Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Power Sources 153 (2006) 29–35

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Short communication

Comparison of the small angle X-ray scattering study of sulfonated poly(etheretherketone) and Nafion membranes for direct methanol fuel cells

B. Yang, A. Manthiram [*]

Materials Science and Engineering Program, The University of Texas at Austin, Austin, TX 78712, USA

Received 7 February 2005; accepted 4 March 2005
Available online 31 May 2005

Abstract

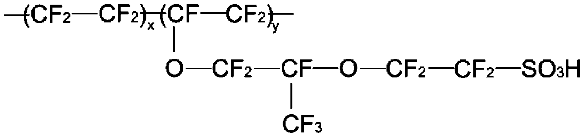
The microstructural evolution and swelling behaviors of sulfonated poly(etheretherketone) (SPEEK) and Nafion polymer membranes have been investigated by small angle X-ray scattering (SAXS) after equilibrating them in 2 M methanol solution at various temperatures, which is relevant for their use in direct methanol fuel cells (DMFC). The relationships among Bragg distance, sulfonation levels of the membrane, equilibrating temperature and transport properties are discussed. The proton conduction properties of the SPEEK and Nafion membranes have been investigated by electrochemical impedance spectroscopy. The network cluster model is employed to retrieve the structural information from the scattering and proton conductivity data. While the SPEEK membranes have narrower pathways for methanol/water permeation at $T < 70\,^{\circ}\mathrm{C}$, the Nafion membranes have a wider channel even at lower temperatures, resulting in a higher methanol permeability in the latter. Based on the differences in the structural/cluster evolutions, the advantages and limitations of the two polymer membranes for use in DMFC are discussed.

Keywords: Small angle X-ray scattering; Nafion membrane; Poly(etheretherketone) membrane; Proton conductivity; Direct methanol fuel cells

1. Introduction

Direct methanol fuel cells (DMFC), which use liquid methanol directly as a fuel, are drawing much attention as promising power sources for portable applications such as cell phones and laptop computers. Currently, Nafion membranes from DuPont are nearly exclusively used as the polymer electrolyte in DMFC due to its favorable mechanical and chemical stabilities along with high proton conductivity in the hydrated state [1,2].

Nafion has the following chemical structure:



in which the values of x and y can be varied to give materials with a range of equivalent weights (900–1400), and the material with an equivalent weight of 1100 is the most common. Nafion consists of an extremely hydrophobic perfluorinated backbone and highly hydrophilic terminal sulfonic acid functional groups ($-SO_3H$) attached to the backbone. The unique properties of Nafion membranes are believed to be closely related to the microscopic phase separation of the ionic parts ($-SO_3H$ groups) from the fluorocarbon matrix. While the polymer backbone provides good mechanical property for

---

[*] Corresponding author. Tel.: +1 512 471 1791; fax: +1 512 471 7681.
E-mail address: rmanth@mail.utexas.edu (A. Manthiram).

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.03.185

the Nafion membrane, the aggregation of the sulfonic acid groups leads to high proton conductivity, especially when the membrane is in the hydrated state.

The clustering of the ionic groups in the low dielectric constant polymer matrix is usually indicated by the existence of a scattering maximum, which is often called “ionomer peak”, in small angle X-ray scattering (SAXS) or small angle neutron scattering (SANS) [1,3–6]. The scattered intensity, $I(q)$, oscillates with increasing wave vector:

$$q = \frac{4\pi}{\lambda}\sin\theta \tag{1}$$

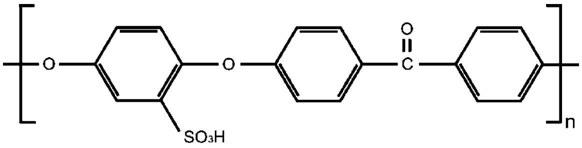
where λ is the wavelength and 2θ is the scattering angle. The Bragg spacing d is related to q as:

$$d = \frac{2\pi}{q} \tag{2}$$

The origin of the scattering maximum has been extensively studied, but it is still a subject of controversy. Since the 1970s, various models have been proposed to interpret the SAXS observations, and they can be generally divided into intraparticle models [7,8], and interparticle models [9–11]. The intraparticle models attribute the “ionomer peak” to the interference within the ionic cluster, implying that the scattering maximum is related to the internal structure of the cluster. On the other hand, the interparticle models attribute the “ionomer peak” to the interference between different ionic clusters, implying that the Bragg spacing obtained from Eq. (2) refers to the center-to-center distance between two clusters. Although the interparticle models are now commonly being accepted, the origin of the ionomer peak is not fully resolved.

Despite the advantages of the Nafion membrane as the electrolyte material for DMFC, its high permeability to methanol has been one of the obstacles that prevent the widespread commercialization of the DMFC technology [12]. To overcome this difficulty along with an aim to lower the cost of the membranes, extensive efforts have been made to develop alternative polymer membranes. In this regard, sulfonated polyketones [13–17], sulfonated polysulfones [18,19] and sulfonated polyimides [20,21] are being actively investigated. These materials show promising results for use in DMFC. For example, the primary properties such as swelling behavior, proton conductivity and methanol permeability of membranes based on sulfonated poly(etheretherketone) (SPEEK) have been characterized, and they have been evaluated in DMFC [14,16,22]. With certain sulfonation level, the SPEEK membranes show low methanol permeability and electrochemical performance comparable to Nafion at temperatures around 60 °C.

However, many of these performance features are not well understood mainly because of the complexity of the membrane structures arising from phase separations when hydrated. The molecular structure of SPEEK membrane is shown below:



According to Kreuer [14,23], the differences in the transport properties and swelling behaviors between the SPEEK and Nafion membranes arise from the differences in their microstructures. They suggested that the separation between the hydrophobic and the hydrophilic groups is smaller, but the separation between the sulfonic acid functional groups is larger in SPEEK compared to that in Nafion. These characteristics of SPEEK were shown to significantly reduce the electro-osmotic drag and water permeation. Therefore, membranes based on SPEEK may help to alleviate the problems associated with high methanol crossover in DMFC.

Generally, SAXS studies of hydrated ionomer membranes use Kapton (polyimide film from DuPont) windows to enclose the samples and keep the water content constant during the measurements. However, it is hard to totally avoid the environmental fluctuations during the long period of SAXS data collection. For those polymer membranes to be used in liquid DMFC, it is highly desirable to obtain the structural information of the electrolyte membranes at conditions close to that in practical fuel cells. Accordingly, we equilibrate the SPEEK membranes with different sulfonation levels in methanol solution at various temperatures and present in this paper a systematic SAXS investigation of the SPEEK membranes. The relationships between the Bragg spacing and the transport of methanol and protons in the SPEEK membranes are discussed and the data are compared with those of Nafion.

2. Experimental

The details of the sulfonation of the poly(etheretherketone) (PEEK) polymer (PEEK450 PF, Victrex) and the preparation of the SPEEK membranes have been given elsewhere [15,16]. Five sulfonation levels (44, 46, 54, 58 and 72%) are used in this study, and they are designated, respectively, as SPEEK-44, SPEEK-46, SPEEK-54, SPEEK-58 and SPEEK-72. For the comparative study, Nafion 115 membranes were used. To prepare SPEEK membranes with different counter ions, the sulfonated polymers were immersed under stirring for 20 h in excess (1.5 times) 0.1 M NaOH or 0.1 M CsCl solution, washed thoroughly with deionized water and dried at around 100 °C overnight. The samples with various levels of sulfonation and the Na^+ or Cs^+ counter ions are designated hereafter as, for example, SPEEK-54-Na, SPEEK-44-Cs, SPEEK-54-Cs and SPEEK-58-Cs.

The SAXS experiments were carried out by placing the sample cell in the path of the X-ray beam. The 1.54 Å Cu Kα X-rays were generated by a rotating copper-anode generator source (Bruker Nonius). The scattering was detected by a multiwire gas-filled 2D detector (Molecular Metrology, Inc.). The experiments were typically carried out at room temperature for a duration of 90 min.

Membranes were equilibrated in 2 M methanol solution at various temperatures for 24 h before conducting the SAXS experiments. To avoid evaporation of the liquid absorbed on the membranes, the samples were embedded in 2 M methanol solution in stainless steel sample holders, and the sample cells were sealed with Kapton films. From our experience and the literature [24], it was observed that both the SPEEK and Nafion membranes exhibit a swelling memory, viz. liquid uptakes obtained at high temperatures remain to room temperature as long as the membranes were kept in the same solution. This ensures the retention of the particular swelling state of the membranes at each temperature and the collection of SAXS data at conditions close to that in practical fuel cells.

Electrochemical impedance spectroscopy studies were conducted with an HP 4192A LF impedance analyzer in the frequency range of 5 Hz to 13 MHz with an applied voltage of 10 mV. Stainless steel blocking electrodes were used for the measurements. The sample fixture was put into an environmental chamber (Model 9000L, VWR Scientific) having the capability to control the temperature and humidity at a desired value. For all the measurements, the membrane samples were first dried at 100 °C in vacuum for about 24 h, and then equilibrated at 80 °C and 20% relative humidity (R.H.) for 12 h before collecting the stable impedance data at various R.H. values. The proton conductivity values of the SPEEK and Nafion membranes were calculated from the impedance data collected.

3. Results and discussion

3.1. SAXS profiles in dry states

The room temperature SAXS spectra of the dry SPEEK and Nafion membranes (pre-dried at 100 °C in vacuum overnight followed by equilibrating in ambient atmosphere) are compared in Fig. 1. It can be seen that in the dry states, no ionomer peaks are observed for SPEEK-44, SPEEK-54, SPEEK 58 and SPEEK-72 membranes, whereas a scattering maximum with a q-value of ~1.93 nm^{-1} is obtained for the Nafion 115 membrane. There are two possibilities for the absence of the ionomer peaks for the SPEEK membranes in the dry states. One is that the ionic clusters do exist, but the electron density contrast between the clusters and the PEEK polymer phase is too small to produce any pronounced SAXS peak structure. The other possibility is that the –SO_3H groups are only statistically attached to the main chains of PEEK during the sulfonation process [25] and no ionic clusters are formed in the dry states by considering the very rigid property of the PEEK backbone to which the –SO_3H groups are attached [26]; the rigidity of PEEK may not provide enough free volume and flexibility for the clustering of the –SO_3H groups.

To clarify this point, SAXS experiments were carried out on the sodium neutralized SPEEK-54 and cesium neutralized SPEEK-44, SPEEK-54 and SPEEK-58 membranes in the dry states. In carboxylated ionomers, the anion packing is determined by the counterion, but it is independent of the cation type in sulfonated ionomers like SPEEK and Nafion investigated in this study [27,28]. In addition, studies have shown that the ionomer peak position is independent of the monovalent counterion; however, the intensity increases as the atomic number Z of the counterion increases due to an increase in the contrast [29]. Therefore, in order to obtain detectable ionomer peaks with dry SPEEK membranes, sodium and cesium ions were used in this study to enhance the electron density contrast between the hydrocarbon PEEK polymer matrix and the ionic clusters, if they exist. The SAXS profiles of the sodium and cesium neutralized membranes are shown in Fig. 2. While the sodium neutralized SPEEK-54 membranes do not exhibit any obvious peak structure, the three cesium neutralized membranes show broad peaks with q-values of around 2.7 nm^{-1}. The results indicate that ionic

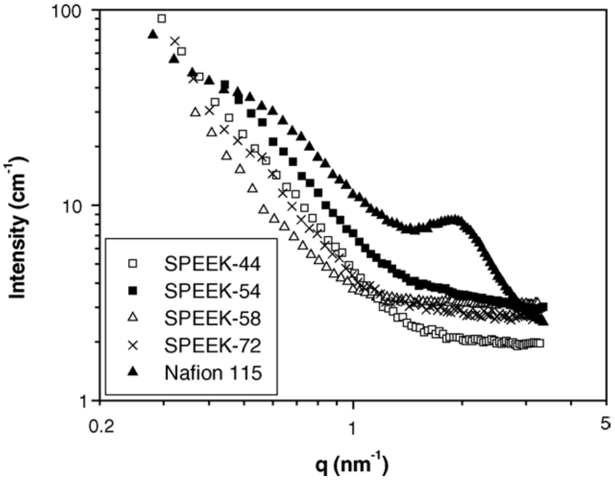


Fig. 1. Comparison of the SAXS profiles of dry Nafion and SPEEK membranes.

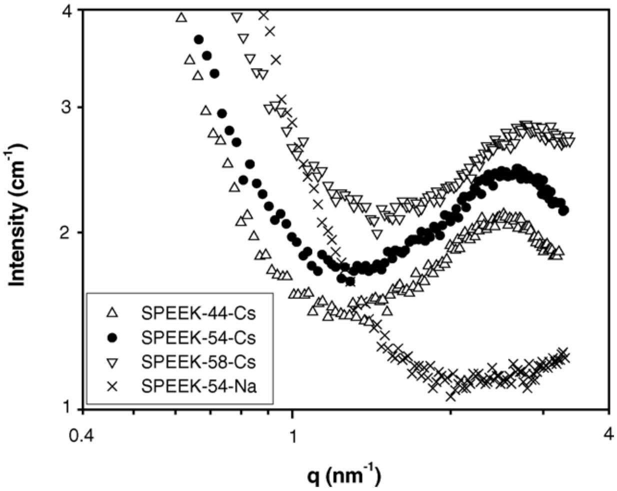


Fig. 2. Comparison of the SAXS profiles of sodium and cesium neutralized SPEEK membranes.

clusters do exist in dry SPEEK membranes, but the cluster size may be small with a small number of ionic –SO_3H groups in each cluster and a small characteristic separation of about 2.3 nm between the clusters. The smaller cluster size is due to the fact that only the closely spaced –SO_3H groups can get clustered due to the high rigidity of the PEEK backbone to which the –SO_3H groups are attached and the smaller free volume. The rigidity of the backbone prevents further structural rearrangement that can lead to larger clusters composed of more ionic groups. On the other hand, in the case of Nafion membrane, the sulfonic acid groups are attached to the PTFE side chains, which due to their high flexibility can provide enough free volume for the ionic groups to cluster easily.

It can also be seen from Fig. 2 that the ionomer peak shifts to slightly higher q-value as the sulfonation level in the cesium neutralized membranes increases from 44 to 58%. This observation indicates that the Bragg distance d (see Eq. (2)) decreases with increasing sulfonation level, suggesting an interparticle origin for the ionomer peak. With increasing sulfonation level, the number of ionic clusters increases, resulting in a smaller center-to-center cluster distance (Bragg spacing).

3.2. Influence of sulfonation level on SAXS profile

Fig. 3 compares the SAXS profiles recorded after equilibrating the SPEEK and Nafion membranes in 2 M methanol solution at various temperatures. Comparison of the data to that in Fig. 1 indicates that ionomer peaks start to appear for the SPEEK membranes on equilibrating in methanol solution. Generally, at each temperature, the scattering maximum shifts toward smaller q-values and the intensity of the peak increases as the sulfonation level increases, especially at higher temperatures (≥60 °C). This trend is different from that obtained for dry membranes in Fig. 2, indicating that microstructural reorganization may be involved upon absorbing methanol/water. In other words, two or more small clusters (clusters composed of small number of ionic groups are called multiplets according to Eisenberg [30]) may combine to form larger clusters containing a larger number of –SO_3H

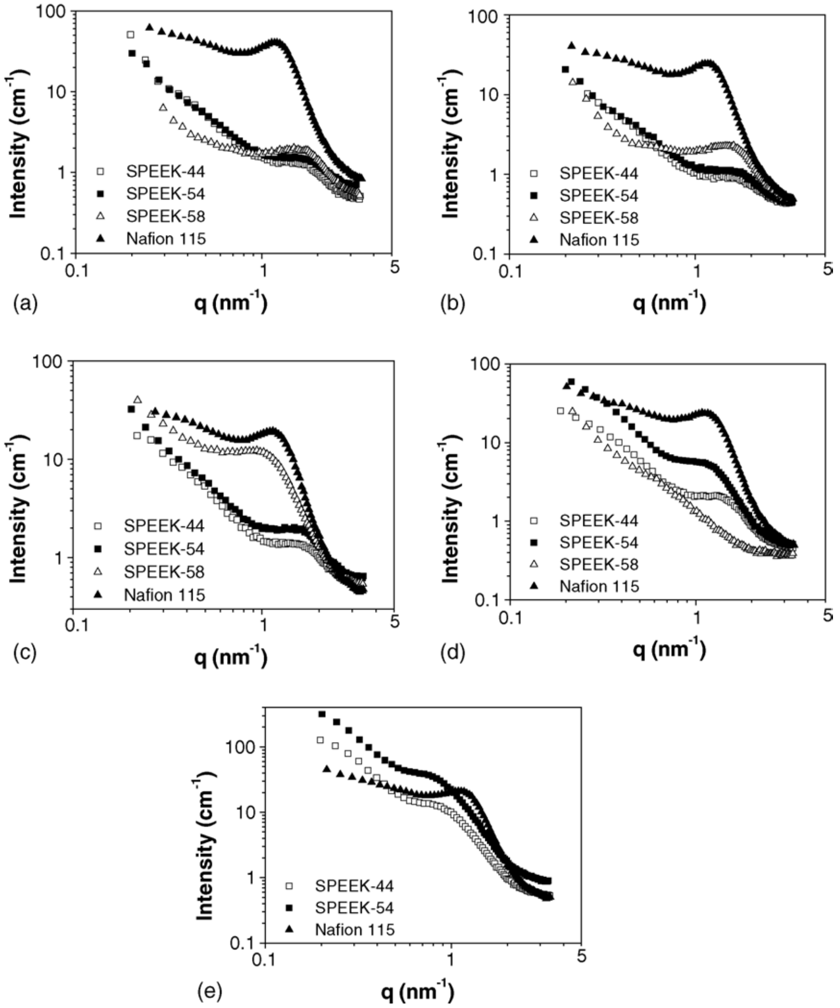


Fig. 3. Comparison of the SAXS profiles of SPEEK and Nafion membranes after equilibrating in 2 M methanol solution at (a) 40 °C, (b) 50 °C, (c) 60 °C, (d) 70 °C and (e) 80 °C.

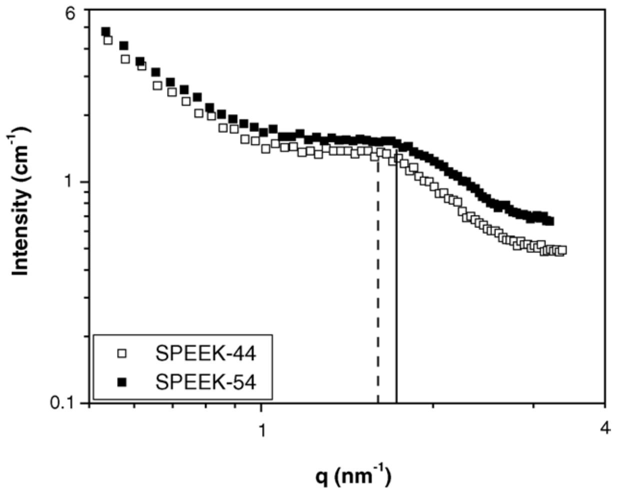


Fig. 4. Comparison of the SAXS profiles of SPEEK-44 and SPEEK-54 membranes after equilibrating in 2 M methanol solution at 40 °C.

ionic groups. While the starting of the structural rearrangement is obvious at lower temperatures for the SPEEK membranes with high sulfonation levels, it becomes obvious only at higher temperatures in the case of membranes with low sulfonation levels. In fact, a careful look at the spectra at a low temperature of 40 °C (Fig. 4) reveals that SPEEK-44 and SPEEK-54 with a low level of sulfonation show characteristics similar to those of cesium neutralized dry SPEEK-44 and SPEEK-54 membranes. SPEEK-54 exhibits a smaller Bragg distance (center-to-center distance of clusters) compared to SPEEK-44, indicating that not too much structural rearrangement and/or cluster combination are involved for these two membranes at low temperatures and the structural characteristics in the dry states are preserved.

It can be seen from Fig. 3(d) that the scattering maximum has disappeared for the SPEEK-58 membrane at 70 °C. The disappearance of the ionomer peak is probably due to a structural reorganization occurring following an excessive swelling as found in our previous study [16]. In contrast, for Nafion membranes, the ionic peak is preserved even at high water contents and high temperatures [31]. These comparisons indicate the advantages of the Nafion membranes over other hydrocarbon based polymer membranes from a thermal stability point of view. In fact, for Nafion membrane, the huge swelling starts only when the temperature is increased to 140 °C, which is much higher than the typical operating temperatures of conventional PEMFC and DMFC.

3.3. *Influence of temperature on Bragg spacing*

To investigate how the ionic clusters in the membrane develop with temperature in methanol solution, the Bragg spacing calculated from the *q*-values of the ionomer peaks in the SAXS profiles is plotted in Fig. 5 against the equilibrating temperature. It can be seen that the Bragg spacing hardly change with temperature in the case of SPEEK membranes with low sulfonation levels (SPEEK-44 and SPEEK-54) at low temperatures (40–60 °C). However, it increases significantly on increasing the temperature above 60 °C.

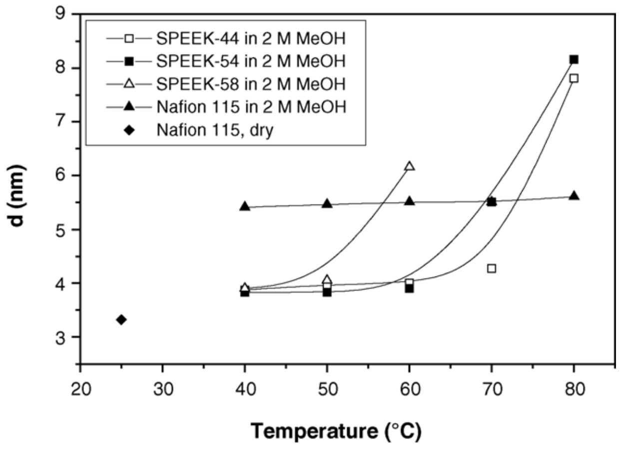


Fig. 5. Variations of the Bragg distance d with the equilibrating temperature in 2 M methanol solution for the SPEEK and Nafion membranes.

The interparticle model can be employed to understand the existence of the two temperature regions (for example, 40–60 and >60 °C for low sulfonation levels of 44 and 54%) in Fig. 5. According to this model, the Bragg spacing is a measure of the center-to-center distance in the ionic clusters. On going from the dry state to the state of being equilibrated in 2 M methanol solution at 40 °C, we may assume that a first stage of cluster combination occurs. In this stage, the first absorbed water/methanol may cause several neighboring small clusters to aggregate to slightly bigger clusters. After this stage, as the temperature is increased from 40 to 60 °C, which is in the low temperature range, most of the liquid is located around the ionic clusters and the size of the cluster increases while the increase in the center-to-center distance between the clusters is relatively smaller. However, as the temperature is increased further (>60 °C), the clusters are getting larger and becoming better connected, and a reorganization may occur to give even larger clusters. In addition, methanol may penetrate into the organic part and plasticize the polymer chain, increasing the flexibility of the polymer backbone and facilitating the reorganization of the clusters. Adjacent clusters may combine to form even larger ones and the number of –SO_3H groups per cluster increases in order to keep the specific surface constant and consequently the total number of clusters decreases [31].

On the other hand, different observations are made with the Nafion membranes. On going from the dry state to the state at 40 °C in methanol solution, the Bragg distance increases from 3.25 to 5.51 nm; after that, the Bragg distance hardly changes upon increasing the equilibrating temperature up to 80 °C. These results suggest that the growth and combination of ionic clusters are almost completed on equilibrating with 2 M methanol solution at 40 °C due to the high flexibility of the side chains to which the sulfonic acid groups are attached.

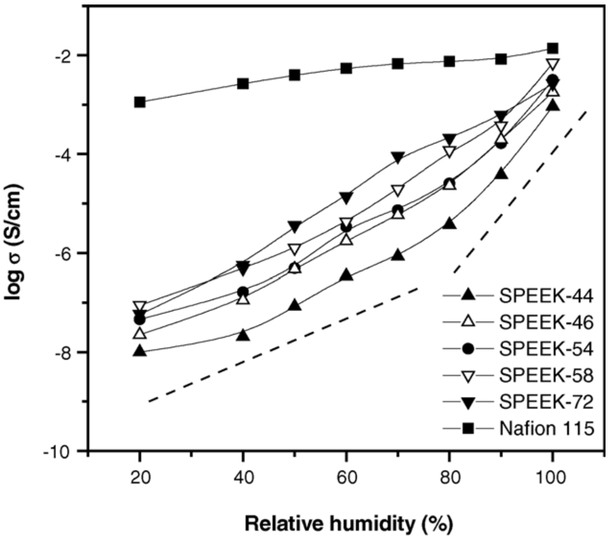


Fig. 6. Comparison of the proton conductivities of Nafion and various SPEEK membranes at 80 °C and various relative humidities.

3.4. *Proton conductivity comparison of SPEEK and Nafion membranes*

The proton conductivities of various SPEEK membranes and Nafion were calculated from the impedance values and the data are shown in Fig. 6 as a function of the relative humidity. The conductivity increases with increasing relative humidity as expected for both the SPEEK and Nafion membranes. However, the conductivity values of the SPEEK membranes are generally lower than that of the Nafion membrane at each relative humidity.

The proton conductivities of the SPEEK membranes in Fig. 6 can be divided into two regions: (i) a region of relatively slow increase in proton conductivity with relative humidity (<80% R.H.) and (ii) a region of relatively faster increase in the proton conductivity with relative humidity (>80% R.H.). These two regions are distinguished in Fig. 6 by the two dashed lines with different slopes. In the region with R.H. <80%, the amount of absorbed water is small and most of them is located around the ionic clusters, which are not well connected. On the other hand, in the region with R.H. >80%, more water is absorbed and the clusters grow and become well connected to each other, increasing the mobility of the protons. In contrast, the proton conductivity of the Nafion membrane increases monotonically in a linear manner with increasing relative humidity, indicating that no significant change in morphology or cluster structure is involved upon swelling.

3.5. *Relationship between SAXS and fuel cell performance data*

We have shown in our previous study [16] that the SPEEK membranes with a sulfonation level of around 50% exhibit much lower methanol permeability than Nafion and an electrochemical performance comparable to that of Nafion 115 in DMFC, but the operating temperature has to be limited to 65 °C. These results are consistent with the SAXS structural evolution data presented in this paper for the SPEEK and Nafion membranes. At $T < 60$ °C, the ionic clusters in SPEEK membranes with low sulfonation levels such as SPEEK-44 and SPEEK-54 are not well connected. So there is no continuous pathway for methanol/water transport through the membrane, leading to lower measured methanol permeability. Also, it can be seen from Fig. 5 that below 70 °C, SPEEK-44 and SPEEK-54 have a smaller center-to-center distance between clusters and smaller cluster sizes. This implies that the membrane can only provide very narrow pathways for methanol/water transportation. The performance loss due to the lower proton conductivity of the SPEEK membranes at these conditions is partly compensated by the advantage gained through the alleviated methanol crossover. On the other hand, continuous pathways for methanol/water permeation can be easily formed in the case of Nafion membranes in contact with the methanol/water solution, leading to high methanol permeability in DMFC. However, other features such as the acidity of the $–SO_3H$ groups and the electro-osmotic drag coefficients in different membranes may also affect their use in DMFC as discussed by Kreuer [14]. It should be noted that the long-term stability of hydrocarbon based polymers such as SPEEK needs to be investigated because methanol may penetrate into the polymer backbone slowly [32,33], leading to further reorganization of the cluster structure and creation of continuous and wide pathways for methanol/water permeation through the membrane.

4. Conclusions

A comparison of the SAXS data of the Nafion and SPEEK membranes has provided important insight regarding their structural features, especially the evolution of clusters. The differences in the structural features are reflected in the differences in the flexibility of their structures. With a sulfonation level of around 50 %, the SPEEK membranes have narrower pathways for methanol/water permeation at $T < 70$ °C, resulting in low methanol permeability. In contrast, wide channels are easily formed in Nafion membranes even at low temperature, which facilitates the transportation of methanol/water and thereby leads to serious methanol crossover problems in DMFC. With a careful control of the processing and operating conditions, the hydrocarbon polymers such as SPEEK may evolve as a promising alternate for the Nafion membranes in DMFC.

Acknowledgement

This work was supported by the Welch Foundation Grant F-1254.

References

[1] A. Eisenberg, H.L. Yeager, Perfluorinated Ionomer Membranes, ACS Symposium Series 180, American Chemical Society, Washington, DC, 1982.

[2] S.R. Samms, S. Wasmus, R.F. Savinell, J. Electrochem. Soc. 143 (1996) 1498.

[3] T.D. Gierke, G.E. Munn, F.C. Wilson, J. Polym. Sci. Polym. Phys. Ed. 19 (1981) 1687.

[4] M. Fujimura, T. Hashimoto, H. Kawai, Macromolecules 14 (1981) 1309.

[5] M. Fujimura, T. Hashimoto, H. Kawai, Macromolecules 15 (1982) 136.

[6] G. Gebel, J. Lambard, Macromolecules 30 (1997) 7914.

[7] J. Kao, R.S. Stein, W.J. Macknight, W.P. Taggart, G.S. Cargill, Macromolecules 7 (1974) 95.

[8] W.J. MacKnight, W.P. Taggart, R.S. Stein, J. Polym Sci. Polym. Phys. 45 (1974) 113.

[9] C.L. Marx, D.F. Caulfield, S.L. Cooper, Macromolecules 6 (1973) 344.

[10] D.J. Yarusso, S.L. Cooper, Macromolecules 16 (1983) 1871.

[11] D.J. Yarusso, S.L. Cooper, Polymer 26 (1985) 371.

[12] X.M. Ren, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 92.

[13] M. Rikukawa, K. Sanui, Prog. Polym. Sci. 25 (2000) 1463.

[14] K.D. Kreuer, J. Membr. Sci. 185, Sp. Iss. SI (2001) 29.

[15] S.P. Nunes, B. Ruffinann, E. Rikowski, S. Vetter, K. Richau, J. Membr. Sci. 203 (2002) 215.

[16] B. Yang, A. Manthiram, Electrochem. Solid State Lett. 6 (2003) 229.

[17] B. Yang, A. Manthiram, Electrochem. Commun. 6 (2004) 231.

[18] F. Lufrano, I. Gatto, P. Staiti, V. Antonucci, E. Passalacqua, Solid State Ionics 145 (2001) 47.

[19] C. Manea, M. Mulder, J. Membr. Sci. 206, Sp. Iss, SI (2002) 443.

[20] C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel, M. Pineri, Polymer 42 (2001) 359.

[21] J.H. Fang, X.X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, Macromolecules 35 (2002) 9022.

[22] L. Li, J. Zhang, Y.X. Wang, J. Membr. Sci. 226 (2003) 159.

[23] K.D. Kreuer, Solid State Ionics 97 (1997) 1.

[24] G. Gebel, P. Aldebert, M. Pineri, Polymer 34 (1993) 333.

[25] R.Y.M. Huang, P.H. Shao, C.M. Burns, X. Feng, J. Appl. Polym. Sci. 82 (2001) 2651.

[26] L.A.S.D. Prado, H. Wittich, K. Schulte, G. Goerigk, V.M. Garamus, R. Willumeit, S. Vetter, B. Ruffmann, S.P. Nunes, J. Polym. Sci. Pol. Phys. 42 (2004) 567.

[27] K.A. Mauritz, J. Macromol Sci. Rev. Macromol. Chem. Phys. C 28 (1988) 65.

[28] J.A. Lefelar, R.A. Weiss, Macromolecules 17 (1984) 1145.

[29] W. Essafi, G. Gebel, R. Mercier, Macromolecules 37 (2004) 1431.

[30] A. Eisenberg, Macromolecules 3 (1970) 147.

[31] G. Gebel, Polymer 41 (2000) 5829.

[32] S. Schlick, G. Gebel, M. Pineri, F. Volino, Macromolecules 24 (1991) 3517.

[33] H. Li, S. Schlick, Polymer 36 (1995) 1141.