

Sulfonated poly(arylene ether sulfone) membranes based on biphenol for direct methanol fuel cells

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Abstract—A series of sulfonated poly(arylene ether sulfone) (PAES) were synthesized through direct aromatic nucleophilic substitution polycondensation of 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS), 4,4'-dichlorodiphenylsulfone (DCDPS) and 4,4'-biphenol (BP). With increasing sulfonate groups in the polymer, water uptake, ion exchange capacity (IEC) and proton conductivities increased, resulting from enhanced membrane hydrophilicity. The membranes exhibited higher thermal stability up to 300 °C, verified by thermogravimetric analysis (TGA). A maximum proton conductivity of 0.11 S/cm at 50 mol% of sulfonation degree was measured at 30 °C, which is slightly higher than Nafion[®]117 membrane (0.0908 S/cm). However, the methanol permeability of the PAES membrane was much lower than that of Nafion[®]117 membrane. As a result, a single cell performance test demonstrated that PAES-BP with 50 mol% sulfonation degree exhibited higher power density than Nafion[®]117.

Key words: Poly(arylene ether sulfone), Polymer Electrolyte Membrane, Fuel Cell, Sulfonation, Biphenol

INTRODUCTION

Direct methanol fuel cells (DMFC) have acquired worldwide attention as candidates for alternative automotive (car, truck and buses) and stationary (fuel cell and laptop) power sources due to features such as their adaptable size and low operating temperatures [1-3]. The vital part of DMFC is the polyelectrolyte membrane for transferring proton ions from anode to cathode as well as providing barrier to fuel crossover between electrodes. The commercially used membranes for fuel cell are perfluorosulfonic polymers such as Nafion[®], Gore-Select, Aciplex, Xus and Flemion. Methanol crossover is a critical property, occurring mostly due to the inability of the commercial perfluorosulfonic acid membranes to prevent methanol from permeating its membrane structure. This crossover methanol reacts with platinum catalyst at cathode, leading to a mixed potential at cathode. This mixed potential on cathode side causes a decrease in cell voltage. Poisoning of platinum catalyst takes place due to methanol oxidation intermediates [4-6].

Nafion[®] is by far the most studied proton electrolyte for fuel cells. Because of its poly(tetrafluoroethylene) backbone, it is chemically inert in both oxidizing and reducing atmospheres. Nafion membranes are highly acidic, and thus have excellent proton conductivity (9×10^{-3} – 12×10^{-2} S/cm at 80 °C in the range 34–100% relative humidity) [7]. These membranes have several limiting factors such as a low conductivity at low relative humidity, a high methanol permeability [8,9], and a low T_g (glass transition temperature) [10], which restricts its application to above 100 °C.

Alternative membrane materials such as sulfonated poly(aryl ether sulfone) (PAES) are being widely studied. Initial method to provide sulfonating group was made by post sulfonation route [11] in which it was difficult to control the location of sulfonation. Then, to the present day, well-controlled sulfonated PAES using persul-

fonated monomer has been developed by various groups [12-16]. Wang et al. [17] studied the synthesis of PAES-BP, but there is very limited study for fuel cell application. In this paper, thus, we report on the synthesis and characterization of PAES based on biphenol (PAES-BP), along with the detailed application of PAES-BP for DMFC. The membrane showed excellent properties, i.e., low methanol crossover, higher proton conductivities as compared to Nafion membrane.

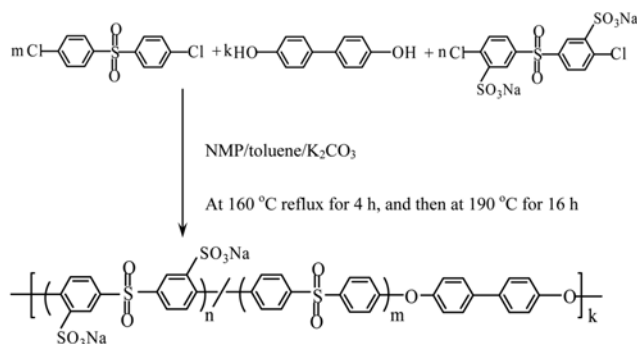
EXPERIMENTAL

1. Materials and Synthesis of Polymers

3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) was synthesized by the process reported by Udea et al. [15] and characterized by ¹H NMR to confirm the structure and purity. Firstly, 1.0242 g (5.5 mmol) of BP, 0.9621 g (3.3 mmol) of DCCPS, and 1.0806 g (2.2 mmol) of SDCDPS (rapidly weighed) were added to a three-necked flask equipped with an overhead mechanical stirrer, a nitrogen inlet, and a Dean-Stark trap. Potassium carbonate (6.3 mmol, 0.88 g) and sufficient NMP (18 ml) were introduced to afford a 20% (w/v) solid concentration. Toluene (9 ml; usually, NMP/toluene=2/1 v/v) was used as an azeotroping agent. The reaction mixture was refluxed at 150 °C for 4 h to dehydrate the system. The temperature was raised to 190 °C by the controlled removal of the toluene and the reaction time was about 16–35 h. The solution was cooled to room temperature and diluted with enough DMAc to allow easier filtering. After these processes, the copolymer was isolated by coagulation in stirred deionized water. And it was washed and immersed in deionized water at 60 °C overnight to extract the salts. Finally, it was vacuum-dried at 120 °C for 24 h.

Nucleophilic substitution condensation polymerization of 4,4'-dichlorodiphenylsulfone (DCDPS), 4,4'-biphenol (BP), and 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) leads to a random sulfonated PAES with two sulfonic acid groups per repeat unit, and in which the sulfonic acid groups are seated on the deactivated

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Scheme 1. Direct polymerization scheme of sulfonated PAES-BP copolymer.

sulfone-linked rings. Sulfonation degree (SD) was calculated through ^1H NMR. A general synthetic scheme of the copolymers is shown in Scheme 1.

2. Membrane Preparation

Membranes were prepared by dissolving the polymer in NMP (10 wt%) and directly casting onto the glass plate. The membranes were dried at 80 °C in a convective oven and further dried at 120 °C under vacuum condition for 2 days. The membranes were converted to acid form by immersing the membranes in 1.5 M sulfuric acid at 30 °C, followed by soaking in deionized water for 24 h. The acidified membrane was dried in a vacuum oven at 90 °C for 48 h.

3. Ion Exchange Capacity (IEC)

IEC of proton exchange membranes was measured by titration. The membranes were equilibrated with 50 mL of standard NaOH solution for 24 h and the IEC [meq/g dry membrane] was determined by back titration by using the following equation.

$$\text{IEC} = \frac{x \times N_{\text{NaOH}}}{W} \quad (1)$$

where x is NaOH quantity determined by back titration in mL and W is weight of polymer membrane in g.

4. Water Uptake

Water uptake was calculated with the following equation.

$$\text{water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

where W_{wet} and W_{dry} are the masses of wet membrane and dry membrane, respectively. The weight (W_{dry}) of proton exchange membranes was measured after drying for 48 hours in the vacuum oven at 80 °C. Then membrane was immersed in deionized water for 24 h, after being fully hydrated the weight was measured for wet weight (W_{wet}).

5. Thermal Analysis

Thermal properties of sulfonated PAES-BP copolymer membranes were investigated by using DSC and TGA. DSC measurements were carried out with a differential scanning calorimeter (TA Instruments, DCS 2010, U.S.A.) at a heating rate of 10 °C/min under nitrogen atmosphere. 15 mg samples were first dried by heating at 20 °C/min to 200 °C, quenched in liquid nitrogen reheated to 250 °C at 10 °C/min. The glass transition temperature, T_g was calculated at the inspection of the tangents to the corresponding DSC curve.

TGA was performed on TGA 1000, TA instrument in nitrogen to evaluate the thermal and thermo-oxidative stability of sulfonated poly(arylene ether) copolymers. Weight loss was measured and reported as a function of temperature. The thermal stability of the polymers was generally reported at the observed temperature of 5% weight loss.

6. Proton Conductivity

Proton conductivity was measured by a galvanostatic four-point-probe ac electrochemical impedance spectroscopy (EIS) technique, which was relatively so insensitive to the contact impedance that it could be adequate to accurately test membranes with high conductivity as reported before [18,19]. The impedance analyzer was worked in galvanostatic mode with ac current amplitude of 0.01 mA over frequency range from 8 MHz to 10 mHz by Nyquist method [18]. The proton conductivity of Nafion® 117 with this method was 0.0908 S/cm at room temperature, which was similar to the value mentioned by Du Pont.

7. Methanol Permeability

Methanol permeability measurement was performed with a home-made diffusion cell. Initially, one compartment (H_2O) of the cell ($V_{\text{H}_2\text{O}}=48.2$ ml) was filled with only deionized water. The other compartment (CH_3OH) ($V_{\text{CH}_3\text{OH}}=55.4$ ml) was filled with 5 wt% methanol solution in deionized water. The membrane that had the diffusion area of 12.76 cm^2 was sandwiched by Teflon O-ring and clamped between the two compartments tightly [18]. The value of methanol permeability for Nafion® 117 was found to be $2.379 \times 10^{-6} \text{ cm}^2/\text{s}$, which is of similar value as measured by Pivovar [20].

8. Single-cell Performance

To fabricate electrode, carbon-supported catalyst (46.1 wt% platinum on Ketjenblack), Nafion® solution (Aldrich, 5 wt% in 15-20%) and poly(tetrafluoro ethylene) (PTFE) suspension (Aldrich, 60 wt% in water) were homogeneously mixed.

The weight ratio of carbon-supported catalyst, Nafion®, and PTFE was fixed at 60 : 25 : 15 in the dry state. The membrane electrode assemblies (MEA) were prepared by placing the above electrodes on both sides of the membranes, followed by hot pressing at 110 °C for 1 min. A single direct methanol fuel cell (DMFC) was operated at a temperature of 110 °C, with an active area of 1 cm^2 . The feed flow rate of the anode was 1.8 ml/min of 2 M methanol solution, and cathode gas (oxygen) was maintained at 300 ml/min with an external pressurization of 2 atm.

RESULTS AND DISCUSSION

1. Synthesis of Sulfonated PAES-BP Copolymer

FT-IR spectroscopy has been commonly used to analyze characteristic bands corresponding to the sulfonate groups in sulfonated polymers, i.e., poly(arylene ether sulfone)s [21-23], polystyrene [24], polyester [25] and poly(phenylene sulfide) [26]. In this study, the successful introduction of the sodium sulfonate groups was confirmed by FT-IR spectra (Fig. 1), with strong characteristic peaks at 1,030 and 1,098 cm^{-1} assigned to symmetric and asymmetric stretching bands of the sodium sulfonate groups, respectively. These peaks were observed for all sulfonated copolymers from PAES-BP10 to PAES-BP50. The densities of these two characteristic peaks increased with higher degree of sulfonation, representing successful polymerization of sulfonated PAES-BP copolymer.

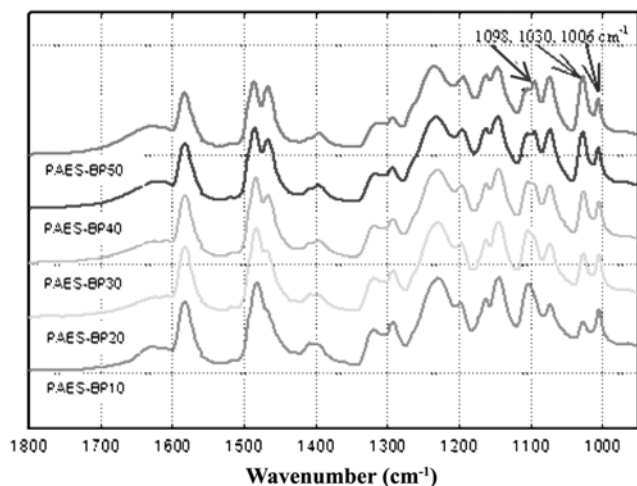


Fig. 1. FTIR spectra of sulfonated PAES-BP with various degrees of sulfonation.

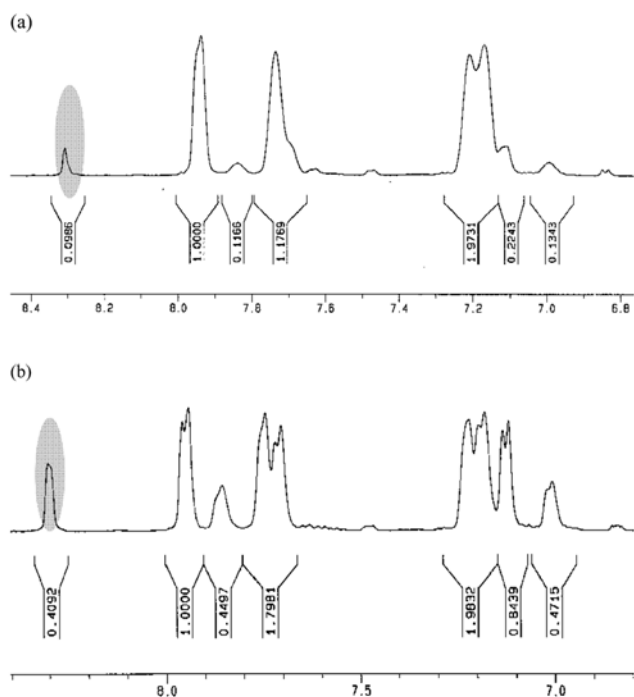


Fig. 2. ^1H NMR of (a) PAES-BP20 and (b) PAES-BP50.

^1H NMR spectroscopy was also used to characterize the series of sulfonated copolymers as NMR allows for compositional and structural determinations of each copolymer. The representative results are presented in Fig. 2. The integration and appropriate analysis of known reference protons of the copolymers allowed the relative compositions of the various copolymers to be determined. The protons adjacent to the sulfonate group derived from the disulfonated dihalide monomer in the copolymer were well separated from the other aromatic protons (8.3 ppm). The degree of sulfonation calculated from NMR data (Fig. 2) of PAES-BP 50 is 46.95% as compared to PAES-BP 20 with 18.89%. This shows the successful polymerization of PAES-BP copolymer.

2. Thermal Analysis

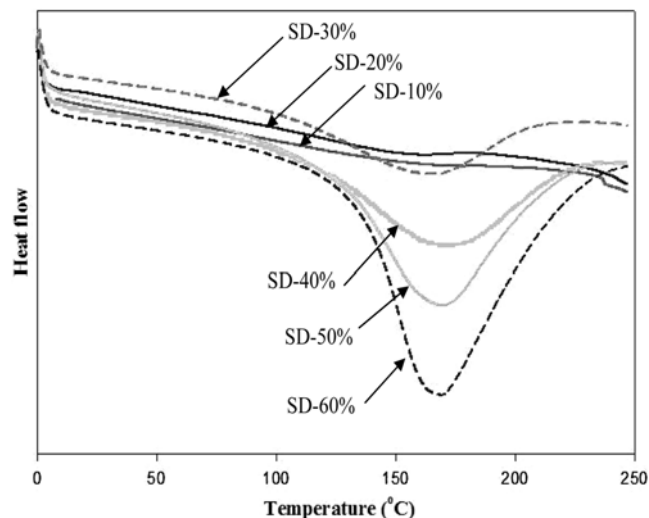


Fig. 3. DSC thermograms of sulfonated PAES-BP with various sulfonation degrees.

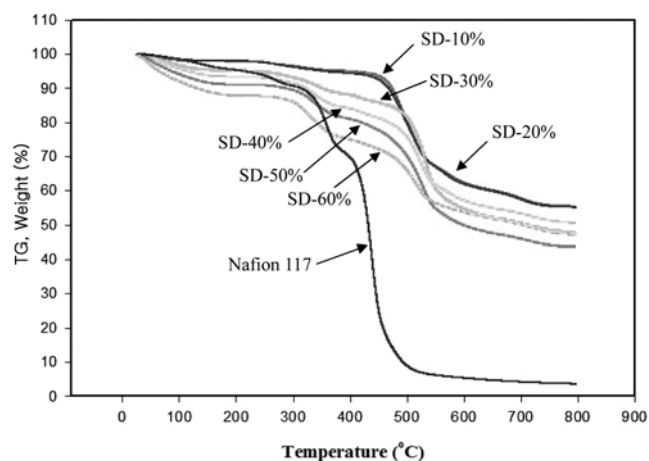


Fig. 4. TGA curves of sulfonated PAES-BP with various sulfonation degrees.

Thermal properties of sulfonated PAES-BP copolymer membranes were investigated by using DSC, as shown in Fig. 3. With increasing degree of sulfonation, T_g values increased from 150 to 170 $^{\circ}\text{C}$ for sulfonated PAES-BP copolymers. Many factors affect the glass transition of a polymer, including polymer structure, molecular symmetry, molecular weight, structural rigidity, and the presence of secondary forces. In the sulfonated polymers, the secondary forces presumably result from the presence of sulfonic acid group, producing additional strong interactions of polymeric chains. Thus, the introduction of sulfonate groups raises the T_g of polymer by increasing chain rigidity in the polymer chains.

The thermal and thermo-oxidative stability as a function of weight loss (%) of the sulfonated PAES copolymers were investigated by TGA. The results are provided in Fig. 4, where the sulfonated PAES copolymers are compared with Nafion[®] 117. All the samples were dried thoroughly in a vacuum oven at 80 $^{\circ}\text{C}$ to remove trace solvent and moisture. Then the TGA experiments were run from room temperature to 800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen

atmosphere. All the sulfonated PAES copolymers exhibited three-step degradation patterns. The weight loss found around 100 °C was due to the loss of residual moisture in the membranes, arising from the highly hygroscopic property of sulfonic acid groups. The second step of degradation around 300 °C exhibited similar second-step degradation temperature regardless of sulfonic acid groups, which was not affected by the chemical backbone of the PAES. The third step indicates the decomposition of the PAES backbone. Generally, all the sulfonated PAES exhibited excellent thermal stability up to around 300 °C.

3. Water Uptake and Ion Exchange Capacity (IEC)

Many significant properties of the PAES-BP membrane, such as proton conductivity and the water uptake, may depend on the IEC of the polymer. Water uptake and the IEC of PAES-BP were compared with common proton exchange membranes in Figs. 5 and 6, respectively. PAES-BP membranes showed higher IEC values than Nafion®117 above 40 mol% of sulfonation level. The high IEC value of the sulfonated PAES-BP implies that the sulfonated PAES-BP have many sulfonic acid groups and can transfer many pro-

tons. The hydrophilic nature of the PAES was examined with water sorption/uptake measurements. All the sulfonated copolymers were swollen by deionized water at 30 °C but were not soluble. Ueda et al. [15] reported lower water contact angles as a function of sulfonation in comparison with those of the unsulfonated control polymer. The water sorption of modified membranes was a function of the degree of sulfonation. The water uptake for sulfonated PAES-BP increased with increasing sulfonation as shown in Fig. 5. With approximately 50-60 mol% increase in sulfonation, a drastic increase in the water uptake was observed. The sulfonated PAES-BP60 copolymer has water uptake around 160%.

4. Proton Conductivity

The proton conductivities at different degree of sulfonation were studied at 30 °C, as shown in Fig. 7. The proton conductivities increased with the increase in degree of sulfonation. The conductivities increased at a steady rate and reached a plateau at 60 mol% sulfonation. In the case of PAES-BP50, a higher degree of ion exchange capacity was required to achieve more proton conductivities as that of Nafion®117. This might be due to the formation of a high-den-

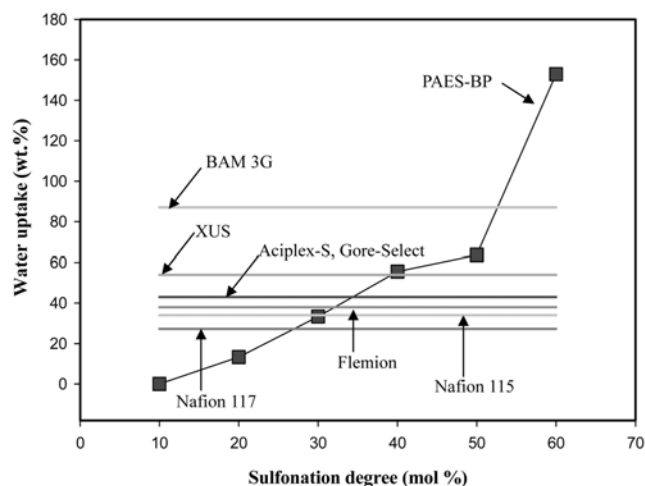


Fig. 5. Water uptake of sulfonated PAES-BP with various sulfonation degrees.

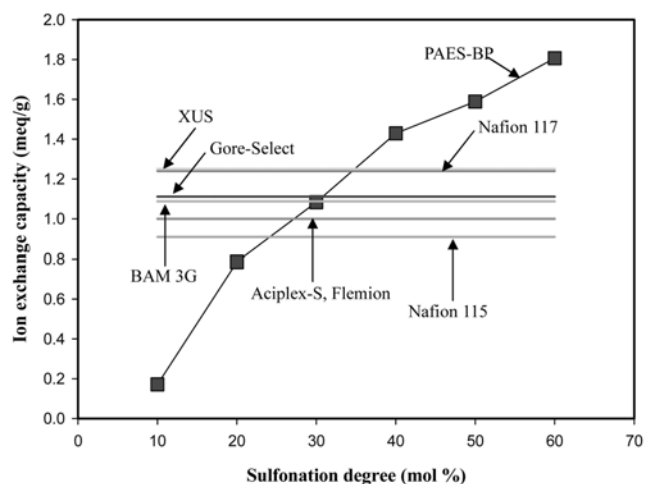


Fig. 6. IEC of sulfonated PAES-BP with various sulfonation degrees.

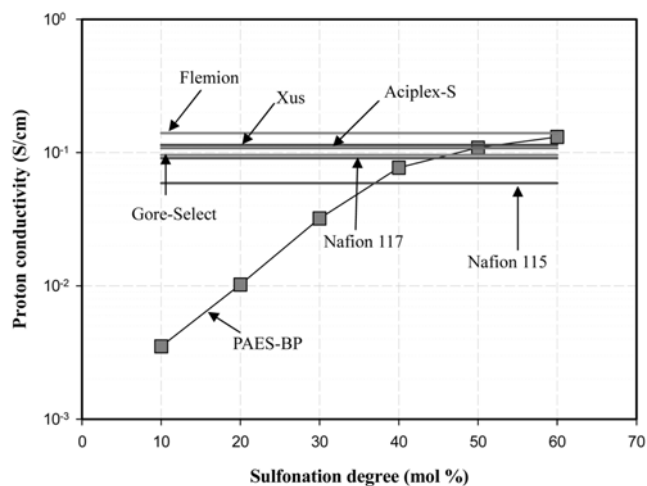


Fig. 7. Proton conductivity of sulfonated PAES-BP with various sulfonation degrees at 30 °C.

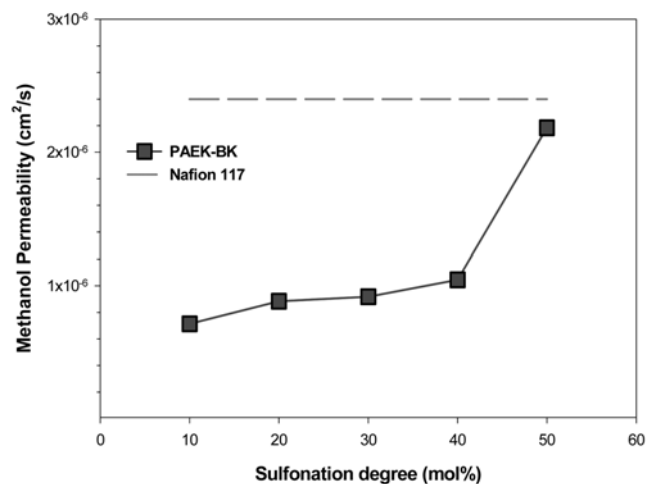


Fig. 8. Comparison of methanol permeability of sulfonated PAES-BP and Nafion117.

sity cluster in the case of Nafion®. The cluster was proposed to form ion channel through the material, which may greatly increase the rate of proton transfer conductivities [27]. However, the proton conductivity of PAES-BP at 60 mol% sulfonation is higher than Nafion®117. This might be attributed to the fact that with increase in number of sulfone groups, proton number increases in the proton exchange membrane. This results in the elevation of water uptake, which in turn is the path for proton movements.

5. Methanol Permeability

Methanol permeabilities of sulfonated PAES membranes were measured as a function of sulfonation level and were compared with Nafion®117 in Fig. 8. The proton conductivities increase as the sulfonation level increases. It is believed that the proton conduction and the methanol permeation mostly take place through the same pathway, because the behavior of both properties follows the same trend. Assuming that methanol mostly passes through a channel where water cluster forms, the sulfonated PAES membranes offer very interesting examples. Methanol permeation does not possibly occur, because of long distance between clusters. However, as sulfonation level increases, the number of hydrophilic domains gradually increases and finally the water cluster begins to be close enough to give rise to an increase in both the proton conductivity by Grotthuss mechanism and vehicle mechanism, and the methanol permeability. Therefore, the methanol transport in less swelling PAES membranes are governed by the population and the average distance of hydrophilic domains rather than the size of water clusters, differing from Nafion. This tremendous reduction of methanol cross-over could indicate a potential feasibility as an excellent electrolyte for DMFC.

6. Single Cell Performance for DMFC

According to the degree of sulfonation of PAES membranes, single cell performance for DMFC was measured as shown in Fig. 9. With the increase of sulfonation degree, the cell performance was also enhanced. At 10% of sulfonation degree, the measurement of cell performance was difficult. The I-V curves of single cell showed that at 0.3 V, the current density (A/cm²) of Nafion 117 was 335 mA/cm² and those of 20%, 30%, 40% and 50% of the sulfonation degree were 18, 72, 117 and 418 mA/cm², respectively. These results

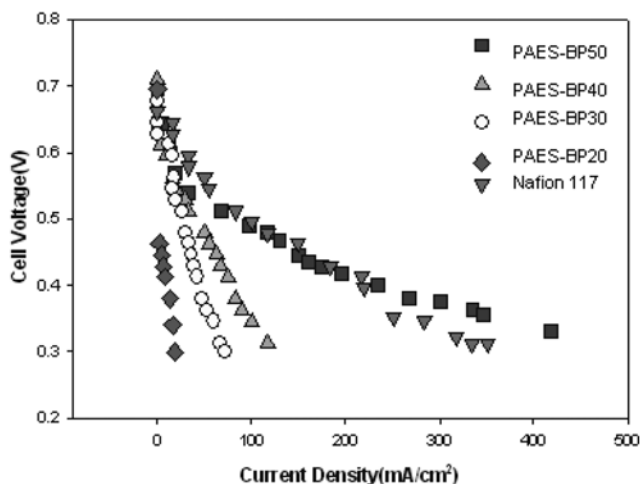


Fig. 9. DMFC performances of PAES-BP membranes and Nafion® 117.

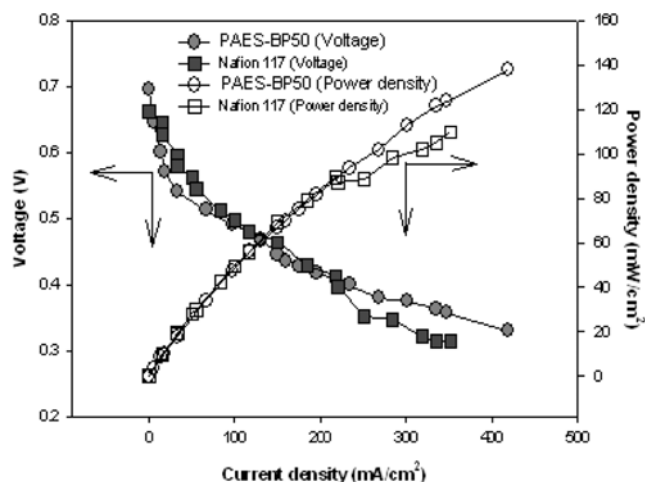


Fig. 10. Single cell DMFC performance of PAES-BP50 membrane and Nafion® 117.

demonstrate that as the degree of the sulfonation increased, the single cell performance was enhanced. Both the current density and the power density of the 50% sulfonation degree of PAES-BP were higher than those of Nafion®117, as shown in Fig. 10.

CONCLUSION

A series of sulfonated PAES copolymers based on BP were synthesized through direct aromatic nucleophilic substitution polycondensation for the polymer electrolyte membranes to DMFC application. The degree of sulfonation influenced the properties of the sulfonated PAES copolymers such as IEC, water uptake and proton conductivity. The IEC values of the sulfonated copolymers were easily controlled by changing the sulfonation degree. The water uptake increased linearly with increasing degrees of sulfonation in PAES-BP up to 50 mol%. Excellent thermal stability of the membranes up to 300 °C was observed by using TGA. PAES-BP with 50 mol% exhibited a slightly higher proton conductivity of 0.11 S/cm at 30 °C, but lower methanol permeability compared to Nafion®117 membrane. In addition, a single cell performance DMFC using PAES-BP with 50 mol% sulfonation degree was slightly higher than that using Nafion®117.

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