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Dynamic Consequences of Ionic Permselectivity. Rapid Ejection from Nafion Coatings of Anions Generated Electrochemically from Cationic Precursors†

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Abstract: The binuclear, cationic complex $(NH_3)_5Co^{III}O_2C\text{-}4\text{-}C_5H_4NRu^{III}(edta)^+$ ($4\text{-}C_5H_4N$ = 4-pyridyl) was synthesized and incorporated as a counterion in Nafion coatings on glassy carbon electrodes. Reduction of the Co(III) center of the incorporated complex causes it to dissociate into mononuclear fragments, one of which is an anionic complex of Ru^{II}(edta). The loss of this complex from the polyanionic Nafion coating was monitored by cyclic voltammetry, and its rapid ejection was observed directly with the aid of a rotating ring-disk electrode. The stability and coordination chemistry of the binuclear complex are altered dramatically by its incorporation in Nafion. The origins of the unusual behavior observed are discussed.

The ideal permselectivity exhibited by electrode coatings prepared from the polyanionic material Nafion[1-3] is most simply understood in terms of a model in which the coatings contain only cationic counterions with virtually complete exclusion of anionic co-ions from the coatngs.[4] We have been interested in exploring the dynamic consequences of such ideal permselectivity by examining the fates of anionic reactants that could be generated from stable, cationic precursors within Nafion coatings. One question that we hoped to answer was whether anions generaed in the interior of the polyanionic coatings would be rapidly ejected by electrostatic forces or whether neutral ion pairs might be formed that would diffuse out of the coating at a more leisurely rate. It was also of interest to determine if the electrode reaction through which the anions were reductively generated would be shifted to much more negative potentials when the anions were produced within the polyanionic coating rather than at the surface of uncoated electrodes in solution.

To perform the desired experiments it was necessary to prepare a cationic reactant that was spontaneously incorporated by polyanionic Nafion coatings and from which an anionic fragment could be subsequently generated and monitored electrochemically. A reactant possessing the necessary characteristics was prepared by reacting a cationic pentaammine(4-pyridinecarboxylato)cobalt(III) complex with an anionic ethylenediaminetetraacetatoruthenium(III) complex to obtain a binuclear, zwitterionic complex with a net positive charge which was readily incorporated by Nafion coatings. Electrochemical reduction of the cobalt(III) center in the binuclear complex produced an anionic fragment whose electroactivity permitted its concentration to be monitored to determine how long it remained in the polyanionic coating. The effects of the Nafion coating on the chemical stability of the unreduced, binuclear, precursor complex were also investigated to compare the behavior resulting from the breaking of the ruthenium(III)-pyridine bond with that obtained when the cobalt-carboxylate bond was severed.

There have been a few previous studies of coordination chemistry that takes place within Nafion coatings,[2,5] but these have not dealt with the possibility that ionic permselectivity could produce large dynamic, as well as equilibrium, effects on the concentrations of ions produced within the coatings.

Experimental Section

Materials. The singly protonated, uncharged complex of ethylenediaminetetraacetate with ruthenium(III), $Ru(Hedta)(OH_2)$, was prepared as previously described[6] from Na_2H_2edta and K_2RuCl_5 (Johnson Mathey). The spectrum and electrochemistry of the product matched those in the previous description.[6] $[(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}](ClO_4)_2$ ($4\text{-}C_5H_4N$ = 4-pyridyl), prepared from $[Co(NH_3)_5OH_2](ClO_4)_3$[7] and 4-pyridinecarboxylic acid as described in ref 8, exhibited a spectrum that matched that previously reported.[8] The Nafion was obtained as a 5 wt % solution of the polyelectrolyte having an equivalent weight of 1100 (Aldrich). This solution was diluted 10-fold with ethanol, and the resulting stock solution was used to prepare electrode coatings by transferring 10 μL of the stock solution to the surface of glassy carbon electrodes and allowing the solvent to evaporate at room temperature. Typical coatings for cyclic voltammetric experiments contained 1.7×10^{-7} mol cm^{-2} of sulfonate groups. Other reagent grade chemicals were used as received. Solutions were prepared from distilled water that was further purified by passage through a purification train (Barnstead Nanopure).

Apparatus and Procedures. Glassy carbon electrodes (Tokai Carbon Co., Tokyo) were mounted and polished as previously described.[9] The electrode area was 0.2 cm^2. A glassy carbon ring-glassy carbon disk electrode was used in rotating ring-disk electrode experiments. The dimensions of the electrode were $r_1 = 0.38$ cm, $r_2 = 0.42$ cm, and $r_3 = 0.55$ cm, where the r values are the distances from the center of the disk to the edge of the disk, the inner edge of the ring, and the outer edge of the ring electrode, respectively. The calculated collection efficiency of 0.41 was in good agreement with the value of 0.40 measured in a solution of ferricyanide. The electrode was coated with Nafion by using a spin-coater. The rotor and dual potentiostat employed in the ring-disk electrode experiments were from Pine Instrument Co. Cyclic voltammetry was carried out with PAR instrumentation (EG&G Industries).

Coating thicknesses were estimated with a profilometer (Dektak, Inc.). The quantities of cation I incorporated in Nafion coatings were determined by coulometric assays in which the Ru^{III}(edta) centers were first reduced to Ru^{II}(edta) and the charge consumed in the subsequent anodic oxidation of the Ru^{II}(edta) centers was measured. This two-step procedure was adopted to avoid losses of Ru(edta) from the coating between the coulometric assays and subsequent experiments with the coatings. Conventional two-compartment electrochemical cells and instrumentation were employed. Solutions were deaerated with prepurified argon. Potentials were measured and are quoted with respect to a sodium chloride saturated calomel electrode (SSCE). Spectra were recorded with a Hewlett-Packard Model 8451 spectrophotometer.

Results and Discussion

In Situ Preparation and Electrochemistry of the Binuclear Complex. The experimental objectives outlined in the introduction required a positively charged electroactive species that could be rapidly converted into a negatively charged product by electroreduction. Our approach utilized a stable pentaammine(4-pyridinecarboxylato)cobalt(III) complex to provide both the cationic charge and the bifunctional, 4-pyridinecarboxylate ligand.

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† Contribution No. 8114.

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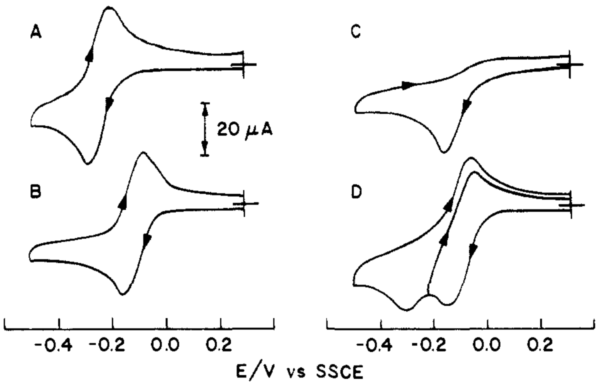
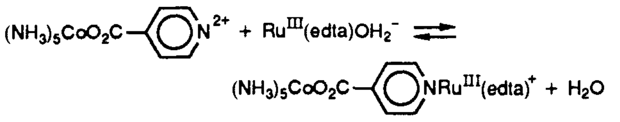


Figure 1. Cyclic voltammetry at an uncoated glassy carbon electrode. (A) 1 mM $Ru^{III}(edta)H_2O^-$; (B) repeat of A in the presence of 3 mM isonicotinic acid; (C) 1 mM $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$; (D) repeat of A in the presence of 1.2 mM $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$. Supporting electrolyte, 0.1 M acetate buffer adjusted to pH 3.9 + 0.2 M CF_3COO-Na. Scan rate, 50 mV s^{-1}.

This dipositive complex $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$ was reacted with $Ru^{III}(edta)OH_2^-$ in which the edta acts as a pentadentate ligand with one carboxylate group uncoordinated and the sixth coordination position of the Ru(III) center occupied by a water molecule.[10] This complex of Ru(III) is unusually labile with respect to substitution of the coordinate water by more strongly bound ligands such as pyridine and isonicotinamide.[10] This feature was exploited to prepare solutions of the binuclear complex by mixing the two reactants in close to stoichiometric quantities.



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The substitutional lability of the $Ru^{III}(edta)OH_2^-$ complex is greatest when the uncoordinated carboxyl group ($pK_a = 2.37$) is deprotonated,[10] and it is desirable to maintain a pH high enough to avoid competition between protons and the Ru(III) center for the exposed nitrogen center in the $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$ complex. Both objectives were realized by carrying out reaction 1 at pH 3.9. The course of the reaction was monitored electrochemically by taking advantage of the significant shift in the formal potential of the $Ru^{III}(edta)/Ru^{II}(edta)$ couple that results when the heterocyclic nitrogen atom replaces the water molecule coordinated to the ruthenium center.

A cyclic voltammogram for $Ru^{III}(edta)OH_2^-$ at a glassy carbon electrode is shown in Figure 1A. The formal potential for the Ru^{III}/Ru^{II} couple obtained from the average of the two peak potentials, −0.23 V, is in good agreement with previously reported values.[6] Addition of 3 mM isonicotinic (4-pyridinecarboxylic) acid to the solution of $Ru^{III}(edta)OH_2^-$ caused an immediate shift in the formal potential to −0.11 V (Figure 1B). The positive shift of 120 mV in formal potential is similar to that obtained when isonicotinamide coordinates to $Ru^{III}(edta)OH_2^-$.[10] The magnitudes of the equilibrium constants for the reaction of pyridine (10^5 M^{-1}) and isonicotinamide (1.2×10^4 M^{-1}) wth $Ru^{III}(edta)OH_2^-$ indicate that the reaction with isonicotinic acid should be essentially complete with reactant concentrations of a few millimolar, and a comparison of the cyclic voltammograms in Figure 1A and B confirms that this is the case.

The rapid substitution on $Ru^{III}(edta)OH_2^-$ also occurs when the anion is mixed with $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$. A cyclic voltammogram for the latter complex is shown in Figure 1C. The cathodic peak at −0.17 V corresponds to the reduction of the cobalt(III) center to cobalt(II). It has no anodic counterpart because the cobalt(II) complex rapidly decomposes into NH_4^+, $Co(OH_2)_6^{2+}$, and isonicotinic acid at the pH employed. In Figure 1D is shown the voltammetric response obtained from a solution to which both $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$ and $Ru^{III}(edta)OH_2^-$ were added. The reversible couple centered at −0.11 V corresponds to the reduction and reoxidation of the Ru center, and the potential where it appears shows that the heterocyclic nitrogen atom of the $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$ complex has replaced the water molecule on the ruthenium center so that the two complexes have reacted to form the binuclear species depicted in reaction 1. (Hereafter this complex will be termed cation I). When the electrode is scanned to more negative potentials a second, irreversible reduction peak appears at −0.3 V (Figure 1D). This peak corresponds to the reduction of the cobalt(III) center in cation I. The substantial negative shift in the potential where this reduction proceeds when $Ru^{II}(edta)$ is coordinated to the remote end of the isonicotinate ligand seems likely to be the result of back-bonding by the Ru(II) center into the orbital that is also involved in the reduction of the cobalt(III) center. Whatever the origin of the shift, it is fortuitous because it permits the electrochemistry of the two metal centers to be inspected separately. Note that there is no change in the anodic peak potential for the reoxidation of the Ru(II) center during the reverse scan when the forward scan is extended beyond −0.3 V so that the cobalt(III) center is reduced and detaches from the isonicotinate ligand, which remains coordinated to the Ru(II) center. Not surprisingly, replacement of the $(NH_3)_5Co^{III}$ center coordinated to the carboxylate end of the isonicotinate ligand with a proton has essentially no effect on the formal potential of the $Ru^{III}(edta)/Ru^{II}(edta)$ couple coordinated to the other end of the ligand.

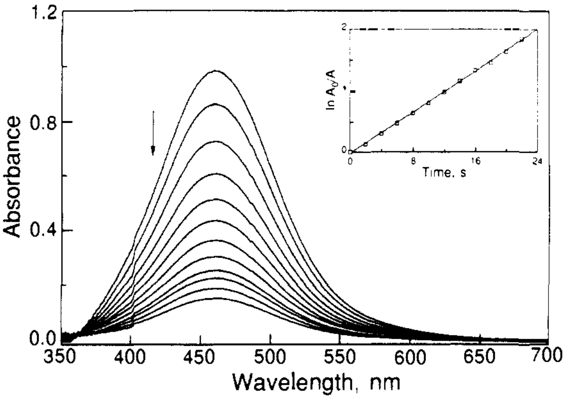

Figure 2. Absorption spectra of $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4NRu^{II}(edta)$ prepared by adding 0.1 mL of 3 mM $Ru(NH_3)_6^{2+}$ to 3 mL of 1 mM $(NH_3)_5CoO_2\text{-}4\text{-}C_5H_4NRu^{III}(edta)^+$. Supporting electrolyte as in Figure 1. Spectra were recorded every 2 s. Inset: First-order kinetic plot prepared from the spectral data.

The electrochemical evidence for the formation of the binuclear complex in Figure 1D is supported by spectral measurements: The absorbance at 350 nm of a 0.5 mM solution of $Ru^{III}(edta)OH_2^-$ is 0.36 and of a 0.5 mM solution of $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$ is 0.034. The absorbance of a solution prepared by mixing equal volumes of 1 mM solutions of the two complexes is 0.98. This increase in absorbance for the mixture resembles that which is reported to occur when $Ru^{III}(edta)OH_2^-$ is mixed with pyridine or isonicotinamide.[10]

The binuclear cation I is similar to the binuclear complexes of Co(III) and Ru(III) prepared by Isied and Taube to study the kinetics of intramolecular electron transfer.[11] The possibility that intramolecular electron transfer might occur between the Ru^{II}(edta) and $Co^{III}(NH_3)_5$ centers in our half-reduced complex was examined by carrying out spectrophotometric measurements similar to those in ref 11. The Ru^{III}(edta) center of cation I was rapidly reduced by added aliquots of $Ru(NH_3)_6^{2+}$ and the transient absorbance of the resulting $(NH_3)_5Co^{III}O_2C\text{-}4\text{-}C_5H_4NRu^{II}(edta)$ complex (Figure 2) was monitored. The absorbance, which was very similar to that reported for the isonicotinamide complex of

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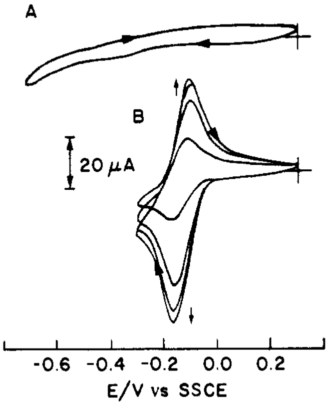

Figure 3. Cyclic voltammetry at a Nafion-coated glassy carbon electrode. (A) 1 mM $\mathrm{Ru^{III}(edta)OH_2^-}$; (B) repeat of A in the presence of 0.8 mM $\mathrm{(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}}$ with continuous scanning of the potential. Supporting electrolyte as in Figure 1. Scan rate, 100 mV s^{-1}. The coating contained 2.5 × 10^{-7} mol cm^{-2} of sulfonate groups.

$\mathrm{Ru^{II}(edta)}$,[10] exhibited a first-order decay (Figure 2 inset) from which a rate constant of 0.08 s^{-1} was estimated.[12] This rate constant corresponds to a half-life of ca. 9 s, which is short enough that, if it also applied to the reaction within Nafion coatings, significant spontaneous intramolecular electron transfer would occur during voltammetric experiments in which the half-reduced complex was generated in Nafion coatings at scan rates of 100 mV s^{-1}. However, as described below, the half-reduced complex persists for several minutes in Nafion coatings so that the rate of intramolecular electron transfer in this complex is apparently diminished substantially when it is incorporated in Nafion.

Incorporation and Electrochemistry of Cation I in Nafion. Nafion is a polyanionic material, which can be used to prepare stable electrode coatings that exhibit ideal permselectivity toward a variety of cationic reactants.[1-3] Anionic reactants such as $\mathrm{Fe(CN)_6^{3-}}$ or $\mathrm{Fe(edta)^-}$ face significant barriers in diffusing through the coatings to reach the underlying surface of Nafion-coated electrodes so that their usual electrochemical responses are lost or greatly diminished.[14] Figure 3A shows that the same is true of $\mathrm{Ru^{III}(edta)OH_2^-}$. The reversible voltammogram obtained at an uncoated electrode (Figure 1A) is completely eliminated at the Nafion-coated electrode (Figure 3A). However, when $\mathrm{(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}}$ is added to the solution used to record Figure 3A, the voltammetry shown in Figure 3B results. The reversible couple appears at the same potential as that for the binuclear cation I at a bare electrode (Figure 1D), and the peak currents increase with time as the reactant is incorporated into the Nafion coating by cation exchange. Both the position of the reversible couple and the fact that is is associated with a complex bearing a net positive charge are consistent with cation I, formed in reaction 1, as the electroactive species that is incorporated by the Nafion coating. It is somewhat surprising that the unipositive cation I competes successfully with the Na^+ ions present at a much higher concentration for incorporation in the Nafion coating. It may be that the interaction of the dipositive end of the binuclear complex with the anionic sulfonate sites within the Nafion is the dominating factor in controlling the incorporation equilibrium.

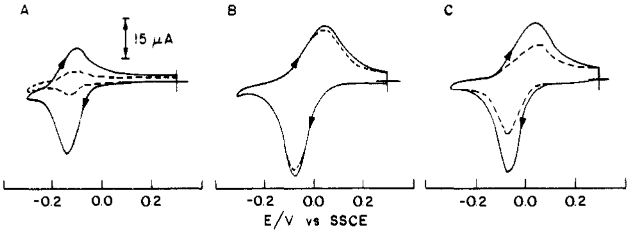

Figure 4. Effect of pH and initial potential on the persistence of voltammetric peaks for the $\mathrm{Ru^{III}(edta)/Ru^{II}(edta)}$ couple of cation I incorporated in Nafion coatings on glassy carbon electrodes. The coatings were exposed to ~1 mM solutions of cation I at pH 3.9 for 10 s and then transferred to pure supporting electrolyte solutions to record the voltammograms. (A) Supporting electrolyte (pH 3.9) as in Figure 1. Electrode potential was scanned from 0.3 V immediately after transfer (solid curve) or after 30 s waiting at 0.3 V (dashed curve). (B) Supporting electrolyte, 0.05 M H_2SO_4. Electrode potential was scanned from 0.3 V immediately (solid curve) or after 5 min waiting at 0.3 V (dashed curve). (C) Repeat of B except that the electrode potential was maintained at −0.3 V during the 5-min waiting period (dashed line). Both scans were initiated from 0.3 V. Scan rate, 100 mV s^{-1}.

In separate experiments directed at monitoring the stability of complex I within Nafion, coated electrodes were exposed to solutions of the complex at pH 3.9 for 10 s and then transferred to a pure supporting electrolyte solution at the same pH; the voltammogram was recorded immediately or after the electrode potential had been maintained at 0.3 V for 30 s. Under these conditions the ruthenium peak disappears at a moderately rapid rate, as is evident from the voltammograms in Figure 4A. The loss of the ruthenium peak was notably slower if the electrode was transferred instead to a supporting electrolyte consisting of 0.05 M H_2SO_4 (Figure 4B). At this pH (1.3) the free carboxylate group of the edta ligand coordinated to the Ru(III) center is protonated[10] so that the net charge on the complex becomes +2, $\mathrm{(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4NRu(Hedta)^{2+}}$.

The charge on the incorporated cation in Figure 4B can be decreased to +1 by holding the electrode potential at −0.3 V, where the Ru(III) center is reduced by Ru(II) without reduction of the Co(III) center. The resulting complex, cation II, is unipositive, just like cation I, but it is lost from the coating much more slowly than is cation I (Figure 4C). The slow decrease in the magnitude of the peak currents for cation II in Figure 4C could be the result of both simple reverse cation exchange and intramolecular electron transfer to produce an anionic Ru(edta) complex. It was not possible to distinguish between these two pathways in the present set of experiments. However, as mentioned earlier, the persistence of cation II in Nafion coatings for over 5 min (Figure 4C) shows that the rate of intramolecular electron transfer in cation II is much slower when it is incorporated in Nafion than when it is generated in solution where its half-life is only ~9 s.

The slower rate of loss of cation II than of cation I (compare Figure 4A and C) depends upon the unusual coordination chemistry exhibited by $\mathrm{Ru^{III}(edta)}$ and $\mathrm{Ru^{II}(edta)}$ complexes as discussed in a later section.

The formal potential of the reversible couple in Figure 4 is 110 mV more positive in 0.05 M H_2SO_4 than in the pH 3.9 buffer. This positive shift in the formal potential of the $\mathrm{Ru^{III}(edta)/Ru^{II}(edta)}$ couple is associated with the protonation of the free carboxylate group in the complex and has been observed at uncoated electrodes in previous studies.[6,15] The voltammetric wave corresponding to the reduction of the Co(III) center in cation II is totally irreversible and the peak shape and potential vary somewhat with the state of the surface of the glassy carbon electrode. However, the potential is always significantly more

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[12] The corresponding rate constant reported by Isied and Taube[11] for the $\mathrm{(NH_3)_5Co^{III}O_2C\text{-}4\text{-}C_5H_4NRu^{II}(NH_3)_4SO_4^{3+}}$ complex is 10^2 s^{-1}. The much lower rate observed for the $\mathrm{Ru^{II}(edta)}$ derivative, in which the $\mathrm{(edta)Ru^{II}\text{-}4\text{-}NC_5H_4CO_2H}$ center is a somewhat stronger reductant than $\mathrm{SO_4(NH_3)_4Ru^{II}\cdot 4\text{-}NC_5H_4CO_2H}$ [E^f = −0.11 and ~0.05 V vs SCE (the latter value is for the analogous chloro complex)[13] respectively], is somewhat surprising. However, we also measured the rate constant for the intramolecular electron transfer with the isomeric nicotinate complex, $\mathrm{(edta)Ru^{II}\text{-}3\text{-}NC_5H_4CO_2Co(NH_3)_5}$. The rate constant obtained, 0.04 s^{-1}, was only 2-fold smaller than that for the isonicotinate complex (k = 0.08 s^{-1}). For the corresponding pair of complexes with $\mathrm{Ru^{II}(NH_3)_4SO_4}$ replacing $\mathrm{Ru^{II}(edta)}$, Isied and Taube[11] found the nicotinate complex to be 200-fold less reactive. Thus, it appears that the $\mathrm{Ru^{II}(edta)}$ and $\mathrm{Ru^{II}(NH_3)_4SO_4}$ centers have substantially different patterns of reactivity toward intramolecular electron transfer to the $\mathrm{Co^{III}(NH_3)_5}$ center.

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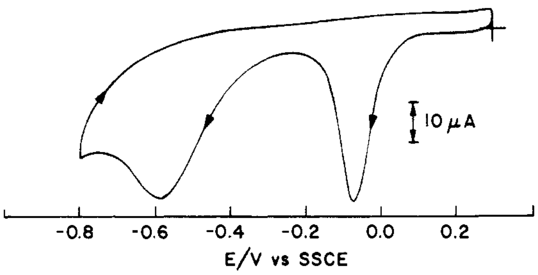

Figure 5. Reductive generation and ejection of (Hedta)Ru-4-$NC_5H_4CO_2H^-$ from Nafion coatings. The coating was loaded with cation I as in Figure 3 and transferred to 0.05 M H_2SO_4 to record the voltammograms. Scan rate, 100 mV s^{-1}.

negative when cation II is incorporated in Nafion (compare Figures 1D, 5, and 7). This negative shift probably results from the stabilizing interaction of the cobalt(III) center with the sulfonate groups in the Nafion as well as the additional activation energy associated with the incipient generation of an anionic complex as the cobalt(III) center is reduced.

The shift from -0.3 to -0.6 V in the potential where the cobalt(III) center is reduced is a rough measure of the decrease in oxidizing strength of the $Co^{III}(NH_3)_5$ center resulting from its incorporation in Nafion. This negative shift, coupled with the positive shift of 0.11 V in the formal potential of the $Ru^{III}(edta)/Ru^{II}(edta)$ couple, means that the driving force for intramolecular electron transfer in the half-reduced complex is decreased by over 0.4 V when it is incorporated in Nafion. This decreased driving force is the probable reason for the much lower rate of intramolecular electron transfer when (protonated) complex II is generated inside Nafion coatings.

Election of $Ru^{III}(Hedta)^-$ from Nafion Coatings. The reversible voltammetric waves for the $Ru^{III}(edta)/Ru^{II}(edta)$ couple of complex I incorporated in Nafion, as shown in Figure 4, are obtained only when the potential scan is restricted to values positive of -0.3 V. At more negative potentials the Co(III) center is reduced. A voltammogram in which both reductive waves are present is shown in Figure 5. It was recorded after the electrode was transferred to the pH 1.3 supporting electrolyte to minimize the spontaneous losses from the coating that occur at pH 3.9 (Figure 4). The reduction of the Co(III) center gives rise to the cathodic peak near -0.6 V and leads to the very rapid breaking of the bond between Co(II) and the carboxylate group of the isonicotinate ligand to produce an anionic ruthenium(II) complex, $HO_2C\text{-}4\text{-}C_5H_4NRu^{II}(Hedta)^-$. This complex is strongly repelled by the polyanionic Nafion coating and its ejection from the coating proceeds quite rapidly. Evidence of this rapid ejection is the absence of anodic peaks during the reverse scan to more positive potentials in Figure 5. The lack of an anodic peak for the oxidation of Co(II) is expected because of the rapid conversion of the reduced cobalt center to $Co(OH_2)_6^{2+}$ (and five NH_4^+ ions), which is not oxidizable at potentials below +1.7 V. However, an anodic peak near 0.05 V would be present if any of the Ru(II) complex remained in the coating (Figure 4B).

The loss of the mononuclear, anionic Ru(II) complex from the Nafion coating proceeds much more rapidly than is the case for a purely diffusion-controlled process. For example, if ferrocenium cations are incorporated in Nafion-coated electrodes as described by Rubinstein[16] and the electrodes are subsequently transferred to pure supporting electrolyte solution where the electrode potential is adjusted to reduce the ferrocenium cations to uncharged ferrocene molecules, voltammetric evidence of the presence of ferrocene in the coating persists for over 2 min (Figure 6). The much more rapid loss of the Ru(II) complex in Figure 5 shows that the electrostatic forces responsible for the permselectivity of Nafion coatings are very effective at ejecting anionic species generated within the coatings.

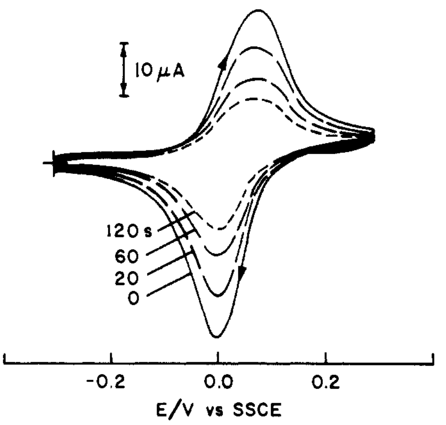

Figure 6. Cyclic voltammetry of the ferrocenium/ferrocene couple incorporated in Nafion coatings. The electrode was maintained at -0.3 V between potential scans. The scans were recorded 0, 20, 60, and 120 s after transfer of the electrode to 0.1 M KCl supporting electrolyte solution.

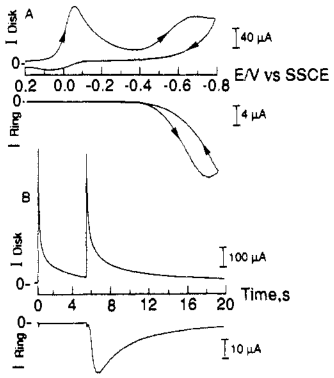

Figure 7. (A) Cyclic voltammogram at a rotating glassy carbon ring–glassy carbon disk electrode. The disk electrode was spin-coated with Nafion and loaded with cation I. Its potential was scanned at 50 mV s^{-1} with the ring potential at 0.2 V. (B) Double-potential-step chronoamperometry with the electrode from part A freshly loaded with cation I. The disk potential was stepped first from +0.2 to -0.3 V for 6 s and then stepped again from -0.3 to -0.8 V. Ring potential, 0.2 V. Rotation rate, 900 rpm. Supporting electrolyte, 0.05 M H_2SO_4.

To observe the ejection of the anionic Ru(II) complex from the Nafion coating more directly, experiments were conducted with a rotating ring–disk electrode.[17] In order to provide a thicker but smoother film, the glassy carbon disk was coated with Nafion by spin-coating using the undiluted (5%) Nafion solution. The Nafion adhering to the concentric glassy carbon ring was carefully removed by gentle abrasion with a fine-pointed wooden pick. Complex I was incorporated in the Nafion coating on the disk and the electrode rotated at 900 rpm as the disk potential was scanned from +0.2 to -0.8 V while the ring electrode potential was maintained at 0.2 V. The resulting, transient disk and ring currents are shown in Figure 7A. The potential of the ring electrode was chosen so that any Ru(II) reaching the ring would be oxidized to produce an anodic ring current. As expected, no ring current resulted when the disk potential was scanned over the $Ru^{III}(edta)/Ru^{II}(edta)$ wave, but when the disk potential reached -0.5 V, where the reduction of the Co(III) center began, a large anodic ring current appeared indicating the arrival of Ru(II) at the ring (Figure 7A). Since the only source of Ru(II) was cation I within the Nafion coating on the disk electrode, it is clear that reduction of the Co(III) center of cation I is accompanied by ejection of the anionic Ru(II) complex from the coating.

Potential-step experiments were also carried out with the rotating ring–disk electrode. The potential of the disk electrode coated with Nafion containing cation I was first stepped from +0.2

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to −0.3 V and subsequently from −0.3 to −0.8 V (Figure 7B) with the ring electrode potential maintained at 0.2 V. No ring current resulted when the disk potential was stepped from +0.2 to −0.3 V because the Ru^{II}(edta) complex produced by reduction of the Ru^{III}(edta) center remained linked to the cationic Co(III) center within the Nafion. However, when the potential step was extended to −0.8 V, where the Co(III) center is reduced, an anodic current flowed at the ring as the Ru(II) complex was ejected from the Nafion coating and swept to the ring electrode. (If the Nafion coating was loaded with the $(NH_3)_5CoO_2C\text{-}4\text{-}C_5H_4N^{2+}$ complex instead of cation I, no ring current resulted when the disk potential was stepped to −0.8 V). Examination of the rising portions of the disk and ring currents showed a delay of ca. 0.4 s between the time the disk potential was stepped to −0.8 V and the time the ring current began to flow. This delay is significantly longer than the time required for species generated at the edge of the disk electrode to reach the inner edge of the ring electrode. For our electrode and rotation rate this transit time was calculated to be ca. 70 ms.[18] The longer observed delay time is presumably a reflection of the time required for the anionic Ru(II) complex to diffuse out of the Nafion coating under the influence of the electrostatic potential. The estimated thickness of the spin-coated coating was ca. 2.5×10^{-4} cm, so that this delay time would correspond to an apparent diffusion coefficient of $(2.5 \times 10^{-4})^2/0.4$ or ca. 2×10^{-7} cm^2 s^{-1}, which is 3–4 orders of magnitude greater than typical diffusion coefficients measured for cationic redox couples in Nafion coatings.[19] The value is somewhat larger than a recently reported[20] diffusion coefficient for ferrocyanide anions in free-standing Nafion membranes.

Integration of ring current transients such as the one in Figure 7B can, in principle, be used to estimate the total quantity of reactant released at the disk electrode if the collection efficiency of the ring–disk electrode is assumed to be unaffected by the presence of a coating on the disk.[21-24] We found ring current integrals that resulted when the disk was stepped from +0.3 to −0.8 V corresponded to ca. 60% of the quantitites of cation I in the Nafion coatings as determined from coulometric assays. The voltammetric results (Figure 5) indicated that the loss of the anionic Ru^{II}(edta) complex from the coating was complete so that we believe the collection efficiency of the ring–disk electrode was lower when the disk was coated with Nafion. In any case, the experimental results shown in Figure 7 demonstrate clearly that when the anionic Ru(II) complex is electrogenerated within a Nafion coating it is ejected from the coating within fractions of a second.

Coordination Chemistry of Cation I within Nafion Coatings. The binuclear cationic species that have been examined in this study exhibit large differences in stability when they are incorporated in Nafion. For example, cation I (at pH 3.9) and cation II (at pH 1.3) are both unipositive but they are lost from Nafion coatings at quite different rates (Figure 4A and B). This contrasting behavior can be understood on the basis of the large effects that pH and oxidation state are known to have on the coordination kinetics of Ru(edta) complexes:[10] The unusual substitutional lability of Ru^{III}(edta)L complexes has been attributed to participation of the uncoordinated carboxylate group of the edta ligand in the mechanism by which the ligand L is replaced by an incoming ligand.[10] With the pH employed in Figure 4A (pH 3.9), the uncoordinated carboxylate group is not protonated and can exert its full potency in accelerating the ligand substitution process. When this reaction involves the substitution of a water molecule for the isonicotinate ligand in cation I, the anionic $Ru^{III}(edta)OH_2^-$ complex that is released is rapidly ejected from the Nafion coating. This is the primary process responsible for the relatively rapid loss of the Ru^{III}(edta)/Ru^{II}(edta) peaks in Figure 4A.

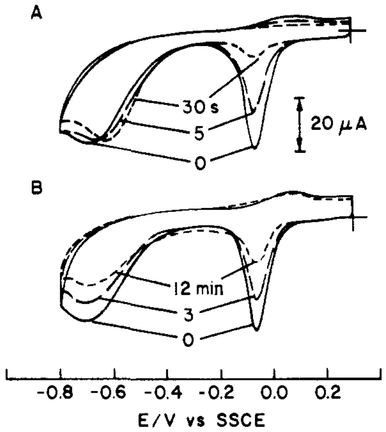

Figure 8. Comparison of the temporal dependence of the peaks for the reduction of Ru(III) and Co(III) centers in Nafion coatings loaded with cation I or cation II. Coatings were freshly loaded before each run by exposure for 10 s to a 1 mM solution of cation I in a pH 3.9 buffer solution followed by rapid transfer to the pure supporting electrolyte of interest for various waiting periods. (A) Electrode was transferred to pH 3.9 supporting electrolyte for 0, 5, or 30 s before a final transfer to 0.05 M H_2SO_4 to quench the loss of cation I and to record the voltammograms. (B) Electrode maintained at −0.3 V in 0.05 M H_2SO_4 for 0, 3, or 12 min before stepping the potential to 0.3 V, waiting for 30 s, and recording the voltammograms. Scan rate, 100 mV s^{-1}.

In addition to the anionic $Ru^{III}(edta)OH_2^-$ complex, the spontaneous dissociation of cation I inside of Nafion coatings yields a cationic complex, $(NH_3)_5Co^{III}O_2C\text{-}4\text{-}C_5H_4N^{2+}$, which is expected to be retained by the Nafion coating. Thus, at pH 3.9 one would expect to observe losses of the voltammetric peaks for Ru^{III}(edta) without a parallel loss of peaks for the cobalt(III) complex. This expectation was confirmed in the experiment shown in Figure 8A, where the cathodic peaks for the Ru(III) and Co(III) centers within a Nafion coating loaded with cation I were recorded at various times after it was transferred to a pH 3.9 buffer. It is evident that the Ru^{III}(edta) that departs from the coating at pH 3.9 is not accompanied by the Co(III) complex to which it was connected in cation I.

The rate of loss of the Ru^{III}(edta)/Ru^{II}(edta) couple from Nafion coatings containing cation I is much slower if the coating is transferred to 0.05 M H_2SO_4 (pH 1.3) with the potential of the coated electrode maintained at 0.3 V (Figure 4B). Several factors may contribute to the longer lifetimes of the incorporated binuclear complex under these conditions. The complex becomes dipositive, which favors its retention, the uncoordinated carboxylate group is protonated at pH 1.3, which makes it less effective in accelerating the rate of ligand substitution at the Ru(III) center,[10] and the complex that is formed by spontaneous dissociation of the Ru^{III}–pyridine bond, $Ru^{III}(Hedta)OH_2$, is uncharged so that time is available for the re-formation of the bond before the complex diffuses out of the coating.

Cation II is produced when a Nafion-coated electrode containing cation I is transferred to 0.05 M H_2SO_4 and the electrode potential is adjusted to −0.3 V to reduce the Ru(III) center. Under these conditions the loss of the Ru^{III}(edta)/Ru^{II}(edta) couple from the coating (Figure 4C) is somewhat faster than in Figure 4B but much slower than in Figure 4A. The reduced ruthenium center in cation II is so much less reactive toward ligand substitution than is Ru^{III}(edta)[10] that very little dissociation of the binuclear complex into its mononuclear components is expected to occur during the times involved in recording Figure 4C. The processes that are responsible for the slow decrease in the voltammetric peaks in Figure 4C are believed to be reverse cation exchange, which results in the removal of the intact binuclear cation II from the coating, and intramolecular electron transfer from the Ru(II) to the Co(III) center. Both processes are evidently much slower than the spontaneous dissociation of cation I at pH 3.9 (Figure 4A) that is the dominating factor in the much more rapid loss of the Ru^{III}(edta)/Ru^{II}(edta) response in Figure 4A. Each of the pro-

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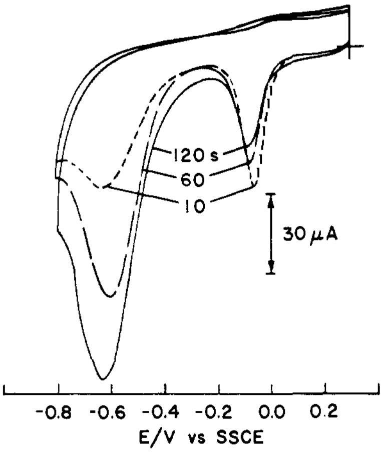

Figure 9. Effects of extended exposure of Nafion coatings to solutions of cation I on the composition of the cations incorporated by the coatings. Nafion-coated electrodes were exposed to 1 mM solutions of cation I at pH 3.9 for increasing times before transfer to a 0.05 M H_2SO_4 supporting electrolyte to record the voltammograms. Scan rate, 100 mV s^{-1}.

cesses responsible for the loss of cation II from the Nafion coatings in Figure 4C would be expected to lead to equal rates of loss of the electrochemical responses from the Ru(III) and Co(III) centers. The voltammograms in Figure 8B show that the two cathodic peaks do indeed decrease at about the same rate under these conditions. The contrast between the behavior shown in Figure 8A and B is evident and supports the interpretation that has been offered to account for the losses of cations I and II from Nafion coatings.

The kinetics of a number of the ligand-exchange reactions engaged in by $Ru^{III}(edta)L$ complexes have been examined by Matsubara and Creutz.[10] For example, they reported rate constants for reaction 2 with L = 4-$NC_5H_4CONH_2$, of k_f = 8.3 ×

$$Ru^{III}(edta)OH_2^- + L \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ru^{III}(edta)L + H_2O \qquad (2)$$

10^4 M^{-1} s^{-1} and k_b = 0.7 s^{-1}. The kinetic parameters within Nafion coatings for the case in hand, where L = $(NH_3)_5CoO_2C$-4-$C_5H_4N^{2+}$, may not be greatly different except for the fact that the concentration of H_2O within Nafion coatings has been estimated to be ~20% of its value in bulk water[25] so that the value of k_b might be correspondingly smaller.

Values of k_b in the range between 0.1 and 1 s^{-1} correspond to the spontaneous breaking off the ruthenium–pyridine bond about once every few seconds. In solutions with millimolar reactant concentrations, the large value of k_f assures that the bond is rapidly re-formed so that the $Ru^{III}(edta)L$ complex is stable. However, the reversible nature of reaction 2 in solution is not expected to persist when cation I is incorporated in Nafion because its spontnaeous dissociation (the reverse of reaction 2) produces the $Ru^{III}(edta)OH_2^-$ anion, which should also be rapidly ejected from Nafion coatings. Thus, exposure of Nafion coatings to stable solutions of cation I for extended periods might be expected to produce coatings that contain both cation I and its cationic dissociation product, $(NH_3)_5CoO_2C$-4-$C_5H_4N^{2+}$. The quantity of the latter dipositive cation incorporated by the coatings could exceed considerably the quantity of cation I. The voltammograms in Figure 9 show that much larger quantities of the $(NH_3)_5CoO_2C$-4-$C_5H_4N^{2+}$ complex than of cation I are indeed incorporated by Nafion coatings exposed to solutions of the latter cation. The behavior makes very clear the major ways in which the coordination chemistry of oppositely charged reactants may be altered by incorporation into Nafion.

Conclusions

The ability of Nafion (and presumably other polyelectrolyte) coatings to affect dramatically the course of electrode, intramolecular electron transfer, and coordination reactions that are carried out with reactants incorporated within the coatings has been demonstrated in this study. The example given emphasized the polyelectrolyte-induced, irreversible dissociation of complexes that are stable outside of the polyelectrolyte domain. The possibility that polyelectrolytes could be utilized in a similar way to effect the inverse process, that is, the association of two counterionic reactants within a polyelectrolyte to generate new complexes that would be unstable outside of the polyelectrolyte domain, is being examined in continuing studies. We are also engaged in experiments designed to measure with more precision the rates of ejection from permselective polyelectrolyte coatings of co-ions generated within them.

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