Polyetheretherketone Membranes for Elevated Temperature PEMFCs

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Membrane electrode assemblies (MEAs) made from polyetheretherketone (PEEK) showed excellent fuel cell performance and thermal stability in the presence of substantial CO at elevated temperatures (i.e., 120°C) in proton exchange membrane fuel cells (PEMFCs). For example, the current from a MEA made from PEEK membrane at 0.6 V and 120°C was 0.50 A/cm² when run on pure hydrogen and 0.45 A/cm² when run on reformate (50% H₂, 1300 ppm CO, and balance N₂). The current density from a MEA made from Nafion at 0.6 V and 120°C was 0.61 A/cm² when run on pure hydrogen. The main difference between these two MEAs is that the ionic conductivity of the PEEK membrane at 120°C was 3.3 × 10⁻² S/cm, which is approximately three times lower than Nafion. Although it is not surprising that CO tolerance increases with increasing temperature, we are the first to show less than 10% drop in performance with 1300 ppm CO at 120°C. Even though Nafion membranes have higher conductivity, PEEK membranes lasted for 350 h thereby outlasting Nafion membranes by seven to eight times.

Polyetheretherketone (PEEK) shows excellent thermal stability and chemical resistance under engineering applications. The glass transition temperature of nonsulfonated PEEK is 146°C. The intermolecular interaction through hydrogen bonding increases with increasing degree of sulfonation resulting in higher glass transition temperatures up to 210°C at 80% sulfonation. Further, PEEK membranes show higher thermal degradation temperature than Nafion and hence are expected to show higher thermal stability at elevated temperatures. Higher thermal stability at temperatures around 120°C and equivalent ionic conductivity make PEEK membranes a promising replacement for Nafion membranes.

The objective of this study is to evaluate the fuel cell performance and long-term stability of PEEK membranes at elevated temperatures (i.e., 120°C) with substantial CO concentration in the anode stream. Ion conducting membranes using sulfonated polyetheretherketone (S-PEEK) were prepared. These membranes were acid treated to improve ionic conductivity, and membrane electrode assemblies (MEAs) were prepared with these treated membranes. Both PEEK and Nafion-based ionomers were used as the electrolyte in the active catalyst layers of the MEA. The performance of these MEAs were tested at 75 and 120°C, and at different concentrations of CO in the fuel stream. The long-term stability of the PEEK membrane was evaluated at 120°C.

Experimental

Membrane preparation.—The membrane sheets were prepared by a solution casting technique. 5-10 wt % solution of commercially available PEEK material was mixed with 6.5 wt % polybenzimidazole (PBI) and 5 wt % polyacrylonitrile (PAN) in dimethyl-acetamide (DMAc), such that the final solid contents were 76, 19, and 5 wt % for PEEK, PBI, and PAN, respectively. The solution was stirred for 16-24 h (typically overnight). The solution was then cast onto a clean glass sheet and air dried overnight. The membrane was then dried under vacuum at 80°C for 15 h to evaporate and cure the membrane, and remove any remaining DMAc. These sheets were then sulfonated by boiling in 1 M sulfuric acid for 1 h to improve ionic conductivity. The ionic conductivity of these membranes was tested at 50 psig using a four-electrode conductivity cell with fully humidified gas streams.

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MEAs contain Nafion ionomer in the catalyst layer. In addition, the membrane.

**Fuel cell testing.**—The MEA was assembled into a fuel cell with single-channel serpentine flow-field plates bought from Fuel Cell Technologies. The cathode side had air flowing at 1.8 standard liters per minute (slm), corresponding to 2.0 stoichs at 1.0 A/cm². The anode side had a flow of either H₂ at a flow rate of 0.6 slm, or reformate at a flow rate corresponding to 1.5 stoichs at 1.0 A/cm² for H₂. All the gases were obtained from Air Products and the pure gases used were certified ultrahigh purity (UHP). Here reformate refers to a mixture of H₂ (50-95%), N₂ (5-40%), and CO (500-1300 ppm) produced in house by mixing H₂ with CO in N₂. To measure the concentration of CO in the inlet gas from the anode, the gas was collected using a sampling bag (200 mL) for 5 min. The gas from the sampling bag was sent through a drying chamber (Drierite bed), then injected into the gas chromatograph (GC) for analysis. Concentration of CO, H₂, and N₂ in reformate was determined using a Varian MicroGC, model CP-2003 equipped with thermal conductivity detector (TCD). The use of sampling bags provided an average concentration of the gases and helped to improve the consistency of the analyses. The concentrations of the gases reported here are averages of at least three analyses from the GC. The experiments were conducted at 75°C with 0 psig and at 120°C with 24 psig back pressures. The back pressures of the anode and cathode streams were such that 100% relative humidity was maintained at 75 and 120°C.

The gas streams were humidified by sparging the gas through humidifying bottles. The anode and cathode humidifier bottles were maintained at 126 and 117°C, respectively, for 120°C operation. Both the anode and cathode operated at 24 psig to maintain 100% relative humidity of the gas streams. The cell was incubated at 75°C under H₂ and air flow conditions for a minimum of 4 h at 0.4 V, before getting the first voltage-current (V-I) data at 75°C. Following which, the temperature was increased. At elevated temperatures after changing the anode gas, the cell was run at 0.4 V until a steady-state current was reached (typically 0.5 to 1 h) before getting V-I curves.

For evaluating the long-term stability of the PEEK membrane, a V-I performance curve for the MEA made from PEEK was generated every few hours (typically 4-5 h). The concentration of CO in the anode gas was set to 600 ppm (76% H₂ and balance N₂), and the cell voltage was set to 0.4 V just minutes before the V-I curve was started. The fuel cell was tested with reformate (greater than 500 ppm CO) at 0.4 V except when the V-I curve was generated.

**Results and Discussion**

**Ionic conductivity.**—The chemical structures of PEEK and sulfonated PEEK are shown in Fig. 1. S-PEEK-based membranes show good thermal stability and ionic conductivity equivalent to Nafion at temperatures above 100°C. However, these membranes under high degree of sulfonation show relatively poor mechanical stability. Lower degrees of sulfonation improve the mechanical stability albeit with a loss in ionic conductivity making it unsuitable for fuel cell applications. Therefore, 83% S-PEEK, which provided a balance between mechanical strength and ionic conductivity, was used in this study. The ionic conductivity of 83% S-PEEK membrane measured at 50 psig using a four-probe conductivity cell is summarized in Table I. At 120°C, the ionic conductivity of the PEEK membrane was 3.38 × 10⁻² S/cm, which is approximately three times lower than the value of 0.11 S/cm reported for Nafion at the same temperature and humidity conditions. The conductivities of these membranes are similar to values reported earlier for PEEK membranes. Further, the ionic conductivity of the membrane increases with increasing temperature.

**Fuel cell testing.**—Figure 2 shows the V-I performance curves of MEAs made from a 4 mil thick PEEK and Nafion 117 membranes run on pure hydrogen. To isolate the effect of the membrane, both MEAs contain Nafion ionomer in the catalyst layer. In addition, the

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**Figure 1.** Chemical structure of PEEK and S-PEEK. The proton attached to the sulfonic acid group on the first benzene ring is responsible for the ionic conductivity of these membranes. Higher degree of sulfonation leads to weaker membranes.

**Figure 2.** Performance curves of MEAs made from (△) Nafion and (●,○) PEEK membranes. The closed and open symbols correspond to 120°C at 24 psig and 75°C at atmospheric pressure, respectively. The solid and dotted lines show the IR corrected potentials of Nafion and PEEK MEA, respectively. The anode side had a catalyst loading of 0.45 mg/cm² of 1:155 atomic ratio Pt-Ru catalyst, while the cathode was made of 0.5 mg/cm² of Pt.

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**Table I.** Ionic conductivity of 83% sulfonated PEEK at 100% relative humidity and 50 psig (balance nitrogen).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Ionic conductivity × 10⁻² (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>2.48</td>
</tr>
<tr>
<td>100</td>
<td>2.73</td>
</tr>
<tr>
<td>120</td>
<td>3.38</td>
</tr>
</tbody>
</table>

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of different concentrations of CO in the anode stream. The performance curve of Nafion operating with pure H₂ is shown for comparison. The anode side had a catalyst loading of 0.45 mg/cm² of 1:155 atomic ratio Pt-Ru catalyst, while the cathode was made of 0.5 mg/cm² of Pt. The tests were conducted at 120°C at 24 psig. The anode and cathode humidifier bottles were maintained at 126 and 117°C, respectively.

The next objective was to determine whether 120°C operation alleviates CO poisoning in these fuel cells. Figure 3 shows the performance of the fuel cell with 76% H₂, 600 ppm CO, and balance N₂. The anode side had a catalyst loading of 0.45 mg/cm² of 1:155 atomic ratio Pt-Ru catalyst, while the cathode was made of 0.5 mg/cm² of Pt. The anode and cathode humidifier bottles were maintained at 126 and 117°C, respectively. The performance curve with H₂ is shown for comparison.

The next objective was to evaluate the long-term stability of the MEA made from PEEK membrane operating at 120°C. Figure 4 shows V-I performance curves generated after running the fuel cell at 0.41 V. As can be seen from Fig. 4, the performance of the fuel cell remained constant (less than 3% drop in current density at 0.6 V) for 225 h. After about 300 h of testing, the performance started to decrease. After 324 h of testing, the current density dropped from 0.499 to 0.46 A/cm², corresponding to a 5.7% drop. After 389 h, the cumulative drop in performance was approximately 15%.

Figure 5 shows the power density (voltage × current density) of a MEA made from PEEK membrane operating at 120°C with 24 psig back pressure as a function of time. The cell voltage was maintained at 0.4 V, the resulting current density was multiplied by this voltage to calculate the power density. The CO concentration in the anode was always maintained above 500 ppm during these tests. The power density of a Nafion MEA operating with simulated reformate (50 ppm CO) at 75 and 120°C is shown for comparison. The power density of an MEA operating at low temperatures is very poor due to CO poisoning. Elevated temperatures alleviate CO poisoning, however the endurance and reliability of the MEA under this conditions is poor. The Nafion MEA operating at 120°C failed after operating for 50 h and the failure was sudden indicating physical failure of the membrane. Post-testing analysis of this MEA showed considerable holes and tearing along the edges of the GDL. The MEA made with PEEK showed relatively stable operation for the initial 200 h. From 200 to 350 h the drop in performance was close to 500 μA/cm² at 0.4 V which is believed to be due to the loss of ionomer in the catalyst layer. After 390 h there was an abrupt drop in the performance due to high gas crossover between the anode and cathode. Post-testing analysis revealed a tear in the membrane along the cata-

Figure 3. Performance curves of a MEA made from PEEK membrane under different concentrations of CO in the anode stream. The performance curve of Nafion operating with pure H₂ is shown for comparison. The anode side had a catalyst loading of 0.45 mg/cm² of 1:155 atomic ratio Pt-Ru catalyst, while the cathode was made of 0.5 mg/cm² of Pt. The tests were conducted at 120°C at 24 psig. The anode and cathode humidifier bottles were maintained at 126 and 117°C, respectively.

Figure 4. Performance curves of a MEA made from PEEK membrane after different durations of testing. The tests were conducted at 120°C at 24 psig with 76% H₂, 600 ppm CO, and balance N₂. The anode side had a catalyst loading of 0.45 mg/cm² of 1:155 atomic ratio Pt-Ru catalyst, while the cathode was made of 0.5 mg/cm² of Pt. The anode and cathode humidifier bottles were maintained at 126 and 117°C, respectively. The performance curve with H₂ is shown for comparison.
bottles were maintained at 126 and 117°C, respectively. The anode and cathode humidifiers were maintained at 1300 ppm. The CO concentration for the Nafion MEA was 50 ppm. Air bleed was not employed in all three cases. The ionic conductivities of these membranes under a relatively low degree of sulfonation can be improved by modifying the polymer structure through grafting or by mixing with precursors like heteropoly acids and other inorganic acids. Further improvements in water retention to realize adequate performance with relatively dry feed gases can be achieved by impregnating with inorganic precursors.

Conclusions

MEAs made from PEEK showed excellent fuel cell performance and thermal stability in the presence of substantial CO at elevated temperatures (i.e., 120°C). For example, the current from a MEA made from PEEK at 0.6 V and 120°C was 0.50 A/cm² when run on pure hydrogen and 0.45 A/cm² when run on reformate (50% H₂, 1300 ppm CO, and balance N₂). The current density from a MEA made from Nafion at 0.6 V and 120°C was 0.61 A/cm² when run on pure hydrogen. The main difference between these two MEAs is that the ionic conductivity of the PEEK membrane at 120°C was 3.38 × 10⁻² S/cm, which is approximately three times lower than Nafion. Even though Nafion membranes showed better performance, PEEK membranes lasted for 350 h thereby outlasting Nafion membranes by seven to eight times. Although it is not surprising that CO tolerance increases with increasing temperature, we are the first to show less than 10% drop in performance with 1300 ppm CO at 120°C. Even though 350 h stability is an order of magnitude less than the target of 4000 h set by the automotive industry, this membrane is far from optimized. In addition, this work is the first to show that an ion conducting membrane can be operated at 120°C with good performance at relatively high CO concentrations. Replacing Nafion ionomer from the catalyst layer with an ionomer made from PEEK should enable operation at temperatures higher than 120°C or increase the endurance of these MEAs further. Also, the ionic conductivities of these membranes under a relatively low degree of sulfonation can be improved by modifying the polymer structure through grafting or by mixing with precursors like heteropoly acids and other inorganic acids. Further improvements in water retention to realize adequate performance with relatively dry feed gases can be achieved by impregnating with inorganic precursors.

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