Polymer-Zeolite Composite Membranes for Direct Methanol Fuel Cells

Brett Libby, W. H. Smyrl, and E. L. Cussler
Dept. of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455

Direct methanol fuel cells require membranes with the dual properties of high proton conductivity and low methanol crossover. Such membranes have a high selectivity, that is a high ratio of proton conductivity to methanol permeability. This research reports such a membrane made of polyvinylalcohol and loaded with mordenite, a proton conducting, methanol impermeable zeolite. Protons travel directly through both the polymer and zeolite phases, but methanol has a more tortuous path around the zeolite particles. The composite membranes show up to twenty times higher selectivity than Nafion, the current benchmark. The improved behavior, a result of the proper tailoring of the polymer and dispersion phase, is predicted using Maxwell's theory for diffusion in composite media.

Introduction

Fuel cells promise more power for less fuel than current thermal engines. This promise has caused a flurry of fuel cell research. Driven by a market that calls for reliable, inexpensive, and environmentally sound sources of energy, researchers are working to boost fuel cell efficiency and performance, while simultaneously reducing size, weight, and cost. Whereas fuel cells were once confined to expensive niche applications like the space program, fuel cells are now expected to broadly impact energy production.

Applications of fuel cells are currently focused in three areas: electric vehicles, stationary electricity generation, and portable electronic devices. The most well publicized fuel cell research efforts are electric vehicles. Concept cars shine at major auto shows, while fuel cell powered buses roam the streets of Vancouver and Chicago. General Motors, Ford, Daimler Chrysler, Honda, and Toyota are all planning production (Business Week, 2000). However, the high costs of current fuel cell powered automobiles will initially prevent their widespread use.

Electricity generation of stationary fuel cells appears more immediate. Over the next 20 years, the electric utilities will need to add about 10 trillion kilowatt-hours of new capacity worldwide (Business Week, 2000). Because of the deregulation of the utility industry, fuel cells are widely investigated as on-site generators of electricity for homes and buildings.

Portable electronic devices may also see widespread acceptance of fuel cells. Fuel cell technology can move into the evolving microelectronic market more easily than into other, more established industries (Libin, 2000). Polymer electrolyte membrane fuel cells are especially attractive as portable battery replacement (Jost, 2000). Such cells, which use a solid polymer membrane as the electrolyte, offer several advantages. The immobilized electrolyte and absence of corrosive liquids simplifies sealing and minimizes corrosion (Jacoby, 1999). The low operating temperatures allow for fast startups and immediate responses to changes in power demand. Most importantly, such compact cells can deliver higher power densities. This results in reduced weight, cost, and volume, along with improved performance.

A polymer electrolyte membrane fuel cell runs best on pure hydrogen as a fuel, so the cell produces only electricity and water. However, hydrogen is hard to store, whether as a compressed gas, as a cryogenic liquid, or in metal hydrides or carbon nanotubes (Appleby, 1999). As a result, many try to utilize hydrogen produced by steam reforming a fuel like methanol, followed by hydrogen separation using a palladium alloy membrane to remove carbon monoxide, which poisons the cell's platinum based electrode catalysts. Such processing dramatically increases the fuel cell's weight and complexity.

Correspondence concerning this article should be addressed to E. L. Cussler.

An alternative cell could directly use an organic fuel like methanol, rather than convert it to hydrogen. The oxidation potential of methanol ($E^o = 1.21V$) is comparable to that of hydrogen ($E^o = 1.23V$), and methanol has a 50% greater volumetric energy density (Dyer, 1999). However, the current membrane used in the cells, a perfluorosulfonic acid membrane like Dupont's Nafion, leaks methanol from the anode to cathode. This methanol crossover has two effects. First, the chemical energy of the methanol is lost when it crosses through the membrane, severely lowering the efficiency of fuel utilization (Ren et al., 1995). Second, the two simultaneous electrochemical reactions at the cathode compete directly for cathodic catalyst sites, reducing the overall cell efficiency. Methanol crossover currently limits direct methanol fuel cells to a 0.5−1.0 M methanol fuel feed. Increasing the methanol feed concentration could potentially increase methanol oxidation kinetics (Narayanan et al., 1996).

This article seeks a new polymer electrolyte membrane with lower methanol crossover. In the following sections, we discuss our target, describe our experiments, and report our results towards this goal.

Theory

The search for new membranes begins by establishing criteria for comparing candidates to the benchmark of Nafion. Transport of protons and methanol is described by the Nernst-Plank equations for the flux j_i

$$-j_i = D_i\left(\nabla c_i + z_i c_i F\frac{\nabla\Phi}{RT}\right) \tag{1}$$

where D_i is the diffusion coefficient, c_i is the concentration and z_i is the charge of species "i"; F is Faraday's constant, R is the gas constant, T is the temperature, and Φ is the electrostatic potential. For the conductance of protons (species "1"), z_1 is $(+1)$ and the concentration c_1 is a constant, so for a membrane of thickness l

$$-j_1 = \left(\frac{D_1 c_1 F}{RT}\right)\frac{\Delta\Phi}{l} \tag{2}$$

This result is more commonly written as a current density i

$$i = -Fj_1 = \sigma(\Delta\phi/l) \tag{3}$$

where the conductivity σ is given by

$$\sigma = D_1 c_1 F^2/RT \tag{4}$$

For methanol species ("2"), z_2 is zero and

$$j_2 = D_2 H_2 (c_{20} - 0)/l \tag{5}$$

where H_2 is a partition coefficient, the product D_2H_2 is the methanol permeability P, and $(c_{20} - 0)$ is the concentration difference of methanol across the membrane. This equation is exact for fuel cells only when electroosmosis does not contribute to the methanol flux.

We are interested in the selectivity of protons vs. methanol offered by different fuel cell membranes. For many membranes separations, selectivity is defined as the ratio of fluxes to driving forces (Ho and Sirkar, 1992)

$$\alpha = \frac{j_1/j_2}{\Delta c_1/\Delta c_2} \tag{6}$$

Because the driving forces for protons and methanol are different here, the selectivity β is better defined as (Pivovar et al., 1999)

$$\beta = \frac{i/j_2}{\Delta\Phi/\Delta c_2} \tag{7}$$

Substituting Eq. 3 and Eq. 5 into Eq. 7 yields

$$\beta = \frac{\sigma}{P} \tag{8}$$

where σ is the proton conductivity and P is the methanol permeability. Note that this new electrochemical selectivity is independent of membrane thickness, but does have units.

In this research, we seek a membrane with high selectivity β. In the past, this goal was taken to imply a high proton conductivity. However, while the current standard fuel cell membrane Nafion 117 has a very high conductivity, its selectivity is compromised due to high methanol permeability. If another membrane had higher selectivity, but lower conductivity, the membrane conductance could be kept large by making the membrane thin. While Nafion 117 is about 200 μm thick, membranes used in commercial separations can be 0.3 μm thick (Ho and Sirkar, 1992). Thus, new membranes could be over a hundred times thinner than the present standard. Mechanical stability can be retained through the use of support layers that do not appreciably affect transport.

To seek a membrane with higher selectivity, we investigated composites consisting of zeolite particles in a hydrophilic polymer. As shown in Figure 1, the components are chosen so that protons are transported through both the dispersed phase and the polymer matrix. If the dispersed material is impermeable to methanol, protons will have a more direct and shorter path compared to methanol. This membrane could enhance the proton selectivity, while reducing methanol crossover.

We chose zeolites as the dispersed membrane phase because their regular pore size promises selective separations based on molecular size and shape (Coronas and Santamaria, 1999). Zeolites can also separate components based on preferential adsorption, in which the strong adsorption of one component blocks or hinders the passage of the other components. However, membranes made of pure zeolites are plagued by defects such as cracks or gaps, exhibit poor mechanical properties such as brittleness and fragility (Berry et al., 2000), and are expensive to manufacture (Caro et al., 2000).

A polymer-zeolite composite membrane represents a compromise between the nonselective polymeric films and the brittle expensive zeolite film. The composite combines the

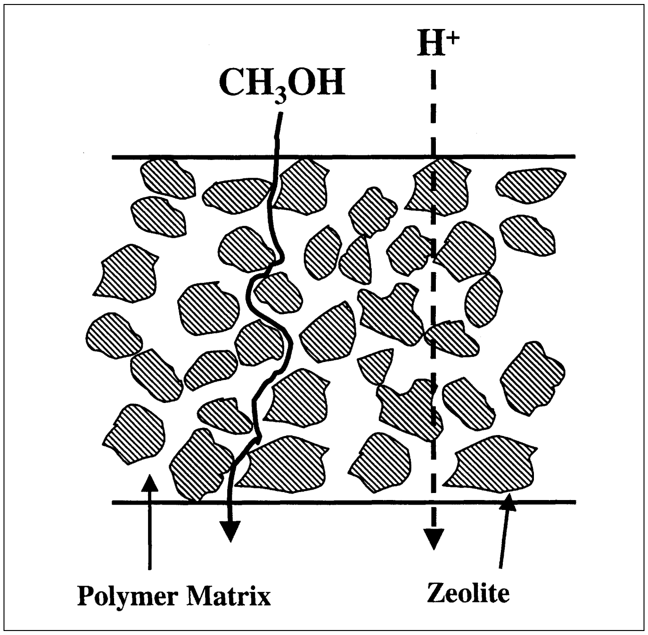

Figure 1. Polymer-zeolite composite membrane.

The membrane consists of highly selective zeolite particles embedded in a polymer matrix. Protons should travel in a direct path through both the polymer and zeolite phases. In contrast, methanol should travel around and between the methanol-impermeable zeolite particles.

highly selective solid-state proton conductor with the flexibility of a polymer matrix. Such membranes have been investigated for both liquid and gas separations, especially for pervaporation (Suer et al., 1994). Applications include dehydration of azeotropic mixtures, separation of organics, and direct methanol fuel cells (Ji and Sikdar, 1996; Rao et al., 1994). Unfortunately, many of these composite membranes are plagued by the formation of voids at the polymer/zeolite interface (Okumus et al., 1994). These voids must be eliminated for a composite membrane to function optimally.

Even without nonselective, interfacial voids, a zeolite-polymer composite must fulfill additional transport requirements to function effectively. To see why, we consider a periodic array of spheres embedded in a continuous medium, as shown in Figure 2. We assume the spheres are impermeable to methanol, so methanol moves entirely in the continuous polymer phase. In contrast, we assume that protons move through both the dispersed and continuous phase. Whether or not the protons take advantage of the pathway through the spheres depends on the relative speed of proton transport in this dispersed phase vs. the continuous phase.

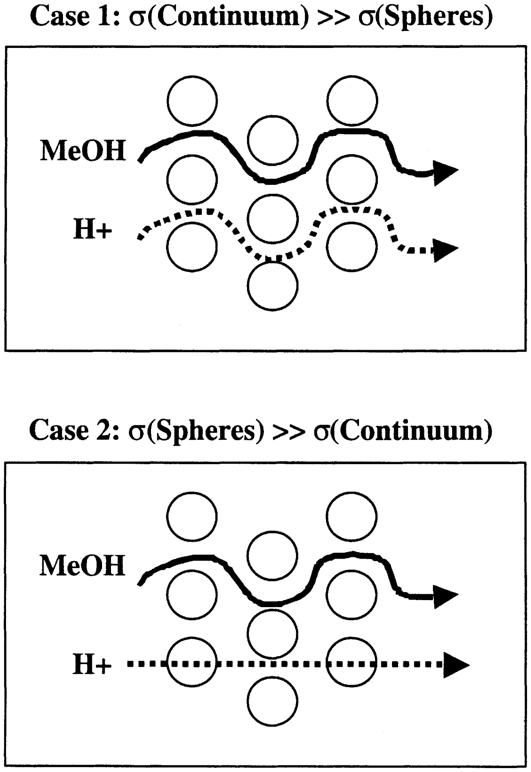

Figure 2. Potential transport scenarios in a composite membrane.

In this idealized situation, the spheres are impermeable to methanol while protons can move through both the continuum and the spheres. In Case 1, protons travel around the spheres because the proton conductivity of the continuum is substantially greater than in the spheres. In Case 2, the spheres offer a highly conducting pathway compared to the continuum. The composite now offers a potential selectivity improvement.

Two limits for transport in this composite system are shown in Figure 2. In Case 1, proton conductivity in the spheres is much less than in the continuum. As a result, the protons move entirely in the continuous phase by traveling around and between the less conductive spheres. Because protons and methanol move by the same pathway through the continuum, the selectivity of the composite is equal to the selectivity of the continuum.

Case 2 is the opposite of Case 1: the proton conductivity in the spheres is now substantially greater than in the continuum. In this scenario, protons quickly move through the spheres, while methanol travels around and between them.

Table 1. Selectivity for Some Typical Compositions*

	Methanol Permeability (10^{-8} cm²/s)				Proton Conductivity (10^{-2} cm²/s)							
									Conductivity of Composite		Selectivty (σ/P)	
Vol. Fraction (φ)	Composite (P)	Polymer in Composite (P_P)	Pure PVA (P_{PVA})	Premeability Reduction (P_{PVA}/P_P)†	Pure PVA (σ_{PVA})	Polymer in Composite (σ_P)	Add Filled Mordenite (σ_M)	Conductivity Ratio (σ_M/σ_P)^a	Theory (σ)	Experiment (σ)	Absolute (10^5)	Relative to Nafion
0	30	30	30	N/A	3.0	3.0	N/A	N/A	3.0	3.0	1.0	2.3
0.25	7.5	11.3	30	2.7	3.0	1.13	40	36	2.1	2.2	2.8	6.5
0.5	1.25	3.13	30	9.6	3.0	0.313	40	128	1.2	1.3	9.7	22

*Note that as the polymer's permeability drops, the selectivity rises.
†Unitless ratio.

This separation of pathways for methanol and proton transport can result in the selectivity of the composite being greater than the continuum. In particular, when the membrane is filled with a periodic array of spheres

$$\frac{D}{D_P}=\frac{2+\dfrac{D_s}{D_P}-2\varphi\left(1-\dfrac{D_S}{D_P}\right)}{2+\dfrac{D_S}{D_P}+\varphi\left(1-\dfrac{D_S}{D_P}\right)} \tag{9}$$

where D is the effective diffusion coefficient in the composite membrane, D_P is the diffusion coefficient in the polymer continuum, D_S is the diffusion coefficient through the spheres, and φ is the volume fraction of spheres (Maxwell, 1881).

We will use Eq. 9 in correlating our experimental data. We will be especially interested in the two limits of this equation given in Figure 2. Because the protons have a direct path through both phases, the proton conductivity (σ) given by an alternative form of Eq. 9

$$\epsilon_1=\frac{\sigma}{\sigma_P}=\frac{2+\gamma-2\varphi(1-\gamma)}{2+\gamma+\varphi(1-\gamma)} \tag{10}$$

where $\epsilon_1(=\sigma/\sigma_P)$ is the ratio of the proton conductivity in the composite vs. proton conductivity in the polymer phase, $\gamma(=\sigma_S/\sigma_P)$ is the ratio of proton conductivity in the spheres to proton conductivity in the polymer, and φ is the volume fraction of spheres. Because methanol cannot go through the spheres, the methanol permeability P is described by Eq. 9 with D_S/D_P equal to zero

$$\epsilon_2=\frac{P}{P_P}=\frac{2(1-\varphi)}{2+\varphi} \tag{11}$$

where $\epsilon_2(=P/P_P)$ is the ratio of the effective methanol permeability in the composite membrane relative to methanol permeability in the polymer phase P_P. Dividing Eq. 10 by Eq. 11 yields the selectivity

$$\beta=\beta_P\left[\frac{2+\gamma-2\varphi(1-\gamma)}{2+\gamma+\varphi(1-\gamma)}\right]\left[\frac{2+\varphi}{2(1-\varphi)}\right] \tag{12}$$

where $\beta_P(=\sigma_P/P_P)$ is the selectivity in the continuous polymer phase.

Equation 12 shows that potential selectivity improvement in a composite membrane is a function of two main factors: γ and φ. To determine the effect of γ on selectivity, we return to the two cases in Figure 2. In Case 1, when the spheres are impermeable to protons, γ is zero, and the bracketed terms of Eq. 12 reduce to one. The selectivity of the composite equals the inherent selectivity of the polymer (that is, $\beta=\beta_\mathrm{P}$). In Case 2 of Figure 2, when proton transport through the spheres is very rapid, γ is infinity, and Eq. 12 becomes

$$\beta=\beta_P\left[\frac{1+2\varphi}{1-\varphi}\right]\left[\frac{2+\varphi}{2(1-\varphi)}\right] \tag{13}$$

Selectivity improvement now depends on the inherent polymer selectivity β_P and the volume fraction of spheres φ. When $\varphi=0.5$, the selectivity of the composite is about 10 times better than in the pure polymer. We will return to these equations in discussing our results.

Experimental Studies

Rationale for this model system

For our studies, we chose mordenite as the zeolite phase and polyvinylalcohol (PVA) as the polymer. The hydrophilic nature of both PVA and mordenite prevents the formation of nonselective voids at the polymer-zeolite interface, while also exploiting the selectivity of the mordenite. Mordenite is one of the most stable zeolites in existence (Breck, 1974), and is one of the most highly conducting (10^{-3} s/cm) and widely studied (Knudsen et al., 1988). Polyvinylalcohol is also a logical choice, because it can be easily formed into membranes and it has a permeability which can be altered with heat. Mordenite is stable up to temperatures above 800°C (Breck, 1974), doesn't decompose in the presence of acids, and has been studied before as a component in composite membranes for methanol fuel cells (Kjaer et al., 1991; Rao et al., 1994). Although these particular materials are not ideal for actual fuel cell use, they do possess the transport properties necessary for demonstrating improved selectivity in such a polymer-zeolite composite membrane.

While we believe that the mordenite-PVA system is a good model for our research, we are concerned that the mordenite used is imperfectly defined. This leads to three more specific concerns: the zeolites Si/Al ratio, its pore size, and its conductivity. Each merits discussion.

The Si/Al ratio of a zeolite dominates adsorption within the zeolite. In particular, increasing the Si/Al is believed to change the selectivity from hydrophilic to hydrophobic. There is debate about where the change occurs. Typical mordenite has a Si/Al ratio of 5, and is hydrophilic. A recent study demonstrated hydrophilic behavior using a zeolite membrane with Si/Al ratio of 15 (Noack et al., 2000). This study utilizes a dealuminated form of mordenite, with a Si/Al ratio of 40, but dealuminated mordenite still preferentially adsorbs water over methanol (Meninghaus and Prins, 2000). However, while adsorption of either species will affect unsteady uptake, it will usually not affect steady-state transport (Cussler, 1997). As we will show below, we see no evidence of adsorption in our experiments.

We are also concerned about pore size. The mordenite used in the present study has most likely been dealuminated through steam treatment at elevated temperatures. In addition to changing the Si/Al ratio, this treatment can increase the pore size. Typical mordenite has a main channel pore size of 0.7 nm, whereas dealuminated mordenite contains pores as large as 20 nm (Meninghaus and Prins, 2000). The larger pore size will substantially reduce the effects of ionic repulsion between mordenite's negatively charged framework and the sulfate anion. Because we always used the same mordenite, we have not investigated this effect.

Finally, we are concerned about the inherently low proton conductivity of 10^{-3} S/cm in mordenite. While typical mordenite is estimated to have an internal molarity of 6M (Rabo, 1976), the acid site concentration of dealuminated mordenite is reduced to about one-sixth of the normal value (Hibino et al., 1993). In this study, we increased the zeolite's effective conductivity by soaking the polymer-zeolite membranes in sulfuric acid solutions. The sulfuric acid solutions should readily absorb into mordenite, similar to the uptake of sulfate species such as 0.5 M ammonium sulfate (Lei et al., 1999) and tin sulfate (Knudsen et al., 1988). Additionally, mordenite impregnated with other ionic species such as antimony (V) chloride (Hix et al., 1994) and phosphotungstic acid (Arico et al., 1995) also shows increased conductivity. Nonetheless, we recognize that soaking the composite membrane in sulfuric acid is a major disadvantage for fuel cells.

Membrane fabrication. Composite membranes of mordenite particles embedded in a polyvinylalcohol (PVA) matrix were fabricated using commercially available materials. The mordenite powder (HM40, Sud-Chemie Inc., Louisville, KY) consisted of 2–4 μm particles, with a Si/Al ratio of 40. Because stability increases and hydrophilicity decreases as the Si/Al ratio increases, this particular value represents a compromise. This mordenite is stable in 1M-H_2SO_4, required for conductivity. The polyvinylalcohol (PVA) (Elvanol 71-30, DuPont, Wilmington, DE) was a medium viscosity, fully hydrolyzed grade with a molecular weight of ~140,000. It is soluble in hot water. The polymer showed excellent adhesion to porous, water-absorbent surfaces. Such adhesion is important in forming a composite membrane with mordenite. Because of its ability to both disperse mordenite and dissolve PVA, water was used as the solvent in solution casting of PVA/mordenite membranes.

Membrane fabrication began by stirring overnight 1 g mordenite powder in 5 g water. A sonicating probe (Ultrasonic Homogenizer-4710 Series, Cole-Parmer Instrument Co., Chicago, IL) further dispersed the mordenite for 5 min at 50% output, followed by 5 min of stirring, and repeated for 1h. Concurrently, a covered 5-wt. % solution of PVA in water was heated at approximately 100°C for 1 h. The PVA solution and the mordenite suspension were then mixed together for 4h at 60°C. Membranes were prepared by casting this solution in a polystyrene dish. After the wet membranes were allowed to air dry for one week, they were made insoluble through heat treatment at 150°C for one to 27 h. Membranes were then hydrated for at least 24 h. Fully hydrated membranes varied in thickness from ~100–300 μm. The procedure for making a pure PVA membrane was the same, but without mordenite.

The color and mechanical properties of the membranes varied with mordenite content and heat treatment. Prior to heat treatment, pure PVA membranes were transparent and flexible. Pure PVA heat-treated membranes retained their flexibility, but turned slightly yellow in color. PVA membranes containing mordenite were beige after drying and were considerably stiffer than pure PVA membranes. After a 1h heat treatment, the membranes became more fragile and the color changed from beige to black. Membranes heat-treated for 27 h were still more fragile but were brown.

Membrane characterization

Scanning electron microscopy (JEOL 840-II) revealed that the 2–4 μm mordenite particles were homogeneously dispersed throughout the membranes. The hydrophilicity of the mordenite was confirmed by the defect free boundary formed at the PVA/mordenite interface. Although mordenite has a higher density than PVA, the viscosity of the PVA solution apparently prevents the mordenite particles from settling. Heat treatment caused no cracking at the PVA/mordenite interface.

The chemical effects of heat treatment were studied with infrared spectroscopy, collected using a Nicolet Magna-IR 550 spectrometer. Results for pure PVA membranes showed that the spectrum of a heat-treated membrane differed from that for an unheated membrane only in an increase in one peak in the C-O stretch region, at ~1,200–1100 cm^{-1}. This peak increase is consistent with the formation of carboxyl groups. Outside of a slight yellowing, he heat treatment of pure PVA does not appreciably affect the chemical or physical nature of the polymer.

Results for PVA membranes containing mordenite also showed spectra before and after a 1h heat treatment at 150°C which were virtually identical. An example is given in Figure 3a. The only noticeable difference was a reduction in the H-

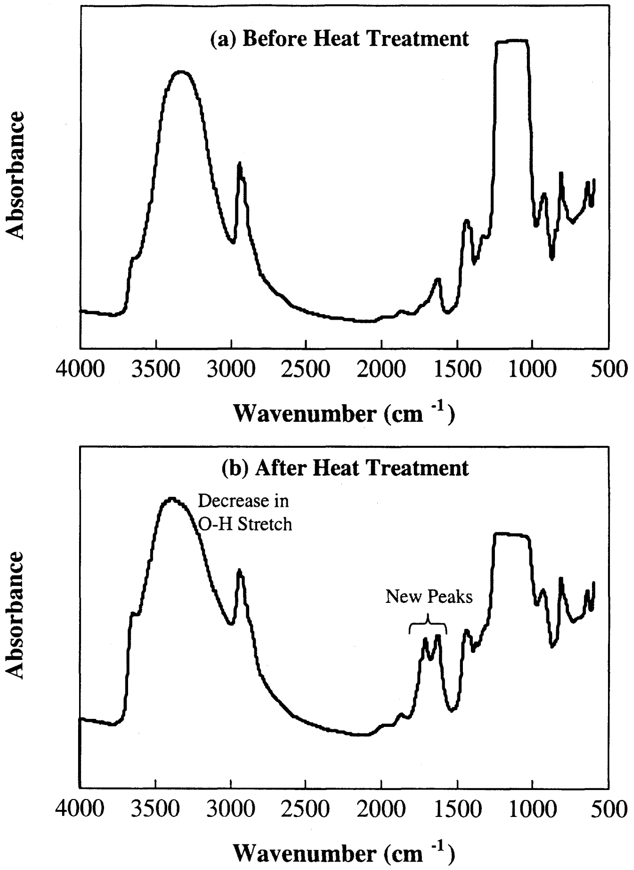

Figure 3. Infrared absorption spectra of a PVA/mordenite (50/50by volume) membrane: (a) before heat treatment and (b) after a 27 h heat treatment.

The heat treatment results in a reduction in the O-H stretch peak at ~3,300 cm^{-1}, while also producing a carbonyl (C = 0) peak at ~1,700 cm^{-1} and an alkene (C = C) peak at ~1,600 cm^{-1}.

O-H bending peak from residual water, a direct result of removing water from the membrane. In contrast, the spectra after a 27h heat treatment were clearly different, as shown in Figure 3b. The heat treatment again resulted in a reduction in the O-H stretch peak at ~3,300 cm^{-1}, but also produced new peaks at ~1,700 cm^{-1} and ~1,600 cm^{-1}. Similar changes have been observed during the dehydration of PVA in the presence of sulfuric acid (Immelman et al., 1993) and of sulfated zirconia (Kim et al., 2001). Partial dehydration of PVA is known to cause the brown discoloration seen here. The acidic hydroxyl groups on the mordenite surface may act as catalysts for the PVA dehydration. The resulting structure contains both carbonyl (C=O) and alkene (C=C) groups, consistent with the new peaks in Figure 3b at ~1,700 cm^{-1} and ~1,600 cm^{-1} (Pritchard, 1970).

To verify the proposed acid-catalyzed dehydration of PVA, membranes were fabricated by dissolving PVA in a weak 0.01M-H_2SO_4 solution instead of water. After solution casting and air drying, the membranes were heated in a 150°C oven for 1h. The final membranes displayed the same dark brown color and IR spectrum characteristics as the PVA/mordenite membranes heated for 27 h, which indicates dehydration of the PVA (Libby, 2001). Thus, mordenite and sulfuric acid both facilitate the dehydration of PVA during heating.

Transport properties

Membranes were tested for both methanol permeability and proton conductivity using methods employed previously by Pivovar et al. (1999). Methanol permeability was measured in a diaphragm cell connected to a differential refractometer. The diaphragm cell had two glass compartments, each about 15 cm^3 in volume, separated by the membrane being tested and stirred at 60 rpm. The membrane was clamped vertically between the adjacent compartments, with a silicone rubber gasket placed on each side of the membrane to ensure a tight seal. The downstream compartment was filled with pure water, while the upstream side was typically filled with a 1 M aqueous solution of methanol. The downstream compartment was connected through the pump to the refractometer (Waters Model 410, Framinghorn, MA) to allow concentration measurements. Typical experiments involved solution sampling every second and data recording every minute.

Proton conductivity of test membranes was determined using the two-point probe technique in which two electrodes on opposite sides of the membrane hold the sample in an acid solution (Libby, 2001). The membranes were soaked in this acid solution for at least 48 h prior to testing. The small gold electrodes, 1.5 mm in diameter, reduced capacitance effects. A spring linked to one of the electrodes kept the membrane under slight but constant pressure, thereby providing good contact between the electrodes and the membrane. The conductivity cell was connected to a Schlumberger Solartron 1286 impedance/gain-phase analyzer, which measured the impedance as a function of frequency. The frequency range was typically 1 MHz to 100 Hz. This unit was interfaced with a Labview 4.0 program on a Macintosh computer for data recording. The apparatus determined the conductivity in the traverse direction of the membrane, which is equivalent to the direction of proton transport in fuel cell membranes.

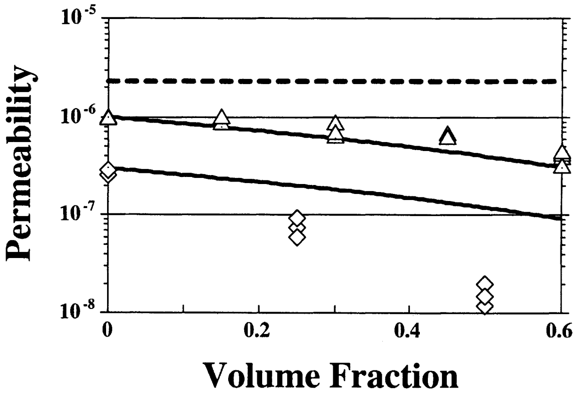

Figure 4. Methanol permeability (cm^2/s) vs. mordenite concentration.

For a short heat treatment (the triangles), permeability demonstrates a 2.5-fold reduction over the mordenite concentration range. In contrast, the long heat treatment (the diamonds) causes permeability to decrease 25 times. Lines representing Maxwell predictions agree well with the short heat treatment data but fail to predict the long heat treatment data.

Results

The goal of this research is the development of composite membranes which are more selective for protons than for methanol. Such membranes may find application in direct methanol fuel cells, which currently use membranes of the perfluorinated, sulfonated polymer Nafion. This research will be successful if the new composite membrane shows a better proton to methanol selectivity than Nafion.

The results of the research are most easily organized as measurements of methanol permeability, determinations of proton conductivity, and values of selectivity. The selectivities are, of course, the ratios of conductivity and permeability. In reporting these data, we will commonly refer to membranes which are heat treated for 1h or for 27 h. Some heat treatment is important to insure that the membranes are insoluble in water. The longer heat treatment retards transport in the PVA component of the membrane and increases selectivity.

Methanol Permeability

The methanol permeability is plotted in Figure 4 vs. the volume fraction of mordenite for both the short heat treatment (1 HR HEAT) and the long heat treatment (27 HR HEAT). The 1 h treated membranes were tested in 1 M-methanol solutions, whereas composite membranes heated for 27 h were tested in 12.3 M methanol (50% methanol by volume). Additional experiments reported elsewhere (Libby, 2001) prove that composite membranes heat-treated for 27 h have methanol permeabilities independent of methanol concentration. Inspection of the 1 HR HEAT data shows a slight drop in permeability as the amount of mordenite increases. In particular, a membrane containing 60% mordenite by volume has about a 2.5 fold decrease in permeability over a pure PVA membrane. The decrease supports the expectation that methanol preferentially moves through the polymer phase, while passing around and between the mordenite particles. The methanol permeability of a pure Nafion 117 membrane is included in Figure 4 as the dashed line spanning the plot. Although the plot may appear to show Nafion permeability as a function of mordenite volume fraction, this is not the case: the line is only for comparing a pure Nafion membrane which does not contain mordenite with the PVA/mordenite composites. For example, a membrane containing 60% mordenite by volume is about 6 times less permeable than Nafion.

As shown in Figure 4, the pure PVA membranes from the 27 HR HEAT data are a little over 3 times less permeable than their 1 HR HEAT counterparts. This is probably due to the increase in crystallinity through removal of residual water, and to the formation of new hydrogen bonds between the macromolecules (Sakurada, 1985). Thus, as heat treatment time increases, molecular packing in the PVA becomes tighter, leading to the lower permeability.

The 27 HR HEAT data fall below the 1 HR HEAT data across the entire mordenite fraction range. The most striking feature of the plot is the steep decline in permeability with increasing mordenite. For example, the permeability of PVA/mordenite membrane (50/50 by volume) is ~ 25 times smaller than the pure PVA membrane. The explanation behind this steep decrease lies in the IR analysis. The acidic mordenite catalyses further dehydration of the PVA structure, which further increases molecular packing, resulting in reduced free volume in the polymer phase. This combination of increased dehydration and increased methanol path length around the mordenite leads to the steep drop shown.

Proton conductivity

The proton conductivities reported in Figure 5 are for membranes equilibrated in 1 M sulfuric acid solutions. As shown, a pure PVA membrane heated for 1 h has a conductivity of ~ 0.06 S/cm, not far below Nafion (~ 0.11 S/cm). As the mordenite content increases, proton conductivity drops slightly to ~ 0.04 S/cm for 60% mordenite despite the 1 M sulfuric acid in the mordenite's pores. The data imply that because the conductivity in the polymer phase is high, the mordenite pores contribute no significant transport. Most protons stay in the polymer phase and travel around the mordenite particles, thus leading to a lower conductivity as the mordenite concentration increases.

The conductivity in membranes heated for 27 h also decreases as mordenite content increases. The pure PVA membrane has a conductivity of ~ 0.03 S/cm, whereas a membrane with 50% mordenite has a conductivity of 0.01–0.015 S/cm. This small decrease, primarily due to changes in the PVA, is much less than the change shown in Figure 4, where methanol permeability dropped by a factor of 25 over the entire mordenite range. The high conductivity of the acid doped mordenite counteracts the decrease in polymer conductivity here, resulting in only a slight decrease in the conductivity of the composite.

Thus, the 1 HR HEAT and 27 HR HEAT treatments demonstrate the importance of the ratio of proton conductivity in the mordenite vs. that in the polymer. For the 1 HR HEAT data, the mordenite is not substantially more conductive than the polymer, so protons are content moving around the mordenite and through the polymer phase. In contrast, for the 27 HR HEAT data, transport in the polymer phase is more hindered, so protons take full advantage of the highly conducting mordenite pathway. This demonstrates the decoupling of transport of protons vs. transport of methanol.

Electrochemical selectivity

Electrochemical selectivity, defined in Eq. 8 as the proton conductivity divided by the methanol permeability, allows a comparison of the new membranes with each other and with the Nafion benchmark. As Figure 6 shows, the 1 HR HEAT and 27 HR HEAT treatments show different behavior as the mordenite content increases. For 1 HR HEAT treatment, the slight decrease in methanol permeability is accompanied by an even smaller decrease in conductivity, which results in a slight improvement over pure PVA. The composite's data are also similar to Nafion's selectivity. In the best case, a PVA membrane containing 60% mordenite by volume demon-

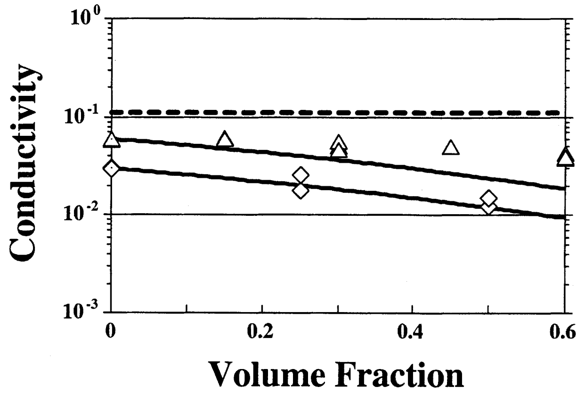

Figure 5. Proton conductivity (S/cm) vs. mordenite concentration.

For both the short heat treatment (the triangles) and the long heat treatment (the diamonds), the conductivity drops as the mordenite content increases. Maxwell predictions (the solid lines) agree well with both the short and long heat treatment data.

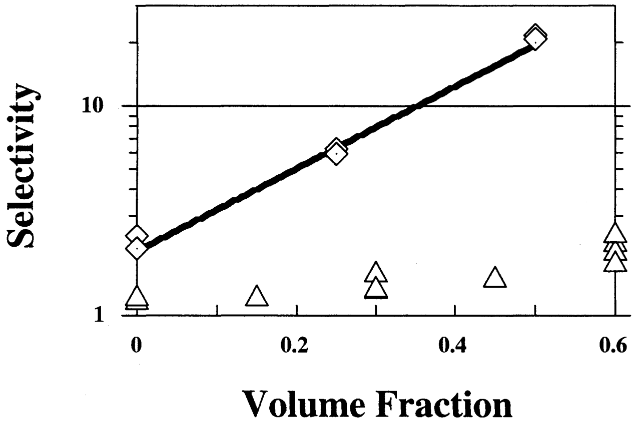

Figure 6. Selectivity relative to Nafion vs. mordenite concentration.

For a short heat treatment (the triangles), the mordenite changes the selectivity less than two times. For the longer heat treatment (the diamonds) the selectivity increases 20 times. Maxwell predictions (the solid line) support the experimental data.

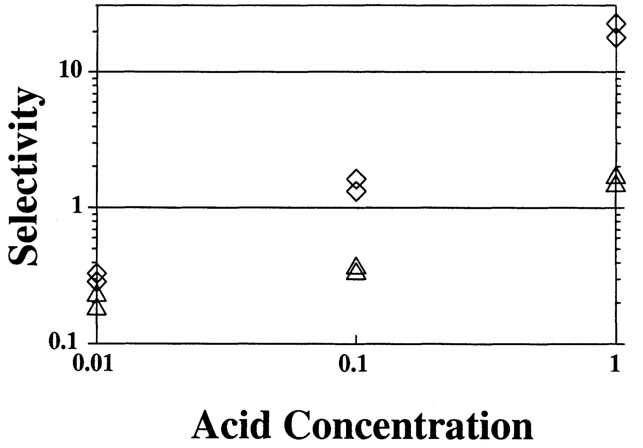

Figure 7. Selectivity of the 27 HR HEAT PVA/mordenite (50/50 by volume) membranes equilibrated in various sulfuric and phosphoric acid solutions.

Only a large sulfuric acid concentration (the diamonds) provides a conductivity value necessary for selectivity improvement. The lower conductivity of phosphoric acid, data (the triangles) yields little.

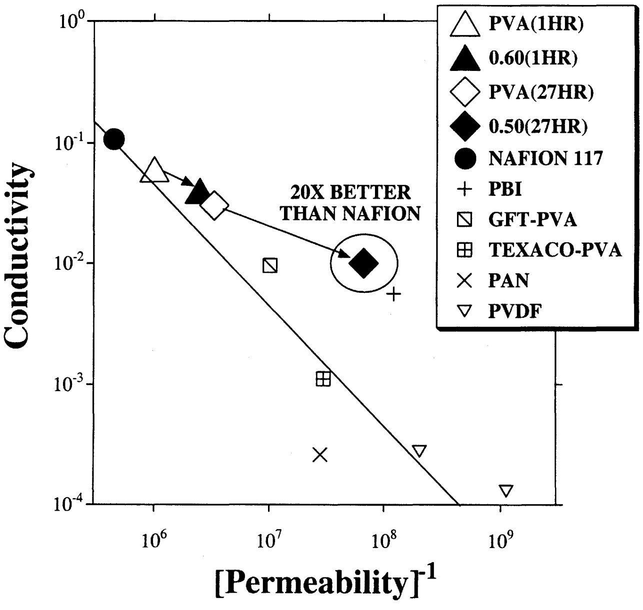

Figure 8. Selectivity plot-proton conductivity of membranes equilibrated in 1M-H_2SO_4 vs. methanol resistance.

Points labeled 0.60(1*HR*) and 0.50(1*HR*) are polyvinyl alcohol membranes containing 60% and 50% mordenite by volume, respectively, heat treated for the time noted. Points labeled PVA are pure polyvinyl alcohol membranes. Reference data are from Pivovar et al. (1999).

strates a mere two-fold increase in selectivity over Nafion. These 1 h heat treatments are not a major improvement.

On the other hand, the 27 HR HEAT data demonstrate a dramatic selectivity improvement as mordenite content increases. The substantial decrease in methanol permeability is not offset by the decrease in proton conductivity, yielding better selectivity. The most successful result by far is a PVA membrane containing 50% mordenite by volume. Compared to Nafion, this membrane demonstrates a 200-fold decrease in methanol permeability, with only an order of magnitude decrease in proton conductivity, which results in ~20-fold increase in selectivity.

The polyvinylalcohol membranes studied here have no fixed charge, and so must be doped with acid to be effective in a direct methanol fuel cell. This is a disadvantage, for acid doping can cause corrosion or reduce catalyst activity. As a result, we explored broadly the effect of acid type and concentration, with results exemplified by those in Figure 7. These data, for membranes containing 50% mordenite by volume heat treated for 27 h, demonstrate a linear increase in selectivity over the acid concentration range. The results are probably due to different partitioning of acid into the membranes.

Discussion

The value of composite membranes developed here and summarized in Table 1 is best judged by replotting the selectivity as shown in Figure 8. The ordinate in this figure is the proton conductivity; the abscissa is the reciprocal of methanol permeability, equivalent to a methanol resistivity. A perfect membrane, with both high proton conductivity and methanol resistivity, would be located in the upper righthand corner of this figure. To compare alternative membranes with Nafion, we plot a line of constant selectivity with a slope of -1 through the value for Nafion. Any membranes falling above this line are more selective than Nafion. Any falling below this line are not.

The composite membranes studied here include pure polyvinyl alcohol membranes heated for 1 h and 27 h, respectively, labeled PVA (1HR) and PVA (27HR). The data also include polyvinyl alcohol membranes containing 60% and 50% mordenite by volume, heated for the time noted in parentheses and labeled 0.60(1HR) and 0.50(27HR). All other data, with the exception of Nafion, are from earlier work (Pivovar et al., 1999). The figure illustrates the dramatically different behavior of membranes heat treated for 1 h vs. 27 h. A pure PVA membrane heated for 1 h has essentially the same selectivity as Nafion. The presence of 60% mordenite by volume increases selectivity slightly. In contrast, a membrane heated for 27 h and containing 50% mordenite shows a huge selectivity gain. Not only is its selectivity ~20 times better than Nafion, but it is better than PBI, another membrane developed for direct methanol fuel cells.

At this point, we may wonder, "Why does the 27 HR HEAT treatment produce better selectivity than the 1 HR HEAT treatment?" The answer to this question depends on the conductivity in the mordenite vs. that in the polymer. For the 1 HR HEAT treatment, the mordenite phase isn't substantially more conductive than the polymer, so the majority of protons are content moving through the polymer phase. In this scenario, shown as Case 1 of Figure 2, both methanol and protons travel around and between the mordenite particles, staying in the polymer. Since both species move by the same pathway through the polymer phase, the composite selectivity is roughly equivalent to the pure PVA selectivity. No selectivity gain is realized.

On the other hand, for the 27 HR HEAT treatment, transport in the polymer phase becomes drastically reduced by mordenite-induced dehydration. The conductivity of the mordenite is now substantially greater than that of the polymer. As shown as Case 2 of Figure 2, protons take full advantage of the highly conducting mordenite pathways, whereas methanol is still forced around the mordenite particles. This separation of transport mechanisms results in the substantial selectivity improvement.

To place this argument on a more quantitative basis, we return to the Maxwell theory for transport through a periodic array of spheres. For 1 HR HEAT treatment, we assume that methanol cannot penetrate the mordenite, so the Maxwell theory reduces to Eq. 11. With the experimental value of $P_P = 1.0 \times 10^{-6}$ cm^2/s from the data in Figure 4, we can use Eq. 11 to predict the composite methanol permeability for various mordenite volume fractions. The results, shown in Figure 4 as the solid line, show that the Maxwell prediction agrees reasonably with the experimental data. The experimental data are slightly higher than predicted, especially at the large mordenite concentration. The discrepancy may be a result of using a theory that is strictly applicable only to dilute suspensions of periodic particles, which is not true here. Nevertheless, this theory has proved applicable for higher concentrations in polymer/zeolite gas separation membranes (Zimmerman et al., 1997). Here, the Maxwell theory provides a reasonable prediction for transport at various mordenite concentrations in the composite membranes.

For the 1 HR HEAT treatment data, the conductivity decreases with increasing mordenite content, just as methanol permeability does. Equation 10 predicts the decrease, as shown in Figure 5, especially at the lower volume fractions where the Maxwell theory is more reliable. Thus, protons and methanol move in a similar manner by transport primarily in the polymer phase, which results in the lack of selectivity improvement seen in Figure 6. The Maxwell predictions with both the methanol and proton conductivity data explain this selectivity.

The 27 HR HEAT treatment gives different results. As shown by the lower solid line in Figure 4, use of Eq. 11 systematically overpredicts the methanol permeability of the composite. The main difference is the mordenite-induced dehydration of PVA during this treatment. Because the extent of the dehydration depends on the amount of mordenite present, the transport properties through the polymer phase became a function of the mordenite content. As a result, the predictions for the longer heat treatment data use a new procedure. Data for the specific example given below clarify how the predictions are made. The data, which appear in parentheses at the end of each step, are for a PVA/mordenite (50/50 by volume) composite membrane, heated for 27 h, and equilibrated in 1M-H_2SO_4. The procedure is as follows:

(1) Start with the methanol permeability of the composite in question. Label this as P.

(*The PVA/mordenite composite membrane has a permeability of* $P = 1.25 \times 10^{-8}$ *cm*^{2}*/s*)

(2) Assuming methanol doesn't permeate through the mordenite, calculate the methanol permeability of the polymer phase $P_{\rm P}$ from Eq. 11.

(*Substitute* $\varphi = 0.5$ *for the volume fraction of mordenite and* $P = 1.25 \times 10^{-8}$ *cm*^{2}*/s to calculate* $P_P = 3.13 \times 10^{-8}$ *cm*^{2}*/s*).

(3) Compare the methanol permeability of pure PVA ($P_{\rm PVA}$) with the polymer phase in the composite ($P_{\rm P}$) to find the permeability reduction

$$\text{Permeability Reduction} = \frac{P_{\rm PVA}}{P_P} \tag{14}$$

(*Substitute* $P_{PVA} = 3.0 \times 10^{-7}$ *cm*^{2}*/s and* $P_P = 3.13 \times 10^{-8}$ *cm*^{2}*/s to yield a Permeability Reduction* = 9.6)

(4) Because experiments show that PVA dehydrated in acid has the same selectivity as pure PVA heated in the absence of acid (Libby, 2001), the reduction in permeability must be accompanied by an equivalent reduction in conductivity

$$\text{Conductivity Reduction} = \frac{\sigma_{\rm PVA}}{\sigma_P} \tag{15}$$

(*The conductivity reduction is* 9.6)

(5) Calculate σ_P using the known values of proton conductivity in pure PVA ($\sigma_{\rm PVA}$) and the conductivity reduction factor.

(*In this case a pure PVA membrane heated for* 27 *h has a proton conductivity* $\sigma_{PVA} = 3.0 \times 10^{-2}$ *S/cm. Thus,* $\sigma_P = (3.0 \times 10^{-2}$ *S/cm*$)/9.6 = 3.13 \times 10^{37}$ *S/cm*).

(6) Assume that the proton conductivity of the mordenite particles equilibrated in acid are equivalent to the proton conductivity of the solution itself (Libby, 2001).

(*From the conductivity of a* $1M - H_2SO_4$ *solution,* $\sigma_M = 0.4$ *S/cm.*)

(7) Calculate the conductivity of the composite (σ) using the Maxwell theory in Eq. 10:

(*Substitute* $\gamma = \sigma_M/\sigma_P = (0.4$ *S/cm*$)(/3.13 \times 10^{-3}$ *S/cm*$)$ *and* $\varphi = 0.5$ *to calculate* $\sigma = 0.012$ *S/cm.*)

(8) Finally, compare the predicted composite conductivity value to the experimental value.

(*The calculated value for composite conductivity of* $\sigma = 0.12$ *S/cm is within the experimentally measured range of* 0.010–0.015 *S/cm.*)

This calculation provides quantitative support for qualitative picture in Figure 2. It not only predicts the result of the example given, but it also predicts the conductivity variations with mordenite concentration shown in Figure 5. Additionally, by combining the methanol permeability results with the conductivity predictions, the Maxwell theory successfully predicts the selectivity changes shown in Figure 6.

We conclude that the Maxwell theory can be a reasonable guide to selectivity changes in these membranes. On this basis, we can ask how much more selective we can hope to make the composites. To explore this, we consider the limit of Eq. 12 as the mordenite conductivity becomes infinite, that is, as $\gamma \rightarrow \infty$. The result, given by Eq. 13, gives a maximum predicted selectivity improvement of 10 when $\varphi = 0.5$. From Figure 6, our experimental results appear to have reached this maximum increase, as the PVA/mordenite (50/50 by volume) composite membrane heated for 27 h is ten times more selective than its pure PVA counterpart. Because the Maxwell theory is successful, we can use Eq. 13 to predict the relative selectivity (β/β_P) as a function of the composite's conductivity ratio γ ($= \sigma_S/\sigma_P$). The result, shown in Figure 9 for two values of mordenite volume fraction φ, suggests that this conductivity ratio must be well above ten to approach the maximum selectivity.

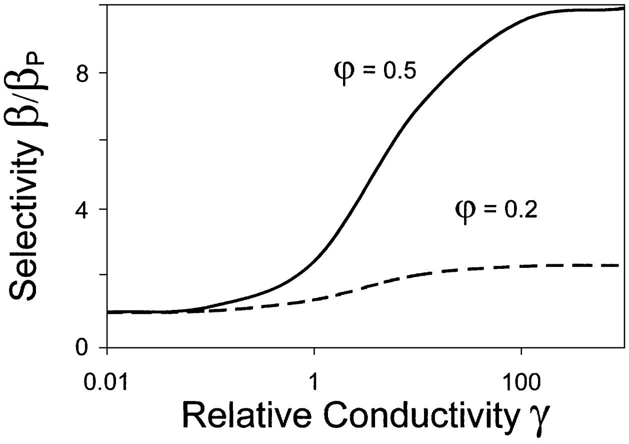

Figure 9. Achieving the largest possible selectivity.

The highest selectivity (β/β_P) requires a zeolite with a relative conductivity more than ten times the polymer continuum.

This key transport ratio criteria sheds light on the commonly asked question of "Why not put mordenite particles into a fuel cell ready membrane such as Nafion?" The answer is that mordenite ($\sigma \sim 10^{-3}$ S/cm) or sulfuric acid filled mordenite ($\sigma \sim 0.4$ S/cm) does not have a conductivity many times greater than Nafion, which is necessary to achieve maximum selectivity in a composite membrane. According to the present theory, the conductivity of the dispersed phase would have to be ~ 10 S/cm, since the typical room temperature conductivity value for Nafion is ~ 0.1 S/cm. Unfortunately, such a solid proton conductor currently does not exist (Norby, 1999).

The results above do suggest that we have achieved the maximum selectivity increase possible with evenly dispersed particles of a proton conductor. However, this is definitely not the maximum selectivity increase which could be achieved. Such a maximum depends strongly on how the proton conducting material is arranged within the composite membrane. For example, if the particles were all on one surface of the membrane, then any selectivity increases would be minor. If they were arranged in conducting channels passing through the membrane, then the selectivity increase could be much larger. This remains a fruitful area for more research.

Conclusions

The PVA/mordenite composite membranes have fulfilled their potential. In particular, a PVA/mordenite membrane containing 50% mordenite by volume, heat-treated for 27 h to make it insoluble, demonstrates a 20-fold improvement in selectivity over Nafion. This successful result contrasts the lack of selectivity improvement seen for the short heat treatment composites, thus demonstrating the importance of tailoring the transport properties between the polymer and zeolite phases in order to achieve selectivity gains. Specifically, the zeolite conductivity must be at least 100 times greater than the polymer phase conductivity to achieve maximum selectivity. The polymer phase cannot solely be responsible for the selectivity gains. The experimental results are well correlated by Maxwell's theory for conducting spheres in a continuum.

Acknowledgments

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Notation

c_i = concentration of species i
D = diffusion coefficient of composite membrane
D_i = diffusion coefficient of species i
F = Faraday's constant
H_i = partition coefficient of species i
i = current density
j_i = flux of species i
ℓ = membrane thickness
P = permeability $D_i H_i$
R = gas constant
T = temperature
z_i = change of species i
α = gas constant
β = electrochemical membrane selectivity
γ = ratio of conductivity in mordenite to that in polymer
ϵ_1, ϵ_2 = ratio in composite to that in polymer for conductivity or permeability, respectively
σ = conductivity
Φ = electrochemical potential
φ = volume fraction

Literature Cited

Appleby, A. J., "The Electrochemical Engine for Vehicles," *Scientific Amer.*, **74**, (July, 1999).

Berry, M. B., B. E. Libby, K. Rose, K.-H. Haas, and R. W. Thompson, "Incorporation of Zeolites into Composite Matrices," *Microporous and Mesoporous Mat.*, **39**, 205 (2000).

Breck, D. W., *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, Wiley, New York (1974).

Business Week, "A Clean Technology Powers Up," *Business Week*, **3680**, 102 (2000).

Caro, J., M. Noack, P. Kolsch, and R. Schafer, "Zeolite Membranes—State of their Development and Perspective," *Microporous and Mesoporous Mat.*, **38**, 3 (2000).

Coronas, J., and J. Santamaria, "Separations Using Zeolite Membranes," *Sep. and Purif. Methods*, **28**, 127 (1999).

Cussler, E. L., *Diffusion*, Cambridge University Press, Cambridge (1997).

Cyer, C. K., "Replacing the Battery in Portable Electronics," *Scientific Amer.*, **88** (July, 1999).

Ho, W. S. W., and K. K. Sirkar, *Membrane Handbook*, van Nostrand Reinhold, New York (1992).

Immelman, E., R. D. Sanderson, E. P. Jacoba, and A. J. Van Reenen, "Poly (Vinyl alcohol) Gel Sublayers for Reverse Osmosis Membranes: 1. Insolubilization by Acid-Catalyzed Dehydration," *J. of Appl. Poly. Sci.*, **50**, 1013 (1993).

Jacoby, M., "Fuel Cells Heading for Sale," *Chem. and Eng. News*, **31** (1999).

Ji, W., and S. K. Sikdar, "Pervaporation using Adsorbent-Filled Membranes," *Ind. Eng. Chem. Res.*, **35**, 1124 (1996).

Jost, K., "Fuel-Cell Concepts and Technology," *Automotive Eng. Int.*, **108**, 173 (2000).

Kim, K.-J., S.-H. Park, W.-W. So, and S.-J. Moon, "Pervaporation Separation of Aqueous Organic Mixtures through Sulfated Zirconia-Poly(vinyl Alcohol) Membrane," *J. of Appl. Poly. Sci.*, **79**, 1450 (2001).

Kjaer, J., J. Yale-Andersen, and N. A. Knudsen, "Solid State Electrolyte Membranes for Direct Methanol Fuel Cells," *Solid State Ionics*, **46**, 169 (1991).

Knudsen, N., E. K. Andersen, I. G. K. Andersen, and E. Skou, "Tin(IV) Oxide Containing Mordenite: Synthesis and Ionic Conductivity Measurements," *Solid State Ionics*, **28–30**, 627 (1988).

Libby, B., "Improving Selectivity in Methanol Fuel Cell Membranes: a Study of a Polymer-Zeolite Composite Membrane," PhD Thesis, University of Minnesota (2001).

Libin, K., "Power Play," *Canadian Business*, **73**, 92 (2000).

Maxwell, J. C., *Treatise on Electricity and Magnetism*, Claredon Press, London (1881).

Meininghaus, C. K. W., and R. Prins, "Sorption of Volatile Organic Compounds on Hydrophobic Zeolites," *Microporous and Mesoporous Mat.,* **35-36**, 349 (2000).

Narayanan, S. R., A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M. Smart, T. I. Valdez, S. Surampudi, and G. Halpert, "Recent Advances in PEM Liquid-Feed Direct Methanol Fuel Cells," *Proc. Battery Conf. on Advances and Applications*, Long Beach, CA (1996).

Noack, M., P. Kolsch, J. Caro, M. Schneider, P. Toussaint, and I. Sieber, "MFI Membranes of Different Si/Al Ratios for Pervaporation and Steam Permeation," *Microporous and Mesoporous Mat.,* **35-36**, 253 (2000).

Norhy, T., "Solid-State Protonic Conductors: Principles, Properties, Progress, and Prospects," *Solid State Ionics*, **125**, 1 (1999).

Okumus, E., T. Gurkan, and L. Yilmar, "Development of a Mixed-Matrix Membrane for Pervaporation," *Sep. Sci. and Technol.*, **29**, 2451 (1994).

Pivovar, B. S., Y. Wang, and E. L. Cussler, "Pervaporation Membranes in Direct Methanol Fuel Cells," *J. Memb. Sci.*, **154**, 155 (1999).

Pritchard, J. G., *Poly(vinyl Alcohol): Basic Properties and Uses*, Gordon and Breach Science Publishers, London (1970).

Rao, N., T. P. Andersen, and P. Ge, "Tin Mordenite Membranes for Direct Methanol Fuel Cells," *Solid State Ionics*, **72**, 334 (1994).

Ren, X., T. A. Zawodzinski, F. Unbe, H. Dai, and S. Gottensfeld, "Methanol Cross-over in Direct Methanol Fuel Cells," *Electrochemical Soc. Proc.*, **95–23**, 284 (1995).

Sakaruda, I., *Polyvinyl Alcohol Fibers*, Marcel Dekker, New York (1985).

Suer, M. G., N. Bac, and L. Yilmar, "Gas Permeation Characteristics of Polymer-Zeolite Mixed Matrix Membranes," *J. Memb. Sci.*, **91**, 77 (1994).

Zimmerman, C. M., A. Singh, and W. J. Koros, "Tailoring Mixed Matrix Composite Membranes for Gas Separations," *J. Memb. Sci.*, **137**, 145 (1997).

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