Measurement of Water Transport Properties Through Membrane-Electrode Assemblies

I. Membranes

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A method using a hydrogen pumping cell to measure the electro-osmotic drag (EOD) coefficient of Gore-Select membranes is described. This technique was verified with the measurement of Nafion membranes, yielding results comparable with those reported in the literature and hence supporting its validity for various types of membranes. The EOD coefficient of Gore-Select membranes was measured to be 1.07 over the wide relative humidity range between ~40% and 95%. An approach was also proposed to characterize the water concentration at the interface between the membrane and the cathode catalyst layer using high-frequency resistance measurement in an operating fuel cell. Based on the information of water concentrations on both sides of the membrane and the water diffusive flux across the membrane, the water diffusion coefficient of Gore-Select membranes was experimentally determined. It was found that the water diffusion coefficient of Gore-Select membranes is roughly half that of Nafion membranes based on the best fit of our available data in this work.
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Water management is an important issue in polymer electrolyte fuel cells (PEFCs). To attain optimal fuel cell performance, it is critical to have a good water balance such that the polymer electrolyte is hydrated for sufficient proton conductivity while cathode flooding and anode dehydration are avoided.[1] Figure 1 displays a schematic of water transport through the membrane. Water transport in the membrane occurs by electro-osmotic drag (EOD) of water with protons from the anode to cathode and by diffusion due to the concentration gradient. An additional source of water comes from the reaction of oxygen reduction at the cathode. Both the EOD and water production result in buildup of water near the cathode. Back diffusion of water from the cathode to anode decreases this trend and flattens the water concentration profile across the membrane.[2,3] Therefore, as the two fundamental properties of water transport through the membrane, the EOD and diffusion coefficient should be well understood. These membrane properties are also instrumental for fundamental fuel cell modeling.[4]

Extensive efforts have been made to investigate these properties of Nafion and other proton exchange membranes (PEMs).[2-24] The EOD coefficients have been measured for liquid-[2,3,5-11] and vapor-equilibrated[12-14] membranes by various techniques including concentration cell method,[2,5-7,13] direct methanol fuel cell (DMFC) analysis,[8,9] electrophoretic NMR technique,[10] and streaming potentials,[14] etc. LaConti et al.[5] used a pair of Ag/AgCl electrodes to derive a constant current across a membrane in contact on both sides with a 0.1 M HCl aqueous solution and obtained the EOD by measuring the transferred water volume using capillaries. They reported that the EOD of Nafion membranes linearly increased from 0 (in a dry state) up to 4 to 5 (in the fully hydrated state) and did not show a temperature dependence. Zawodzinski et al.[2,6] used a similar apparatus with Pd/H electrodes and obtained EOD equal to 2.5 and 0.9 at 30°C for a fully hydrated Nafion 117 membrane (i.e., $\lambda = [H_2O]/[SO_3H] = 22$) and a treated sample ($\lambda = 11$, dried at 105°C before the measurement), respectively. Recently, Cussler et al.[7] followed the same procedure to measure the EOD of Nafion 117, polystyrene sulfonic acid (PSSA), and polybenzimidazole (PBI) membranes at fully hydrated state in the presence of phosphoric, sulfuric, and hydrochloric acid. Their results showed that the EOD of Nafion membranes ranged between 3 and 6 depending on external acid concentration, and the values for PSSA and PBI membranes were about 2.0 and less than 1.0, respectively. Xie and Okada[3] measured EOD equal to 2.6 for a fully hydrated Nafion 117 membrane

using the streaming potential method. Ren et al.[8,9] developed a measurement for fully hydrated Nafion 117 membranes in DMFC and found that the EOD strongly increased with temperature from 2.0 at 15°C to 5.1 at 130°C. Ise et al.[10] applied electrophoretic NMR (ENMR) method to measure the EOD of Nafion and polyetheretherketone (PEEK) membranes and attained the values equal to 2.6 for Nafion ($\lambda = 20$) and 3.1 for PEEK membranes ($\lambda = 40$). Motupally et al.[11] utilized a HCl gas electrolyzer to measure EOD of Nafion membranes with one side contact with liquid water and the other side with gaseous anhydrous HCl. They fitted the EOD from a model that is equal to 3.84 at 80°C and 3.50 at 60°C, respectively.

The reported EOD values of the membranes equilibrated with water vapor are much smaller than those of the same membranes equilibrated with liquid water. Fuller and Newman[12] experimentally determined the EOD of Nafion 117 membrane using a concentration cell. They concluded that its value at 25°C decreased from 1.4 toward zero as the activity of water in the vapor phase dropped from unity to zero. Zawodzinski et al.[13] adopted Fuller and Newman's method and observed that the EOD values were closely equal to 1.0 for Nafion and other PFSA membranes equilibrated with water vapor over a large range of activities. Weng et al.[14] utilized a specially designed cell consisting of a large gas reservoir and a small gas chamber and determined the EOD of the membranes from the gas chamber's partial pressure change. They reported that the EOD for Nafion/H_3PO_4 membrane varied from 0.2 to 0.6, but was essentially
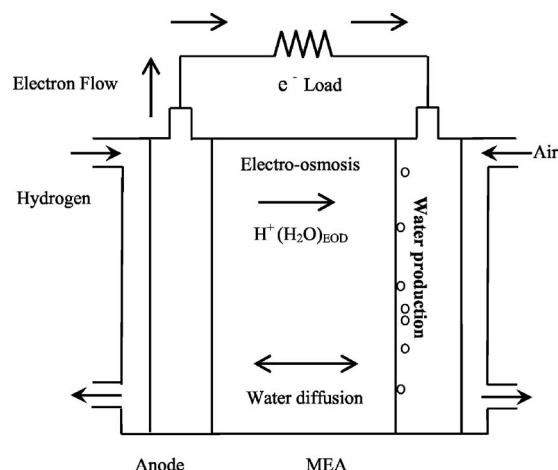
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Figure 1. Schematic of water transport through the membrane.

zero for phosphoric acid-doped PBI membranes over the range of the water activity between 0.05 and 0.35 at temperatures above 125°C.

The water diffusion coefficients of Nafion membranes relative to both a concentration and a chemical-potential driving force have been measured by such methods as NMR,[2,6,15-17] transient sorption kinetics,[18,19] steady state permeation,[20-23] and others.[24,25] The values of the self-diffusion coefficient measured by Zawodzinski et al.,[2,6,15] Zelsmann and Pineri,[16] and Inglefield and co-workers[17] using NMR techniques, the intradiffusion coefficients measured by Morris and Sun[18] and Yeo and Eisenberg[19] using the transient sorption kinetics method, and the Fickian diffusion coefficients reported by Fuller and Newman,[20] Rivin et al.,[21] Motupally et al.,[22] and Ye and LeVan[23] using steady state permeation methods, varied significantly with one another. The diffusion coefficients from Zawodzinski et al.,[2,6,15] Springer et al.,[24] Morris and Sun,[18] Motupally and co-workers,[22] and Ye and LeVan[23] pass through a maximum at a water content between $\lambda = 3$ and 4. In contrast, most of the other researchers' results show a monotonic increase of the diffusion coefficient with water content. For the dependence of the diffusion coefficient on the membranes' water content, Fuller and Newman[20] obtained a linear relationship, whereas Zawodzinski et al.,[2,6,15] Springer et al.,[24] Rivin et al.,[21] Motupally and co-workers,[22] and Ye and LeVan[23] proposed more complicated functional formulas.

It can be seen from the above discussion that the EOD values and water diffusion coefficients for Nafion membranes reported in the literature show a large scatter, and almost all of them were obtained ex situ due to the difficulty in performing measurements in an operating fuel cell. To account for the effects caused by current loads and the special fuel cell environment, measurements in an operating fuel cell are certainly desirable.

In recent years, Gore-Select membranes have been widely used in state-of-the art membrane electrode assemblies (MEAs) because of their high performance and good reliability.[26-28] However, their water transport properties have not been reported, and researchers had to assume that they have similar properties to Nafion membranes due to lack of data in their modeling work.[29]

In this paper, we present techniques to measure the EOD and water diffusion coefficients of Gore-Select membranes in an operating fuel cell and to investigate the membrane's actual hydration state under current loads. Our objectives are (*i*) to provide water transport data of Gore-Select membranes to enable proper water management in the fuel cells based on Gore-Select membranes and MEAs and (*ii*) to present techniques for determination of water transport properties, i.e., EOD and diffusion coefficient, under in situ fuel cell conditions for a variety of membranes, e.g., hydrocarbon membranes.

Theory

When a fuel cell is charged with a direct current (dc) and hydrogen gas is supplied on both anode and cathode sides, the following two reactions take place at the anode and cathode, respectively

$$H_2 \leftrightarrow 2H^+ + 2e$$

$$2H^+ + 2e \leftrightarrow H_2$$
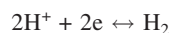
Hydrogen is oxidized into protons at the anode side. The protons are transported through the MEA to the cathode, where they are reduced into hydrogen. With proton transport water molecules are dragged from the anode to cathode as a form of $H^+(H_2O)_{EOD}$. The water molecules build up at the cathode, and back diffusion may occur due to the water concentration gradient. The back diffusion of the water diminishes with the membrane thickness. When the membrane is sufficiently thick, it becomes negligible. The EOD of the membrane can thus be determined by measuring the water flux through the thick membrane at constant currents. At steady state, the relationship between the water flux aroused from EOD and the imposed current density can be described by[1]
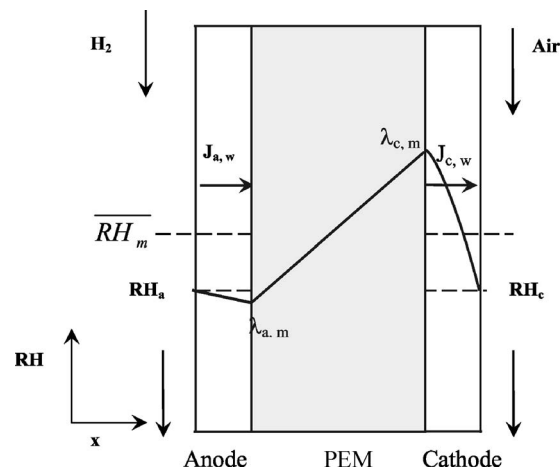

Figure 2. Water concentration profile through the MEA in an operating fuel cell.

$$J_{EOD} = EOD\frac{I}{F} \qquad [1]$$

where J_{EOD} (mol/m^2 s) is the water flux through the membrane, I the current density (A/m^2), F the Faraday constant, and EOD the electro-osmotic drag coefficient, J_{EOD}, can be obtained from water balance, i.e.

$$J_{EOD} = J_{a,in} - J_{a,out} = J_{c,out} - J_{c,in} \qquad [2]$$

where $J_{a,in}$, $J_{a,out}$, $J_{c,in}$, and $J_{c,out}$ (mol/m^2 s) are the water fluxes of the gas streams on the anode and cathode side and at the inlet and outlet, respectively. If a linear relationship exists between $J_{EOD} \times F$ and current density, the value of EOD can then be obtained from the slope of the line.

One advantage of using the hydrogen pumping mode to measure EOD lies in that the hydrogen pumping cell does not generate net water as opposed to a H$_2$/air fuel cell so that water buildup on the cathode and hence water back diffusion through the membrane is minimized. This enables more accurate determination of EOD values.

In contrast, measurement of water diffusion coefficient in Gore-Select membranes was performed in an operating H$_2$/air fuel cell using relatively thin membranes. A schematic of the water concentration profile through the MEA is shown in Fig. 2. Due to the EOD and water production from oxygen reduction reaction, water builds up at the interface between the membrane and CCL forming a concentration profile shaped like a watershed. The water concentration at the membrane/CCL interface, which is higher than that in the cathode gas channel, must be known in order to determine the water diffusion coefficient through the membrane. As the binary water diffusion coefficient in hydrogen is about four times that in air,[30,31] and the water flux through the anode side ($J_{a,w}$) is much smaller than that through the cathode side ($J_{c,w}$) due to additional water production at the cathode, the water concentration gradient through the anode catalyst layer is believed to be much smaller than that through the cathode. Thus, it is assumed that the membrane on the anode side is equilibrated with water vapor in the anode gas channels as controlled through a fuel cell test station.

It has been reported in literature[24,32] that the water concentration profile within a thin membrane is approximately linear. Thus, the water concentration at the membrane/CCL can be obtained from the following equations

$$\lambda = f_1(a) \qquad [3]$$

$$\lambda = \lambda_{a,m} + (\lambda_{c,m} - \lambda_{a,m})\frac{x}{l_m} \qquad [4]$$

$$\kappa = \kappa(\lambda) \qquad [5]$$

$$\bar{R}_m = \int_0^{l_m} \frac{dx}{\kappa(\lambda)} = \frac{l_m}{\lambda_{c,m} - \lambda_{a,m}} \int_{\lambda_{a,m}}^{\lambda_{c,m}} \frac{d\lambda}{\kappa(\lambda)^-} \qquad [6]$$

where a is the activity of water vapor in the gas phase. λ, $\lambda_{a,m}$, and $\lambda_{c,m}$ are the water contents of the membrane expressed as molar ratio of water molecules to charged SO_3H^+ sites (mol H_2O/mol SO_3H^+) at a transverse position, x, and at the interfaces between the membrane and anode as well as cathode catalyst layers, respectively. l_m is the thickness, and κ is the conductivity of the membrane. $\bar{R}_m$ is the membrane resistance measured by high-frequency resistance (HFR).

The other term needed for determination of water diffusion coefficient through a membrane is the diffusive flux, which can be measured by performing water balance on the anode and cathode sides, respectively. That is

$$J_{net} = J_{a,in} - J_{a,out} \qquad [7]$$

and

$$J_{net} = J_{c,out} - J_{c,in} - J_{prod} \qquad [8]$$

where J_{net} is the net water flux through the membrane, which is the sum of the EOD and back diffusion terms, i.e.

$$J_{net} = J_{EOD} + J_D \qquad [9]$$

The flux of water produced at the cathode is calculated as

$$J_{prod} = \frac{I}{2F} \qquad [10]$$

Hence, the water flux due to back diffusion can be determined by Eq. 9 based on the predetermined EOD value and water balance on either the anode or the cathode side. Simultaneously, this water flux caused by back diffusion can be expressed by[24,33,34]

$$J_D = -\frac{I}{l_m} \int_{C_{a,m}}^{C_{c,m}} D_m dC_- \qquad [11]$$

where D_m (m²/s) is the water diffusion coefficient of the membrane. $C_{a,m}$ and $C_{c,m}$ (mol/m³) are the water concentrations at the interface between the membrane and the anode and CCL, respectively. Eq. 11 can be rearranged as

$$J_D = -\frac{\rho_m}{EW_m l_m} \int_{\lambda_{a,m}}^{\lambda_{c,m}} D_m d\lambda_- \qquad [12]$$

where ρ_m and EW_m are the membrane's density (kg/m³) and equivalent weight (kg/mol), respectively. The water diffusion coefficients of the membrane can then be experimentally obtained when the EOD and $\lambda_{c,m}$ become available.

Experimental

Materials.— Thick MEAs with multilayer Gore-Select membranes (200 μm thick) and multilayer Nafion 115 membranes (250 μm thick) were used in the hydrogen pumping cell to measure the EOD of these membranes. These MEAs were self-prepared from 8 layers of 25 μm Gore-Select membranes and two layers of Nafion 115 membranes, respectively. The multilayer membranes were made by hot pressing at 125°C and 100 kgf/cm² for 3 min. Great care was taken to ensure that no air bubbles were formed between layers and that the whole membrane had an excellent integrity. The catalyst-coated membranes (CCM) were fabricated by a decal technique.[35,36] The catalyst ink was prepared by mixing carbon supported catalyst (40% Pt/Vulcan XC72, E-TEK, Inc., Somerset, NJ) with an appropriate amount of Nafion solution (5 wt % in alcohols/water, Aldrich). The ink mixture was first coated onto a Telfon substrate and then was transferred onto both sides of the membrane by hot pressing. The catalyst loading for both the anode and cathode is
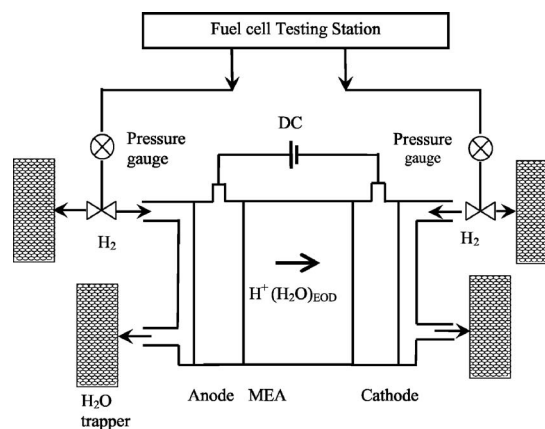
0.4 mg/cm². Commercially available MEAs, 5 cm² Gore-PRIMEA-18 and -25 (12 μm catalyst layer, 0.4 mg/cm² loading, and 18 and 25 μm membrane thickness, respectively) were used in the fuel cell to determine water diffusion coefficient through Gore-Select membranes. The gas diffusion layers (GDL) in both hydrogen pumping cell and fuel cell were self-fabricated from TGPH-60 Toray carbon paper by a paste casting process. The paste was prepared by dispersing a certain amount of poly(tetrafluoroethylene) (PTFE) powder into an appropriate carbon powder solution.

Experimental setup and apparatus.— A schematic diagram of the experimental setup for the hydrogen pumping cell is illustrated in Fig. 3. A single cell fixture of 5 cm² with serpentine flow channels was used as a "differential cell." Arbin 12-channel integrated FCTS Fuel Cell Testing System (Arbin Corporation, College Station, TX) was used as a dc power source. Teledyne MEDUSATM RD 890C 50 W Fuel Cell Test Station (Teledyne Energy Systems, Inc. Hunt Valley, MA) was employed for gas supply, humidification, and electronic load (for the fuel cell mode). Solatron 1255B frequency response analyzer (FRA, Solartron Inc., Houston, TX) and the Teledyne Test Station were combined for HFR measurements at various current densities. ZView softare (Scribner Associates, Inc., Southern pines, NC) was used to analyze the collected ac impedance data.

The MEAs were sandwiched between GDLs, and the cell was assembled by application of a uniform torque of 20 in. lbs between the two copper plates on either side. Two silicon rubber gaskets were used to ensure good sealing. The cell, pressure gauges, and tubing connections were all carefully checked to ensure a leak-free system. Water flux measurements at the inlet and outlet on the both sides of the fuel cell were carried out by trapping water in the gas streams into two laboratory gas-drying columns filled with Drierite desiccants (W. A. Hammond Drierite Co. Ltd, Xenia, OH). A 100% water trapping efficiency was attained within the period of each experiment. A mass balance with 0.01 g accuracy was used to weigh the amount of the water trapped.

Experimental procedure.— The success of the experiments for measuring EOD in the hydrogen pumping cell and determination of water diffusion coefficient in an operating fuel cell hinges on the accuracy of water flux measurement and on the stability of the humidifiers' performance. Special care was taken to improve the experiments' reliability. Before the initiation of measurements with both hydrogen pumping cell and fuel cell operation, the MEAs were sufficiently activated by preconditioning for over 10 h until a stable performance was achieved so that the measurements were obtained at the MEA's steady state. Two gas streams (H_2/H_2 and H_2/air for hydrogen pumping and fuel cell operation, respectively) with a sufficiently large stoichiometry rate and roughly equal relative humidity (RH) were passed on the both sides of the cell. A good compro-
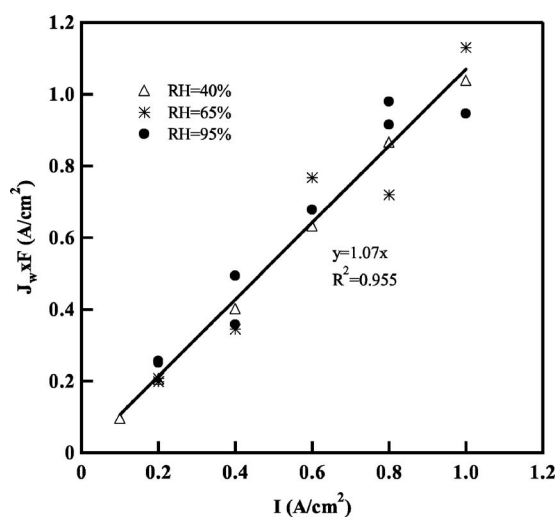

Figure 3. Schematic diagram of the hydrogen pumping cell.

Figure 4. Flux of water by EOD vs current density for Gore-Select multilayer membranes.
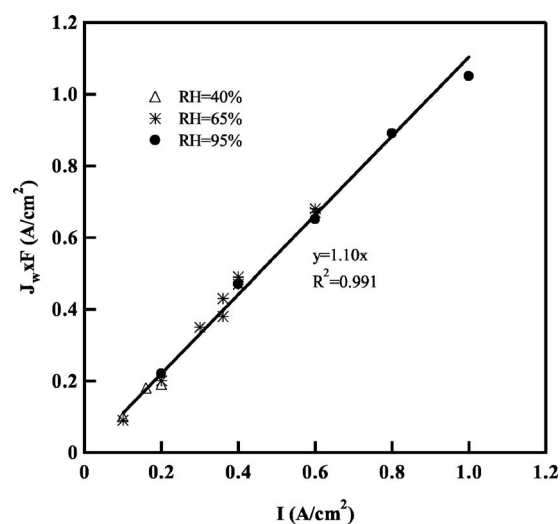

Figure 5. Flux of water by EOD vs current density for Nafion multilayer membranes.

mise was made between the uniform RH level along the gas channels and the reliable measurement of water flux through the membrane. To eliminate the effect of hydraulic pressure difference across the membrane on water transport, the pressures on the anode and cathode side were kept equal using the backpressure regulators during each measurement. To reduce the influence of the humidifiers' unstable performance and improve the measurement accuracy, the amount of the trapped water from the gas streams was usually more than 10 g. The water flux measurement for the inlet gas streams was carried out immediately after that for the outlet gas streams, and the readings of the pressure gauges were kept identical in the whole measurement process such that the possible effect of pressure on the actual performance of the humidifiers was eliminated. In the operational fuel cell, the measurement of HFR values under various conditions was continuously carried out within the possibly shortest time in order to minimize the effect of performance degradation, if any.

Results and Discussion

Electro-osmotic drag coefficient.— The EOD values for Gore-Select and Nafion membranes were measured at 80°C under atmospheric pressure. The membranes were equilibrated with coflowing hydrogen gas streams of equal RH and of the same flow rate coflowing in the gas channels on the both sides of the cell. The average RH level of the gas streams varied from about 40% to 95%. At each level, the RH variance along the differential cell was maintained within 5–7% using a sufficiently large gas flow rate. The stoichiometry of hydrogen gas streams fell in the range between 20 and 60 depending on the RH level. The higher the RH level, the smaller the gas flow rate. The RH on the anode side decreased due to the EOD while that on the cathode increased by a similar amount. The water balance between the anode and cathode achieved in most of the experiments were greater than 98.5%. To minimize further the inaccuracy caused by slight mass imbalance, the water flux through the membrane was calculated from the average value based on the both sides instead of on either side. At high RH levels the imposed current densities varied over a large range between 0.1 and 1.0 A/cm^2 while at lower RH levels smaller current densities were applied due to much higher membrane resistance.

Because the membranes used in this study are sufficiently thick, the water flux due to back diffusion was negligible compared to the EOD. Plots of the water flux through the membrane vs the current density at various RH levels are shown in Fig. 4 and 5 for Gore-Select and Nafion membranes, respectively. It can be seen that a good linear relationship exists between the water flux and the cur-

rent density for both membranes. The EOD values as obtained from the slope of the lines are 1.07 and 1.10 for Gore-Select and Nafion membranes, respectively.

Note that the present method of measuring EOD critically depends on the membrane thickness. Too thin a membrane will give rise to the influence of back diffusion and hence erroneous EOD coefficient. Our experimental data showed that the EOD value so obtained for a 25 μm Gore-Select membrane was only 0.51, as shown in Fig. 6. In addition, deviation from the linearity is clearly seen for higher current densities at 95% RH.

We validated the methodology of hydrogen pumping cell with the measurement of Nafion membranes. A summary of the results reported in the literature for EOD values of Nafion membranes is shown in Fig. 7. If not mentioned, they were for Nafion 117 membrane at ambient temperatures. Note that the EOD value we obtained for Nafion 115 membrane at 80°C agrees well with that reported by Zawondzinski et al. for Nafion 117 at 30°C,[13] which has been widely used in the literature (see Ref. 4 and references therein). They are all closely equal to 1.0 over a large range of water content albeit at different temperatures. The EOD value of Gore-Select membranes, measured for the first time to the best of our knowl-
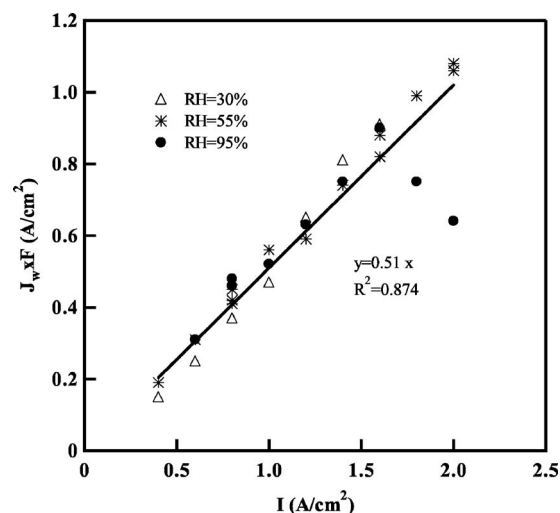

Figure 6. Net flux of water vs current density for Gore-Select 25 μm membrane in a hydrogen pumping cell.
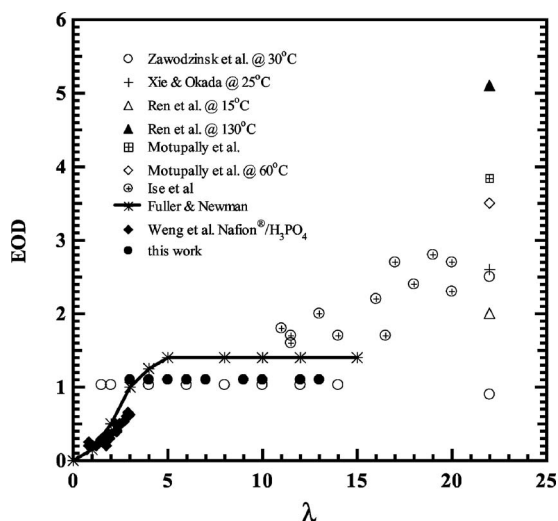
Figure 7. Comparison of Nafion membrane's EOD measured in this work with those in the literature.

Figure 8. Measured membrane resistance in an operating fuel cell under current load at various RH levels.

edge, is identical to that of Nafion membranes. This demonstrates that the composite PTFE reinforced structure of the Gore-Select membranes does not affect the membrane's EOD.

HFR and hydration state of the membrane in the operational fuel cell.— The fuel cells with 5 cm^2 Gore-PRIMEA-18 and -25 MEAs were operated at 80°C under atmospheric pressure over a large RH range between 35% and 100% (the average RH value based on the gas streams of the both sides). At each RH level they were operated at three current densities of 0.4, 0.8, and 1.2 A/cm^2, respectively. The flow rates of hydrogen and air are 0.28 and 0.70 standard liters/min (slm), respectively. It was found that a good compromise could be maintained between a uniform RH level and a reliable measurement of water flux through the membrane under these conditions. A similar practice to that used in the hydrogen pumping cell was employed for the water flux measurement. The ac impedance spectroscopy for HFR values of the operating fuel cells was carried out by incorporation of Teledyne Test Station with FRA, which can perform measurements under high current loads. The ac impedance data were collected by frequency scan from 10 kHz to 10 Hz using the ac amplitude of 10% of the dc current. The high-frequency impedance at 1 kHz was chosen as the sum of the membrane's resistance and the related contact resistances.[37,38] Given a proton conductivity of the membrane at 100% RH characterized independently, the total contact resistance was calibrated from the cell's HFR and the membrane's resistance at 100% RH level, i.e., contact resistance = cell HFR − membrane resistance at 100% RH. We assume that the term of the total contact resistance was a constant independent of current density and gas RH over the period of the experiments. Then, the membrane resistance under a current load and at a RH level was obtained from the cell's HFR. It was compared with that at open circuit under the same conditions (e.g., RH level, gas flow rates, etc.), and, consequently, the effect of the current load on the resistance and thus on the hydration state of the membrane was clearly differentiated. Because the ac impedance measurement for an operating fuel cell needs to be carried out under a dc current load above a certain value, the HFR value at "open circuit" was actually achieved at a very small current density of 0.06 A/cm^2. Figure 8 displays dependence of the obtained membrane's resistance on the RH level at three current densities for Gore-PRIMEA-18 MEA. It was found that the resistance of the membrane under current load was smaller than that of the membrane at open circuit, and the difference between them increased with the current density. This trend became more obvious at lower RH levels. It can thus be found that the hydration state of the membrane under current load is wetter
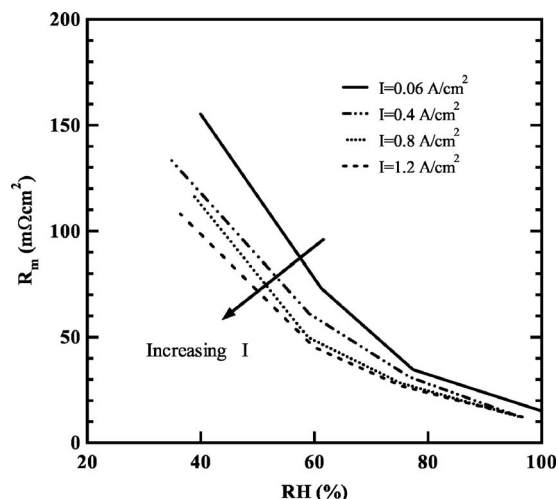
than that of the membrane at open circuit under the same conditions, and this tendency became stronger with increasing current density. Therefore, for a thin membrane as we used in this study EOD does not dehydrate the membrane at the anode. Instead, the net effect of current load is that the membrane becomes wetter due to the production of water at the cathode and the strong back diffusion sufficiently compensating for EOD. This observation is in agreement with those reported in the literature. Buchi and Scherer[39,40] reported that the resistance decreased with current density for the thin Nafion 112 membrane but increased for thick membranes.

Water diffusion coefficient of Gore membranes.— To characterize water diffusion coefficient of the membrane, we need to obtain accurately the water concentration at the membrane/CCL interface from HFR measurements via the membrane's proton conductivity as a function of water activity such as the following

$$\kappa = 0.12a^{2.80} \qquad [13]$$

Equation 13 was fitted from separate measurements of HFR at open circuit with anode and cathode gases of known water activity, as shown in Fig. 9.

Considering the chemical similarity in functional groups between Gore-Select and Nafion membranes, we assume that their diffusion
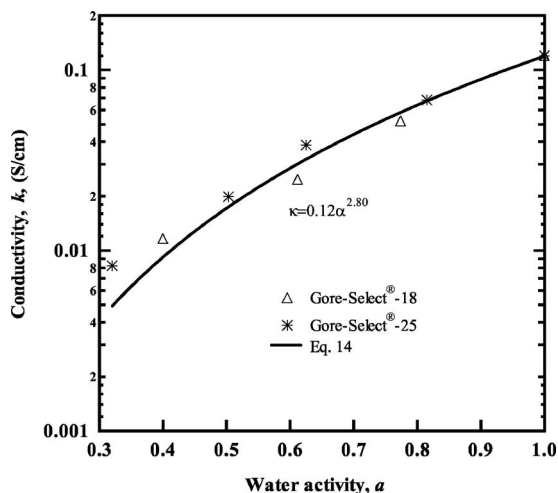

Figure 9. Proton conductivity measured by HFR at various water content levels.
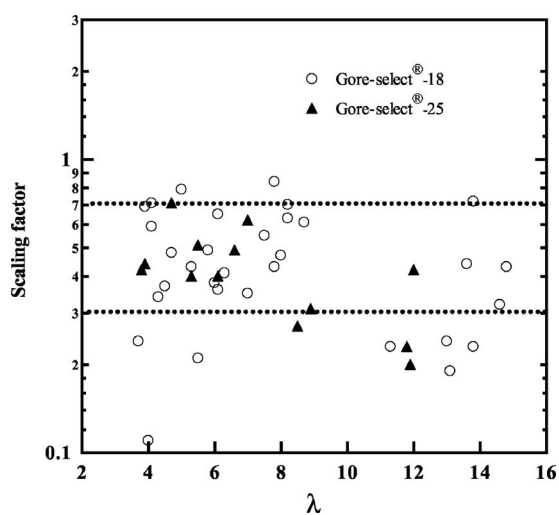
Figure 10. Scattering of the scaling factor for the water diffusion coefficient of Gore-Select membranes relative to that of Nafion membranes.

Figure 11. Comparison of water diffusion coefficients between Gore-Select and Nafion membranes.

coefficients exhibit a similar function of water content and differ only by a scaling factor, k, to account for the microscopically reinforced composite nature of Gore-Select membranes. Springer's formula was chosen as an expression of the water diffusion coefficient of Nafion membranes because it has been widely adopted in the literature.[4,11,24,41] Thus, the formula for water diffusion coefficient of Gore-Select membranes can be given by

$$D_{\lambda>4} = k \times 10^{-6} \exp\left[2416\left(\frac{1}{303} - \frac{1}{273+80}\right)\right]$$

$$\times \ (2.563 - 0.33\lambda + 0.0264\lambda^2 - 0.000671\lambda^3) \quad [14]$$

The values of k at various water content levels ($\lambda > 4.0$) were experimentally determined by using Eq. 12. As shown in Fig. 10, the k values are smaller than 1.0 and mostly fall in the range between 0.3 and 0.7. Much scattering of k values occurred to the data points at high water contents because it may be more difficult to determine the accurate $\lambda_{c,m}$ values due to the possible presence of liquid water. From the best fit of our available data we obtained the value of k equal to 0.50. This implies that the water diffusion coefficient of Gore-Select membranes is half that of Nafion membranes.

A comparison of the diffusion coefficients of Gore-Select membranes with those of Nafion membranes reported in the literature is shown in Fig. 11. Considering the large variation in the reported results for Nafion membranes, the scattering of the scaling factor, k, for Gore-Select membranes may be deemed satisfactory. Note also that our results were obtained from an operating fuel cell, which may reveal more reliably the membrane's water diffusion property in the fuel cell environment.

Conclusions

In this work, the EOD of Gore-Select membranes was measured to be 1.07 over a large RH range between 40% and 95% using a hydrogen pumping cell. This technique was verified with the measurement of Nafion membranes and the results were found to be comparable with those in the literature. The water concentration at the membrane/CCL interface as well as the actual hydration state of the membranes in an operating fuel cell was characterized with HFR measurement. It was found that for a fuel cell with thin membranes as used in the present study, EOD does not dehydrate the anode side of membranes. Rather, the membrane is wetter due to the production of water at the cathode and strong back diffusion to the anode. The water diffusion coefficients of Gore-Select membranes have been experimentally determined in situ in an operating fuel cell. According to the best fit of our data, they are roughly half those of Nafion
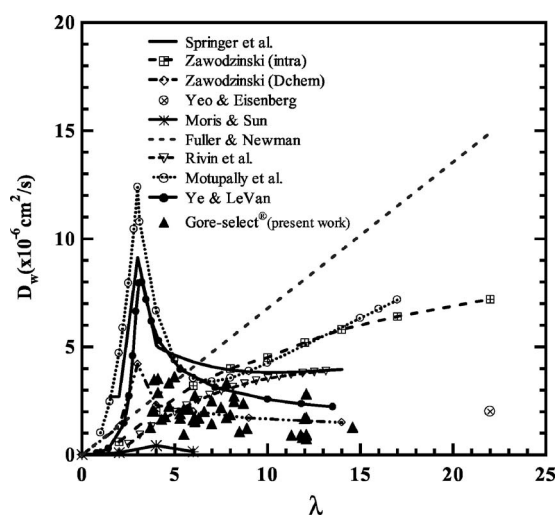
membranes at similar levels of water content. The fundamental properties of water transport through Gore-Select membranes reported herein are useful not only for proper water management and also as input parameters in models for Gore MEA-based fuel cells.

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