

MORPHOLOGICAL AND ELECTROMECHANICAL CHARACTERIZATION OF IONIC LIQUID / NAFION POLYMER COMPOSITES

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Abstract

Ionic liquids have shown promise as replacements for water in ionic polymer transducers. Ionic liquids are non-volatile and have a larger electrochemical stability window than water. Therefore, transducers employing ionic liquids can be operated for long periods of time in air and can be actuated with higher voltages. Furthermore, transducers based on ionic liquids do not exhibit the characteristic back relaxation that is common with water-swollen materials. However, the physics of transduction in the ionic liquid-swollen materials is not well understood. In this paper, the morphology of NafionTM / ionic liquid composites is characterized using small-angle X-ray scattering (SAXS). The electromechanical transduction behavior of the composites is also investigated. For this testing, five different counterions and two ionic liquids are used. The results reveal that both the morphology and transduction performance of the composites is affected by the identity of the ionic liquid, the cation, and the swelling level of ionic liquid within the membrane. Specifically, speed of response is found to be lower for the membranes that were exchanged with the smaller lithium and potassium ions. The response speed is also found to increase with increased content of ionic liquid. Furthermore, for the two ionic liquids studied, the actuators swollen with the *less* viscous ionic liquid exhibited a *slower* response. The slower speed of response corresponds to less contrast between the ionically conductive phase and the inert phase of the polymer. This suggests that disruption of the clustered morphology in the ionic liquid-swollen membranes as compared to water-swollen membranes attenuates ion mobility within the polymer. This attenuation is attributed to swelling of the non-conductive phase by the ionic liquids.

INTRODUCTION

Ionic polymer transducers are polymeric materials that exhibit electromechanical coupling due to their chemical makeup. These devices consist of an ionomer membrane plated on both surfaces with conducting metal electrodes. The most common polymer utilized for ionic polymer transducers is DuPont's NafionTM material. Transduction in NafionTM was first discovered by Sadeghipour *et al.* in 1992¹ and

was patented by Oguro in 1993.² The chemical structure of NafionTM is shown in Figure 1 below. As can be seen, NafionTM consists of a perfluorinated TeflonTM backbone with attached pendant side chains. These side chains are terminated in sulfonic acid groups and each of these acid groups is neutralized by an associated cation. Transduction in these materials is thought to arise from the electrically- or mechanically-induced motion of these cations; the anions are covalently bound to the polymer and cannot move. Therefore, these ionic polymer transducers can function as either sensors or actuators.

There are several key aspects of these materials that are intimately linked to the transduction. First, because the mechanism of transduction is charge motion, the electromechanical coupling is maximized by increasing the charge capacity (capacitance) of the device. This is done typically by plating the membrane with interpenetrating platinum electrodes using an "impregnation / reduction" process. This process was first developed by Millet *et al.* in 1989 and has since been studied and improved significantly.³⁻⁶ Recently, Akle and Leo have developed a direct assembly process for fabricating the electrodes from high-surface area metal powders.⁷ These authors have shown that the strain generated by an ionic polymer transducer is linearly proportional to its capacitance.

A more important consideration for the current work is the requirement of a solvent in order for these transducers to function. In its dry form, the cations within the NafionTM membrane are tightly bound to the sulfonate exchange sites and cannot move in response to an input. In this case, the ionic conductivity of the membrane (a measure of the mobility of the ions within the polymer) is very low and transduction cannot occur. Therefore, the polymer must be swollen with a solvent that will associate with both the cations and the anionic exchange sites, thus allowing the cations to move about within the polymer matrix. Traditionally, water has been the solvent of choice for ionic polymer transducers. This is because water is protic and highly polar and will therefore effectively solvate both the cations and the exchange sites. The water serves to shield the charges from each other and allows cation motion to occur.⁸ The ionic conductivity is increased and transduction can

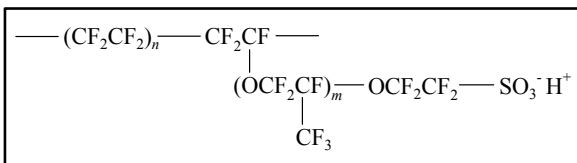


Figure 1. The chemical structure of Nafion™ polymer.

now occur. Water has several disadvantages as a solvent for ionic polymer transducers, however. First, water is volatile and will quickly evaporate out of the membrane. This prohibits the use of these devices for long periods of time in an air environment. Bennett and Leo have shown that an ionic polymer actuator swollen with water would only operate for about 2000 cycles in air.⁹ Water-swollen transducers could also clearly not be used in space applications. Second, the maximum voltage that can be applied to an ionic polymer transducer is determined by the electrochemical stability limit of the solvent. For a platinum electrode, electrolysis of water will occur at a potential of 1.23 V.

In order to move ionic polymer transducer technology out of the laboratory, a new solvent must be found that maintains or improves the performance of water-based devices while allowing for long-term operation outside of a water environment. The current work focuses on the use of ionic liquids in this regard. Ionic liquids are salts that exist in their liquid state at low temperature. The low melting temperature of these materials arises from the bulky and cumbersome nature of the corresponding ions. Ionic liquids are attractive for use in ionic polymer transducers because they have an immeasurably low vapor pressure, a large electrochemical stability window, and a high inherent ionic conductivity. Therefore, the use of ionic liquids to replace water in ionic polymer transducers could potentially allow these devices to be operated in air for long periods of time and could allow for higher actuation voltages, thus increasing the transducers' energy density.

The concept of using ionic liquids to replace water in ionic polymer transducers was first demonstrated by Bennett and Leo in 2004.⁹ In this work, actuation of an ionic liquid-swollen Nafion™ transducer was demonstrated for more than 250,000 cycles in air. However, several inconsistencies were observed between the electromechanical response of the ionic liquid samples as compared to water-based materials. For example, the speed of response of the ionic liquid-swollen materials is reduced. This effect could possibly be explained by the higher viscosity of the ionic liquids as compared to water. Also, the charac-

teristic back-relaxation that has often been observed in water-based ionic polymer transducers is notably absent in the ionic liquid-based devices. Additional work by Bennett and Leo has also suggested that the cation has little effect on the electromechanical response of the transducers.¹⁰ Again, this is a departure from the behavior of conventional water-swollen ionic polymer transducers. For example, Abe *et al.* and Nemat-Nasser and Wu have characterized the response of water-swollen transducers in various cation forms and have noted striking differences in the characteristics of the response.^{11, 12}

In order to understand the causes of the behavior of the ionic liquid-swollen transducers, a detailed study of the polymer / ionic liquid composites must be carried out. This study will include a characterization of electromechanical transduction in these materials. Another portion of this study will be an analysis of the ionic interactions within the composite. For the water-swollen materials, the interaction of water with the cations and sulfonate exchange sites is relatively straightforward. However, upon incorporation of an ionic liquid into the membrane, two new ions are introduced. The interaction that these ions will have with the polymer is not well understood.

This paper will focus on understanding the effect of the ionic liquids on the morphology of the polymer and how this effect relates to transduction. The process for fabricating the ionic liquid-based transducers will be presented, and a discussion of the morphological characterization of the Nafion™ / ionic liquid composites will be provided. The results of the electromechanical characterization will also be presented and conclusions linking the transducers' performance to morphology will be formulated.

TRANSDUCER FABRICATION

The transducers studied in this work are based on the Nafion™-117 membrane, which has a nominal thickness of 183 microns and an equivalent weight of 1100. Two ionic liquids are used are 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-Im). The structures and relevant properties of these ionic liquids are shown in Figure 2 and Table 1, respectively. As can be seen, the cation of these two ionic liquids is the same di-substituted imidazolium ring but the anions differ. The anion of the EMI-Im ionic liquid is larger and more fluorinated; this is responsible for the more hydrophobic nature of this ionic liquid. The EMI-Im ionic liquid also has a slightly lower viscosity than the EMI-Tf ionic liquid and is more dense, but

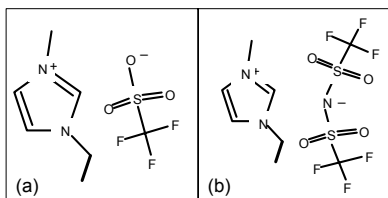


Figure 2. The structure of the (a) EMI-Tf ionic liquid and (b) EMI-Im ionic liquid.

Table 1. Relevant properties of the ionic liquids studied.

| ionic liquid | viscosity (cP @ 25°C) | density (g/cm ³) | melting point (°C) |
|--------------|--------------------------|---------------------------------|-----------------------|
| EMI-Tf | 45 ¹³ | 1.390 ¹³ | -9 ¹³ |
| | 43 ¹⁴ | 1.383 ¹⁴ | -10 ¹⁴ |
| EMI-Im | 34 ¹³ | 1.520 ¹³ | -3 ¹³ |

| ionic liquid | conductivity (mS/cm @ 25°C) | sat. water content (mass % @ 20°C) |
|--------------|--------------------------------|---------------------------------------|
| EMI-Tf | 8.6 ¹³ | soluble ¹³ |
| | 9.3 ¹⁴ | |
| EMI-Im | 8.8 ¹³ | 1.4 ¹³ |

most of the other properties of these two materials are very similar.

The preparation of the NafionTM membranes involves plating the surfaces of the membrane with interpenetrating platinum electrodes using the “impregnation / reduction” process. In this process, the NafionTM membrane is alternately soaked in solutions of tetraammineplatinum chloride and sodium borohydride. The process is repeated 4-6 times and results in a disperse platinum layer that covers the surface of the membrane and penetrates into the thickness of the membrane to a depth of 10-20 microns. This process has been described in detail by Rashid and Shahinpoor⁴ and Millet *et al.*^{5,6} After the platinum plating process the membrane is boiled in 1.0 M sulfuric acid in order to exchange it into the proton ion form. The membrane is then soaked in a 0.5 M chloride salt of the desired ion in order to exchange it into a specific ion form. The five cations used in the present study are lithium (Li), potassium (K), cesium (Cs), tetraethylammonium (TEA), and 1-ethyl-3-methylimidazolium (EMI). After soaking for several days in the salt solutions, the membranes are soaked for one day in de-ionized water to remove and unbound co-ions and are then dried under vacuum at 110°C overnight. The dry membranes are then swollen with an ionic liquid.

In order to incorporate these ionic liquids into the NafionTM membrane, a volatile solvent that is highly miscible with the ionic liquid and the membrane is used. For this work, methanol was chosen as the swelling agent. Gebel *et al.* have reported that dry

NafionTM membranes will increase in volume by 51% when equilibrated in pure methanol.¹⁵ Methanol is also miscible with both of the ionic liquids used and is highly volatile so it can be easily removed after the incorporation process. In the current process, the ratio of ionic liquid to methanol is held constant at 1 to 1 by volume. The dry membranes are soaked in the methanol / ionic liquid mixture for a period of 3 hours, after which time the membranes are removed from the methanol / ionic liquid mixture and dried under vacuum at 110°C for 3 hours. The soaking process is carried out either at room temperature (25°C) or in an oven at 70°C; the use of a higher temperature soak results in more ionic liquid being absorbed into the membrane. The incorporation process has also been performed at 90°C, but at this temperature the methanol evaporates very quickly and the swelling is less controlled. Results obtained for all three processes will be presented. The amount of swelling of the membranes has also been observed to be a function of the counterion within the membrane. This is attributed to the use of methanol as a swelling agent during the swelling process. Because the smaller ions (Li, K) have a higher charge density and are more hydrophilic, they will have a greater affinity for methanol and will therefore result in more of the methanol / ionic liquid mixture being absorbed into the membranes.

After the incorporation of the ionic liquids, a second electrode is applied to the membranes to improve the surface conductivity of the transducers. This electrode consists of a thin gold foil and is applied by hot-pressing. For the samples that were tested by SAXS, no platinum or gold electrode was applied to the polymer, but the exchange of the membrane into the appropriate cation form and incorporation of the ionic liquid was performed as described above. The content of ionic liquid in the membranes reported is the volume of ionic liquid in the membrane as a percentage of the dry volume of the membrane. The dry volume of the membrane and the volume of the ionic liquid were computed from the dry and swollen weights of the membrane and the densities of the dry membrane and the ionic liquid. The densities of the platinum-plated and un-plated dry membrane in all five cation forms were calculated from weight and volume measurements.

MORPHOLOGICAL CHARACTERIZATION

Although the specific morphology of the NafionTM polymer is still a source of debate,¹⁶ one of the most common morphological models of NafionTM is that of inverted micellar clusters containing the ionic species and solvent and embedded in an inert fluorocarbon

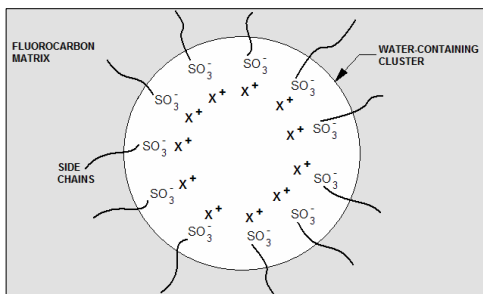


Figure 3. A visual representation of the inverted micelle model proposed by Gierke *et al.*^{18, 26}

phase—see Figure 3. This model of ion clustering in NafionTM membranes was first proposed by Gierke.¹⁷ The clustered morphology of NafionTM has been studied by small-angle X-ray scattering (SAXS),^{18, 19} by atomic force microscopy (AFM),^{20–22} and by transmission electron microscopy (TEM).^{23–25} Based on these studies, the clusters are thought to be about 4–5 nm in diameter and interconnected by narrow channels about 1 nm in diameter. It is this networked cluster morphology of NafionTM that is responsible for its unique ion transport properties.

One of the available means of characterizing the morphology of a polymer is small-angle X-ray scattering (SAXS). In SAXS, an X-ray beam is passed through a sample and collected on a detector screen. The interaction of the X-rays with the sample creates a constructive / destructive interference pattern that is related to order in the sample, such as crystallinity or phase separation. In NafionTM, SAXS has been used to characterize the order created by the presence of the ionic cluster domains within the fluorocarbon matrix. The test provides two useful pieces of information. First, the contrast between the constructive and destructive fringes is related to the regularity of the order within the material. Second, the location of the constructive fringes (relative to the test geometry) correlates to the spacing of the ordered domain in the material. Therefore, in NafionTM SAXS can be used to measure the relative degree of contrast between the cluster phase and the fluorocarbon phase and also the mean spacing between the clusters. It cannot be used to measure the size or shape of the clusters, however. Furthermore, the lattice spacing as measured by SAXS is the *center-to-center* distance between the clusters. Information cannot be gained from this test about the proximity of the cluster boundaries.

The SAXS testing in this work was performed at the Army Research Laboratory, Multifunctional Materials Branch with the assistance of Dr. Rick Beyer. The X-ray generator was of the rotating drum type

and it was excited at 40 kV, with a driving current of 60 mA. The wavelength of the resulting X-rays was 1.542 Å. The positions of the periodic fringes observed in the SAXS data are related to the lattice spacing through Bragg’s law:

$$n\lambda = 2d\sin(\theta), \quad (1)$$

where λ is the wavelength of the incident X-rays, θ is the scattering angle, d is the lattice spacing (mean intercluster distance), and n is an integer value related to the periodicity of the fringe pattern. Similarly, the length of the scattering vector, q is given by

$$q = \frac{4\pi}{\lambda}\sin(\theta). \quad (2)$$

The mean intercluster spacing is therefore related to the length of the scattering vector by:

$$d = \frac{2\pi}{q}, \quad (3)$$

where n is assumed to be 1, corresponding to the primary scattering harmonic.

The results of the SAXS testing are summarized in Figures 4 and 5. Note that the absolute amplitude of the curves is arbitrary and they have been shifted vertically for clarity. The low swelling results shown are for those polymers that were swollen with the methanol / ionic liquid mixture at room temperature whereas the high swelling results are for the polymers treated at 70°C. The peak or shoulder in the data at high q values corresponds to the ionic domains in the material. In some of the plots a shoulder is observed at low q values. This could be related to crystallinity within the polymer. As can be seen from the plots, the mean intercluster spacing is around 3–5 nm. This is similar to the values observed by Gierke and Hsu for NafionTM swollen with water to similar swelling levels.¹⁹ In some of the plots, a distinct upturn is observed at low q values. The origins of this feature are unknown, but it has been observed in water-swollen samples and has been tentatively attributed to large-scale order resulting from agglomeration of the ionic clusters.²⁷

A very interesting feature of the results shown in Figures 4 and 5 is that the shape of the SAXS curves seems to be relatively independent of the counterion within the membrane. This is contrary to the findings of Gierke and Hsu for water-swollen NafionTM in different cation forms.¹⁹ Those authors found that the height of the clustering peak increased substantially as the size of the cation was decreased. In their work the membranes were hydrated by boiling in de-ionized

water and therefore the hydration level was not controlled directly but rather was a function of the size of the cation. Because the smaller cations are more hydrophilic, those membranes that were neutralized with the smaller cations exhibited a larger degree of swelling. For the inverted micelle “cluster” model discussed here, the water will reside exclusively within the clusters. Therefore, increasing the amount of water inside the membrane will result in an increase in the water content of the clusters with no corresponding change to the fluorocarbon matrix phase. This will result in an increase in the electron density contrast between the cluster phase and the matrix phase, which will result in an increase in the height of the SAXS peak associated with the regularity of the clusters.

The fact that the height of the clustering peak seems to be relatively independent of the cation and the degree of swelling could suggest that the ionic liquid does not swell the clusters exclusively. Based on the results, it seems reasonable that the ionic liquid could be partially incorporated into the fluorocarbon phase. This argument is supported by the fact that the height of the clustering peak is much lower for the EMI-Im ionic liquid than for the EMI-Tf ionic liquid, even at low swelling levels. At the higher swelling level, the clustering peak in the samples swollen with the EMI-Im ionic liquid almost disappears completely. Because the EMI-Im ionic liquid is more fluorinated and is hydrophobic, it should be more miscible with the hydrophobic fluorocarbon phase of NafionTM than the EMI-Tf ionic liquid. Therefore, it seems that the presence of the ionic liquids within the NafionTM polymer disrupts the clustered morphology as compared to water. This is observed as a decrease in the phase contrast as measured by SAXS. Also, the EMI-Im ionic liquid seems to disrupt this morphology to a greater extent than the EMI-Tf ionic liquid.

Although the height of the clustering peak does not seem to change as the cation or swelling level is changed, the position of the peak does shift. The position of the peak corresponds to the lattice spacing in the material; in the case of NafionTM it is a measure of the mean intercluster distance. As can be seen from Figure 6, the cluster spacing increases linearly as the amount of ionic liquid within the polymer is increased. This same linear trend was observed by Gierke and Hsu for NafionTM swollen with water.¹⁹ A very interesting phenomenon is observed that is not consistent with their findings, however. The relationship between the intercluster spacing and the swelling level of the polymer is found to also be a function

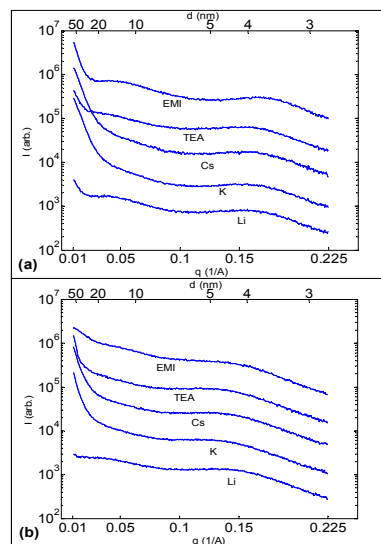


Figure 4. SAXS result for NafionTM-117 membranes in various counterion forms swollen with EMI-Tf ionic liquid at (a) low swelling level, (b) high swelling level.

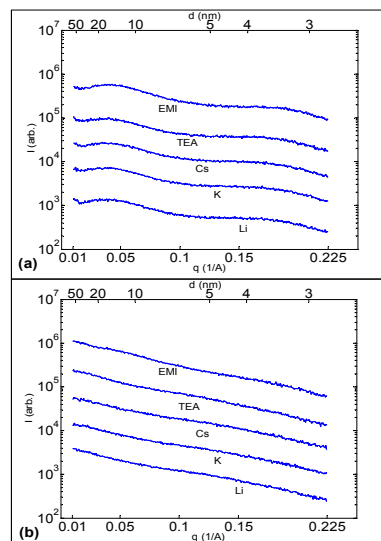


Figure 5. SAXS result for NafionTM-117 membranes in various counterion forms swollen with EMI-Im ionic liquid at (a) low swelling level, (b) high swelling level.

of the counterion. Two linear trends are observed in Figure 6, one that corresponds to the lithium and potassium ions, and one that corresponds to the other three ions (Cs, TEA, EMI). This distinction is very clear for the EMI-Tf ionic liquid. Although this effect is not as clear for the EMI-Im ionic liquid, this can likely be attributed to the difficulty in accurately determining the position of the peaks in the EMI-Im SAXS data. The result of this is that the clusters will be more closely spaced for the lithium and potassium ion forms of the membrane than for the other ion forms, for an equivalent level of swelling with ionic

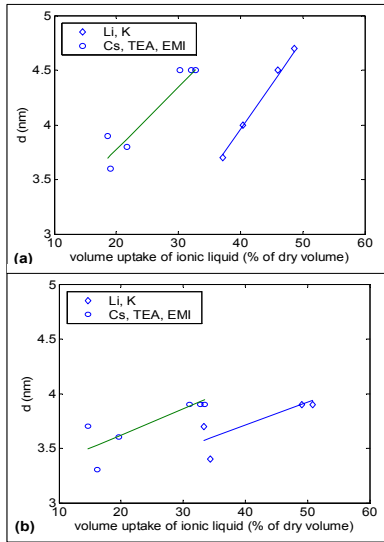


Figure 6. Mean intercluster spacing versus swelling level for (a) the EMI-Tf ionic liquid, (b) the EMI-Im ionic liquid.

liquid. The specific reasons for this are unclear, but the lithium and potassium ions are smaller and have a higher charge density than the other ions. This could indicate that the size of the counterion affects the ion associations within the ionic liquid-swollen membrane and therefore the way that the ionic liquid swells the membrane. The mean intercluster spacing is also found to be higher for the EMI-Tf ionic liquid than for the EMI-Im ionic liquid. Again, the reasons for this are at this point unclear, but this could be related to the decrease in phase contrast observed in the EMI-Im membranes as compared to the EMI-Tf membranes.

ELECTROMECHANICAL CHARACTERIZATION

In addition to the morphological characterization discussed thus far, a group of ionic liquid-swollen and metal-plated NafionTM membranes were also studied as electromechanical transducers. These transducers were fabricated according to the procedures described in Section 2. These transducers were characterized in the time domain by measuring their response to a step voltage input and in the frequency domain by measuring the frequency response function between applied voltage and generated strain and between applied charge and generated strain. The electrical impedance of each transducers was measured. For a detailed description of the testing methods refer to Bennett and Leo.⁹

A representative free strain frequency response is shown in Figure 7a; the first resonant peak of the transducer can be seen at about 17 Hz. As can be seen from the figure, there is some rolloff in the re-

sponse as the frequency is increased. This rolloff is indicative of limited charge mobility and is associated with a slower speed of response in the ionic liquid-swollen materials as compared to the water-swollen materials. Several possible reasons for the limited charge mobility are the viscosity of the ionic liquid, the amount of ionic liquid present in the polymer, the morphology of the ionic liquid-swollen polymers, and the ion associations within the polymer. The ion mobility is also manifested in the impedance measurement—see Figure 7b. The high impedance of about 70 Ω at high frequencies indicates that the ions within the material are not able to respond to a rapidly changing input signal; the high frequency impedance of water-swollen transducers is typically less than 5 Ω . If the generated strain is normalized by the charge accumulated on the transducer and the size of the transducer (because the charge capacity is a function of the device area) then the frequency dependence of the response is removed. For these materials, the normalized strain per unit charge was found to be between 20 and 45 $\mu\epsilon/(C/m^2)$. This value does not depend on the identity of the ionic liquid, on the amount of ionic liquid within the polymer, or on the cation in the polymer. This is evidence for the notion that strain generation in ionic polymer actuators arises from charge motion. Akle and Leo have performed similar measurements on water-swollen materials and have shown that the normalized strain per charge remains constant even among transducers with dramatically different voltage response characteristics.²⁸

The time response of these transducers to a step voltage input was also measured—see Figure 8. There are several interesting features of this response. First of all, neither of the ionic liquids exhibit the back relaxation that has commonly been observed with water-swollen transducers. In fact, the materials seem to exhibit some forward relaxation. This is especially true for the EMI-Tf ionic liquid. As can be seen, the actuator swollen with this ionic liquid responds quickly when the step is first applied, then continues to move slowly towards the anode. The step response has also been measured for longer times and this forward relaxation is sometimes found to continue for 6-8 minutes. Also interesting is the distinct difference in the shape of the step responses for the two ionic liquids. The EMI-Tf ionic liquid samples clearly respond faster than the EMI-Im samples. Additionally, the response of the EMI-Tf samples seems to involve several stages with different time constants. This could indicate that multiple actuation mechanisms are responsible for this motion. By contrast, the actuators swollen with the EMI-

Im ionic liquid move more slowly and the response more closely approximates an exponential rise. Also, the EMI-Im samples moved to an average maximum strain of $1000 \mu\epsilon$ for a two-minute step as compared to $1300 \mu\epsilon$ for the EMI-Tf samples. While this difference could be due to the difference in the speed of the response of the actuators, it could also be indicative of a fundamental difference in the transduction mechanism between these two materials.

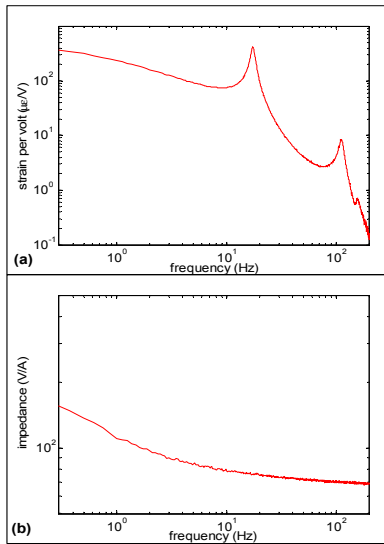


Figure 7. (a) Strain-to-voltage frequency response and (b) electrical impedance for a Nafion™ transducer in the cesium ion form and swollen with 47.0% EMI-Tf ionic liquid.

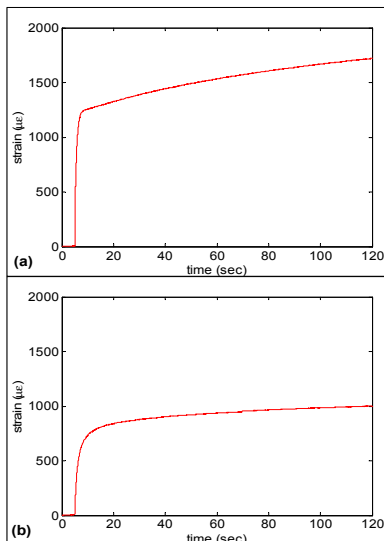


Figure 8. Response to a 1.5 V step for Nafion™ transducers in the cesium ion form and swollen with (a) 47.0% EMI-Tf ionic liquid, (b) 35.4% EMI-Im ionic liquid.

In addition to the differences between the two ionic liquids, the content of ionic liquid within the trans-

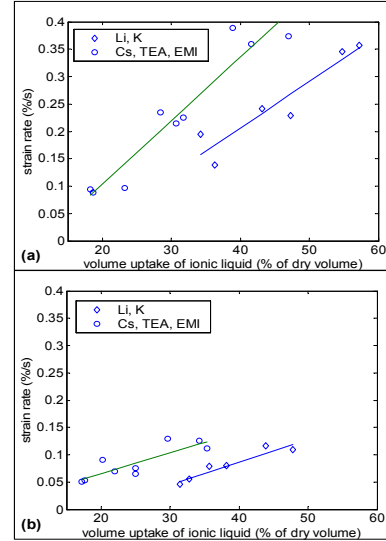


Figure 9. The initial strain rate vs. swelling level for the transducers swollen with (a) the EMI-Tf ionic liquid, (b) the EMI-Im ionic liquid.

ducer has also been found to have a profound effect on the response. Specifically, the speed of the response is affected by the amount of ionic liquid in the polymer. Figure 9 shows the initial slope of the step response over the range of swelling levels for both of the ionic liquids. As can be seen, the initial strain rate increases as the amount of ionic liquid is increased. This is due to the increase in the mobility of the ions in the more swollen samples. The initial strain rate is also higher for the EMI-Tf ionic liquid than for the EMI-Im ionic liquid. The rolloff in the strain-to-voltage frequency response has also been used as a measure of the speed of response of the transducers, although the data is not shown due to space restrictions. For the EMI-Tf ionic liquid this rolloff was found to vary from 8-17 dB/decade and for the EMI-Im ionic liquid it was found to vary from 10-19 dB/decade. The results are consistent with the results obtained from the step responses in that the rolloff decreases as the swelling level is increased. The increase in the speed of the response as the swelling level is increased is accompanied by a decrease in the high frequency resistivity of the samples, which also indicates increased mobility of the ions within the polymer—see Figure 10. The resistivity is calculated from

$$\rho = \frac{\Omega A}{t}, \quad (4)$$

where Ω is the mean impedance from 100 Hz to 200 Hz, A is the area of the transducer (parallel to the electrodes), and t is the thickness of the transducer.

One of the most interesting aspects of these plots is the clear distinction that can be observed between

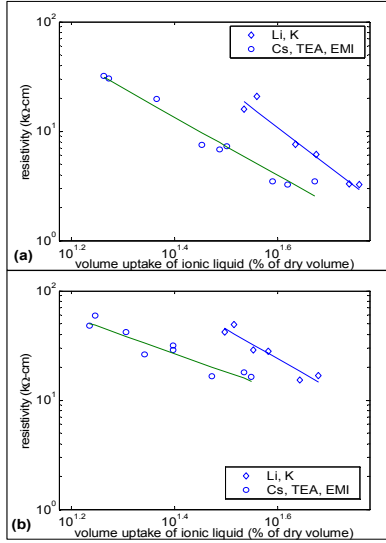


Figure 10. High frequency resistivity vs. swelling for the transducers swollen with (a) the EMI-Tf ionic liquid, (b) the EMI-Im ionic liquid.

the behavior of the lithium and potassium ions and the other ions. This distinction was also observed in the morphological characterization of these materials. The SAXS results revealed that the mean intercluster spacing was smaller for the lithium and potassium ions than for the other ions at equivalent swelling levels. The transduction results reveal that the high frequency resistivity was higher and the speed of response lower for the lithium and potassium ions than for the other ions. The frequency domain analysis also exhibited a clear distinction between the two groups of ions, as the lithium and potassium ions tended to exhibit more rolloff in the strain-to-voltage frequency response than the other ions, for equivalent levels of swelling.

Both the dependence of resistivity on swelling and speed of response on swelling are found to be a function of the cation, although the results seem to indicate that for the group of cations selected, only two distinct relationships are observed. However, both of these metrics relate to the mobility of the ions within the polymer. Therefore, the relationship between response speed and resistivity should not exhibit a dependence on the cation. This is in fact the case—see Figure 11. Interestingly, although Figure 11 exhibits no distinction between the different cations, the EMI-Tf ionic liquid is shown to produce a faster response than the EMI-Im ionic liquid for similar resistivity values. This could indicate a fundamental difference in the physics of transduction between the two materials.

By plotting the speed of response against the mea-

sured resistivity, the differences between the two groups of ions are reduced and a true relationship between electrical impedance and mechanical actuation is revealed. In the same way, the speed of response has also been plotted against the mean intercluster spacing—see Figure 12. In this case the data was fitted to an analytical curve, as the transduction results were obtained for a different group of samples than the SAXS results, although the processing was the same for both groups. As can be seen, the trend is for the speed of response to increase as the mean intercluster spacing is increased. Although the lithium

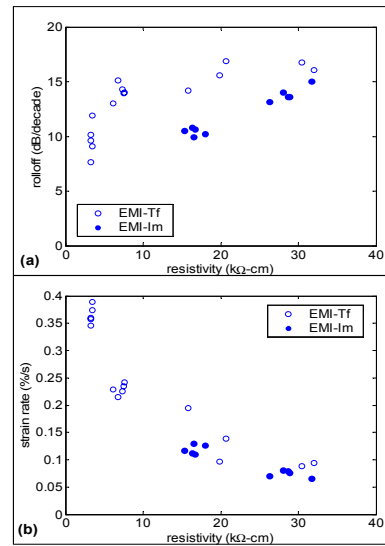


Figure 11. (a) Rolloff of the strain-to-voltage frequency response and (b) Initial slope of the step response vs. high frequency resistivity.

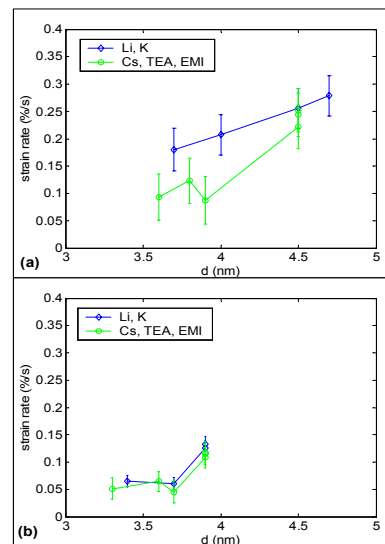


Figure 12. The initial slope of the step response vs. the mean intercluster spacing for (a) the EMI-Tf samples, (b) the EMI-Im samples.

and potassium ions appear to exhibit a slightly faster response speed than the others, the relationship between transduction and morphology does not exhibit a strong dependence on the cation. The relationship is distinctly different for the two ionic liquids, however. Again, this could indicate that the ionic liquids interact with the membrane in fundamentally different ways.

DISCUSSION OF RESULTS

A morphological and electromechanical characterization of NafionTM polymer transducers swollen with ionic liquids has been presented. For this study, two ionic liquids were used and the absorption of the ionic liquids into the membranes was varied over a range. The membranes were neutralized with one of five different cations. In this way, the effect of the cation, the ionic liquid, and the degree of swelling on the morphology and electromechanical response have been investigated. Although this data taken alone does not support any indisputable conclusions, clear trends can be observed and theories can be formulated to explain these trends. For example, the mean intercluster spacing, high frequency resistivity, and speed of actuation response are all found to depend on the cation. For these parameters, two distinct relationships are observed: one for the lithium and potassium cations and another for the cesium, tetraethylammonium, and 1-ethyl-3-methylimidazolium cations. The main difference between these two groups of ions is that the lithium and potassium ions are much smaller than the others. For this reason, they have a higher charge density; the charge density will affect the strength of associations with adjacent ions. Therefore, the most likely explanation for the observed phenomenon is that the ion associations within the NafionTM / ionic liquid composite are fundamentally different for the NafionTM that is neutralized with the smaller cations than for the NafionTM that is neutralized with the larger cations. Infrared spectroscopy and nuclear magnetic resonance (NMR) testing are currently underway to probe the ion associations within these composite materials.

The relationship between the speed of the actuation response and the high frequency resistivity are found to be independent of the cation. This is reasonable as both of these metrics are related to the mobility of the ions in the polymer. Thus, the response speed should be directly related and independent of the cation, the ionic liquid, or the amount of ionic liquid within the polymer. The data seems to indicate that the relationship between response speed and resistivity is indeed independent of the cation and the

degree of swelling, but the same relationship is not observed for both of the ionic liquids. In fact, the samples that were swollen with the EMI-Tf ionic liquid exhibit a faster speed of response than the samples swollen with the EMI-Im ionic liquid, even for equivalent values of resistivity. This would seem to indicate that the two ionic liquids participate in the transduction in different ways.

In fact, differences in the polymer / ionic liquid interactions can be immediately observed in the SAXS results. For example, the height of the SAXS peak associated with the ionic domains is much lower for the EMI-Im ionic liquid than for the EMI-Tf ionic liquid. Also, the mean intercluster spacing for the EMI-Im ionic liquid is smaller than for the EMI-Tf ionic liquid. Although specific conclusions about the morphology of the polymer cannot be drawn from the SAXS data alone, the results would seem to suggest that the presence of the EMI-Im ionic liquid disrupts the clustering within the material and reduces the contrast between the ionic domains and the fluorocarbon phase. This is reasonable as the EMI-Im ionic liquid is likely more miscible with the fluorocarbon phase than the EMI-Tf ionic liquid.

The net result of this disruption seems to be an attenuation of the mobility of the ions within the polymer. This can be seen in the relationship between response speed and mean intercluster spacing. Even for equivalent cluster spacings, the response speed of the EMI-Im samples is lower than the speed of the EMI-Tf samples. This can be explained as follows. Because the EMI-Tf ionic liquid swells the clusters of the polymer, the increase in mean intercluster spacing is due primarily to the increase in the size of the clusters. When the clusters grow larger, their centers become farther apart and this is reflected in the SAXS data. The edges of the clusters become closer together and ion transport between adjacent clusters becomes easier. However, based on the data, the EMI-Im ionic liquid seems to swell both the clusters and the fluorocarbon phase. In this case, the increase in the mean intercluster spacing is not caused solely by the increase of the cluster size. Rather, it is partially due to the size increase of the space *between* the clusters. Based on this argument, the proximity of the clusters to each other would be less in the polymer swollen with EMI-Im ionic liquid than in the polymer swollen with the EMI-Tf ionic liquid, *even though the center-to-center distance (mean intercluster spacing) may be the same*. For this reason, it would be more difficult for the ions to move between adjacent clusters in the EMI-Im-swollen polymer and therefore the speed of response would be lower. From

a morphological standpoint, this argument explains why the membranes swollen with the EMI-Tf ionic liquid exhibit superior transduction performance, although more data is needed to strengthen the claim.

CONCLUSIONS

Ionic liquids are demonstrated as viable solvents for ionic polymer transducers. The advantages of ionic liquids over water is their low volatility and large electrochemical stability window. Small-angle X-ray scattering is used to probe the morphology of Nafion™ membranes swollen with two different ionic liquids. This data reveals that the ionic liquids disrupt the clustered morphology of Nafion™ as compared to water, and that one of the ionic liquids disrupts this morphology to a greater degree. Electro-mechanical characterization reveals that this disruption inhibits ion motion within the polymer. This can be attributed to swelling of the non-conductive phase in the ionic liquid-swollen membranes. The characteristics of the transducers' response is also seen to be a function of the cation within the polymer. This is initially attributed to differences in the ion associations within the membrane, although further testing is underway to confirm this.

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