Composite Membranes for Fuel-Cell Applications

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One of the major obstacles to overcome for the realization of economical hydrogen-oxygen, polymer-electrolyte fuel cells is the high capital cost of the inert perfluorosulfonic acid (PSA) membranes, which provide a pathway for ionic transport between the cell electrodes. It has recently been shown that composite polymer membranes can be synthesized by depositing PSA polymers onto porous poly(tetrafluoroethyene) (PTFE) substrates. The resulting membranes are mechanically durable and quite thin relative to traditional PSA membranes; we expect the composite membranes to be of low resistance and cost. In this experimental study, we examine the composite membrane properties as a function of the membrane composition. Our results allow us to form a conceptual model to explain both the equilibrium and transport characteristics of these materials. For high PSA contents, the membrane behavior is similar to that of the PSA polymer; the water permeability, however, is reduced significantly. For intermediate PSA contents, the membranes have a high porosity and match the thickness of the PTFE substrate (≈ 50 μm); membranes of this composition range are potentially useful candidates for fuel cells because of their high resistance to water transport and reduced ionic resistance. Composite membranes of very low PSA content demonstrate characteristics similar to the hydrophobic PTFE substrate and are not of interest for fuel cells.

Introduction

While it is generally accepted that hydrogen-oxygen membrane fuel cells present an attractive alternative to traditional power sources, the cost of the cell components precludes their immediate implementation for most stationary and vehicular applications. A primary contributor to the membrane fuel cell's high cost is the perfluorosulfonic acid (PSA) membrane (Ticianelli et al., 1988; Verbrugge and Hill, 1990). In this work, we investigate composite ion-exchange membranes made from poly(tetrafluoroethyene) (PTFE) and PSA polymers (Penner and Martin, 1985). From a cost perspective, it is important to note that the composite PTFE/PSA membranes contain much less of the expensive PSA polymer than traditional PSA membranes such as Nafion 117 of E. I. du Pont de Nemours and Co.

To form the composite PTFE/PSA membranes, it is necessary to deposit PSA polymers from solution; Rubinstein and Bard (1980) published on the successful deposition of PSA polymers onto a relatively inert substrate (graphite in their study). Subsequent investigations have shown that it is possible to deposit PSA films on a variety of substrates. [See, for example, Moran and Majda (1986).] Alcohol-PSA solutions are used typically for film deposition; the dissolution of PSA polymers in alcohol solutions at elevated temperatures and pressures has been studied by a number of researchers. [See, for example, Martin et al. (1982).] It is noted frequently that deposited PSA films do not retain the durable mechanical and chemical strength of the original PSA membrane. In recent work, Moore and Martin (1986) reported that deposition of PSA films from aprotic solvents at elevated temperatures produced membranes of superior quality relative to the traditional, low-temperature cast films; experiments in our laboratory and elsewhere have confirmed these findings. In this study, we employ the high-temperature deposition technique to form composite PTFE/PSA membranes.

Experimental Studies

Composite membranes were made using 0.2-μm pore size

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PTFE films (GORE-TEX of W. L. Gore and Associates, Inc.) and PSA polymer solutions. The void volume of the PTFE films was approximately 80%. The PSA solution (Solution Technology, Inc.) contained Nafion polymer obtained from solubilizing PSA films with 1.1 mols of sulfonate sites for every gram of dry polymer in an alcohol solution.

PTFE disks of 1.5-cm diameter were cut from Gore-tex sheets with a cork borer. These disks were cleaned by refluxing in concentrated nitric acid and then in 30% hydrogen peroxide. After two 1-hour refluxes in microfiltered, distilled, deionized water, each disk was placed in a vial containing 6-mL ethyl alcohol, 2-mL dimethyl sulfoxide, 1-mL tetrahydrofuran, and 1-mL dimethylformamide. These chemicals were all Baker Analyzed Reagent Grade. Differing amounts of the PSA solution were added to each vial. (The amounts correspond to the abscissa values of the data points shown in Figure 1). The solutions were evaporated from the vials at 160°C for 5 hours. It should be noted that the PTFE disks stay intact throughout the process; they do not dissolve at any time during the formation of the composite membrane.

The resulting composite films were cleaned by alternate refluxing in water and ethyl alcohol solutions; subsequently, they were refluxed in the 1M sulfuric acid solution that was used for the characterization tests. The transport experiments utilized a cell comprising two reservoirs separated by the composite membrane to be tested. A schematic illustration of the cell at the beginning of the radiotracer transport experiments can be represented as:

Cold Reservoir	Membrane	Hot Reservoir
H^+	H^+	H^+
HSO_4^-	HSO_4^-	HSO_4^-
		$(^3H)OH$
		$H(^{35}S)O_4^-$
	$\leftarrow \Delta\Phi \rightarrow$	
	$\leftarrow i$	
	$\leftarrow v$	

A more complete drawing of the cell can be found in the article by Verbrugge and Hill (1990). The voltage drop across the membrane is represented by $\Delta\Phi$, the current is given by i, and the pore fluid's velocity by v. (For theoretical treatments of electro-osmotic convection, which is responsible for the convective processes in this study, see Verbrugge and Hill, 1990, or Guzmán-Garcia et al., 1990, and references cited therein.) In all of the current-passage experiments, current flow was from the hot reservoir to the cold reservoir (in the same direction as the diffusion of the radiotracer species). Both the hot- and cold-side reservoirs contained 50 mL of acid solution. At the anode in the hot side, water is converted to oxygen and protons ($H_2O \rightarrow 2H^+ + 2e^- + 1/2O_2$), and at the cathode in the cold side, protons were reduced to hydrogen ($2H^+ + 2e^- \rightarrow H_2$). The hot side contained initially $\approx 8\ \mu$ Ci/mL each of tritium and sulfur-35. Aliquots of 10 μL were withdrawn periodically from the cold side to determine the rate of tritiated water $(^3H)OH$ and tagged bisulfate anions $H(^{35}S)O_4^-$ transporting across the membrane. All radiotracers were received from New England Nuclear. For the radiotracer counting done in this work, a Packard Trib-Carb 2200CA liquid-scintillation spectrometer was used; the system contained a multichannel analyzer allowing display and analysis of the energy spectra for the radionuclides' β decay.

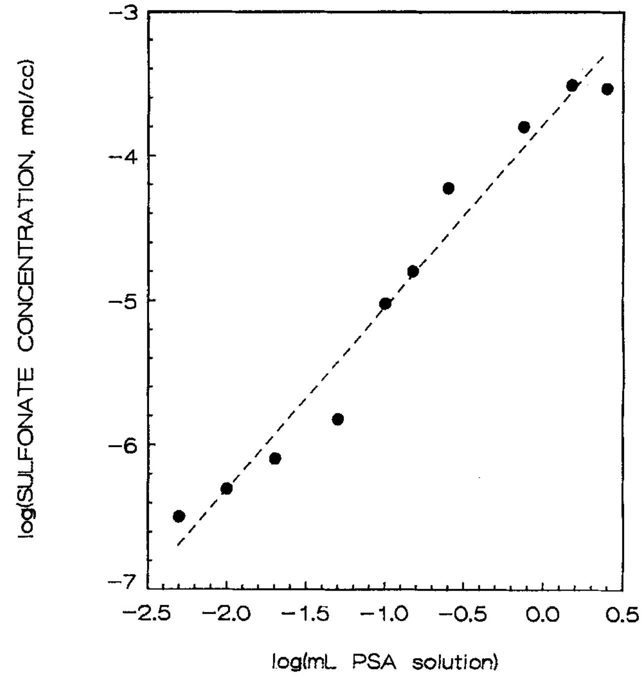

Figure 1. Sulfonate contents of the composite membranes.

The deposition solutions contained 6 mL of ethyl alcohol, 2 mL of dimethyl sulfoxide, 1 mL of tetrahydrofuran, 1 mL of dimethylformamide, and the PSA solution volumes corresponding to the abscissa values of this figure.

Resistance measurements employed a geometry similar to the schematic above. Capillary ports placed near the membrane housed reference electrodes (mercury-mercurous sulfate), and working electrodes placed within the well-stirred reservoirs were used to pass current across the membrane. A Princeton Applied Research Model 273 Potentiostat/Galvanostat controlled the cell current. The potential drop between the reference electrodes was measured and recorded with a Nicolet 4094A storage oscilloscope. The membrane resistance was taken to correspond to the measured potential difference between the reference electrodes with the membrane in place less the same measurement made with the membrane removed from the cell.

The equilibrium uptake measurements to determine water and acid absorption by the membranes began by equilibrating the cleaned membrane under study with a tagged 1M acid solution similar in tracer concentrations to that of the hot-side reservoir concentrations of the transport experiments. To remove surface moisture, the membranes were blotted with filter paper. The imbibed membranes were placed in counting vials containing 15 mL of liquid scintillation solution (Insta-Gel, Packard Instruments).

To determine the sulfonate concentration of the composite membranes, the cleaned membranes were equilibrated with purified water after they had been treated with sulfuric acid; these membranes were consequently in their H^+ form: that is, the membrane pores contained only H^+ and H_2O mobile species. Tritiated water was then placed in the vial containing the membrane and H_2O; the vial was placed subsequently in a vacuum oven to evaporate the free water and $(^3H)OH$. Upon drying, the sulfonate sites had associated with them H^+ and $^3H^+$. The dried membrane was placed in 15 mL of counting solution; the resulting count data were then used to determine the sulfonate concentration, as the ratio of $^3H^+/H^+$ was initially measured and constant. (We do not attempt to account for any chemical differences introduced by the added two neutrons in the tritium relative to hydrogen. Treating the isotopes as chemically identical is well within the error bounds of the present analysis.)

Results and Discussion

The most important characteristic of the composite membranes is the fixed charge concentration (sulfonate ion concentration). We shall ultimately use the membrane sulfonate concentration as the independent variable in our analyses. (That is, we shall plot our experimental measurements against the sulfonate concentration.) As will be made clear in the analysis to follow, the membranes with low PSA contents and correspondingly low sulfonate contents are the most promising membranes from a fuel-cell point of view. It is unfortunately the case that the measurement of the sulfonate concentration represents a difficult problem. The weight change for small PSA contents is not easily measured by standard laboratory analytical balances. The radiotracer method outlined in the Experimental Section appeared to yield sufficient accuracy for our purposes. The data shown in Figure 1 indicate that, as expected, lower PSA concentrations in the reaction vial yield lower sulfonate concentrations within the membrane. Plotted is the logarithm of the sulfonate concentration based on the total wet membrane volume (imbibed with 1M H_2SO_4) vs. the milliliters of PSA solution added to the solution used to form the composite membrane. The corresponding sulfonate content of Nafion 117, the PSA membrane used to form the PSA solution, is 1.2×10^{-3} mol/cm^3 (Verbrugge and Hill, 1990); this corresponds to an ordinate value of -3 in Figure 1. Thus, in this work, polymers ranging from essentially that of pure Nafion to nearly pure Gore-tex, as judged by the sulfonate content, were prepared.

Shown in Figure 2 are the water and acid partition coefficients for the composite membranes. Throughout this work, we compare our data to analogous results for equilibrium and transport data of the Nafion 117, 1M sulfuric acid system (Verbrugge and Hill, 1990). The water partition coefficient represents the concentration of water within the membrane (based on the total membrane wet volume) divided by the concentration of water in the 1M acid. Since excess surface moisture is removed by blotting the membrane surfaces with filter paper, and the area to volume ratio is much larger for the low-sulfonate-concentration membranes, the error in the partition coefficient measurements is larger for small abscissa values in Figure 2. The general trends observed in Figure 2 do reflect what we expect from these materials. Large PSA contents yield membranes similar in uptake properties to those of Nafion 117. As the PSA content is reduced, more $H(^{35}S)O_4^-$ anions are allowed into the membranes, since they have both a larger porosity and a reduced anion-repulsive, fixed-charge concentration. The explanation we provide is based on the concept that the porous PTFE acts as a support, and that the PSA polymer coats the PTFE support. Relative to the high PSA content membranes, the intermediate PSA content membranes, we speculate, have nearly identical PTFE support structures: that is, the porous PTFE support does not change significantly in physical dimension. Hence, the PSA polymer coating of the PTFE gives the membrane its hydrophilic character. Consequently, lower PSA contents yield larger membrane pores (with hydrophilic pore walls). For very low PSA contents, the membranes begin to take on more of the characteristics of hydrophobic PTFE; consequently, $(^3H)OH$ concentrations are reduced as are those of $H(^{35}S)O_4^-$.

The above-cited trend is also apparent in the resistance measurements of Figure 3. Shown in this figure is the measured

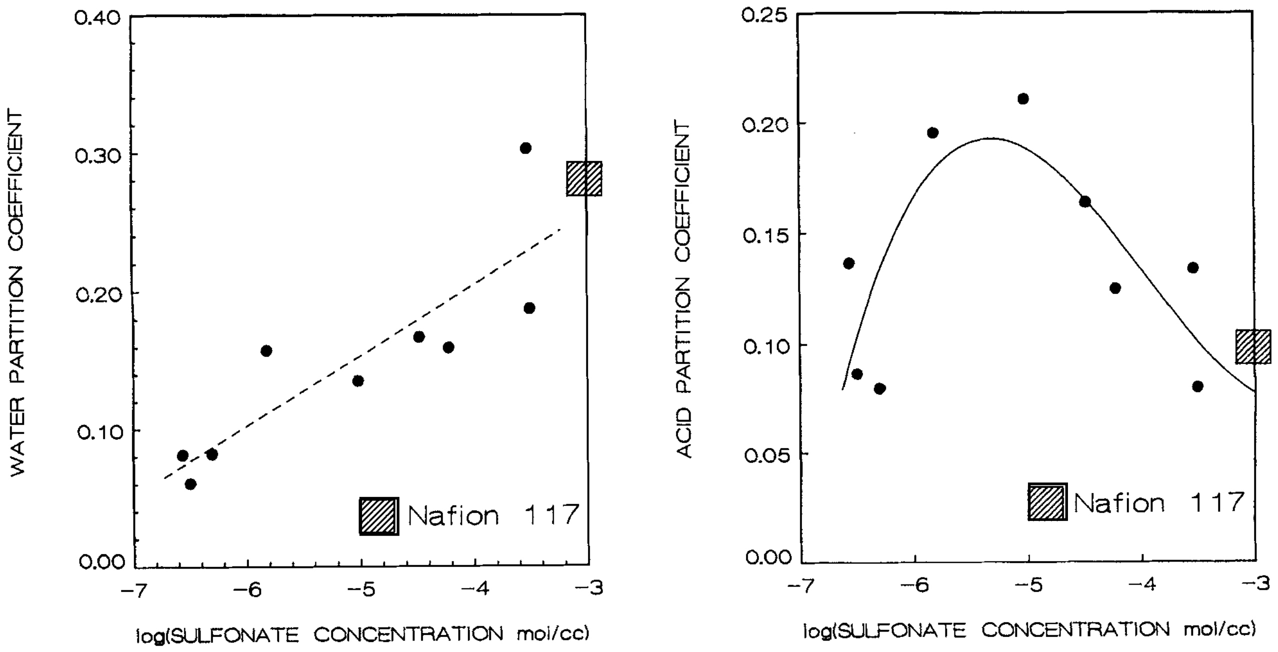

Figure 2. Partition coefficients: water (left panel) and acid (right panel).

The hatched box corresponds to values for Nafion 117.

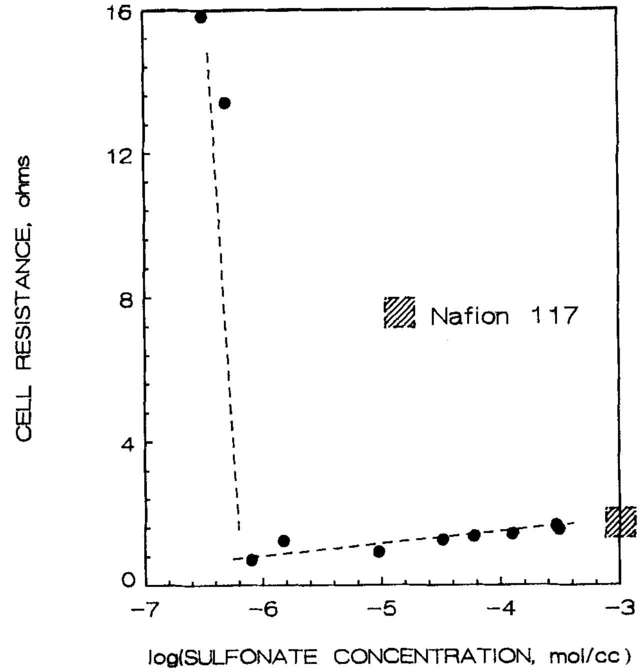

Figure 3. Cell resistance measurements.

The hatched box corresponds to values for Nafion 117.

resistance between the reference electrodes adjacent to the membrane surface as a function of the membrane sulfonate ion content. It is clear that the larger sulfonate contents approach resistance behavior similar to Nafion 117, which is in agreement with the uptake data of Figure 2. Very small sulfonate contents lead to large measured resistances, as the membrane begins to reflect the properties of hydrophobic PTFE, which is an ionic insulator relative to Nafion 117. The intermediate sulfonate contents yield lower resistances, since they are quite thin and porous relative to the higher PSA content membranes.

For log(sulfonate concentration, mol/cm^3) below about -4.5, we cannot obtain accurate values for the membrane resistance using this electrochemical technique, as the membrane resistance is only a small fraction of the measured cell resistance. This is a general problem faced by fuel-cell membrane researchers as more conductive, thinner membranes become available. The ideal fuel-cell membrane would have a very high fixed (anion) charge concentration and would be very thin; such a membrane would yield a high proton concentration in a fuel cell, which in turn would yield a high membrane conductivity. Obviously, thinner membranes, all other physical properties taken constant, yield lower resistances. Radiotracer techniques are limited, since one cannot tag the proton species in the presence of water—most of the tagged hydrogen isotope exchanges onto more abundant water molecules and sensitivity to proton transport rates is lost. An approach that we plan to follow in the future in this laboratory is to use tritium to tag the water, another suitable anion tracer such as sulfur-35 or chlorine-36, and sodium-22 as the mobile cation. While this approach does not yield directly the proton diffusion coefficient, it does allow for the measurement of the

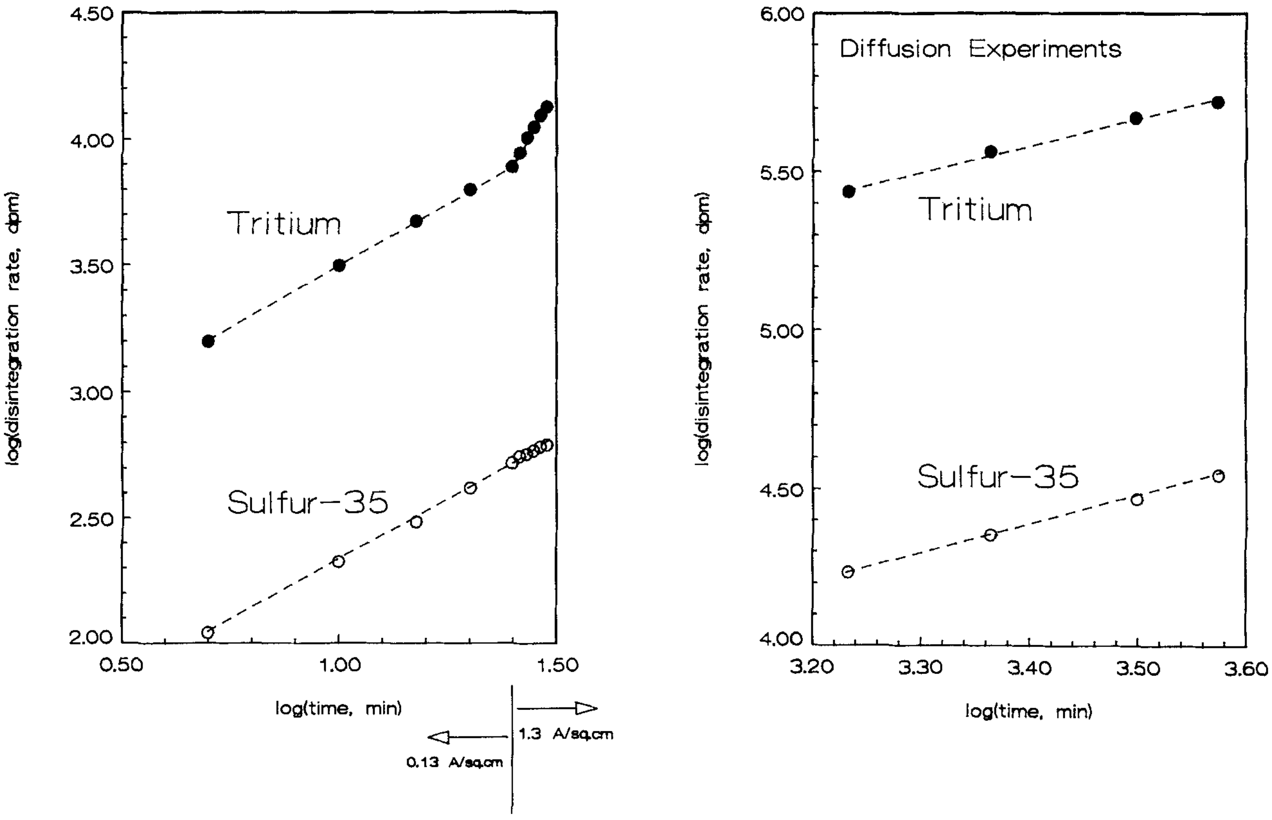

Figure 4. Radiotracer results for the transport experiments.

For these data, log(sulfonate concentration, mol/cm^3) = -4.2. For the first 25 minutes, the current was maintained at 0.1 A (0.13 A/cm^2); 1.3 A/cm^2 were used for the next five minutes. The diffusion experiments (right panel) were run after the current-passage experiments.

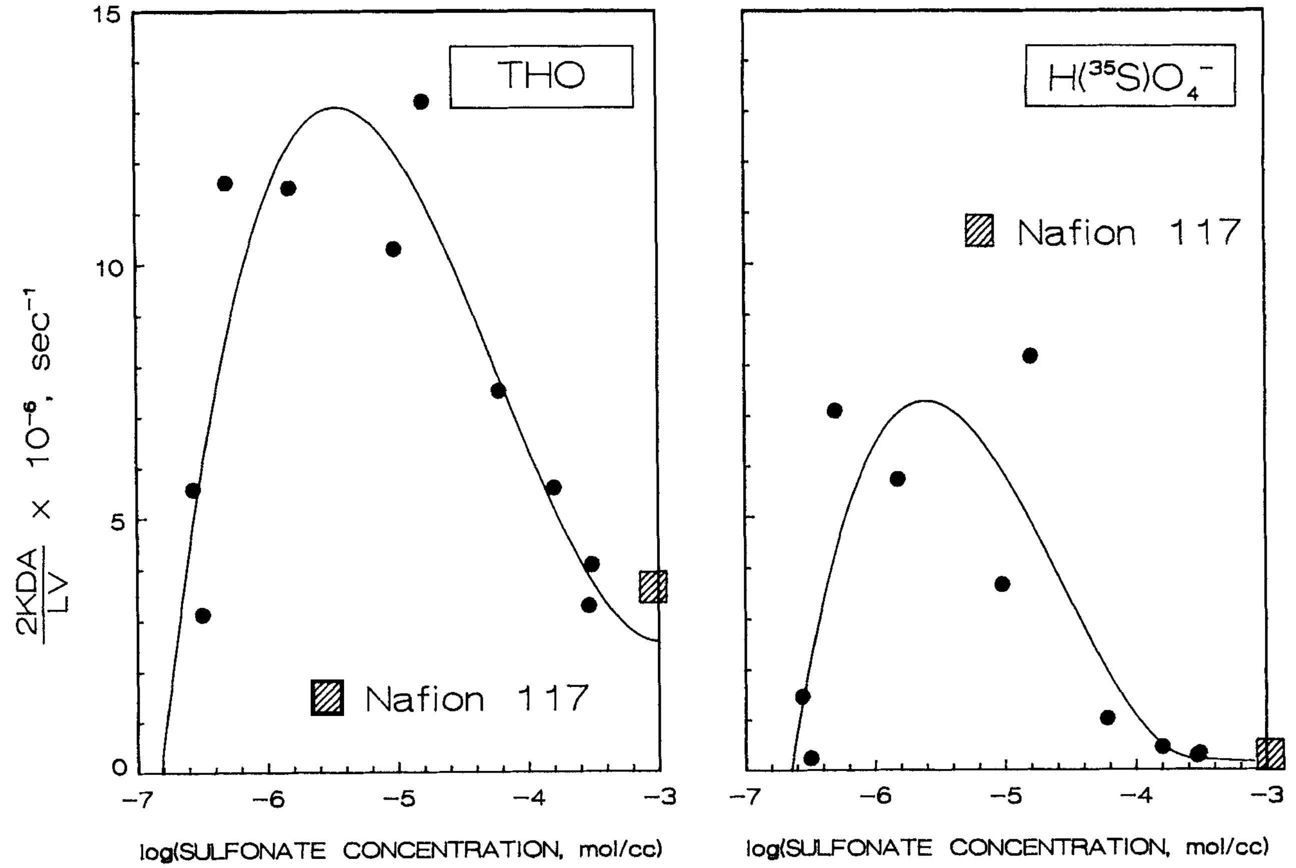

Figure 5. Diffusion results: (^{3}H)OH data (left panel) and $H(^{35}S)O_4^-$ data (right panel).

The hatched box corresponds to values for Nafion 117. The quantity $2\,KDA/(LV)$ is a constant; K is the partition coefficient; D is the diffusion coefficient; A is the superficial area of the membrane normal to the direction of transport; L is the membrane thickness; and V denotes the volume of the reservoirs.

$^{22}Na^+$ diffusion coefficient and the consequent measurement of the membrane tortuosity associated with a cation species. (The anion transport rates are useful for the determination of membrane properties, although anions are typically not present in SPE fuel cells.)

Shown in Figure 4 are data characteristic of the radiotracer transport analyses. For the data of this plot, the logarithm of the sulfonate concentration was −4.2. The current-passage experiments were run before the diffusion experiment. For the first 25 minutes, a 130 mA/cm^2 current source was used, and aliquots were withdrawn every 5 minutes. During the last 5 minutes, the current was maintained at 1,300 mA/cm^2, and aliquots were taken every minute. After the current-passage tests, the diffusion experiments were initiated; aliquots were taken every 4 hours. The reproducibility of the transport results for a given membrane was excellent; however, significant spread is seen in the transport characteristics as a function of the PSA content.

Diffusion results for (^{3}H)OH and $H(^{35}S)O_4^-$ are displayed in Figure 5. For these self-diffusion experiments, the following long-time relationship applies:

$$\ln \frac{(c_i^{COLD} - c_i^{HOT})|_{\text{initial}}}{c_i^{COLD} - c_i^{HOT}} = \frac{2K_iD_iA}{LV}\, t,$$

where

i = (^{3}H)OH or $H(^{35}S)O_4^-$
c = concentration
HOT, $COLD$ = reservoir
K = partition coefficient
D = diffusion coefficient
A = superficial area of the membrane normal to the direction of transport
L = membrane thickness
V = reservoir volumes
t = time

For each membrane, the diffusion results analogous to those of Figure 4 (right panel) were used to calculate $2\,KDA/(LV)$; for all of the membranes, a linear relationship between the logarithmic concentration term and time was obtained. The flux N_i of each tracer i is given by:

$$N_i = \frac{K_iD_i}{L}\,(c_i^{HOT} - c_i^{COLD}).$$

We do not attempt to further treat the quantity $2\,KDA/(LV)$, since we can immediately compare this grouping with Nafion 117 (which is sufficient for the present purpose) and it is very difficult to get precise measurements of the membrane thicknesses for the thinner membranes. As observed in the acid partition coefficient and the resistance measurements, the species fluxes for the thicker membranes are similar to those for Nafion 117. Intermediate PSA contents lead to more facile diffusion of (^{3}H)OH and $H(^{35}S)O_4^-$ because of the reduced composite membrane thickness and the increased porosity.

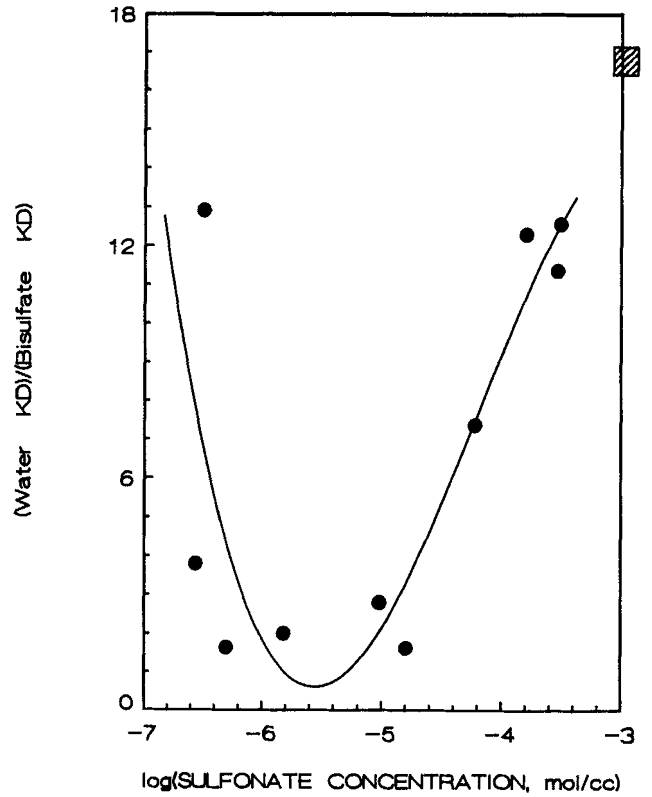

Figure 6. Ratio of *KD* for (^{3}H)OH relative to *KD* for H(^{35}S)O$_4^-$.

The species fluxes were constant over the course of the experiment and are proportional to *KD*. The hatched box corresponds to values for Nafion 117.

Similar trends in transport within composite membranes containing a high PSA polymer content as the hydrophilic component have been reported by Moran and Majda (1986) and by Liu and Martin (1990). Very low PSA contents yield more of the PTFE character, resulting in reduced transport rates.

The significance of Figure 5 can be clarified by a similar interpretation of the data shown in Figure 6. Plotted on the abscissa is $K_{H_2O}D_{H_2O}/(K_{HSO_4^-}D_{HSO_4^-})$, and the ordinate gives the sulfonate content. For large PSA contents, Nafion-like behavior is observed. (The hatched box in Figure 6 corresponds to Nafion 117). For intermediate PSA contents, the composite membranes are not very ion-selective, and the ratio $K_{H_2O}D_{H_2O}/(K_{HSO_4^-}D_{HSO_4^-})$ nears order unity. Since the membranes are porous under these conditions of intermediate PSA content, it is probable that both the water and co-ion partition coefficients are nearly equal to the membrane porosity and that the ratio of $K_{H_2O}D_{H_2O}/(K_{HSO_4^-}D_{HSO_4^-})$ is nearly constant and of order unity since $D_{H_2O}/D_{HSO_4^-}$ is of order unity. For very low PSA contents, the membrane changes significantly as it takes on more of the characteristics of PTFE and the membrane selectivity increases relative to the intermediate PSA-content membranes (that is, co-ion transport is reduced relative to water transport). It should be noted that the low PSA content membrane may be useful in processes where ohmic drop is unimportant and very high selectivity is required, for example, dialysis devices.

The (^{3}H)OH and H(^{35}S)O$_4^-$ fluxes during current passage are given in Figure 7. Initial inspection of the data indicates a strong analogy with those of Figure 5; it is important to note, however, that although the same trend with sulfonate content is observed in Figures 5 and 7, the composite materials appear

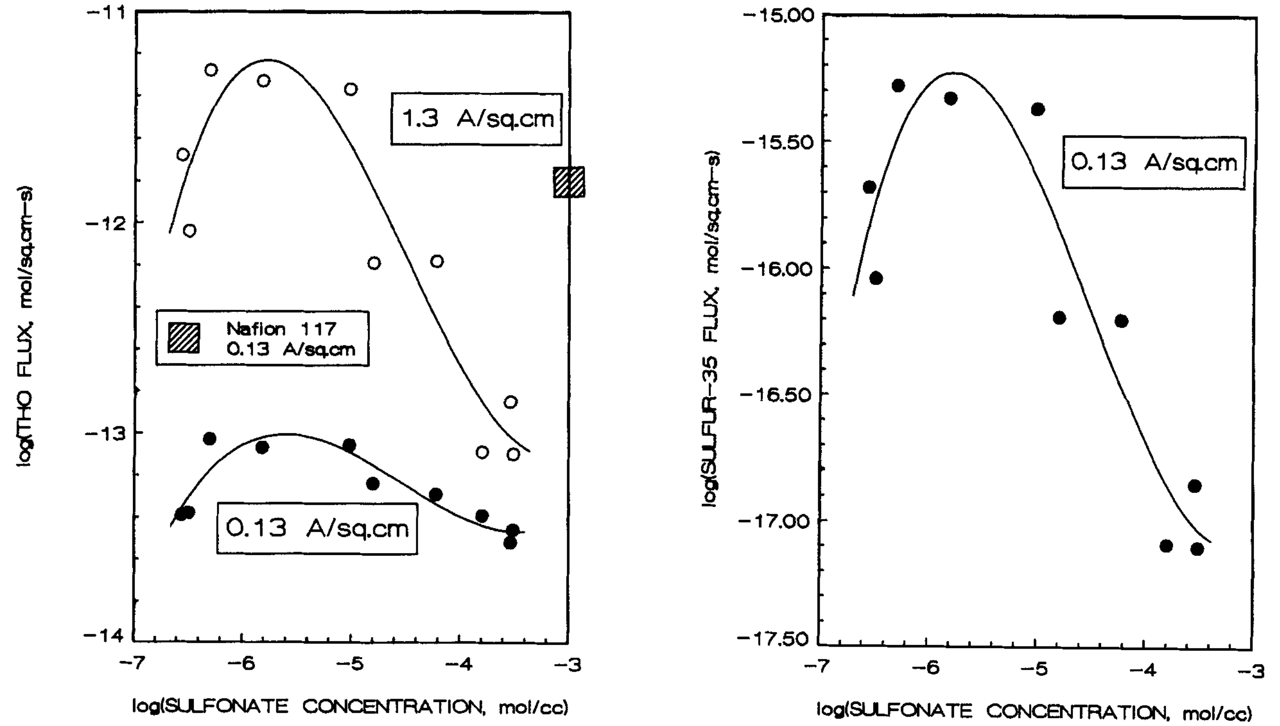

Figure 7. Current-passage results.

The hatched box corresponds to values for Nafion 117 at 0.13 A/cm^2.

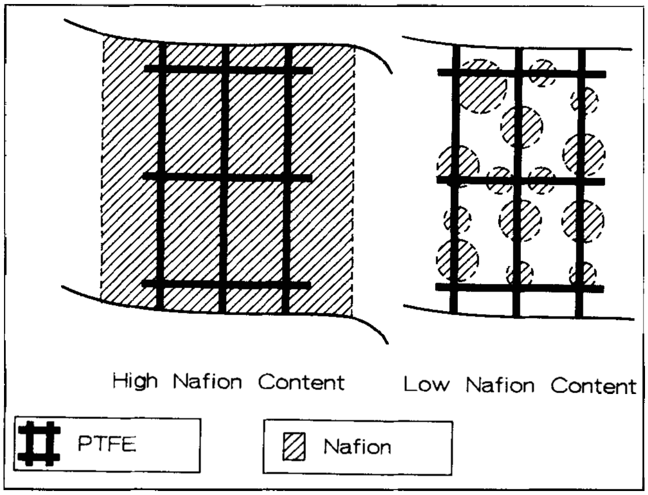

Figure 8. Cross-section of the composite membrane.

The thickness of the PTFE support remains nearly constant and is equal to about 50 μm. The thickest composite membrane was 200 μm.

to have a much lower membrane permeability than Nafion 117. Up to this point, we have shown that composite membranes with high PSA content tend to perform similar to Nafion 117. It is clear from an analysis of Figure 7, however, that although the equilibrium and diffusion characteristics for the high-PSA-content membranes are similar to Nafion 117, the current-passage characteristics are not. Apparently, the backbone PTFE matrix onto which the PSA material is deposited tends to retard convection through the composite material. The effect of surfaces on water viscosity, which is especially apparent in pores of small breadth, is an active area of research, and a quantitative treatment has not been achieved (Lyklema and Overbeek, 1961; Anderson and Quinn, 1972; Babchin et al., 1976; Eisenberg and Yeager, 1982; and Guzmán-Garcia et al., 1990). It is usually thought that reduced water mobility in fuel-cell membranes is a benefit relative to facile water transport, as the "bound" (immobile) water will keep the membrane hydrated and consequently maintain ionic conductivity. The interpretation of the right panel in Figure 7 is not as straightforward; while diffusion of $H(^{35}S)O_4^-$ is in the direction of current passage, the migration component of $H(^{35}S)O_4^-$ transport is from the COLD to the HOT side. For the $(^3H)OH$ species, diffusion and convection are the only two modes of $(^3H)OH$ transport, and the analysis is less ambiguous. It is clear from a comparison of the panels in Figure 7 that the $H(^{35}S)O_4^-$ flux is much smaller than that of $(^3H)OH$.

Figure 8 shows how we view the composite membranes; despite its simplification, it can be used to explain our results. For high PSA contents, it appears that the membrane maintains equilibrium and diffusion characteristics similar to Nafion 117. As lower PSA (Nafion 117) contents are utilized, the membrane thickness eventually reaches that of the PTFE (Gore-tex) support. From a fuel-cell membrane perspective, the optimal geometry corresponds to the point at which the membrane thickness is essentially determined by the Gore-tex, and all of the Nafion is anchored inside the film. As indicated in the analysis of Figure 3, we do not have enough sensitivity in the polarization measurements to get a $^3H^+$ diffusion coefficient; however, we can place what is probably an upper bound on the composite membrane performance. For composite membranes with log(sulfonate concentration, mol/cm^3) < -5, the thickness is essentially invariant and ≈ 50 μm; thus, the membrane corresponding to a logarithm concentration term of -5 is probably the most promising fuel-cell membrane. In the absence of electro-osmotic effects, the sheet resistance R_{sheet} can be expressed as (Verbrugge and Hill, 1990):

$$R_{\text{sheet}} = \frac{\Delta\Phi}{i},$$

$$\approx \frac{L}{\kappa},$$

$$\approx \frac{L}{D_{H^+} c_{SO_3^-} F^2/(RT)}.$$

For $L = 0.005$ cm, $D_{H^+} = 9 \times 10^{-5}$ cm^2/s, $c_{SO_3^-} = 1 \times 10^{-5}$ mol/cm^3 and $T = 298$/K, we obtain a sheet resistance of 1.47 ohm·cm^2. (For a cell operating at 100 mA/cm^2, 0.147 V of ohmic drop would be attributable to the membrane.) To find this upper bound on the membrane's performance, we have used a free-solution diffusion coefficient for H^+. A number of PSA membranes are known to have a lower sheet resistance than 1.47 ohm·cm^2 (Verbrugge and Hill, 1990). Although this abbreviated analysis indicates that the composite membranes may not be used in fuel cells because of their proton-resistance characteristics, one cannot dismiss this possibility entirely since it is not clear at this time just how much of the total fuel-cell resistance is due to ohmic drop. For instance, the modeling work of Bernardi and Verbrugge (1991) indicates that the membrane contributes less than 25% of the cell resistance below 0.5 A/cm^2. It may be that the lower cost of the composite membranes relative to the parent PSA membrane and the reduced water permeability could justify the use of composite PTFE/PSA polymers in hydrogen-oxygen membrane fuel cells.

Conclusions

For the composite PTFE/PSA membranes of this study, which were formed by deposition from a combination of aprotic solvents, we have provided a conceptual model that can be used to explain the equilibrium and transport characteristics of these materials. Our description is supported by both electrochemical and radiotracer data. For high PSA contents, the membrane behavior is similar to that of the PSA polymer, except that the water permeability is reduced significantly. For intermediate PSA contents, it appears that the membranes obtain a high porosity and match the thickness of the PTFE substrate (≈ 50 μm); in essence, membranes of intermediate PSA content can be viewed conceptually as highly porous glass frits covered with a surfactant that makes the resulting structure hydrophilic. (The glass frit corresponds to the PTFE substrate, and the PSA polymer corresponds to the surfactant). Composite membranes of very low PSA content demonstrate characteristics similar to the hydrophobic PTFE substrate.

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