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Small-Angle X-ray Scattering Study of Water Free Fuel Cell Membranes Containing Ionic Liquids[†]

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The effect of polymeric membranes containing ionic liquids in replacement of water on the morphology and the formation of ionic aggregates has been studied using mainly small-angle X-ray scattering (SAXS) techniques. The polymeric membranes were based on recast Nafion and sulfonated poly(aryl ether ketone) (SPAEK-6F) containing ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) and 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIPF_6$). The small-angle scattering maximum (ionomer peak) has been observed in the recast Nafion membranes containing the ionic liquids (Nafion/$EMIBF_4$, Nafion/$EMIPF_6$), whereas it was absent in the membranes based on SPAEK-6F (SPAEK-6F/$EMIBF_4$, SPAEK-6F/$EMIPF_6$). This has been explained to be due to the different level of ion-clustering ability of the hydrophilic parts (i.e., sulfonic acid groups) in the Nafion and SPAEK-6F polymers. It is also confirmed in that the mean Bragg distance between the ionic clusters, which is reflected in the position of the ionomer peak, is larger in the membranes containing $EMIBF_4$ than the $EMIPF_6$. In addition, the ionic conductivity of the membranes follows the same trend and is higher for the membranes containing $EMIBF_4$. However, the matrix peak is present at low scattering angles in all the membranes based on recast Nafion and SPAEK-6F due to the crystalline content of the membranes. The membranes containing ionic liquids have ionic conductivity ~0.01 S cm^{-1} above 100 °C under ambient humidity, good mechanical strength, and thermal stability up to temperatures above 300 °C and are hence suitable for potential use in polymer electrolyte fuel cells (PEFCs) at medium temperatures (100−200 °C) in the absence of external humidification.

Introduction

In polymer electrolyte fuel cells (PEFCs), Nafion membranes are generally used as they possess high ionic conductivity along with good mechanical properties.[1] A PEFC is normally operated at 80 °C under fully hydrated conditions. However, due to the carbon monoxide (CO) poisoning of the platinum catalyst, the hydrogen fuel used in fuel cells should be very pure (< 20 ppm CO), which increases the cost of PEFCs.[2] This problem can be avoided if the PEFC is operated at higher temperatures in the 100−200 °C range as the CO tolerance has been reported to increase with an increase in temperature and hydrogen fuel containing up to 3% CO can be used at 200 °C.[3] However, Nafion membranes cannot be used at higher temperatures (> 80 °C) as the ionic conductivity is strongly dependent on humidity, and 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.[4] This problem can be addressed by either of the following general approaches:[5−11]

- by using membranes which can be operated at higher temperatures but still require humidity for obtaining high ionic conductivity

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- by using membranes which do not require water for high ionic conductivity but instead use an alternative solvent with higher boiling point and other suitable properties
- by the covalent immobilization of such solvents (imidazole, benzimidazole, phosphonic acid, etc.) leading to fully polymeric systems (no free solvent)

A number of alternative proton conducting polymer membranes based on aforementioned approaches have been reported,[1-8] but most of them follow the first approach and still require humidity for high ionic conductivity.

The higher ionic conductivity of water swollen Nafion membranes is generally explained on the basis of phase-separated morphology which has been widely studied by small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), atomic force microscopy (AFM), transmission electron microscopy (TEM), etc. Although the exact morphology of Nafion is still not resolved clearly, different models have been proposed to explain the morphology of such membranes,[12-17] which recently have been reviewed.[5] The most comprehensive results for membranes with different water contents starting from dry ionomer to the Nafion solutions have been reported by investigating their structural evolution using small-angle scattering techniques.[18-20] However, on the basis of quantitative analysis of the published SAXS data, it has been recently reported that none of the models match the experimental SAXS data.[21]

The morphology has been reported to be correlated with the ionic conductivity of these membranes. Generally, so do alternative membranes which are based on hydrocarbon polymers. In case of high temperature membranes for which ionic conductivity still depends upon humidity, the results of morphology obtained by SAXS and SANS are generally compared with those of Nafion membranes. However, in case of membranes in which water has been replaced with another solvent (phosphoric acid, imidazole, pyrazole, heterocycles, ionic liquids, etc), such morphological studies are very scarce and no standard reference material is known with which such SAXS results could be compared. In the absence of any reference material, the SAXS results for any new fuel cell membrane are generally compared with water swollen Nafion membranes. Thus there is a growing need to obtain SAXS data for high temperature proton conducting membranes, particularly those which do not use water for swelling, and the present study is a step in that direction.

One of the various approaches used to develop anhydrous membranes was by replacing water as the proton solvent with a liquid that has a higher boiling point.[22,23] Ionic liquids (ILs) have also shown much promise as a replacement for water as they are nonvolatile and also have a larger electrochemical stability window than water.[24] Membranes based on different polymers (commercial polymers, recast Nafion, sulfonated copolymers, etc.) containing ILs have been also reported[25-28] for use in PEFCs at higher temperatures and under anhydrous conditions. Initial results for the membranes based on commercial polymers showed lower fuel cell power density due to the lower ionic conductivity of the membranes under low humidity conditions. For optimizing the design of such membranes to obtain high ionic conductivity along with other suitable properties such as good mechanical stability, high thermal stability, wide electrochemical window, etc., establishment of the extensive knowledge on their morphology is very essential. While developing alternative membranes based on ionic liquids for PEFCs, it was observed that a proper pairing of the polymer and the ionic liquid is also very important for obtaining the optimum properties.[27,29] The hydrophilic/hydrophobic nature of the polymer and the ionic liquid also plays an important role in this regard. Proton conducting membranes based on recast Nafion and sulfonated poly(aryl ether ketone) (SPAEK-6F) containing different ionic liquids showed the possibility of being operated at higher temperature under anhydrous conditions and the hydrophilic ionic liquid, 1-ethyl-3-methylimidazolium tetraflouroborate ($EMIBF_4$), was found to show higher ionic conductivity.[27] In addition, the membranes based on recast Nafion were found to possess relatively higher ionic conductivity than those based on SPAEK-6F. However, SPAEK-6F-based membranes are more suitable for use in PEFCs due to their better ability for entrapment of the ionic liquids than recast Nafion-based ones.[27] A correlation between membrane morphology and transport properties was reported for the membranes based on recast Nafion and SPAEK-6F containing a pair of hydrophilic/hydrophobic ionic

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Table 1. Properties of Ionic Liquids and Anions

(a) Some Important Properties of Ionic Liquids[34,35]

IL	temp (°C)	molecular weight (g mol^{-1})	melting point (°C)	density (gm cm^{-3})	conductivity (mS cm^{-1})	viscosity (cP)	window (V)
$EMIBF_4$	25	197.97	11−15	1.28	13.8 − 15.8	25−43	4.5
$EMIPF_6$	26	256.13	58−62	1.52	5.2		

(b) Calculated Anion Properties

anion	molecular weight (g mol^{-1})	molecular volume (Å^3)	equivalent spherical radius (Å)
BF_4^-	86.8	50.5	2.29
PF_6^-	145	84.3	2.72

liquids (1-ethyl-3-methylimidazolium triflate (EMITf) and 1-ethyl-3-methylimidazolium imide (EMIIm)).[30]

The present study deals with water free fuel cell membranes based on recast Nafion and SPAEK-6F containing a pair of ionic liquids such as $EMIBF_4$ and $EMIPF_6$. The formation of ionic clusters in the membranes containing ionic liquids has been studied by SAXS and TM-AFM. The effect of the nature of the polymers and ionic liquids and the crystalline content on the morphology of the membranes has been investigated and the results have been correlated with the ionic conductivity results for those membranes. The thermal stability of the membranes has been checked by TGA measurements.

Materials and Methods

Materials. Sulfonated poly(aryl ether ketone) (SPAEK-6F) random copolymers with degree of sulfonation (DS), 40, were synthesized via a nucleophilic aromatic substitution method described in our previous work.[31] The Nafion solution (perfluorosulfonic acid/TFE copolymer resin (5−6%), 1-propanol (42−54%), water (40−50%), ethyl alcohol (< 8%), mixed ethers, and other volatile organic compounds (VOCs; < 2%)) was purchased from Dupont (USA). The ILs used in the present study, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) and 1-ethyl-3-methylimidazolium hexafluorophosphate ($EMIPF_6$) were purchased from TCI (Japan).

Synthesis. Polymer electrolytes containing IL and polymer in equal weight ratio (50 wt % polymer + 50 wt % ionic liquid) were prepared by the solution casting method described elsewhere.[27,32] The requisite amount of each IL was added into 10 wt % polymer solutions in *N*,*N*-dimethylacetamide (DMAc), and the solutions were stirred overnight. All the samples were cast in Petri dishes and were finally dried in a vacuum oven at 60 °C for 24 h to evaporate the solvent slowly. All the samples studied in the present case contain equal amount of polymer and IL, and it has been done to compare the results for different samples.

Characterization. The electrochemical properties of the ionic liquids and composite membranes were investigated at elevated temperatures and under ambient humidity conditions. Ionic conductivity of the composite membrane samples was measured by the four-point-probe conductivity cell described elsewhere.[33] The conductivity cell was placed in the headspace of a temperature controlled sealed vessel, which maintained an anhydrous atmosphere. The size of membrane samples was 2 cm long and 1 cm wide. The impedance data for ionic conductivity of the membranes were obtained by using Solartron 1260 gain phase analyzer, interfaced to Solartron 1480 multistat. The measurements were carried out in a potentiostatic mode in the frequency range of 0.1 Hz to 10 MHz with 5 mV oscillating voltage. The electrochemical data were averaged using three measurements, and the standard deviation of all data was below 1%.

The thermal stability of the ILs and 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^{-1} was used over the temperature range of 50−600 °C.

Morphology characterization of the membranes was studied by the small-angle X-ray scattering (SAXS) and tapping mode atomic force microscopy (TM-AFM). 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. AFM images were obtained by a Bio-AFM D3100 (Veeco) in the tapping mode with the standard etched silicon probe tips. All the images shown in this study are phase images scanned at 1.0 Hz frequency and 256 scan rates and have been filtered through the "planefit" procedure. The crystalline/amorphous nature of composite membranes was studied by X-ray diffraction (XRD) analysis using a Rigaku D/MAX-RB X-ray diffractometer.

The mechanical strength of the membranes was measured with a tensile strength instrument Instron 5583 (Instron Corporation) at a constant separating speed of 5 mm min^{-1} in an air atmosphere at room temperature.

Results and Discussion

The important physical properties of the anions and ILs are listed in Table 1.[34−36] The weakly coordinating nature of these anions (BF_4^-, PF_6^-) has been reported to result in ILs with high thermal and chemical stability, large density, high ionic conductivity, and wide electrochemical window. $EMIBF_4$ has higher ionic conductivity and lower viscosity as compared with $EMIPF_6$. The ILs have been selected due to their very similar chemical properties with anions (BF_4^- and PF_6^-) having

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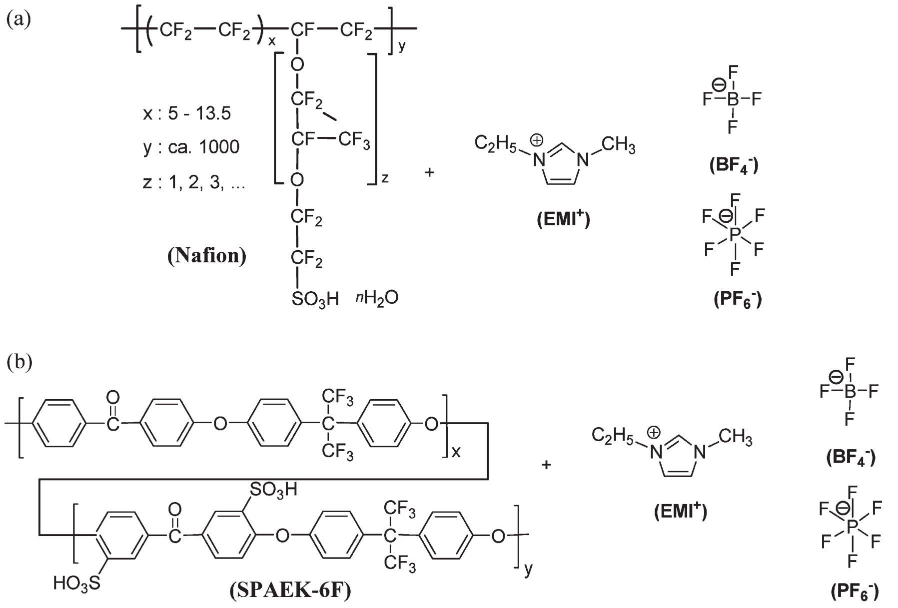
Scheme 1. Preparation of Nafion and SPAEK-6F Based Composite Membranes with Ionic Liquids Comprising of Anions (BF_4^-, PF_6^-) and the Cation (EMI^+) Used in This Study



a spherical distribution of fluorides around a central atom with the negative charge and have radii 2.29 and 2.72 Å, respectively. The chemical structure of the two polymers (Nafion and SPAEK-6F) used in the present study is shown in Scheme 1.

The ionic conductivity of the composite membranes based on recast Nafion containing $EMIBF_4$ and $EMIPF_6$ was measured at different temperatures under ambient humidity conditions, and the variation of ionic conductivity with temperature is given in Figure 1a. Both the membranes show ionic conductivity of the order of 10^{-2} S cm^{-1} above 100 °C, and the Nafion/$EMIBF_4$ membrane shows higher ionic conductivity than the Nafion/$EMIPF_6$ membrane at all temperatures. In general, the ionic conductivity of the membranes containing hydrophilic ILs ($EMIBF_4$) is higher than that of the membranes containing hydrophobic ILs ($EMIPF_6$). The straight line behavior observed in the plot between logarithmic conductivity and reciprocal temperature suggests thermally activated Arrhenius relationship with activation energies 8.1 and 11.1 kJ mol^{-1} for the Nafion/$EMIBF_4$ and Nafion/$EMIPF_6$ membranes, respectively. The smaller size, lower viscosity and hydrophilic nature of the IL ($EMIBF_4$) contribute to the higher ionic conductivity of Nafion/$EMIBF_4$ membranes.

SPAEK-6F having higher IL entrapment ability[27] has been also used in the present study and the ionic conductivity of the membranes based on this polymer containing the same pair of ionic liquids (SPAEK-6F/$EMIBF_4$ and SPAEK-6F/$EMIPF_6$) was measured at different temperatures under ambient humidity condition. Figure 1b shows the variation of ionic conductivity with temperature. The ionic conductivity of the SPAEK-6F/$EMIBF_4$ membrane is higher than that of the SPAEK-6F/$EMIPF_6$ membrane at all temperatures studied. However, the difference in the ionic conductivity

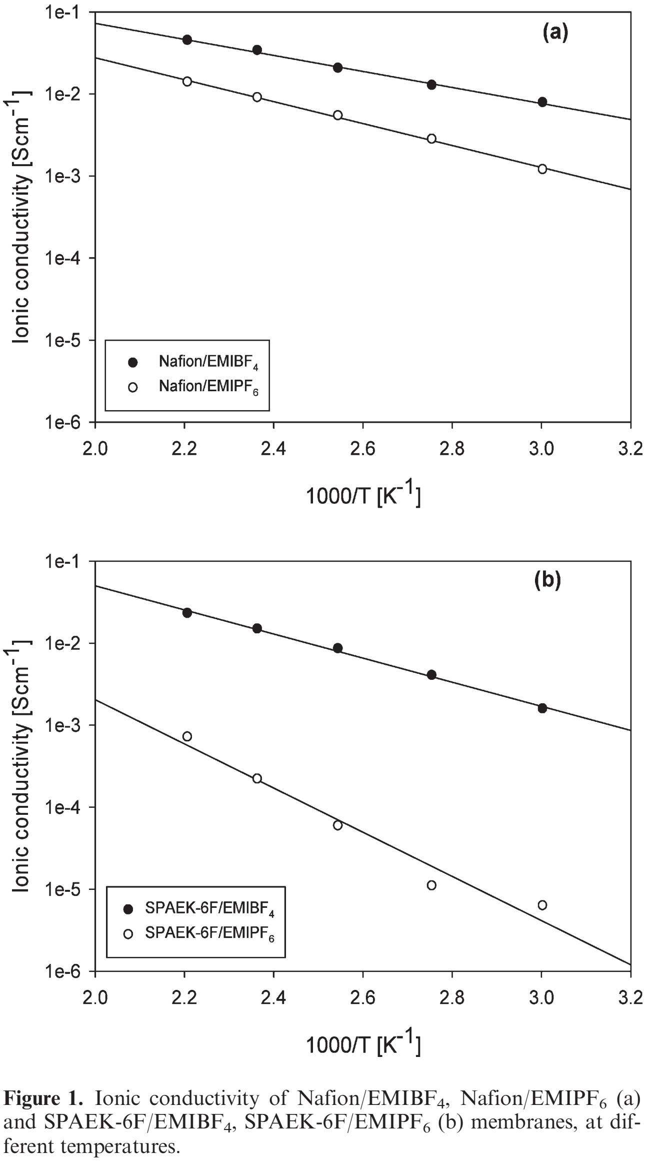


Figure 1. Ionic conductivity of Nafion/$EMIBF_4$, Nafion/$EMIPF_6$ (a) and SPAEK-6F/$EMIBF_4$, SPAEK-6F/$EMIPF_6$ (b) membranes, at different temperatures.

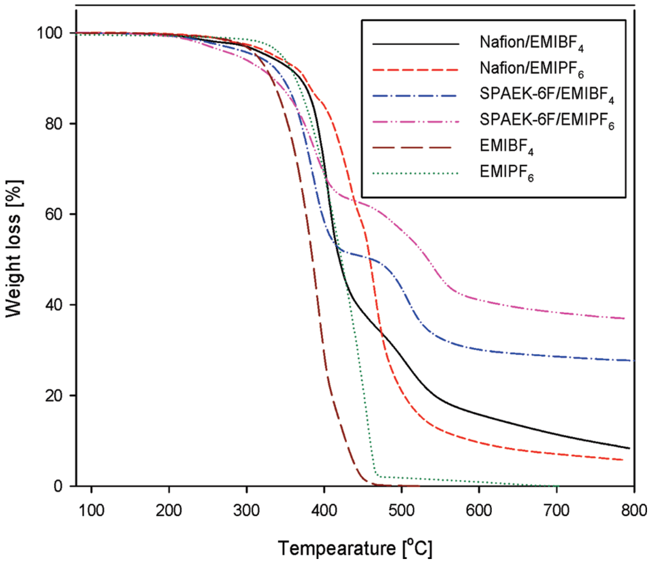


Figure 2. Thermogravimetric analysis (TGA) weight loss curves for $EMIBF_4$, $EMIPF_6$, Nafion/$EMIBF_4$, Nafion/$EMIPF_6$, SPAEK-6F/$EMIBF_4$, and SPAEK-6F/$EMIPF_6$.

value for the SPAEK-6F/$EMIBF_4$ and SPAEK-6F/$EMIPF_6$ membranes is much more than that for the similar membranes based on recast Nafion containing the same pair of ILs. The ionic conductivity of the SPAEK-6F/$EMIBF_4$ membrane at temperatures above 100 °C is $>10^{-2}$ S cm^{-1}, whereas for the SPAEK-6F/$EMIPF_6$ membrane it is 1 order of magnitude lower and approaches a value of $\sim 10^{-3}$ S cm^{-1}. The lower ionic conductivity of the membranes containing $EMIPF_6$ (Nafion/$EMIPF_6$ and SPAEK-6F/$EMIPF_6$) is partly due to the relatively higher viscosity of the IL ($EMIPF_6$). Although the viscosity data is not available for $EMIPF_6$, it is reasonable to consider that this salt would be more viscous than $EMIBF_4$. This indicates that the viscosity along with the hydrophilic/hydrophobic nature of the IL significantly affects the ionic conductivity to a greater extent in SPAEK-6F than in the membranes based on recast Nafion. The lower ionic conductivity of the SPAEK-6F based-membranes is due to the lower ion-clustering ability of SPAEK-6F than Nafion polymer in ionic liquids.[27] This highlights the importance of the nature of the IL for the membranes based on SPAEK-6F. The straight lines observed in the plot between logarithmic conductivity and reciprocal temperature show Arrhenius behavior with activation energy 12.2 and 22.4 kJ mol^{-1} for the SPAEK-6F/$EMIBF_4$ and SPAEK-6F/$EMIPF_6$ membranes, respectively. Although the membranes based on recast Nafion show higher ionic conductivity, the interest in the SPAEK-6F-based membranes is mainly due to their higher IL entrapment ability.[27]

Table 2. TGA Data for the ILs and Composite Membranes

sample	temperature at 5 and 10 wt % loss	
	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)
$EMIBF_4$	313	332
$EMIPF_6$	345	363
Nafion/$EMIBF_4$	327	368
Nafion/$EMIPF_6$	335	375
SPAEK-6F/$EMIBF_4$	311	346
SPAEK-6F/$EMIPF_6$	287	334

The thermal stability of all the membranes and ionic liquids has been studied and Figure 2 shows the thermogravimetric analysis (TGA) mass loss curves for the membranes based on recast Nafion and SPAEK-6F along with the results for the neat ILs used in the membranes. Normally a temperature corresponding to 10% mass loss is taken as the dissociation temperature (T_d), and in the present case, also temperatures corresponding to 5 and 10% mass loss have been determined for different samples from Figure 2 and are listed in Table 2. The ILs ($EMIBF_4$ and $EMIPF_6$) used in the present study are thermally stable up to temperatures above 300 °C, and the weight loss takes place by a one-step weight loss process. The hydrophobic IL ($EMIPF_6$) has been found to be thermally more stable than the hydrophilic IL ($EMIBF_4$). The temperatures at 10% mass loss are 332 and 363 °C for $EMIBF_4$ and $EMIPF_6$, respectively. For the two Nafion-based membranes, the small weight loss features at ~250 °C are shown due to the solvent used in the preparation of the membranes. The temperatures corresponding to 5 and 10% mass loss are 327 and 368 °C for the Nafion/$EMIBF_4$ and 335 and 375 °C for the Nafion/$EMIPF_6$ membranes, respectively. The weight loss takes place by a two-step weight loss process: the first at ~350 °C due to the loss of IL and the second at 450−500 °C due to the loss of polymer. This shows that the recast Nafion membranes containing ILs are thermally stable up to temperatures well above 350 °C. The recast Nafion membrane containing hydrophobic IL ($EMIPF_6$) is relatively more stable than membrane containing hydrophilic IL ($EMIBF_4$). Similarly, the temperatures corresponding to 5 and 10% mass loss have been observed to be 311 and 346 °C for the SPAEK-6F/$EMIBF_4$ and 287 and 334 °C for the SPAEK-6F/$EMIPF_6$ membranes, respectively. The weight loss also takes place by a two-step weight loss process with the first weight loss at ~330 °C due to the loss of IL, and the second at temperature of ~500 °C is due to the loss of polymer. In the case of the sulfonated polymer SPAEK-6F, the membrane containing $EMIBF_4$ (hydrophilic) is thermally more stable than the membrane containing $EMIPF_6$ (hydrophobic). This shows that, in addition to the hydrophobic/hydrophilic nature of the IL, the nature of polymer also affects the thermal stability of the membranes. A proper choice of the polymer and IL can thus lead to membranes with relatively higher thermal stability. However all the membranes studied in the present case are found to be thermally stable up to temperatures above 300 °C and can be used at temperatures in the 100−200 °C range for PEFCs.

In the presence of water, the hydrophilic domains containing the ionic groups ($-SO_3H$) have been proposed to swell and form ionic clusters which are separated from the hydrophobic domains. With an increase in water content, these ionic domains grow in size and get interconnected to one another by channels which provide paths for the migration of ions.[18−20,37,38] The SAXS results are explained on the basis of different models which are generally classified into intraparticle[13,14] and interparticle[15−17] models. The intraparticle models explain the ionomer peak due to the interference within the ionic cluster, which indicates that the scattering maximum is related to the internal structure of the cluster. The interparticle models explain the ionomer peak due to the interference between different ionic clusters, which indicate that the Bragg spacing is the center to center distance between the clusters. The cluster network model[12,15] and the core shell model[13,14] are the two main models widely used to explain the correlation between morphology and ionic conductivity of water swollen Nafion membranes based on SAXS results. In the cluster network model, the ionic clusters are proposed to be distributed within an inert fluorocarbon matrix and these ionic clusters are interconnected by narrow channels which lead to the unique transport properties of Nafion. In the core shell model, the ionic clusters, surrounded by a fluorocarbon phase, are embedded in an intermediate ionic phase, which consists of both fluorocarbon polymer and nonclustered ionic sites. A third model[38] is based on the assumption of nonspherical ionic clusters and the presence of a third phase which is intermediate between the ionic clusters and the fluorocarbon phase. A recently proposed model[21] consists of parallel cylindrical water channels which are lined with hydrophilic groups and are stabilized by hydrophobic backbone. Scattered intensity, $I(q)$, calculated from this model, can be reproduced as a function of the ionomer peak along with the q^{-1} or q^{-4} scaling at low and high scattering vector (q) values, respectively. However, the validity of this model for Nafion at low hydration levels is not known.

The morphology of water swollen Nafion membranes has been studied by SAXS and the overall SAXS profile has been reported[39−41] to show the following general features:

An upturn of the intensity $I(q)$ at very small values of q ($< 10^{-2}$ Å^{-1}) is strongly related to the ionic clusters and is generally associated with the long-range inhomogeneities in the spatial distribution of the ionic clusters.[42] The presence of a small peak (shoulder), centered at intermediate q values, is called the matrix peak. The intensity of this peak depends upon the crystalline content of the Nafion films or the presence of crystallites in the fluorocarbon hydrophobic phase.[43] The small-angle scattering maximum ("ionomer peak"), which originates from either the shape of the ionic clusters or their spatial distribution and the position of the ionomer peak, corresponds to the mean center to center spacing between the ionic clusters. The tail region of the SAXS profile shows an asymptotic behavior in the large q region and follows Porod's law ($I(q) \propto q^{-4}$), which is an indication that the polymer−solvent interface is sharp and also supports the idea that the phase separation[44] has taken place.

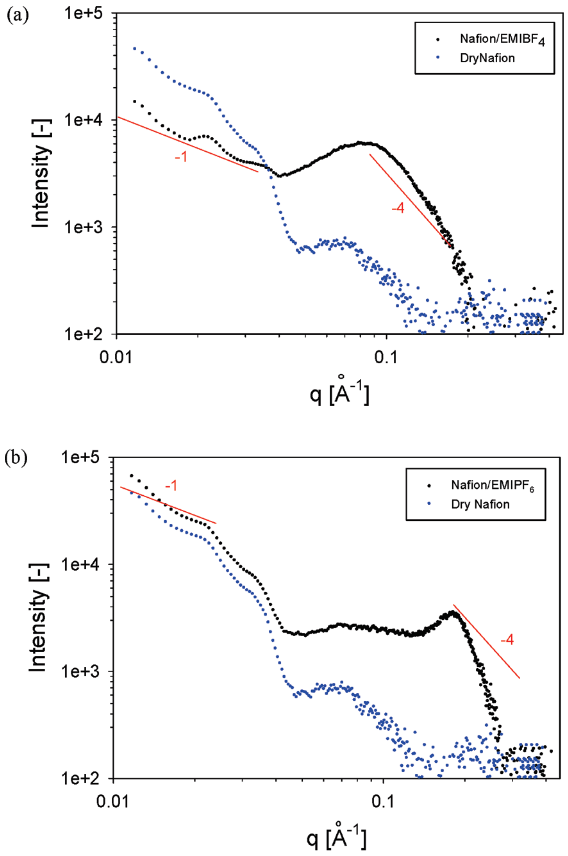


Figure 3. SAXS spectra of recast Nafion membranes: Nafion/EMIBF$_4$ (a) and Nafion/EMIPF$_6$ (b).

The morphology of the membranes based on recast Nafion containing EMIBF$_4$ and EMIPF$_6$ has been studied by SAXS, and the SAXS spectra (Figure 3) shows the variation of scattered intensity as a function of the scattering vector q. The SAXS results for the Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes are different and depend upon the hydrophilic/hydrophobic nature of the IL. From the results given in Figure 3, the following general observations can be made:

A small peak along with a shoulder related to the matrix peak has been observed at $q = 0.0211$ and 0.0334 Å^{-1} for the Nafion/EMIBF$_4$ and at $q = 0.0221$ and 0.0334 Å^{-1} for the Nafion/EMIPF$_6$ membrane. The slope of the intensity line in the small q region is −1.20 for the Nafion/EMIBF$_4$ and −1.68 for the Nafion/EMIPF$_6$ membranes, respectively. A broad ionomer peak has been observed at $q = 0.0841$ Å^{-1} for the Nafion/EMIBF$_4$ and

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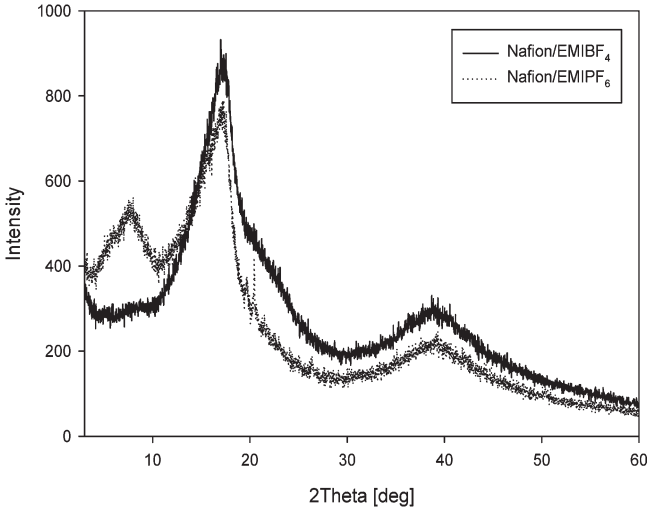

Figure 4. X-ray diffraction pattern for Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes.

at $q = 0.1810$ Å^{-1} for the Nafion/EMIPF$_6$ membrane. This indicates that the ion aggregation also takes place in water free recast Nafion membranes containing ILs. The ionomer peak in the Nafion/EMIBF$_4$ membrane appears at relatively lower q values as compared with the Nafion/EMIPF$_6$ membrane which indicates that the Bragg spacing between the ionic clusters is relatively larger in the membranes containing EMIBF$_4$. After the position of the ionomer peak, a sharp fall in intensity has been observed for the Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes in the high q region, $q = 0.12-0.25$ Å^{-1} for the Nafion/EMIBF$_4$ and at $q = 0.22-0.27$ Å^{-1} for the Nafion/EMIPF$_6$ membrane. The slope of the scattered intensity curve in this region is -3.53 for the Nafion/EMIBF$_4$ and -4.94 for the Nafion/EMIPF$_6$, which is over a very narrow range of q values. The upturn in intensity at very low values of q has not been observed in the present case as it is normally observed by ultra-small-angle X-ray scattering (USAXS) at $q < 10^{-2}$ Å^{-1}, and this range of q values has not been studied in the present case. Another peak at $q = \sim 0.35$ Å^{-1} has been also observed in the SAXS spectra of all the membranes based on Nafion and SPAEK-6F. This peak was due to a component of the beamline/instrument and was confirmed in the SAXS spectrum of blank (no sample) not shown here. Thus, this peak at $q = \sim 0.35$ Å^{-1} in the SAXS spectra of all the membranes has been subtracted by the SAXS spectrum of blank.

The intensity of the matrix peak at low q values observed in the SAXS spectra of water swollen Nafion membranes is generally related to the crystalline content of the membranes. This was checked by the wide-angle X-ray diffraction, and Figure 4 shows the XRD patterns for the Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes. The presence of the two broad peaks at d values of 2.3 ($2\theta = 38.7°$) and 5.1 Å ($2\theta = 17°$) in both the membranes is generally attributed to the crystalline stacking in the hydrophobic microphase. The broadness of different peaks observed in the XRD patterns indicates the amorphous nature of the membranes. The small intensity of the matrix peak, as observed in Figure 3 in the SAXS spectra also suggests that the membranes have a large amorphous content. This is due to the plasticizing effect of the ILs used in the present membranes, which increases the amorphous content of the membranes.

The SAXS spectra (Figure 3), shows that after the position of the ionomer peak, a sharp fall in intensity has been observed for the Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes. The slope of the $I(q)$ versus q curve for the Nafion/EMIBF$_4$ membrane is -3.53, whereas, for the Nafion/EMIPF$_6$ membrane, the slope is -4.94 despite being over a very narrow q range, indicating the presence of an interface between the two phases. This also shows that the recast Nafion membranes containing ILs show phase separation.

The asymptotic behavior of the scattering intensity curve at large q values contains information about the nature of the interface between the hydrophilic and hydrophobic domains in water swollen Nafion membranes. On the basis of the SAXS data of Figure 3, the graphs between $\ln[q^4 I(q)]$ versus $10q^2$ have been plotted for the Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes in Figure 5. However, these plots are for a narrow q range as Porod's law is obeyed in the narrow q regions as observed in Figure 3. The slope of the $\ln[q^4 I(q)]$ versus $10q^2$ plot provides information about the distance between the two phase interface region.[45,46] The straight lines have been observed in Figure 5, and the slope of the lines has been found to be 1.75 and 0.17 Å^2 for the Nafion/EMIBF$_4$ and the Nafion/EMIPF$_6$ membranes, respectively. The larger value of the slope for the Nafion/EMIBF$_4$ membrane is generally related to the larger interface thickness between the hydrophilic and hydrophobic phases and the phase-separated structure of the membranes containing the ILs.[45,46] These results are also consistent with the ionic conductivity trend for these membranes as given in Figure 1a.

Nafion membranes show the presence of an ionomer peak[47] in the dry state as well as in other solvents, and this suggests that it may also be present in the Nafion membranes containing ILs. The SAXS spectrum for the Nafion/EMIBF$_4$ membrane shows the presence of a broad ionomer peak at $q = 0.0841$ Å^{-1}. The SAXS spectrum for the Nafion/EMIPF$_6$ membrane also shows the presence of an ionomer peak but at a relatively larger value of $q = 0.1810$ Å^{-1} in comparison with the Nafion/EMIBF$_4$ membrane. The observation of the ionomer peak at higher q values for the Nafion/EMIPF$_6$ indicates that the Bragg distance between the ionic clusters is smaller as compared with the Nafion/EMIBF$_4$ membrane. This may be related to the hydrophobic nature of the IL (EMIPF$_6$) used in this membrane because there is the possibility that the IL may penetrate into the hydrophobic part of the Nafion polymer (Note that an equal quantity of IL is present in all membranes). However, the q^{-4} scaling of the scattering intensity

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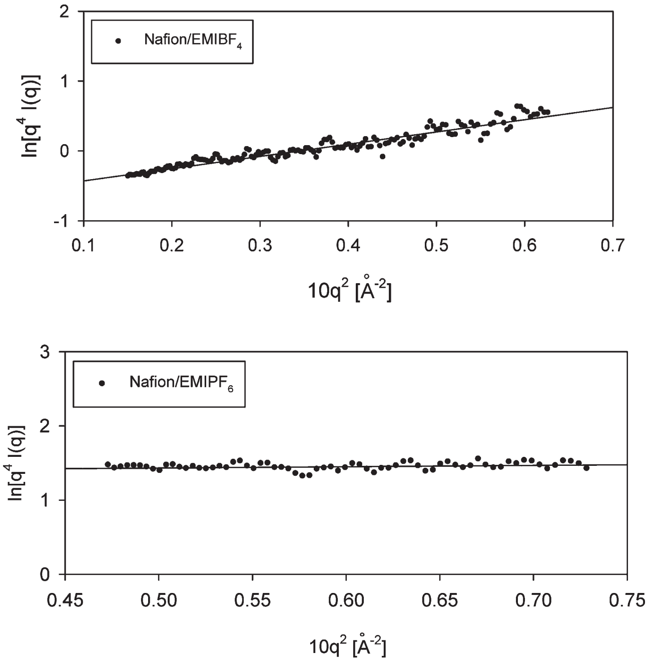

Figure 5. $\ln[q^4 I(q)]$ versus $10q^2$ curves for Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes.

after the ionomer peak suggests that phase separation has taken place. Although SAXS can be used to measure the contrast between the cluster and the fluorocarbon phase and also the mean distance between the clusters, it can not be used to measure the size or shape of the clusters.

The information about the presence of ionic clusters and phase separation obtained from the SAXS data (Figure 3) for the recast Nafion membranes containing ILs was also checked by TM-AFM studies. The micrographs (phase images) obtained by TM-AFM for the Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes are given in Figure 6. The relatively lighter regions in the micrographs are generally ascribed to be due to the softer domains, which represent the hydrophilic sulfonated ionic clusters, and the darker regions are assigned to the neutral hydrophobic regions in the membranes. Ionic clusters of different sizes are present, and this is reflected in the broadness of the ionomer peak in Figure 3. The size and the connectivity of the ionic clusters also affect the ionic conductivity and other properties of proton conducting polymer membranes. In Figure 6, the micrograph for the Nafion/EMIBF$_4$ membrane containing the hydrophilic IL shows the clusters of relatively larger and of varying sizes and having better connectivity, whereas, in case of the Nafion/EMIPF$_6$ membrane containing the hydrophobic IL, the size of ionic clusters is relatively small and the connectivity between different ionic clusters is also not so good as in case of the Nafion/EMIBF$_4$ membrane. These results are consistent with the SAXS results for these membranes in which the $2\pi/q_{\max}$ or $d_{\max}$ was found to be 74.7 and 34.7 Å for the Nafion/EMIBF$_4$ and Nafion/EMIPF$_6$ membranes, respectively. The interface region for these membranes was also found to be thicker in the Nafion/EMIBF$_4$ than in the Nafion/EMIPF$_6$ membrane.

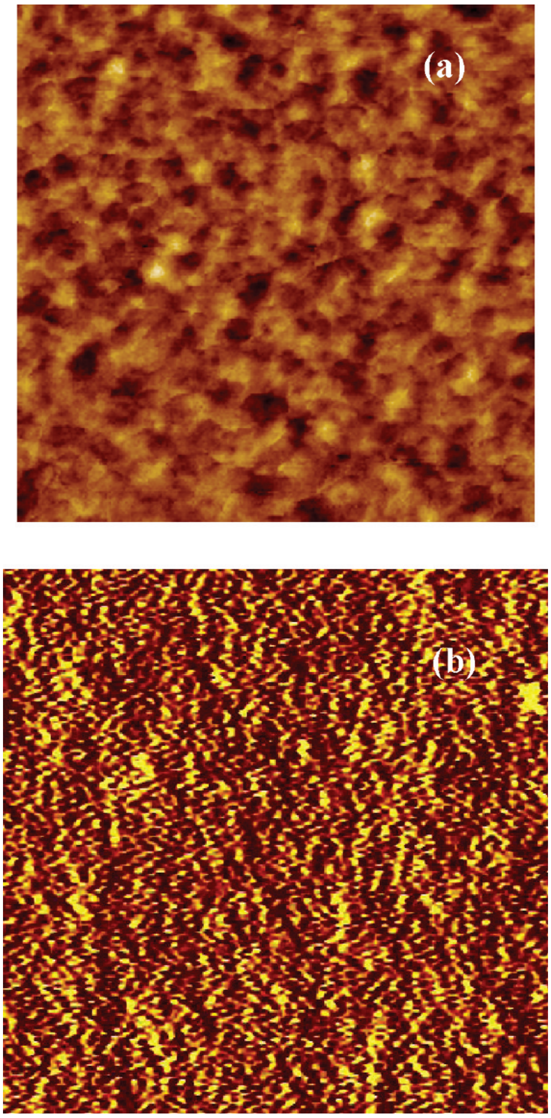

Figure 6. Tapping mode atomic force microscopy (TM-AFM) phase images (size 1 μm) of Nafion/EMIBF$_4$ (a) and Nafion/EMIPF$_6$ (b) membranes.

From the ionic conductivity results given in Figure 1, it has been observed that the membranes based on SPAEK-6F have slightly lower ionic conductivity as compared with the recast Nafion membranes containing the same ILs. It is due to the different morphology as transport properties and ionic conductivity is related to the morphology of membranes. For optimizing the ionic conductivity of such membranes, an understanding of the membrane morphology will be very helpful. The SAXS plots for the SPAEK-6F/EMIBF$_4$ and SPAEK-6F/EMIPF$_6$ membranes are given in Figure 7.

The SAXS spectra for the membranes based on SPAEK-6F containing ILs are very similar. The membranes show small matrix peak and a shoulder at q = 0.0211 and 0.0335 Å^{-1} for the SPAEK-6F/EMIBF$_4$ and at q = 0.0219 and 0.0334 Å^{-1} for the SPAEK-6F/EMIPF$_6$ membranes, and the intensity of these peaks is related to the crystalline content of the membranes. A dotted line with a slope of -1 has been drawn in Figure 7 at small values of q, and the scattered intensity plots show

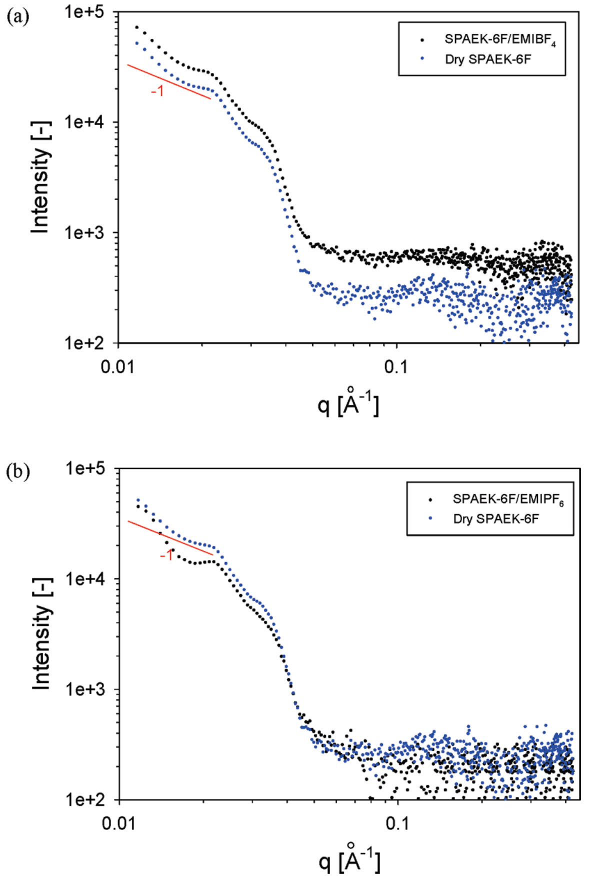

Figure 7. SAXS spectra of composite membranes: SPAEK-6F/EMIBF$_4$ (a) and SPAEK-6F/EMIPF$_6$ (b).

a slope of ~ -1 at small values of q. The matrix peak is related to the crystalline content of the membranes, and this was checked by the wide-angle X-ray diffraction given in Figure 8. The XRD pattern for the SPAEK-6F/EMIBF$_4$ membrane shows some sharper peaks superimposed on a broad peak at $2\theta = 16-23°$, which indicates the presence of a crystalline component in the amorphous membrane. However the small intensity of the peaks suggests that the amount of crystalline component is very small as compared with the amorphous part. The XRD pattern of the SPAEK-6F/EMIPF$_6$ membrane also shows a broad halo on which a sharp peak is superimposed, which also suggests the amorphous nature of the membrane. The presence of ILs has a plasticizing effect and increases the amorphous content of these membranes. The presence of small intensity sharp peaks is possibly due to the presence of some crystalline compounds in these membranes.

The absence of an ionomer peak in the SPAEK-6F based membranes can be either due to (i) a small difference in the electron density of the ionic clusters and the neutral hydrophobic polymer phase which does not lead to the formation of a small-angle scattering peak or (ii) the ionic groups which are randomly dispersed in the polymer matrix which accordingly results in the small size of ionic domains—not large enough to give rise to a visible peak. The different synthesis method used in the case of the random copolymer (SPAEK-6F) can also lead to a different structure. The absence of an ionomer peak in some cases is also explained to be due to an excess of the polymer chain rigidity as the presence of the ionomer peak is correlated to the flexibility of the neutral sequence (hydrophobic part) much more than that of the ionic sequence (hydrophilic part). Thus, the rigidity of the hydrophobic part also affects the reorganization of the structure as well as the formation of ionic domains. The polymer (SPAEK-6F) used in the present study is a random copolymer, and such polymers do not generally phase separate easily. In the case of sulfonated poly(aryl ether ketones), no side chains are present and there is a smaller difference between the hydrophilic/hydrophobic parts which lead to a less pronounced distinction in hydrophilic and hydrophobic domains as compared with Nafion.[38] The use of polymers with very dissimilar hydrophilic and hydrophobic parts may be desirable for improving the ion-clustering ability, provided the membranes fulfill other requirements needed for their use in PEFCs.

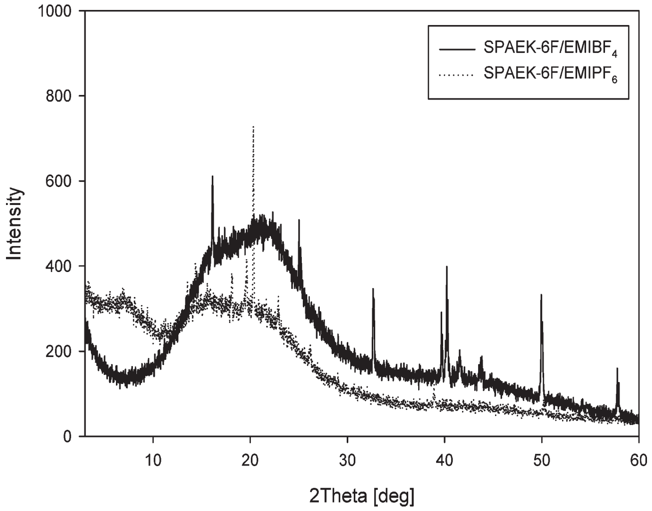

Figure 8. X-ray diffraction pattern for SPAEK-6F/EMIBF$_4$ and SPAEK-6F/EMIPF$_6$ membranes.

The general shape of the SAXS curves plotted on double-logarithmic scale for the SPAEK-6F based membranes containing the ILs (Figure 7) is quite similar to that observed for some other water swollen membranes based on various sulfonated polymers such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(ether ether ketone ketone) (SPEEKK), and sulfonated polyimides (SPIs).[45,46,48]

The morphology of the SPAEK-6F based membranes containing the ILs was also studied by TM-AFM and the micrographs (phase images) of the SPAEK-6F/EMIBF$_4$ and SPAEK-6F/EMIPF$_6$ membranes are given in Figure 9. The ionic domains appear to be randomly distributed in the polymer matrix, and as a result, the ionomer peak is also not observed in these membranes. The connectivity between ionic domains (which appears lighter) is also very poor, which contributes to lower value of ionic conductivity for these membranes as given in Figure 1b. The phase image for the SPAEK-6F/EMIPF$_6$ membrane shows ionic domains of varying sizes. The relatively better connectivity between ionic

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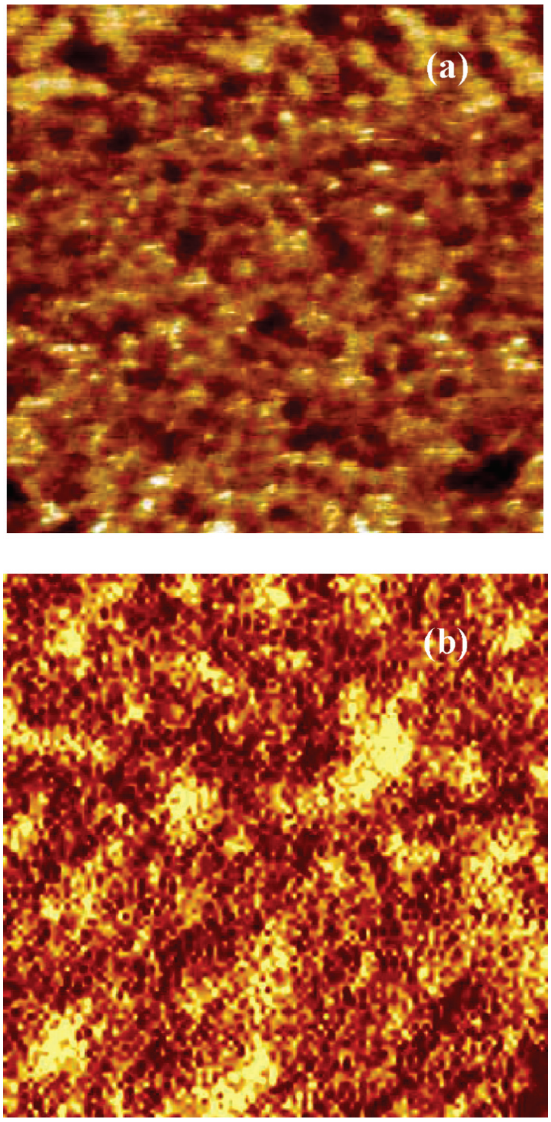

Figure 9. Tapping mode atomic force microscopy (TM-AFM) phase images (size 1 μm) of SPAEK-6F/EMIBF$_4$ (a) and SPAEK-6F/EMIPF$_6$ (b) membranes.

domains in the SPAEK-6F/EMIBF$_4$ membrane also supports the higher value of the ionic conductivity of this membrane as compared with the SPAEK-6F/EMIPF$_6$ membrane. This may also be related to the hydrophilic nature and lower viscosity of the IL (EMIBF$_4$) used in this membrane.

The ionic conductivity of sulfonated polymers generally increases with an increase in the degree of sulfonation (DS) and is also accompanied by deterioration in the mechanical properties of the membranes. For having reasonable mechanical strength along with higher value of ionic conductivity, the different membranes in the present work used polymer (SPAEK-6F) sulfonated with a DS equal to 40. The mechanical strength of the high conducting membranes containing EMIBF$_4$ was measured at room temperature. The tensile strength and strain of the Nafion/EMIBF$_4$ membrane at break are 5.496 MPa and 129%, respectively, whereas for the SPAEK-6F/EMIBF$_4$ membrane, the tensile strength and strain at break are 3.660 MPa and 186.2%, respectively. These values are lower as compared with the mechanical strength of dry Nafion (10 MPa), and as expected, sulfonated polymers show lower mechanical strength. However, the mechanical strength of the membranes containing ILs is sufficient for PEFC applications.

Conclusions

On the basis of SAXS and other studies on water free proton conducting polymer membranes based on recast Nafion and SPAEK-6F containing a pair of ionic liquids (EMIBF$_4$ and EMIPF$_6$), the following general conclusions can be made:

- Water free recast Nafion membranes containing ionic liquids show the presence of an ionomer peak, whereas it is not observed for membranes based on SPAEK-6F.
- The broadness of the ionomer peak indicates a wide distribution of the Bragg distance between ionic aggregates.
- The average distance between ionic aggregates is larger in the Nafion/EMIBF$_4$ than in the Nafion/EMIPF$_6$, and the ionic conductivity of the membranes also follows the same trend.
- The presence of the matrix peak at low q values in all the membranes based on recast Nafion and SPAEK-6F is due to the crystalline content of the membranes.
- The lower ionic conductivity of the membranes containing EMIPF$_6$ is due to the higher viscosity and the hydrophobic nature of the IL.
- The membranes have high ionic conductivity, are mechanically strong and thermally stable up to ~300 °C, and thus can be used at temperatures up to 200 °C .

The water free membranes containing ILs, studied in the present work, have been prepared by the solution casting technique and are not solvent swollen. The observation of an ionomer peak in the SAXS spectra of the membranes based on recast Nafion suggests the formation of ionic clusters, whereas its absence in the SPAEK-6F based membranes is due to the lower ion-clustering ability of the polymer in which the hydrophilic and hydrophobic parts are not very dissimilar due to the absence of any side-chain. Although a direct comparison of the SAXS results with water swollen Nafion membranes is not proper, the SAXS results for such water free membranes will be quite helpful in understanding the ion conduction mechanism of these membranes and will also help in the improvement of the design of such high temperature membranes being developed for PEFCs.

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