

Ion exchange resin/polystyrene sulfonate composite membranes for PEM fuel cells

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Abstract

A new composite proton exchange membrane was made by casting a polystyrene sulfonate (PSS) solution with suspended micron sized particles of a crosslinked PSS ion exchange resin. The chemical compatibility of the resin and the PSS allow stable composites with up to 50 wt.% resin. The resin/PSS composite membranes have greater ion exchange capacity than PSS membranes, but the ion conductivity is similar to that of PSS. Swelling of the composite membranes as a function of water uptake is lower than that of PSS. The composite membranes are mechanically more robust and display greater chemical stability in a fuel cell than the PSS membranes. The polarization curves show long-term degradation of the membranes; the cell potential decreased by 60% in 55 h for a PSS membrane, and in 340 h for a composite membrane. The reduced rate of degradation of the composite membranes suggests that with further refinement they may have potential as an inexpensive alternative for PEM fuel cells.

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1. Introduction

Nafion[®] (DuPont) [1], a perfluorosulfonic acid polymer, is the most widely used proton conductor in polymer electrolyte membrane fuel cells (PEMFCs). It possess near ideal physical characteristics for a PEMFC, high ionic conductivity, good thermal stability, adequate mechanical strength and excellent chemical stability. However, the high price of Nafion[®] (~\$800 m⁻² corresponding to ~\$160 kW⁻¹) [2] and the environmental hazards associated with its disposal have prompted research for low-cost non-perfluorinated ionomer membranes, which are more environmentally friendly. Some of the polymer electrolyte membranes investigated include polyether ether ketone (PEEK) [3–5], poly(arylene-ether-sulfone) (PSU) [6–8], PVDF-graft styrene [9–11], acid doped polybenzimidazole

(PBI) [12,13], and polyphosphazene [14,15]. The ideal fuel cell membranes should have low-cost (less than \$10 kW⁻¹ in a PEMFC), high proton conductivity, good chemical stability, and maintain mechanical integrity in hot water. To date none of the proposed materials satisfy the desired specification. For example, the sulfonated PEEK, PSU, and polyphosphazene membranes are cheap and chemically stable, but they have low proton conductivity. At higher sulfonation levels they have better conductivity, but they become water soluble, and they have insufficient mechanical strength. The sulfonation process of these polymers to provide the ionic groups necessary for proton conduction is also difficult.

In order to improve proton conductivity, some researchers have impregnated the membranes with low molecular weight strong acids (e.g. phosphoric acid, sulfuric acid, and CFSO₃H) [13,16,17]. The conductivity of acid doped membranes can be as twice high as that of Nafion[®] [17]. Unfortunately these low molecular weight acids are leached out of the membranes over tens to hundreds of hours. Increased me-

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chanical strength and decreased swelling has been achieved by crosslinking the polymer chains in the membrane. The polymer may be crosslinked before the sulfonation process [18,19], but diffusional limitations in the crosslinked polymer limited the degree of sulfonation. Alternatively the polymer may be crosslinked after the sulfonation. This process generally involves the coupling of sulfonic acid groups on different molecules [8], resulting in decrease of conductivity in the polymer membrane.

Polystyrene sulfonate (PSS) membranes may be prepared from a sulfonated copolymer of styrene–ethylene–butylene or styrene–butadiene, with the aromatic rings being sulfonated. The ethylene–butylene or butadiene makes the polymer flexible, which is necessary to make a good contact with the electrode. This kind of membrane has high proton conductivity and low-cost, but it has a low tensile modulus and is susceptible to chemical degradation in the oxidizing environment of the fuel cell. In this article, we present the results of our study of resin/PSS composite membranes. The resin is a crosslinked polystyrene sulfonate ion exchange resin. The resin is very rigid. It is not a thermoplastic, nor is it soluble in any solvent. Hence it cannot be cast or extruded into a membrane. The resin is nanoporous to permit water and cations to diffuse through the crosslinked network, but the crosslinking limits the water uptake and inhibits swelling. The resin is chemically similar to the PSS copolymer so it can be blended with the PSS with good interfacial adhesion. We have prepared blends with the solid resin content as high as 50%. The addition of the resin in the composite membrane increases the ion exchange capacity, decreases the extent of swelling with water absorption, increases the mechanical strength, and reduces the rate of oxidative degradation.

2. Experimental

2.1. Materials

Partially sulfonated poly(styrene–ethylene–butylene) (Fig. 1) was obtained as a solution in a mixture of propanol, dichloroethane and THF from Dais-Analytic Co. The molecular weight of the polymer and the monomer stoichiometry were proprietary. The ion exchange capacity (IEC) was 1.50 mmol/g. Ion exchange resin was purchased from

Scientific Polymer. The ion exchange resin is poly(styrene sulfonic acid) crosslinked with divinylbenzene; its IEC is 3.77 meq/g (by titration). Isopropanol was purchased from Fisher Chemicals.

2.2. Membrane recasting

A special device was made for membrane recasting. The membrane recasting setup consists of a cylindrical glass tube open at both ends (6.35 cm diameter) placed on a glass plate with a level adjustment. The end of the glass tube was polished flat to match the glass plate, when the polymer solutions were poured into the cylinder no liquid leaked out between the plate and the cylinder. The level of the glass plate was adjustable to assure uniform film thickness to $\pm 2 \mu\text{m}$.

2.3. Synthesis of resin/PSS composite membranes

The ion exchange resin was suspended in isopropanol and ground into a powder with average particle size $< 3 \mu\text{m}$. The resin dispersion was added to the PSS solution and the solution was stirred vigorously for 10 min to ensure uniform particle dispersion. The solution with the dispersed particles was transferred into the cylindrical glass tube and the level of the glass plate was adjusted carefully. The solvent was evaporated at 80–90 °C (typically 6–8 h for a 100 μm thick membrane). The dried membranes were annealed at 160 °C in an argon atmosphere; we found the annealing improved their mechanical strength against tearing. The membranes were soaked in 1 M H_2SO_4 for 4 h and washed completely with DI H_2O to remove any metallic ion impurities.

2.4. Synthesis of Nafion[®]-layered membranes

Layer membranes with the polystyrene sulfonated composite sandwiched between thin Nafion[®] membranes were prepared to reduce the oxidation of the PSS at the membrane electrode interface. Two 10 μm Nafion[®] membranes were cast by the procedures described above from a Nafion[®] solution (emulsion) obtained from Ion Power (LIQUION 1100, 5% solution). A composite membrane was cast of a desired thickness. Finally, the 10 μm Nafion[®] membranes were pressed on to both sides of PSS or resin/PSS membranes at 100 °C and 500 kPa.

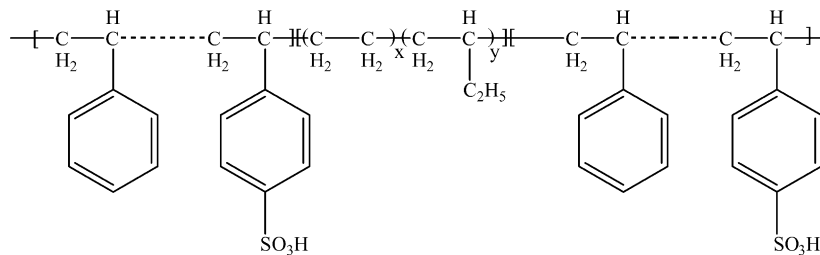


Fig. 1. The structure of Dais polymer electrolyte. The polymer is a block co-polymer of blocks of polystyrene, and then blocks of ethylene/butylene. A portion of the phenyl rings are sulfonated.

2.5. Conductivity measurements

Conductivity measurements were performed using a two probe method with a Princeton Applied Research potentiostat/galvanostat Model 273 A and Princeton Applied Research lock-in amplifier Model 5210 connected to a PC running electrochemical impedance software. The desired humidity was controlled barometrically by injecting aliquots of water into a container of known volume holding the sample at controlled temperature. The pressure in the barometric container equals the water vapor pressure, and the difference in the water aliquot added to the container and the water content in the vapor phase is assumed to be absorbed into the membrane [20,21].

2.6. IEC measurement

The membranes were vacuum dried at $\sim 80^\circ\text{C}$ for 3 h, then weighed. The membranes were placed in 1 M NaCl solutions overnight to exchange all the H^+ with Na^+ . The proton content in the salt solution was determined by titration with 0.01 N NaOH solution using phenol red as the endpoint indicator.

2.7. Swelling measurement

Membranes approximately $3\text{ cm} \times 3\text{ cm} \times 100\ \mu\text{m}$ thick were vacuum dried at $\sim 80^\circ\text{C}$ for 3 h, then weighed and the length measured. The membranes were then placed in liquid H_2O for 10 h at 25°C , the external water was wiped off and the samples were weighed and the length measured. The linear expansion rate (L , %) and H_2O absorption (W , %) were obtained using the Eqs. (1) and (2)

$$L(\%) = \frac{L_1 - L_0}{L_0} \times 100 \quad (1)$$

$$W(\%) = \frac{W_1 - W_0}{W_0} \times 100 \quad (2)$$

where L_0 and L_1 are the length of membranes before and after water absorption, respectively; W_0 and W_1 are the mass of membranes before and after water absorption, respectively.

2.8. Fuel cell performance evaluation of membranes

Membrane–electrode assemblies (MEAs) were prepared with 5 cm^2 ETEK electrodes with 0.4 mg/cm^2 Pt loading. The electrodes were impregnated with $1\text{ mg Nafion}^\circledast/\text{cm}^2$, and then pressed onto both sides of the membrane. For PSS and resin/PSS membranes, the MEAs were pressed at room temperature and 500 kPa; for $\text{Nafion}^\circledast$ -layered membranes, the MEAs were pressed at 130°C and 2 MPa. The MEAs were tested in a Globetech fuel cell test station. Humidified H_2 and O_2 were fed to the anode and cathode, respectively. The flow rates of H_2 and O_2 were 100 ml/min , which are considerably higher than the stoichiometric rates. The hu-

midity of the reactant streams was controlled by bubbling the gas streams through bottles of water at controlled temperature. Our standard test conditions were with the fuel cell at 80°C , the anode humidification bottle was at 88° and the cathode humidification bottle was at 86°C . The feed humidification was estimated to be $\sim 80\text{--}90\%$ relative humidity at 80°C , based on independent measurements of humidification of $100\text{ cm}^3/\text{min}$ N_2 flowed through the humidification bottles at 90°C . A few tests were done with the cell temperature at 120°C . Both humidification bottles were kept at 130°C for those tests. During preconditioning and for steady operation the cell voltage was controlled with a potentiostat. After the fuel cell had reached a stable voltage and temperature, cyclic voltammograms were done at a sweep rate of 100 mV/s and in the range of $0.1\text{--}1\text{ V}$ versus hydrogen electrode until they were reproducible and indicated no traces of impurities. Polarization curves of cell potential versus current were obtained by varying the external resistance with an electronic load.

3. Experimental results and analysis

Because the resin and PSS are chemically compatible it was possible to make composites with high loadings of resin; we prepared membranes with 50 wt.% of solid resin with no evidence of mechanical failure. By contrast, the incompatibility in $\text{SiO}_2/\text{Nafion}^\circledast$ composite membranes limited the SiO_2 content to less than 10 wt.% SiO_2 before the membranes became brittle and were unstable to handle [22].

The membranes were examined by a Philips XL-30 scanning electron microscope. The sample was sputter-coated with 3 nm of gold. As is seen in Fig. 2, the resin particle size is less than $3\ \mu\text{m}$ and the particle distribution was uniform.

The physical–chemical characteristics of the membranes are shown in Table 1, and for comparison, the properties of $\text{Nafion}^\circledast 115$ are also included. The values in Table 1 are averages of two or three measurements of samples from a single membrane. The water absorption and linear expansion in liquid water of the resin/PSS composite membranes decrease with the resin content in the membrane. The ion exchange capacity increased proportionally to the resin content in the composite membranes. However, the proton conductivity of the PSS composite membranes was nearly constant, independent of the resin content or ion exchange capacity. The PSS membranes are compared to $\text{Nafion}^\circledast 115$ in Table 1. The water absorption, swelling, and proton conductivity of all three PSS membranes is higher than $\text{Nafion}^\circledast 115$.

Neither water absorption nor proton conductivity scale with the sulfonic acid group density in the membrane. The water absorption and linear expansion both decreased with ion exchange capacity, and the proton conductivity was nearly independent of all ion exchange capacity for the PSS membranes. The PSS membranes swelled more than $\text{Nafion}^\circledast$ membranes. The PSS membranes are physically more flexi-

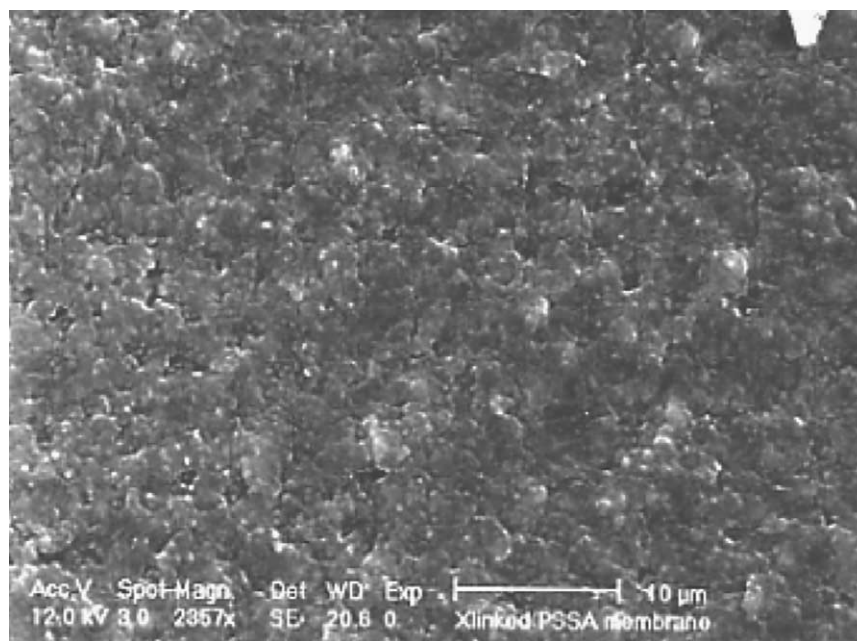


Fig. 2. Scanning electron micrograph of resin/PSS membrane with resin content being 45 wt.%. The area shown is $55 \mu\text{m} \times 40 \mu\text{m}$ (magnification $2357\times$). The graininess from the $3 \mu\text{m}$ resin particles is evident.

ble than Nafion[®], which permits greater swelling and water absorption

The composite membranes combine a stiff crosslinked polystyrene material with a rubbery poly(styrene–ethylene–butylene) polymer. Since the crosslinked resin cannot be processed to make well-defined sheets we were unable to measure the properties of the pure resin. However, by visual inspection the resin beads were hard glassy polymers; they did not swell more than 10–15% when exposed to boiling water. Crosslinking constrains the polymer network giving the resin rigidity and restricting the water absorption in the resin, even though it had greater ion exchange capacity. The surprising result was that the composite membranes had nearly constant proton conductivity with resin content, independent of the water absorption or ion exchange capacity. Since the composite

consists of resin particles embedded in a continuous phase of PSS we suggest that the proton conductivity in both phases is nearly the same. The low expansion of crosslinked resin results in smaller hydrophilic channels for proton mobility, and therefore, lower conductivity. On the other hand, the higher IEC of the resin increases its conductivity. The two opposite factors compensate each other, resulting in the conductivity of the resin being almost the same as that of PSS.

The fuel cell performances as a function of time of operation of up to 70 h for the composite membrane and plain PSS membrane are shown in Figs. 3 and 4, respectively. The steeper slope of the current voltage curve with time of operation reflects an increase in membrane resistance, suggestive of degradation of the membrane. PSS degradation is fast, the membrane resistance at 1 A/cm^2 increased from 0.23 to

Table 1
Characterization of the membranes

| | Membranes | | | |
|---|-----------|----------------------------|----------------------------|-------------------------|
| | PSS | 20% resin/PSS ^a | 45% resin/PSS ^a | Nafion [®] 115 |
| Ion exchange capacity (IEC, meq/g) | 1.50 | 2.02 | 2.72 | 0.91 |
| Swelling and water absorption from liquid water | | | | |
| Linear expansion (%) | 41.2 | 37.3 | 31.4 | 13.3 |
| H ₂ O take up (wt.%) | 340 | 318 | 288 | 149 |
| Conductivity, at 100% relative humidity (S/cm) | | | | |
| 60 °C | 0.280 | 0.250 | 0.236 | – |
| 80 °C | 0.304 | 0.308 | 0.303 | 0.142 |
| 100 °C | 0.320 | 0.315 | 0.320 | 0.154 |
| 120 °C | 0.303 | 0.310 | 0.323 | 0.166 |

^a 20% resin/PSS: composite membrane containing 20 wt.% resin and 80 wt.% PSS; 45% resin/PSS: composite membrane containing 45 wt.% resin and 55 wt.% PSS.

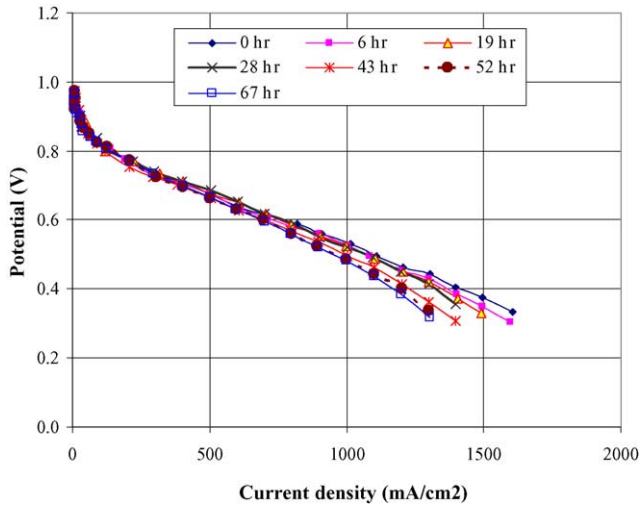


Fig. 3. The fuel cell performance of 45% resin/PSS membrane. Polarization curves taken after time-on-line as shown on the graph. (Membrane thickness: 100 μm ; operating conditions: anode: 88 $^{\circ}\text{C}$, cell: 80 $^{\circ}\text{C}$, cathode: 86 $^{\circ}\text{C}$, 1 atm H_2/O_2 .)

0.47 Ω after 55 h. The PEMFC with the composite membrane degraded more slowly, its resistance increased from 0.27 to 0.29 Ω over the same 50 h period. The results in Figs. 3 and 4 also suggest that the virgin PSS membrane gave slightly better performance in the fuel cell than the PSS–resin composite. This is a small difference, but seems to be in agreement with the results in Table 1, where the conductivity of the PSS was greater than the composite at lower temperatures.

It has been suggested that the degradation of fuel cell membranes occurs at the membrane/electrode interface [23,24]. In order to increase the chemical stability of membranes at the MEA interface, Nafion[®]/PSS/Nafion[®]-layered membranes were made by pressing 10 μm Nafion[®] membrane on both

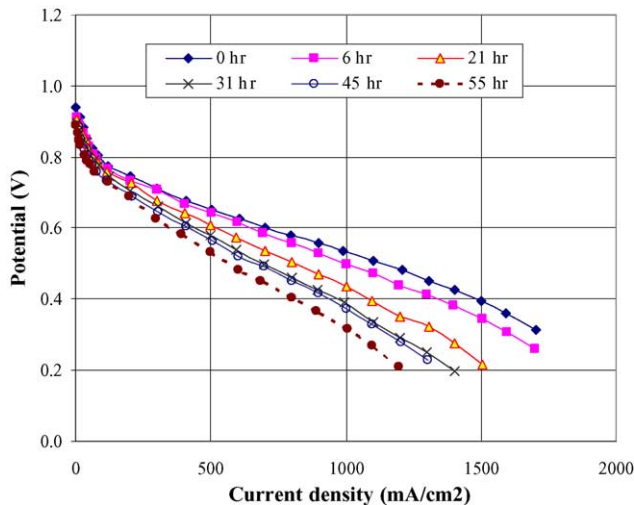


Fig. 4. The fuel cell performance of plain PSS membrane. Polarization curves taken after time-on-line as shown on the graph. (Membrane thickness: 90 μm ; operating conditions: anode: 88 $^{\circ}\text{C}$, cell: 80 $^{\circ}\text{C}$, cathode: 86 $^{\circ}\text{C}$, 1 atm H_2/O_2 .)

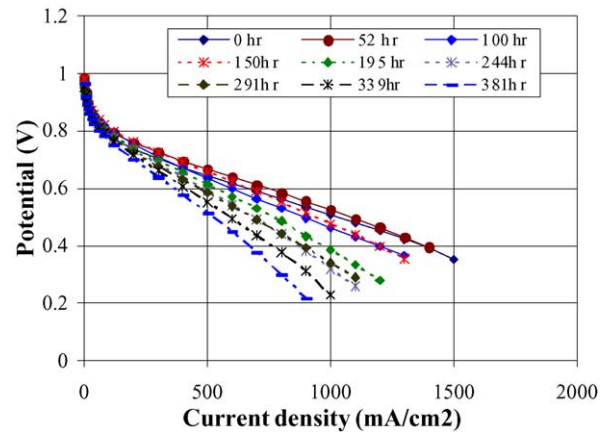


Fig. 5. The fuel cell performance of Nafion[®]/45% resin-PSS/Nafion[®] membrane (10/90/10 μm). Polarization curves taken after time-on-line as shown on the graph. (Operating conditions: 88/80/86 $^{\circ}\text{C}$, 1 atm H_2/O_2 .)

sides of PSS membranes. The fuel cell performance of a layered membrane is shown in Fig. 5. The Nafion[®] layers only slowed the rate of degradation a small amount, the increase in the membrane resistance with time was still significant after 381 h. The degradation of the layered membranes is also much greater than observed for Nafion[®] membranes (our experience is that Nafion[®] membranes operated in fuel cells for thousands of hours with minimal degradation [25]). This suggests that degradation of PEMFC membranes happens not only at the electrode–membrane–interface surface, but also throughout the membranes.

Our results do show that the addition of the ion exchange resin to the membrane slows the rate of membrane degradation. This is shown more clearly in Fig. 6 where the cell potential has been followed as a function of time at constant current density. The composite membranes, with or without a Nafion[®] barrier layer, showed a much slower decline of the cell voltage over time.

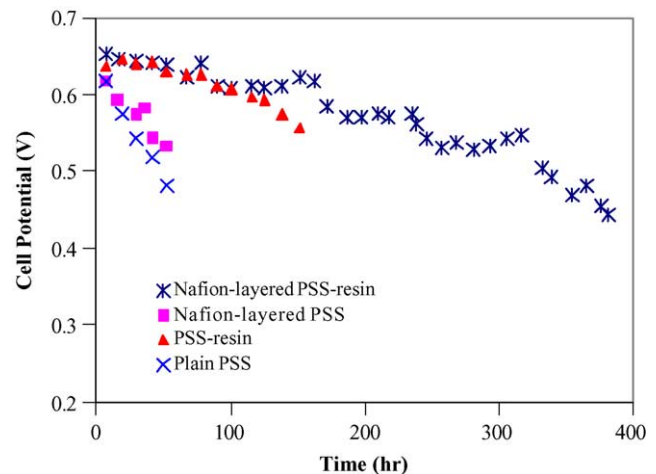


Fig. 6. Cell potential changes with time at fixed current density of 600 mA/cm^2 for different membranes. (Fuel cell conditions: 88/80/86 $^{\circ}\text{C}$, 1 atm H_2/O_2 .)

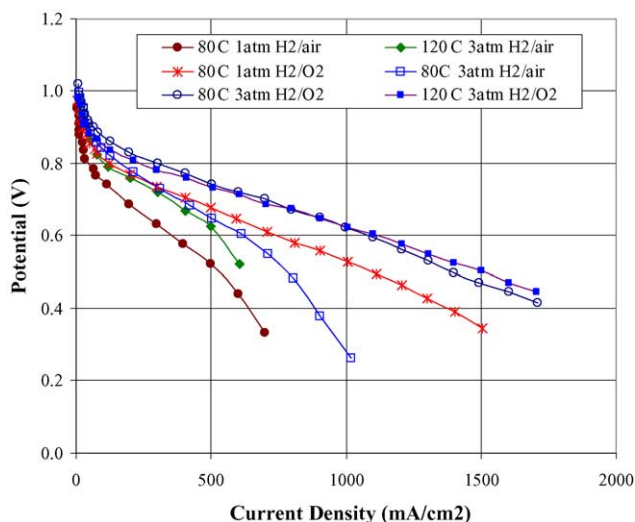


Fig. 7. Fuel cell performance of layered Nafion[®]-45% resin-PSS (10/89/10 μm) (H_2/O_2 and air). All the polarization curves were taken during the first 24 h of operation.

The mechanism that causes the increased resistance of the polystyrene membranes is not known. A possible mechanism is that reactive species formed at the electrodes diffuse into the polymer membrane and result in some chemical degradation of the polymer. During the reduction process of oxygen at the cathode, some free radicals, such as HOO^\bullet and HO^\bullet are formed. These free radicals can diffuse into the membranes attack the polymer chains degrading the performance of fuel cell. The accepted view is that the PSS structure can be attacked at the $\alpha\text{-C}$ by free radicals [26], and this could result in polymer chain scission as well as loss of the sulfonated phenyl groups from the polymer chain. The reason for the improved stability of fuel cell performance for the resin/PSS composite membranes could be due to the crosslinking restricting the diffusion of radicals through the resin phase of the composite. Additionally the crosslinked resin has a nearly infinite molecular weight so the time to break down the molecule by multiple radical reactions is increased. As a consequence, owing to the very large molecular weight and small channel for diffusion of free radicals, the resin/PSS composite membranes are much more stable than plain membranes.

Nafion[®]-layered resin/PSS membranes were also tested in fuel cells at 120 °C. To maintain the membranes humidified at the higher temperature the pressure in the fuel cell must be increased to 3 atm. The fuel cell performance was also tested at 80 °C and 3 atm, pressure and using both oxygen and air as oxidant. The results for the 45% resin/PSS membrane are shown in Fig. 7. The fuel cell performance of 20% resin/PSS membrane was similar to that of 45% resin/PSS membranes. At the same current density, the greater the reactant pressure, the higher the cell potential. Increasing the temperature also led to higher voltages at the same current. Because air contains only ~ 20 vol.% oxygen, the cell potential of air is lower than that of using oxygen as oxidant; however, the decrease in much greater than expected based on thermodynamics sug-

gesting that mass diffusion limitations also contribute to the decrease in cell voltage.

4. Conclusion

A new kind of composite proton exchange membranes was made composed of PSS and as high as 50 wt.% of a polystyrene ion exchange resin. The resin/PSS composite membranes have much higher IEC than PSS membrane, but the ion conductivity is similar to that of PSS. The water swelling of the composite membranes is lower than that of PSS. The PSS structure is attacked by the free radicals, so that the PSS degrades during the fuel cell operation. Nafion[®] layers between the PSS and the electrodes do not prevent the membrane degradation during the fuel cell operation, indicating degradation reaction occurs throughout the membrane. However, the resin/PSS composite membranes degraded much more slowly than PSS membranes suggesting that the very large molecular weight and small channel for diffusion of free radicals inhibit the rate of degradation.

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