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Synthesis and characterization of proton exchange membranes based on sulfonated poly(fluorenyl ether nitrile oxynaphthalate) for direct methanol fuel cells

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ABSTRACT

A series of sulfonated poly(fluorenyl ether nitrile oxynaphthalate) (SPFENO) copolymers with different degree of sulfonation (DS) are synthesized via nucleophilic polycondensation reactions with commercially available monomers. Incorporation of the naphthalenesulfonate group into the copolymers and their copolymer structures are confirmed by ¹H NMR spectroscopy. Thermal stability, mechanical properties, water uptake, swelling behavior, proton conductivity and methanol permeability of the SPFENO membranes are investigated with respect to their structures. The electrochemical performance of a direct methanol fuel cell (DMFC) assembled with the SPFENO membrane was evaluated and compared to a DMFC with a Nafion 117 membrane. The DMFC assembled with the SPFENO membrane of proper DS exhibits better electrochemical performance compared to the Nafion 117-based cell.

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1. Introduction

Direct methanol fuel cell (DMFC) is a type of proton exchange membrane fuel cell (PEMFC) that generates electricity using liquid methanol as a fuel [1,2]. In the DMFC, methanol is oxidized at the anode, generating electrons, protons, and carbon dioxide. The proton is transported through a proton exchange membrane from the anode to the cathode, followed by combination with oxygen and an electron to complete the electrochemical reaction. Perfluorosulfonic

polymers such as Nafion are widely used in DMFCs as the proton-conducting membrane because they exhibit high proton conductivity and good mechanical, chemical and thermal stability [2–5]. However, there are some drawbacks to these materials, including high cost and high methanol permeability. Especially, the high methanol crossover from the anode to the cathode not only decreases fuel utilization but also causes mixed potentials at cathode, which reduces cell voltage and decreases the efficiency of the fuel cell system. Therefore, there have been significant efforts placed

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in the development of new proton exchange membranes possessing low methanol crossover in conjunction with high ionic conductivity. There has been particular focus on sulfonated aromatic polymers such as sulfonated poly(arylene ether sulfone), sulfonated poly(arylene ether ketone), sulfonated poly(ether sulfone ketone), sulfonated polyimide and so on [6–15], due to their excellent thermal and mechanical properties, as well as their resistance to oxidation under acidic conditions. However, the low sulfonation level leads to the low proton conductivity, which makes them unsuitable for using in fuel cells. To improve the proton conductivity, the sulfonation content should be increased, which results in deterioration in mechanical properties and high methanol permeation. It has been found that the introduction of nitrile groups into sulfonated aromatic polymer could reduce water uptake and improve the dimensional stability at similar sulfonation level [16–19].

With the goal of developing proton exchange membranes with high ionic conductivity, low methanol permeability and good dimensional stability, a series of sulfonated poly(fluorenyl ether nitrile oxynaphthalate) (SPFENO) containing nitrile groups were synthesized by nucleophilic substitution polycondensation of various amounts of 2,7-dihydroxynaphthalene-3,6-disulfonic acid disodium salt and 9,9-bis(4-hydroxyphenyl) fluorene with 2,6-difluorobenzonitrile. The degree of sulfonation (DS) and ion exchange capacity (IEC) in these polymer materials were controlled by adjusting the molar ratio of the reactants. The proton exchange membrane was prepared by casting from organic polymer solution dissolving SPFENO copolymer. It offered a more convenient and less expensive process than fabricating perfluorosulfonic acid membrane. Proton conductivity, thermal stability, water uptake, swelling behavior, mechanical strength and methanol permeability of the SPFENO-based membranes were investigated and compared with those of Nafion 117 membrane. Finally, the electrochemical performances of DMFCs assembled with the SPFENO membranes of different DS were evaluated and compared to that of DMFC with a Nafion 117 membrane under the same operating conditions.

2. Experimental

2.1. Materials

9,9-bis(4-hydroxyphenyl)fluorene (HPF) was purchased from TCI (Tokyo Chemical Industry, Japan) and recrystallized before use. 2,6-difluorobenzonitrile (DFBN) and 2,7-dihydroxynaphthalene-3,6-disulfonic acid disodium salt (DHNS) were purchased from TCI and used without further purification. Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), toluene, anhydrous potassium carbonate and Nafion 117 membrane were purchased from Sigma–Aldrich and used as received.

2.2. Copolymer synthesis

The SPFENO copolymer was synthesized by the nucleophilic substitution polycondensation reaction, as shown in Fig. 1. As an example, 10 mmol DFBN, 6 mmol HPF, 4 mmol DHNS and 11.6 mmol K_2CO_3 were added into a three-neck flask equipped with a mechanical stirrer, a Dean–Stark trap and an argon gas inlet. Then, 40 ml DMSO and 25 ml toluene were charged into the reaction flask. Argon gas was purged through the reaction mixture with stirring, and the mixture was refluxed at 140 °C for 4 h. After dehydration and removal of toluene, the reaction temperature was maintained at 170 °C for 20 h. The reaction mixture was then cooled to room temperature and precipitated in a large excess of de-ionized water with vigorous stirring. The precipitate was filtered and washed with water several times to remove inorganic salts. The fibrous polymer was collected and dried under vacuum at 110 °C for 24 h. The resulting polymer was denoted “SPFENO-40”, where 40 refers to the molar ratio of DHNS to diol monomers (HPF and DHNS). The chemical structure of the SPFENO copolymers was determined by 1H NMR spectrum using a VARIAN (Mercury 300) NMR spectrometer with DMSO- d_6 as the solvent. The chemical shift of tetramethylsilane (TMS) was used as an internal standard reference.

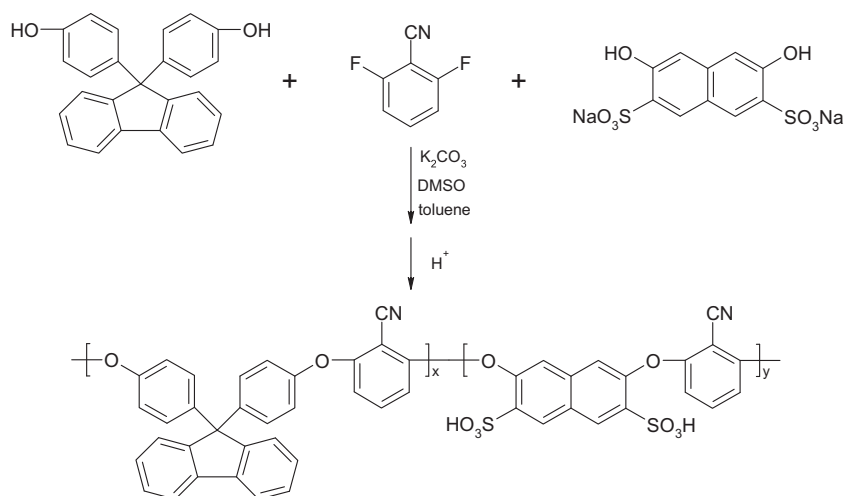


Fig. 1 – Reaction scheme for synthesis of SPFENO copolymers.

2.3. Preparation of the proton exchange membrane

The sulfonated copolymer in sodium salt was dissolved in NMP (10%, w/v) and filtered through a 0.45 μm Teflon[®] syringe filter. The filtered solution was poured onto a glass casting tray and dried at 50 °C for 24 h. The membrane was peeled from the glass plate by immersion in de-ionized water. The acid form of the SPFENO membrane was obtained by boiling the sodium form of the membrane in 0.5 N H_2SO_4 for 2 h, followed by washing with boiling water to remove excessive H_2SO_4 from the acidified membrane. Finally, a transparent and yellowish membrane was obtained.

2.4. Membrane characterization

The thermal stability of the membranes was examined using a TA instrument apparatus (TGA, model SDP 2960). Prior to analysis, the polymers were dried at 100 °C for 12 h to remove moisture. Dried polymer samples were heated at a rate of 10 °C min^{-1} in the temperature range of 100–600 °C under an air atmosphere. The mechanical properties of the acidified dry membranes were measured using a universal test machine (AGS-J, Shimadzu) with the ASTM D882 method. Each membrane was strained at a speed of 1 mm min^{-1} . For measurements of water uptake and swelling ratio, the membranes were first vacuum dried at 100 °C overnight. After measuring the weight and length of the dried membranes, the membranes were immersed in de-ionized water for 24 h at a specified temperature. Next, the water-swollen membranes were taken out, wiped with tissue paper and weighed immediately. Water uptake was calculated using the equation (1)

$$\text{water uptake}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where W_{dry} and W_{wet} are the weight of the dried and hydrated membranes, respectively. The swelling ratio was calculated by equation (2)

$$\text{swelling ratio}(\%) = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100 \quad (2)$$

where l_{dry} and l_{wet} are the lengths of the dried and hydrated membranes, respectively. The water uptake and swelling ratio of each sample were measured at least five times to ensure data reproducibility. The IEC values of the membranes were determined by titration. The dried membranes were immersed in 1 M NaCl solution for 24 h to facilitate the exchange of protons with sodium ions. After that, the IEC value was determined by back-titration of the solution with 0.01 M NaOH solution in order to evaluate the amount of protons released. The IEC value was calculated using the following equation (3)

$$\text{IEC}(\text{mequiv g}^{-1}) = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_{\text{dry}}} \quad (3)$$

where V_{NaOH} is the volume of NaOH solution consumed during the titration, C_{NaOH} is the molarity of the NaOH solution, and W_{dry} is the weight of the dry membrane. Proton conductivity was measured by the four-electrode AC impedance method using an impedance analyzer (ZAHNER, IM6) over a frequency

range of 1 Hz–100 kHz with an oscillating voltage of 10 mV. Proton conductivity was calculated from the membrane resistance (R) by the equation (4)

$$\sigma = \frac{d}{RA} \quad (4)$$

where d is the distance between the electrodes and A is the cross-sectional area of the membrane. Methanol permeability was measured using a liquid diffusion cell composed of two compartments. One compartment (A) was filled with a 10 M methanol/water solution and the other compartment (B) was filled with de-ionized water. The membrane was placed between the two compartments. Both compartments were slowly stirred during the permeation experiments. The amount of methanol diffusing from A to B across the membrane was measured over time with a refractive index detector (model RI750F, Younglin, Korea). The methanol permeability (P) was calculated by the equation (5):

$$P(\text{cm}^2\text{s}^{-1}) = \frac{k \times V_B \times L}{A \times C_A} \quad (5)$$

where k is the slope of the straight-line plot of methanol concentration in solution B versus permeation time (mol s^{-1}), V_B is the volume of solution B (ml), C_A is the concentration of methanol in the A cell (mol l^{-1}), A is the membrane area (cm^2), and L is the membrane thickness (cm).

2.5. Single-cell performance

Single-cell tests were performed on single cells with an active area of 9 cm^2 , as reported previously [20]. The membrane-electrode assembly (MEA) was fabricated with a Nafion 117 or SPFENO membrane, PtRu/C (HISPEC 12100, Johnson Matthey) as the anode catalyst, and Pt/C (HISPEC 13100, Johnson Matthey) as the cathode catalyst. The gas diffusion layer of the anode was Toray TGP-H-060 carbon paper (Toray Co., Japan) treated with 5 wt% PTFE, and that of the cathode was 25BC carbon paper (SGL, Germany). Pt loadings were 2.0 mg cm^{-2} for both anode and cathode. The polarization curves were obtained with an electrochemical measurement system capable of recording the voltage, current and temperature of the cell. The performance of the cells was measured with 1.0 M methanol solution under air atmosphere at 60 °C.

3. Results and discussion

The chemical structures of the sulfonated copolymers were confirmed by ^1H NMR spectra. Fig. 2 shows the ^1H NMR spectra of the aromatic protons for the series of SPFENO copolymers in sodium form. The proton signals (peak j) from the naphthalenesulfonate group are observed downfield due to both the deshielding ring current effect of the adjacent benzene rings and the presence of an electron-withdrawing sulfonate group. It can be clearly seen that the relative intensity of the corresponding protons in the naphthalenesulfonate increases with the molar ratio of DHNS in the reaction feed. Other proton peaks are also assigned to the synthesized molecular structure, as can be seen in the figure. The degree of sulfonation in the copolymer could be easily estimated from the

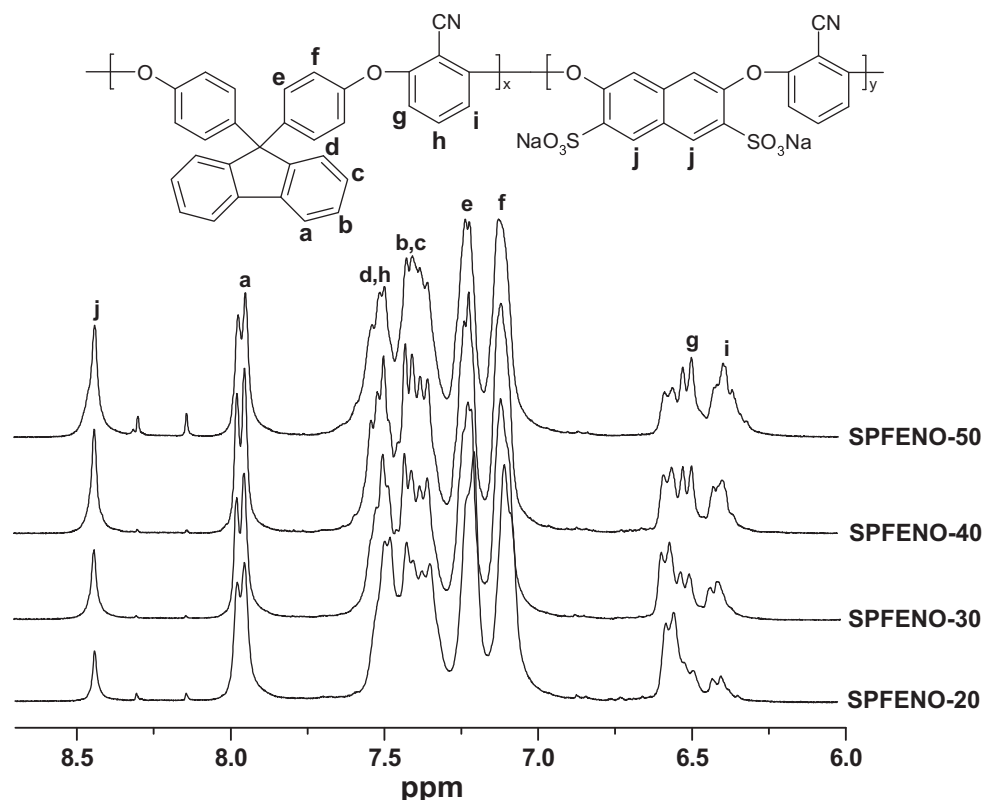


Fig. 2 – ^1H NMR spectra of the aromatic protons for the series of SPFENO copolymers in DMSO-d_6 .

relative ratio of integral values of peak a and peak j; these results are summarized in Table 1. The calculated DS values were very close to the expected values for all copolymers, indicating that the naphthalenesulfonate groups are quantitatively introduced into the polymer chains according to their feed ratio. The expected and measured IEC values of the polymer membranes in acid form are also given in Table 1. The experimentally measured IEC values were basically consistent with theoretical values, and the IEC values increased with DS, as expected. All SPFENO membranes have higher IEC than Nafion 117.

Thermal stabilities of the proton exchange membranes prepared with SPFENO copolymers were investigated by TGA analyses, and the results are shown in Fig. 3. For the purpose of comparison, the TGA curve of Nafion 117 membrane is also given in Fig. 3. The SPFENO membranes first began to slightly lose weight at temperatures above 300 °C, which corresponds

to the elimination of sulfonic acid groups in the copolymers. The significant weight loss observed in the 500–600 °C range can be attributed to the degradation of the main chain of the SPFENO copolymers. The higher degradation temperature of SPFENO membranes compared to Nafion 117 membrane implies superior thermal stability of the proton exchange membranes based on SPFENO copolymers. Membranes with higher DS degrade more quickly than those with lower DS. Accordingly, the membrane based on the SPFENO-20 copolymer exhibited the highest thermal stability among the membranes considered in this study.

The mechanical properties of the proton exchange membranes were evaluated by measuring their tensile strength. Fig. 4 compares the tensile strength of proton exchange membranes prepared with SPFENO copolymers. The tensile strength of a Nafion 117 membrane is also shown in the figure for comparison. An increase in the relative molar

Table 1 – Synthesis and characterization of SPFENO copolymers.

| Copolymer | DFBN (mmol) | HPF (mmol) | DHNS (mmol) | DS expected | DS from ^1H NMR | IEC expected (mequiv g^{-1}) | IEC measured (mequiv g^{-1}) |
|------------|-------------|------------|-------------|-------------|--------------------------|---|---|
| SPFENO-20 | 10 | 8 | 2 | 0.20 | 0.21 | 0.92 | 0.90 |
| SPFENO-30 | 10 | 7 | 3 | 0.30 | 0.31 | 1.36 | 1.30 |
| SPFENO-40 | 10 | 6 | 4 | 0.40 | 0.40 | 1.76 | 1.64 |
| SPFENO-50 | 10 | 5 | 5 | 0.50 | 0.51 | 2.24 | 2.17 |
| Nafion 117 | – | – | – | – | – | 0.90 | 0.89 |

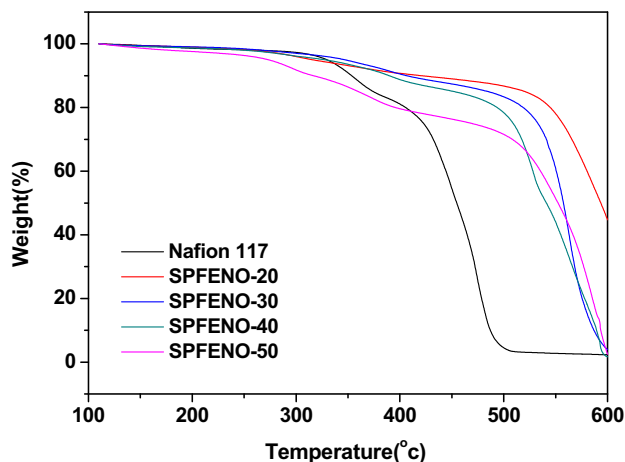


Fig. 3 – TGA curves of Nafion 117 and SPFENO membranes.

ratio of DHNS in the copolymer degrades the mechanical properties of the resulting polymer membrane. This result implies that the introduction of naphthalene disulfonic acid groups into the copolymer has a negative effect on the mechanical properties of the resulting membrane. Accordingly, the proton exchange membrane based on SPFENO-20 exhibited the highest tensile strength, with a tensile strength much higher than that of the Nafion 117 membrane. On the other hand, the proton exchange membrane prepared with SPFENO-50 was rather fragile in the dry state.

Water uptake and swelling behavior of the proton exchange membranes prepared with SPFENO copolymers and Nafion 117 are compared in Fig. 5. It can be seen that the membranes absorbed 3.9–93.2% of water, depending on DS and temperature. The membrane based on SPFENO-50 exhibited the highest water absorption over all temperatures, and its water uptake significantly increased with temperature. The swelling behaviors of the membranes were similar to those of their water uptake. The difference in water uptake and swelling behavior of the proton exchange membranes with changing DS can be attributed to the

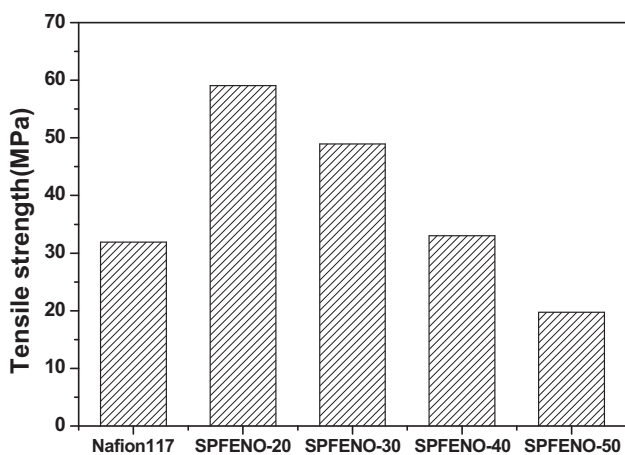


Fig. 4 – Comparison of the tensile strength of Nafion 117 and SPFENO membranes.

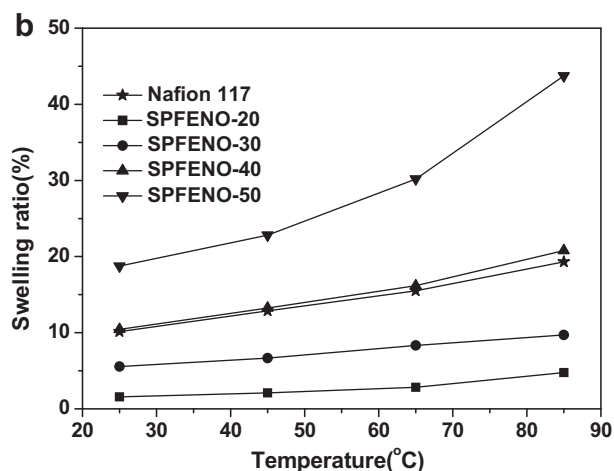
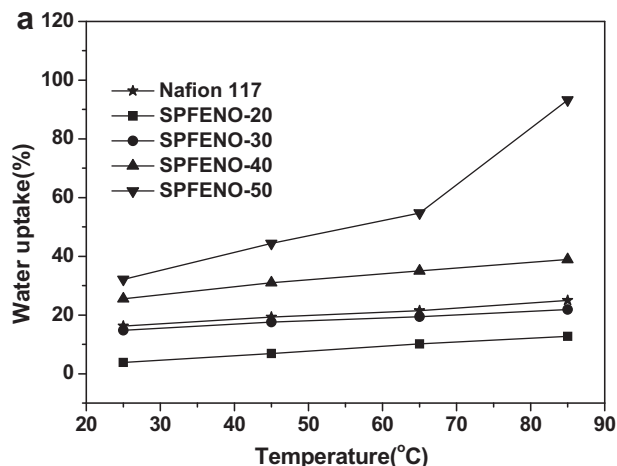


Fig. 5 – (a) Water uptake and (b) swelling ratio of Nafion 117 and SPFENO membranes as a function of temperature.

different molecular structures of the copolymers. The naphthalene sulfonic acid groups in the SPFENO main chain have much higher hydrophilicity than fluorenyl groups, resulting in enhanced water absorption. However, the membranes did not dissolve even in hot water and did not exhibit a significant loss in mechanical strength at a high degree of sulfonation. The nitrile groups on the aromatic rings of the main chain may enhance inter- or intramolecular interactions in the SPFENO copolymer; this consequently improves the dimensional stability of the membranes, even in a wet state.

Proton conductivities of the proton exchange membranes prepared with SPFENO copolymers and Nafion 117 were measured at 100% RH and are plotted as a function of temperature in Fig. 6. The proton exchange membranes prepared with SPFENO copolymers of higher DS exhibited higher proton conductivities over the entire temperature range. This can be explained by the higher ion exchange capacity of the corresponding membrane and the existence of many water molecules in the membrane. The membranes prepared with SPFENO-40 or SPFENO-50 exhibited high proton conductivities from 5.6×10^{-2} to 1.7×10^{-1} S cm⁻¹ over the temperature ranges of 25–85 °C, comparable to those of the Nafion 117 membrane in the same temperature range.

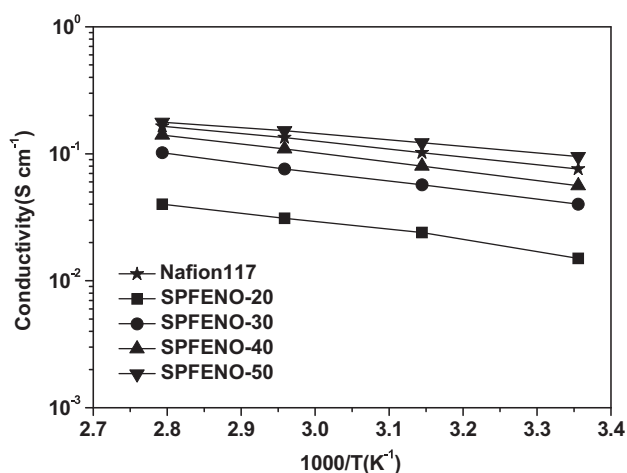


Fig. 6 – Temperature dependence of proton conductivities of Nafion 117 and SPFENO membranes.

Fig. 7 shows the methanol permeability of the various membranes. The methanol permeability of the membranes rapidly increased with increasing DS for the SPFENO copolymer. Although proton conductivities of the membranes based on SPFENO-50 are higher than those of the SPFENO-20 membrane (Fig. 6), the membrane prepared with SPFENO-50 has much higher methanol permeability than the SPFENO-20 membrane. Since, both high proton conductivity and low methanol permeability are important properties for proton exchange membranes in DMFCs, we expect that there is an optimum DS in SPFENO membrane for achieving good performance of DMFC.

In order to optimize the DS of SPFENO membrane in terms of cell performance, we assembled DMFCs with the SPFENO membranes of different DS. Unfortunately, we failed to fabricate a MEA with SPFENO-50 by hot-pressing process, because the SPFENO-50 membrane was too brittle to prepare the MEA. Fig. 8 compares the electrochemical single-cell performances of MEAs based on Nafion 117 and SPFENO membranes, measured at 60 °C under feed flow rates of

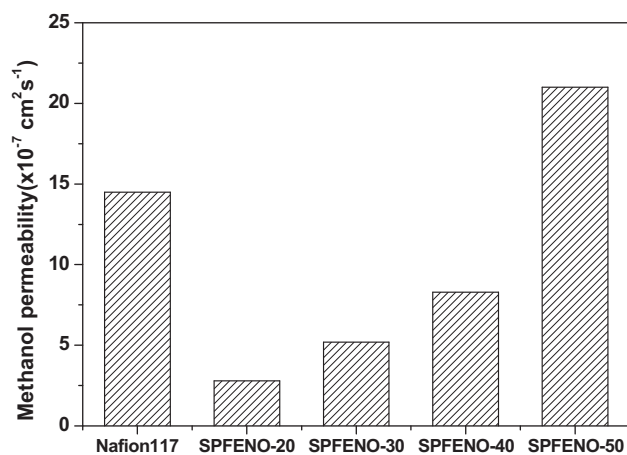


Fig. 7 – Methanol permeability of Nafion 117 and SPFENO membranes.

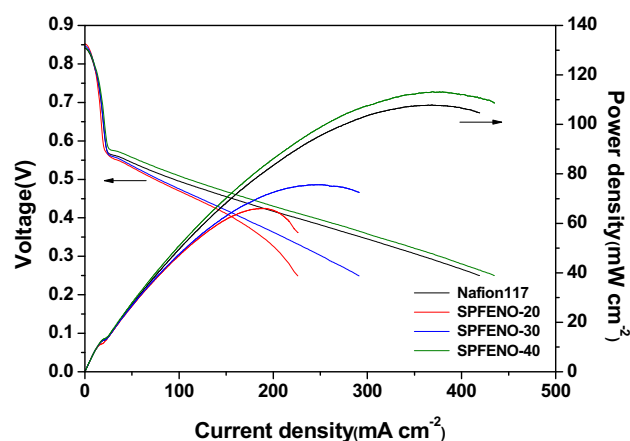


Fig. 8 – Polarization and power density curves of a single-cell assembled with Nafion 117 and SPFENO membranes of different DS. The measurements were carried out with 1.0 M methanol solution and air at 60 °C.

3 cc min⁻¹ of 1.0 M methanol and 400 cc min⁻¹ air at atmospheric pressure. It is clearly seen that the polarization curves and power density of DMFC are dependent on DS of SPFENO membrane. An open circuit voltage (OCV) of the cell slightly decreases with increasing DS of the membrane. All the cells assembled with SPFENO membrane shows the higher OCV than that of Nafion 117-based cell. This result suggests that the SPFENO membranes can suppress the methanol crossover in DMFC, because the OCV is closely related to the methanol permeation and increases when the methanol crossover is decreased. The cell performance was found to be improved with DS of SPFENO membrane, which may be ascribed to their high proton conductivity. It was very encouraging that SPFENO-40 membrane exhibited better cell performance than that of Nafion 117 in the whole range of current density. The maximum power density of the SPFENO-40 membrane reached 113.2 mW cm⁻², which is also higher than the value obtained for Nafion 117 (107.8 mW cm⁻²). The improved fuel cell performance may be associated with the higher selectivity of the SPFENO-40 membrane, which is defined as the ratio of proton conductivity to methanol permeability. These results suggest that the SPFENO-40 membrane with a proper balance between high conductivity and low methanol permeability is a promising candidate for a proton exchange membrane in DMFCs. More studies on long-term stability and efforts to improve the cell performance are currently in progress.

4. Conclusions

A novel series of sulfonated poly(flourenyl ether nitrile oxynaphthalate) copolymers with varying DS were synthesized by nucleophilic substitution polycondensation. DS was controlled by varying the molar ratio of DHNS to HPF. The SPFENO membranes exhibited good thermal stability and mechanical strength. The membrane prepared with high DS (SPFENO-50) showed high proton conductivity, but mechanical weakness and high methanol permeability limited its

practical use as a membrane in a DMFC. Evaluation of single-cell performance showed that the cell assembled with the SPFENO-40 membrane exhibited superior performance compared to a Nafion 117-based cell. These results demonstrate that proton-conducting membranes based on SPFENO copolymers with optimum sulfonation level are of practical interest for use in direct methanol fuel cells.

Acknowledgments

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