A new type of reinforced composite perfluorinated polymer electrolyte membrane, GORE-SELECT™ (W. L. Gore & Assoc.), is characterized and tested for fuel cell applications. Very thin membranes (5-20 μm thick) are available. The combination of reinforcement and thinness provides high membrane conductances (80 S/cm² for a 12 μm thick membrane at 25°C) and improved water distribution in the operating fuel cell without sacrificing longevity or durability. In contrast to non-reinforced perfluorinated membranes, the x-y dimensions of the GORE-SELECT membranes are relatively unaffected by the hydration state. This feature may be important from the viewpoints of membrane/electrode interface stability and fuel cell manufacturability.

INTRODUCTION

To a large extent, the evolution of the polymer electrolyte fuel cell (PEFC) is linked to ionomeric membrane advances. Perhaps the single most significant advancement in PEFC membrane technology was the replacement of the polystyrene sulfonate based membranes, as used in the Gemini program, with perfluorinated membranes that provided substantially improved durability, longevity, and performance.1 These perfluorinated membranes, such as Nafion™ 117 (from DuPont), were originally developed for chlor-alkali or other non-fuel cell applications. Aside from some incremental advances tailored towards fuel cell applications, the membrane products from DuPont, Dow and Asahi Glass employed at present for fuel cell applications are fundamentally similar to the perfluorinated membranes introduced in the 1960’s. Although some advantages were gained by lowering the membrane equivalent weights (EW), perhaps the most substantial improvements in fuel cell performance were realized by simply thinning the membranes.3,4 The advantages gained with this simple strategy include lower membrane resistance, lower material utilization (which obviously relates to costs), and improved hydration of the entire membrane. The latter is facilitated by the enhanced back-diffusion of water from the cathode side of the membrane to the anode side, the latter of which tends to become dehydrated as a result of the electroosmotic drag.2 However, there is a limitation to the extent to which such membranes can be thinned because of difficulties with durability and reactant cross-over.

Conceivably, some of these difficulties could be alleviated using reinforced membranes. Fluoroionomer membranes reinforced with woven polytetrafluoroethylene (PTFE) are used in industrial electrochemical membranes (such as Naflons 324 or 417). The relatively coarse weave of the woven PTFE reinforcements results in membranes that are much too thick for high fuel cell performance. Some experimental non-woven
PTFE/fluoroionomer composite membranes have been formulated for fundamental ion transport studies\textsuperscript{5,6} and for investigations of other properties relevant to chlor-alkali\textsuperscript{7,8} and fuel cell\textsuperscript{9} applications.

Advancements in materials and processing technology have resulted in the introduction of a new series of PTFE/fluoroionomer composite membranes from W. L. Gore and Associates, Inc. under the GORE-SELECT trademark. Samples of these membranes were provided in nominal thicknesses of about 5, 10, and 20\,\mu m. The membranes were supplied with either 900 or 1100\,EW ionomeric components.

**MEMBRANE CHARACTERIZATION**

The GORE-SELECT reinforced membranes are transparent, very much like the non-reinforced Nafion or developmental Dow membranes. The membrane appears to be uniform and homogeneous. Nevertheless, some of the physical properties of the membrane reflect a preferred orientation, as is observed with the extruded Nafion 117 product.

| Membrane  | EW  | Thickness (\mu m) | Ionic Conductivity (S/cm) | Conductance (S/cm\(^2\)) |
|-----------|-----|------------------|---------------------------|---------------------------|
| Nafion 117| 1100| 200              | 0.14\textsuperscript{a}, 0.10\textsuperscript{b} | 5-7                       |
| Nafion 112| 1100| 60               | 0.10\textsuperscript{b} | 17                        |
| Dev. Dow  | 800 | 100              | 0.15\textsuperscript{b} | 15                        |
| GORE-SELECT  | 1100 | 20          | 0.052\textsuperscript{a}, 0.053\textsuperscript{b} | 26                        |
| GORE-SELECT  | 1100 | 5           | 0.028\textsuperscript{a} | 56                        |
| GORE-SELECT  | 900  | 12           | 0.096\textsuperscript{b} | 80                        |

\textsuperscript{a} z-direction, sulfuric acid immersed sample measured with a four-point probe

\textsuperscript{b} x-y direction, high-frequency measurement for membrane immersed in deionized water.

**Ionic Conductivities**

For comparison, the ionic conductivities of several thicknesses of GORE-SELECT membranes and various other commercial membranes were measured using four-point probe and high-frequency response methods. All membrane samples were boiled for at least 30 minutes in deionized water prior to use. Transverse (z-direction) ionic conductances of sample membranes were obtained using a standard "Kelvin" four-point probe (Palico Model 9100-2) in which the membrane samples were immersed in 1\,M sulfuric acid maintained at 25\,\textdegree\,C. Longitudinal (x-y) conductances of the membranes in the fully hydrated state were provided by the real axis intercept of a 1\,Hz to 10\,kHz impedance spectrum using a Solatron 1260 Frequency Response Analyzer.\textsuperscript{10} Results for several thicknesses of GORE-SELECT membrane are compared to values obtained for
developmental Dow and Nafions 112 and 117 in Table I. Although the conductivities of the higher equivalent weight GORE-SELECT membranes are much lower than the unreinforced Nafion membranes, the conductances are significantly higher due to the thinness of the reinforced membranes. The similarities in the x-y and the z direction conductivities for the 20 µm thick GORE-SELECT membrane suggest that the material is relatively isotropic, so far as ionic conductivity is concerned. However, it should be noted that sulfuric acid imbibed in the membranes during the four-point probe experiments may have influenced the measured conductivities.

**Water Content and Hydraulic Permeability**

Water contents of several commercial and GORE-SELECT membranes are listed in Table II. The water contents of the GORE-SELECT membranes are surprisingly high compared to the other commercial membranes considering they possess a substantial non-ionic reinforcement component. The water content variations within the GORE-SELECT membrane values roughly correspond to the differences in the EW’s.

Table II. Membrane water content and hydraulic permeability.

| Membrane     | EW  | Thickness (µm) | Water Uptake<sup>a</sup> (%) | Hydraulic Permeation<sup>b</sup> (Relative Rate) |
|--------------|-----|----------------|-----------------------------|-----------------------------------------------|
| Nafion 117   | 1100| 200            | 34                          | 1.0                                           |
| Nafion 112   | 1100| 60             | 34                          | 3.3                                           |
| Dev. Dow     | 800 | 100            | 56                          | 4.0                                           |
| GORE-SELECT  | 1100| 20             | 32                          | 3.7                                           |
| GORE-SELECT  | 900 | 12             | 43                          | 12.9                                          |

<sup>a</sup>Expressed as percent of membrane dry weight.  
<sup>b</sup>Hydraulic permeability relative to Nafion 117

Table II also shows that the hydraulic permeability of the 20 µm thick 1100 EW GORE-SELECT membrane is about 4 times as great as Nafion 117, much as might be expected for a composite material that is about one-ninth as thick. On the other hand, the permeability of the 12 µm thick 900 EW membrane is somewhat higher than expected based on the 20 µm thick membrane results. Indeed, the general trend across all types of membranes suggest that the lower equivalent weight (and corresponding higher water uptake) enhances the water transport, after factoring in the relative thicknesses.

**Shrinkage**

The x and y direction dimensional stabilities of the GORE-SELECT and Nafion 117 membranes were measured upon dehydration using a Thermomechanical Analyzer 2940. A predetermined force was applied to 25.4 mm by 3 mm samples that were first fully hydrated by boiling in deionized water for 30 minutes. A quartz probe in contact with the samples detected the changes in sample dimensions during drying. The amounts of shrinkage are noted in Table III.
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Table III. Membrane shrinkage upon dehydration.

| Membrane   | Thickness (µm) | Transverse Direction (%) | Machine Direction (%) |
|------------|----------------|--------------------------|-----------------------|
| Nafion 117 | 200            | -11.80                   | -10.55                |
| GORE-SELECT| 20             | -2.95                    | -2.90                 |

Tensile strengths

The tensile strengths of membrane samples were measured using an Instron Model 1122 instrument, in accordance with ASTM D 638-91. Membrane samples were oven dried, tested, fully hydrated by boiling in deionized water and then retested. Table IV provides the average normalized stresses at maximum load for the various sample conditions.

Nafion 117 and GORE-SELECT tensile strengths are fairly similar in the dried state. Upon hydration, however, the Nafion 117 ionomer loses over half of its strength due to the "plasticization" of the membrane by the rather substantial water component. While the ionomeric component of the GORE-SELECT membrane would be similarly compromised, the loss in the hydrated membrane strength is quite modest because the reinforcement component of the membrane is unaffected by the presence of water.

Table IV. Membrane tensile strengths.

| Membrane      | Thickness (µm) | Transverse Direction (Pascals x 10^7) | Loss (%) | Machine Direction (Pascals x 10^7) | Loss (%) |
|---------------|----------------|---------------------------------------|----------|------------------------------------|----------|
| Nafion 117    | 180-200        | 2.47^a 0.95^b                          | 62       | 2.98^a 1.39^b                      | 53       |
| GORE-SELECT   | 20^c           | 2.39 1.77                              | 26       | 3.44 3.25                          | 6        |

^a Based on a 180 µm dry thickness.
^b Based on a 200 µm fully hydrated thickness.
^c Thicknesses are relatively invariant to hydration state.

FUEL CELL TESTING

Several of the available membrane thicknesses were tested in 5 cm² fuel cell hardware. The single-cell components, hardware, testing equipment, and membrane catalyzation process for low platinum loadings (< 0.2 mg Pt/cm²/electrode) are for the most part similar to those described previously. A 20 µm thick GORE-SELECT membrane, with an 1100 EW ionomeric component, was catalyzed in this manner with 0.14 mg Pt/cm²/electrode. Polarization and high frequency resistance curves for the cell operating on H₂/Air after about 210 hours of continuous operation are shown in Figure 1. Typical humidification conditions of anode/cathode humidifiers of 105/80°C were used. Under these conditions, Figure 1 suggests that the cell evidently dried out slightly at low
current densities, but quickly recovered with the increase in current density. Fairly quickly, the cell resistance stabilized at a low value of only 0.06 Ω cm², of which, Table I suggests that about 0.04 Ω cm² is attributable to the membrane. Shortly after the data for Figure 1 were acquired, a testing equipment mishap terminated the test (after about 240 h total).

More extensive testing was accomplished with a 12 μm thick, 900 EW (ionomeric component) GORE-SELECT membrane with a GORE-CARBEL™ carbon composite cathode that was catalyzed with 0.2 mg Pt/cm² at W. L. Gore and an anode prepared at Los Alamos. Polarization curves for varying reactant pressures are shown in Figure 2. At the higher pressures, about 0.8 W/cm² maximum power was attained. Even at a low cathode air pressure of only 1.2 atm, the cell yielded a commendable 0.45 W/cm². Life test performance (ongoing 3000 h), as indicated by the current density at a continuous 0.5 V (Tcell = 80°C, H₂/Air = 2.8/4.2 atm), is shown in Figure 3. Long term performance of the cell has been quite good and the high-frequency cell resistances were also stable and uniformly below 0.06 Ω cm². The early variations in the current density evident in Figure 3 are primarily due to variations in the humidification conditions. In this cell, lower levels of humidification than are typically optimal for 5 cm² cells provide improved performance when operating under maximum power conditions. For example, the increase in performance evident at about 700 h resulted after the cathode humidifier temperature was decreased from 80° to 25°C. In contrast, lowering the anode humidifier temperature substantially below 90°C does impair the performance of the cell. It still may be possible to realize a non-humidified system with these membranes on a larger scale, since we find that larger cells invariably require less external humidification than these 5 cm² ones.

Concerns of excessive reactant cross-over or membrane failure are common with such thin membranes. Even minute defects could become potential failure sites in very thin membranes. While routine testing for pin-holes eliminates some difficulties, composite membranes have a natural advantage in minimizing weak spots. In the limited testing accomplished, the cells with the 12 and 20 μm GORE-SELECT membranes, catalyzed with thin-film catalysts layers by either the Los Alamos process¹¹ or at W. L. Gore, demonstrated reasonable open circuit voltages of at least 0.92 V and did not experience membrane failures. An even thinner membrane, 5 μm thick, is available but only limited testing has thus far been accomplished.

DISCUSSION

For the most part, the fuel cell membranes currently under consideration for commercial products are not particularly thin because of concerns about durability and cross-over in the operating cell. However, these types of high performance membranes are not reinforced and depend upon the entanglement of the ionomer chains for their structural integrity. Naturally, mechanical properties are compromised when the membranes are well hydrated and heated somewhat, such as might be expected in fuel cell applications. While it is possible to obtain good, long term cell performance with some of the thin, non-reinforced, perfluoroionomer membranes,¹¹ they are clearly more susceptible to cross-over and failure than their thicker brethren. On the other hand, in the case of a reinforced membrane, the structural element is relatively unaffected by heat and hydration and can provide a stable base for the ionomeric element. Table IV demonstrates the increase in strength of a fully hydrated membrane over that of the
relatively robust 1100 EW Nafion product. This advantage is not only relevant for the operating fuel cell but also in membrane/electrode assembly fabrication and cell assembly.

A significant advantage of the reinforced GORE-SELECT products is that the dimensional stability of the membranes in the x-y plane is relatively unaffected by the hydration level of the membrane, as is shown in Table III. This may be important in types of fuel cell electrodes in which the catalyst layer is bonded to a relatively rigid structure that will not easily accommodate variations in the membrane hydration state and may tend to delaminate. The x-y stability may be even more advantageous from a manufacturing point of view. A membrane that maintains the same dimensions independent of the hydration state should simplify the manufacturing process, increase part consistency, and improve product reliability.

While there may be some material consumption factors, the primary motivation for developing thin membranes is to enhance fuel cell performance. This is realized by not only a decrease in the membrane resistance but also by more effective water management within the membrane. As shown in Table I, the conductances of the GORE-SELECT membranes are substantially higher than Nafion 117, the baseline material for comparison. Although Table I also demonstrates that the inherent bulk conductivities of the GORE-SELECT membranes are relatively low, their high membrane conductances are made possible by the extreme thinness of the membranes. Table IV suggests that water transport is not adversely affected by the presence of the reinforcement component. Good water transport is also indicated in the operating cells by a lack of increase in the cell resistance with current density, as is shown in Figure 1.

CONCLUSION

Conventional high performance fuel cell membranes require that both structural and electrochemical functions be achieved by a single material. As is observed in the chlor-alkali industry, there are advantages to using membranes with distinct structural and functional components. This dual-component advantage has apparently been realized for fuel cells with the GORE-SELECT membranes. The thin, yet durable, membranes made possible by the composite construction provide the high ionic conductances and enhanced water transport necessary for high performance fuel cells. Other desirable properties include minimal dimensional changes during hydration/dehydration cycles and the maintenance of good mechanical properties in the fully hydrated membrane.

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FIGURES

Figure 1. Polarization and high-frequency resistance curves for a 0.14 mg Pt/cm² catalyzed 20 μm thick, 1100 EW (ionomeric component) GORE-SELECT membrane. Tcell = 80°C, H₂/Air = 2.8/4.2 atm.
Figure 2. Polarization curves for a 0.20 mg Pt/cm² catalyzed 12 μm thick, 900 EW (ionomeric component) GORE-SELECT membrane at various reactant pressures. T_{cell} = 80°C.

Figure 3. Life test current density at 0.5 V of the cell shown in Figure 2. T_{cell} = 80°C, H₂/Air = 2.8/4.2 atm.