

Proton Exchange Membrane Based on Sulfonated Poly (Aromatic Imide-Co-Aliphatic Imide) for Direct Methanol Fuel Cell

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A new sulfonated poly(aromatic imide-co-aliphatic imide) (SPI) for the use as a polymer electrolyte membrane was successfully synthesized from 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid disodium salt (S-DDM), hexamethylenediamine, and 3,3',4,4'-benzophenonetetracarboxylic dianhydride in a one-step reaction. S-DDM was prepared by the direct sulfonation of DDM monomer. The degree of sulfonation of the sulfonated copolyimide was varied by using various molar concentrations of S-DDM. The sulfonated copolyimide with the highest degree of sulfonation possessed the proton conductivity of 0.0032 S.cm^{-1} in a wet state. The highest methanol permeability of the sulfonated copolyimide was $2.75 \times 10^{-8} \text{ cm}^2.\text{s}^{-1}$ which is ~425 times lower than that of the Nafion 117. The highest membrane selectivity belonged to the membrane with 34% degree of sulfonation with the value of $1.65 \times 10^6 \text{ s.S.cm}^{-3}$ which is three orders of magnitude higher than the commercial Nafion 117.

Keywords: sulfonated poly(aromatic imide-co-aliphatic imide), proton conductivity, direct methanol fuel cell, methanol permeability.

1. Introduction

Direct methanol fuel cell (DMFC) has received much attention due to their high power density, high energy conversion efficiency, low emissions, as well as low pollution levels¹. The main applications for DMFC are energy sources of small vehicles such as a forklift, consumer goods such as laptops, mobile phones, and digital cameras. The essential part of DMFC is the polymer electrolyte membrane (PEM) which acts as an electrolyte for transferring protons from the anode to the cathode, and a separator that prevents the mixing of the reactant gases. At present, various sulfonated perfluoropolymers such as Nafion, Flemion, and Aciplex have been perceived as the highest proton conductive membranes in their fully hydrated states because they exhibit high proton conductivities and excellent chemical and mechanical stabilities. However, these commercial membranes have several drawbacks including high cost, high methanol crossover, and loss of proton conductivity at temperatures above 80 °C, which limit their application in DMFC². Alternatively, J. Lobato *et al.*, (2006)³ used a perfluorsulphonic polymer to produce a less expensive membrane namely the Sterion membrane; the Sterion L-180 and the Nafion 117 possessed the ionic resistances of 0.122 Ohms and 0.182 Ohms, respectively.

Recently, various types of polymer electrolyte membranes have been developed-poly(styrene sulfonic acid), sulfonated poly(ether ether ketone), sulfonated polysulfone². Among these proton exchange membrane candidates, the sulfonated polyimide

has gained much attention because it has high mechanical, thermal, and chemical stabilities⁴⁻³⁰. In addition, the chemical structure of its polymer backbone can be varied in different ways depending on the monomer selected. A variety of monomers can bring about flexibility or rigidity to the main chain.

In this work, a new sulfonated poly(aromatic imide-co-aliphatic imide) (SPI) with different degrees of sulfonation were synthesized from 4,4'-diaminodiphenylmethane (DDM), sulfonated 4,4'-diaminodiphenylmethane (S-DDM), hexamethylenediamine (HDA), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (DTDA). The structure design of this SPI membrane was to combine the hydrophilic part namely the sulfonic acid side group to increase proton conductivity, and the hydrophobic aromatic polymer backbone to increase strength and flexibility and to lower methanol permeability. Fourier transform infrared spectroscopy was used to determine the structure of the synthesized sulfonated copolyimides. The ion exchange capacity (IEC), thermal stability, water uptake, degree of sulfonation (DS), proton conductivity, and methanol permeability were measured and investigated and compared with the commercial Nafion membrane.

2. Experimental

2.1 Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA; Aldrich, 96%), 4,4'-diaminodiphenylmethane

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(DDM; Aldrich, 97%), and hexamethylenediamine (HDA; Aldrich, 98%) were used as starting monomers. For the sulfonation process, fuming sulfuric acid (Merck, 65%) and concentrated sulfuric acid (Univar, 98%) were used as the solvents. Benzoic acid (Univar, 99.9%) as a catalyst, and triethylamine (Fluka, 98%) were used in the membrane synthesis. Hydrochloric acid (HCl; Univar, 37%) was used to protonate the synthesized membrane. Sodium chloride (Lab-Scan, 99.0%) and sodium hydroxide (Univar, pellet purity 97%) were used to determine the degree of sulfonation (DS) and the ion exchange capacity (IEC). Methanol (MeOH; Lab-Scan, 99.9%) and ethanol (EtOH; Lab-Scan, 99.9%) were used in the methanol permeability measurement.

2.2 Synthesis of 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid disodium salt (S-DDM)

To a round bottom flask, 4,4'-diaminodiphenylmethane (10 g, 50 mmol) and 20 mL of 98% sulfuric acid at 0 °C were added. Then, the reaction mixture was stirred until the 4,4'-diaminodiphenylmethane was completely dissolved, after which fuming sulfuric acid (5 ml) was added. The reaction mixture was continuously stirred at 0 °C for 2 h, followed by stirring at 80 °C for 2 h. After cooling to room temperature, the solution was carefully poured over crushed ice. A sodium hydroxide solution was added to salt out the monomer precipitate. The resulting monomer precipitate was filtered off, washed with deionized water, and dried in vacuum for at least 24 h.

2.3 Synthesis of Sulfonated Poly(aromatic imide-co-aliphatic imide)

The synthesis of SPI was performed by a one-step reaction. The molar ratio of S-DDM: DDM: HDA was fixed at 1: 4: 5. In a round bottom flask, 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid disodium salt (S-DDM) (0.1219 g, 0.34 mmol), triethylamine, hexamethylenediamine (0.1955 g, 1.6 mmol), and DDM (0.2654 g, 1.33 mmol) were dissolved in dimethyl sulfoxide (15 ml). The solution mixture was mechanically stirred under nitrogen atmosphere at 70 °C. Next, BTDA (3.3 g, 10.0 mmol) was then added to the reaction mixture and benzoic acid (0.1610 g, 1.32 mmol) was used as a catalyst for the polymerization process. The reaction was continuously stirred at ambient temperature for 24 h to obtain the synthesized polymer.

2.4 Membrane Formation and Protonation

The sulfonated poly(aromatic imide-co-aliphatic imide) film was prepared by a solution casting method. Polymer solution in DMSO was cast onto glass plate and dried in a vacuum oven at 80 °C for 24 h, followed by 100 °C for 24 h, 120 °C for 16 h, and 160 °C for 18 h. The SPI membrane was deprotonated by immersing the membrane in a 1.0 M

HCl solution at room temperature for 48 h. The resulting membrane was thoroughly washed with de-ionized water until neutral and then dried in the vacuum oven at 80 °C for 24 h.

2.5 FTIR and ¹H NMR Spectroscopy

Fourier transform Infrared (FTIR) spectra of DDM, S-DDM and BTDA were recorded on a Thermo-Nicolet NEXUS 670 FTIR spectrometer using a KBr pellet as the background material. The FTIR spectra were measured in the wavenumber range of 400 cm⁻¹ to 4000 cm⁻¹. ATR-FTIR technique was used to record the spectrum of SPI with ZnSe as a background material.

¹H-NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. Deuterated dimethylsulfoxide (DMSO-*d*₆) was used as a solvent.

2.6 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed to investigate the thermal stability of the polymer membranes with a Perkins Elmer Pytis Diamond TG/DTA instrument. The samples were heated at a heating rate of 20 °C/min under nitrogen atmosphere from 50 °C to 900 °C.

2.7 Ion Exchange Capacity

Ion exchange capacities (IECs) of the sulfonated polyimide membranes were determined by the titration method¹³. The membranes were cut into small pieces and then immersed in 1.0 M NaCl solution and stirred for 2 days at room temperature. The solution was titrated with a 0.01 M NaOH solution with phenolphthalein used as an indicator. The IEC values were calculated with the following equation:

$$\text{IEC (meq/g)} = \frac{V_{\text{NaOH}} (\text{ml}) \times C_{\text{NaOH}} (\text{M})}{W_{\text{dry}} (\text{mg})} \quad (1)$$

where V_{NaOH} is the added volume of sodium hydroxide solution at the equivalent point, C_{NaOH} is the molar concentration of the sodium hydroxide solution, and W_{dry} is the dry weight of the sample in H⁺ form (mg).

2.8 Degree of sulfonation

The polymer membranes were acidified by a 0.1 M HCl solution at room temperature for 24 h. The membranes were washed with deionized water and dried at 80 °C for 24 h, followed by immersion in a NaCl solution for 24 h. The DS of the solution was determined by the titration method with 0.01 M NaOH using phenolphthalein as an indicator. The DS of the membrane was calculated with the following equation:

$$\text{DS (\%)} = \frac{(V_{\text{NaOH}} (\text{ml}) \times C_{\text{NaOH}} (\text{Molar})) / 1000}{\text{Mole of polymer membrane}} \times 100 \quad (2)$$

where V_{NaOH} is the volume of NaOH consumed, and C_{NaOH} is the molar concentration of NaOH.

2.9 Water uptake

Water uptake (%) was determined by immersing the membranes in distilled water at 80 °C for 5 h. The membranes were taken out, quickly wiped with tissue paper, and weighed on a microbalance. The percentage of water uptake was calculated by the following equation²⁸:

$$\text{Water uptake(\%)} = \frac{W_s - W_d}{W_d} \times 100\% \quad (3)$$

where W_s and W_d are the weights of the wet and dry membrane samples, respectively.

2.10 Proton conductivity

Proton conductivities (σ) of the membranes were determined by an electrochemical impedance spectroscopy (EIS) technique using an Agilent E4980A Precision LCR Meter⁸. The 16451B dielectric test fixture with the type C electrode was used. The sulfonated films were cut into 0.5 cm × 0.5 cm pieces and submerged in water for 24 h, then the excess water was wiped off, coated with a silver paint before measurement. This measurement condition is referred to as a wet state. The measurement was then carried out at room temperature at 50%RH. The coated membrane was measured at a 1 V potential using an alternating current in the frequency range of 20 Hz to 2 MHz. The proton conductivity was calculated by the following equation:

$$\sigma (S.cm^{-1}) = \frac{d}{R \times A} \quad (4)$$

where σ is the proton conductivity, d is the thickness of the membrane, A is the area of the interface of the membrane in contact with the electrodes, and R is the resistance which can be derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) or Z' axis.

2.11 Methanol permeability

Methanol permeability (P) was determined by using a liquid permeation cell consisting of two compartments (A and B) separated by a tested membrane¹¹. A 2.5 M methanol solution was placed in compartment A and de-ionized water was placed in compartment B. The concentration of the methanol in compartment B was analyzed using gas chromatography (GC) at 30 °C and 60 °C. Methanol permeability (P) was calculated by the following equation:

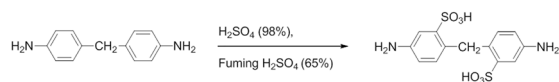
$$P (cm^2/s) = \frac{K_B V_B L}{A(C_A - C_B)} \quad (5)$$

where C_A and C_B are the initial methanol concentrations in the feed and permeated compartment, respectively, V_B is the volume of the permeate solution, A is the effective area of the membrane, L is the thickness of the membrane, and k_b is the methanol concentration gradient vs. time (the slope of methanol concentration profile in the compartment B).

3. Results and Discussion

3.1 Monomer synthesis

DDM was converted into S-DDM via the direct sulfonation using fuming sulfuric acid as a sulfonating agent, as shown in Scheme 1. In the first step, concentrated sulfuric acid (98%) reacted with the amino group of the DDM to create the quaternary ammonium salt of sulfuric acid. In the second step, SO_3 in the fuming sulfuric acid reacted with the DDM to produce the S-DDM. The S-DDM monomer was characterized by ¹H-NMR spectroscopy. Signals assigned to the three aromatic protons of S-DDM appear at $\delta = 7.16$, 7.12, and 6.71 as shown in figure 1. The attachment of sulfonic group onto the polyimide chain at the aromatic ring can be referred to the work of Deligoz *et al.*, (2008), the primary amine resonance is apparent as a broad singlet at $\delta = 5.55$, whereas the methylene protons resonate at $\delta = 3.82$ ¹³.



Scheme 1. Synthesis of S-DDM.

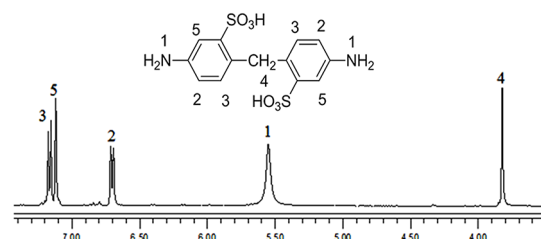
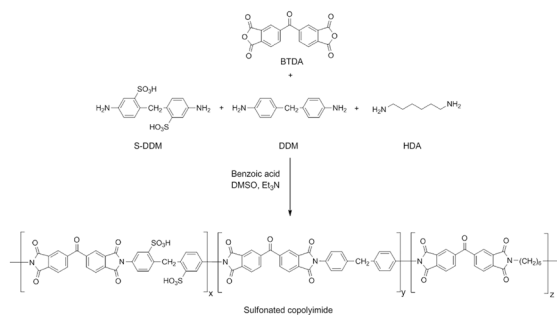


Figure 1. The ¹H-NMR spectrum of S-DDM in DMSO-*d*₆.

3.2 Copolymer synthesis

The new SPI was successfully synthesized by copolymerization of SDDM, DDM and HDA, as shown in Scheme 2. The molar ratio of SDDM:DDM:HDA was fixed at 1:4:5. The chemical structure of the resulting sulfonated copolyimide was confirmed by FTIR measurements. The unsulfonated copolyimide was also synthesized with the molar ratio of DDM:HDA = 5:5. Figure 2 shows that the FTIR spectra of both copolyimides possess the characteristic absorption bands of the imide groups at 1777 cm⁻¹ and 1709 cm⁻¹, which can be attributed to the C=O asymmetric and C=O symmetric stretchings, respectively^{24,26,28}. The band at 1662 cm⁻¹ corresponds to the carbonyl group of benzophenone²⁶. The absorption band at 1368 cm⁻¹ is attributed to the characteristic C-N stretching of the imide group^{24,26,28}. The observation of all characteristic imide bands in both copolyimides indicates complete thermal imidization. In the case of the sulfonated copolyimides, the absorption bands of sulfonic acid groups namely the symmetric and asymmetric S-O stretchings appear



Scheme 2. Synthesis of poly(aromatic imide-co-aliphatic imide) (SPI).

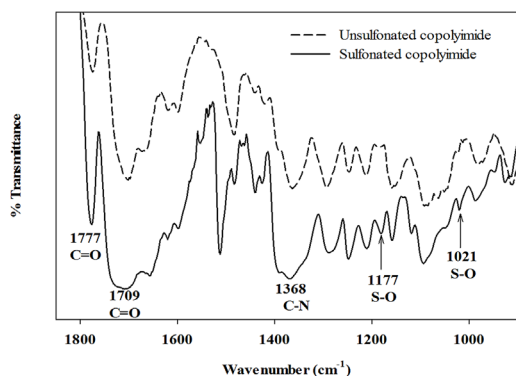


Figure 2. FTIR spectra of unsulfonated and sulfonated copolyimides.

at 1182 cm^{-1} and 1019 cm^{-1} , respectively²⁴. The FTIR band at 1050-1100 cm^{-1} is due to the stretching of sulfoxide group (S=O). The sulfonated copolyimide shows a higher peak area and intensity relative to the unsulfonated copolyimide due to the amount of the S=O group present²³.

3.3 Thermal Stability

The thermal stability of the membrane is important in DMFC operation. The membrane should be stable when the fuel cells are operated at an elevated temperature in the range of 70-100 °C. Thermogravimetric analyses for sulfonated copolyimide membranes with different molar ratios of S-DDM: DDM: HDA (**SDH 0**, **SDH 1**, **SDH 2**, **SDH 3**, **SDH 4**, and **SDH 5**) were investigated, as tabulated

in Table 1. Figure 3 shows that the unsulfonated copolyimide membrane (**SDH 0**) exhibits only one main weight loss at temperature about 450 °C, corresponding to the degradation of the polymer main chain^{10,12,13,18}. All other sulfonated copolyimide membranes (**SDH 1-SDH 5**) demonstrate a typical two steps degradation pattern. The first weight loss at 200-300 °C can be ascribed to the decomposition of sulfonic acid groups by desulfonation^{10,12,13,18}. This weight loss at 200 °C is due to the phosphoric acid degradation³¹. It is apparent that weight loss (%) increases in proportion to the molar concentration of S-DDM or the degree of sulfonation. The second weight loss at ~450 °C is attributed to the decomposition of the polymer main chain^{10,12,13,18}. Thus, all synthesized sulfonated copolyimides show high thermal stability.

3.4 Degree of sulfonation, ion exchange capacity, and water uptake

The measured DS values are tabulated Table 1; the maximum DS value is as high as 96% for the SDH 5 membrane.

IEC is the number of milli-equivalents of ions in 1 g of dry membrane. The experimental IEC values of the membranes were determined by the titration method, while the theoretical IEC values were computed by the content of the sulfonic acid groups incorporated into the polymer backbone. In this work, the measurements were carried out for the series of sulfonated copolyimides. The IEC values of copolyimides with the different molar ratios of S-DDM: DDM: HDA are tabulated in Table 1 and the titration method details can be found in Supplementary section, table S1. The experimental IEC values are 0, 0.84, 1.28, 2.20, 2.82, and 3.12 meq.g^{-1} ; they are slightly lower than the theoretical IEC values which are 0, 0.87, 1.49, 2.23, 2.97, 3.24 meq.g^{-1} for the SDH 0 - SDH 5 membranes, respectively. This might be caused by the incomplete proton exchange^{12,29}. On the other hand, the experimental IEC value of the commercial Nafion 117 is much lower; it is only 0.95. Figure 4 shows the plots of DS and IEC of the copolyimides at different molar ratios of S-DDM: DDM: HDA. It can be seen that the IEC value increases linearly with increasing DS.

Table 1. Ion exchange capacity and water uptake (%) of the sulfonated copolyimides.

Copolymer	[SDDM]:[DDM]: [HDA]	Degree of sulfonation (%)	IEC (meq.g^{-1}) (30 °C)	Water uptake (%) (30 °C)
SDH 0	0: 5: 5	0	0	2.18
SDH 1	1: 4: 5	19.32	0.84	2.14
SDH 2	2: 3: 5	34.46	1.28	2.18
SDH 3	3: 2: 5	58.94	2.20	3.82
SDH 4	4: 1: 5	75.96	2.82	3.20
SDH 5	5: 0: 5	96.29	3.12	1.99
Nafion 117	-	-	0.95	39.07

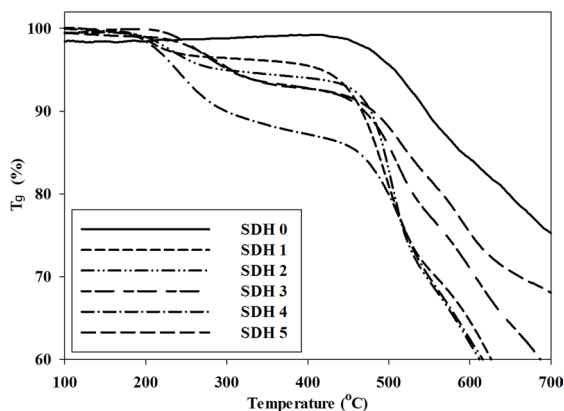


Figure 3. TGA thermograms of the sulfonated copolyimides as **SDH 0:** [SDDM]: [DDM]:[HDA] = 0:5:5 **SDH 1:** [SDDM]: [DDM]:[HDA] = 1:4:5; **SDH 2:** [SDDM]: [DDM]:[HDA] = 2:3:5; **SDH 3:** [SDDM]: [DDM]:[HDA] = 3:2:5; **SDH 4:** [SDDM]: [DDM]:[HDA] = 4:1:5; **SDH 5:** [SDDM]: [DDM]:[HDA] = 5:0:5

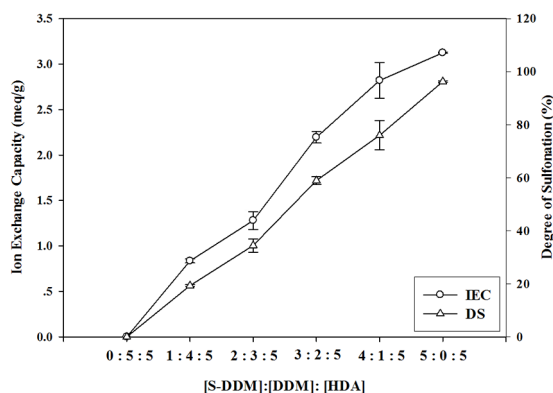


Figure 4. Degree of sulfonation and ion exchange capacity of sulfonated copolyimides.

Water uptake values of the sulfonated copolyimide membranes were measured at 30 °C and are tabulated in table 1. The water uptakes of the sulfonated copolyimides are 2.18, 2.14, 2.18, 3.82, 3.20, and 1.99% corresponding to the **SDH 0 - SDH 5**, respectively. The water uptake firstly increases with increasing degree of sulfonation due to more available hydrophilic sulfonic groups, then the water uptake decreases for the **SDH 4 and SDH 5** (at the 75.96 and 96.29% degrees of sulfonation) due the higher amount of bulky sulfonic groups present leading to lesser water adsorption capacity. For comparison, the water uptake of the **SDH 1** membrane (water uptake 2.14 %), which has an IEC value (0.84) close to Nafion 117 (0.95), is about ten times lower than that of the Nafion 117 (water uptake 39.07%)⁹. This can be explained by the rigidity of the polymer chain. The main chain of the **SDH 1** consists of the highly rigid aromatic groups whereas the Nafion 117 is composed of much more flexible linear fluorinated aliphatic chains.

3.5 Proton conductivity and methanol permeability

Proton conductivity (σ) of the SPI membranes was measured after immersing in deionized water for 24 h at room temperature (30 °C); this condition is referred hereafter as a wet state. The present work was focused at room temperature since the SPI membranes for DMFC are intended to be used in portable electrical devices which are operated at or near room temperature. Proton conductivity monotonically increases with increasing degree of sulfonation as shown in Figure 5. For the sulfonated copolyimides, the proton conductivity values are in the range of 1.603×10^{-3} to 3.241×10^{-3} S.cm⁻¹ at room temperature. The initial increase in the proton conductivity with the degree of sulfonation can be attributed to the available sulfonic groups present. The SDH 5 membrane possesses the highest proton conductivity value of 3.241×10^{-3} S.cm⁻¹. The proton conductivity was calculated from equation 4, where R was the resistance as obtained from the intersect of the high frequency semi-circle on a complex impedance plane with the $\text{Re}(Z)$ or Z' axis of the Nyquist plot as shown in figure

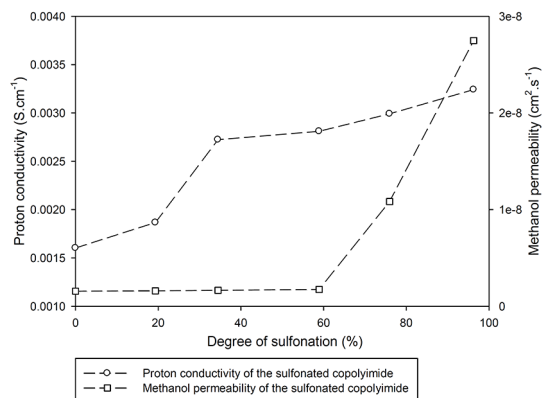


Figure 5. Proton conductivity of sulfonated copolyimides at various DS in the wet state at 30 °C and methanol permeability of the sulfonated copolyimide membranes measured at 60 °C.

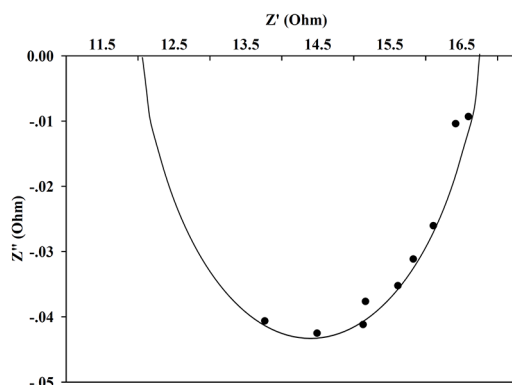


Figure 6. Nyquist plot of SDH 3.

6 for the SDH 3 membrane. The SDH 5 value is higher than those of the sulfonated polybenzimidazoles produced from 3,3'-disulfonate-4,4'-dicarboxylbiphenyl (2.79×10^{-3} S.cm⁻¹ at 80 °C)³⁰ and the sulfonated polybenzimidazoles produced from 4,8-disulfonol-2,6-naphthalenedicarboxylic acid (2.70×10^{-3} S.cm⁻¹ at 90 °C)³⁰. Low proton conductivity of the sulfonated polybenzimidazoles can be attributed to the strong ionic interactions between the basic benzimidazoles and the sulfonic acid groups³⁰. The proton conductivity of the sulfonated copolyimide SDH 3 is higher than that of the Nafion 117 under the same condition (3.17×10^{-3} S.cm⁻¹), but less than that of the Nafion 117 previously reported (6.83×10^{-3} S.cm⁻¹)¹⁷. The latter result of the lower proton conductivity may have resulted from the difference in the water uptake of the previously measured Nafion 117. In another related work, the proton conductivity of the sulfonated PBI membrane at 125 °C showed the highest value of 0.18 S.cm⁻¹, a higher value than measured at room temperature³¹.

Methanol permeability (*P*) is an important parameter for PEMs used in DMFC. To achieve the highest fuel cell performance, PEMS should have low methanol permeability because the methanol crossover from the anode to the cathode causes a lower cell voltage and decreases fuel cell efficiency²⁷. Methanol permeability of the sulfonated copolyimide membranes was measured at both 30 °C and 60 °C during the measurement period of about one week. The copolymers synthesized had the ability to prevent methanol permeation at 30 °C; the methanol did not sufficiently permeate through the membrane to be measurable within 7 days. At 60 °C, the methanol did not pass through the membranes within the first two days, after that the methanol slightly passed through the membranes and concentration was measurable. Methanol permeability of the sulfonated copolyimide membranes was determined and the results at 60 °C are displayed in Figure 5. Methanol permeability values of the sulfonated copolyimides fall between 1.56×10^{-9} and 2.75×10^{-8} cm².s⁻¹. It can be seen that the membrane with a higher sulfonation level possesses higher methanol permeability. Methanol permeation is controlled by the hydrophilic channel size which is composed of the sulfonic acid groups along the copolyimide backbone⁷. Thus, the increase in the sulfonic acid groups result in enlarged interspaces or free volumes between the polymer backbones, through which methanol can pass⁸. The highest measured methanol permeability of the sulfonated copolyimides prepared in this study at 60 °C is 2.75×10^{-8} cm².s⁻¹ which is still ~ 425 times lower than that of the commercial Nafion 117 which was measured at same condition (1.17×10^{-5} cm².s⁻¹ at 60 °C). The methanol permeabilities of Nafion 117 and Sterion L-180 were 1.2×10^{-6} and 1.4×10^{-6} cm².s⁻¹ at 55 °C³. The present SPI membranes possess lower methanol permeability values relative to the the Sterion L-180 by about 50 times. The low methanol permeability of the sulfonated copolyimides

may be explained by the physical crosslinking between the polymer chains, the lower water uptake, and the rigidity of the aromatic backbone, preventing methanol crossover. In summary, low methanol permeability data obtained suggest that the synthesized sulfonated copolyimides have a high potential for DMFC applications. The membrane selectivity (s.S.cm⁻³) was calculated from the ratio between the proton conductivity (S.cm⁻¹) and the methanol permeability (cm².s⁻¹); the higher membrane selectivity is preferable for DMFC. The membrane selectivities of the copolyimide membranes are 1.02×10^6 , 1.17×10^6 , 1.65×10^6 , 1.61×10^6 , 2.76×10^5 , and 1.18×10^5 s.S.cm⁻³ belonging to the SDH 0 - SDH 5 membranes, respectively. On the other hand, the membrane selectivity of the Nafion 117 is relatively low at 1.82×10^3 s.S.cm⁻³. The highest membrane selectivity, the ratio between proton conductivity and methanol permeability, is 1.65×10^6 s.S.cm⁻³ belonging to the SDH 2 membrane with the 34.46% degree of sulfonation. The highest membrane selectivity value suggests that the SDH 2 membrane to be the most suitable for the DMFC application.

4. Conclusions

Sulfonated copolyimides, of various DS, were successfully synthesized and characterized by FTIR spectroscopy. The synthesized sulfonated copolyimides withstood well at high temperature where the first degradation of the sulfonic group occurred at 200-300 °C. The IEC value increased with increasing sulfonation level. Water uptake of the sulfonated copolyimides was less than 4%. Proton conductivities of the sulfonated copolyimides at room temperature depended on the proportion of S-DDM, and the proton conductivity values were in the range of 1.603×10^{-3} S.cm⁻¹ to 3.241×10^{-3} S.cm⁻¹. Methanol permeability of the sulfonated copolyimides also depended on the DS; a higher sulfonation level can be correlated with a higher methanol permeability. The highest measured methanol permeability of the sulfonated copolyimides obtained in this work was 2.75×10^{-8} cm².s⁻¹, which is much lower than that of Nafion 117. The highest membrane selectivity of 1.65×10^6 s.S.cm⁻³ belonged to the sulfonated copolyimide membrane with the 34.46% degree of sulfonation (SDH 2) for use in DMFC. Overall, the fabricated SPI membranes possessed higher selectivity values when compared to the commercial Nafion 117.

5. Acknowledgements

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The following online material is available for this article:

Table S1. Ion Exchange Capacity (IEC)

Figure S1. Dynamic mechanical analysis (DMA)