Journal of the Korean Electrochemical Society
Vol. 14, No. 1, 2011, 9-15
DOI:10.5229/JKES.2011.14.1.009

Effect of Annealing of Nafion Recast Membranes Containing Ionic Liquids

Jin-Soo Park*, Mun-Sik Shin, S.S. Sekhon†, Young-Woo Choi††, and Tae-Hyun Yang††

Department of Environmental Engineering, College of Engineering, Sangmyung University, 300 Anseo-dong, Dongnam-gu, Cheonan, Chungnam Province 330-712, Republic of Korea

†Department of Applied Physics, Guru Nanak Dev University, Amristar-143005, India

††Fuel Cell Research Center, New and Renewable Energy Research Division, Korea Institute of Energy Research (KIER), 102 Gajeong-ro, Yuseong-gu, Daejeon 305-343, Republic of Korea

(Received November 8, 2010 : Accepted December 6, 2010)

Abstract : The composite membranes comprising of sulfonated polymers as matrix and ionic liquids as ion-conducting medium in replacement of water are studied to investigate the effect of annealing of the sulfonated polymers. The polymeric membranes are prepared on recast Nafion containing the ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$). The composite membranes are characterized by thermogravitational analyses, ion conductivity and small-angle X-ray scattering. The composite membranes annealed at 190°C for 2 h after the fixed drying step showed better ionic conductivity, but no significant increase in thermal stability. The mean Bragg distance between the ionic clusters, which is reflected in the position of the ionomer peak (small-angle scattering maximum), is larger in the annealed composite membranes containing $EMIBF_4$ than the non-annealed ones. It might have been explained to be due to the different level of ion-clustering ability of the hydrophilic parts (*i.e.*, sulfonic acid groups) in the non- and annealed polymer matrix. In addition, the ionic conductivity of the membranes shows higher for the annealed composite membranes containing $EMIBF_4$. It can be concluded that the annealing of the composite membranes containing ionic liquids due to an increase in ion-clustering ability is able to bring about the enhancement of ionic conductivity suitable for potential use in proton exchange membrane fuel cells (PEMFCs) at medium temperatures (150-200°C) in the absence of external humidification.

Keywords : Annealing, High temperature proton exchange membrane fuel cell, Composite membrane, Ionic liquid, Proton conductivity

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) generally use perfluorosulfonic acid polymers such as Nafion since they possess high ionic conductivity along with good mechanical properties, and are normally operated at 80°C under fully hydrated conditions.[1] However, the demand on high temperature (150-200°C) and no external humidification operation of PEMFCs is recently increasing due to the carbon monoxide (CO) poisoning of the platinum catalyst and system complexity in conventional PEMFCs, which increase the cost of PEFC.[2] However, Nafion membranes can not be used at higher temperatures (>80°C) since the ionic conductivity is strongly dependant on humidity and thus an increase in temperature above 80°C leads to a loss in fuel cell performance due to a drastic decrease in ionic conductivity by the loss of water by evaporation.[3] This problem can be addressed by using membranes which do not require water for ionic conduction but use an alternative solvent with higher boiling point and other necessary properties.

*E-mail: energy@smu.ac.kr

Recently, E. Cho *et al.*[4] have reported that the characteristics of composite membranes containing ionic liquids were very similar to those of water swollen membranes, which are an increase in ionic conductivity with an increase in the degree of sulfonation of polymers and in the content of ionic liquids. S.S. Sekhon *et al.*[1,5,6] have concluded that the morphology studies of composite membranes containing ionic liquids by small-angle X-ray scattering (SAXS) confirmed the formation of ionic clusters in the composite membranes and the proportional correlation between the size of clusters obtained by SAXS and ionic conductivity. The composite membranes containing ionic liquids should have more content of ionic liquids to get higher ionic conductivity, but more content of ionic liquids causes poor mechanical strength and significant gas permeation. In an effort to reduce the content of ionic liquids without a significant loss in ionic conductivity, J.-S. Baek *et al.*[7] have found that the addition of the acids with common anion of ionic liquids into the composite membranes containing ionic liquids brought about an increase in the size of ionic clusters by SAXS and in ionic conductivity.

Annealing studies of sulfonated polymers have been reported numerously in literature. The preparation or annealing temperature has been reported to have much influence on the crystallinity and microstructure of Nafion electrolytes and accordingly the favor formation of ionic clusters, leading to an increase in ionic conductivity.[8] Moore *et al.*[9,10] annealed Nafion ionomers at temperatures in the range of 120-250°C and suggested that the elevated temperature could provide sufficient thermal energy to the polymer chains to improve the mechanical behavior of the membranes. Early research about casting Nafion electrolyte membranes demonstrated that the elevated annealing temperature could increase crystallinity and promote the formation of ionic clusters in the membrane.[11] Another research on casting PFSA membranes revealed that the annealing process decreased the crystallinity of the membranes and provided sufficient thermal energy to activate the movement of the SO_3 site buried in the C-F chains, forming more stable and larger ionic clusters in the electrolyte membrane.[12]

In this study, composite membranes containing ionic liquids were prepared using Nafion dispersion as polymer matrix and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) as ion-conducting medium by solution casting with various annealing conditions. In order to investigate the annealing effect of the composite membranes containing ionic liquids, the properties such as ionic conductivity, thermogravitational analysis and small-angle X-ray scattering were compared between non- and annealed composite membranes.

2. Experimental

Polymer

The Nafion solution (perfluorosulfonic acid/TFE copolymer resin (5-6%), 1-propanol (42-54%), water (40-50%), ethyl alcohol (< 8%), mixed ethers and other VOCs (< 2%)) was purchased from Dupont (USA).

Ionic liquids

The ILs used in this study, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) was purchased from TCI (Japan).

Composite membranes

The composite membranes containing the same concentrations of the IL (50 wt%) and the polymer (50 wt%) were prepared by the solution casting method described elsewhere.[4,5] The 10 wt% of *N,N*-dimethylacetamide (DMAc) was added into the polymer solutions, and then the solutions were stirred overnight. As summarized in Table 1, all the samples (non-annealed and annealed ones) were cast in Petri dishes and were finally dried in a vacuum oven at 40°C for 12 h under no vacuum and then at 110°C for 12 h under vacuum to evaporate the solvent slowly and completely.

Annealing

All the membrane samples were annealed under various conditions summarized in Table 1. As summarized in Table 1, the recast Nafion membranes and the composite ones containing $EMIBF_4$ used the same drying condition for solvent evaporation, and then each membrane applies for the same annealing at atmosphere for 2 h. Annealing temperatures studied were 150, 170 and 190°C.

Characterization

Ionic conductivity of the composite membrane samples was measured by the four-point-probe conductivity cell described elsewhere.[13] The conductivity cell was placed in the head-space of a temperature controlled sealed vessel, which maintained required relative humidity, i.e., ~100% for recast Nafion membranes or anhydrous for composite membraens containing ionic liquids. The size of the membrane samples was 2 cm long and 1 cm wide. The impedance data for ionic conductivity of the membranes were obtained by impedance spectroscopy using a Bio-Logic SP-150. The measurements were carried out in potentiostatic mode in the frequency range of 0.1 Hz to 0.5 MHz with 5 mV oscillating voltage. Ionic conductivity of the samples was calculated from the impedance data using the equation (1):

$$\sigma = \frac{L}{RWd} \quad (1)$$

where σ is the ionic conductivity (S cm^{-1}), L the distance between two potential sensing platinum wires, R the membrane resistance derived from the impedance value at zero phase angle, W the width between the potential sensing platinum wires and d the hydrated membrane thickness. The electrochemical data were averaged using three measurements, and the standard deviation of all data was below 1%. The density of membrane was measured from a known membrane dimension and weight after memebrane casting.

Morphology characterization of the membranes was studied by the SAXS. SAXS experiments were performed at a Rigaku D/max-2500 (5 kW) with an image plate system equipped using X-rays with a wavelength of 1.5406 Å. The crystalline nature of composite membrane was studied by X-ray diffraction (XRD) analysis using Rigaka D/MAX-RB X-ray diffractometer.

The ion exchange capacity (IEC) for recast Nafion membranes was measured by a back titration method. Dried composite membranes were firstly soaked in a 1 M NaOH solution and titrated with 0.01 M HCl using phenolphthalein as an indicator.

The water uptake of recast Nafion membranes was determined as the following equation (2):

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (2)$$

where W_{dry} is the weight obtained after the membrane was completely dried in a vacuum oven and W_{wet} is the weight measured at the fully hydrated state for 1 day.

The thermal stability of the thorough dried composite membranes was examined by thermogravimetric analysis (TGA) using a TGA 2050 instrument (TA instruments). Heat scans were carried out under nitrogen and a heating rate of 10°C/min under a nitrogen atmosphere was used over the temperature range of 100 to 600°C.

3. Results and discussion

The proton conduction of water swollen membranes is carried out by hopping (transport by hydronium ions, H_3O^+) and vehicular (transport by diffusion) mechanisms. Most of protons in sulfonated polymers are conducted by hopping from a hydronium ion to a water molecule. High water content in the polymer results in high ionic conductivity since water channels are formed significantly for proton conduction. Too much water content, however, brings about a decrease in mechanical and dimensional stability and an increase in gas permeation during fuel cell operation. Thus, the favor formation of water cluster network at low water content is of importance. Perfluorosulfonic acid (PFSA) polymers such as Nafion well forms water cluster network at low content of water due to great difference between hydrophobicity of backbone and hydrophilicity of long side chain. Similarly, the composite membranes containing ionic liquids also need to form cluster network by ionic liquids since proton is mainly transported by hopping from one imidazole group of cation of ionic liquids to another. Hence, more content of ionic liquids is necessary for higher ionic conductivity, but too much content of ionic liquids might make the aforementioned problems during fuel cell operations significant.

In this study, annealing of composite membranes containing ionic liquids was carried out to make polymers more dense, which might increase crystallinity and promote the formation of ionic clusters in the membrane, and investigation on polymer density of Nafion before and after annealing at 190°C has confirmed a 3.7% increase from 1.91 to 1.98 g cm^{-3}, respectively. Firstly, in order to study the effect of annealing on properties of a polymer matrix, annealing of recast Nafion membranes was carried out with various annealing conditions. Fig. 1 shows the variation of membrane properties such as ionic conductivity, ion exchange capacity and water content of recast Nafion membranes with annealing temperature and compares the membrane properties of annealed recast Nafion membranes to those of a non-annealed one. The inset lines indicate the reference values of a non-annealed recast Nafion mem-

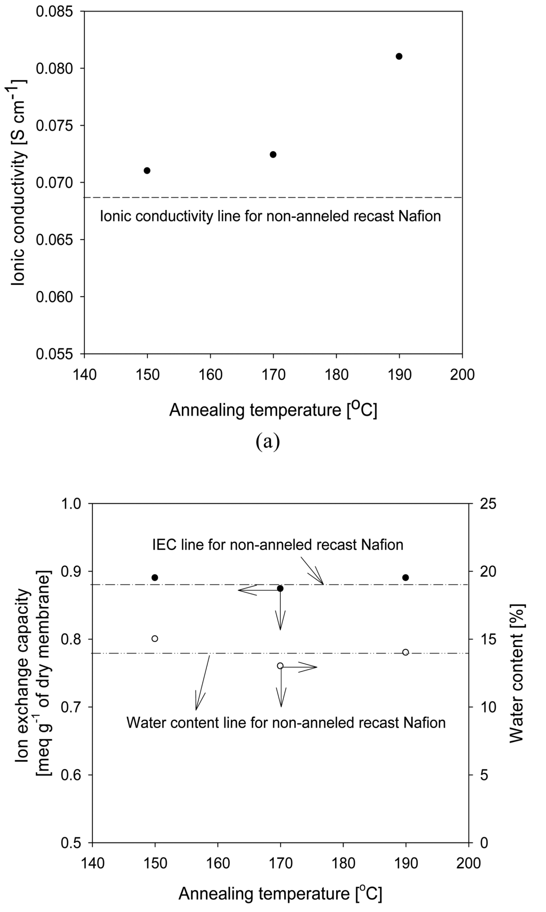

Fig. 1. (a) Variation of ionic conductivity (at fully hydrated status and room temperature) (b) variation of ion exchange capacity (IEC) and water content with annealing temperature for recast Nafion membranes.

brane in Fig. 1. It is found that ionic conductivity of all the annealed membranes is higher than that of a non-annealed one at all the annealing temperatures studied in this study. As annealing temperature from 150 to 190°C increases, ionic conductivity also increases. However, no change of other membrane properties, i.e., ion exchange capacity and water content, is observed. It is thought that the annealing temperatures tested in this study cause no decomposition of sulfonic acid groups during an annealing step. Therefore, no change of water content is obtained since the same number of ion-exchangeable sites by sulfonic acid groups is kept. It can be inferred that annealing promotes the formation of ionic clusters in recast Nafion membranes and thus the composite membrane containing ionic liquids in which recast Nafion is used as polymer matrix is influenced in membrane properties.

Fig. 2 shows the variation of ionic conductivity of the Nafion recast membranes containing $EMIBF_4$ before and after annealing. It can be observed under anhydrous status that ionic conductivity of the composite membranes increases with temperature. As discussed in other literature,[1,4-6] it is believed that ionic liquids well provide pathways to conduct ions through the composite membranes. A previous study found that the ionic conductivity of composite membranes containing ionic liquids increases as the ionic conductivity of the polymer matrix used in the composite membranes increases[4] In this point of view, if annealing increases crystallinity of the composite membranes containing $EMIBF_4$ and promotes the formation of ionic clusters in the membrane, the ionic conductivity of annealed composite membranes has to be higher than that of non-annealed ones. As expected, Fig. 2 shows higher ionic conductivity of the annealed composite membranes containing $EMIBF_4$ than that of the non-annealed ones. It is found that the difference in ionic conductivity between the annealed and the non-annealed composite membranes increases as temperature increases. At low temperatures, the composite membranes containing $EMIBF_4$ is not thermally activated, and the property enhanced by annealing does not projects the

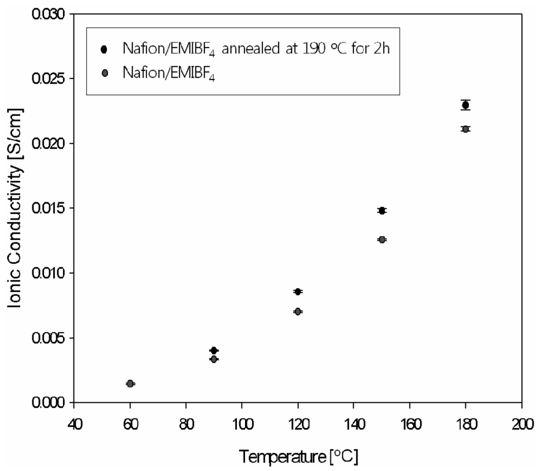

Fig. 2. Variation of ionic conductivity (under anhydrous status) with temperature for the composite membranes containing $EMIBF_4$ before and after annealing at 190 °C for 2 h.

property, in particular, ionic conductivity of the composite membranes. However, as the composite membranes are thermally getting activated, the difference in ionic conductivity can be observed to increase. In addition, it was found by XRD studies that the annealing of the recast Nafion polymer has increased polymer crystallinity (note that crystallinity of recast Nafion polymer non-annealed was 12.8%) and an increase in crystallinity of recast Nafion polymer annealed has been observed to be 13.3, 13.9 and 14.7 at annealing temperatures of 150, 170 and 190°C, respectively. It can be concluded that an increase in polymer crystallinity results in an increase in ionic conductivity.

As mentioned earlier, enhanced ionic conductivity of the composite membranes containing $EMIBF_4$ is due to the effect of annealing which is capable of the formation of better ionic cluster. Ionic cluster network is a proposed structure comprised of spherical ionic clusters and connection between ionic clusters.[14-18] The formation of spherical ionic clusters in membranes is done by the reorganization of hydrophilic side chains solvated by solvents such as water (in general) or ionic liquids (in this study). SASX is usually being used to study scattering of intermolecular like scattering between clusters. Fig. 3 shows the SAXS curves of dry recast Nafion and composite membrane containig $EMIBF_4$. The SAXS profile for water swollen Nafion membranes generally shows the presence of (i) an upturn in the intensity at very small q values ($< 10^{-2}$ Å^{-1}), (ii) matrix peak, (iii) an ionomer peak and (iv) Porod (tail) region at high q values. A representative SAXS curves are given in Fig. 3 for dry recast Nafion membrane and the composite membrane containing $EMIBF_4$ of 50 wt%. The upturn at small q values ($< 10^{-2}$ Å^{-1}) for both the membranes is not observed in the present case since scattering curve is recorded for q values greater than 10^{-2} Å^{-1} only. The ionomer peaks in the mid q region which is generally attributed to the presence of ionic clusters in perfluorinated ionomer membranes has been observed in both the membranes. In case of the dry recast Nafion membrane, two ionomer peaks have been observed at q values of ~0.06 and above 0.2 Å^{-1}. The peak at relatively lower q value (~0.06 Å^{-1}) was earlier attributed to long period between lamellar crystallites in water swollen Nafion membranes.[19)]

Fig. 4 shows a similar look of the SAXS curve of the composite membranes containing $EMIBF_4$ shown in Fig. 3. It is, however, noted that the SAXS curve of the annealed composite membrane has a little different look compared to that of the non-annealed one. This change might be brought about by the effect of annealing. Interestingly the ionomer peak of the annealed composite membrane becomes much sharper and shifts to a lower q value. It means that the formation of ionic clusters in the composite membrane is promoted by annealing. The position of the scattering maximum q_{max} can be related to the Bragg distance d_{max} by the relation $d_{max} = 2\pi/q_{max}$. The evolution of the Bragg distance has been calculated for the composite membranes

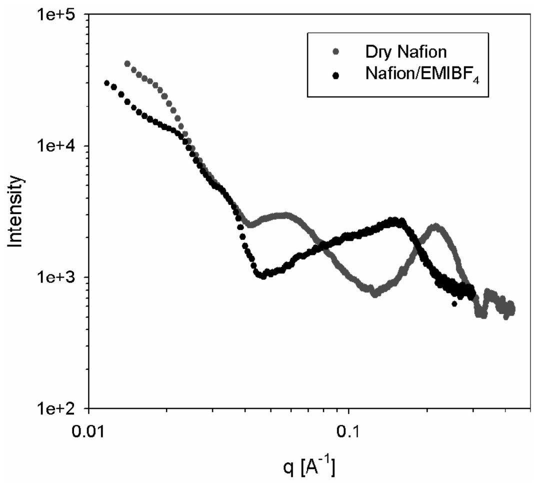

Fig. 3. SAXS of the Nafion recast membranes and the composite ones containing $EMIBF_4$.

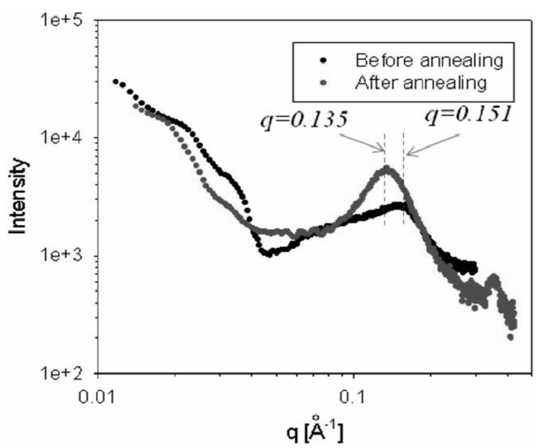

Fig. 4. SAXS of the composite membranes containing $EMIBF_4$ before and after annealing at 190 °C for 2 h.

containing $EMIBF_4$.[19,20,21] As shown in Fig. 4, the maximum q value was shifted from 0.151 to 0.135 before and after annealing, respectively. For the non-annealed and annealed composite membranes, the Bragg distances have been observed to be 41.6 and 46.5 Å, respectively. An increase in Bragg distance means that the size of ionic clusters has increased since annealing is affected to promote the formation of ionic clusters. This result is in good agreement with the result of ionic conductivity of the composite membranes before and after annealing as shown in Fig. 1. In other words, the greater Bragg distance is, the higher ionic conductivity is.

Fig. 5 shows the SAXS curves of the composite membranes containing $EMIBF_4$ with different annealing conditions. The SAXS of the composite membrane annealed at 150°C for 2 h (not shown here) is very similar to that annealed 170°C for 2 h, and has shown almost the same maximum q value. For the composite membrane annealed 190°C for 2 h, a whole look of the SAXS are very similar to one annealed 170°C for 2 h, but the maximum q value decreases from 0.138 to 0.135, which means that Bragg distance increases from 45.5 to 46.5 Å. It is found that annealing temperature need to be optimized. Among the annealing temperatures tested in this study, i.e., 150, 170 and 190°C, annealing at 190°C significantly influences to promote the morphology of the composite membranes and then the membrane property such as ionic conductivity.

Fig. 6 shows the thermogravimetric analysis (TGA)

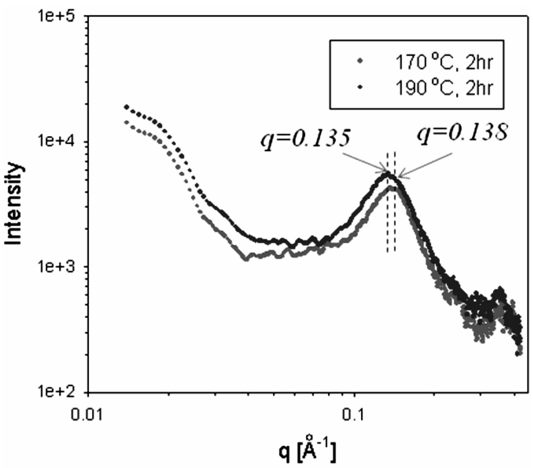

Fig. 5. SAXS of the composite membranes containing $EMIBF_4$ at 170 and 190 °C for 2 h.

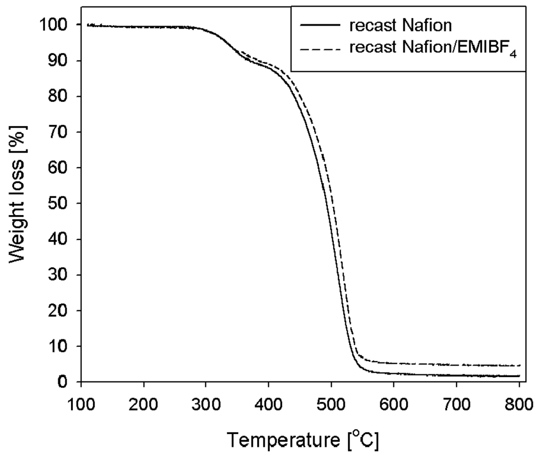

Fig. 6. Thermogravimetric analysis curves of recast Nafion and composite membranes containing $EMIBF_4$ under nitrogen atmosphere.

curves of the recast Nafion membranes and the composite ones containing $EMIBF_4$. The TGA curves of both membranes have two distinguishable steps which are affected by a decomposition of sulfonic acid groups at ~300°C and by a decomposition of main chain ~400°C. However, the TGA curve of the composite membrane shows better thermal stability after a temperature at which sulfonic acid groups are decomposed. It might be due to the effect of the ionic liquid contained since the recast Nafion was totally dried for TGA. It was found that the TGA curves of annealed recast Nafion and composite membranes were almost the same to those of non-annealed ones (not shown here). Thus, it can be inferred that the annealing used in this study significantly influences no change of thermal stability.

4. Conclusions

The effect of annealing of the composite membranes comprising of recast Nafion as polymer matrix and $EMIBF_4$ as ion-conducting medium on membrane properties was investigated in terms of ionic conductivity and SAXS. It was found that annealing of recast Nafion itself promotes the formation of ionic clusters to have better ionic conductivity and causes no decomposition of sulfonic acid groups. This resulted in an increase in ionic conductivity for the composite membranes containing $EMIBF_4$. In addition, the enhancement of ionic conductivity was confirmed by lower-shifting of ionomer peaks in SAXS of the composite membranes containing $EMIBF_4$ which means an increase in the size of Bragg distance. As a result, it can be concluded that annealing of the composite membranes containing $EMIBF_4$ is able to increase the size of ionic clusters by making the polymer matrix of the composite membranes more dense, and thus it is possible to reduce the content of ionic liquids of composite membranes containing ionic liquids with no loss in ionic conductivity for anhydrous and high temperature proton exchange membrane fuel cells.

Acknowledgement

This work was supported in part by the Grant of the Korean Ministry of Education, Science and Technology (The Regional Core Research Program/Zero Energy Green Village Technology Center), and in part by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Korean Ministry of Education, Science and Technology (2010-0021541).

References

1. S. S. Sekhon, J.-S. Park, J.-S. Baek, S.-D. Yim, T.-H. Yang, and C.-S. Kim, 'Small-angle X-ray scattering study of water free fuel cell membranes containing ionic liquids' *Chem. Mater.*, **22**, 803 (2010).
2. Q. Li, R. He, J. O. Jensen, and N. J. Bjerrum, 'Approaches and Recent Development of Polymer Electrolyte Membranes for Fuel Cells Operating above 100°C' *J. Chem. Mater.*, **15**, 4896-4915 (2003).
3. J. Roziere and D. J. Jones, 'Non-fluorinated polymer materials for proton exchange membrane fuel cells' *Annu. Rev. Mater. Res.*, **33**, 503 (2003).
4. E. Cho, J.-S. Park, S. S. Sekhon, G.-G. Park, T.-H. Yang, W.-Y. Lee, C.-S. Kim and S.-B. Park, 'A Study on Proton Conductivity of Composite Membranes with Various Ionic Liquids for High-Temperature Anhydrous Fuel Cells' *J. Electrochem. Soc*., **156**, B197 (2009).
5. S. S. Sekhon, J.-S. Park, and Y.-W Choi, 'A SAXS study on nanostructure evolution in water free membranes containing ionic liquid: from dry membrane to saturation' *Phys. Chem. Chem. Phys*., **12**, 13763 (2010).
6. S. S. Sekhon, J.-S. Park, E. Cho. Y.-G Yoon, C.-S. Kim, and W.-Y. Lee, 'Morphology studies of high temperature proton conducting membranes containing hydrophilic/hydrophobic ionic liquids' *Macromolecules*, **42,** 2054 (2009).
7. J.-S. Baek, J.-S Park, S. S. Sekhon, T.-H. Yang, Y.-G Shul, and J.-H. Choi, 'Preparation and characterization of non-aqueous proton-conducting membranes with the low content of ionic liquids' *Fuel Cells*, **10**, 762 (2010).
8. J. Li, X. Yang, H. Tang, and M. Pan, 'Durable and high performance Nafion membrane prepared through high-temperature annealing methodology' *J. Membr. Sci.*, **361**, 38 (2010).
9. C. R. M Robert and B. Moore, 'Procedure for preparing solution-cast perfluorosulfonate ionomer films and membranes' *Anal. Chem*., **58**, 2570 (1986).
10. C. R. M. R. B. Moore, 'Chemical and morphological properties of solution-cast perfluorosulfonate ionomers, Macromolecules' **21**, 1334 (1988).
11. G. Gebel, P. A. Aldebert, and M. Pineri, 'Structure and related properties of solution cast perfluorosulfonated ionomer films' *Macromolecules*, **20**, 1425 (1987).
12. Y. H. Luan, Y. M. Zhang, H. Zhang, L. Li, H. Li, and Y. G. Liu, 'Annealing effect of perfluorosulfonated ionomer membranes on proton conductivity and methanol permeability' *J. Appl. Polym. Sci.*, **107**, 396 (2008).
13. Y. Woo, S. Y. Oh, Y. S. Kang, and B. Jung, 'Synthesis and characterization of sulfonated polyimide membranes for direct methanol fuel cell' *J. Membr. Sci*., **220**, 31 (2003).
14. T. D. Gierke, G. E. Munn, and F. C. Wilson, 'The morphology in nafion perfluorinated membrane products, as determined by wide- and small-angle x-ray studies' *J. Polym. Sci.*: *Polym. Phys. Ed.*, **19**, 1687 (1981).
15. B. Dreyfus, G. Gebel, G. P. Aldebert, M. Pineri, and M. Escoubes, 'Distribution of the « micelles » in hydrated perfluorinated ionomer membranes from SANS experiments' *J. Phys. France*, **51**, 1341 (1990).
16. G. Gebel and J. Lambard, 'Small-Angle Scattering Study of Water-Swollen Perfluorinated Ionomer Membranes' *Macromolecules*, **30**, 7914 (1997).
17. S. Kumar and M. Pineri, 'Interpretation of small-angle x-ray and neutron scattering data for perfluorosulfonated ionomer membranes' *J. Polym. Sci. B.*, **24**, 1767 (1986).
18. A. S. Ioselevich, A. A. Kornyshev, and J. H. G. Steinke, 'Fine Morphology of Proton-Conducting Ionomers' *J. Phys. Chem. B*., **108**, 11953 (2004).
19. G. Gebel, 'Structural evolution of water swollen perfluorosulfonated ionomers from dry membrane to solution' *Polymer*, **41**, 5829 (2000).
20. L. Rubatat, A. L. Rollet, G. Gebel, and O. Diat, 'Evidence of Elongated Polymeric Aggregates in Nafion' *Macromolecules*, **35**, 4050 (2002).
21. L. Rubatat, A. L. Rollet, G. Gebel, and O. Diat, Fibrillar 'Structure of Nafion: Matching Fourier and Real Space Studies of Corresponding Films and Solutions' *Macromolecules*, **37**, 7772 (2004).