
A comparison of physical properties and fuel cell performance of Nafion and zirconium phosphate/Nafion composite membranes

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Abstract

The physiochemical properties of Nafion 115 and a composite Nafion 115/zirconium phosphate (∼25 wt.%) membranes are compared. The composite membrane takes up more water than Nafion at the same water activity. However, the proton conductivity of the composite membrane is slightly less than that for Nafion 115. Small angle X-ray scattering shows that the hydrophilic phase domains in the composite membrane are spaced further apart than in Nafion 115, and the composite membrane shows less restructuring with water uptake. Despite the lower proton conductivity of the composite membranes they display better fuel cell performance than Nafion 115 when the fuel cell is operated at reduced humidity conditions. It is suggested that the composite membrane has a greater rigidity that accounts for its improved fuel cell performance.

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I. Introduction

Polymer electrolyte fuel cells based upon perfluorinated membranes have typically been operated in a temperature range between approximately 50 and 90 ◦C [1–3]. This temperature range is a compromise between competing factors. Increasing the operating temperature above room temperature will improve the electrode kinetics of the oxygen reduction reaction [4,5]. The upper limit of temperature results from the difficulty in maintaining membrane water content at temperatures at or above 100 ◦C. In addition, temperatures above the polymer glass transition temperature (∼110 ◦C for protonated Nafion) can cause polymer chain rearrangements, which can lead to structural changes in the membrane and lower the membrane stability, performance, and lifetime [6–8].

Polymer membranes able to operate above 120 ◦C could benefit from both enhanced carbon monoxide (CO) tolerance and improved heat removal [9]. The most significant barrier to running a polymer electrolyte fuel cell at elevated temperatures is maintaining the proton conductivity of the membrane. Higher temperature increases the water vapor pressure required to keep a given amount of water in the membrane, thereby increasing the likelihood that water loss will occur and significantly reduce proton conductivity. The conductivity of a dry membrane is several orders of magnitude lower than a fully saturated membrane. A number of alternative strategies have been investigated to maintain membrane conductivity in a dehydrating environment (i.e. elevated temperature and reduced relative humidity). Two recent reviews summarize these strategies well [5,10].

The addition of an inorganic material into a polymer membrane can alter and improve physical and chemical polymer properties of interest (such as elastic modulus, proton conductivity, solvent permeation rate, tensile strength, hydrophilicity, and glass transition temperature) while retaining its important polymer properties to enable operation in the fuel cell. A number of investigators have examined composite membranes for use in polymer electrolyte fuel cells [5,10–25]. The hydration properties of membranes are key characteristics that can influence fuel cell performance. The composite membranes may improve the water-retention properties of these membranes under low humidity conditions.
conditions. The conductivity of perfluorinated sulfonic acid membranes vary over many orders of magnitude depending upon the water activity and temperature. Models for proton conduction in Nafion have been proposed that provide a good semi-quantitative prediction of the conductivity at wa-
ter activities greater than 0.2 [26–27]. However, very little has been done to characterize the conductivity of Nafion above 100 °C or to characterize the proton conductivity in compos-
ite membranes [19]. We have compared water uptake, proton conductiv-
ity, microstructure morphology and fuel cell performance of Nafion and Nafion/zirconium phosphate com-
posite membranes as functions of temperature (80–140 °C) and water activity. We also tested the performance of composite polymer/inorganic membranes (Nafion/zirconium phosphate) in fuel cells at elevated temperatures. In this paper we compare the chemical and physical properties of Nafion membranes and Nafion/zirconium phosphate composite membranes to elucidate the role of zirconium phosphate in altering the membrane performance in PEM fuel cells.

2. Experimental

2.1. Membrane preparation

Nafion/zirconium phosphate (Nafion/ZP) composite membranes were prepared using Nafion® 115 films (Du-
Pont) as the base material. To obtain uniform high-purity Nafion membranes as starting material, the membranes were cleaned with a standard treatment procedure: (i) boiling in 3% hydrogen peroxide for 1 h to oxidize organic impurities; (ii) rinsing with boiling water for several hours; (iii) boiling in 1 M sulfuric acid for 1 h to remove any metallic/ionic impurities; and (iv) rinsing again in boiling water to remove any excess acid.

Zirconium hydrogen phosphate (Zr(HPO$_4$)$_2$·H$_2$O) was the desired additive to Nafion-based membranes because of its attributes, including: (i) it has moderate proton conduc-
tivity when humidified (~10$^{-3}$ S/cm) [28–37]; (ii) it is a Bronsted acid with the ability to donate protons; (iii) it is thermally stable to temperatures above 180 °C; (iv) it is hy-
groscopic and hydrophilic; and (v) it is easily synthesized in a manner that is compatible with the chemical and phys-
ical limits of the polymer membrane [24]. In practice the zincium phosphate phase may vary from amorphous to

Zirconium phosphate was incorporated into Nafion using the procedure first described by Grot and Rajendran [14]. The synthesis involves the reaction of a solution of Zr$^{4+}$ ions with phosphoric acid (H$_3$PO$_4$) leading to the precipi-
tation of the insoluble zirconium phosphate. To accomplish this synthesis within the membrane, the procedure takes ad-

dvantage of the fact that Nafion and other perfluorosulfonic

acid ionomers are ion-exchange membranes. The protons are exchanged with zirconium ions and the zirconium ions are subsequently reacted in place with phosphoric acid.

First, the membranes were weighed in the dry state, and then swollen in a boiling methanol–water solution (1:1 (v/v)) to expand the membrane and facilitate ionic diffu-
sion. The membranes were then dipped into a 1 M solution of zirconyl chloride, ZrOCl$_2$ (Aldrich) for several hours at 80 °C. The ZrOCl$_2$ solution diffuses into the membrane and the excess of Zr$^{4+}$ ions within the membrane leads to an exchange with sulfonic acid protons in the membrane. The membranes were then rinsed in cold water to remove the zirconyl chloride solution from the surface and then immersed in 1 M phosphoric acid (H$_3$PO$_4$) overnight at

80 °C. The phosphoric acid has two purposes: (i) it reacts with the Zr$^{4+}$ ions to precipitate insoluble zirconium hy-
drogen phosphate in situ, and (ii) the acidic solution can re-protonate the sulfonate anions to regenerate the acidity of the membrane. The membranes were then repeatedly boiled for several hours in distilled water to remove any excess acid and ZrOCl$_2$ solution. After drying, membrane weight and thickness increased about 25 and 30%, respectively, as compared with the unmodified membrane.

2.2. Physical/chemical characterization

The cross-sections of several Nafion and composite Nafion/zirconium phosphate membranes were analyzed using a Cameca SX50 experimental microprobe to deter-
mine the presence and distribution of zirconium phosphate. Micrographs revealed that the control Nafion contains neg-
ligible quantities of Zr and P, while the composite mem-
bres have Zr and P uniformly distributed throughout the cross-section.

Powder X-ray diffraction (XRD) patterns for the compos-

te membranes were obtained at CNR-ITAE using a Philips

X-Pert 3710 X-ray diffractometer using Cu K$_\alpha$ source op-

erating at 40 kV and 30 mA. Ion-exchange capacity (IEC) was determined by an ex-

change of acidic protons with Na$^+$ ions in solution [38,39]. The membranes were dried and weighed and then placed in a 1 M NaCl solution at 80 °C overnight to exchange Na$^+$ ions with H$^+$. A large excess of Na$^+$ ions in the solution ensured nearly complete ion exchange. The membranes were removed from solution and the solution was titrated to the phenolphthalein end point with 0.1 M NaOH solu-
tion to determine the quantity of exchanged H$^+$ ions. The ion-exchange capacity and equivalent weight (grams of poly-

mer per mole of H$^{+}$) were calculated using the dry weight of the polymer and the quantity of exchanged protons.

2.3. Water uptake and membrane conductivity

The water uptake and the proton conductivity mea-
surements were carried out in a temperature-controlled barometric sorption vessel. The barometric sorption appa-
Fig. 1. Schematic of the barometric sorption apparatus for measuring water uptake and conductivity of membranes. A membrane sample was mounted between two graphite electrodes inside the temperature-controlled pressure vessel. The sorption vessel is shown placed in an oven to maintain a uniform temperature everywhere and avoid temperature gradients inside the sorption vessel.

The sorption vessel volume, $V$, is 430 mL. It is equipped with an Omega pressure transducer, copper and thermocouple wire feedthroughs, and Swagelok® fittings with a septum for water injection. The unconstrained dry membrane is placed within the sorption vessel, which is evacuated at the measurement temperature (80–140 $^\circ$C) for over an hour to dry the membrane and remove any residual water from the vessel. Water is injected into the vessel through the septum using a microliter syringe.

At temperatures between 80 and 140 $^\circ$C, the small mass of water, $m_{H_2O}$, that is injected (typically 5–50 L) evaporates quickly and increases the pressure in the vessel. Using the ideal gas law, the expected pressure, $P_{exp}$, associated with the vaporization of the injected water can be calculated:

$$P_{exp} = \frac{m_{H_2O}RT}{18V}$$  \hspace{1cm} (1)

The difference between the expected pressure and the actual measured pressure, $P_{act}$, is attributed to water uptake by the membrane and the number of moles of water in the membrane, $N_{H_2O}$, can be calculated. The number of moles of sulfonic acid in the membrane is calculated from the dry weight of polymer in the membrane, $m_{mem}$, and equivalent weight, EW:

$$N_{SO_3^-} = \frac{m_{mem}}{EW}$$  \hspace{1cm} (3)

Finally the membrane water content parameter, $\lambda$, the number of moles of water per mole of sulfonate, can be calculated:

$$\lambda = \frac{N_{H_2O}}{N_{SO_3^-}}$$  \hspace{1cm} (4)

After allowing at least 30 min for membrane equilibration with the vapor phase, another small quantity of water is injected and the pressure is measured again. This procedure is repeated until no pressure rise is detected with the water injection, which indicates that the saturation vapor pressure, $P_{sat}$, is reached.

Within the sorption vessel, the membrane conductivity was measured using an ac impedance technique to isolate the bulk membrane resistance from other resistance factors. The conductivity of the perfluorinated sulfonic acid membranes is measured along the longitudinal direction (in plane) of the membrane. A small piece of the membrane is placed between a set of graphite blocking electrodes spaced 1 cm apart. The graphite electrodes are connected through the vacuum feedthroughs on the sorption vessel to the measurement equipment. The two-probe frequency-dependent impedance measurement was carried out on a Princeton Applied Research (PAR) Model 398 Electrochemical Impedance System, consisting of a potentiostat/galvanostat Model 273A and a lock-in amplifier Model 5210 which are connected to a PC running Electrochemical Impedance Software (EIS). The applied signal is a single sine wave of 5 mV with frequencies varying between 10$^3$ and 10 Hz. The membrane resistance was taken from the zero frequency limit of the impedance.
2.4. Small angle X-ray scattering (SAXS)

2.4.1. SAXS sample preparation

Nafion membranes and Nafion/zirconium phosphate composite membranes were used after the cleaning treatment procedure described above. Before each set of runs, the membrane was placed in boiling de-ionized water to ensure full hydration. The membrane was then placed in a viton-sealed copper sample cell with mica windows. The cell was opened and the membrane was slowly dehydrated between runs. Membrane water content, $\lambda$, was determined gravimetrically.

2.4.2. SAXS data collection and analysis

The sample cell was placed in the path of the X-ray beam. Membrane water loss during the data collection was minimized by filling the flight tube with helium rather than a vacuum. The 1.5418 Å Cu Kα X-rays were generated by a Philips XRG-3000 sealed tube generator source. The beam was slit collimated and the scattering was detected by an Anton-Paar compact Kratky camera equipped with a Braun OED-50M detector. Samples were typically run at room temperature for 10 min. Background beam scattering, sample transmittance, and detector response were corrected for in the data analysis. The data reduction and desmearing procedures are described in detail by Register and Bell [40]. The invariant scattering intensity ($q^2I$) is plotted as a function of scattering angle or distance and the Bragg spacing is determined by the location of the peak in scattering intensity.

2.5. Water transport

The water flux through different membranes was measured at 80 °C. Liquid water was fed to the one side of the membrane and a dry gas was flowed to the opposite side. Nafion 115, Nafion 117, and Nafion 115/zirconium phosphate membranes were prepared as previously described. Each of these membranes was hot-pressed at 135 °C without electrodes, between sealing gaskets for 2 min at 10 kN (1 metric ton).

The membrane was placed in a 5-cm$^2$ fuel cell housing with triple-pass serpentine flow fields and heated to 80 °C. Liquid water was passed through the flow field on one side of the membrane and a dry N$_2$ stream was passed through the other side. The water vapor in the nitrogen outlet was condensed in a cold trap at 0 °C and collected in a graduated cylinder. The water flux through the membrane was determined as a function of the nitrogen flow rate to extrapolate to zero gas side mass transfer resistance.

2.6. Fuel cell tests

2.6.1. Membrane electrode assembly (MEA) preparation

Commercial gas-diffusion electrodes (20% Pt-on-carbon, 0.4 mg Pt/cm$^2$, purchased from E-TEK) were brushed with 5 wt.% solubilized Nafion (Aldrich) to impregnate the active layer (0.6 mg/cm$^2$) and then dried at 80 °C for 1 h. The geometrical area of the electrodes was 5 cm$^2$. A membrane was sandwiched between two electrodes and gas sealing gaskets, and the membrane electrode assembly was then pressed for 2 min at 135 °C at 20 MPa using a Carver hot press.

2.6.2. Single cell test fixture and performance evaluation

The MEAs, coupled with gas-sealing gaskets, were placed in a single cell test station. H$_2$ and O$_2$ gases were fed to the single cell at 100 scm. The gases were bubbled through water in temperature-controlled stainless steel bottles to humidify the feeds prior to entry to the fuel cell. The baseline test was total pressure of 1 bar, cell temperature of 80 °C, and the humidifier bottles at $T_{anode} = 90^\circ$C and $T_{cathode} = 88^\circ$C, respectively. Performance evaluations were carried out at 120–140 °C with backpressure regulators at the effluents from the fuel cell fixed at 3 bar. The temperatures of the humidifier bottles were varied to alter the water vapor pressure (water activity) of the feed. The maximum temperature of the humidifier bottles was 130 °C, corresponding to an equilibrium water vapor pressure of 2.65 bar (the actual water vapor pressure is less due to finite mass transport rates in the bubbler). H$_2$ and O$_2$ partial pressures were always the difference between the total pressure of 3 bar and the water vapor pressure.

The fuel cell performance was characterized by current–voltage measurements (polarization curves). These were recorded at 80 °C and atmospheric pressure as well as in the range of temperatures between 80 and 140 °C, and total pressure of 3 bar pressure. The fuel cell was preconditioned by operating at 0.3 V and high current density prior to the performance measurement.

Current–voltage measurements were obtained by connecting the fuel cell to a load resistance (either carbon film resistors or an electronic Amrel load), and allowing the current and voltage output of the single cell to settle to fixed values (~5–20 s). After the values of current and voltage were recorded, a new load condition was used and the single cell output was recorded. The measurements were made starting at open circuit (zero current) and increasing current with each subsequent load condition. Because the entire current–potential curve for a given temperature/humidification condition is obtained in a couple of minutes, it is assumed that the membranes have constant water content throughout the measurement.

3. Results

3.1. Physical/chemical characterization

Table 1 compares the density change and ion-exchange capacity for Nafion 115 and the Nafion/zirconium phosphate composite membrane. The membranes were dried at 80 °C in vacuum for >4 h prior to the measurements. The density of the composite membrane is significantly lower than expected...
Table 1

<table>
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<tr>
<th>Membrane</th>
<th>Thickness (μm)</th>
<th>Density (g/cm³)</th>
<th>IEC (μeq/g)</th>
<th>EW (g/mol H⁺)</th>
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<tr>
<td>Nafion 115</td>
<td>130</td>
<td>2.6</td>
<td>996</td>
<td>1004</td>
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<tr>
<td>Nafion/zirconium phosphate (25%)</td>
<td>170</td>
<td>1.6</td>
<td>1464</td>
<td>683</td>
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</table>

Table 2

<table>
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<tr>
<th>Membrane treatment</th>
<th>Liquid water uptake (25°C)</th>
<th>Water vapor uptake (80°C)</th>
</tr>
</thead>
<tbody>
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<td>Nafion 115</td>
<td>41</td>
<td>18</td>
</tr>
<tr>
<td>Nafion 115/ZP (25%)</td>
<td>33</td>
<td>25</td>
</tr>
</tbody>
</table>

The ion-exchange capacity and equivalent weight (grams of polymer per mole of H⁺) were calculated using the dry weight of the polymer and the quantity of exchanged protons. Table 1 shows the results of ion-exchange experiment. The IEC of the composite Nafion/ZP membranes have an increased ion-exchange capacity (~40–50%) as compared to Nafion. Zirconium hydrogen phosphates have protons that can be exchanged which give the composite membrane a much greater ion-exchange capacity.

3.2. Water uptake and conductivity

Table 2 summarizes the water content of Nafion and Nafion/ZP composite membranes equilibrated with 100%
Fig. 3. Water uptake of Nafion 115 and Nafion 115/ZP (25 wt.%) composite membranes at 80 °C. The data were fit to finite layer BET isotherms (Eq. (7)) with fitting parameters—Nafion 115: \( \lambda_m = 2, c = 35, n_L = 9.2 \); Nafion/ZP composite: \( \lambda_m = 2.6, c = 17, n_L = 12.8 \).

relative humidity air at 80 °C and immersed in liquid water at 25 °C. Both these conditions correspond to water activity of 1. The membranes were removed from the water or the barometric sorption vessel and surface water is brushed off to get an accurate membrane water content measurement gravimetrically. The water content, \( \lambda \), is calculated from the mass of water and Eqs. (4) and (5). Even though 100% relative humidity and liquid water both correspond to water activity of 1, there is a difference in the water uptake. Liquid water uptake is greater than water vapor uptake. This difference has been attributed to the osmotic pressure of the membrane swelling in the liquid that can increase water content considerably (Schroeder’s paradox).

The water uptake isotherms at 80 °C for Nafion 115 and the Nafion/ZP composite membranes are shown in Fig. 3. As the water activity in the vessel is increased, the membrane water content increases. The isotherm shows a rapid rise at low water activity, a slow rising plateau at intermediate water activities, and the majority of water uptake occurring at high water activity \( a_w > 0.6 \). At 80 °C and water activity, \( a_w = 1 \), the Nafion membrane contains around 11 waters per sulfonate or about 18 wt.% of water. The solid line in Fig. 3 shows the results of the BET finite layer isotherm model describing the membrane water content dependence on relative humidity.

While the uptake of water from the extruded Nafion membranes has been characterized in the literature [7,43], water uptake by composite membranes has not received much attention. As seen in Fig. 3 the composite membrane contains more water than a Nafion membrane at the same water activity. The number of waters is based only on the sulfonic acid content in the Nafion and neglects the interaction of water with the zirconium phosphate. However, even on a total weight basis the Nafion/ZP membrane absorbs more water than Nafion.

The water uptake was not very sensitive to the temperature over the range 80–140 °C. Our data could not discern any change in the water uptake with temperature for fixed water activity.

The conductivity of Nafion 115 as a function or water activity over a range of temperatures from 80 to 140 °C is shown in Fig. 4. The data have been plotted on both log and linear scales. Most obvious from the log graph is the very large change in conductivity with water activity. The conductivity increases by five orders of magnitude with water activity increasing from 0 to 1. The conductivity values at \( a_w = 0 \) may be high because of incomplete water removal during the initial evacuation of the barometric sorption vessel can have a large impact. The most reliable conductivity measurements are for intermediate water activity, 0.15 < \( a_w < 0.95 \), and the conductivity increases by more than two orders of magnitude with increasing water activity over that range. The temperature effect on conductivity is much smaller than the effect of water activity. By plotting the data on a linear scale the temperature effect becomes more evident. The conductivity increases by approximately a factor of 2 from 80 to 140 °C at fixed water activity.

We expected Nafion/zirconium phosphate membranes to have an increased conductivity compared to unmodified Nafion. The water content was higher in the composite membrane and the zirconium phosphate may contribute extra protons to increase the charge carrier concentration. Fig. 5 compares the conductivity of the Nafion/zirconium phosphate composite membrane with Nafion 115. The composite membranes had lower proton conductivity than Nafion over the entire range of water activities and temperatures. Similar to Nafion 115, the major conductivity change
for the composite membrane is associated with the water activity. The conductivity of the composite membranes increased with temperature, but the variation of the composite membrane conductivity with temperature was slightly less than that observed with Nafion 115.

### 3.3. Small angle X-ray scattering

The slit collimated scattering data collected by the multi-channel detector were converted into the scattering intensity versus scattering angle. The raw data were analyzed to account for several factors following the procedure recommended by Register and Bell [40]:

(i) Scattering due to interaction with the helium sample environment was subtracted.

(ii) The absolute scattering intensity of the sample was determined quantitatively with a standard polyethylene sample.

(iii) The data were desmeared to correct for the slit width.

The invariant scattering intensity \(q^2I\) profile is plotted against Bragg spacing (determined from the scattering angle) for each membrane sample as a function of water content, \(\lambda\), in Fig. 6. The data obtained show that increasing water content leads to an increase in the intensity of the scattering peaks for both an extruded Nafion 115 and a Nafion 115/ZP
composite membrane. The scattering intensity increases linearly with water content. Ionomers, such as Nafion, will micro-phase separate into a Teflon-like region and an ionic region containing the sulfonic acid groups [6,44–46]. In the pure Nafion membranes, the electron density of the ionic inclusions is slightly lower than that of the polymer backbone while in the zirconium phosphate composite membrane the electron densities of the two phases are almost equal. For this reason there is little electron density contrast between the two phases when the membranes are dry and no scattering peak is obtained [47]. Water has a significantly lower electron density than the fluorocarbon polymer matrix. Absorbed water partitions into the ionic regions of Nafion. As a result, the electron density contrast between the ionic and Teflon-like phases of Nafion increases with increasing water content, resulting in greater scattering intensity and an increasingly well-defined scattering peak [45]. The scattering peaks for the zirconium phosphate membrane in Fig. 6B are significantly wider than the peaks for the unmodified Nafion 115 membrane, indicating greater structural heterogeneity. In addition, the shift in the spacing between inclusions with water content is much less for the composite membrane than for Nafion. The maximum spacing between ionic inclusions at the highest water content is nearly the same for the Nafion 115 and the Nafion 115/ZP composite. The scattering maximum for Nafion shifts to smaller spacing with decreasing water content; however, the scattering maximum for the composite membrane is almost unchanged with decreasing water content.

3.4. Water transport

The flux of water through the membranes as a function of the nitrogen flow through the test cell is shown in Fig. 7. The Nafion 117 membrane has almost the same thickness as the Nafion 115/ZP composite membrane, permitting us to distinguish between the effects of membrane thickness and membrane composition. The data in Fig. 7 show that the water flux increases with nitrogen flow rate through the test cell at low flow rates and then plateaus at a limiting flux. The limiting flux corresponds to the minimum mass transfer resistance at the membrane gas interface, and diffusion through the membrane is the dominant mass transfer resistance. The limiting flux is greatest for the Nafion 115 membrane. The flux was reduced through the Nafion 117 membrane due to increased membrane thickness. The limiting water flux through the composite membrane is less than that for Nafion 117 suggesting that water diffusion through the composite membrane is reduced relative to diffusion through Nafion.

3.5. Fuel cell performance of Nafion/zirconium phosphate composite membranes

Polarization curves for fuel cells with membrane electrode assemblies containing Nafion 115 and Nafion 115/zirconium phosphate membranes were measured at four different sets of operating conditions. The base case was for humidified feeds near water activity of 1 with a cell temperature of 80 °C and pressure of 1 bar. The other three conditions were at elevated temperature and a total pressure of 3 bar. The conditions tested are defined by the total pressure in the fuel cell and the temperature of the humidifier bottle for the anode feed ($T_{anode}$), the cell temperature ($T_{cell}$), and the temperature of the humidifier bottle for the cathode ($T_{cathode}$).

Polarization curves are shown in Fig. 8 for fuel cells with Nafion 115 and Nafion 115/zirconium phosphate membranes at conditions 1 and 3. At 80 °C the fuel cell performance was nearly identical for both membranes, with the effective MEA resistance being slightly greater for the composite membrane than Nafion 115. When the temperature was
Fig. 6. (A) SAX scattering intensity ($q^2 I$) for extruded Nafion 115 film. The scattering peaks result from water absorbed into the Nafion clustering creating electron density contrast with the fluorocarbon phase. The water content as determined by weight is given by the parameter $\lambda$. (B) Scattering intensity ($q^2 I$) vs. Bragg spacing for the composite Nafion/zirconium phosphate (25 wt.%) membrane. The water content as determined by weight is given by the parameter $\lambda$.

$130 ^\circ C$ the MEA resistance was substantially less for the composite membrane than for the Nafion 115 membrane.

The polarization curves for fuel cells with Nafion 115 and Nafion 115/zirconium phosphate composite membranes at different levels of humidification are shown in Fig. 9. By maintaining the humidification temperatures fixed the water vapor pressure of the feeds are fixed. At fixed feed humidification increasing the cell temperature will decrease the water activity in the cell, $a_w = P_w / P_{sat}(T_{cell})$. The effective MEA resistance increased less with decreased water activity
Fig. 7. Water flux through Nafion 115, Nafion 117, and Nafion 115/zirconium phosphate composite membranes as functions of gas flow on the opposite side of the membrane. The limiting fluxes are denoted by the horizontal lines.

for the composite membrane than observed with the Nafion 115 membrane.

The MEA polarization curves have been fitted to Eq. (5):

\[ E = E_{rev} - b \log \left( \frac{i}{i_0} \right) - R_{MEA} \]

(5)

where \( E_{rev} \) is the reversible cell potential, \( b \) the Tafel slope, \( i_0 \) the exchange current density, \( i \) the current density and \( R_{MEA} \) the membrane electrode resistance. The fit parameters at different operating conditions are summarized in Table 3. The composite membranes show reduced exchange current density compared to the Nafion membranes. The MEA resistance of the composite membranes is substantially less than the resistance of Nafion 115 at the higher fuel cell temperatures.

The composite membranes operated more stably at elevated temperatures. The cell was operated at 130 °C for 1 h, and then the cell temperature was raised to 140 °C. After 1 h of operation under the latter condition, the cell temperature was returned to 130 °C. After this procedure with the composite membrane the current–voltage curves returned to their initial (pre-140 °C operation) values. The unmodified Nafion 115 membranes, by contrast, were altered by the brief exposure (∼20–30 min) to the high temperature. The effective ohmic resistance of the Nafion 115 MEA increased from 1.3 to over 2 Ω after operation at 140 °C.

4. Discussion

When we initiated our studies with composite membranes the working hypothesis was that addition of zirconium phosphate to Nafion would increase the water uptake by the membrane at elevated temperature, thereby increasing the proton conductivity and thus improving the fuel cell performance. We were surprised that the proton conductivity was diminished in the composite membrane relative to Nafion in spite of the increased water uptake, and we were even more surprised that the fuel cell performance of the composite membranes exceeded Nafion even though the proton conductivity was reduced. Our data do not fully resolve these conflicting observations, but the data are consistent with the suggestion that mechanical properties of the composite membranes may be the key to the performance of composite membranes.

4.1. Water uptake and ion-exchange capacity

The ion-exchange capacity of the composite membrane is greater than the ion-exchange capacity of Nafion [48,49]. Zirconium phosphate has exchangeable protons; the number of protons depends on the chemical form of the zirconium phosphate. The ion-exchange capacity for the composite membrane listed in Table 1 can be divided into contributions
Fig. 9. (A) PEM fuel cell performance of an MEA employing a Nafion 115 membrane. The cell voltage is plotted as a function of average current density in the fuel cell. The cell operating conditions are: (●) 1; (□) 2; (▲) 3; (○) 4. (B) PEM fuel cell performance of an MEA employing a Nafion 115/ZP composite membrane. The cell voltage is plotted as a function of average current density in the fuel cell. The cell operating conditions are: (●) 1; (□) 2; (▲) 3; (○) 4.

Table 3
Fuel cell performance parameters

<table>
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<th>Membrane</th>
<th>Operating condition</th>
<th>(\delta) (mV/dec)</th>
<th>(i_0) (\times 10^3) mA/cm(^2)</th>
<th>(R_{MEA}) (Ω cm(^2))</th>
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<td>Nafion 115</td>
<td>1</td>
<td>84.7</td>
<td>3.7</td>
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<tr>
<td></td>
<td>2</td>
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</tbody>
</table>

Operating conditions: (1) \(P = 1\) bar, \(T_{anode}/T_{cell}/T_{cathode} = 90/80/88\); (2) \(P = 3\) bar, \(T_{anode}/T_{cell}/T_{cathode} = 130/120/130\); (3) \(P = 3\) bar, \(T_{anode}/T_{cell}/T_{cathode} = 130/130/130\); (4) \(P = 3\) bar, \(T_{anode}/T_{cell}/T_{cathode} = 180/130/130\).
water adsorption, and
has kept it extended. The membrane does not swell much because the inorganic scaffold is amorphous and XRD cannot quantify the amorphous zirconium phosphate.

Liquid water uptake by Nafion 115 and the Nafion115/ZP composite were the same when normalized by the sulfonic acid concentration. The mass uptake of liquid water normalized by the mass fraction of Nafion in the membrane is the same in both membranes.

Water uptake from the vapor is reduced compared to water uptake from liquid water. The composite membranes showed substantially greater water uptake from the vapor phase than water uptake by Nafion 115. The water uptake as a function of water activity, shown in Fig. 3, was fit by a finite layer BET isotherm [27]:

$$\lambda = \frac{\lambda_m}{(1 - \alpha w)(1 - \alpha w + n_L n^m(w) \alpha_w)}$$

$$\lambda = \frac{\lambda_m}{(1 - \alpha w)(1 - \alpha w + c_w n^m(w) \alpha_w)}$$

The Eikerling model uses a single-bond effective medium approximation (SB-EMA) to solve for the conductivity of this random network. Swelling and structural changes (i.e. ionic cluster reorganization) within the membrane are described by Eqs. (8) and (9):

$$n(w) = n_0(1 + \alpha w)$$

$$\nu(w) = \nu_0(1 + \beta w)^3$$

4.2. Proton conductivity

Protons are transported through the membrane by two pathways. The first is a proton shuttling (or Grotthus) mechanism that involves the formation and breaking of hydrogen bonds between the proton and water [50,51]. The second pathway for proton conduction is equivalent to traditional cation conduction where the hydrated proton diffuses through the aqueous media in response to an electrochemical gradient [52,53]. The proton conductivity via the Grotthus mechanism is considerably faster than hydrogen ion diffusion, and it is estimated that approximately 90% of proton conductance occurs via the Grotthus pathway [50].

We fit our proton conductivity data to two models from the literature in an effort to identify the role of the zirconium phosphate in proton conductivity. The random network model for membrane proton conductivity proposed by Eikerling et al. [26] is based upon the inverted micelle structure of Nafion and other ionomer membranes. The micelles, or "pores", are either dry with low conductivity or wet with high conductivity. As a membrane absorbs water and swells, the fraction of wet pores in the membrane increases, while the fraction of dry pores decreases. The distributions of wet and dry pores are governed by the membrane water content and swelling behavior.

The Eikerling model uses a single-bond effective medium approximation (SB-EMA) to solve for the conductivity of this random network.
pores, \( x(w) \), depends on the water fraction, the swelling parameters and a scaling parameter, \( \gamma \):

\[
x(w) = \frac{\gamma w}{(1 + \beta w)^{\gamma}} - \frac{\gamma w^2}{\alpha}
\]

The conductivity of the membrane is the weighted average of the conductivities of the wet and dry pores:

\[
\sigma = x(w)\sigma_{\text{wet}} + (1 - x(w))\sigma_{\text{dry}}
\]

The small angle X-ray scattering data and the cluster swelling model proposed by Gierke and Hsu [54] were employed to calculate the values for the number of sulfonates per pore and the pore volume \( n \) and \( v \) as a function of water content, \( w \). The calculated values of \( n \) and \( v \) were plotted as a function of \( w \) and the best fit for parameters \( \alpha \) and \( \beta \) were calculated. The parameter \( \gamma \) was obtained by equating \( x(w) = 0 \) when \( w = 0.41 \) in Eq. (10). Table 4 shows the parameter values obtained from the SAXS data and conductivity at saturation. A critical caveat in determining these swelling parameters is that the SAXS data were collected at room temperature (25 °C), while it is being applied to the membrane conductivity model at 80°C.

The model fit to the experimental conductivity data is shown in Fig. 10. The model consistently overestimates the conductivity. The values of the swelling parameters \( \alpha \) and \( \beta \) are less for the composite membrane than those obtained for Nafion 115, which reflect the decreased swelling of the composite membrane. The conductivity of the dry pores is nearly an order of magnitude greater for the composite membrane. Those two membranes have comparable thickness. If water diffusion is limited to the organic phase of the composite, then the water transport data suggest that the zirconium phosphate plays no role in water diffusion.

The Thampan model as well as the models of Gierke et al. [45] and Paddison [56] assume a threshold water content.
below which no proton conduction occurs. Experimentally
Nafion membranes have a small but non-zero conductivity
even at “zero” water content. The model presented by Tham-
pan et al. neglects tunneling and other diffusion mechanisms
that may dominate at low water content. We have shown a
single parameter empirical fit to the conductivity data for
Nafion in Fig. 4A:
\[ \sigma = \sigma_{aw=0} \exp(c_1 c_2 w) \]  
(13)
\[ c_2 \] is the conductivity of a dry membrane, \( c_1 = \ln(\sigma_{aw=1}/\sigma_{aw=0}) \), and \( c_2 \) is an adjustable parameter. This
empirical equation fits the conductivity as a function of wa-
ter activity very well with only one adjustable parameter.
The empirical fit is useful for modeling PEM fuel cells.

4.3. Fuel cell performance

The most surprising result from our studies is that fuel
cell performance, as judged by the polarization curves, is
improved for composite membranes even though the pro-
ton conductivity is poorer. This improvement in fuel cell
performance appears to be limited to conditions where the
water activity is significantly less than 1. We estimated the
water activity in the fuel cell for different temperatures of
the humidifier bottles assuming the same mass transfer effi-
ciency at the different temperatures. (The mass transfer effi-
ciency was estimated from a separate experiment where dry
air flowing at 100 mL/min was bubbled through the humid-
ifier at 50 °C and the outlet humidity was measured.) The

![Graph showing model fits of the proton conductivity in Nafion 115.](image)

![Graph showing model fits of the proton conductivity in Nafion 115/zirconium phosphate composite membrane.](image)
estimated water vapor pressure of the gases humidified at 140, 130, and 120 °C are 2.4, 2.0, and 1.7 bar, respectively, so the water activity in the fuel cell for the three cases are $a_w(140/130/140) = 1.0$, $a_w(130/130/130) = 0.85$, and $a_w(120/130/120) = 0.70$.

Reducing the water activity from 1.0 to 0.7 should increase the membrane resistance for Nafion 115 from 0.20 to 0.22 $\Omega \cdot \text{cm}^2$. However, from the fuel cell data the membrane resistance increased from 0.24 to 9.8 $\Omega \cdot \text{cm}^2$. The increase in the effective MEA resistance is much greater than that predicted from the conductivity measurements. Why is there such a large discrepancy and why does the effective MEA resistance only increase from 0.27 to 0.79 $\Omega \cdot \text{cm}^2$ for the composite membrane?

We suggest that the discrepancy is due to the constrained environment of the membrane in the fuel cell. The MEA is compressed between the bipolar plates. The applied pressure on the MEA limits the swelling of the membrane. Absorbed water swells the membrane creating a “swelling pressure” that must overcome the applied sealing pressure of the fuel cell. The greater the water activity the greater the swelling pressure exerted by the membrane. In the fuel cell environment the water content of the membrane is probably much less than that expected based on ex situ measurements because the sealing pressure squeezes water from the membrane.

We suggested that the zirconium phosphate in the composite membrane forms rigid internal scaffolding, which would resist compression of the sealing pressure. At the reduced water activity the composite membrane can take up water and swell without having to overcome the applied sealing pressure. We suggest that the zirconium phosphate provides mechanical strength to the membrane; the data suggest that the zirconium phosphate plays little role in the actual conduction of protons through the membrane. This explanation is also consistent with our group’s results with other Nafion/metal oxide composite membranes. We have routinely found improved fuel cell performance of the composite membranes at reduced water activity, and there has been little sensitivity to the choice of metal oxide [57–59].

The effect of clamping the fuel cell is accentuated at higher temperatures because the elastic modulus of the membrane decreases with increasing temperature. The glass transition temperature of dry Nafion is ~100–110 °C, and decreasing with water content. Above the glass transition temperature the swelling pressure is greatly reduced.

5. Conclusions

Nafion 115/zirconium phosphate composite membranes show improved fuel cell performance compared to Nafion 115 at elevated temperature and reduced water activity. A Nafion 115/zirconium phosphate composite membrane had a greater ion-exchange capacity and took up more water than Nafion 115 membranes, but the composite membranes showed reduced proton conductivity and water transport. Small angle X-ray scattering data indicated that the spacing between hydrophilic phases in the composite membrane were greater than in Nafion 115, and there appeared to be less restructuring of the composite membrane with water absorption. The data suggest that the zirconium phosphate forms an internal rigid scaffold within the membrane that permits increased water uptake by the membrane in the confined environment of the fuel cell membrane electrode assembly.

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References


