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Molecular Weight Effect of Partially Sulfonated PS-*b*-PDMS Diblock Copolymers as Proton Exchange Membrane for Direct Methanol Fuel Cell

Seulgi Kim[1], Hae Woong Park[2], Hyunjung Lee[*,3], Taihyun Chang[2], and Wonmok Lee[*,1]
[1]Department of Chemistry, Sejong University, 98 Gunja-dong, Gwngjin-gu, Seoul 143-747 Korea
[2]Department of Chemistry, Pohang University of Science and Technology, San 31 Hyoja-dong, Gyeongbuk 790-784, Korea
[3]School of Advanced Materials Engineering, Kookmin University, 861-1 Jeongneung-dong, Seoul 136-702, Korea

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Abstract: Partially sulfonated polystyrene-*b*-poly(dimethylsiloxane) (sPS-*b*-PDMS) block copolymer membranes were prepared using three different polymers with various molecular weights and block ratios. Eleven different products were obtained with controlled degree of sulfonation (DS) of PS block ranging from 22% to 48%, and they were cast into proton exchange membranes (PEMs). Each PEM was rigorously characterized to see the effect of molecular weight and PS content to PEM for direct methanol fuel cells (DMFC). The first set of sPS-*b*-PDMS with the highest molecular weight and 50% PS block ratio generally showed high mechanical strength and selectivity (proton conductivity/ methanol permeability), and the second set with medium molecular weight and 60% PS ratio showed high proton conductivity. The last PEM with the lowest molecular weight and 80% PS ratio exhibited a poor tensile strength which is not suitable for PEM application. When the membrane/electrode assemblies (MEAs) were fabricated using the sPS-*b*-PDMS PEMs with moderately high DS (~40%), one from the second set (moderate molecular weight, 60% PS content) showed the best power performance (90 mW/cm^2 at 70 $^\circ$C) in active mode DMFC operation, which was found to be 20% higher than that of Nafion 115 MEA.

Keywords: partially sulfonated polystyrene-*b*-poly(dimethylsiloxane), proton exchange membrane, direct methanol fuel cell, molecular weight.

Introduction

For decades, there have been active researches worldwide to develop alternative renewable energy sources which can be applied as stable power source for small mobile devices. Direct methanol fuel cells (DMFC) are regarded as one of the renewable energy sources particularly suitable for small electronic devices such as cell phones and laptop computers owing to advantageous features such as high energy density and simple device fabrication.[1,2] In DMFC, methanol oxidation occurs at the anode producing six protons which are consumed at the cathode for water production. Two electrodes are separated by a thin proton exchange membrane (PEM) through which protons are transported from anode to cathode in hydronium form. The redox reactions in DMFC result in electromotive force corresponding to 1.2V ideally, which is diminished due to many realistic reasons. PEM is a key material to constitute DMFC single cell, and there are requirements for PEM such as proton conductivity, mechanical/chemical stabilities, and compatibility with the respective electrodes to avoid unwanted potential drops and consequently maximize the fuel cell performance. Nafion, a short-branched perfluorinated polymer with sulfonyl pendants is mostly used for PEM in DMFC since it meets most of requirements for DMFC PEM, while high methanol permeability and high manufacturing cost remain to be the obstacles for Nafion to become one of a kind choice for practical DMFC applications.[3-5] Hence, there have been efforts to develop alternative PEMs by sulfonating the hydrocarbon based engineering plastics such as poly(styrene),[6] poly(ether ether ketone),[7-9] poly(imide),[10] poly(phosphazene),[11] poly(ether sulfone)[12-14] exhibiting low methanol permeability and cost effectiveness. Some of those examples showed excellent membrane properties and usefulness as DMFC PEM, but there are still limitations in most of the membranes due to trade-off characteristics of proton conductivity *vs*. methanol permeability. From this point of view, the polymer systems with more sophisticated nanostructures such as microphase separated block copolymers have been considered to provide a clue to the trade-off game of PEM by forming nanostructured hydrophilic channels which can selectively allow proton transport while efficiently blocking methanol crossover.[15] Due to relative easiness of post-sulfonation, the block copolymers containing polystyrene (PS) as a channel-forming block

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*Corresponding Authors. E-mails: wonmoklee@sejong.ac.kr or hyunjung@kookmin.ac.kr

have been actively utilized with systematic engineering of degree of sulfonation (DS) on PS or morphological control of the microphase.[16-18] In those reports, however, the hydrocarbon rubbery blocks are often vulnerable to acidic environment during fuel cell operation showing deteriorated long term stability. Recently, we investigated the diblock copolymer containing a sulfonated PS (sPS) as hydrophilic block and poly(dimethylsiloxane) (PDMS) as a rubbery block to find out an improved stability of membrane electrode assembly (MEA) in DMFC condition without loss of long term stability.[19,20] High performance and long term stability of the sPS-*b*-PDMS was attributed to the unique chemical stability and hydrophobicity of PDMS block.

In this study, we investigate the effect of molecular weight and block composition in sPS-*b*-PDMS on PEM properties in a systematic manner. Three different PS-*b*-PDMS's are sulfonated to various DS's, and the PEM properties of the resulting ionomers are rigorously characterized. Using a selected PEM, MEA fabrication and DMFC performance test are carried out.

Experimental

Materials. Three different PS-*b*-PDMS diblock copolymers were used in this study, and they were distinguished by number in order of decreasing molecular weight. PSPDMS1 was synthesized by anionic polymerization in cyclohexane through sequential addition of monomers. PSPDMS2 and PSPDMS3 were obtained from Polymer source Inc., and used as purchased. Nafion® dispersion (10 wt%, E.W. 1100) and Nafion 115 membrane were obtained from Dupont. Sulfuric acid (Aldrich, 95-98%), acetic anhydride (Samchun, 99.0%), dichloroethane (DCE, Dae-jung, 99%), i-propanol (IPA, Duksan, 99.5%), tetrahydrofuran (THF, Duksan, HPLC grade) and methanol (Duksan, 99.8%) were respectively purchased and used without further purification. Deionized (DI) water was prepared by water purifier (Human technology) equipped with ion exchange resins.

Partial Sulfonation of PS-*b*-PDMS: 1 gram of PS-*b*-PDMS powder and 20 mL of DCE were added in a 2-neck round-bottom-flask (RBF, 50 mL) and gently purged by nitrogen gas for 1 h under stirring. In the other 50 mL RBF, 10 g DCE and 6.5 g acetic anhydride were mixed with 3.3 g sulfuric acid under iced water condition to prepare acetyl sulfate. Aacetyl sulfate was added dropwise into the dissolved PS-*b*-PDMS, and temperature was raised to 60 °C. Sulfonation reaction was carried out for 2.5 h under N_2 environment. Reaction was terminated by addition of 10 mL isopropyl alcohol (IPA). DCE and liquid byproducts were removed by rotary evaporator, and the crude product was repeatedly washed with water and methanol for 3-4 days. The sulfonated products were dried in a vacuum oven for one day.[6] By using different amount of acetyl sulfate, DS of each sPS-*b*-PDMS was controlled.

Membrane Preparation. Partially sulfonated sPS-*b*-PDMS sample was dissolved in THF at 2.5 wt% for one day, and the polymer solution was filtered through a 1 μm pore disk filter (Whatman). The solution was poured in a glass petri-dish and membrane casting was carried out for 40 °C for 4 h, followed by annealing for 12 h at 70 °C. The cast membrane was delaminated from the petri-dish by immersing it in DI water.

Characterization. Molecular weights of three PS-*b*-PDMS samples were characterized by gel permeation chromatography(GPC, Acme9000, Younglin) analysis in THF through standard calibration using PS standards. The block compositions of PS-*b*-PDMS and DS's of sPS-*b*-PDMS's were characterized by ^{1}H nuclear magnetic resonance spectroscopy (NMR) (Bruker, 500 MHz).[20] For NMR analysis, PS-*b*-PDMS was dissolved in $CDCl_3$ and sPS-*b*-PDMS was dissolved in DMSO-d_6. The glass transition temperature (T_g) of sPS-*b*-PDMS was analyzed by differential scanning calorimetry (DSC, Scinco). The mechanical property of sPS-*b*-PDMS membrane was characterized by tensile strength measurement of 1×4 cm^2 hydrated sample strip using universal testing machine (UTM, Series-5567, Instron). Surface and cross-sectional morphologies of sPS-*b*-PDMS membranes were respectively characterized by tapping mode atomic force microscopy (AFM, Asylum) and scanning electron microscopy (SEM, S4700, Hitachi). The sample for AFM imaging was prepared by dissolving sPS-*b*-PDMS in n-butanol at 1 wt%, which was spin coated on a pre-cleaned Si wafer for 20 s at 500 rpm spin rate. A thin film was annealed at 160 °C under vacuum and cooled down to room temperature before imaging. For SEM, sPS-*b*-PDMS was dissolved in THF at 5 wt%, and one drop of the solution was slowly cast in between two glass cover slips. Upon complete drying, a sandwiched sample was directly immersed in liquid nitrogen and a frozen sample was broken to expose a clean-cut cross-section.

Proton Conductivity and Methanol Permeability. Proton conductivity (σ) of sPS-*b*-PDMS PEM was measured *via* four-point probe method by using an AC impedance analyzer (compactstat, IVIUM).[13,21] A 1×4 cm^2 strip of PEM sample was fixed at a custom-made measurement cell, and AC voltage scan was carried out to obtain AC impedance (R) from which σ was calculated from a relationship $\sigma = L/(A \times R)$, where A is the membrane cross-sectional area, and L is the distance between two platinum probe). With this measurement, σ of Nafion 115 was measured to be 0.078 S/cm at room temperature. Methanol permeability of PEM was measured by diffusion cell method using a custom-made diffusion cell at room temperature.[7] Experimental details of the measurement procedures can be found elsewhere.[19]

MEA Fabrication and DMFC Single Cell Test. MEAs for DMFC performance test were fabricated.[22] Catalyst slurries of Pt black (Highspec 4000, Johnson-Matthey) as a cathode and Rt-Ru black (Highspec 12100, Johnson-Matthey) as an anode were prepared by respectively mixing them with Nafion binder at 20 wt%, and coating on Toray 060 and SGL-25BC carbon papers respectively. A sPS-*b*-PDMS PEM was placed between two electrodes and hot-pressed at 50 MPa pressure and 80 °C temperature for 1 min to complete MEA fabrication. Using an MEA, a DMFC single cell was constructed, and the cell was activated by flowing 1 M methanol for 4 h at 3 mL/min rate. Then, active DMFC performance of the MEA was measured under constant voltage mode at the temperature range of 30~70 °C with 400 mL/min air flow at cathode. For comparison, an MEA was prepared using Nafion 115 as PEM by hot-pressing it at 5 MPa and 150 °C for 1 min, and a DMFC performance test was carried out under the same condition as described above.

Results and Discussion

The molecular weights and the block compositions of three PS-*b*-PDMS's used in this study are summarized in Table I. PSPDMS1 showed the highest molecular weight (220 kg/mol) and the smallest PS block ratio (50%), while PSPDMS3 had the smallest molecular weight (65,000 g/mol) and the largest PS ratio (80%).

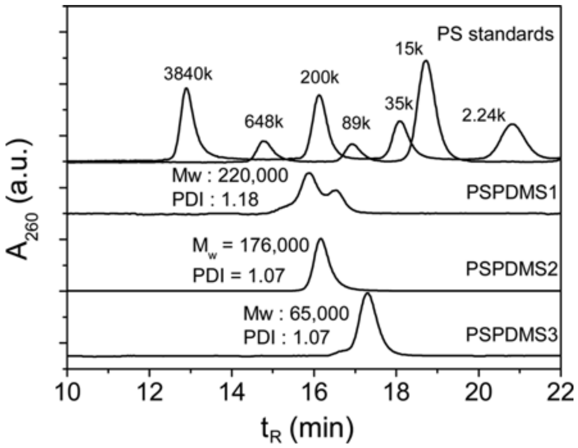
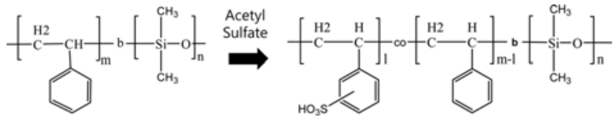


Figure 1. GPC chromatograms of three PS-*b*-PDMS's used in this study overlaid with seven PS standards for molecular weight comparison.



Scheme I. Partial sulfonation of PS-*b*-PDMS using acetylsulfate.

Since the block copolymers used in this study were prepared by anionic polymerization, their polydispersity index (PDI) values were as narrow as 1.07. However, GPC analysis revealed that PSPDMS1 contains significant amount of PS homopolymer which appeared at a retention time of t_R~16.7 min as shown in Figure 1 to result in a larger PDI than others.

Table I. Characterization Results of PS-*b*-PDMS

Sample Name	PSPDMS1	PDPDMS2	PSPDMS3
Mol. Wt.[a] (g/mol)	220,000	176,000	65,000
PDI[b]	1.18	1.07	1.07
PS mol%[c]	50%	60%	80%

[a,b]Measured by GPC using THF solvent and PS calibration standards. [c]Measured by ^1H NMR in $CDCl_3$.

The PS block of each polymer was partially sulfonated by reacting with acetylsulfate with controlled DS as shown in Scheme I. As summarized in Table II, eleven sPS-*b*-PDMS products having various DS's (22~48%) were prepared by controlling the concentration of acetyl sulfate in the sulfona-

Table II. Properties of PEM Samples Used in this Study[a]

Sample (Mol. Wt., PS mol%)	Degree of Sulfonation (%)	Glass Transition Temp. (°C)	Proton Conductivity (S/cm)	MeOH Permeability (cm^2/s)	Selectivity (normalized to Nafion 115)
sPSPDMS1 (220,000, 50%)	22	131	0.019	1.38×10^{-7}	4.02
	34	148	0.082	5.33×10^{-7}	4.59
	39	158	0.078	1.73×10^{-6}	1.35
sPSPDMS2 (176,000, 60%)	23	139	0.032	4.95×10^{-7}	1.94
	30	138	0.037	5.82×10^{-7}	1.91
	31	146	0.036	6.27×10^{-7}	1.70
	32	149	0.049	1.21×10^{-6}	1.21
	42	164	0.114	4.70×10^{-6}	0.72
	46	170	0.101	4.70×10^{-6}	0.64
	48	172	0.106	2.18×10^{-6}	1.46
sPDPDMS3 (65,000, 80%)	41	157	0.08	2.26×10^{-6}	1.06
Nafion 115	·	128	0.078	2.70×10^{-6}	1.00

[a]Proton conductivity and methanol permeability were measured at room temperature.

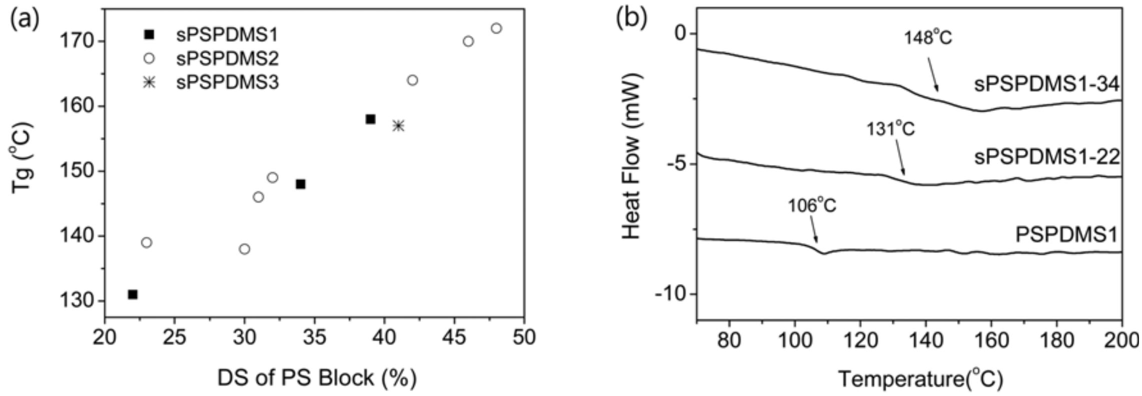


Figure 2. (a) Plot of T_g measured from the eleven sPS-*b*-PDMS products. (b) DSC Thermograms of PSPDMS1 and its sulfonated products with indication of T_g.

tion reactions. Upon sulfonation, it was reported that T_g of the sPS block in block copolymer increases in proportion to DS.[20] Through DSC analysis, the T_g of every sulfonation product has been measured and summarized in Table II. T_g of the unsulfonated PS block was measured to be 106 °C, and Figure 2(a) shows that T_g has monotonously increasing tendency with DS up to 173 °C regardless of the molecular weights of the pristine samples used in this study, due to their sufficiently high molecular weights.

As an example, DSC thermograms of sPSPDMS1 series are shown in Figure 2(b). Since T_g of rubbery PDMS block is very low (-127 °C), it was not shown in the scanned temperature range.

Proton conductivity of sPS-*b*-PDMS membrane is a key property for PEM application. Figure 3 shows the proton conductivities of the cast PEMs measured at room temperature as a function of DS, which again show increasing tendencies while no visible dependence of the molecular weight of the polymers was observed. However, there is an abrupt increase of proton conductivity at around 32-34% of DS which can be attributed to the existence of percolation threshold due to effective linking of ionic clusters to form proton channels.[15,23,24] Among the three different PSPDMS sources, sPSPDMS2 series showed relatively high proton conductivities at the similar DS's probably due to a higher purity of the original polymer. Since the unique PEM property of the block copolymer ionomer stems from the formation of well-defined hydrophilic channels provided by block copolymer's nanostructures, existing homopolymer impurities may deteriorate the effective formation of nanochannels for proton transport.

The mechanical strengths of the selected PEMs were tested by UTM. Three PEMs having a similarly high DSs obtained from each PS-*b*-PDMS (39-42%) were chosen, and tensile strength of each PEM was measured. It is shown in Figure 4 that sPSPDMS1-39 exhibited the highest tensile stress as well as a large elongation due to high molecular weight. sPSPDMS2-42, however, was revealed to have low tensile stress although elongation was as large as that of sPSPDMS1-39. In addition to a relatively lower molecular weight, slightly higher DS may have caused a higher swelling of PEM during hydration and therefore have resulted in lower tensile stress. Such a reasoning can be supported by relatively high proton conductivities of sPSPDMS2 series shown in Figure 3. A PEM of sPSPDMS3-41, having the lowest molecular weight and

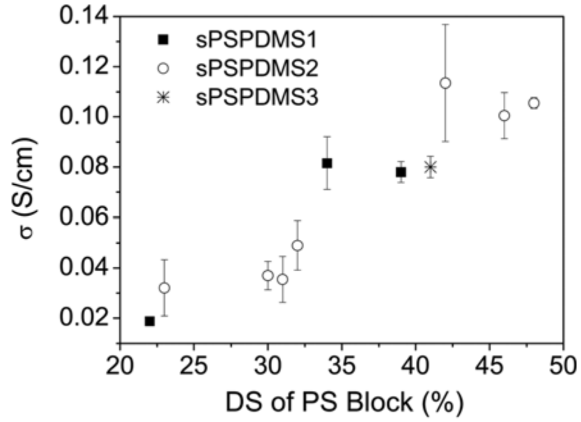


Figure 3. Plot of proton conductivity *vs*. DS of PS block of the eleven sPS-*b*-PDMS PEMs showing increasing tendency with DS.

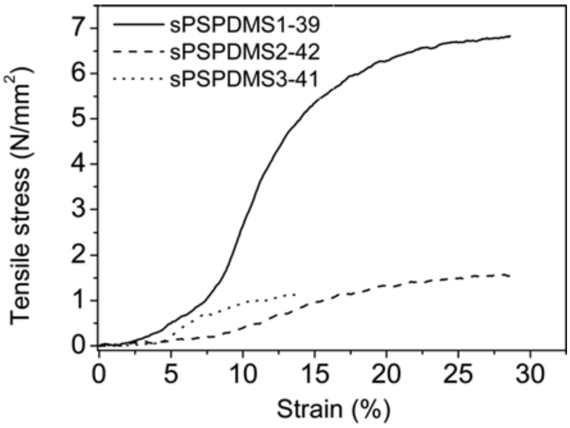


Figure 4. Tensile strength measurements of three sPS-*b*-PDMS PEMs.

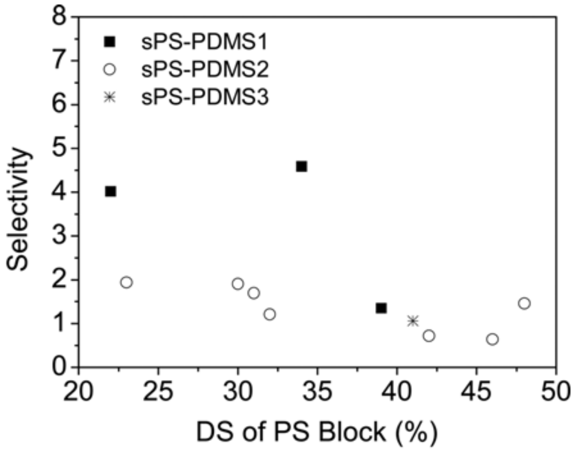


Figure 5. Plots of selectivity *vs*. DS of PS block for the eleven PEMs used in this study.

the highest PS content, showed a higher tensile stress compared to sPSPDMS2-42 at the initial strain, but was torn apart before reaching 15% of strain. Low tensile strength and strain of sPSPDMS3-41 PEM can be partly attributed to low molecular weight and also due to a low PDMS content which will provide a lesser flexibility to the membrane.[14,20]

As summarized in Table II, the methanol permeabilities of sPS-*b*-PDMS PEMs measured at room temperature constantly showed increasing tendency with DS due to the increased number of proton channels. At high DS, enhanced formation of hydrophilic channel generally brings about increases in both proton conductivity and methanol permeability.[25] In order to better describe the PEM property, the ratio of proton conductivity and methanol permeability (*i.e.*, selectivity) was calculated for each PEM synthesized in this study, and it was normalized to the value of Nafion 115. Shown in Figure 5 are the normalized selectivity *vs*. DS revealing slightly decreasing tendency with increased DS. It is noteworthy that the PEMs derived from PSPDMS1 showed high selectivities at low DS while those above the DS of 33% (percolation threshold) became indistinguishable regardless of molecular weight.

Figure 6 shows the cross-section SEM images of three freeze-fractured sPSPDMS PEMs which were used for tensile measurements. It is noteworthy that the domains which look like standing posts are normal to the cross-sectional planes. The post-like domains are believed to be those from PDMS blocks. Even at low temperature of liquid N_2, PDMS blocks are still at their rubbery states and will be elongated during freeze-fracturing where they will finally end up having the selectively deformed shapes at the fractured surface.

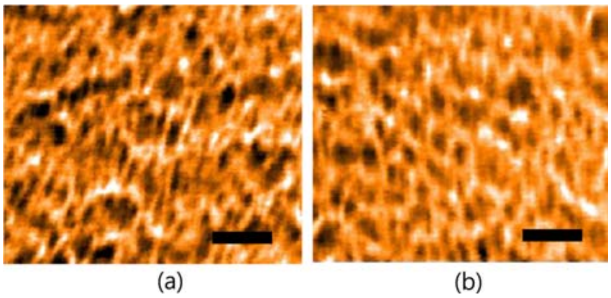


Figure 7. Tapping mode AFM phase images obtained at the surface of two PEMs of (a) sPSPDMS1-39, (b) sPSPDMS2-42, showing more dark spots in sPSPDMS1-39 due to higher PDMS content. Scale bar in each image stands for 100 nm.

Compared to the surfaces of sPSPDMS1 and sPSPDMS2, that of sPSPDMS3 showed a relatively flatter cross-section which can be attributed to low PDMS content (20%) in the block copolymer. In order to compare the surface nanostructures sPSPDMS1 and sPSPDMS2 more rigorously, tapping mode AFM analysis was conducted on the surface of each membrane. Shown in Figure 7 are the phase images of two PEMs where dark regions stand for soft rubbery domains.[14,20] Both PEMs showed the interconnected nanostructures of bright domains which are presumably consisted of sPS domains with higher T_g. Although the surface morphologies of two PEMs appeared similar, there are more dark spots in sPSPDMS1-39 due to higher PDMS content.

To compare the sPSPDMS membranes and Nafion 115 as PEM materials for DMFC, 150 μm thick membranes were prepared from high DS ionomers and the MEA's were fabricated by hot-pressing each membrane between PtRu and Pt as anode and cathode respectively. Standard fabrication procedures optimized for Nafion 115 PEM in active mode DMFC

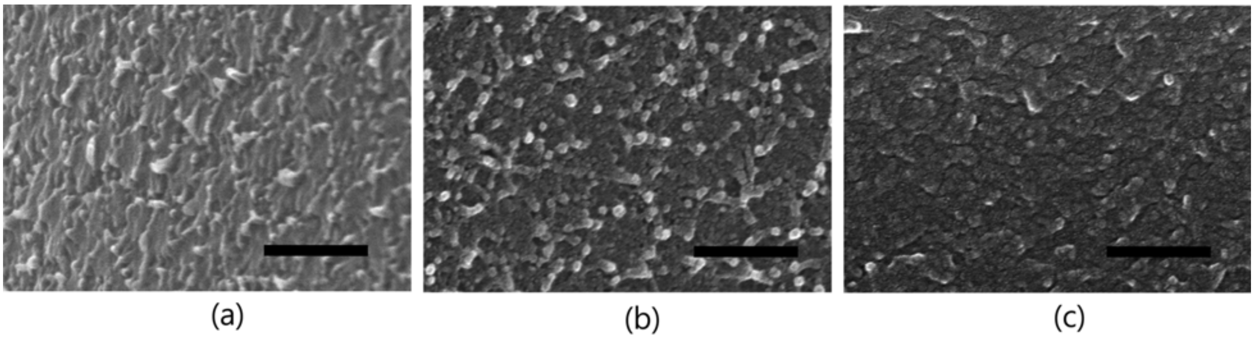


Figure 6. SEM Images obtained from the freeze-fracture samples of (a) sPSPDMS1-39, (b) sPSPDMS2-42, (c) sPS-PDMS3-41. Scale bars stand for 300 nm for all images.

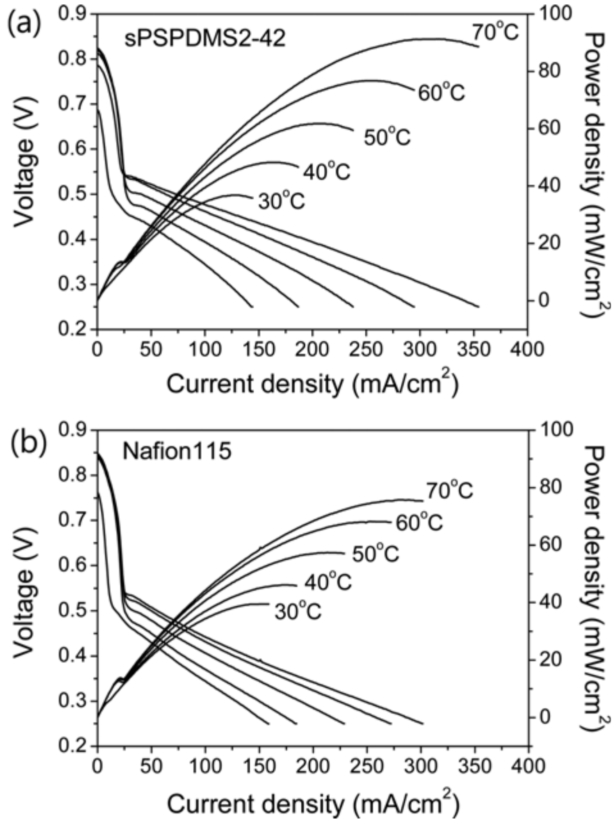


Figure 8. Active mode DMFC polarization curves obtained at various temperatures using (a) sPSPDMS2-42, (b) Nafion 115 as PEM.

were adopted. After activating an MEA in 1 M methanol, a polarization curve was obtained at the temperature ranges of 30~70 °C (Figure 8).

We prepared the MEAs using sPSPDMS PEMs with similar DS's as used for SEM analysis, but only the one with sPSPDMS2-42 exhibited meaningful data. The failure of sPSPDMS3-41 PEM can be attributed to its weak mechanical property originating from low molecular weight. However, since sPSPDMS1-39 exhibited better PEM properties in tensile strength and selectivity than other membranes, it was expected to show a good DMFC performance. As briefly mentioned earlier in Figure 1, a significant amount of PS homopolymer contained in PSPDMS1 could have caused a membrane failure during the activation process. The sulfonated PS molecules without hydrophobic PDMS block could be dissolved much more easily in harsh DMFC operation conditions to end up forming holes or cracks in the PEM. As shown in Figure 8, the maximum power density of the MEA with sPSPDMS2-42 PEM was measured to be 90 mW/cm^2 at 70 °C while that of Nafion 115 MEA was 75 mW/cm^2 at the same temperature. Considering that the MEA fabrication is optimized for Nafion membrane, a 20% improvement in the power performance with sPSPDMS-containing MEA is noteworthy. From the results obtained in this study, it was found that a high molecular weight as well as a high purity is required for sPSPDMS to be properly used as a PEM for DMFC.

Conclusions

In this study, three PS-*b*-PDMS's with different molecular weights and block compositions were partially sulfonated to be tested as PEM for DMFC. Eleven sPS-*b*-PDMS's were obtained with various DS's (22~48%) on PS block, and rigorous PEM characterizations were carried out. From the proton conductivity measurements, a percolation threshold was found at ~33% of DS, and the second set of sPSPDMS2 PEM with medium molecular weight (176 kg/mol) and 60% PS ratio showed the largest proton conductivities at the given DS. The tensile measurement revealed that the sPSPDMS1-39 PEM with the highest molecular weight (220 kg/mol) shows the largest mechanical strength. sPSPDMS3-41, a low molecular weight product (65 kg/mol), showed too poor mechanical strength to be used as an actual PEM. Although a large molecular weight PEM was expected to be the best PEM material, their MEA failed during the activation process for active mode DMFC operation presumably due to existence of a homo-PS impurity in the precursor block copolymer. The MEA with sPSPDMS2-42 showed a significantly higher power performance than that of Nafion 115.

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