes in coordination and, as will be illustrated below, the very slow growth rate of the wave at -0.21 V is consistent with the assignment as a cobalt(3+/2+) process.

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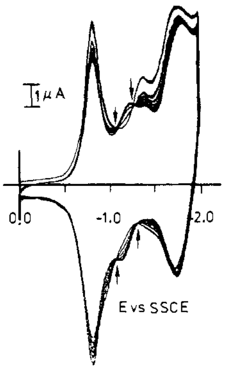
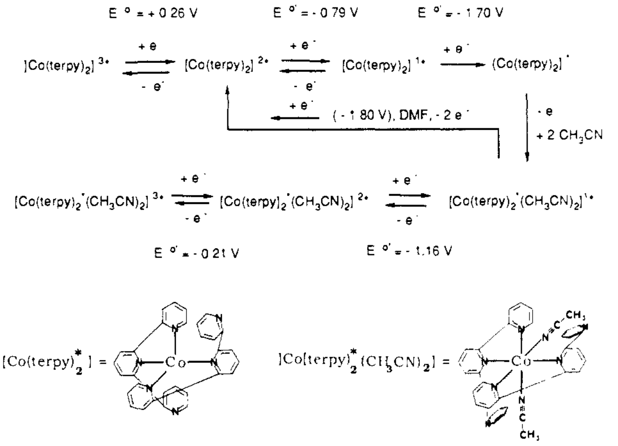


Figure 3. Cyclic voltammograms at 100 mV/s in acetonitrile/0.1 M TBAP for a platinum electrode modified with a film of $[Co(v\text{-}terpy)_2]^{2+}$ after it had been cycled in DMF/0.1 M TBAP and potentiated at −1.80 V for 5 min (arrows indicate isopotential points).

Scheme I



A rational explanation for the displacement of the pyridine ligands rests in the weakening of the cobalt–terpyridinyl bond and the presence of a moderately strong coordinating solvent (acetonitrile). No such substitution was observed in poorly coordinating solvents such as DMF and dichloromethane. In addition, if an electrode that has been cycled in acetonitrile (and thus contains the acetonitrile complex) were placed in dimethylformamide containing 0.1 M TBAP and the potential scanned and held at −1.80 V for 5 min, the majority of the $[Co(terpy)_2]^{2+}$ was regenerated. This reflects the presence of a dynamic equilibrium, and in the absence of a coordinating solvent, triscoordination by both terpyridinyls is retained. If such a regenerated electrode were again placed in acetonitrile and the potential scanned out to −1.8 V, the acetonitrile complex was again formed. The appearance of isopotential points[3,12] during consecutive scans (Figure 3) lends strong supporting evidence to this mechanism.

Spectroscopic studies provide further evidence in support of this reaction sequence. A tin oxide electrode was coated with an electropolymerized layer of $[Co(v\text{-}terpy)_2]^{2+}$. In this case the potential was only scanned out to −1.2 V during the polymerization so that none of the acetonitrile complex was generated. We have previously demonstrated that at this potential there will be polymerization; however, the deposition rates are greatly diminished. The visible spectrum of such a modified electrode was virtually identical with that of the $[Co(v\text{-}terpy)_2]^{2+}$ complex in acetonitrile/0.1 M TBAP with absorbances at 446 and 518 nm. A potential of −1.80 V was then applied to the modified electrode for a period of 10 min, after which the spectrum was measured again. In this case the absorbances at 446 and 518 nm due to $[Co(v\text{-}terpy)_2]^{2+}$ were greatly attenuated and a new, prominent absorbance at 366 nm was present. For comparison, an acetonitrile solution of $[Co(bpy)_3]^{2+}$ was electrolyzed at −1.80 V. This gave rise to the four-coordinated bis(bipyridinyl) cobalt complex, which upon oxidation (exposure to air) generates the bis(bipyridinyl)–bis(acetonitrile) complex, i.e. $[Co(bpy)_2(CH_3CN)_2]^{2+}$. The spectrum of the electrolyzed solution had a very prominent absorbance at 360 nm, and this correlates very well with the absorbance of the modified electrode after electrolysis at −1.8 V. These spectral studies, along with the electrochemical studies, lend strong support to our proposed reaction sequence.

To our knowledge, this represents one of the more dramatic effects on reactivity changes upon incorporation of a transition-metal complex into a polymeric film. In addition, the fact that empty coordination sites can be reversibly generated makes this approach very attractive for potential electrocatalytic applications.

(b) Transport Studies. The study of charge transport at chemically modified electrodes is an area that has received a great deal of attention, and various models and mechanisms have been postulated.[13] Factors such as the physical movement of species, electron self-exchange, morphology of the deposited layer, and counterion transport have all been shown to be intimately related to the measured rates of charge transport, and depending on the details of the specific system involved, any of these processes can be rate limiting. It has also been recognized that the rate of charge propagation through these modified interfaces can be described in terms of an apparent diffusion coefficient.[13c,g]

Two aspects that have received particular attention are the contributions of physical diffusion and electron self-exchange rate to the measured values of the diffusion coefficient. According to the theories of Dahms[14] and Ruff and co-workers,[15] an electrochemically determined diffusion coefficient has two main contributions: one arising from the physical diffusion of the species and a second due to electron self-exchange. This is generally expressed as

$$D_{\mathrm{exptl}} = D_0 + (\pi/4)k_{\mathrm{ex}}\delta^2 C$$

where D_0 is the diffusion coefficient that would be measured in the absence of self-exchange, C is the sum of the concentrations of the oxidized and reduced forms of the redox couple, δ is the distance between centers when the electron transfer takes place, and k_{ex} is the second-order self-exchange rate constant.

For freely diffusing species in solution, the contribution due to electron self-exchange is negligible. However, at modified electrodes where physical diffusion can be slower by many orders of magnitude, the term due to self-exchange can be significant, and in some cases dominant. The effect of self-exchange rate on the apparent diffusion coefficient has been studied by various authors. Anson and Buttry[16] have studied these effects for $[Co(bpy)_3]^{2+}$ and $[Co(terpy)_2]^{2+}$ incorporated by ion exchange into electrodes modified with a thin film of Nafion (Nafion is a trademark of E. I. du Pont de Nemours and Co.). These systems are particularly well suited for these studies due to the very large differences in self-exchange rates for the $Co^{3+/2+}$ ($k = 2\ M^{-1}\ s^{-1}$)[17] and $Co^{2+/+}$ ($k = 10^8\ M^{-1}\ s^{-1}$)[18] couples. These authors demon-

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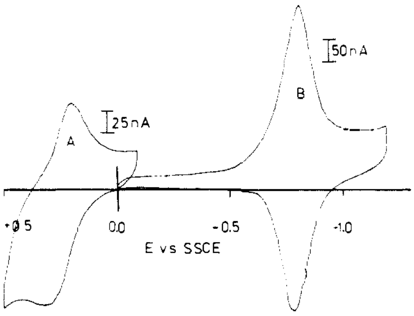

Figure 4. Cyclic voltammograms for the Co$^{3+/2+}$ and Co$^{2+/+}$ couples at 50 mV/s in acetonitrile/0.1 M TBAP for an electrode modified with about a monolayer equivalent of [Co(v-terpy)$_2$]$^{2+}$ (notice the difference in wave shapes and current scales).

strated that the measured values and concentration dependences of the apparent diffusion coefficients for the two couples were consistent with the very large differences in their self-exchange rates. One complication in their system, however, is that of the partitioning of the complexes between the hydrophobic and hydrophilic domains within the Nafion film.

Oyama and co-workers[19] have studied the concentration dependence of the transport properties of pendant viologen grafted onto chloromethylated polystyrene. In this case they were able to observe a linear dependence of D_{app} with concentration although the exact slope was different from that predicted by theory. At the lowest loadings they report a D_{app} value of about 2.5×10^{-11} cm^2/s, which is surprisingly large considering that the redox centers are physically anchored to the polymer backbone.

In our studies, the first indication of the drastic differences in the diffusion coefficients of the Co$^{3+/2+}$ and Co$^{2+/+}$ couples was during the electropolymerization reaction (Figure 1C) when it was observed that the [Co(v-terpy)$_2$]$^{3+/2+}$ wave and the corresponding 3+/2+ wave for the acetonitrile complex centered at about −0.20 V grew at much slower rates than the others. Furthermore, the currents observed at modified electrodes (Figure 2) showed that the peak currents for the 3+/2+ couples were significantly smaller than for the corresponding 2+/1+ couples. Further evidence was provided by the differences in the voltammetric wave shapes for the Co$^{3+/2+}$ and Co$^{2+/+}$ processes at slow sweep rates (Figure 4), with the former having the wave shape typical of a diffusional process whereas that for the wave centered at −0.80 V (2+/1+ couple) is typical of a surface-confined redox couple. In addition, the peak current is proportional to the square root of the sweep rate in the former and directly proportional to the sweep rate in the latter. At high coverage values or at sweep rates beyond 200 mV/s, the voltammetric wave shape for the Co$^{2+/+}$ process was also diffusional.

According to the Dahms and Ruff formalism, couples with a small self-exchange rate constant should exhibit apparent diffusion coefficients that are independent of concentration. This is in contrast to couples with large values of self-exchange rates whose diffusion coefficients should exhibit a linear dependence with concentration.

A brief explanation of the variation and determination of surface concentration is appropriate at this time. Unlike experiments performed in Nafion and similar ion-exchange polymers where the surface concentration of redox centers can be controlled by varying the solution concentration or time of incorporation from solution, our polymers were deposited by electropolymerization on the electrode surface. Thus, one would a priori anticipate that the concentration of redox material would not change significantly. However, we found that at least for the polymers employed in this study, the concentration was a function of coverage. In general, the concentration increased linearly with coverage and then leveled off a high coverage, and we attribute this effect to variations in the packing density with coverage. In order to determine the relationship between surface coverage and concentration, a coverage/concentration curve was constructed as described in the Experimental Section.

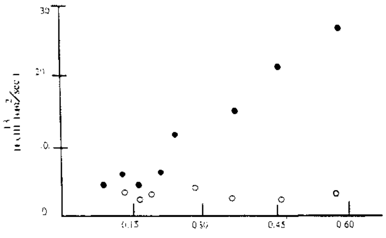

Figure 5. Plot of D_{app} vs concentration for the Co$^{3+/2+}$ (○) and Co$^{2+/+}$ (●) couples for electrodes modified with electropolymerized films of [Co(v-terpy)$_2$]$^{2+}$.

It should also be mentioned that Murray[20] has employed electropolymerized films of vinylpyridinyl complexes of ruthenium and osmium, and by controlling the ratio of solution concentrations of monomers from which the polymerization was performed, he was able to prepare electropolymerized films of one complex diluted by the other. This process allowed him to vary the mole ratio of the complexes. In addition, he studied the effect of mole ratio on the effective diffusion coefficient.

Figure 5 shows a plot of D_{app} vs concentration for both the 3+/2+ and 2+/1+ couples. The former shows no dependence on concentration, whereas the 2+/1+ couple shows the predicted linear dependence with concentration. (However, the exact slope is somewhat larger than 1.) The value of the diffusion coefficient for the Co$^{3+/2+}$ couple is $\sim 3 \times 10^{-13}$ cm^2/s, which is significantly smaller than that reported by Anson and Buttry for the [Co(bpy)$_3$]$^{3+/2+}$ couple in Nafion ($\sim 2 \times 10^{-12}$ cm^2/s).

This last point needs to be considered in more detail since the Dahms–Ruff theory should only be applicable to species that are relatively free to move, as is the case for species dissolved in Nafion. In our case the cobalt complexes are in a much more restricted environment, and this may be responsible for the much smaller apparent diffusion coefficient. However, only slightly larger values were obtained for electropolymerized films of [Co(v-terpy)(terpy)]$^{2+}$, which cannot cross-link by virtue of the fact tht it has only one vinyl group.

Furthermore, the values reported by Oyama and co-workers[19] for viologens grafted onto chloromethylated polystyrene are about 2 orders of magnitude higher than those measured here even though the viologen centers are also relatively immobile. Thus, there may also be other processes involved.

(c) Electrocatalysis of CO$_2$ Reduction. The electrocatalytic reduction of carbon dioxide represents a truly challenging problem due to the mechanistic complexities involved and the fact that multielectronic transfers are required. A number of systems have been shown to reduce carbon dioxide, with varying catalytic efficacy,[21] to various products including carbon monoxide, formate,

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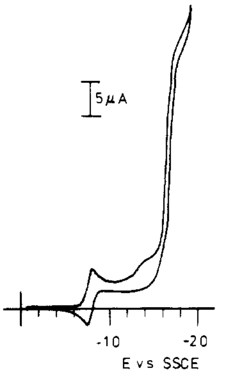

Figure 6. Cyclic voltammogram at 100 mV/s for a platinum electrode in a DMF/0.1 M TBAP solution containing $[Co(terpy)_2]^{2+}$ at a concentration of 1.02×10^{-3} M and under a CO_2 atmosphere. Notice the large enhancement of the current for the wave at about −1.70 V vs that at −0.80 V.

and others. It is generally recognized that in order to achieve a high electrocatalytic activity in the reduction of carbon dioxide (or activation of small molecules in general) with a transition-metal complex, a free coordination site should be made available for the molecule to bind. On the basis of the observed behavior of the electropolymerized layer of $[Co(v\text{-}terpy)_2]^{2+}$, we decided to investigate its potential electrocatalytic activity toward carbon dioxide since Lewis and co-workers[21c] had previously demonstrated the electrocatalytic activity of cobalt phthalocyanine for the reduction of carbon dioxide in aqueous media.

To obtain a preliminary assessment of the catalytic activity of the modified electrode, we initially investigated the reactivity of $[Co(terpy)_2]^{2+}$ in solution. As mentioned previously, cyclic voltammograms in argon-saturated acetonitrile or DMF solutions showed two reversible processes at $E^{\circ\prime}$ values of −0.79 and −1.70 V, respectively (Figure 1A). Under an atmosphere of carbon dioxide, the wave at −0.70 V remained relatively unaltered, whereas the second wave (at −1.65 V) was enhanced manyfold, indicative of a very strong catalytic effect, although at a rather negative potential (Figure 6).

For the corresponding $[Co(v\text{-}terpy)_2]^{2+}$ modified electrode system, however, a large catalytic effect was noted for the wave centered at −0.79 V. This is shown in Figure 7, which illustrates a rotating-disk voltammogram (at 3000 rpm) for the modified electrode under argon (curve A) and carbon dioxide (curve B) saturated DMF solutions, respectively. The very large enhancement in the current and the fact that there was no current in the reverse sweep are indicative of a very fast reaction. If the solution were again saturated with argon, the response reverted back to that of curve A, pointing to the stability of the polymeric film. In addition, the very low potential observed for the process is indicative of the very strong catalytic effect. Furthermore, the difference in reactivity between the complex in solution and that in the electropolymerized layer is truly remarkable and emphasizes some of the unique advantages of reagent immobilization.

Preliminary mass spectrometric analysis indicates that carbon monoxide is one of the reaction products. We are currently performing further coulometric experiments to determine more precisely the nature and ratio of the reaction product(s), as well as rotating-disk voltammetric studies to estimate the rate of the reaction.

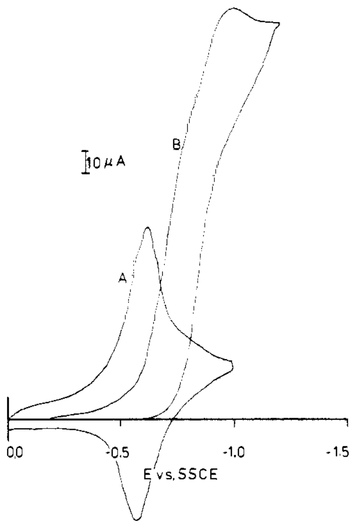

Figure 7. Rotated-disk voltammograms at 3000 rpm and 10 mV/s for an electrode modified with $[Co(v\text{-}terpy)_2]^{2+}$ and in contact with a DMF/0.1 M TBAP solution saturated with (A) argon and (B) CO_2.

Conclusions

We have shown that electropolymerized layers of $[Co(v\text{-}terpy)_2]^{2+}$ exhibit properties and chemical reactivity that are significantly different from those shown by $[Co(terpy)_2]^{2+}$ in solution. We attribute these differences to constraints imposed by inclusion of the metal complex in a polymeric system. We have also shown that these polymeric films of $[Co(v\text{-}terpy)]^{2+}$ exhibit charge-transport properties that closely follow the formalism of Dahms and Ruff, especially with regard to the dependence of the apparent diffusion coefficient on concentration. Finally, the electrocatalytic ability of electropolymerized films of $[Co(v\text{-}terpy)_2]^{2+}$ for the reduction of carbon dioxide was demonstrated.

We believe that these reactivity differences result from constraints imposed by the polymer film. However, it is also important to note that having a tridentate ligand also enhances this effect. For example, such reactivity differences have not been reported for any electropolymerized film based on a vinylpyridine or vinylbipyridine transition-metal complex. With this hypothesis, we are preparing electropolymerizable complexes containing quinquidentate ligands, which not only will enhance this effect but will in addition carry an empty coordination site. We anticipate that very active electrocatalysts will result from these types of complexes.

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Registry No. $[Co(v\text{-}terpy)_2]\cdot 2PF_6$ polymer, 108270-57-1; $[Co(v\text{-}terpy)_2]^{2+}$, 108270-36-6; $[Co(bpy)_3]^{2+}$, 15878-95-2; $[Co(terpy)_3]^{2+}$, 18308-16-2; $[Co(v\text{-}bpy)_3]^{2+}$, 113705-10-5; CO_2, 124-38-9; CH_3CN, 75-05-8.