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Nafion-layered sulfonated polysulfone fuel cell membranes

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Abstract

Sulfonated polysulfone (SPSU) with high ion exchange capacity (IEC) and ion conductivity was synthesized through deep sulfonation of polysulfone using the trimethysilyl chlorosulfonate as sulfonation agent. The silicon-containing compounds formed during the synthesis of SPSU were completely removed from the SPSU by simple evaporation. Water swelling, ion exchange capacity, conductivity and fuel cell performance were measured for the SPSU membranes. SPSU membranes with IEC twice that of Nafion-115 were prepared. The conductivity of the SPSU increased exponentially with the relative humidity (RH), achieving conductivities of 0.1 S cm^{-1} for RH > 70%. A Nafion-layered SPSU PEM fuel cell membrane was synthesized through pressing a thin Nafion-115 layer on to both sides of SPSU membrane. The Nafion layers on the SPSU prevented the water-soluble SPSU from being washed out of MEA, and the membrane was stable during the fuel cell operation up to 120 °C.

Keywords: Fuel cells; Polymer electrolyte membranes; Sulfonation; Polysulfone; Layered membranes

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted the attention because of their high-energy conversion efficiency, zero pollution emission and low operation temperature suitable for transportation and residential applications. Nafion (DuPont) [1], a perfluorosulfonic acid polymer, is the most widely used as proton conductor in the PEMFCs, due to its high ionic conductivity, good thermal stability, mechanical strength and chemical stability. However, its high price (presently, \$800 m^{-2}) [2] and the difficulty involved in its disposal [3] have spurred investigations for low-cost non-perfluorinated ionomer membranes, which are environmentally disposable. Proton conducting membranes investigated to date include polysulfonated triflurostyrene [4], polyether ether ketone (PEEK) [5,6], poly(arylene ether sulfone) (PSU) [7–9], PVDF-graft styrene [10–12], acid-doped polybenzimidazole (PBI) [13,14], polyphosphazene [15,16] and ion resin/polystyrene sulfonate composite materials [17]. The ideal fuel cell membranes should have low-cost (less than \$10 kW^{-1} in a PEMFC), high chemical stability, high mechanical strength and high conductivity. To date, none of the proposed materials have satisfied the desired specification.

PEEK, PSU and polyphosphazene are cheap and chemically stable [6,8,17]. To achieve good proton conductivity these materials must be highly sulfonated; as a result, these polymers swell substantially with water uptake and some are even soluble in water. Sulfonated poly(arylene ether sulfone) (SPSU), shown in Fig. 1, contains many polar groups (e.g. $-SO_2-$(sulfone) and $-O-$) along the backbone chain which contribute to the water uptake, but contribute little to proton conductivity.

Cross-linking may be employed to decrease the water swelling of these membranes. The Cross-linking has usually

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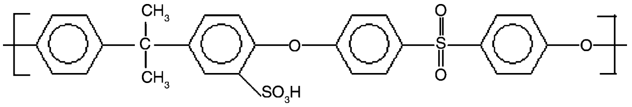

Fig. 1. Chemical structure of sulfonated poly(arylene ether sulfone) (SPSU).

involved multivalent cations bonding to sulfonic acid groups on different molecules [8,18]. This improves the mechanical strength of the polymer but results in decreased proton conductivity. Literature reports of the conductivity of SPSU are circa 0.01 S cm^{-1} [7], one magnitude order lower than that of Nafion-115.

We report here the preparation of layered Nafion/SPSU/Nafion membranes. The Nafion keeps the SPSU from being washed out of the membrane electrode assembly (MEA). The layered membranes have two thin Nafion membranes (∼10 μm) pressed on to both sides of a SPSU membrane. Because the SPSU molecules are large and carry the same kind of charges as Nafion, SPSU cannot penetrate through the Nafion layers, preventing the SPSU from being washed out of the MEA. Fuel cell performance of the layered membranes was comparable to that of Nafion, much better than that previously reported in the literature.

2. Experimental

2.1. Materials

Poly(arylene ether sulfone) (PSU), P-3500, was obtained from Solvay Advanced Polymers Company. The weight average molecular weight is about 77 000. 1,2-Dichloroethane, trimethysilyl chlorosulfonate, *N*,*N*-dimethylacetamide and methanol were purchased from Aldrich. Nafion-1100 solution (5 wt.%) was purchased from Ion Power Inc.

2.2. Synthesis of SPSU

The sulfonation process of the SPSU was similar to that used by Lufrano et al. [7] and Nolte et al. [8]. However, the highly sulfonated SPSU we prepared is soluble in the methanol and ethanol which required an alternative method to recover the SPSU product from the Si-containing compounds. The procedure is as follows. The PSU was dissolved in stirred dichloroethane at room temperature for about 5 h under Ar atmosphere. Trimethysilyl chlorosulfonate was added at room temperature as the sulfonation agent. During the reaction, Ar was purging continuously through the reaction solution and HCl was continuously produced and released out of the reactor with Ar. The degree of sulfonation was controlled by varying the mole ratio between sulfonating agent and monomer. After about 36 h, methanol was added to quench the reaction, and to cleave the silyl sulfonate moieties yielding sulfonated polysulfone. The primary reactions involved in the synthesis are shown in Fig. 2. Silicon-containing compounds, methyl sulfate, dichloroethane, methanol and water were removed through evaporation first at 1 atm and then vacuum (1–2 mmHg) at the temperature of 120 °C.

2.3. Analysis of Si content of the SPSU

The Si content was determined through the energy dispersive X-ray spectrometry (EDS) and ashing of the SPSU samples. The EDS were performed on Hitachi SEM S4200 and the sample was sputter-coated with 3 nm of gold. The ash test was carried out through heating the SPSU samples from room temperature to 750 °C in air and then maintaining temperature for 1 h.

2.4. Synthesis of membranes

Membranes were recast from solution in 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 thickness to ±2 μm.

The SPSU polymer was dissolved in a mixture of methanol–*N*,*N*-dimethylacetamide to make a 10 wt.% SPSU solution. An aliquot of SPSU solution for the desired membrane thickness was added to ∼20 ml isopropanol and poured into the membrane recasting setup which was at 70 °C. The solvents were evaporated at 70 °C for ∼3 h and then at 130 °C for about ∼5 h. After the solvents were completely removed, the membranes were removed from the glass plate, soaked in 1 M H_2SO_4 for 4 h and then washed completely with DI water to remove any metallic ion impurities. The SPSU membranes were transparent. Two ∼10 μm transparent Nafion membranes were cast by the procedures described above using Nafion-1100 solution (emulsion). Nafion-layered SPSU membranes were obtained by pressing the 10 μm Nafion membranes on both sides of SPSU membranes at 100 °C and 50 kg cm^{-2}.

2.5. Conductivity measurements

Conductivity measurements were performed at controlled humidity and temperature. Aliquots of water were injected 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.

2.6. IEC measurement

The membranes were vacuum-dried at ∼80 °C for 3 h, and then weighed. The membranes were placed in 1 M NaCl

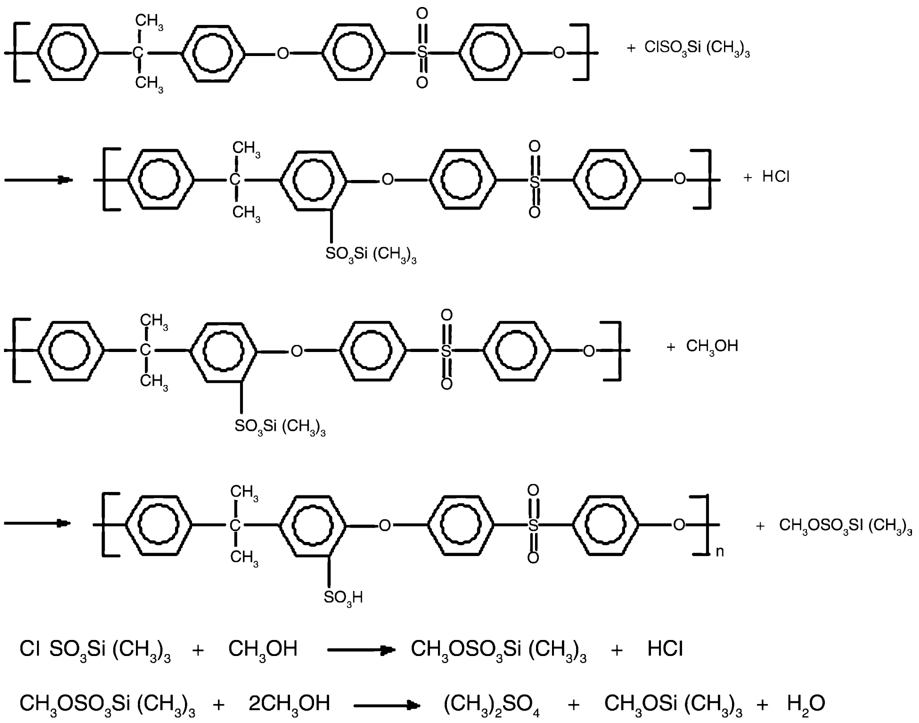

Fig. 2. The reactions involved in the sulfonation process of PSU. $(CH_3)_2SO_4$ and $CH_3OSi(CH_3)_3$ are volatile under vacuum at high temperature.

solutions overnight to exchange all the H^+ with Na^+. The proton content in the salt solution was determined by titration with 0.01N NaOH solution using phenolred as the endpoint indicator.

2.7. Swelling measurement

Membranes ∼4 cm × 4 cm were vacuum-dried at ∼100 °C for 3 h, weighed and the length measured. The membranes were then placed in liquid H_2O for 10 h, the external water was wiped off and the samples were weighed and the length measured. The linear expansion (L%) and water absorption (W%) were obtained using the Eqs. (1) and (2).

$$L\% = \frac{L_1 - L_0}{L_0} \times 100 \tag{1}$$

$$W\% = \frac{W_1 - W_0}{W_0} \times 100 \tag{2}$$

where the 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 made by first impregnating 1 mg Nafion1100 cm^{-2} into the electrodes and then pressing the electrodes (E-TEK 0.4 mg cm^{-2} Pt loading carbon cloth) onto both sides of the membrane at 130 °C and 200 kg cm^{-2}. The electrode area was 5 cm^2. The MEAs were tested in a Globetech fuel cell test station. Pure H_2 and O_2 or air was fed to the anode and cathode, respectively. The flow rates of H_2 and O_2 were 100 ml min^{-1}, which are considerably higher than the stoichiometric rates. Mass transfer resistance between the electrodes and reactants streams was negligible. The humidity of the reactant streams was controlled by bubbling the gas streams through sealed water bottles of water at controlled temperature. The cell voltage was controlled with a potentiostat. After the fuel cell had reached a stable voltage and temperature, the cyclic potential scanning was done at a sweep rate of 100 mV S^{-1} and in the range of 0.1–1 V versus hydrogen electrode for 1 h. Polarization curves of cell potential versus current were obtained by varying the external resistance with an electronic load.

3. Experimental results and analysis

3.1. Synthesis and silicon analysis of the SPSU

The sulfonation reaction conditions are shown in Table 1. Excess sulfonation agent was employed to obtain highly sulfonated PSU. The degree of sulfonation of PSU, (defined as the mole ratio of sulfonic acid group per monomer), was determined by IEC (results summarized in Table 1). With a large excess of sulfonation agent more than 100% degree of sulfonation was achieved, indicating that more than sulfonic

Table 1
Synthesis conditions and characterization of the SPSU

Membranes	SPSU-1	SPSU-2	Nafion-115
Sulfonation reaction conditions			
X[a]	1.43	2.86	
T(°C)	24–25	24–25	
t (h)	36	36	
IEC, meq g^{-1}	1.68	2.33	0.91
Degree of sulfonation[b] (%)	87	127	
Conversion of sulfonation agent[c] (%)	60.8	44.4	
Ashes content (mass) (%)	0.0	0.0	
Swelling and water absorption			
Linear expansion (%)			
@20 °C	13.6	136	8.0
@80 °C	Dissolved completely	Dissolved completely	13.3
H_2O take up (wt.%)			
@20 °C	38.8	1012	13
@80 °C	Dissolved completely	Dissolved completely	22

[a] Moles of sulfonating agent used per monomer of polysulfone (Fig. 1 shows one monomer of the polysolfone).
[b] Moles of $-SO_3H$ group attached on one monomer of polysulfone.
[c] The ratio of moles sulfonation agent reacted with the polymer to moles of total sulfonation agent.

acid residue was added per monomer unit. The conversion of trimethysilyl chlorosulfonate is 60.8 and 44.4% for SPSU-1 and -2, respectively, indicating that conversion decreased with degree of sulfonation.

Based on the amount of sulfonation agent used for the sulfonation reaction, the SiO_2 content of the SPSU-1 and -2 should be 14.3 and 24.0 wt.%, respectively. Previous investigators removed the silicon by precipitation of the polymer [7,8]. Lufrano et al. [7] added the SPSU solution dropwise into stirred ethanol. For low degree of sulfonation SPSU is insoluble in ethanol and hence it precipitated, while the silicon-containing compounds were soluble in ethanol. The precipitated polymer was free of silicon-containing moieties. Methanol was used by Nolte et al. [8] to precipitate the reaction products.

The SPSU prepared in this work was soluble in methanol and ethanol due to the high degree of sulfonation; hence evaporation of the solvent and Si compounds was employed instead of precipitation. The trimethylmethoxy silane by-product of sulfonation is sufficiently volatile to remove by evaporation. To determine the residual silicon content of the SPSU, the SPSU samples were heated to 750 °C in air for 1 h to burn away the organic polymer. Any residual Si should remain in the ashes as SiO_2. The ash content was below detectable limits for the SPSU samples, indicating that no Si-containing compounds remained in the SPSU samples. Further confirmation was obtained by EDS performed with a Hitachi SEM S4200; the EDS results are shown in Fig. 3. The SPSU samples contain only C, O, and S; Au was from the sputter-coating of the sample for the SEM. The EDS result was agree well with that of the ash test. We conclude that Si-containing compounds can be completely removed from the SPSU samples through the evaporation methods used in this work.

3.2. *The physical–chemical characteristics of the membranes*

The ion exchange capacity (IEC) and water swelling data for the membranes are shown in Table 1, and for comparison, the properties of Nafion-115 are also included. At room temperature, the linear expansion rate of the SPSU in water and the water take-up are higher than Nafion-115. The water take-up and linear expansion of the SPSU-2 are much greater than those of SPSU-1; the water swelling of SPSU increases dramatically with the IEC. The conductivity of the membranes is shown in Fig. 4. The SPSU-2 has higher conductivity than Nafion-115 when relative humidity (RH) is higher than 80%, and the conductivity is almost one order higher than that of SPSU prepared by other investigators [7–9]. Although the SPSU-1 could be completely dissolved in 80 °C liquid water, it was mechanically stable in water vapor of 100% RH for several hours, so that the conductivity measurements at 100% RH were possible. SPSU-2 was mechanically unstable in water vapor of 100% RH; conductivity measurements were limited to a maximum of 87% RH. Although the IEC of SPSU-1 is higher than that of Nafion-115, the conductivity is the same as Nafion-115 at 100% RH, indicating the proton conductivity of the polymer electrolyte depends on the structure of the polymer. The conductivity of SPSU-2 is higher than SPSU-1, owing to its higher IEC than SPSU-1. The conductivity of SPSU increases more rapidly with relative humidity than Nafion-115. The RH at which the SPSU conductivity increased exponentially was lower with increased degree of sulfonation. A possible explanation of the difference between Nafion and SPSU is the sulfonic acid placement. The sulfonic acid groups in Nafion are attached to side chains, which they are attached along the backbone of SPSU. The hydrophilic domains can separate more effectively in Nafion providing

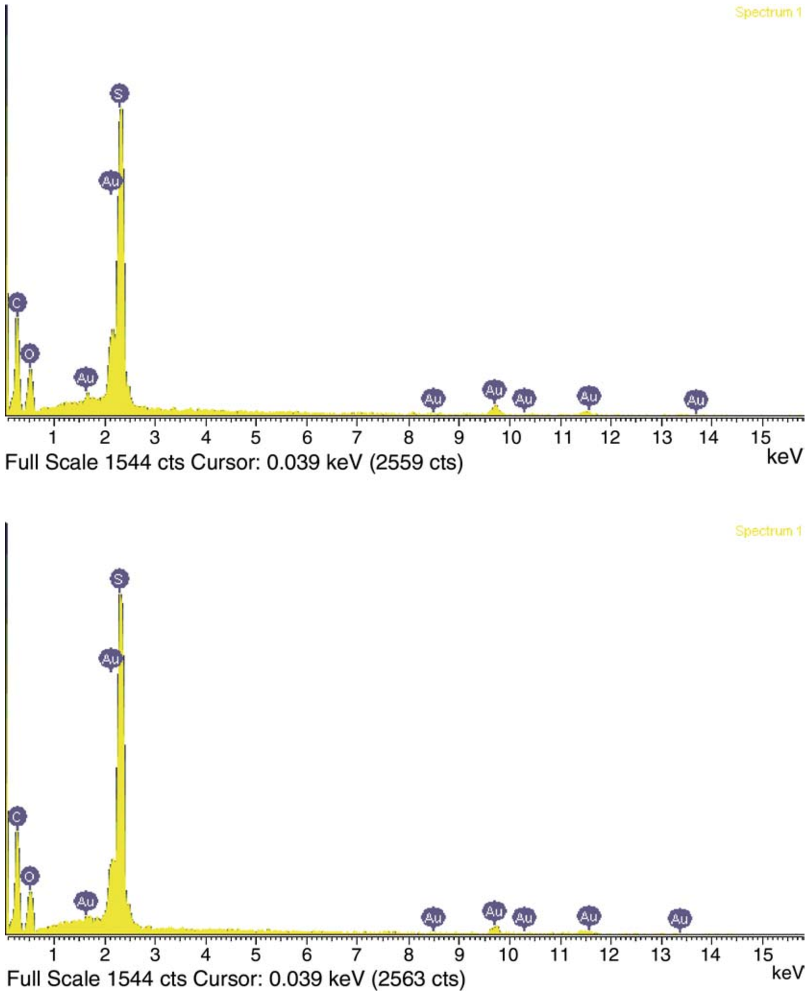

Fig. 3. The EDS of the SPSU samples. Standard: C: $CaCO_3$; O: Al_2O_3; S: FeS_2; Au: Au.

percolation channels at lower water content. This permits Nafion to have higher proton conductivity than SPSU with the same IEC.

3.3. The fuel cell performances of membranes

The SPSU membranes prepared in this work are soluble in water at the fuel cell operation temperature. To keep the SPSU from being washed out of MEA, Nafion/SPSU/Nafion-layered membranes were prepared as shown in Fig. 5. Nafion (10 μm)/SPSU (77 μm)/Nafion (10 μm) membranes were prepared and tested in a fuel cell test station. After running for 140 h, the experiment was shut down to examine the layered membrane. The SPSU was still intact between the Nafion layers, indicating that the thin Nafion layer confined the water-soluble SPSU inside the MEA. For comparison, a MEA was made from a plain SPSU-1 membrane of 100 μm thickness and was tested at 80 °C in the fuel cell test station. After 1 h the fuel cell effluent reached 100% relative humidity, the current from the cell dropped to zero and an explosive pop was heard from the fuel cell. The MEA apparently failed

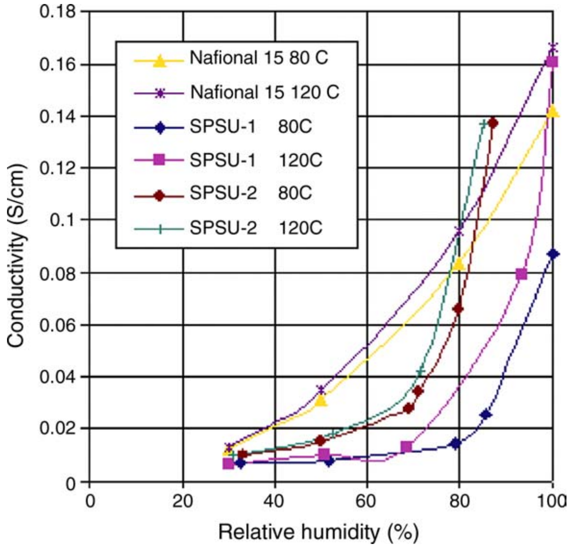

Fig. 4. The conductivity of sulfonated polysulfone membranes.

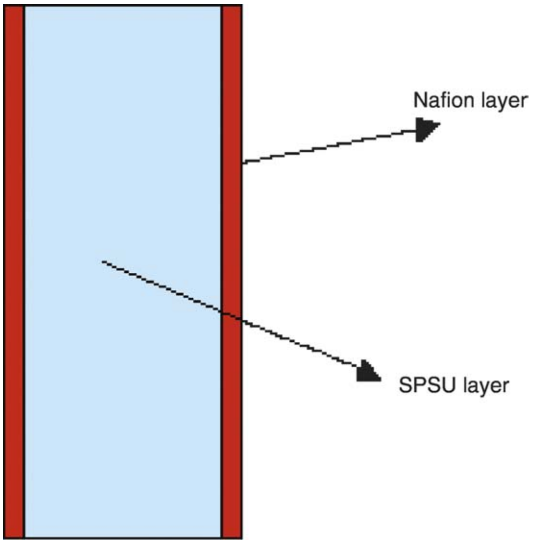

Fig. 5. Schematic diagram of Nafion/SPSU/Nafion-layered membranes.

when the SPSU membrane dissolved in water and began to flow out through the gas diffusion layer into the gas flow channels. The explosion occurred when the membrane failed and the H_2 and O_2 mixed and reacted on the Pt catalysts.

The layered membranes have two thin Nafion membranes (∼10 μm) pressed on to both sides of the SPSU membranes. The SPSU molecule is large with fixed negative charges. There is both size and charge exclusion of the SPSU from the Nafion. The SPSU membrane remains confined between the Nafion even at 100% relative humidity and up to 120 °C. As a result, highly sulfonated PSU can be used as fuel cell membranes.

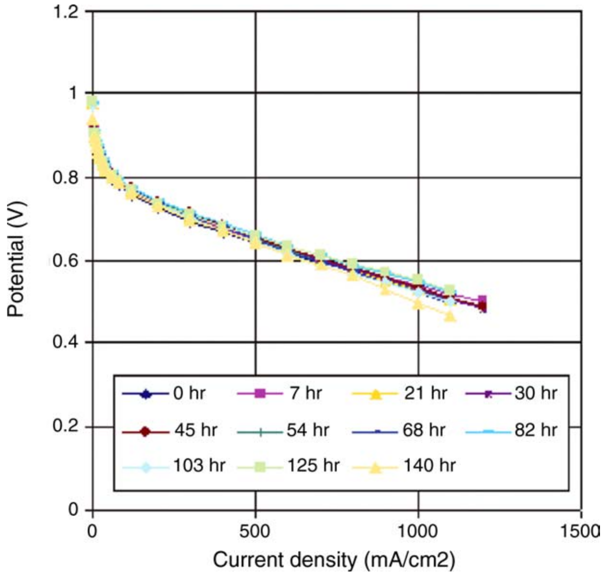

Fig. 6. The fuel cell performances of the Nafion-layered SPSU-1(10/77/10 μm) vs. operation time (operation conditions: 88/80/86 °C, total $P = 1$ atm, H_2/O_2).

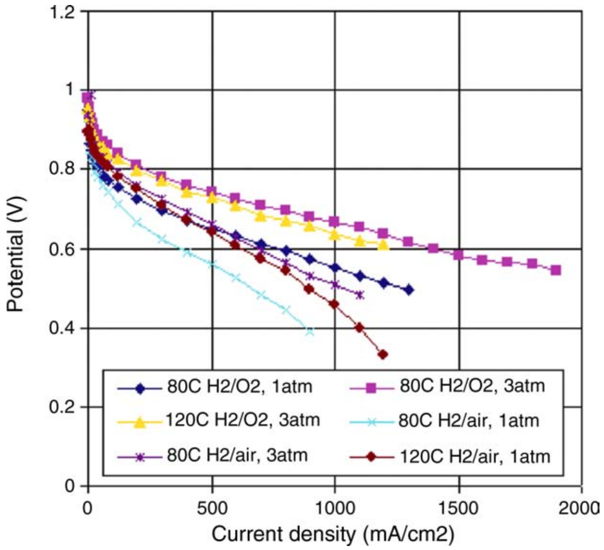

Fig. 7. The fuel cell performance of the Nafion-layered SPSU-1(10/77/10 μm) using O_2 and air as oxidants at different T and P.

The layered membrane's fuel cell performance was very stable as shown in Figs. 6 and 7. The Nafion-layered SPSU membranes were much more stable than the Nafion-layered polystyrene sulfonate (PSS) membranes [17], which were prepared by pressing two thin Nafion layers onto both sides of PSS membranes.

Fig. 7 compares the fuel cell performance of the Nafion-layered SPSU-1 using O_2 and air as oxidants at different temperature and pressure. The cell potential using air is lower than that with oxygen; however, the decrease was much greater than expected based on thermodynamics, suggesting that mass diffusion limitations, in the case of air as oxidant, also contribute to the decrease in cell voltage.

4. Conclusions

Sulfonated polysulfone (SPSU), with IEC more than twice that of Nafion-115, can be synthesized through deep sulfonation of polysulfone using the trimethysilyl chlorosulfonate as sulfonation agent. The silicon-containing compounds formed during the synthesis of SPSU can be completely removed from the SPSU by simple evaporation. The proton conductivity of the SPSU increases with the relative humidity (RH) and exceeds the conductivity of Nafion-115 above 80% RH. The higher the IEC, the higher is the conductivity of SPSU. Through pressing thin Nafion-115 layers on to both sides of SPSU membrane, a PEM fuel cell composite membrane—Nafion-layered SPSU was prepared. The Nafion layers on the SPSU serves as a shield preventing the water-soluble SPSU from being washed out of MEA, and the membrane is stable during the fuel cell operation up to 120 °C. The high fuel cell performance and high chemical stability makes the Nafion-layered SPSU be a promising PEM fuel cell membrane.

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