The Effect of Composition of Nafion Deposition Solutions on the Diffusional Properties of the Films

1 author:

Ze'ev Porat
Nuclear Research Center - Negev
48 PUBLICATIONS   **1,095** CITATIONS

Some of the authors of this publication are also working on these related projects:

Project   Materials Science, Nanotechnology, Nanobio-technology View project

The Effect of Composition of Nafion Deposition Solutions on the Diffusional Properties of the Films

Ze'ev Porat, Israel Rubinstein and Baruch Zinger

The Effect of Composition of Nafion Deposition Solutions on the Diffusional Properties of the Films

Ze'ev Porat[a] and Israel Rubinstein*

Department of Materials and Interfaces, The Weizmann Institute of Science, Rehovot 76100, Israel

Baruch Zinger

Department of Applied Chemistry, Soreq Nuclear Research Center, Yavne 70600, Israel

ABSTRACT

The properties of Nafion films on electrodes were studied as a function of the water content in the deposition solutions (0.7% Nafion in mixed ethanol/water). The rate of loading and unloading (*i.e.*, ion-exchange) of the complex ion $Ru(bpy)_3^{2+}$, loading into films which were thermally treated, and penetration of the anion $Fe(CN)_6^{4-}$ were examined. All these measurements show a nearly linear dependence of the voltammetric peak currents (for the oxidation of the incorporated ions) on the percentage of water in the deposition solutions. These results lead to the conclusion that films that are cast from solutions of higher water content have more "open" structures that allow faster diffusion of ions. It is also suggested that $Ru(bpy)_3^{2+}$ exists in the films in two forms: one is strongly bound to the sulfonic groups by ion-pairing, for which the mass-transport mechanism is primarily electron self-exchange (characterized by D_{et}). The other is bound to the polymer by weak electrostatic or hydrophobic interactions, for which mass transport proceeds mainly by physical diffusion (D_o). The two diffusion coefficients were determined separately in each kind of film, and they both show nearly linear dependence on the percent of H_2O in the Nafion solutions from which the films are deposited.

Nafion films as a coating material for chemically modified electrodes have been the subject of numerous studies for more than a decade.[1] Three major properties have made Nafion particularly suitable for this purpose: (*i*) an exceptional chemical and thermal stability; (*ii*) the multiphase structure, that includes a fluorocarbon backbone, interconnected ionic clusters, and an interfacial region;[2] (*iii*) the ability, as a cation-exchange polymer, to extract high concentrations of electroactive cations, even from dilute solutions.

Three factors may be involved in transport processes in Nafion films on electrodes: (*i*) diffusional motion of electroactive species in the film, (*ii*) electron transfer between redox centers (electron hopping), (*iii*) migration of counterions.

Physical diffusion of ions, although much slower in Nafion than in fluid solvents, is the mechanism responsible for ion exchange between the loading solution and the film. Its relative contribution to the charge propagation in Nafion films varies for different kinds of incorporated ions, as discussed below.

Electron hopping appears experimentally as a diffusion process, characterized by D_{et}

$$D_{et} = 1/6k\delta^2 C_p \quad [1]$$

where k is the second-order rate constant for the self-exchange reaction, δ is the distance between the centers of the reactants, and C_p is the concentration of the electroactive species in the polymer. The numerical coefficient (1/6) has recently been corrected;[3] the previous value was believed to be $\pi/4$.[4]

The contribution of electron transfer to the charge propagation is usually negligible in solution electrochemistry, where physical diffusion is the predominant effect. It can, however, be significant in polymer films, where the physical diffusion is much slower, and the electron-exchange rate constant is large enough. The combination of physical diffusion (D_o) and electron transfer diffusion (D_{et}) results in an apparent diffusion coefficient, which is given by the Dahms-Ruff equation.[4,5]

$$D_{app} = D_o + D_{et} \quad [2]$$

The relative contributions of the two are different for different ions. For instance, the diffusional mode of the cation

[(trimethylammonio)methyl] ferrocene (C_pFeTMA^+) was found by White *et al.* to be almost exclusively physical, whereas for tris(2,2' bipyridine) ruthenium ion [$Ru(bpy)_3^{2+}$] it is mostly electron transfer.[6] Moreover, Buttry and Anson have found that D_{app} for the couple $Co(bpy)_3^{2+/1+}$ in Nafion is much larger than that for $Co(bpy)_3^{2+/3+}$, and attributed this result to a significant contribution from electron hopping to D_{app} only for the 2+/1+ couple. Cross electron transfer between two different species, incorporated into a polycationic film, was shown by Facci and Murray to substantially enhance the rate of transfer diffusion relative to physical diffusion in the film.[8]

Migration of counterions is essential for maintaining the electroneutrality in the film during an electrochemical reaction. For instance, reduction of a substrate within the polymeric film involves the incorporation of cations from the solution and/or expelling of anions from the film, irrespective of the relative contributions of the two diffusion mechanisms discussed above. The effect of the counterion migration in Nafion films on the value of D_{app} for $Ru(bpy)_3^{2+}$ was examined by Martin *et al.*[9] They assumed that such an effect would result in a dependence of D_{app} on the size of the counterions (or co-ions). Experimental results showed no such dependence, and it was concluded that the motion of counterions or co-ions has no effect in that case.

Nafion films are usually deposited from alcoholic solutions of the polymer, usually containing a certain amount of water. The effect of the depositing conditions on the properties of the resultant films were only partially studied. Moore and Martin reported that solution-cast films ("recast films") have poor mechanical properties (compared with as-received Nafion membranes) and are soluble, at moderate temperatures, in a variety of organic solvents.[10] They developed a solution processing procedure which produced high quality films. The key element in this procedure was the replacement of the ethanol-water mixture with a high boiling point solvent, followed by removal of the solvent at an elevated temperature.

The effect of thermal treatment on the properties of recast films was also studied by Gebel *et al.*[11] They found that crystalline order develops with temperature and is strongly affected by annealing. They proposed that prior to thermal treatment, the films are composed of fractions of low crystallinity, randomly distributed over the amorphous phase. Upon annealing, rearrangement of the crystalline sites takes place, that includes an increase in the crystallite size, improvement of their internal order and development of a

---

Fig. 1. Loading voltammo-grams for Pt/Nafion (deposited from EtOH/H₂O 30:70) in 0.5 mM Ru(bpy)$_3^{2+}$ in 0.1 M H₂SO₄, taken at 1 min intervals (see numbers). (A) Quiescent solution. (B), (C) Increasing stirring rates (qualitative). The potential at the negative limit is 0.20 V (vs. MSE).
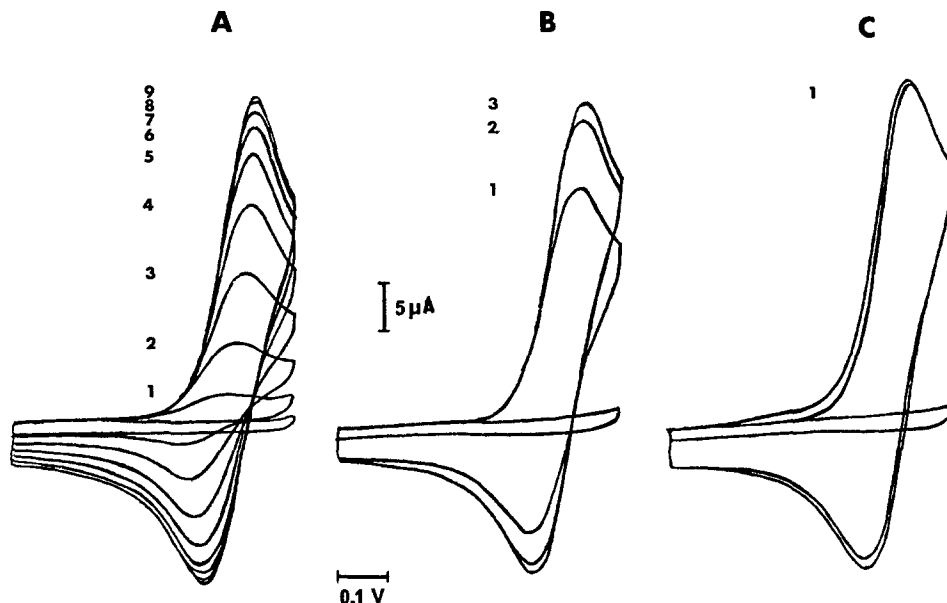
long-range order. The changes in the solubility and mechanical properties upon annealing were related to these structural modifications.

Recently, Striebel et. al. studied the effect of humidity level during film deposition on the properties of the films.[12] They evaporated ethanolic solutions of Nafion on electrodes under a glass cover, that also contained either pure water ("wet-cured films") or P₂O₅ dessicant ("dry-cured films"), and tested the permeability of Ru(bpy)$_3^{2+}$ and Cl⁻ in the films. It was found that loading of Ru(bpy)$_3^{2+}$ ions was much faster into the wet-cured films than into the dry-cured films, while the permselectivity of wet-cured films towards Cl⁻ was lower, i.e., chloride ions could permeate more easily into those films.

In the present paper we focus on the composition of the solvent in the depositing Nafion solution, i.e., the ratio ethanol/water. We examine the effect on the properties of the resultant films and the modes of binding and diffusion of Ru(bpy)$_3^{2+}$ in these films.

Experimental

Chemicals.—Nafion coating solutions in water/ethanol were prepared from soluble powder of Nafion 1100 EW (Solution Technology, Incorporated), triply distilled water, and analytical grade ethanol. The exact concentration (expressed as percent w/v) was determined by drying and weighing known volumes of the parent Nafion solution, followed by two times dilution with the desired composi-, tion of the solvent. Tris (2,2′ bipyridine) ruthenium(II) chloride and potassium ferrocyanide were analytical grade and were used as received.

Film deposition.—Coating of the electrode was carried out by applying a drop of 7 μliter Nafion solution (0.7% w/v in mixed ethanol-water) on the entire surface (Pt + glass), followed by room-temperature evaporation of the solvent. The volume of the film was calculated from the concentration and the volume of the Nafion drop, the density of wet Nafion 1100 EW (1.58 g/cm³ for Nafion-Na⁺),[13] and the geometric area (0.24 cm² for the Pt-glass surface). The calculated thickness of the films was 1.3 μm. The amount of the incorporated Ru(bpy)$_3^{2+}$ in the films was determined by coulometry and its concentration was calculated from the "effective" volume of the film, i.e., over the Pt disk only.

Electrochemical measurements.—A conventional three-electrode cell was used, with a platinum disk (0.018 cm²), sealed in a soda-glass tube, as a working electrode, a platinum coil as a counterelectrode and a mercurous sulfate electrode (MSE) as a reference. The instrumentation in-

cluded a Model 303C potentiostat and an electrochemical programmer, both from the Department of Chemistry, Technion, Haifa; a Houston Instrument 100 X-Y recorder and an ESC 630 digital coulometer from the Electrosynthesis Company, East Amherst, NewYork. The coulometry was performed as follows: the potential was stepped to 0.83 V (vs. MSE), positive of the oxidation potential of Ru(bpy)$_3^{2+}$, and held there for 60 s. The potential was then scanned back to a potential negative of Ru(bpy)$_3^{2+}$ reduction, and the number of coulombs for the reduction recorded. A coulometric measurement of the background (i.e., the unloaded film) was subtracted from the total reduction charge. The experimental error in the coulometric measurements was up to 10%.

Results

Loading and unloading.—The conversion of a Nafion film to the Ru(bpy)$_3^{2+}$ form ("loading") was carried out by soaking the coated electrode in an aqueous acid solution of Ru(bpy)$_3^{2+}$ dichloride. Two parameters seem to govern the rate of complex incorporation: the rate of material supply to the film-solution interface and the rate of mass-transport in the polymer.

When the coated electrode is immersed in an unstirred solution of the complex, the rate of material supply is limited by diffusion in the solution. Stirring the solution accelerates significantly the incorporation rate, which increases with the speed of stirring up to a saturation point. Hence, a film that required 8 min for full loading in an unstirred solution was fully loaded within 1 min in a vigorously stirred solution, as indicated by the peak currents of the voltammograms recorded at 1 min intervals (Fig. 1).

The rate of permeation (and transport) in the polymer was found to be dependent upon the nature of the specific film. As noted above, coating of the electrode was carried out upon applying a volume of a few microliters of Nafion solution (0.7% w/v) in mixed ethanol-water onto the surface, followed by room temperature evaporation of the solvent. It was found that the composition of the depositing solvent, i.e., the EtOH/H₂O ratio, strongly affects the rate of permeation. Nafion solutions that contain higher amounts of water appear to form more "open" films, allowing more facile incorporation of the complex. A set of measurements, carried out in an unstirred solution of 0.5 mM Ru(bpy)$_3^{2+}$ in 0.1M sulfuric acid, is shown in Fig. 1A. Films were prepared from Nafion solutions of different water content, ranging from 10 to 70%. Cyclic voltammograms of incorporated Ru(bpy)$_3^{2+}$ were recorded at time intervals of 1 min, showing the growth of the complex concentration in the polymer. Plots of the loading rates of the different films,
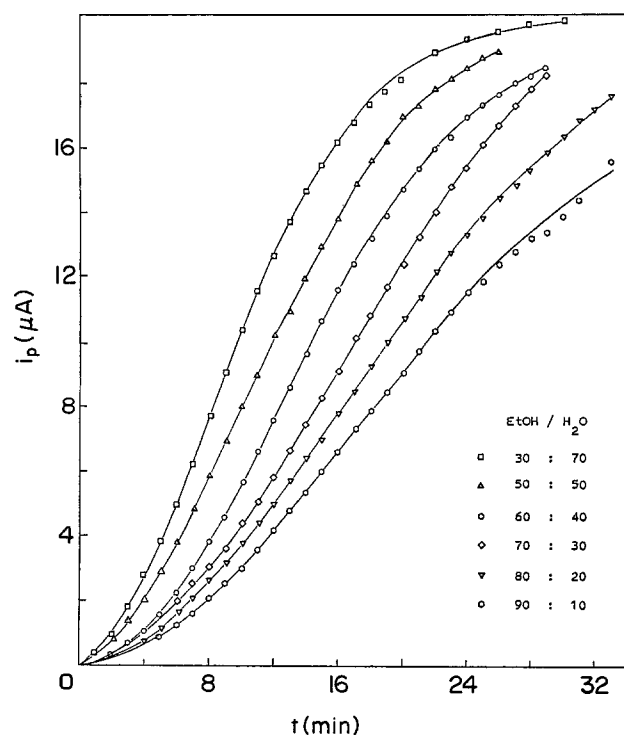
Fig. 2. Loading curves for Pt/Nafion in an unstirred solution of 0.5 mM Ru(bpy)$_3^{2+}$ in 0.1M H$_2$SO$_4$, as a function of the composition of the Nafion deposition solution.

Fig. 3. Loading curves for Pt/Nafion in a stirred solution of 0.5 mM Ru(bpy)$_3^{2+}$ in 0.1M H$_2$SO$_4$, measured after 1 (filled circles) and 2 (open circles) min, as a function of water content in the deposition solution.

presented as the oxidation peak currents *vs.* time, are shown in Fig. 2. There is a clear correlation between the peak current at a certain time and the percentage of water in the depositing Nafion solution.

The rate of incorporation of the complex into the film in the unstirred solution is almost completely governed by mass transport in the solution (see Fig. 1). One can therefore reasonably assume that, at any given time, the complex concentration in the film is independent of the film deposition solution and is approximately equal for all the films. The difference in i_p (at any given time) for the various films can, therefore, be attributed to different diffusion coefficients in the films, resulting from the different solvent mixtures used for film deposition, as discussed below.

Since the rate of complex incorporation in a quiescent solution (Fig. 1A and 2) is limited primarily by mass transport in the solution, it does not demonstrate fully the effect of film structure. Therefore, loading experiments were repeated under vigorous stirring, as shown in Fig. 1B, C. Films were prepared from Nafion solutions with water content ranging from 5 to 90%. Measurements taken after 1 min of loading show a nearly linear relationship between i_p and percent H$_2$O in the deposition solution (Fig. 3). Measurements taken after 2 min show a similar linearity for some films, but films cast from solutions of higher water content (70% or higher) are already close to saturation. Thinner films, loaded under the same conditions, were mostly saturated within 1 min. The measurements under forced convection again show a clear effect of the water content in the deposition solution on the rate of complex ion incorporation, presumably due to the influence of the water content in the deposition solution on the structure and properties of the resultant polymer. Here, unlike the results in unstirred solutions, one cannot assume equal concentrations in the different films at equal loading times; hence, i_p may be influenced by both the complex concentration and its diffusion coefficient in the film. The trend, however, is qualitatively similar to that in Fig. 2.

It should be noted that the pure ethanolic solution of Nafion (0% H$_2$O) sometimes shows Ru(bpy)$_3^{2+}$ incorporation currents close to those obtained for films deposited from 30% water solutions. This deviation is discussed later.

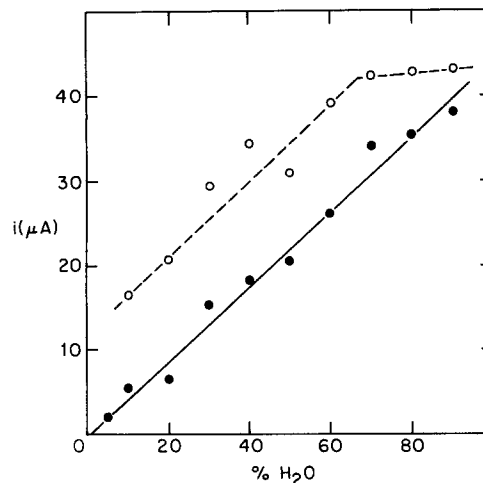The rate of unloading of Nafion films in background solution was also monitored by cyclic voltammetry. Unloading of complex ions from the film in background solution indicates ion exchange with cations of the supporting electrolyte (in our case, protons). The electrode was removed from the loading solution, rinsed, and cycled periodically in pure sulfuric acid which was well stirred. The stirring was aimed at minimizing mass-transport limitations in the solution, *i.e.*, accumulation of the complex near the solution/film interface, which would slow the process. A continuous decrease in peak heights is observed, as shown in Fig. 4. The unloading is fast at the beginning and then slows down until it practically stops, at ca. 40% of the initial peak current. (Peak currents in Fig. 4 are normalized to the initial peak current i_{max}.)

Here too, the correlation between the rate of transport in the polymer and the composition of the deposition solution is clearly shown. This is well demonstrated during the first minute of unloading, where the rate of material loss from the film is the highest. A plot of the normalized peak currents *vs.* the percentage of water in the deposition solution
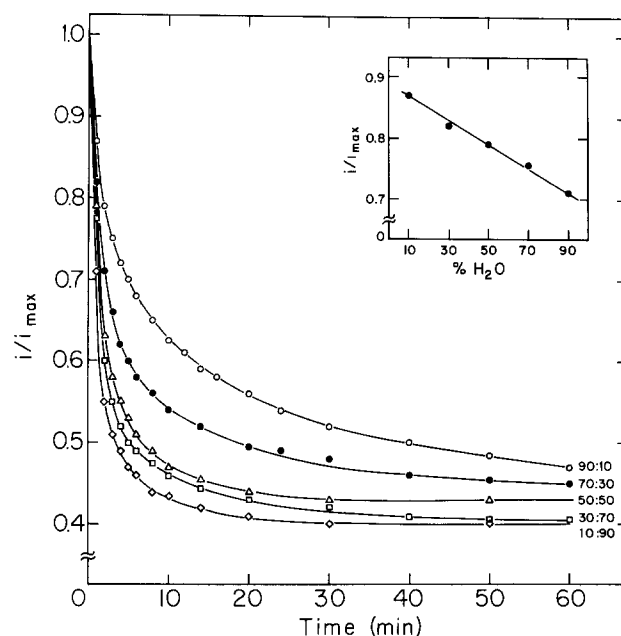

Fig. 4. Unloading curves for Ru(bpy)$_3^{2+}$ from Pt/Nafion in a stirred 0.1M H$_2$SO$_4$ solution. The compositions of the deposition solutions are marked (as EtOH/H$_2$O). Insert: loss of Ru(bpy)$_3^{2+}$ after 1 min unloading, as a function of water content in the deposition solution.

Table I. Dependence of the diffusion coefficients and of the maximal loading charge of $Ru(bpy)_3^{2+}$ in Nafion films on the composition of the deposition solution.

| Solvent EtOH:H₂O	$D_{app}{}^{a}$ ($\times 10^{10}$ cm²/s)	$D_{et}{}^{a}$ ($\times 10^{10}$ cm²/s)	$D_o{}^{b}$ ($\times 10^{10}$ cm²/s)	q (μC)
20:80	20.0	7.9	12.8	88
30:70	19.0	4.8	11.4	104
40:60	12.0	3.2	9.8	122
60:40	12.6	4.7	7.1	126
70:30	7.4	1.2	5.5	140
80:20	5.4	1.5	4.0	167
100:0	3.6	1.2	1.5	168

[a] Experimental value.
[b] Calculated from the lines in Fig. 5.

shows a nearly linear relationship (Fig. 4, insert), a behavior rather similar to that observed during loading.

Diffusion coefficients in the various films.—Since the rate of mass transport in the film is characterized by an apparent diffusion coefficient, it was of interest to see whether a correlation can be found between the measured values of D_{app} for $Ru(bpy)_3^{2+}$ in the loaded polymer and the degree of "openness," shown above to be dependent upon the percent H₂O in the deposition solution. White *et al.*[6] and Buttry and Anson[7] argued that the major contribution to mass transport of $Ru(bpy)_3^{2+}$ in Nafion films is by electron hopping rather than physical diffusion. Hence, a set of experiments was set up in order to evaluate the two terms separately, in the following manner: the films were fully loaded as before, from a stirred solution of 0.5 mM $Ru(bpy)_3^{2+}$. Cyclic voltammetry at several scan rates was then carried out in the loading solution; the diffusion coefficient thus measured[14] is assumed to include the full contribution of the two mass-transport mechanisms (D_{app}). Under these conditions unloading is avoided, and the measurement of D_{app} in fully loaded films is possible. The complex concentration in the film was determined by coulometry (see the Experimental section). The electrode was then transferred to a pure electrolyte solution for prolonged unloading (90 min) until a steady state was obtained, *i.e.*, the voltammetric peak current decreased to a constant value. Here we assume that the complex that stays in the polymer is strongly bound to the sulfonic groups and that mass transport in the film is almost entirely governed by electron hopping, and hence measurements under these conditions provide D_{et} in the various films. D_o can then be obtained using Eq. [2]; the results are summarized in Table I.
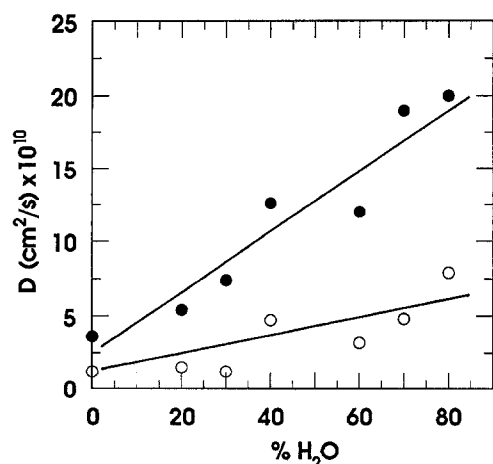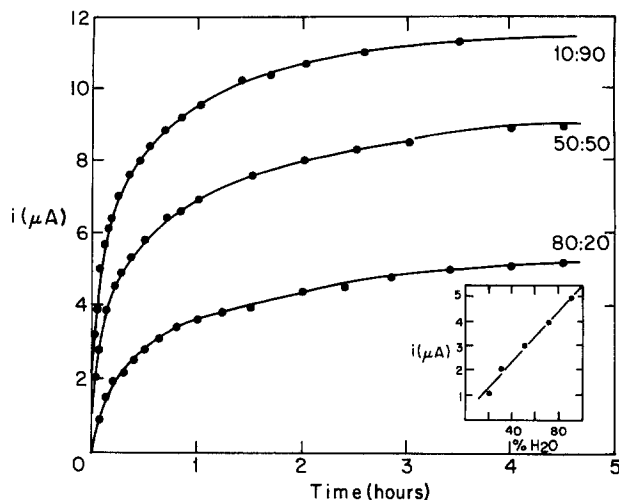
Fig. 6. Loading curves for Pt/Nafion, annealed (see text) in a stirred solution of 0.5 mM $Ru(bpy)_3^{2+}$ in 0.1M H₂SO₄. The composition of the deposition solution is marked as EtOH/H₂O. Insert: peak currents recorded after 4 min, plotted vs. the water content of the deposition solution.

Several conclusions can be drawn from the data presented in Table I:

1. The apparent diffusion coefficients (D_{app}) measured with the fully loaded films exhibit a prominent dependence on the water content in the Nafion solutions, with a near-linear relationship between D_{app} and percent H₂O in the deposition solution (Fig. 5). This is attributed to a systematic modification of the film inner structure upon changing of the film deposition conditions.

2. The electron-transfer diffusion coefficients (D_{et}) also exhibit an increase with percent H₂O and, as expected, the values are smaller than the corresponding values of D_{app}. The physical diffusion coefficients (D_o) also vary in the same manner as a function of the percent H₂O in the Nafion deposition solution.

3. The maximal ion capacity of the film decreases upon increasing the water content of the deposition solution. This conclusion, however, should be taken with some caution, as the coulometric measurement itself involves 1 min at +0.85 V (*vs.* MSE), where the complex is triply charged. It was reported that the 3+ state of the complex is less stable in the polymer[9] and hence expected to diffuse out more easily from the more hydrated ("open") films.

4. Changes in D_{app} may, in principle, be due to some extent to differences in $Ru(bpy)_3^{2+}$ concentration in the film. This effect appears to be of little importance here, based upon the observation that the same trend in D_{app} is seen in Fig. 2, where the concentrations in the different films are approximately equal (at any given time), as explained above.

The effect of annealing.—Thermal treatment of recast Nafion films was reported to increase their stability in organic solvents, *i.e.*, render them rather insoluble.[10] This effect is probably associated with the increased degree of crystallinity of the fluorocarbon phase. Annealing of Nafion above its glass-transition temperature may also cause rearrangement of the side chains and thus changes in the morphology of the ionic clusters, which may be reflected in their ion-exchange properties.
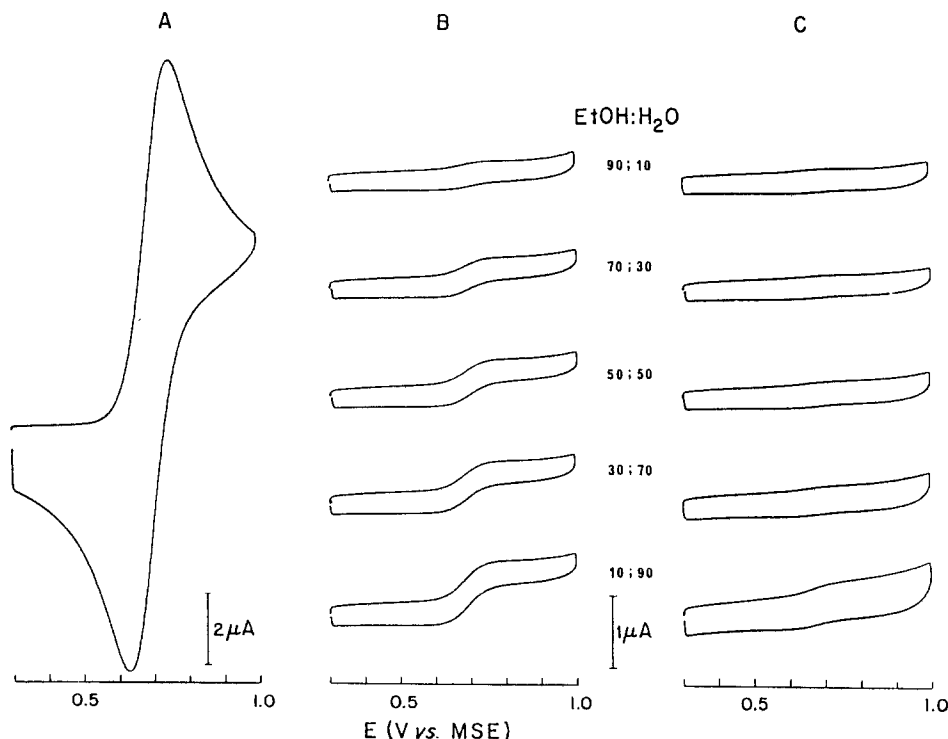

Fig. 5. Plot of the diffusion coefficients D_{app} (filled circles) and D_{et} (open circles) of $Ru(bpy)_3^{2+}$ in Nafion films vs. the water content in the deposition solutions.

Fig. 7. Anion rejection at Pt/ Nafion film in 3.0 mM Fe(CN)$_6^{4-}$ + 0.1M Na$_2$SO$_4$. (A) Bare Pt electrode; (B) same Pt electrode, coated with Nafion films deposited from solutions of different water content (as indicated); (C) same as (B), with the films loaded with Ru(bpy)$_3^{2+}$.

The effect of annealing of Nafion films on electrodes was examined in the following manner: coating of the Pt/glass electrode was carried out as described above. After drying, the coated electrode was held for 30 min at 120°C, *i.e.,* above the reported glass-transition temperature of Nafion-H⁺, [15] and then left to cool for 5 min in air. Loading was performed as before from a stirred solution of 0.5 mM Ru(bpy)$_3^{2+}$, monitored by continuous cyclic voltammetry and by coulometry. The following results have been obtained:

1. The currents for the incorporated complex and the rates of incorporation are considerably lower in annealed films. After 5 h of loading the peak currents are 12-25% of corresponding currents in unannealed films.

2. The rate of incorporation into annealed films exhibits the familiar dependence on the composition of the deposition solution (Fig. 6). A plot of the peak currents measured after 4 min *vs.* percent H$_2$O shows again a near linear relationship (Fig. 6, insert).

3. The maximal loading currents of annealed films are also a function of the water content in the Nafion solutions. Thus, after 4.5 h loading, the current for a film prepared from 90% H$_2$O solution is more than twice that for a film prepared from 20% H$_2$O solution.

4. Soaking of the electrode in a mixture of acetonitrile/ water (3:1) for several hours has a pronounced effect on annealed films, and enhancement of Ru(bpy)$_3^{2+}$ incorporation is evidenced by the growth of the voltammograms. The current increase is not as fast as that observed in loading of unannealed films but still is very significant.

5. The annealed Nafion films remain intact after several hours in acetonitrile/water (as well as in other organic solvents), indicating the dramatic decrease in the solubility of recast Nafion in organic solvents and in water/organic mixtures.

Anion rejection.—While a bare Pt electrode, dipped in a solution of K$_4$Fe(CN)$_6$, exhibits normal redox peaks corresponding to the reversible couple Fe(CN)$_6^{4-/3-}$ (Fig. 7A), the same electrode coated with a Nafion film and dipped in the same solution shows very small peaks. This clearly demonstrates the perm-selectivity of Nafion films (Donnan exclusion).

Anion rejection was studied here in the context of the influence of Nafion film deposition conditions on the film structure and properties. The major observations are:

1. The peak currents for Fe(CN)$_6^{4-/3-}$ show the familiar dependence on the amount of water in the deposition solution (Fig. 7B). Higher currents are obtained with films prepared from Nafion solutions of higher water content, and the relationship is nearly linear (Fig. 8). A qualitatively similar trend was observed by Striebel *et. al.* for Cl⁻ ions in Nafion films.[12]

2. The currents for the Fe(CN)$_6^{4-/3-}$ couple are markedly reduced when the film is preloaded with Ru(bpy)$_3^{2+}$ (Fig. 7C), indicating either a lower concentration of ferrocyanide ions in the film, or a slower diffusion in the film, or both.

The dependence of the peak currents for anions on the composition of the deposition solution (Fig. 8) is in agreement with the assumption that films with more "open" structure are formed from water-rich solutions. Permeation of anions through pores in the film would be more energetically favorable when the repulsion forces between the sulfonic groups and the permeating anions are weaker.

The substantial decrease in the peak currents for Fe(CN)$_6^{4-/3-}$ in the presence of Ru(bpy)$_3^{2+}$ in the film can be explained by blocking of diffusion channels and/or by elec-
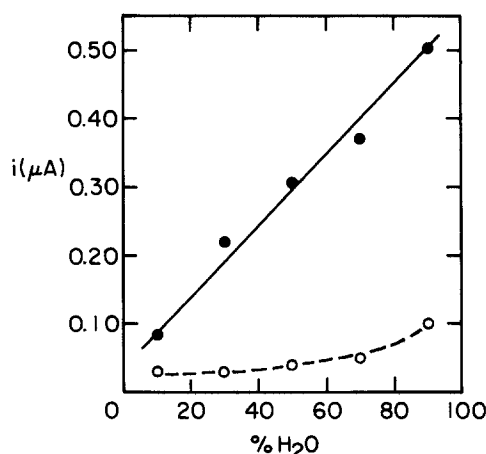

Fig. 8. Plots of the oxidation peak currents for Fe(CN)$_6^{4-}$ at Pt/ Nafion electrodes *vs.* the water content of the deposition solution. Solid line: Pt/Nafion; dashed line: Pt/Nafion, Ru(bpy)$_3^{2+}$ (results from Fig. 7).

trostatic cross-linking of side chains by the multiply charged ions. It is clear, in any event, that the structure of the polymer is largely modified by the incorporation of Ru(bpy)$_3^{2+}$ ions, as was previously shown.[16]

Discussion

The main property of Nafion films on electrodes that was observed in this study is their "memory" for the composition of the deposition solution, which strongly affects the film behavior as a medium for electrochemical processes. The influence of the amount of water in the Nafion solution on the mobility of incorporated ions in the film was evidenced in essentially all the measurements: permeation of cationic and anionic complexes [Ru(bpy)$_3^{2+}$ and Fe(CN)$_6^{4-}$], unloading of Ru(bpy)$_3^{2+}$ and loading into annealed films. Furthermore, in all the above cases the relationship between the percentage of water and the rate of loading/unloading was found to be nearly linear. (Note that in several cases the currents observed with films deposited from 100% ethanolic solution were higher than expected. This is probably due to poor physical integrity and cracking of the films in the absence of any water in the deposition solutions and will not be considered in the discussion below.)

The rates of these processes were evaluated from voltammetric peak currents of the incorporated ions and are therefore related to the mechanism of mass transport in the films. In the case of Ru(bpy)$_3^{2+}$, it was previously shown that both physical diffusion and electron self-exchange contribute to charge propagation. However, the apparent diffusion coefficient was found to be concentration-independent,[9] unlike what is expected from the Dahms-Ruff equation. This was suggested by White et al., to be due to inhomogeneous distribution of the complex among the different phases of Nafion,[6] as discussed in the introductory paragraphs.

We assume that the higher rates of loading and unloading observed with films deposited from Nafion solutions of higher water content are due to the more open structure of these films. This is caused by a different organization of the side chains, resulting from higher solvation of the sulfonic groups by water molecules and/or due to longer evaporation times of the more water-rich mixtures. Thus, in the more open films the ionic clusters might be larger and the interconnecting channels might be wider, which would enhance both physical diffusion and hopping diffusion.[16]

More information on the partitioning of Ru(bpy)$_3^{2+}$ in the film is obtained from the unloading measurements. First, although the affinity of Nafion to "hydrophobic" cations was reported to be high,[17] the unloading experiments exhibit a rapid drop of the peak currents right at the beginning. Second, in spite of the strong dependence of the unloading rates on the water content in the deposition solution (Fig. 4), the final peak currents for the different films are rather close, i.e., between 0.4-0.45 of the initial current in the fully loaded films.

These observations strongly suggest the existence of two types of incorporated Ru(bpy)$_3^{2+}$ in the polymer: a fraction of the ions which is strongly bound to the sulfonic groups by ion pairing, and another which is bound by weak electrostatic or hydrophobic interactions and is more free to undergo physical diffusion. The latter form of incorporated complex is the one which undergoes unloading, i.e., is rapidly lost from the polymer upon transferring the coated electrodes to pure electrolyte solution. The strongly bound complex remains in the film even after hours in background solution, and charge transport among these ions is assumed to proceed mainly via electron hopping.

Additional support for the suggested model of two types of bound complex ions is obtained from the ratios of the voltammetric peak currents and of the coulometric measurement, taken after full loading and after prolonged unloading of Ru(bpy)$_3^{2+}$ in a Nafion film (Fig. 9). Hence, the peak current for a film prepared from a 50:50 Nafion solution, recorded after 1.5 h of unloading, is 27% of the peak current at full loading, while the coulometric value after
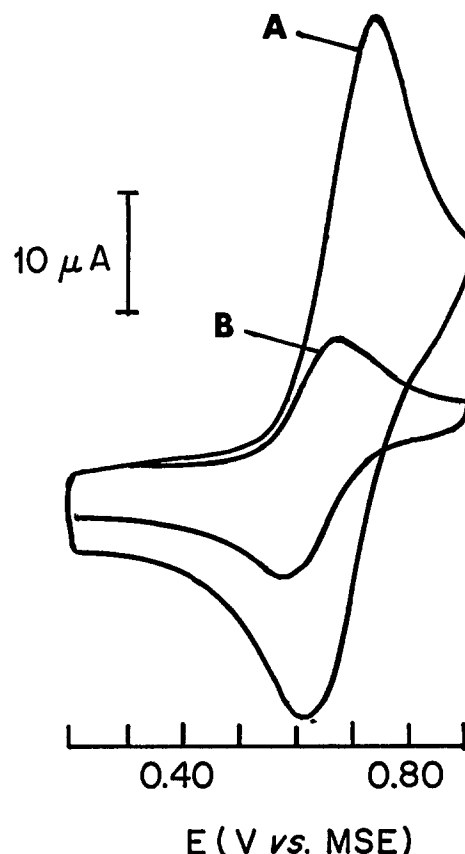

Fig. 9. Cyclic voltammograms for Pt/Nafion, Ru(bpy)$_3^{2+}$ followed by coulometric measurements: (A) at full loading, $q = 59$ μC; (B) after prolonged unloading, $q = 37$ μC.

unloading is much higher, i.e., 63% of the initial value before unloading.

Such results allow the calculation of the diffusion coefficients of Ru(bpy)$_3^{2+}$ under full loading and prolonged unloading (Fig. 5). When the films are fully loaded, the contribution of physical diffusion to the apparent diffusion coefficient is significant, i.e., about 2.5 times larger than the contribution of electron hopping. Thus, the value of D_{app} for Ru(bpy)$_3^{2+}$ in highly loaded films is about 2×10^{-9} cm^2/s, which is about five times the value commonly reported for this complex in Nafion films. The reason that electron hopping is usually reported to be the dominant mechanism of transport[6,7] is evidently the rapid loss of the weakly bound complex ions, which occurs in pure electrolyte solutions before or during the measurements. Measuring of D_{app} in the loading solution enables the determination of the high values of D_{app} in fully loaded films.

The above conclusion can be also supported by a simple calculation, using the Einstein-Smoluchowski equation for the diffusion length[18]

$$X = (2Dt)^{1/2} \qquad [3]$$

Assuming, for the sake of the calculation, that all incorporated complex ions diffuse physically with a diffusion coefficient of 4×10^{-10} cm^2/s, then the time required for nearly complete unloading of the complex from a film of 1.3 μm would be ~20 s. The experimental results are quite different, i.e., a large fraction of the complex ions remains in the film after hours of unloading conditions, clearly indicating that the diffusion mechanism for these ions is electron self-exchange.

Conclusions

1. The structure of recast Nafion films is affected by the composition of the deposition solution. Films cast from solutions that contain a larger fraction of water acquire a more open structure, in which physical diffusion is faster.

2. The complex ion Ru(bpy)$_3^{2+}$ is exchanged into Nafion films upon forming two types of sites: (*i*) ions bound by strong pairing with the sulfonic groups, for which the transport mechanism is primarily electron hopping, and (*ii*) ions bound by weak electrostatic and hydrophobic interactions, which allow physical diffusion of the ions in the polymer.

3. The majority of complex ions in the film are of the first kind, *i.e.*, strongly bound. However, most of the current in highly loaded films is carried by physical diffusion of the complex in the film, for which the diffusion coefficients are much higher.

4. Incorporation of large ions of hydrophobic nature [such as Ru(bpy)$_3^{2+}$] results in changes in the microstructure of Nafion *i.e.*, rearrangement of the phases.

5. Thermal treatment, at temperatures above the glass transition, renders the films insoluble in organic solvents, and considerably less permeable to ions. Soaking of annealed films in a mixture of acetonitrile/water "re-opens" the films for ionic permeation while maintaining their insolubility in organic solvents.

REFERENCES

1. I. Rubinstein, in *Applied Polymer Analysis and Characterization*, Vol. II, J. Mitchell, Jr., Editor, p. 236, Hanser, Munich (1991).
2. H. L. Yeager and A. Steck, *This Journal*, **128**, 1880 (1981).
3. F. C. Anson, D. N. Blauch, J.-M. Savéant, and C.-F. Shu, *J. Am. Chem. Soc.*, **113**, 1922 (1991).
4. I. Ruff and V. J. Friedrich, *J. Phys. Chem.*, **75**, 3297 (1971).
5. H. Dahms, *ibid.*, **72**, 362 (1968).
6. H. S. White, J. Leddy, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 4811 (1982).
7. D. A. Buttry and F. C. Anson, *ibid.*, **105**, 685 (1983).
8. J. Facci and R. W. Murray, *J. Phys. Chem.*, **85**, 2870 (1981).
9. C. R. Martin, I. Rubinstein, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 4817 (1982).
10. R. B. Moore and C. R. Martin, *Macromolecules*, **21**, 1334 (1988).
11. G. Gebel, P. Aldebert, and M. Pinery, *ibid.*, **20**, 1425 (1987).
12. K. A. Striebel, G. G. Scherer, and O. Haas, *J. Electroanal. Chem.*, **304**, 289 (1991).
13. C. R. Martin and K. A. Dollard, *ibid.*, **159**, 127 (1983).
14. A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 218, Wiley, New York (1980).
15. S. C. Yeo and A. Eisenberg, *J. App. Polym. Sci.*, **21**, 875 (1977).
16. I. Rubinstein, *J. Electroanal. Chem.*, **188**, 227 (1985).
17. M. N. Szentirmay and C.R. Martin, *Anal. Chem.*, **56**, 1989 (1984).
18. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Vol 1, p. 333, Plenum Press, New York (1977).

Corrosion Inhibition of Cobalt with a Thin Film of Cu-BTA

V. Brusic,* G. S. Frankel,* A. G. Schrott and T. A. Petersen

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

B. M. Rush

Department of Chemical Engineering, University of California, Berkeley, Berkeley, California 94720

ABSTRACT

Electrochemical techniques, ellipsometry and x-ray photoelectron spectroscopy were used to evaluate the use of benzotriazole, alone or in combination with boric acid/borate buffer and dilute copper sulfate for the protection of cobalt. The data indicate that in slightly alkaline solutions benzotriazole is a strong inhibitor for cobalt corrosion, whereas in water and neutral solutions it produces a barely measurable effect. In the presence of benzotriazole and Cu^{+2} ions, spontaneous reduction of copper ions leads to the formation of a thin film of Cu-BTA on the cobalt surface. This film acts as a corrosion protector that is better than benzotriazole, with a significant reduction of the corrosion rate even during subsequent exposure to solutions without inhibitors.

Corrosion is a spontaneous process and a ubiquitous problem for all but a few noble metals and metals that form a passivating oxide layer. Cobalt does not belong to either of these two groups. It is less noble than some other magnetic metals, such as nickel, and cobalt oxide is less passivating than nickel oxide on Ni. Due to their magnetic properties, Co and its alloys are widely used in thin film magnetic disks and heads. These thin film structures are particularly sensitive to corrosion loss, both during fabrication and in the field.

For magnetic recording applications, any passivation scheme that degrades the magnetic properties of the Co alloy is not viable. Alloying with metals such as Cr, thermal oxidation and application of conversion layers are all problematic. Corrosion could be reduced in a fabrication step during which Co or a Co alloy is in contact with a process solution by the use of inhibitors. However, many of the recommended corrosion inhibitors for Co offer only limited protection *in situ*, and even less once the part is removed from the solution containing the inhibitor.

Copper is more noble than cobalt, and copper oxides, like cobalt oxide, are marginal surface passivators. Much of the usefulness of Cu results from the very successful inhibiting action of benzotriazole (1 H-BTA to be referred to here simply as BTA) and its derivatives.[1] This compound reacts with Cu to form a Cu-BTA surface film, which, depending on the details of preparation, might be only 2 nm thick but very protective. Once formed, the film reduces the corrosion rate of Cu in water (with or without BTA) by more than two orders of magnitude.[2] This work describes the use of BTA, alone or in combination with other compounds such as boric acid/borate buffer and dilute CuSO$_4$, for the protection of cobalt. The intention of the work is to evaluate if the spontaneous reduction of Cu^{+2} ions could lead to the formation of Cu(I)-BTA on Co. In order to be practical, the overall protection scheme should be such that the inhibiting solution itself is not aggressive and the treatment results in some lasting protection.

Experimental

The samples were 150 nm thick sputter-deposited films of cobalt. The corrosion inhibiting electrolytes were pre-