

Ion Distribution in Ionomer and High Temperature Ionic Liquid Actuators

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Abstract:

Proper understanding of the ion transport and concentration distribution in low voltage ionomer-based actuators is crucial for optimizing their performance in medical and optical devices. Actuators were built using Aquivion™ swelled with ionic liquid of 1-butyl-2,3-dimethylimidazolium chloride ([BMMI⁺][Cl⁻]). Electrical impedance, I-V characteristics, and charging current for the actuator were characterized using both room temperature, and a temperature above the 99°C melting point for [BMMI⁺][Cl⁻] [1]. The direct current (DC) conductivity of the actuator was found to be 30 μS/cm at 100°C and two orders of magnitude higher, compared to room temperature measurements. The electrochemical window of the device was determined to be 3V. Charge accumulation was measured to be one order of magnitude greater at 100°C compared to room temperature. Bending actuation under 2.5 V was observed at 100 ± 10°C, but not at room temperature. A semi-quantitative depth profile of ion concentration was measured by using SIMS imaging. Depth profiling suggests that, in a charged actuator, concentration gradients for [BMMI⁺] are thicker compared to corresponding [Cl⁻] gradients. The charged actuator also demonstrated unexpected accumulation of [Cl⁻] in the cathode and [BMMI⁺] in the anode which was due to a clustering effect in ionic liquids.

Introduction and Objective:

Ionomer and ionic liquid actuators show great promise for effectively converting electrical stimulus into mechanical motion. Application of a few volts of bias across the actuator causes ion accumulation near the electrodes. These ion accumulations swell the electrode region causing expansion of the polymer matrix and, due to the larger size of the cation compared to the anion, subsequent bending of the actuator towards the anode [2].

This project analyzed the ion distribution inside a charged actuator. Prior work with these types of actuators generally used ionic liquids with a melting point below room temperature. These ionic liquids were unsuitable for use in this analysis since the ions would quickly discharge or evaporate while inside a room temperature spectroscopy chamber. To avoid this issue, actuators were built using the ionic liquid 1-butyl-2,3-dimethylimidazolium chloride ([BMMI⁺][Cl⁻]) from Aldrich, due to its high melting point of 99°C.

Synthesis:

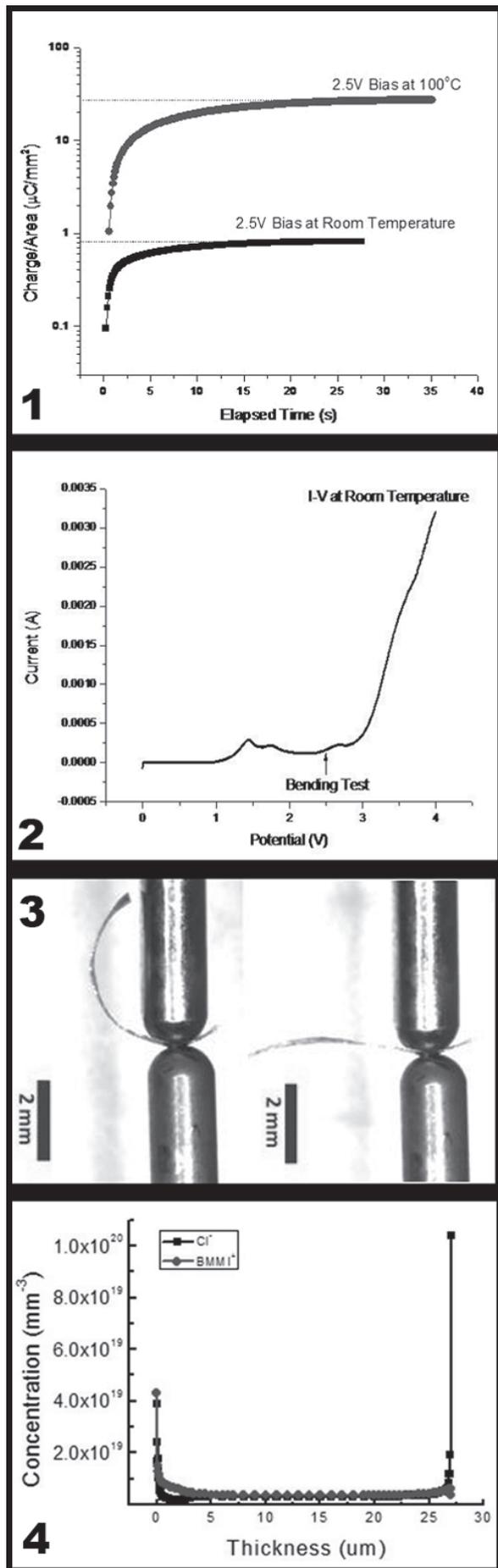
The use of a solvent was necessary to precisely control the uptake of [BMMI⁺][Cl⁻] into the Aquivion™ polymer purchased from Solvay Solexis. A solution by mass of 66% [BMMI⁺][Cl⁻] and 34% ethanol was prepared and held at 63°C. A sample of 30 μm thick Aquivion polymer was immersed into the solution and soaked for 20 minutes,

before solvent removal. Filter paper was used to remove residual solution from the sample surface. The sample was then placed in a vacuum oven held at a temperature of 50°C for two hours to evaporate the ethanol. The final uptake of [BMMI⁺][Cl⁻] was found to be 45.6%, a level sufficient for observable actuator performance.

Two layers of 50 nm gold were hot-pressed to the prepared Aquivion™ with 3100 N of force at 90°C for approximately 45s. If inspection revealed inadequate binding, the hot pressing procedure was repeated with the same parameters for one minute. Prepared samples were stored in a dry box to minimize water contamination before actuation tests. Actuators tested in this experiment were 1.5 mm by 12 mm.

Results and Conclusions:

Electrical measurements were performed at both room temperature and 100°C to ensure the device deactivated by lowering temperature. Figure 1 demonstrates the charge density increased by over an order of magnitude at the higher temperatures. Other tests also demonstrated a two-order of magnitude increase in the DC conductivity for the device at the higher temperatures. This shows that the higher temperatures yielded a greater free ion concentration and thus more potent electrical activity.



The I-V curve for the device, shown in Figure 2, was used to determine the electrochemical window within which the device may reliably operate. Only the room temperature curve is shown since the curve at 100°C has the same shape except with higher currents. The linear increase in current draw at greater than 3V indicated the presence of reduction-oxidation reactions. To prevent device damage, the maximum operating voltage for these devices was set as 2.5 V. Figure 3 shows the device tip moved 5 mm with applied DC voltage at 100°C.

The results of these electrical tests and presence of bending indicated that, at high temperatures, actuators constructed with $[\text{BMMI}^+][\text{Cl}^-]$ have comparable behavior as similar actuators with room temperature ionic liquids. This allowed for conclusions drawn from analysis to be applied to the actuators in general.

Secondary ion mass spectroscopy (SIMS) with 40 KeV C_{60} sputtering was employed to depth profile the actuator. Four 5-7 μm deep craters were created for probing the ion distribution near two electrodes. Figure 4 shows the determined concentrations in the polymer calculated from the SIMS data, and ensuring conservation of charge between the ionic liquid and ionomer. The remarkable increase of $[\text{BMMI}^+]$ in anode and $[\text{Cl}^-]$ in cathode indicated the ions do not fully separate and instead remained strongly attracted to each other, forming clusters. These formations contrasted with qualitative explanations given in literature.

Another notable result was the significantly higher concentration of $[\text{Cl}^-]$ at the anode compared to more widely distributed $[\text{BMMI}^+]$ at the cathode. This indicated the smaller size of $[\text{Cl}^-]$ versus $[\text{BMMI}^+]$ permitted denser accumulation near the actuator surface.

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References:

- [1] Merck Chemical. "Ionic Liquid Product Brochure." <http://www.emdchemicals.com/ionic-liquids-brochures/c_qAGb.s1OHEIAAAEH2AURLYY3>
- [2] Liu, Y. et al. "Ion Transport and Storage of Ionic Liquids in Ionic Polymer Conductor Network Composites." *Appl. Phys. Lett.* 96, 223503-1,2 (2010).

Figure 1: Charge density increases with temperature.

Figure 2: Electrochemical window limited to 3V.

Figure 3: Before/After photos of bending with 2.5V bias applied at 100°C.

Figure 4: Concentrations from SIMS suggests ion clustering effects.