Sulfonated Polyimide and Poly (ethylene glycol) diacrylate based Semi-Interpenetrating Polymer Network Membranes for Fuel Cells

Seokkyu Lee, Wonbong Jang, Seunghyuk Choi, Kannan Tharanikkarasu, Yonggun Shul, Haksoo Han

Department of Chemical Engineering, Yonsei University, Seodaemun-gu, Seoul 120-749, Korea

ABSTRACT: Semi-interpenetrating polymer network (semi-IPN) membranes based on novel sulfonated polyimide (SPI) and poly (ethylene glycol) diacrylate (PEGDA) have been prepared for the fuel cell applications. SPI was synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride, 4,4′-diaminobiphenyl 2,2′-disulfonic acid, and 2-bis [4-(4-aminophenoxy) phenyl] hexafluoropropane. PEGDA was polymerized in the presence of SPI to synthesize semi-IPN membranes of different ionic contents. These membranes were characterized by determining, ion exchange capacity, water uptake, water stability, proton conductivity, and thermal stability. The proton conductivity of the membranes increased with increasing PEGDA content in the order of 10^{-1} S cm^{-1} at 90°C. These interpenetrating network membranes showed higher water stability than the pure acid polyimide membrane. This study shows that semi-IPN SPI membranes based on PEGDA which gives hydrophilic group and structural stability can be available candidates comparable to Nafion® 117 over 70°C. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2965–2972, 2007

Key words: sulfonated polyimide; poly ethylene glycol diacrylate; interpenetrating polymer networks; polyelectrolyte membrane; fuel cell

INTRODUCTION

Fuel cell is a prominent technology for a potentially wide variety of applications including micro-power, auxiliary power, transportation power, and stationary power owing to its ability to generate high power density with both zero level toxic gas emissions and an added advantage of silence. Because of these advantages, polymer electrolyte membrane fuel cell (PEMFC) at low operating temperatures is a forerunner especially in both the automobile and portable power applications.[1–3] Among the different parts of the fuel cell, electrolyte membrane is the most important element in any fuel cell system, which essentially plays a leading role to transport the hydrogen ions and prevent the fuel crossover. In addition, it also serves as a separator which separates the electrode structures to prevent the mixing of reactant gases and the formation of an electrical short between anode and cathode.[2,3] To satisfy these requirements, until now, a variety of per-fluorinated polyelectrolyte membranes (Nafion®, Flemion®, and Aciplex® families) and various modified per-fluorinated, partially per-fluori-

nated, and nonper-fluorinated polymer electrolytes are under development for PEMFC applications.[4]

Among the per-fluorinated membranes, Nafion® has been successful in real commercial PEMFC systems because of its outstanding high proton conductivity and long life.[5–7] However, it has fatal drawback i.e., the unreacted methanol at the anode can diffuse through the membrane and react at the cathode, lowering the voltage efficiency of the cell, and reducing the system's fuel efficiency in direct methanol fuel cell (DMFC). Besides these, it is also quite costly owing to the difficult fluorinated synthetic process and it losses its performance at high temperature because of the low humidity. These drawbacks force membrane researchers to develop alternative polymer electrolyte membranes.

Because of the salient features like high thermal stability, thermo-oxidative stability, high mechanical strength, and superior chemical resistance, which are inherent characterization of polyimide, aromatic sulfonated polyimides (SPIs) are good alternative polyelectrolyte membranes.[8–11] Basically, SPIs are synthesized by reacting dianhydrides and sulfonated aromatic diamines.[12–15] For the higher ionic conductivity, the larger amount of sulfonated diamines should be required during the synthesis of SPI, but the membrane with higher sulfonation degree will be easily swelled and even broken by the water more than that with the lower sulfonated one. Hence nonsulfonated

diamine is used along with sulfonated diamine during the polyimide synthesis. But these partially SPIs have still the lower water stability when a certain sulfonation degree (ion-exchange capacity of 1.4–1.6 mequiv SO_3H/g) or a certain operation temperature (60–80°C) is exceeded.[16–20] Therefore, it is required to reduce the swelling degree of the membranes without losing their proton conductivity too much. These requirements can be achieved by forming a semi-interpenetrating polymer network (semi-IPN) structures. Earlier, benzimidazoles terminated poly (ethylene glycol) and poly (ethylene glycol)–poly (thiophenylenesulfonic acid) composites were reported to exhibit non aqueous proton conduction.[21,22] In our lab, polyethylene glycol was already reacted with maleic anhydride terminated SPI to synthesis crosslinked polyelectrolyte membrane.[23] Here poly (ethylene glycol) diacrylate (PEGDA) having flexible hydrophilic poly (ethylene glycol) backbone is expected to render flexible crosslinking and hold water at high temperature to give good proton conductivity.

In this study, we prepared the semi-IPN membranes based on the linear SPI chains and PEGDA chains and reported that the electrical and thermal properties of these semi-IPN membranes for PEFMC. Moreover, on the basis of effort of semi-IPN structure, the conductivity and its activation energy as a function of temperature and water stability were studied in detail.

EXPERIMENTAL

Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA), 2,2′-benzidine-disulfonic acid (BDSA), and 2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (HFBAPP) were purchased from Tokyo Kasei, Japan. PEGDA (average $M_n = 258$.) and 4,4′-azobis(4-cyanovaleric acid) (ACVA) were purchased from Aldrich, USA. Triethylamine (TEA), m-cresol, benzoic acid, and acetone were purchased from Duksan, Korea. NTDA, BDSA, HFBAPP, and benzoic acid were dried under vacuum before use and m-cresol was distilled under reduced pressure. PEGDA, ACVA, TEA, and acetone were used without any further purification.

Synthesis of sulfonated polyimide

To synthesize the SPI, BDSA (10 mmol), m-cresol (60 mL), and TEA (6 mL) were successively added to a 250 mL 3-neck round bottom flask under nitrogen flow. When BDSA was completely dissolved, 10 mmol of HFBAPP was added. To this solution, 20 mmol of NTDA and 28 mmol of benzoic acid were added. The mixture was stirred at room temperature for a few minutes until it became homogeneous and then they were

chemically imidized. Detailed procedure is reported elsewhere.[13–14] The synthesized SPIs were precipitated in acetone and dried in vacuum.

Synthesis of SPI-PEGDA semi-IPN membranes

Calculated amount of already synthesized SPI was taken in a 50-mL conical flask to which anhydrous m-cresol was added (30 wt %) and vigorously stirred at room temperature under N_2 purging until the SPI was completely dissolved. For preparing semi-IPN membranes, calculated and various amounts of the PEGDA was added to the already dissolved SPI solution. The ratio of SPI and PEGDA is given in Table I. Then the initiator, ACVA (4 mol % of the PEGDA) was also added and the solution was stirred at room temperature for 1 h for well mixing. Then the solution was cast onto glass plates using spin coater. The glass plate were prebaked at 80°C for 1 h and then cured in a curing oven at 80, 120, and 180°C for 4, 6, and 3 h, respectively. The resulting semi-IPN membranes were soaked in deionized water overnight to release the membranes from the glass plates and then soaked in methanol at 60°C for 1 h and in 1.0M HCl at room temperature for 20 h successively. The proton-exchanged membranes were thoroughly washed with deionized water and then dried in vacuum at 100°C for 20 h.

Measurements

The infrared (FTIR) spectra were collected using Excalibur series FTIR (DIGLAB) instrument. Thermo gravimetric analysis was carried out using thermo gravimetric analyzer (Q 50, TA instruments), at a heating rate of 10°C/min in N_2 atmosphere. The ion exchange capacity (IEC) of semi-IPN membranes was measured by titration method as follows. First, the semi-IPN membranes were thoroughly washed with deionized water for several times and was soaked in 0.1M NaCl for 18 h. The protons released due to the exchange reaction with Na^+ ions were titrated against 0.01M NaOH, using phenolphthalein as an indicator. The IEC was determined from the following equation.

$$\text{IEC (mequiv/g)} = \frac{X \times N_{\text{NaOH}}}{\text{Weight (polymer)}}$$

where X is the volume of NaOH consumed and N_{NaOH} is the normality of NaOH.

For water uptake studies, the semi-IPN membranes, after exchange of protons, were first dried in vacuum oven at 100°C for 24 h. The weight of the completely dried samples (W_d) was initially measured using microbalance (Sartorius, Fisons Instruments, Sensitivity of 1 μg mass capacity). Then the membranes were kept in a humidified chamber with deionized water until no further water uptake took place (~ 6 h). Water

TABLE I
Synthesis and Characterization of Semi-IPN Membranes[a]

Polymer Code	Composition (wt %)		IEC (mequiv g^{-1})		Water uptake (%)			
	SPI	PEGDA	Theoretical	Experimental	30°C	50°C	70°C	90°C
SP-100	100	0	1.475	1.460	11.7	15.3	19.2	22.4
SP-80	80	20	1.180	1.171	10.9	14.5	18.5	20.8
SP-60	60	40	0.885	0.804	10.0	13.5	19.8	23.9
SP-50	50	50	0.737	0.699	9.3	13.1	18.4	21.2
SP-40	40	60	0.590	0.558	8.6	11.6	15.8	19.8

[a] Phase separation formed when the PEGDA content was increased above 60 wt %.

uptake studies were carried out at 30, 50, 70, and 90°C. When there was no water uptake, the films were removed out of the chamber and the free water was removed from the membranes by using blotting paper. Again, the weight of the membranes were measured (W_s) with micro balance. Then the water uptake (S) was calculated using the following equation.

$$S\ (\%) = \frac{(W_s - W_d)}{W_d} \times 100$$

Here, six semi-IPN membranes were used to get one average value of S. The proton conductivity of the semi-IPN membranes was measured using electrochemical impedance spectroscopy technique over the frequency range of 100 kHz–10 Hz. The resistance of semi-IPN membranes was measured using Autolab Impedance Analyzer at different temperatures. The outline of the electrochemical cell used in this experiment was given in our earlier reports.[13,14] The proton conductivity (σ) was calculated using the following equation.

$$\sigma\ (S/cm) = \frac{1}{\Omega} \times \frac{d}{A}$$

where, d is the distance between of electrodes and A and Ω are the area and resistance of the semi-IPN membrane, respectively. The water stability of the semi-IPN membranes was evaluated using two methods as follows: universal testing machine (UTM, LR-10K, LLOYD Instrument) and soaking and folding methods. In the UTM method, eight specimens (30 mm ×5 mm ×0.02–0.04 mm) were prepared from the semi-IPN membranes respectively, and those were immersed in hot water at 80°C for 1 h and then subjected to tensile measurement as soon as they were taken out. The crosshead speed was 1 mm/min at (23 ± 2)°C and (50 ± 5)% RH. To get the reliable data, only the average value among the six data was taken after discarding the maximum and minimum value after measurements. While in the soaking and folding method, the membranes were immersed in hot water at 80°C and the water was continuously stirred at constant speed, ~300 rpm if the semi-IPN membranes

broken into pieces during immersion in stirring hot water or when semi-IPN membranes are folded it is mentioned as brittle after folding it for three times. The experiments were continued until the semi-IPN membranes become brittle.[15,23]

RESULTS AND DISCUSSION

In continuation of our efforts to synthesize polymer membranes[13–14] for fuel cell applications, semi-IPN technique is used in this study. The SPI (Theoretical IEC is 1.475) was synthesized using NTDA, BDSA, and HFBAPP and used as a un-crosslinked backbone. PEGDA was used as a crosslinked backbone. PEGDA was reacted in presence of SPI to get semi-IPNs. Scheme 1 gives the schematic representation of the synthesis of semi-IPN membranes.

FTIR analyses

To confirm the chemical structure of the semi-IPN membranes, FTIR spectroscopic technique was used and the FTIR spectra are shown in Figure 1. The >C=O vibration of the anhydride (1778 and1737 cm^{-1}) shifted to lower frequency upon conversion into imides. The presence of characteristic absorption band of imide carbonyl group at 1715 cm^{-1} (asymmetric) and 1666 cm^{-1} (symmetric) confirmed the formation of polyimides. The SO_2 vibration of the sulfonic acid group was observed as a broad bands around 1165 and 1093 cm^{-1}. The C—N—C absorption of the imide ring was observed around 1342 cm^{-1}.[24,25] It is interesting to note that the peaks corresponding to PEGDA (1636 cm^{-1} for vinyl group stretching, 1407 cm^{-1} for vinyl group bending) are disappeared. This suggests that the crosslinking reaction involves the opening of double bonds forming the semi-IPN structures with linear SPI chains.

Ion exchange capacity

Many important properties of the SPI such as the proton conductivity and the water uptake depend on IEC which is indicative of the actual ion exchange sites
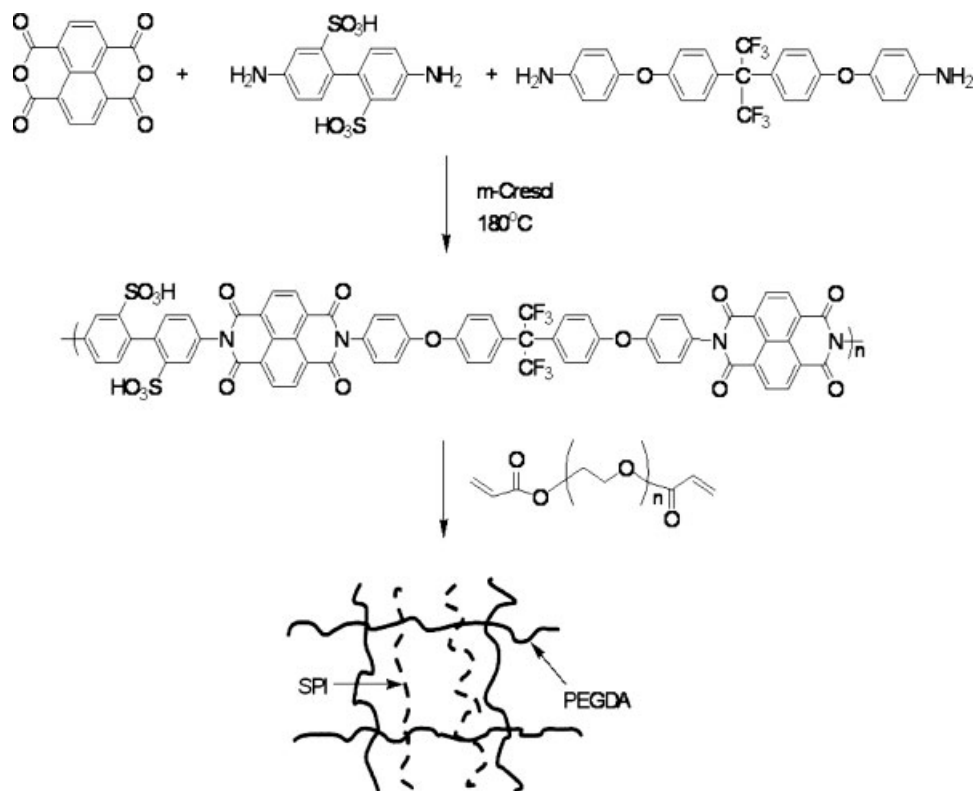
Scheme 1 Synthesis of Semi-IPNs.

available for proton conduction. This IEC directly depends on the content of sulfonic acid groups having free protons present in the polymer.[26] Generally, the higher IEC shows higher proton conductivity, whereas it results in the lower stability towards water in fuel cell system because of solubility stability and swelling stability by its hydrophilic nature. To optimize between the high proton conductivity and strong water stability, it is essential to optimize the content of the sulfonic acid group by designing the ratio between the sulfonated and nonsulfonated diamine monomers ratio. In this investigation, IEC values decreased in the order SP-100 > SP-80 > SP-60 > SP-50 > SP-40 as given in Table I. These values were calculated for a particular weight of the polymer.[13,14] With the increase in the PEGDA content, the amount of SPI decreased and hence IEC also decreased. This is due to the reason that the number of sulfonic acid group will decrease in a particular weight of the taken semi-IPN membranes, when the PEGDA weight content increases and SPI decreases resulting in decreased IEC. Hence, water uptake and proton conductivity of the semi-IPN membranes are expected to decrease with the decrease in IEC, because they generally depend on IEC.

Water uptake

Water uptake capacity is important character to find application in fuel cell. Generally, the proton conductivity of the electrolyte membranes increases with

increase in water uptake capacity. This is because with more water uptake it improves the formation of the hydrophilic domain carrying the proton conductivity.[27] The water uptake of the semi-IPN membranes was determined by micro balance and the results are
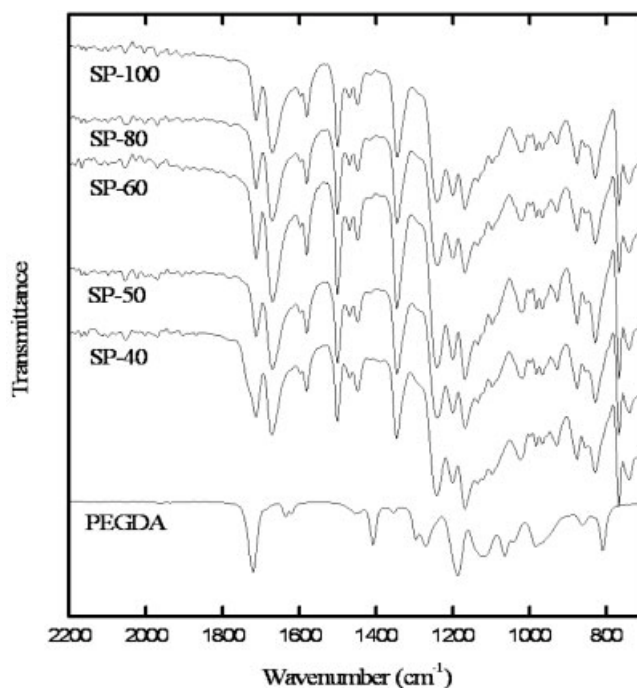

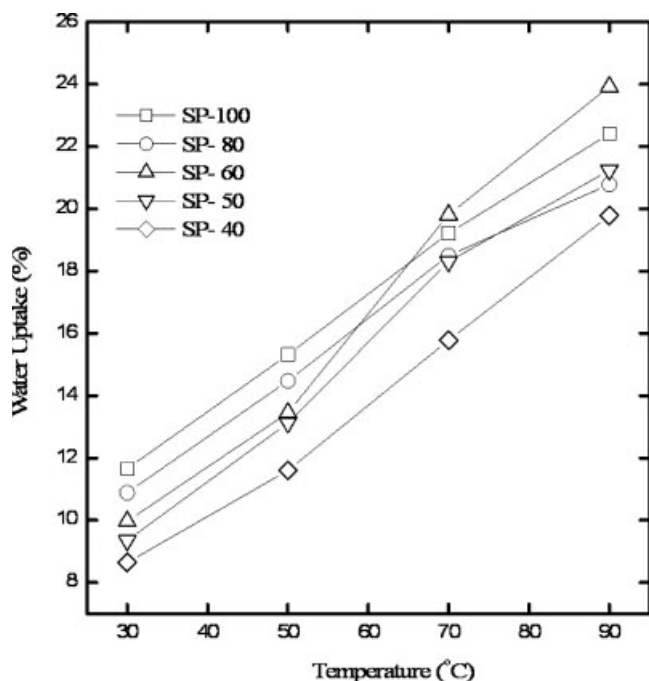**Figure 1** FTIR spectra of semi-IPN membranes.

Figure 2 Water uptake of semi-IPN membranes.

presented in Table I and Figure 2. In the nearest temperature condition, at 30°C, the water uptake varied as follows: SP-100 > SP-80 > SP-60 > SP-50 > SP-40. The water uptake decreased with increase in PEGDA content because of the presence of less quantity of the sulfonated acid groups. However, the same trend is not observed in all temperatures. As the temperature was increased above 50°C, the SP-60 and SP-50 were faster to take water than other membranes and this lead water uptake finally in the following order at 90°C: SP-60 > SP-100 > SP-50 > SP-80 > SP-40. In general, water uptake values of SPIs are directly proportional to IEC values. It is interesting to note here that semi-IPN membranes, such as SP-50 and SP-60, with relatively lower IEC values showed more water uptake at higher temperatures than the semi-IPN membranes with higher IEC values. This is clearly due to the presence of more hydrophilic PEG groups, which is presented in semi-IPN structure, in SP-50 and SP-60. However SP-40 had lower water uptake than the SP-60 or SP-100, even though it contains the largest amount of the PEGDA. This result might be drawn from the reason too small degree of sulfonic acid group. In other words, the degree of sulfonic acid group in semi-IPN membranes is strongly subject to attract water uptake as driving force compared to the hydrophilicity of PEGDA. This water uptake behavior will be compared with the following results of the proton conductivity.

Proton conductivity

Generally, the proton conductivity of the polymer increases with increase in IEC and water uptake. This is

TABLE II
Proton Conductivity of Semi-IPN and Nafion® 117 Membranes

| Polymer | Proton conductivity (S cm^{-1}) | | | |
	30°C	50°C	70°C	90°C
SP-100	0.034	0.066	0.093	0.140
SP-80	0.031	0.054	0.081	0.115
SP-60	0.026	0.050	0.097	0.154
SP-50	0.023	0.046	0.078	0.132
SP-40	0.021	0.037	0.066	0.105
Nafion® 117	0.060	0.105	0.147	0.187

because, with more IEC and water uptake, the formation of the hydrophilic domain increase and hence the proton conductivity increases.[13,27] The proton conductivity of the SPI based semi-IPN membranes and Nafion® 117 at different temperature was measured and the results are given in Table II. The proton conductivity of the semi-IPN membranes and Nafion® 117 increased with increase in temperature. The increase in temperature favors both the dynamics involved in proton transfer and structural reorganization, which are required for fast proton conductivity.[27] Figure 3 shows an Arrehnius plot of conductivity as a function of temperature of the semi-IPN (SP-100, 60, and 40) and Nafion® 117 membranes. The activation energies of the semi-IPN membranes are from 12.6 to 16.0 kJ mol^{-1} while the Nafion® 117 has 10.5 kJ mol^{-1}, which is similar to that value reported in the literature for Nafion® 117 membrane along with the con-
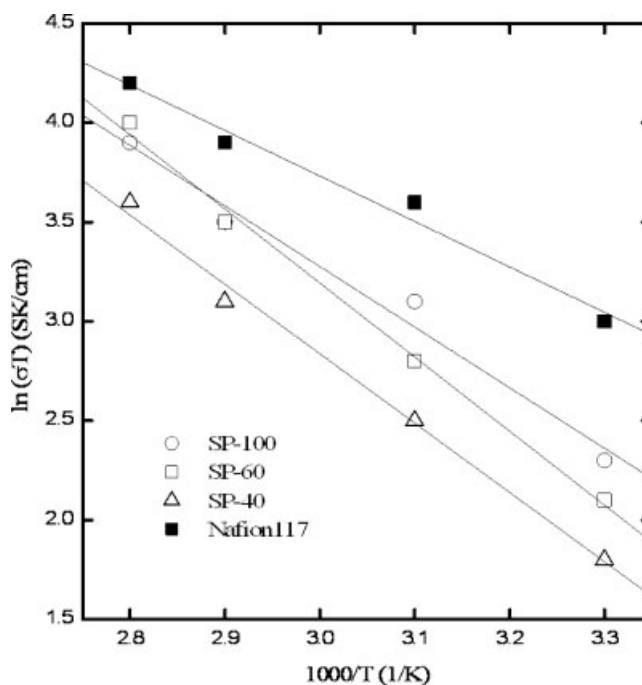

Figure 3 Temperature dependence of semi-IPN and Nafion® 117 membranes on conductivity.

TABLE III
Water Stability of Semi-IPN Membranes

		UTM method		Soaking and folding method
Polymer	Film pretreatment[a]	Young's modulus (GPa)	Tensile strength (MPa)	Time taken to become brittle (h)
SP-100	Before	1.06	32.80	46
	After	0.20	12.93	
SP-80	Before	1.12	46.13	65
	After	0.30	15.95	
SP-60	Before	1.14	48.38	87
	After	0.31	16.09	
SP-50	Before	1.21	51.00	125
	After	0.33	17.50	
SP-40	Before	1.33	56.63	178
	After	0.37	20.60	

[a] Before: dried in vacuum oven at 100°C for 24 h; After: immersed in hot water at 80°C for 1 h.

ductivity at 70°C.[28] This means that proton migration in the semi-IPN membranes is more influenced by temperature variation. Among the semi-IPN membranes, the proton conductivity at 30°C decreased as SP-100 > SP-80 > SP-60 > SP-50 > SP-40. In other words, proton conductivity at 30°C is decreased with increasing PEGDA content. This is the same trend as in the case of IEC and water uptake at 30°C. But at 90°C, the SP-60 (0.154 S cm^{-1}, IEC = 0.804) shows the highest conductivity among the all semi-IPN membranes although it has smaller quantity of the sulfonic acid groups. This may be due to the higher water uptake as mentioned in the water uptake analysis. But the proton conductivity of semi-IPN membranes is lower than the benchmark Nafion® 117 membrane. This may be explained that the unique structure of the Nafion, which has a noncrosslinked ion-exchange (ionomer) polymer comprised of a perfluorinated backbone with sulfonated ionic groups attached to pendant side chains. These hydrophobic fluorocarbon chains and the hydrophilic sulfonated groups are arranged to maximize the interaction between the similar fragments. This is thought to result in the formation of inverted micelles or ion clusters when it swells in water condition and those water clusters help to transport the proton more easily so that it shows higher proton conductivity even though it has lower IEC value (0.91) than that of the SP-100 (1.46).[29,30] From this result, it is presumed that the proton conductivity is affected not only by the IEC value but also by the membrane structure. The results with incorporating hydrophilic PEG groups into SPI membrane increase proton conductivity in spite of lower IEC values.

Water stability

Membrane stability as well as proton conductivity is one of the important factors that greatly affect the fuel cell performance. The water stability of the SPI mem-

branes has been studied by many researchers and our laboratory also.[31] Poor water stability of the SPI membranes may arise from two reasons. First, the incorporation of the sulfonic acid group to polyimide leads to absorption of water and hence results in swelling of membrane, which might give stress to the swelled membrane. In results, the mechanical stability of the swelled membrane is generally poor. Second, the chemical degradation of SPI occurs because of the nucleophilic attack of hydroxyl ion at the imide linkage which could be called as hydrolytic stability. This results in decreased molecular weight which leads to poor mechanical stability.[16] The water stability of the semi-IPN membranes was evaluated and the results are given in Table III. In the UTM method, the Young's modulus and tensile strength of the all membranes were decreased by approximately 60–70% after water soaking when compared with the dried films. Among the hot water soaked membranes, the tensile modulus of the SP-40 (20.60 MPa) was greater than that of the SP-100 (12.93 MPa). This is mainly attributed to the assistant of the PEGDA, which is relatively more flexible than the pure sulfonated rigid polyimide and the PEGDA forming the crosslinked network structure physically reduce the extra swelling of the SPI chains. In addition, it is also natural that decreasing IEC from 1.460 (SP-100) to 0.558 (SP-40) of the membranes increases the water stability. This UTM results were well corresponded with the soaking and folding test results. Hence, semi-IPN membranes pre-

TABLE IV
Thermal Properties of Semi-IPN Membranes

	Onset temperature (°C)		
Polymer	2nd step	3rd step	Residue (%)
SP-100	278.52	522.16	54.23
SP-80	274.19	516.98	53.57
SP-60	271.25	512.27	53.18
SP-50	263.01	514.14	53.03
SP-40	259.19	491.37	47.54

pared from SPI and PEGDA could be a candidate to increase water stability of the membrane for fuel cell.

Thermal stability

The thermal stability of the semi-IPN membranes was investigated by thermo gravimetric analysis. The onset temperatures for degradation steps in a nitrogen atmosphere are given in Table IV and representative thermograms were given in Figure 4. The semi-IPN membranes exhibited higher thermal stability than the intended use temperature, i.e., around 150°C, indicating their suitability as fuel cell membrane. All the semi-IPN membranes exhibited three-step degradation pattern. The first weight loss was observed around 100°C, which is due the loss of absorbed moisture by the hygroscopic sulfonic acid groups in the polyimides. The second step of degradation corresponds to the degradation of aromatic sulfonic acid groups.[32] The thermal stability of the pure acid form, SP-100 exhibits higher thermal stability than the semi-IPN membranes such as SP-80, 60, 50, and 40. The second step degradation temperature decreased with the decrease in the SPIs content. This is attributed to the decomposition of PEGDA group because of its lower thermal stability when compared with SPI. The third step indicates the decomposition of the polyimide backbone, which showed thermal stability above 500°C. These results show that the semi-IPN structures except the SP-40 are good candidates as polymer electrolyte membranes in high temperature operating fuel cells.
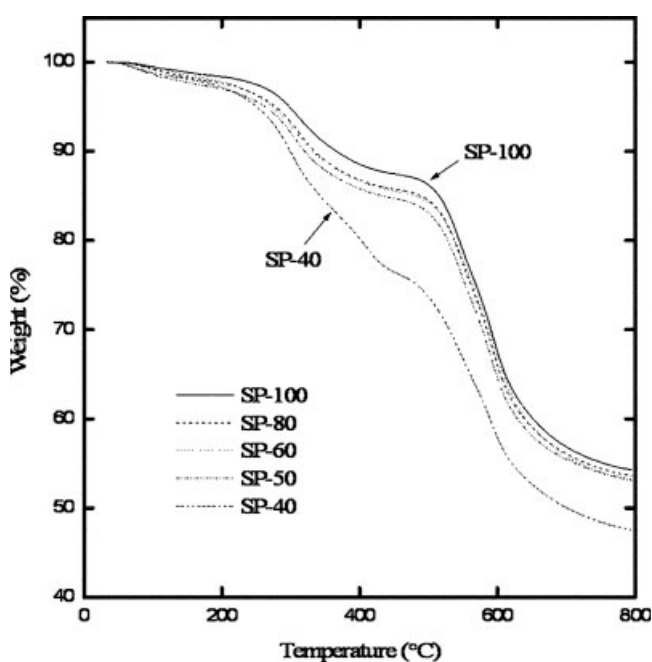

Figure 4 TGA thermograms of semi-IPN membranes.

CONCLUSIONS

The SPI was synthesized and this was reacted with PEGDA to form the semi-IPN structures. These semi-IPN membranes were evaluated the suitability for the DMFC application in terms of the thermal stability, IEC, water uptake, proton conductivity, and water stability. Among the semi-IPN membranes, the SP-60 had higher water uptake than the pure SPI (SP-100) even though SP-60 had smaller amount of the sulfonic acid group in higher temperature at 90°C by the help of the well crosslinked PEGDA network structures, which helps the water retention capability of the sulfonic acid group because of its hydrophilic ethylene oxide group. This higher water uptake resulted in the higher proton conductivity of the SP-60 at 90°C. Water stability was improved as the PEGDA content increased owing to its flexibility and semi-IPN structures, which enhances the mechanical stability of the SPI in water condition. Hence it may concluded that the SP-60 semi-IPN membrane is the most optimum candidate among the semi-IPN membranes prepared in this study owing to its good water stability without any loss of the proton conductivity.

References

1. National Energy Technology Laboratory. Fuel Cell Handbook; University Press of the Pacific: Honolulu, 2005.
2. Larminie, J.; Dicks, A. Fuel Cell Systems Explained; Wiley: England, 2000.
3. Doyle, M.; Rajendran, G.; Vielstich, W.; Lamm, A.; Gasteiger, H. A. Handbook of Fuel Cells, Vol. 3.; Wiley: England; 2003
4. Savadago, O. J Power Sources 2004, 127, 135.
5. Yeo, R. S.; Chin, D. T. J Electrochem Soc 1980, 127, 546.
6. Wilson, M. S.; Gottesfeld, S. J Appl Electrochem 1992, 22, 1.
7. Ren, X. M.; Wilson, M. S.; Gottesfeld, S. J Electrochem Soc 1996, 143, 12.
8. Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. Chem Rev 2004, 104, 4587.
9. Miyatake, K.; Fukushima, K.; Takeoka, S.; Tsuchida, E. Chem Mater 1999, 11, 1172.
10. Hasiotis, C.; Deimede, V.; Kontoyannis, C. Electrochim Acta 2001, 46, 401.
11. Caretta, N.; Tricoli, V.; Piccioni, F. J Membr Sci 2000, 166, 189.
12. Vallejo, E.; Pourcelly, G.; Gavach, C.; Mercier, R.; Pineri, M. J Membr Sci 1999, 60, 127.
13. Lee, C.; Sundar, S.; Kwon, J.; Han H. J Polym Sci Part A: Polym Chem 2004, 42, 3612.
14. Lee, C.; Sundar, S.; Kwon, J.; Han H. J Polym Sci Part A: Polym Chem 2004, 42, 3621.
15. Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H. Macromolecules 2002, 35, 9022.
16. Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 359.
17. Faure, S.; Cornet, N.; Gebel, G.; Mercier, R.; Pineri, M.; Sillion, B. In Proceedings of 2nd International Symposium on New

Materials for Fuel Cell and Modern Battery Systems; Sava-dogo, O.; Roberge, P. R., Ed.; Montreal, Canada, July 6–10, 1997; p 818.

18. Cornet, N.; Diat, O.; Gebel, G.; Jousse, F.; Marsacq, D.; Mercier, R.; Pineri, M. J New Mater Electrochem Syst 2000, 3, 33.

19. Kim, H.; Litt, M. Polym Prepr (Am Chem Soc Div Polym Chem) 2001, 42, 486.

20. Watari, T.; Fang, J.; Tanaka, K.; Kita, H.; Okamotoa, K.; Hirano, T. J Membr Sci 2004, 230, 111.

21. Persson, J. C.; Jannasch, P. Chem Mater 2003, 15, 3044.

22. Miyatake, K.; Fukushima, K.; Takeoka, S.; Tsuchida, E. Chem Mater 1999, 11, 1171.

23. Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. Macromolecules 2002, 35, 6707.

24. Kim, S.; Lee, Y.; Cho, C. Polymer 1995, 36, 4497.

25. Pitarresi, G.; Licciardi, M.; Craparo, E.; et al. Radiat Phys Chem 2002, 65, 159.

26. Poppe, D.; Frey, H.; Kruer, K. D.; Heinzel, A.; Mulhaupt, R. Macromolecules 2002, 35, 7936.

27. Kreuer, K. D. Chem Mater 1996, 8, 610.

28. Silva, R.F.; De Francesco, M.; Pozio, A. J Power Sources 2004, 134, 18.

29. Slade, S.; Campbell, S. A.; Ralph, T. R.; Walsh, F. C. J Electrochem Soc 2002, 149, A1556.

30. Sumner, J. J.; Creager, S. E.; Ma, J. J.; Desmarteau, D. D. J Electrochem Soc 1998, 145, 107.

31. Jang, W.; Lee, C.; Sundar, S.; Shul, Y.; Han, H. Polym Degrad Stab 2005, 90, 431.

32. Gao, Y.; Robertsons, G. P.; Guiver, M. D.; Jian, X.; Mikhailenko, S. D.; Kaliaguine, S. Solid State Ionics 2005, 176, 409.