# The Effect of Viscosity and Ion Size on the Transduction of Ionic Polymer Metal Composite Actuators

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## Abstract

Ionic polymer membranes plated with platinum and gold serve as actuators when a small potential is applied. However, the water used to hydrate the membrane evaporates during use, decreasing actuator performance. Ionic liquids are being considered as a replacement for water because of their low vapor pressure. Prior studies show that the large ion size and high viscosity of ionic liquids slow the response time of the polymer membrane when a voltage is applied. This study examines the relationships of ion size and viscosity to transduction by modeling ionic liquids with inexpensive salts of varying ion size and glycerol/water solutions. Based on these results several ionic liquids were selected and tested for use as membrane solvents. This study includes frequency response, step response, and impedance tests of samples impregnated with $Li^+$, $K^+$, $Cs^+$, $TMA^+$, $TEA^+$, and $TBA^+$. Actuators solvated in solutions with a viscosity similar to 70–80 wt. % glycerol solutions (18–46 cP) and cation size similar to that of $TMA^+$ (0.347 nm) appear to yield the best results. When used as the membrane solvent, the ionic liquid 1-ethyl-3-methyl imidazolium trifluoromethanesulfonate (IL #3) resulted in the greatest strain per charge per area of the three ionic liquids tested in this study.

## 1. Introduction

Ionic polymer metal composites (IPMCs) are smart materials being investigated for applications as actuators and sensors. These materials require low operation voltages of 1–5 V and act as simple mechanical devices. When an electric field is applied across the IPMC, the movement of cations and water molecules inside the membrane causes the actuator to bend toward the anode. Optimum transduction occurs when an actuator exhibits maximum deflection, quick response time, and no back relaxation toward the original position after deflection. IPMCs act as transducers because they convert electrical energy to mechanical motion, or vice versa.

The IPMCs are manufactured by plating an ionic polymer membrane with a thin layer of metal. The majority of work in this area uses a Nafion™ polymer membrane plated with a thin layer of platinum metal, then with a layer of gold metal to improve surface conductivity.[1, 2] Previous work established a procedure for manufacturing IPMCs with repeatable mechanical and electrical properties.[1]

The degree of hydration of the polymer is critical to membrane transduction, but previous work has been limited by the evaporation of the water from the membrane during testing. This dependency on hydration limits the applications of IPMCs to aqueous environments.[3] Ionic liquids are being considered to replace water as the IPMC membrane solvent, which would extend their use to non-aqueous environments. Some potential applications for the actuators are heart-assist devices, catheter guidance, and blood pressure measurement devices.[4]

Ionic liquids are room temperature molten salts made up of dissociated cations and anions.[5] These liquids have low vapor pressure at room temperature and therefore evaporate more slowly than water. It is estimated that approximately one trillion room-temperature ionic liquids exist.[6]

Preliminary experiments using ionic liquids as membrane solvents show that transduction and the resulting deflection occur more slowly than when water is used. Slow actuation may result from the viscosity of the solution and the relatively large ion size. Seven ionic liquids were selected for characterization and evaluation on the basis of similar cation and anion combinations. The seven ionic liquids chosen were:

- tetramethylammonium bis(trifluoroethyl)imide
- tetramethylammonium tris(pentafluoroethyl) trifluorophosphate
- 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
- 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate
- trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide
- trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl) trifluorophosphate
- 1-ethyl-3-methylimidazolium trifluormethansulfonate

## 2. Procedure

The use of ionic liquids as membrane solvents in IPMCs has only recently been studied, and the characterization of the effects of using ionic liquids is not well documented. These liquids have a large range of viscosities and ionic radii, both of which are thought to have an effect on the transduction of IPMCs. Therefore, this study used membrane solvents of varying viscosity and ion size to model the effects on the transduction of IPMCs to help determine an optimum range of viscosity and ionic radius for selecting an ionic liquid.

Six salt solutions were mixed using lithium ($Li^+$), cesium ($Cs^+$), potassium ($K^+$), tetramethylammonium ($TMA^+$), tetraethylammonium ($TEA^+$), and tetrabutylammonium ($TBA^+$) as the cations and water as the solvent. A sheet of platinum-plated and gold-plated Nafion™ was cut into 36 specimens measuring 4 by 35 mm. Six IPMCs were placed in each of the salt solutions and put into an oven at 100°C for two days. Several days prior to testing, the six IPMCs in each salt solution were removed from the solution and dried for 48 hours at approximately 80°C between steel plates with copper spacers. Six glycerol and water solutions of 0, 60, 70, 80, 90, and 100 wt. % glycerol were produced to effectively study a range of different viscosities. After verifying the six solution viscosities using a Brookfield DV-II$^+$ viscometer, published values were used for the remainder of the project.[7] One cation-impregnated IPMC was placed into each glycerol solution and held at 100°C for 24 hours. This resulted in 36 samples impregnated with six cations and solvated in six fluids of varying viscosity.

## 3. Results and Discussion

### 3.1 Frequency Response Characterization

Frequency response tests conducted on each of the 36 samples measured voltage, current, and tip displacement to determine the strain, impedance, and capacitive properties of IPMCs when a random voltage is applied. Figure 1 shows the frequency response test data for $TMA^+$ as a representative sample of results for all sample sets. Figure 2 contains the frequency response test data for the 70 wt. % glycerol samples as a representative sample for all the sets.

The displacement was calculated with the laser output data and the laser gain setting. The impedance at a given frequency was determined by calculating the resistance, R, from the measured current, I, and voltage input, V, according to Equation 1.

$$R = \frac{V}{I} \qquad (1)$$

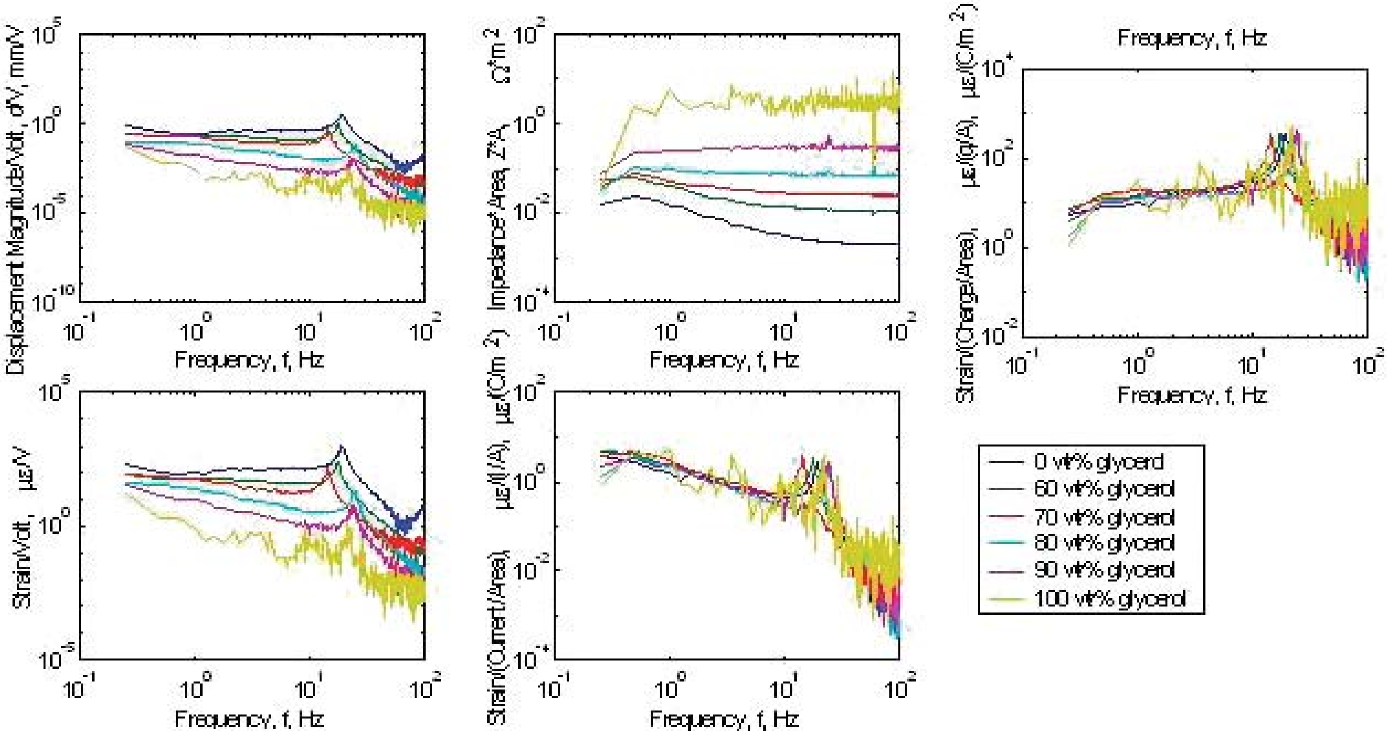

**Figure 1. Frequency responses of TMA+ samples**

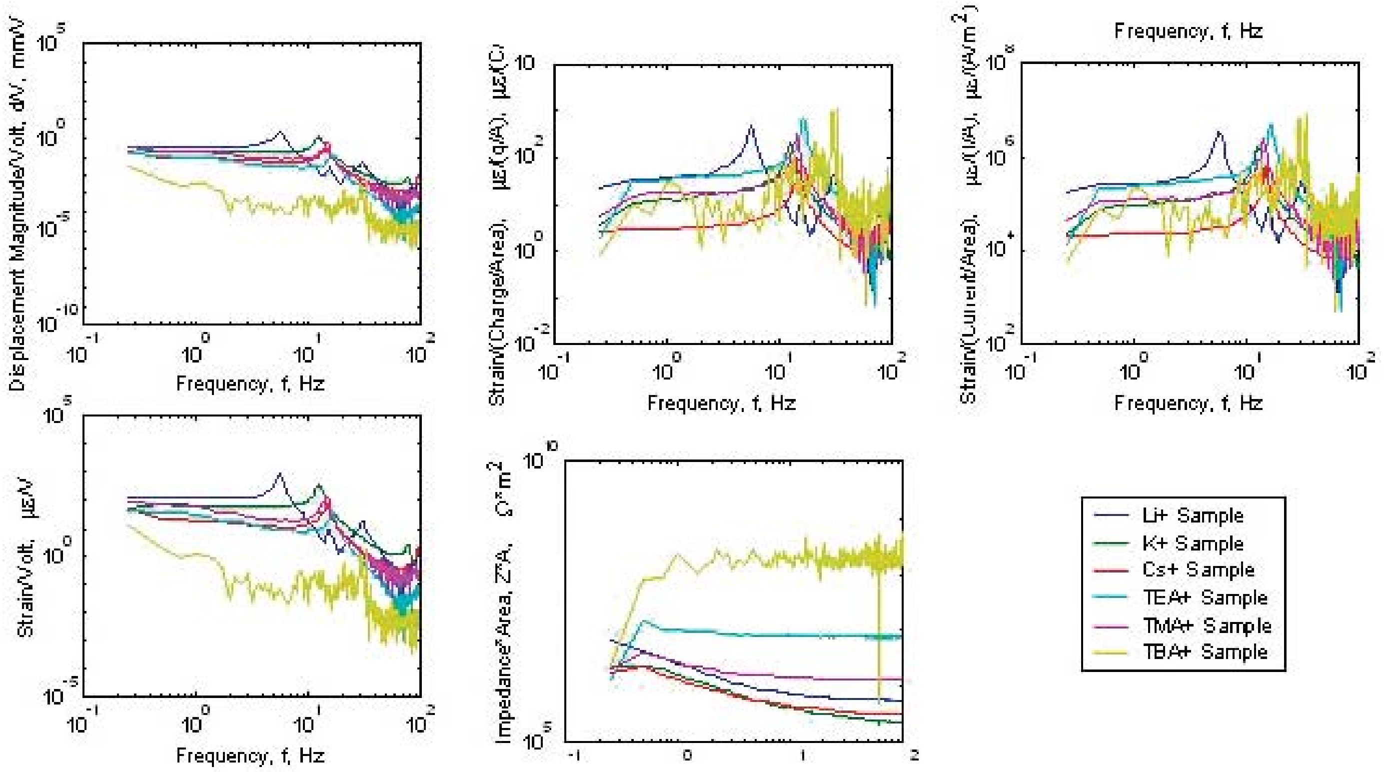

**Figure 2. Frequency responses of 70 wt. % glycerol samples**

Constant impedance indicates that the actuator behaves as a resistor. The resistance is due to the low mobility of the large cations through the membrane. However, smaller cations, such as $Li^+$ or $K^+$, behave as capacitors, as indicated by the negative slope of impedance.

$$Strain = \frac{Displacement \times t}{L^2} \qquad (2)$$

The strain was determined by multiplying the magnitude of displacement by a geometric factor in Equation 2, where t is the sample thickness and L is the length of the actuator. The strain per current at a given frequency was determined by multiplying the strain by the impedance. The strain per charge at a certain frequency was calculated by multiplying the strain per current by ω, the angular frequency, in Equation 3.

$$\omega = 2\pi f \qquad (3)$$

The impedance is consistently higher for samples with more viscous membrane solvents, as shown in Figure 3. The impedance of the samples impregnated with $TBA^+$, the largest cation, is less sensitive to changes in viscosity than those impregnated with smaller cations, such as $Cs^+$ or $K^+$. This trend is shown by the constant impedance for $TBA^+$ as a single frequency in Figure 3.

Ionic polymers with lower viscosity membrane solvents and small cations deflect the largest distance and result in the greatest amount of strain at low frequencies as shown in Figure 4. The strain measured on IPMCs impregnated with $TBA^+$ is less dependent on solvent viscosity than for the IPMCs impregnated with smaller cations. As shown in Figure 5, the cations with radii less than approximately 0.45 nm have the largest resulting strain upon deflection. When the strain per charge is normalized by the area of the actuator, the electromechanics of each actuator can be compared directly. These data suggest that once charge is stored in the actuator, the electromechanics are very similar, regardless of solvent viscosity or ionic radius, and indicate that differences in actuation are a function of the electrode

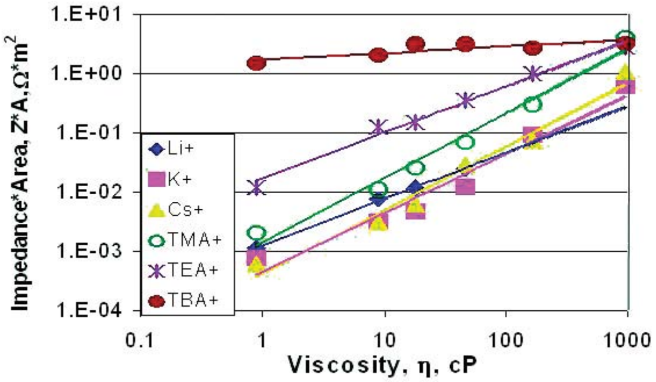

**Figure 3. Impedance*area at 100 Hz vs. viscosity**

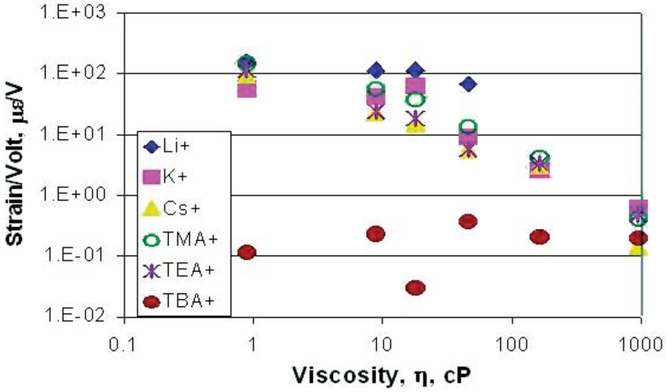

**Figure 4. Strain/volt at 2 Hz vs. viscosity**

### 3.2 Ionic Liquids

Based on the evaluation of transduction using various viscosities and ion sizes, actuators with a viscosity similar to 70–80 wt. % glycerol solutions and cation size similar to that of $TMA^+$ appear to yield the best results. The viscosities of the three ionic liquids evaluated range from 35 to 224 cP. The viscosities of 70 and 80 wt. % glycerol solutions at room temperature are 18 cP and 46 cP, respectively. Frequency response tests were performed on actuators solvated in the following ionic liquids (IL):

- 1-butyl-1-methyl pyrolidinium bis(trifluoromethylsulfonyl)imide (IL #1)

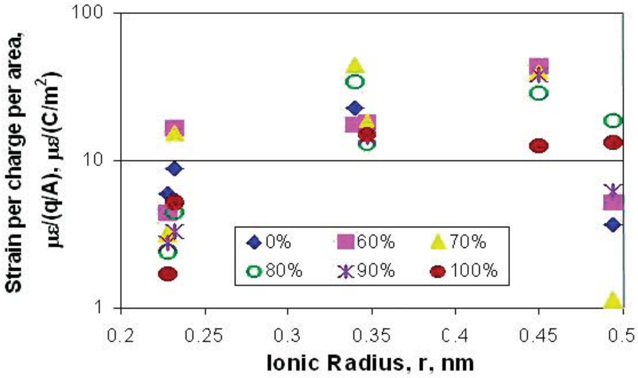

**Figure 5. Strain/(charge/area) at 2 Hz vs. ionic radius**

- 1-butyl-1-methyl pyrolidinium tris(pentafluoroethyl)trifluorophosphate (IL #2)
- 1-ethyl-3-methyl imidazolium trifluoromethanesulfonate (IL #3)

The results of these tests are shown in Figure 6. IL #3 was impregnated with $H^+$ and $Li^+$, while IL #1 and IL #2 were only impregnated with $H^+$. The viscosities for IL #1, IL #2, and IL #3 are 76 cP, 224 cP, and 35 cP, respectively.

Actuators solvated in ionic liquids have electromechanical properties similar to actuators solvated in glycerol solutions of comparable viscosity, as shown in Figure 3. Although the exact ionic radii of the ionic liquids tested are unknown, the cations in the liquids are large, and their frequency response behavior can help predict the ionic radii based on preliminary experimental data using various cation sizes. Figure 6 shows a plot of the frequency response test data for the three ionic liquids.

Actuators solvated in IL #1 and IL #2 behave in the same manner as actuators impregnated with large ions, such as TBA$^+$. Although the viscosity of IL #1 was much lower than that of IL #2, the strain per charge per area plots of the two actuators are approximately the same. This agrees with the trend noted in the preliminary testing, which indicates that as the cation becomes larger, the strain and impedance of the actuator become independent of viscosity. The behavior of the two actuators solvated in IL #3 is similar to those impregnated with TMA$^+$ and TEA$^+$. The impedance per area for both of these actuators is low, indicating capacitive characteristics. The strain per charge per area plots give smooth curves with resonant frequencies resembling those of TMA$^+$.

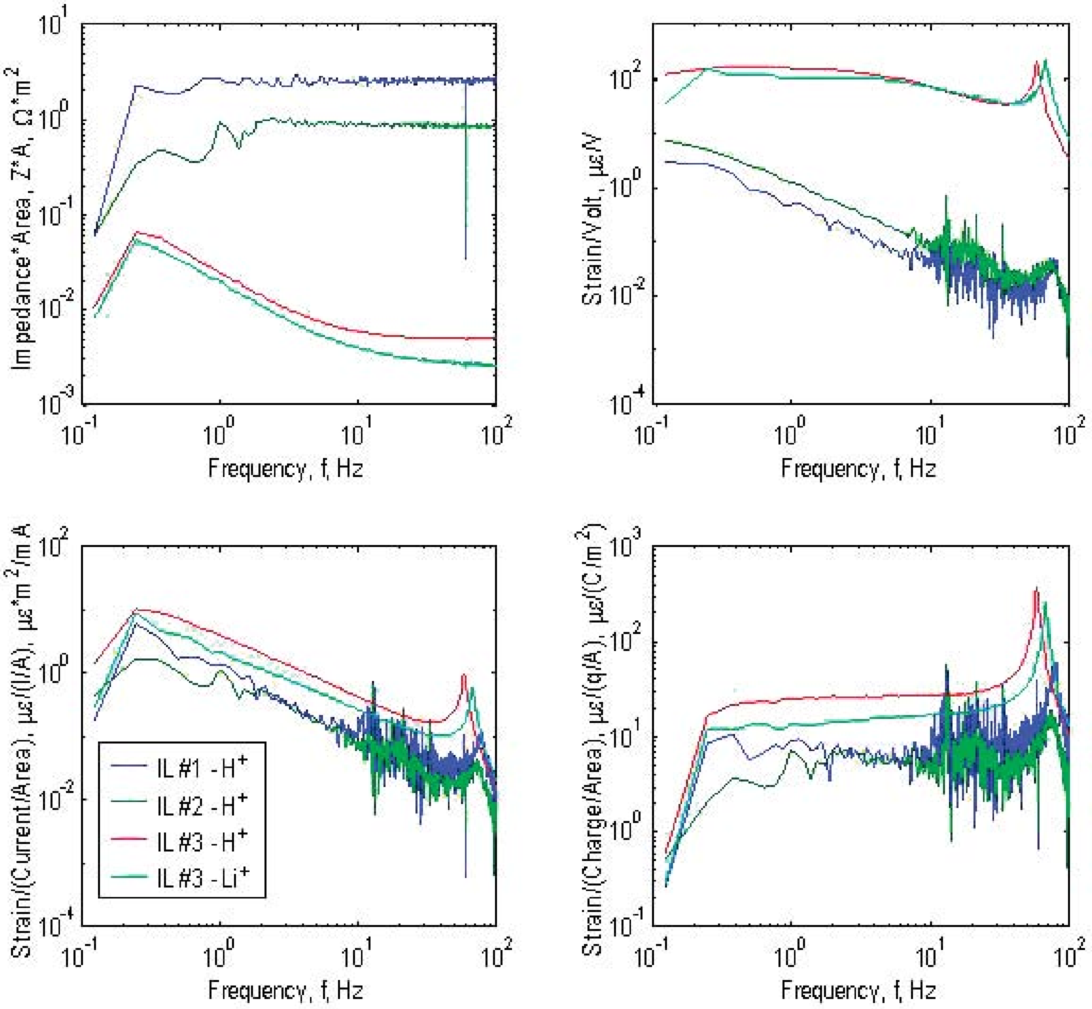

**Figure 6. Frequency responses of ILs**

## 4. Conclusions

The results of the study indicate that ionic liquids may be suitable replacements for water as the membrane solvent. Of the three different ionic liquids tested as membrane solvents, those exhibiting successful frequency response data had cations approximately the size of $TMA^+$ and viscosities near that of 70 to 80 wt. % glycerol. Therefore, the most effective ionic liquids were characterized by an ionic radius of approximately 0.347 nm and a viscosity between 18 and 46 cP. Actuators solvated in ionic liquids with these characteristics had low impedance and high strain per charge per area. These actuators stored charge and current flowed through the membrane, causing a displacement.

Based on the frequency response testing, viscosity played a larger role in the transduction when smaller ions were used to impregnate the polymer. The smaller ions possessed greater mobility inside the polymer membrane, allowing transduction to occur more easily. Similarly, the larger ions were less dependent on viscosity because their bulky size limited movement inside the polymer membrane. As the ionic radius of the cation increased, the deflection and resulting strain decreased. Additionally, the IPMCs impregnated with larger cations had higher impedance. Increasing viscosity resulted in higher impedance of the IPMC. Small ion size and low viscosity would produce the IPMC with the most favorable frequency response.

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