Sulfonated poly(arylene ether sulfone) as a methanol-barrier layer in multilayer membranes for direct methanol fuel cells

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ABSTRACT

Novel poly(arylene ether sulfone) copolymers containing different amount of pendant sulfonic acid groups have been synthesized by an aromatic substitution polymerization reaction. The properties of the synthesized sulfonated poly(diphenylsulfone-diphenol) (SDPS-DP) copolymers depend on the sulfonic acid group content in the copolymers. Although all the copolymers show good thermal stability, low liquid uptake, and low methanol crossover, they exhibit lower proton conductivity than Nafion or sulfonated poly(ether ether ketone) (SPEEK). Taking advantage of the low methanol crossover, multilayer membranes consisting of the SDPS-DP copolymer as a methanol-barrier center layer and SPEEK as the proton-conducting outer layers have been fabricated and characterized. The SPEEK/SDPS-DP-60/SPEEK multilayer membranes with an optimized center layer thickness are found to exhibit better performance and higher power density in DMFC than plain SPEEK and Nafion 115 membranes.

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1. Introduction

Proton exchange membrane (PEM) is one of the main components in direct methanol fuel cells (DMFCs), and it plays an important role on the fuel cell performance. While high proton conductivity is desirable for a good PEM, low methanol permeability is also a critical property of PEM for DMFC. The methanol crossover from the anode to the cathode side through the PEM will waste the fuel, poison the cathode Pt catalyst, and generate a mixed potential through the unwanted methanol oxidation reaction at the cathode side. These will not only lead to performance loss, but also result in a degradation of the long-term stability of DMFC [1,2].

Extensive investigations have been made with poly(perfluorosulfonic acid) (PFSA) membranes such as Nafion (Dupont), Aciplex (Asahi Chemical company), Flemion (Asahi Glass Company), and XUS (Dow) [1,2] due to their high proton conductivity and good resistance to chemical attack. However, the PFSA membranes usually suffer from high cost and high methanol permeability when used in DMFC. In this regard, aromatic polymers with sulfonic acid groups attached to them have been widely investigated as candidate materials to replace the PFSA electrolytes in DMFC as the aromatic backbone could provide good thermal stability with suppressed methanol permeability while lowering the cost compared to the PFSA membranes.

Sulfonated derivatives of commercially available polymers such as sulfonated poly(ether ether ketone) (SPEEK) [3,4], sulfonated polysulfone (SPSf) [5–7], sulfonated poly(ether sulfone) (SPES) [8–10] are among those being investigated due to the easy access of the unsulfonated precursor raw materials as well as the simple reaction procedure amenable for easy scale up. The degree of sulfonation (DS) could be controlled by the reaction time and the amount of sulfonating agent (H_2SO_4, SO_3) used in the reaction. Also, sulfonated aromatic polymers could be synthesized through the polymerization reactions of different sulfonated monomers [11–24]. With this strategy, several PEMs with controllable chemical structures (controllable degree of sulfonation and sulfonation sites) and well-defined microstructures have been investigated. It has been found that to improve the osmotic and hydrolytic stability of the sulfonated polymers, an increasing hydrophilic–hydrophobic separation is desired by locating the sulfonic acid groups away from the polymer main chains [18–23].

With this perspective, our group reported recently novel sulfonated copolymers consisting of pendant sulfonic acid groups synthesized by a nucleophilic displacement polymerization reaction [24]. The resulting sulfonated poly(diphenylsulfone-diphenol) copolymer formed with a degree of sulfonation of 60%, which is designated as SDPS-DP-60, showed low methanol permeability and liquid uptake in water and methanol solutions compared to Nafion 115 membrane and some sulfonated aromatic polymer (SPEEK, SPSf) with similar proton conductivity [4,5,24], which makes it a promising electrolyte material for DMFC application. However, the experimentally measured IEC value of the resulting SDPS-DP-60 was lower than that expected for a degree of sulfonation of 60% in

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our previous study due to unoptimized reaction conditions. Also, due to the low proton conductivity of the copolymer, thinner membranes compared to SPEEK or Nafion are needed for DMFC operation to achieve low cell resistance. Unfortunately, very thin membranes will sacrifice the mechanical property and generate issues related to membrane-electrode assembly (MEA) fabrication since brittle thin membranes tend to break during the hot-pressing process.

One approach to make use of the low methanol permeability of the membranes without introducing too big a cell resistance is to adopt a multilayer membrane approach [25–38] in which a thin layer of the low methanol permeability polymer forms the center layer and a relatively high proton-conducting polymer forms the outer layers. For example, our group [36] reported that multilayer membranes with SPEEK as the methanol-barrier center layer and recast Nafion as the proton-conducting outer layers increase the overall cell performance significantly because of the suppressed methanol crossover. Si et al. [37] also reported the use of a Nafion/PVDF/Nafion (PVDF refers to polyvinylidene fluoride) tri-layer membrane in DMFC, but PVDF is a proton insulator. Jiang et al. [38] reported that SPEEK with different degrees of sulfonation could also be used to fabricate the tri-layer membranes, but the proton conductivity of the methanol-barrier SPEEK is still too low when low methanol permeability is desired.

To have better understanding of the relationship between the degree of sulfonation and the properties of the SDPS-DP copolymers, we present here first a further investigation of the chemical and thermal properties of the SDPS-DP copolymers with different degrees of sulfonation (20–60%) that could be achieved by higher reaction temperature and longer reaction time. The SDPS-DP copolymers with a degree of sulfonation of 20, 40, and 60% are hereafter designated as, respectively, SDPS-DP-20, SDPS-DP-40, and SDPS-DP-60. Then the fabrication and characterization of tri-layer membranes consisting of a thin inner layer of SDPS-DP-60, which has the highest proton conductivity among the three copolymers, and two outer layers of SPEEK are presented. The low methanol permeability of the thin SDPS-DP layer is expected to suppress the methanol crossover significantly without adversely increasing the cell resistance. The multilayer membranes could also offer good mechanical strength with long-term stability due to the similar backbone structures of SPEEK and SDPS-DP polymers. The electrochemical performance, methanol crossover in DMFC, and the structural stability of the multilayer membranes with different thicknesses of the methanol-barrier center layer are presented here.

2. Experimental

2.1. Materials synthesis

The materials used for the synthesis of the SDPS-DP copolymers have been reported before [24]. N,N′-dimethylacetamide (DMAc, 99+%,) was purchased from Acros organics. Poly(ether ether ketone) (PEEK450 PF) was obtained from Victrex. All chemicals were used as-received.

The sulfonated poly(ether ether ketone) (SPEEK) was synthesized by sulfonating PEEK with concentrated sulfuric acid for certain amount of time to get the desired degree of sulfonation [39]. Although the proton conductivity of SPEEK increases with increasing degree of sulfonation, SPEEK membranes with degree of sulfonation higher than 55% exhibit high water uptake and methanol permeability, which could degrade the mechanical stability and increase the methanol crossover during fuel cell operation. Generally, SPEEK membranes with degree of sulfonation between 40% and 55% show reasonable proton conductivity, low solubility, and good mechanical stability [4,38]. Accordingly, SPEEK with an ion exchange capacity (IEC) of 1.56 and a degree of sulfonation (DS) of 51% was used in this study.

As shown in Fig. 1, the sulfonated poly(arylene ether sulfone) copolymers were synthesized by an aromatic substitution polymerization reaction as reported by our group before [24].

2.2. NMR, FT-IR, and thermal characterization of the copolymer

[1]H Nuclear magnetic resonance (NMR) spectra were recorded with a Varian INOVA-500 NMR spectrometer at a proton frequency of 499.4 MHz using deuterated dimethyl sulfoxide (DMSO-d_6) as a solvent. Fourier transform infrared (FT-IR) spectra of the copolymers were recorded with a Perkin-Elmer Spectrum BX instrument. The thermal stability and the glass transition temperature of the copolymers were evaluated with Perkin-Elmer Series 7 thermogravimetric analyzer (TGA) in flowing air with a heating rate of $5\,^{\circ}C\,min^{-1}$ and differential scanning calorimeter (DSC) in flowing nitrogen with a heating rate of $10\,^{\circ}C\,min^{-1}$.

2.3. Membrane preparation

The plain SPEEK, SDPS-DP, and the multilayer membranes were prepared by a solution casting method employing SPEEK/DMAc (10%, w/w) or SDPS-DP/DMAc (10%, w/w) solutions. For the
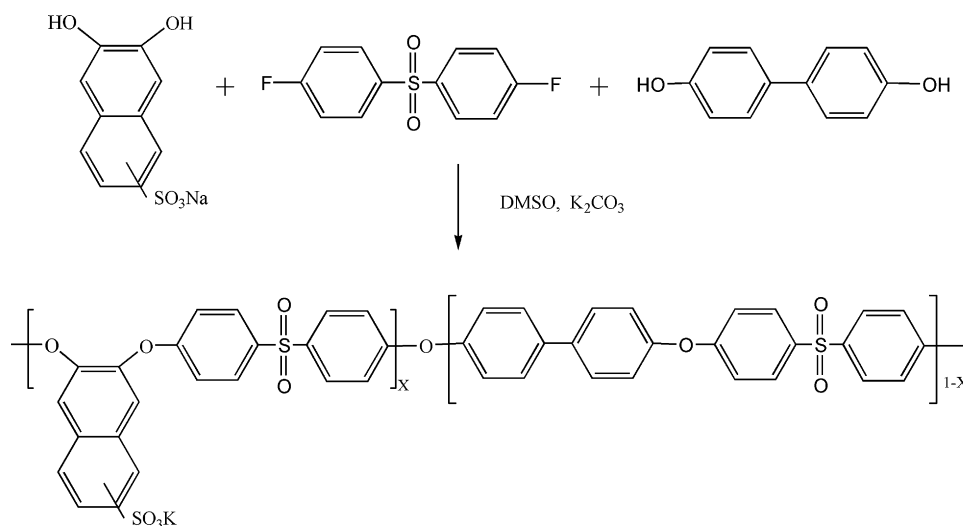

Fig. 1. Synthesis scheme for the SDPS-DP copolymers.

multilayer membranes, a thin SDPS-DP-60 membrane with various thickness values (5–30 μm) was first casted, followed by casting two layers of SPEEK membrane on each surface. After casting all the layers, the membranes obtained were hot-pressed at 130 °C and 20 psi for 2 min. All the plain and multilayer membranes were dried at 90 °C overnight, held in a vacuum oven at 130 °C for 6 h, and washed thoroughly with boiled de-ionized water several times to remove the residual solvent. The thickness of the membrane was controlled by changing the amount of SDPS-DP or SPEEK during the casting process, and all the membranes in this study had the same total thickness of 60 μm with 5 cm^2 active area.

2.4. Ion exchange capacity (IEC) and liquid uptake measurement

The ion exchange capacity (IEC) values were determined by suspending the SDPS-DP copolymers (0.15–0.2 g) in 2.0 M NaCl solution (30 mL) for 24 h to liberate the H$^+$ ions and then titrating with standardized 0.05N NaOH solution (Fisher Scientific) using phenolphthalein as an indicator.

Equilibrium liquid uptake of the polymer membranes (W_{uptake}) was determined at room temperature by first measuring the weight of the wet membrane (W_{wet}) and the weight of the dry membrane (W_{dry}) as

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

2.5. Proton conductivity measurement

Proton conductivity values of the water equilibrated membranes were obtained from the impedance data collected in the lateral direction (i.e. in plane) using an open window framed two platinum electrode cell [39] with a HP 4192A LF impedance analyzer in the frequency range of 5 Hz to 10 kHz with an applied voltage of 10 mV. The measurement setup with the membrane was held in a VWR humility chamber oven with water vapor at 100% relative humidity (R.H.) at the desired temperatures for 2 h before the tests.

2.6. Membrane-electrode assemblies (MEAs) fabrication

The electrodes (consisting of gas-diffusion and catalyst layers) for testing in DMFC were prepared as reported elsewhere [40]. The anode and cathode catalysts consisted of, respectively, commercial 60 wt.% Pt–Ru (1:1) alloy on Vulcan carbon (E-TEK) and 60 wt.% Pt on Vulcan carbon (Alfa Aesar). The loadings for cathodes (Pt) and anode (Pt–Ru) were 2.5 mg cm^{-2} on both sides, and the Nafion loading for both the anode and cathode catalysts was 0.45 mg cm^{-2}. After the catalyst layers were deposited onto the gas diffusion layers (A-6 ELAT/SS/NC/V2 carbon cloth, E-TEK), the resultant anode and cathode electrodes were hot pressed onto the membrane at 120 °C, 40 psi for 2 min.

2.7. DMFC performance and methanol crossover evaluation

Fuel cell tests were performed with a single-cell hardware (active area of 5 cm^2) by feeding methanol solution at a flow rate of 2.5 mL min^{-1} and humidified oxygen at a flow rate of 200 mL min^{-1} without backpressure. The steady state fuel cell polarization data were collected after operating the fuel cell for two consecutive days including the period of shut down overnight.

Methanol crossover was evaluated by measuring with a voltammetric method [41] the steady-state limiting current density arising from the oxidation of the permeated methanol at the cathode side. In the measurement, methanol solution was fed at a flow rate of 2.5 mL min^{-1} into the anode side of the MEA while the cathode side was kept in an inert humidified N$_2$ atmosphere. The steady-state limiting current density resulting from complete electro-oxidation at the membrane/Pt catalyst interface at the cathode side was measured by applying a positive potential at the cathode side.

2.8. Membrane cross-sectional characterization

Before and after the DMFC durability evaluation, the cross-sectional structure of the multilayer membrane was studied with a JEOL JSM-5610 scanning electron microscope (SEM). The samples were prepared by freezing the membrane in liquid nitrogen followed by breaking the frozen membrane with forceps.

3. Results and discussion

3.1. FT-IR and NMR characterization

The chemical structure of the sulfonated polymers (in acid form) was characterized by FT-IR and ^{1}H NMR spectroscopies (Figs. 2 and 3). Fig. 2 compares the FT-IR spectra of the sulfonated copolymers obtained with different acid monomer contents. The characteristic absorption peaks of the copolymers could be assigned as reported before [24,42]. It is worth to point out that the intensity of the absorption peaks corresponding to the aromatic sulfonic acid group (1030 cm^{-1}) increases with increasing sulfonated monomer content, which is consistent with the NMR results discussed below. Fig. 3 compares the ^{1}H NMR spectra of the SDPS-DP copolymers with different degrees of sulfonation. The chemical shifts of the protons in the polymer main chains could be readily assigned as reported elsewhere [24,43,44]. The increasing intensities of the hydrogen at H4 position on the naphthalenesulfonate containing units with increasing sulfonated monomer content reflects the increasing degree of sulfonation. Interestingly, by comparing the intensities of the H4 (1H) signal with the H8 (4H) signal of the diphenol segment, we can calculate the degree of sulfonation of the products. For example, the intensity ratio of the H8 (4H) to H4 (1H) proton signal for SDPS-DP-40 was 6.68, implying 0.63 diphenol units and hence 0.37 DHNS units containing the sulfonic acid groups. All the IEC values calculated from the NMR data are listed in Table 1 with other properties of the copolymers.
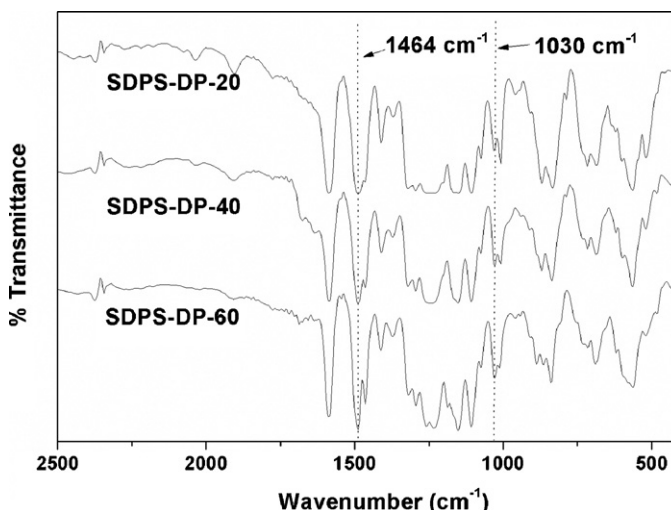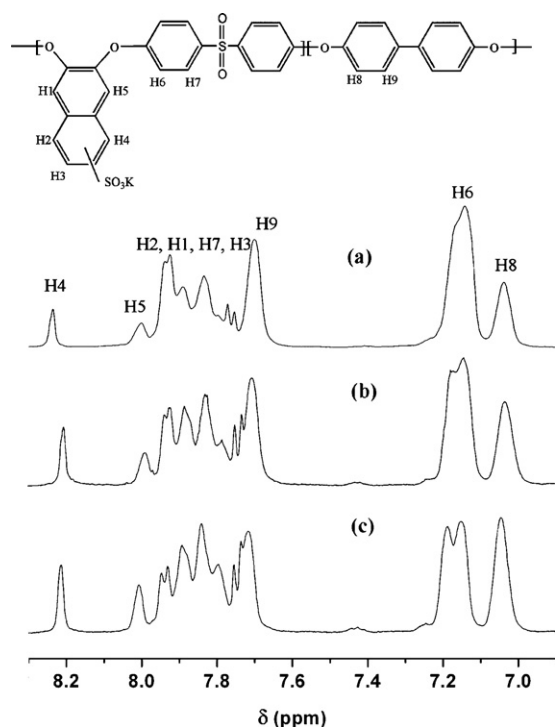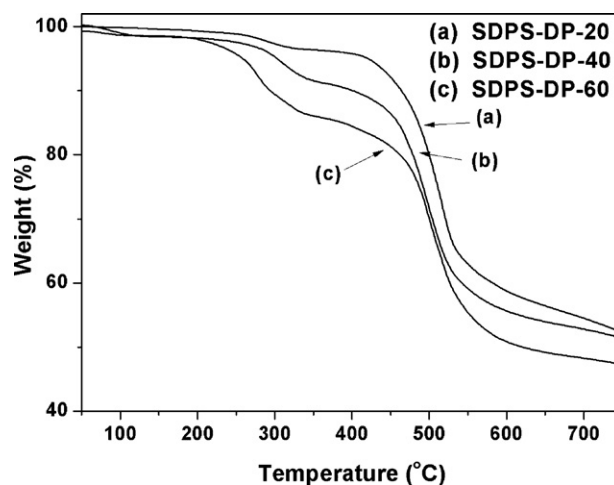

Fig. 2. FT-IR spectra of the SDPS-DP copolymers.

Fig. 3. ^{1}H NMR spectra of the SDPS-DP copolymers with different sulfonated monomer content in DMSO-d_6: (a) SDPS-DP-20, (b) SDPS-DP-40, and (c) SDPS-DP-60.

Fig. 4. TGA plots of the SDPS-DP copolymers recorded in flowing air.

3.2. Thermal stability data

The thermal properties of the copolymers were investigated by TGA and DSC analyses. As seen in Fig. 4, with increasing degree of sulfonation, the weight loss corresponding to the loss of sulfonic acid groups (in the temperature range of 250–450 °C) increases and the decomposition temperature shifts to lower temperature. For DSC measurements, all the copolymers were first pre-heated at 10 °C min^{-1} to a temperature below their decomposition temperatures, which were derived from the TGA curves collected in nitrogen atmosphere. After cooling down, they were heated again at a rate of 10 °C min^{-1} to their decomposition temperatures. The data from the second scan are compared in Fig. 5. The copolymers show an increase in the glass transition temperature (T_g) with increasing degree of sulfonation (as seen in Fig. 5), which is consistent with other copolymers synthesized from the same sulfonated monomer. The increase in the T_g value with increasing sulfonic group concentration is consistent with that normally observed for ionomeric polymers due to the strong interaction between sulfonic acid groups [42,45,46]. The high decomposition temperature (T_d) and T_g values of the copolymers suggest that they have adequate thermal stabilities for DMFC applications.
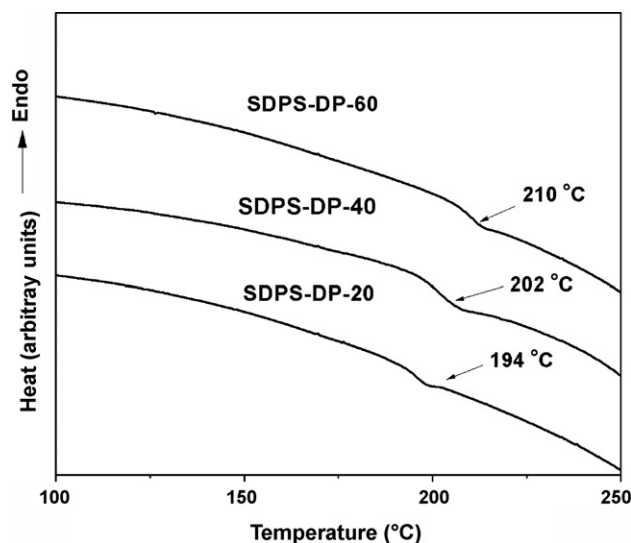
3.3. IEC, liquid uptake, and proton conductivity

Table 1 gives the ion exchange capacity (IEC) values, liquid uptake in water and methanol solution, and the proton conductivity values measured under 100% R.H. at 25 °C for the sulfonated copolymers with different degrees of sulfonation as well as those of the SPEEK membrane.

The SDPS-DP copolymers show IEC values in the range of 0.46–1.32 with increasing degree of sulfonation. The IEC values obtained from the titration data are reasonably close to those cal-

Fig. 5. DSC plots of the SDPS-DP copolymers recorded in flowing nitrogen.

Table 1
Ion exchange capacity (IEC), liquid uptake, and proton conductivity (σ) of SPEEK and SDPS-DP membranes with different degrees of sulfonation.

Polymer	IEC from titration (mequiv. g^{-1})	IEC from NMR (mequiv. g^{-1})	Theoretical IEC (mequiv. g^{-1})	Liquid uptake				σ^a (mS cm^{-1})
				In water (%)		In 1 M methanol solution (%)		
				25 °C	65 °C	25 °C	65 °C	
SDPS-DP-20	0.46	0.47	0.48	4.9	5.2	5.9	6.2	11
SDPS-DP-40	0.89	0.90	0.94	13.1	16.5	16.7	17.3	18
SDPS-DP-60	1.31	1.32	1.36	17.6	27.8	18.2	30.9	31
SPEEK	1.56	–	–	32.9	47.5	36.3	58.6	45

[a] In 100% RH at 25 °C.

culated from the ^{1}H NMR results. The close agreement between the IEC values obtained by the two methods also confirms that the observed degrees of sulfonation are close to the expected values. Additionally, the IEC value obtained with 60% degree of sulfonation is more close to the expected value due to the more optimized synthesis conditions compared to that in our previous report [24] due to unoptimized synthesis condition. When considering the liquid uptake, even though the sulfonated polymers show an increase in the liquid uptake with increasing temperature and methanol concentration, the values are much lower than those found with the SPEEK membrane at a given temperature and methanol concentration. This is not only due to the low IEC values of the SDPS-DP copolymer compared to that of SPEEK, but also due to the larger distance between the sulfonic groups and the backbone compared to that of the SPEEK membrane [22–24].

The proton conductivity values determined with the copolymer films range from 0.011 to 0.031 S cm^{-1} at room temperature depending on the sulfonic acid group content. Even though the sulfonated copolymers show lower proton conductivities compared to that of the Nafion (0.090 S cm^{-1}) and SPEEK membrane (0.045 S cm^{-1}), all of them show better dimensional stability and lower methanol permeability. To take advantage of the low methanol permeability of the SDPS-DP copolymers, SDPS-DP-60 was further used as a methanol-barrier layer in multilayer membranes since it showed the highest proton conductivity among all the copolymers and much lower methanol permeability compared to SPEEK and Nafion membranes [24].

3.4. Effect of the thickness of the center layer on methanol crossover and membrane resistance

A series of multilayer membranes was fabricated for DMFC as shown in Fig. 6. The SDPS-DP-60 copolymer with a lower methanol permeability was used as the methanol-barrier center layer, while SPEEK with an IEC of 1.56 and higher proton conductivity was used as the outer layer on either side of the inner layer. While the total membrane thickness was maintained constant at 60 μm, the thickness of the inner layer was varied from 5 to 30 μm.

Fig. 7 shows variations of methanol crossover current density and membrane resistance with the thickness of the methanol-barrier center layer. As seen, at 65 °C with 1 M methanol solution, the methanol crossover current density of the SDPS-DP-60 membrane (35 mA cm^{-2}) is only 30% of that of the plain SPEEK membrane (115 mA cm^{-2}) with the same membrane thickness. Due to the methanol blocking effect of the SDPS-DP-60 copolymer, the methanol crossover of the multilayer membranes is significantly reduced. The methanol crossover is only 66 and 42% of that of plain SPEEK with, respectively, 5 and 15 μm thick methanol-barrier center layers. On increasing the center layer thickness to 30 μm, the methanol crossover is further reduced to 37%, which is very close to that of the SDPS-DP-60 copolymer.

However, the resistance of the multilayer membrane increased significantly with increasing thickness of the center layer. For example, the resistances of the multilayer SPEEK/SDPS-DP-60/SPEEK membranes with 5 and 15 μm center layer thicknesses
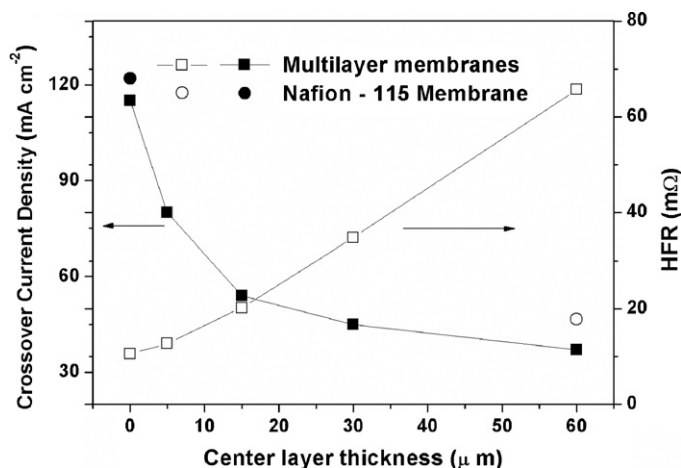

Fig. 7. Methanol crossover current density and high frequency resistance (HFR) of the 60 μm thick SPEEK/SDPS-DP-60/SPEEK multilayer membrane with different SDPS-DP-60 center-layer thickness.

are, respectively, 13 and 20 mΩ. Moreover, the resistance of the multilayer membrane with 30 μm thick center layer is almost 3 times higher than that of plain SPEEK membrane. Furthermore, the electrochemical selectivities of the multilayer and plain SPEEK and SDPS-DP membranes, which is defined as the ratio of reciprocal resistance to methanol permeability [47], were calculated using the methanol permeability (*P*) determined from the methanol crossover current density with electro-osmotic drag correction [41] and the resistance data listed in Fig. 7. With a thickness of 5 and 15 μm for the SDPS-DP-60 methanol-barrier center layer, the selectivity of the multilayer membrane is, respectively, 1.3 and 1.5 times higher than that of the plain SPEEK membrane. On increasing the center layer thickness further, the selectivity value becomes lower than that for plain SPEEK membrane due to the significantly increased membrane resistance. Thus, the optimized thickness for the center layer is found to be ∼15 μm.

3.5. Fuel cell performance

Fig. 8 compares the polarization curves of the multilayer membranes (with different SDPS-DP-60 methanol-barrier center layer thickness) in DMFC with those of the plain SPEEK, SDPS-DP-60 copolymer, and Nafion-115 membranes at 65 °C with 1 M methanol solution. The multilayer membranes with 5 and 15 μm center layer thickness exhibit higher performance in DMFC than plain SPEEK membrane despite a higher membrane resistance mainly due to the much suppressed methanol crossover through the multilayer membrane (Fig. 7). However, with a larger thickness (>30 μm) of the SDPS-DP-60 methanol-barrier center layer, the membrane resistance increases significantly while the methanol crossover is limited by the properties of the center layer polymer, resulting in a decrease in the overall fuel cell performance. In addition, with increasing center layer thickness, the open circuit voltage (OCV) of the multilayer membranes increases from 0.66 V for 5 μm center layer thickness to 0.73 V for 30 μm center layer thickness due to the suppressed methanol crossover through the membrane and the consequent smaller voltage loss at the cathode side [48]. The polarization loss seen with the multilayer membrane with 30 μm center layer thickness is also higher than that seen with the multilayer membrane with 15 μm center-layer thickness, which is attributed to a higher membrane resistance arising from its lower proton conductivity as shown in Fig. 7.

Fig. 9 compares the polarization curves and power density of the plain SPEEK membrane, multilayer SPEEK/SDPS-DP-60/SPEEK membrane with an optimized center layer thickness of 15 μm, and
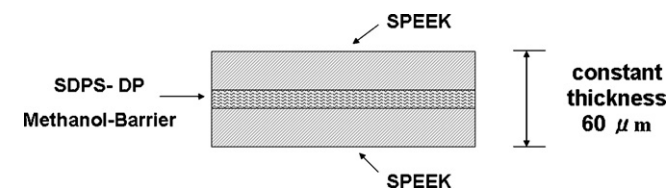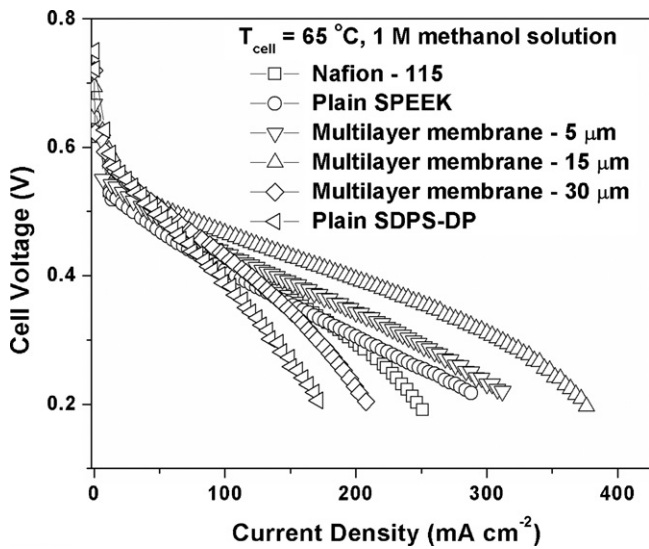

Fig. 6. Schematics of the multilayer membrane structure (SDPS-DP corresponds to SDPS-DP-60).

Fig. 8. Comparison of the polarization curves recorded with Nafion 115, plain SPEEK, plain SDPS-DP-60, and SPEEK/SDPS-DP-60/SPEEK multilayer (with different SDPS-DP-60 center-layer thickness) membranes in DMFC. Methanol concentration: 1 M, cell temperature: 65 °C. The thickness values indicated in μm with the multilayer membranes refer to the center layer thickness.
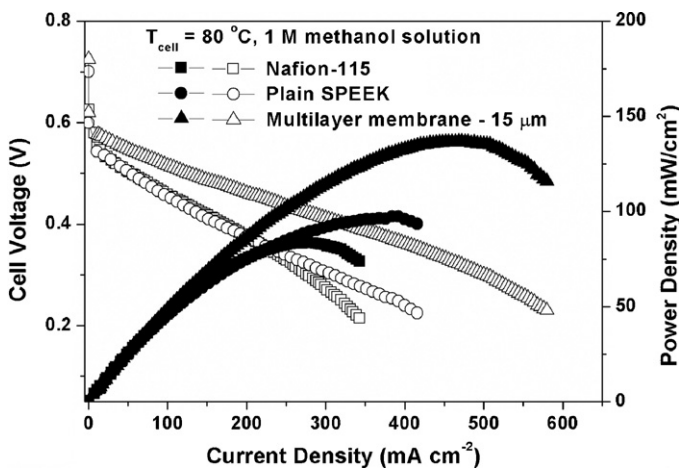

Fig. 9. Comparison of the polarization curves and power densities recorded with Nafion 115, plain SPEEK, and SPEEK/SDPS-DP-60/SPEEK (15 μm SDPS-DP-60 central-layer thickness) membranes in DMFC. Methanol concentration: 1 M, cell temperature: 80 °C.

Nafion 115 membrane at 80 °C with 1 M methanol solution. Due to the better reaction kinetics in the electrodes at elevated temperatures, the polarization loss is decreased and the current density values are increased compared to that observed at 65 °C in Fig. 8. More importantly, the maximum power density of the multilayer membrane (140 mW cm^{-2}) is much higher than those of both the plain SPEEK (96 mW cm^{-2}) and Nafion 115 (82 mW cm^{-2}) membranes, which is 1.4 and 1.7 times higher, respectively.

3.6. Cross-sectional characterization by SEM of the MEAs

In multilayer membranes, the delamination phenomenon during fuel cell operation has been observed after the fuel cell operation when different materials were used in various layers. For example, Nafion/SPEEK/Nafion multilayer membranes have been reported by other researchers to encounter delamination [38]. To investigate the performance and structure durability of the multilayer membrane, the DMFC testing of the membrane was carried
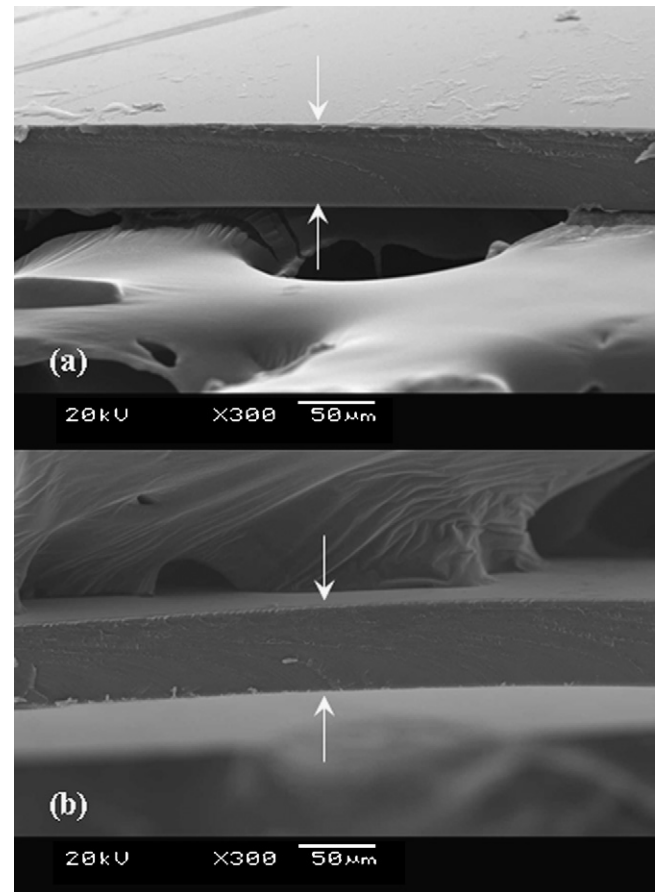
Fig. 10. Cross-sectional SEM images of the multilayer SPEEK/SDPS-DP-60/SPEEK membranes: (a) before and (b) after DMFC evaluation.

out for two weeks (including the overnight shutting down time) by holding the potential at 0.4 V. Then the cross-section of the membrane (with a center-layer thickness of 15 μm) was characterized by SEM before and after the DMFC evaluation. The multilayer membrane shows good performance stability after the DMFC operation. For example, the current density value at 0.4 V and the maximum power density remain at 93% and 95% of the initial values after 2 weeks of operation, which is better than that found with the SPEEK/SPEEK/SPEEK multilayer membrane before [38]. The SEEK/SDPS-DP-60/SPEEK multilayer membrane shows good structural stability under the DMFC operating conditions. As seen in Fig. 10(a) and (b), no structural delamination is observed in the cross-section of the same membrane after the DMFC evaluation. It is mainly due to the similar main-chain chemical structures of the SPEEK and SDPS-DP-60 polymers. Also, the solution-casting procedure used for fabricating the multilayer membrane might have helped to generate stronger interlayer bonding between the different layers as has been indicated in the literature [38].

4. Conclusions

A series of sulfonated poly(arylene ether sulfone)s with various contents of sulfonic acid groups has been synthesized via a nucleophilic displacement polycondensation reaction and characterized. The sulfonated SDPS-DP polymers are thermally stable up to 250 °C in air, and the T_g, liquid uptake, and proton conductivity of the sulfonated copolymers increase with increasing degree of sulfonation. Although these membranes exhibit lower proton conductivity than SPEEK and Nafion 115, they exhibit a significantly

reduced methanol crossover and liquid uptake compared to Nafion and SPEEK membranes.

Taking advantage of the low methanol crossover of these copolymers, a series of multilayer membranes with the SDPS-DP-60 copolymer as the methanol-barrier center layer and the high proton-conducting SPEEK as the outer layers have been fabricated and characterized. The multilayer membranes show significantly decreased methanol crossover without significantly increasing the membrane resistance compared to SPEEK and Nafion 115 membranes. The multilayer membranes with an optimized center-layer thickness of 15 μm show much improved fuel cell performance and power density at 65 and 80 °C with 1 M methanol solution compared to plain SPEEK membrane due to the much suppressed methanol crossover. The performance of the multilayer membranes could be improved further employing SPEEK as an ionomer in the electrode instead of Nafion during MEA fabrication to reduce the interfacial resistance between the membrane and the catalyst layers [48,49].

Acknowledgements

References

[1] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. 104 (2004) 4587.
[2] V. Neburchilov, J. Martin, H.J. Wang, J.J. Zhang, J. Power Sources 169 (2007) 221.
[3] P.X. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K.P. Wang, S. Kaliaguine, J. Membr. Sci. 229 (2004) 95–106.
[4] B. Yang, A. Manthiram, Electrochem. Solid-State Lett. (2003) A229.
[5] Y.-Z. Fu, A. Manthiram, J. Power Sources 157 (2006) 222.
[6] C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel, M. Pineri, Polymer 42 (2001) 359.
[7] J.H. Fang, X.X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, Macro-molecules 35 (2002) 9022.
[8] J.A. Kerres, J. Membr. Sci. 185 (2001) 3.
[9] R. Nolte, K. Ledjeff, M. Bauer, R. Mulhaupt, J. Membr. Sci. 83 (1993) 211.
[10] K. Miyatake, Y. Chikashige, M. Watanabe, Macromolecules 36 (2003) 9691.
[11] N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uchida, M. Watanabe, J. Am. Chem. Soc. 128 (2006) 1762.
[12] P.X. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, S. Kaliaguine, J. Polym. Sci.: Part A 42 (2004) 2866.
[13] Y. Gao, G.P. Robertson, M.D. Guiver, X.G. Jian, J. Polym. Sci.: Part A 41 (2003) 497.
[14] Y. Gao, G.P. Robertson, D.-S. Kim, M.D. Guiver, S.D. Mikhailenko, X. Li, S. Kaliaguine, Macromolecules 40 (2007) 1512.
[15] A.S. Badami, A. Roy, H.-S. Lee, Y.X. Li, J.E. McGrath, J. Membr. Sci. 328 (2009) 156.
[16] W.L. Harrison, F. Wang, J.B. Mecham, V.A. Bhanu, M. Hill, Y.S. Kim, J.E. McGrath, J. Polym. Sci.: Part 41 (2003) 2264–2276.
[17] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, J. Membr. Sci. 197 (2002) 231.
[18] B. Lafitte, P. Jannasch, Adv. Funct. Mater. 17 (2007) 2823.
[19] S. Matsumura, A.R. Hlil, C. Lepiller, J. Gaudet, D. Guay, A.S. Hay, Macromolecules 41 (2008) 277–280.
[20] S. Matsumura, A.R. Hlil, C. Lepiller, J. Gaudet, D. Guay, Z. Shi, S. Holdcroft, A.S. Hay, Macromolecules 41 (2008) 281.
[21] Y. Gao, G.P. Robertson, D. Kim, M.D. Guiver, S.D. Mikhailenko, X. Li, S. Kaliaguine, Macromolecules 40 (2007) 1512.
[22] Y. Gao, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, X. Li, S. Kaliaguine, Poly-mer 47 (2006) 808.
[23] D.S. Kim, Y.S. Kim, M.D. Guiver, B.S. Pivovar, J. Membr. Sci. 321 (2008) 199.
[24] J.K. Lee, W. Li, A. Manthiram, J. Membr. Sci. 330 (2009) 73.
[25] T.R. Farhat, P.T. Hammond, Adv. Funct. Mater. 15 (2005) 945.
[26] T.R. Farhat, P.T. Hammond, Adv. Funct. Mater. 16 (2006) 433.
[27] D.M. DeLongchamp, P.T. Hammond, Langmuir 20 (2004) 5403.
[28] F.D. Martino, N. Vatistas, V. Tricoli, J. Electrochem. Soc. 156 (2009) B59.
[29] L.J. Hobson, H. Qzu, M. Yamaguchi, S. Hayase, J. Electrochem. Soc. 148 (2001) A1185.
[30] L.J. Hobson, Y. Nakano, H. Oza, S. Hayase, J. Power Sources 104 (2002) 79.
[31] M. Walker, K.M. Baumgartner, M. Kaiser, J. Kerres, A. Ullrich, E. Rauchle, J. Appl. Polym. Sci. 74 (1999) 74.
[32] M.A. Smit, A.L. Ocampo, M.A. Espinosa-Medina, P.J. Sebastián, J. Power Sources 124 (2003) 59.
[33] M. Walker, K.M. Baumgartner, J. Feichtinger, M. Kaiser, Surf. Coat. Technol. 116 (1999) 996.
[34] J. Feichtinger, R. Galm, M. Walker, K.M. Baumgartner, Surf. Coat. Technol. 142 (2001) 181.
[35] L. Li, Y.M. Zhang, J. Power Sources 175 (2008) 256.
[36] B. Yang, A. Manthiram, Electrochem. Comm. 6 (2004) 231.
[37] Y.C. Si, J.-C. Lin, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc. 151 (2004) A463.
[38] R.C. Jiang, H.R. Kunz, J.M. Fentona, J. Electrochem. Soc. 153 (2006) A1554.
[39] W. Li, A. Bellay, Y.-Z. Fu, A. Manthiram, J. Power Sources 180 (2008) 719.
[40] W. Li, Y.-Z. Fu, A. Manthiram, M.D. Guiver, J. Electrochem. Soc. 156 (2009) B258.
[41] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466.
[42] Y. Gao, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, X. Li, S. Kaliaguine, Macro-molecules 37 (2004) 6748.
[43] D. Xing, J. Kerres, J. New Mater. Electrochem. Syst. 9 (2006) 51.
[44] J.K. Lee, J. Kerres, J. Membr. Sci. 294 (2007) 75.
[45] X. Jin, M.T. Bishop, T.S. Ellis, F.E. Karasz, Br. Polym. J. 17 (1985) 4.
[46] F.G. Wilhelm, I.G.M. Punt, N.F. van der Vegt, H. Strathmann, M. Wessling, J. Membr. Sci. 199 (2002) 167.
[47] B.S. Pivovar, Y. Wang, E.L. Cussler, J. Membr. Sci. 154 (1999) 155.
[48] J.K. Lee, W. Li, A. Manthiram, M.D. Guiver, J. Electrochem. Soc. 156 (2009) B46.
[49] J.K. Lee, W. Li, A. Manthiram, J. Power Sources 180 (2008) 56.