Sulfonated poly(ether sulfone)/sulfonated polybenzimidazole blend membrane for fuel cell applications

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Article info
Article history:
Received 7 November 2009
Received in revised form 25 February 2010
Accepted 7 March 2010
Available online 11 March 2010

Keywords:
Polymer electrolyte fuel cells
Polymer blends
Proton exchange membrane
Sulfonated poly(ether sulfone)
Sulfonated polybenzimidazole

Abstract
Polymer blending is used to modify or improve the dimensional and thermal stability of any two different polymers or copolymers. In this study, both sulfonated polybenzimidazole homopolymer (MS-p-PBI 100) and sulfonated poly(aryl ether benzimidazole) copolymers (MS-p-PBI 50, 60, 70, 80, 90) were successfully synthesized from commercially available monomers. The chemical structure and thermal stability of these polymers was characterized by 1H NMR, FT-IR and TGA techniques. Blend membranes (BMs) were prepared from the salt forms of sulfonated poly(ether sulfone) (PES 70) and MS-p-PBI 100 using dimethylacetamide (DMAc). These blend membranes exhibited good stability in boiling water. The blending of 1 wt.% of MS-p-PBI 100 and 99 wt.% of PES 70 to produce the blend membrane BM 1 reduced membrane swelling, thus leading to good dimensional stability and comparable proton conductivity. Hence, BM 1 was chosen for the fabrication of a membrane electrode assembly (MEA) for proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) applications. This paper reports on PEMFC and DMFC performance under specific conditions.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are one of the most promising worldwide alternative power sources for applications in stationary, automotive, and portable devices. PEFCs are electrochemical energy converters which directly transform chemical energy into electricity using a series of electrochemical redox reactions. To date, perfluorosulfonic acid polymer membranes, produced by DuPont, have been the most widely studied polymer electrolytes in the fuel cells. Although they show high proton conductivity and excellent chemical stability, their high cost and the environmental hazards they pose have led scientists to search for lower cost and more environmentally friendly membranes. Therefore, various alternative polymer electrolytes have been studied and reported for fuel cell applications [1–4].

Aromatic polybenzimidazoles (PBIs) have received considerable attention in the past decade due to their potential application in PEFCs [5–21]. Recently, phosphoric acid-doped sulfonated PBI membranes have shown higher proton conductivities than the corresponding phosphoric acid-doped non-sulfonated PBI membranes [22]. Especially, the synthesis and characterization of sulfonated PBIs from sulfonated monomers have been studied widely. The direct polymerization method from the sulfonated monomers has proved to be better at precisely controlling the degree...
of sulfonation. Nonetheless, at this time very few sulfonated monomers are commercially available [18,23–26].

PBI s are inexpensive heterocyclic polymers possessing high thermal stability and excellent chemical resistance in various environments. Due to the rigid structure of the main-chain, they have a high glass transition temperature. They have both proton donor (–NH−) and proton acceptor (–N=) hydrogen-bonding sites which exhibit specific interaction to form blend membranes for fuel cell applications. Most of the polymer blend research reports have explained their miscibility, thermal stability, mechanical properties, structural morphologies, dimensional stability, etc., but very few fuel cell test results have been reported using PBI-based blend membranes [27–33]. More recently, Hong et al. studied the direct methanol fuel cell (DMFC) performances of blend membranes for fuel cell assemblies (MEAs) based on sulfonated poly(arylene ether sulfone) (SPAES) acid polymer with the sulfonated poly(aryl ether benzimidazole) amphiphilic polymer (SPAEBI) blend system. The single cell DMFC performance of the modified blend membrane (SPAES-SPAEBI-50-5) was found to be 1.2 times higher than that of the commercial Nafion® 117 membrane under similar operating conditions [34].

The use of PBIs has been limited, however, because many are only soluble in strong acids and cannot be processed from organic solvents, yet improved solubility and processability have been accomplished by the incorporation of meta-substituted linkages, aryl ether linkages, and main-chain alkyl substitutents into the monomers prior to polymerization. In this report, we synthesized novel PBI which is very soluble in common organic solvents. Among several PBIs, poly[2,2-(m-phenylene)-5,5′-bibenzimidazole] (mPBI) derivatives have been mostly studied, whereas poly[2,2-(1,4-phenylene)-5,5′-bibenzimidazole] (p-PBI) could not be utilized due to its poor solubility in organic solvents. We introduced sulfonated group to p-PBI to improve its solubility in organic solvents and blended it with sulfonated poly(ether sulfone) copolymer (PES 70). The low cost PES 70 membrane reported in our previous paper exhibited two main disadvantages. One was the contradiction between high proton conductivity and instability in boiling water. The other was poor dimensional stability [35]. Due to its high proton conductivity and low methanol permeability encouraged further investigation of this copolymer. The main aim of the present work is the study of a blend system consisting of acid polymer PES 70 with amphiphilic sulfonated polybenzimidazole (MS-p-PBI 100). These blend membranes enhance boiling water stability as well as dimensional stability as compared to that of pristine PES 70 membranes, so with this in mind, blend membranes using different compositions of MS-p-PBI 100 and acid polymer PES 70 were prepared. Moreover, the basic properties of the resulting membranes were studied. Our investigation additionally looked at single cell performance for a proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) using the blend membrane as a proton exchange membrane. Identifying an appropriate system for blending acid polymer PES 70 with amphiphilic polymer MS-p-PBI 100 paves the way to a promising new polymer electrolyte for fuel cell applications.

2. Experimental

2.1. Materials

3,3′-diaminobenzidine (99% Aldrich), 2-sulfoterephthalic acid monosodium salt (TCI), 4,4′-oxybis(benzoic acid (99% Aldrich), polyphosphoric acid (PPA, 115% as H3PO4 equivalent Sigma–Aldrich), N, N-dimethylformamide (DMF, Sigma–Aldrich) and methanol (J.T. Baker HPLC grade) were purchased and used without further purification. The other chemicals and solvents used in this work have been described elsewhere [35].

2.2. Synthesis of sulfonated poly(aryl ether benzimidazole) copolymers

The general process for producing the solution copolycondensation for synthesizing random copolymer MS-p-PBI 70 was as follows. Poly(phosphoric acid) (PPA) with a magnetic bar was placed into a 100 mL round bottom flask equipped with a condenser and an argon inlet. The flask was immersed in an oil bath and the PPA solution was allowed to stir at 100 °C for 2 h under an argon atmosphere. A stoichiometric ratio mixture of 3,3′-diaminobenzidine (0.86 g, 4.0 mmol), 2-sulfoterephthalic acid monosodium salt (0.75 g, 2.8 mmol), and 4,4′-oxybis(benzoic acid (0.31 g, 1.2 mmol) was added slowly during the stirring. After complete dissolution of the monomers at 200 °C, the solution was maintained at this temperature for 20 h. The brown fiber polymer was isolated by adding the resulting viscous solution to 1000 mL of deionized water. The polymer was filtered and washed several times with deionized water until a neutral pH of the washing water was achieved. The brown fibrous polymer obtained was dried at 100 °C under vacuum for 12 h. The polymer was then allowed to stir in a 10% potassium carbonate solution for at least 24 h. Finally, the resultant fibrous polymer was filtered and washed with deionized water after which it was dried at 100 °C under reduced pressure. Other sulfonated poly(aryl ether benzimidazole) copolymers (MS-p-PBI 50, MS-p-PBI 60, MS-p-PBI 70, MS-p-PBI 80 and MS-p-PBI 90) were also synthesized by the same method but with different molar ratios of monomers. 1H NMR (δ, ppm, in DMSO-d6): MS-p-PBI 70; 12.83–13.77 (3s, 2.6H, ArNH), 8.83–9.04 (s, 1.0H, ArH), 8.16–8.73 (m, 3.7H, ArH), 7.43–8.16 (m, 8.5H, ArH); 7.18–7.40 (m, 1.7H, ArH); FT-IR (cm⁻¹) 803, 1023, 1071, 1172, 1234, 1447, 1601, 1627 and 3161.

2.3. Synthesis of sulfonated polybenzimidazole homopolymer

The sulfonated polybenzimidazole homopolymer was also synthesized by solution polycondensation using the above mentioned method with 3,3′-diaminobenzidine (0.86 g, 4.0 mmol), 2-sulfoterephthalic acid monosodium salt (1.10 g, 4.0 mmol) and PPA. 1H NMR (δ, ppm, in DMSO-d6): MS-p-PBI 100; 13.05–13.83 (2s, 2H, ArH/N), 8.83–9.08 (s, 1H, ArH); 8.24–8.78 (m, 2H, ArH), 7.27–8.24 (m, 6H, ArH); FT-IR (cm⁻¹) 802, 1022, 1069, 1166, 1224, 1444, 1622 and 3059.
2.4. Synthesis of sulfonated poly(ether sulfone) copolymer

The sulfonated poly(ether sulfone) PES 70 was synthesized by aromatic nucleophilic substitution polycondensation, according to the procedure reported in our earlier paper [35]. The salt form PES 70 was used to prepare the blend membranes. $^1$H NMR (δ, ppm, in DMSO- $d_6$): 1.57–1.73 (s, 6.0H, $-\text{CH}_3$), 6.93–7.37 (m, 26.0H, ArH), 7.39–7.52 (s, 2.3H, ArH), 7.77–8.07 (m, 13.3H, ArH); FT-IR (cm$^{-1}$) 1013, 1075, 1103, 1144, 1225, 1289, 1405, 1470 and 1584.

2.5. Membrane preparation and acidification

The sulfonated polybenzimidazole homopolymer and sulfonated poly(aryl ether benzimidazole) copolymer membranes were prepared from their 6 to 7 wt.% cast solutions in N, N'-dimethylacetamide (DMAc). The cast solutions were heated to 130–140°C in an argon atmosphere for the fast dissolution of polymers. When clear solutions were obtained, they were filtered and spread on clean glass plates using a doctor’s blade, and the solvent was evaporated in a vacuum oven at 100°C for 48 h. The glass plates with the polymer films were allowed to attain room temperature. The glass plates were then soaked in a deionized water bath. The membranes were slowly removed from the glass plates.

For the blend membranes, DMAc was used as a solvent. The salt form PES 70 polymer was added into the clear salt form MS-p-PBI 100 solution. The blend solutions (~15 wt.%) were allowed to stir until transparent solutions were obtained. The blend solution was then filtered and cast in the same conditions. Blend membranes were also removed from the glass plates in a similar method to that mentioned before. Both the polymer membranes and blend membranes were treated first in 10% HCl solution at 70°C and then rinsed with water several times. Finally, the membranes were stored in deionized water at room temperature.

2.6. Characterization techniques

Fourier transformed infrared spectra were recorded on a Nicolet Magma II FT-IR spectrometer. Samples were used as thin polymer films. The $^1$H NMR (300 MHz) spectra were obtained on a Varian instrument at room temperature. The solvent dimethylsulfoxide (DMSO-$d_6$) with tetramethylsilane (TMS) was used as an internal reference. The thermal stability of the membranes was analyzed by means of thermogravimetric analysis with a 2050 TGA V5.4A instrument. The stability of the membranes was analyzed by means of thermal gravimetric analysis with a 2050 TGA V5.4A instrument.

2.7. Water uptake, swelling ratio, water solubility and proton conductivity

Water uptake was measured for the acid form polymer membranes and blend membranes. Five samples (~20 mg each) of membrane were dried at 120°C in a vacuum oven. The samples were soaked in deionized water at room temperature for 48 h. Then, each sample was taken out, quickly wiped with paper, and weighed. The water uptake could then be calculated from the following equation:

\[
\text{Water uptake} = \frac{W_w - W_d}{W_d} \times 100
\]

where $W_w$ and $W_d$ represent the weight of the wet and dry membranes, respectively. The water uptake values reported in this paper correspond to the average of the five samples.

For the swelling ratio measurement, 3 × 3 cm membrane samples were placed in a Soxhlet extraction device with deionized water for 48 h. The swelling ratios of the membranes were calculated as

\[
\text{Swelling ratio} \% = \frac{L_a - L_b}{L_b} \times 100
\]

where $L_a$ and $L_b$ are the lengths before and after Soxhlet extraction, respectively.

The water stability test was performed for the acid form blend membrane (BM 1). The BM 1 membrane (3 × 3 cm) was placed in a Soxhlet extraction device with deionized water for 300 h. After 300 h subjected BM 1 membrane was characterized by FT-IR technique.

The proton conductivity of the hydrated membranes was measured using a four-probe conductivity cell with an IM6 (ZAHNER® elektrik) analyzer [36].

2.8. Membrane electrode assembly and single cell test

For the PEMFC single cell test, a catalyst solution was prepared by mixing 45.5 wt.% Pt/C (Tanaka Kikinzoku Kogyo K.K) with isopropyl alcohol (J.T. Baker analyzed HPLC reagent) and then the solution was ultrasonicated for 1 h. A 5 wt.% Nafion® solution (EW 1100, Dupont Inc.) was added to the catalyst solution, which was again ultrasonicated for 1 h. The MEA was prepared by the catalyst coated membrane (CCM) method, in which the prepared catalyst solution was sprayed on the BM 1 (a blend of 1 wt.% of MS-p-PBI 100 and 99 wt.% of PES 70) membrane using an automated spraying machine. The active electrode area was 25 cm$^2$ with a platinum loading of 0.3 and 0.4 mg cm$^{-2}$ for the anode and cathode, respectively. The single cell was assembled with the prepared CCM, gas diffusion media (SGL 10BC, Sigracet®, Carbon Inc.), Teflon® gaskets, graphite field-flow plates, and end plates. Hydrogen and air were fed to the anode and cathode, respectively, after passing through a bubble humidifier at a temperature of 70°C (anode) and 65°C (cathode) under ambient pressure. The cell temperature was 70°C. The single cell performance was evaluated by measuring the current–voltage ($i$–$V$) characteristics using an electronic load (Daegil Electronics, EL500P). The $i$–$V$ measurement of the single cell was recorded after activation for 24 h at a constant current density of 640 mA cm$^{-2}$.

For the DMFC single cell test, catalyst ink was prepared by dispersing the unsupported Pt-Ru (50:50 wt.%) and Pt black (Johnson Matthey Co.) with a mixture of deionized water, 5 wt.% Nafion® (EW 1100, Dupont®) ionomer solution, and isopropyl alcohol. The MEA was prepared by the CCM method, in which the prepared catalyst inks were sprayed on the BM 1 membrane directly using an air brush
gun-piece (GP-2, Fuso Seiki Co., Japan). The Pt-Ru and Pt loadings in the anode and cathode were 3 mg cm⁻². Carbon paper (ETEK) was used for the anode side gas diffusion layer (GDL). The 0.6 mg cm⁻² of the micro porous layer (MPL) based GDL containing Vulcan XC-72R carbon, IPA, and PTFE was used for the cathode side. The single cell test was performed using a commercial test station (SMART-II Wona Tech PEM/DM hybrid fuel cell test system, Korea) with an active area of 10 cm² at 70°C with different methanol feed concentrations at a flow rate of 5 mL min⁻¹ and humidified air at a flow rate of 1250 mL min⁻¹ without backpressure.

3. Results and discussion

3.1. Synthesis and characterization of sulfonated polymer

Both homopolymer (MS-p-PBI 100) of 2-sulfoterephthalic acid monosodium salt with 3,3'-diaminobenzidine and copolymers (MS-p-PBI 50 ~ MS-p-PBI 90) of 3,3'-diaminobenzidine, with a mixture of a different mole ratio of 2-sulfoterephthalic acid monosodium salt and 4,4'-oxybis(benzoic acid), were synthesized via solution polymerization in PPA (Scheme 1). PPA is a relatively inexpensive, non-oxidizing medium that acts as the solvent, catalyst, and dehydrating agent in polymerization. The number after the polymer code indicates the degree of sulfonation of the polymers. The ¹H NMR and FT-IR characterization techniques are used to investigate the polymer structural compositions and functional groups. The ¹H NMR spectra of acid form MS-p-PBI 100, MS-p-PBI 70, along with their proton designations, are depicted in Fig. 1. It is interesting to note that the signal peak, due to the imidazole –NH protons of MS-p-PBI 100 (H₄ and H₅), was obtained at 13.65 and 13.31 ppm. The imidazole –NH protons of MS-p-PBI 70 (H₄, H₅, and H₆) were also obtained at 13.65, 13.31 and 12.99 ppm. This is due to the effect of the electron withdrawing –SO₃H group and the presence of aryl ether linkage [25]. The proton next to the sulfonic acid group (H₆) signal appeared at 8.95 ppm. Signals appeared at 8.64 ppm for H₇ and 8.44 ppm for H₈ protons. The signal peaks of the other three protons, H₈, H₉, and H₁₀, were detected at 8.05, 7.8, and 7.65 ppm, respectively. The copolymer structural composition (MS-p-PBI 70) was confirmed from the integral values of its ¹H NMR spectrum. The aromatic proton signal at 8.83–9.04 ppm is from the proton (H₈) which is located next to the sulfonic acid group. The signal at 7.18–7.40 ppm represents the ortho proton (H₇) to aryl ether linkage in the polymer repeating unit. Theoretically, the peak integration ratio of two peaks (H₈/H₇) should be 1/1.7. The expected integration values were obtained from the ¹H NMR spectrum. The copolymer PES 70 was synthesized via nucleophilic aromatic polycondensation reaction. The contents of the calculated monomers were in good agreement with the feed ratio as revealed in the ¹H NMR spectrum of PES 70 (Fig. 2).

The FT-IR spectra of all polymers were scanned using thin films. The FT-IR spectra of MS-p-PBI 100, MS-p-PBI 70, and PES 70 are presented in Fig. 3. The characteristic absorption band of the C=N stretching of the imidazole ring at 1622 cm⁻¹ for MS-p-PBI 100, and at 1627 cm⁻¹ for MS-p-PBI 70, confirms the formation of polybenzimidazole. The peak located at 1601 cm⁻¹ is attributed to the ring vibration of conjugation between the benzene and imidazole rings. The absence of the carbonyl absorption band between 1780 and 1650 cm⁻¹ is further evidenced by the complete imidazole ring closer under the reaction conditions. The stretching vibration of the –NH groups involved in the hydrogen-bonding interaction peaks appeared at 3161 cm⁻¹ for MS-p-PBI 100 and at 3059 cm⁻¹ for MS-p-PBI 70, and 1584 cm⁻¹ and 1470 cm⁻¹ for PES 70 confirms the formation of polybenzimidazole. The peak at 1601 cm⁻¹ is attributed to the ring vibration of conjugation between the benzene and imidazole rings. The absence of the carbonyl absorption band between 1780 and 1650 cm⁻¹ is further evidenced by the complete imidazole ring closer under the reaction conditions. The stretching vibration of the –NH groups involved in the hydrogen-bonding interaction peaks appeared at 3161 cm⁻¹ and 3059 cm⁻¹ for MS-p-PBI 70 and MS-p-PBI 100, respectively [23]. The aromatic ring skeleton peaks for PES 70 appeared at 1584 cm⁻¹ and 1470 cm⁻¹. The characteristic aryl oxide peak for MS-p-PBI 70 appeared at 1234 cm⁻¹. However, it appeared at 1225 cm⁻¹ for PES 70 [35]. The peaks at 1444 cm⁻¹ for MS-p-PBI 100 and 1447 cm⁻¹ for MS-p-PBI 70 are attributed to vibration of the aromatic ring skeleton. The hetero-

![Scheme 1](image-url)
cyclic ring vibration absorption band appeared at 802 cm$^{-1}$ and 803 cm$^{-1}$ for MS-p-PBI 100 and MS-p-PBI 70, respectively [23]. The characteristic band of the aromatic sulfone group appeared at 1166 cm$^{-1}$ for MS-p-PBI 100, 1172 cm$^{-1}$ for MS-p-PBI 70, and 1144 cm$^{-1}$ for PES 70. Also, the two absorption peaks appeared at 1069 cm$^{-1}$, 1022 cm$^{-1}$ for MS-p-PBI 100, 1071 cm$^{-1}$, 1023 cm$^{-1}$ for MS-p-PBI 70, and 1075 cm$^{-1}$, 1013 cm$^{-1}$ for PES 70 which are character-

Fig. 1. $^1$H NMR spectra of MS-p-PBI 100 and MS-p-PBI 70.
istic of the aromatic SO$_2$ stretching vibrations [35]. On the basis of $^1$H NMR and FT-IR studies, the proposed polymer structure was synthesized successfully.

### 3.2. Solubility, water uptake, swelling ratio, proton conductivity, and hydrolysis resistance of the membranes

Solubility behavior of the sulfonated polybenzimidazole polymers was studied by dissolving 5 mg of polymers in 1 mL of solvents such as DMAc, DMSO, and DMF. The transparent, tough, and flexible sulfonated polybenzimidazole membranes were obtained from DMAc solutions. The blend membranes were prepared from different amounts of salt form MS-p-PBI 100 (0.5, 1, 1.5 and 2 wt.%) with the salt form of PES 70 using the same solvent. Even though non-sulfonated p-PBI is not soluble in polar aprotic solvents, the salt form sulfonated polymers (MS-p-PBI 50 ~ MS-p-PBI 100) are readily soluble in polar aprotic solvents at ambient temperature.

Table 1 shows the solubility behavior, proton conductivity, water uptake, and swelling of the membranes. The proton conductivity value for the PES 70 polymer we used was 0.12 S cm$^{-1}$ at room temperature. It exhibited a very large dimensional change when immersed into deionized water at 70 °C and was soluble in boiling water. Even though the PES 70 had high proton conductivity, the extreme swelling and dimensional change that occurred makes this membrane unsuitable as a PEM material in practical fuel cell applications. For these reasons, the amphiphilic polymer (MS-p-PBI 100) was used to improve the properties of PES 70 as a blend system. The water uptake of the blend membranes was obviously lower than that of the acid form PES 70 membrane. The swelling behavior, as well as dimensional stability of the blend membranes, improved greatly. It is interesting to note that the swelling ratio values for blend membranes decreased.
with increasing amounts of MS-p-PBI 100. This indicates that the blend membranes have higher hydrolytic stability than the pristine PES 70 membrane. The BM 1 was subjected to a 300 h water stability test to ensure its hydrolytic stability. The FT-IR results for the BM 1 membranes before and after the 300 h water stability test are shown in Fig. 4. The FT-IR results prove that the sulfonic acid group and backbone of the BM 1 did not degrade after the 300 h water stability test. Such remarkable dimensional stability may be due to the presence of ionic cross-linking and/or ionic bonding between the acid polymer and amphilic polymer [34]. In other words, the lower proton conductivity and water uptake of the BM 1 compared to the pristine PES 70 could be an additional reason for increased hydrolytic stability. This behavior of the blend membranes is very advantageous for application in fuel cells.

### 3.3. Thermal stability of sulfonated polymer membranes and blend membranes

The thermal stability of the acid form PES 70, sulfonated polybenzimidazole (MS-p-PBI 100, MS-p-PBI 70) and PES 70/MS-p-PBI 100 blend membrane (BM 1) were analyzed and the TGA of the four membranes are shown in Fig. 5. This figure shows that all membranes exhibited a three-step weight loss. The first step weight loss appeared below 150 °C due to the loss of water molecules absorbed by SO$_3$H groups. The second step of weight loss was observed at around 292 °C for PES 70 and BM 1 due to thermal desulfonation of the sulfonic acid group. However, the sulfonic acid contained in polybenzimidazole (MS-p-PBI 100, MS-p-PBI 70) did not change until the temperature exceeded 400 °C when the second step of weight loss was observed in these blend membranes. This is attributed to the position of the sulfonic acid group which is situated in the deactivated part of the polybenzimidazole due to the electron withdrawing nature of imidazole rings. It also indicates that complete cyclization of the imidazole rings occurred in the reaction condition. The third step of weight loss was associated with the decomposition of the polymer backbone. For MS-p-PBI 100 and MS-p-PBI 70, the onset of the third step of weight loss started around 600 °C, but for PES 70 and BM 1, the onset of the third step of weight loss was earlier, at around 450 °C, due to the decomposition of the PES 70 backbones. These results suggest that the membranes are a good alternative PEM candidate for fuel cell applications.

### 3.4. Single cell performance of BM 1 for PEMFCs operated under fully humidified conditions

The blend membrane BM 1 was chosen as a PEM material due to its high proton conductivity and insolubility in boiling water. The catalyst slurry was sprayed directly onto the membrane and the catalyst loading was 0.3 and

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solubility$^a$</th>
<th>Solubility$^b$</th>
<th>Proton conductivity$^c$ (S/cm)</th>
<th>Water uptake (%)</th>
<th>Swelling ratio (%)</th>
</tr>
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<tbody>
<tr>
<td>PES 70</td>
<td>++</td>
<td>++</td>
<td>0.121</td>
<td>98</td>
<td>NR</td>
</tr>
<tr>
<td>MS-p-PBI 100</td>
<td>++</td>
<td>–</td>
<td>0.035</td>
<td>28</td>
<td>R</td>
</tr>
<tr>
<td>BM 0.5</td>
<td>–</td>
<td>+</td>
<td>0.072</td>
<td>53</td>
<td>23</td>
</tr>
<tr>
<td>BM 1.5</td>
<td>–</td>
<td>+</td>
<td>0.058</td>
<td>46</td>
<td>5</td>
</tr>
<tr>
<td>BM 2</td>
<td>–</td>
<td>+</td>
<td>0.049</td>
<td>32</td>
<td>R</td>
</tr>
</tbody>
</table>

$^a$ Solubility in polar aprotic solvents such as DMAc, DMSO and DMF at room temperature.

$^b$ Solubility in boiling water (++ soluble, – not soluble, - not tested, + partially soluble, SW swelling, R Resistant, NR Non-resistant).

$^c$ Proton conductivity at room temperature.

$^d$ Salt form.

$^e$ Acid form.

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**Fig. 4.** FT-IR spectra of the blend membranes (BM 1) before and after a 300 h water stability test. (a) BM 1 fresh and (b) BM 1 after the test.

**Fig. 5.** TGA spectra for acid form membranes. (a) MS-p-PBI 70; (b) MS-p-PBI 100; (c) BM 1; and (d) PES 70.
at a cell temperature of 70 °C are shown in Fig. 7. A noticeable decrease in open circuit voltage (OCV) was observed as methanol feed concentration increased. This reflects the increase in methanol cross-over through the membrane. A maximum current density value of 230 mA cm\(^{-2}\) was obtained at 0.4 V with 1 M methanol feed at 70 °C. A maximum peak power density of 110 mW cm\(^{-2}\) was achieved, which is comparable to commercial membrane Nafion® 115-based MEA. Based on this observation, the BM 1-based MEA brought about better DMFC performance as compared to the findings reported in our previous study [36,37]. This is due to greater membrane thickness and lower methanol permeability of the blend membrane. Further study on the enhancement of current density through the development of MEAs and electrode structures will be undertaken in the near future.

4. Conclusions

Aromatic sulfonated polybenzimidazole homopolymer (MS-p-PBI 100) and sulfonated poly(aryl ether benzimidazole) copolymer (MS-p-PBI 50 ~ MS-p-PBI 90) were successfully synthesized in PPA. The sulfonic acid content in the copolymers was controlled by varying the ratio of the sulfonated di-acid to non-sulfonated di-acid. The MS-p-PBI homopolymer and copolymers were soluble in organic solvent and could be easily cast into membrane films. The films were tough and flexible in the dry state. The resulting sulfonated polybenzimidazole polymers were thermally stable up to 400 °C in their acid from. Although these sulfonated polybenzimidazole polymers have reasonable proton conductivity, thermal stability and insolubility in boiling water, they did not prove to be a good PEM material in a real fuel cell environment. Highly sulfonated, water soluble poly(ether sulfone) PES 70 was modified into a robust membrane by adding MS-p-PBI 100. The lower proton conductivity, swelling behavior and water uptake of the blend membranes evidenced the presence of ionic cross-linking and/or ionic bonding between the acid–amphiphilic polymers. The blend membrane BM 1 was used for PEMFC and DMFC operation. A current density of 800 mA cm\(^{-2}\) was obtained at 0.4 V with a stoichiometric flow rate (H\(_2\)/air = 1.5/2) of gases. The current density value of 230 mA cm\(^{-2}\) was obtained at 0.4 V for 1 M methanol feed at 70 °C. Both PEMFC and DMFC fuel cell test results prove that this blend membrane is an alternative PEM material for fuel cell applications.

Acknowledgements

This work was supported by New and Renewable Energy R&D program (2008-N-FC12-J-01-2-100), and a Grant (M2009010025) from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy (MKE), Republic of Korea.

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