Improving electroactive polymer actuator by tuning ionic liquid concentration

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ABSTRACT

We have fabricated actuators from a blend of fluoropolymer (FP) with ionic liquid (IL). Here a combination of graphene, graphite, and silver nanoparticles is used to raise the electrode conductivity. As the electrode composition is fixed, we found that the actuator displacement increases with decreasing amount of ionic liquid in the polymer gel electrolyte. A maximum strain of 0.48% was observed from peak-to-peak displacement for an actuator with IL/FP = 0.3 in the polymer gel electrolyte. The simulation results indicate that lowering IL concentration leads to a more compact ion distribution in the electrode layers and hence explains the increased strain in the actuators.

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1. Introduction

Electroactive polymers have enabled soft, lightweight actuators, sensors, and energy harvesting devices that are widely applicable to robotics, haptics, and biomimetic systems [1–3]. Among the various types of electroactive materials, fluoropolymers blended with ionic liquid (IL) allow device operation in air at low applied voltages. The polymer blends can be deposited over large area, patterned into arbitrary shapes through solution printing [4,5], and integrated into flexible organic electronics [6–8]. Here we use solution casting to change the IL concentration and enhance the performance of a bimorph actuator.

A bimorph actuator is comprised of a polymer gel electrolyte layer sandwiched between two electrodes, in which IL is incorporated in all three layers. Upon applying a bias, the IL cations and anions are redistributed by the electric field, and the ion migration leads to volume change in the structure because of steric repulsion and electrostatic

effects between the charged ions [9,10]. Due to the size difference between cations and anions, one of the electrodes shrinks while the other one swells, resulting in a bending motion. This type of ionic gel actuator is based on the bucky gel actuators pioneered by Asaka et al. They have shown that the generated strain depends on the size and transport properties of the IL species [11,12], as well as on the fluoropolymer support [13], and the composition of the electrodes [14–16]. The interaction between electrode, polymer matrix, and electrolyte is key to the actuator's final performance. The electrodes are typically made from integrating conductive carbon nanoparticles and/or nanotubes into the fluoropolymer-IL blend. Structures with graphene hybrids [17,18] and graphene-stabilized silver electrodes [19] have shown improved actuator frequency response and displacement. Here a combination of graphene, graphite, and silver nanoparticles is used to raise electrode conductivity and is shown to be another viable choice for electrode materials. As for the polymer gel electrolyte film, previous studies have often treated it as a mere transport layer. However, the role of the polymer gel electrolyte layer extends beyond ions transport, and this paper investigates how the electrolyte composition affects the actuation mechanics in bimorph structures.

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[1] Experiments were completed at Palo Alto Research Center, when this author was there on sabbatical.

In this work, we show that actuation strain is improved by tuning the IL concentration in the polymer gel electrolyte. The ratio of IL to fluoropolymer (IL/FP) is varied in the polymer gel electrolyte layer, as the electrode composition remains fixed. The actuator properties are measured and examined alongside simulation results. We demonstrate that adjustment of the polymer gel electrolyte composition provides a new method to increase actuator displacement.

2. Experiments

2.1. Materials and fabrication procedure

All of the materials were used as received. The ionic liquid was 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF$_4$, Aldrich). The fluoropolymer was fluoride-cohexafluoropropylene (PVDF-HFP, Kynar Flex 2801, Arkema). The electrode materials were graphite (Aldrich), graphene composite (Vorbeck F101), and silver nanoparticle ink (Sun Chemicals). N,N-dimethylacetamide (DMAc), 4-methyl-2-pentanone (MP), and propylene carbonate (PC) were purchased from Aldrich and used as solvents.

Six different weight ratios of EMIBF$_4$:PVDF-HFP were prepared for the polymer gel electrolyte layers, ranging from 0.3, 0.4, 0.6, 0.8, 1, to 1.5. The ratio of 1.5 was the maximum limit, because beyond that the ionic liquid started to form a separate band in the solution mixture. Each solution had 200 mg PVDF-HFP, 60–300 mg EMIBF$_4$, dissolved in 6 mL MP and 0.5 g PC solvents. The solution was stirred for one day at 70 °C, and then 2 g was cast onto a circular mold with 25 mm radius. The mixture was dried in air at 50 °C for one day and in vacuum oven at 80 °C for three days. The resulting polymer gel electrolyte films were measured to be 40 μm in thickness.

The electrode layers had a fixed composition made from a solution of 100 mg graphite, 200 mg EMIBF$_4$, 100 mg PVDF-HFP, mixed in 10 mL DMAc solvent. The solution was stirred for one day, and then 1.5 g was cast onto a circular mold with 25 mm radius. The mixture was dried in air at 50 °C for one day and in vacuum oven at 80 °C for three days. The electrode films were measured to be 40 μm in thickness. The surface resistance of these films was 200 Ω/□, and the graphite films were made more conductive (150 Ω/□) by spin-coating a micron-thick layer of the graphene composite ink. This composite conductor also acted as a blocking barrier to seal in the IL. A silver ink was spin-coated upon the blocking layer, and the silver film (50 nm) drastically reduced the electrode resistance to 20 Ω/□. We observed that without the silver film, the resistivity of the electrode was too high and the actuator device did not show movement. In general, resistivity of tens of ohms is required for effective actuation. While future experiments are needed to quantify the lifetime of actuators using non-noble metals, this method of using a blocking layer expands the choices of conductor materials, to allow low-cost metals in devices with ionic liquid.

The electrode films were cut into 20 mm by 5 mm strips. They were laminated [20] with the polymer gel electrolyte films to form actuator structures as illustrated in
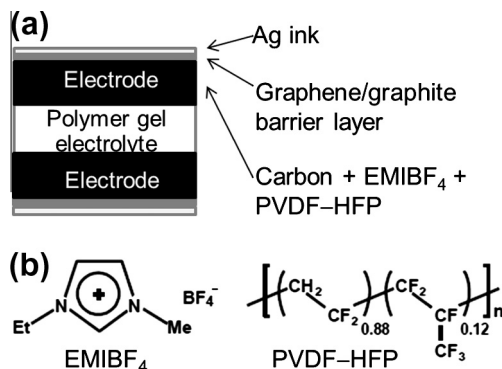

Fig. 1. (a) Schematics of the actuator. (b) Chemical structures of the ionic liquid EMIBF$_4$ and the fluoropolymer PVDF-HFP.

Fig. 1. The lamination was done at 2 atm and 70 °C for one minute. It was observed that for films with EMIBF$_4$:PVDF-HFP (IL/FP) ratio below 0.3, the adhesion was poor between the polymer gel electrolyte and electrodes. Thus, IL/FP = 0.3 was the minimum composition ratio. The total thickness of a typical device was around 120 μm.

2.2. Measurement procedure

Electrical and mechanical measurements were simultaneously captured. The electrical contacts to the bimorph actuator, as shown in Fig. 2 inset, were made from aluminum foils soldered to wires, and the contacts were located on the two isolated sides of a spring-loaded clip, which clamped down on the actuator electrodes. As voltage was applied to one electrode, the other electrode was connected to an electrometer (HP model 617) to monitor current through the actuator. The actuator motion was concurrently recorded by a video camera at 60 frames per second to measure displacement. The video sequence
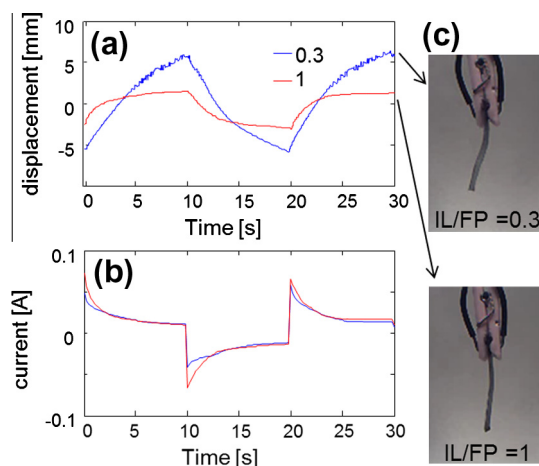

Fig. 2. (a) Displacement and (b) current of actuators under ±4 V square waveform at 0.05 Hz. The amount of ionic liquid in the polymer gel electrolyte is at 0.3× or at 1× of polymer weight. (c) Photos of the bending actuators at 4 V.

(available in the supplemental information, along with the image analysis schematics, supplemental Fig. 1) was processed by an edge-detection algorithm to extract the actuator profile. The edge-detection algorithm is an image analysis program from Labview (National Instruments). An ROI (region of interest) is defined around the actuator to specify the image analysis area. In the rectangular ROI, two edges of the actuator were detected, and the actuator profiles were obtained. From the extracted profile, the end-point location is determined and plotted as the actuation displacement in Fig. 2. The actuator end-point, indicated by an arrow in the supplemental schematics, was tracked to compare the displacement of the six actuators with different IL amounts in their polymer gel electrolyte layers.

3. Results and discussions

Fig. 2 displays the actuators' displacement and current when a square waveform of 0.05 Hz and ±4 V amplitude was applied to the electrodes. The photos compare the actuators' position after applying +4 V for 10 s. The actuator with IL/FP = 1 showed smaller displacement than the one with reduced ionic liquid. The tip displacement δ was converted into strain ε by the equation [12] $\varepsilon = 2d\delta/(L^2 + \delta^2)$, where d = 120 μm is the thickness of the actuator, L = 20 mm is the free beam length. At an applied voltage of 4 V, the maximum strain calculated from peak-to-peak displacement was 0.18% for the actuator with IL/FP = 1. In comparison, for the actuator with reduced IL (IL/FP = 0.3), the strain was higher by 2.7 times, reaching up to 0.48%. The actuator with IL/FP = 1 had similar polymer gel electrolyte composition as the devices in previous literature [14,15,20], but the electrode composition here is different from the previous work with carbon nanotube gel electrode. The maximum strain in Ref. [15] was measured to be 0.78%, and we believe that the device in Ref. [15] showed higher strain value than ours (0.18%) due to better conductivity in the nanotube electrodes. However, the previous works did not mention the effect of varying IL/FP in the polymer gel electrolyte. The applied voltage of ±4 V had exceeded the electrochemical window [21] of the IL, but the measurements were reproduced in independent sets of actuators, as well with ramping waveforms of ±4 V (supplemental Fig. 2). Degradation over many cycles has not been tested yet and may be worse at high applied voltage. Nevertheless, the electrochemical data (supplemental Fig. 3) shows that the current response was consistent during the three sweep cycles at 2 V/s. In this report, in order to isolate the effect of varying the IL/FP ratios in the polymer gel electrolyte, the electrode composition and applied voltage remains fixed for the following measurements.

The electrical current through the actuators increased with higher IL concentration, as shown in Fig. 3. The sheet resistance of the films with different IL/FP ratios are shown in Table 1 and increased monotonically with higher IL concentration, until the resistance saturates at ratio IL/FP ⩾ 1. The ratio of 1.5 was the maximum limit, because beyond this ratio, the ionic liquid was not homogeneously dispersed in the fluoropolymer. The rate of current change
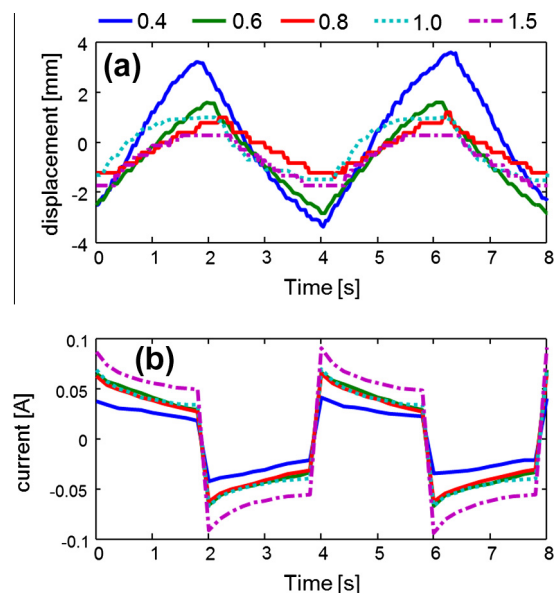

Fig. 3. (a) Displacement and (b) current of actuators under ±4 V square waveform at 0.25 Hz, upon varying the weight ratio of ionic liquid to fluoropolymer in the polymer gel electrolyte.

Table 1
Sheet resistance of the films with different IL/FP ratios.

| Ionic liquid-to-fluoropolymer ratio	Sheet resistance (ohm/square)
0.3	380
0.4	300
0.6	270
0.8	240
1.0	220
1.5	220

was faster for the more conductive polymer gel electrolyte. However, higher current did not directly translate to larger displacement. After one second at a constant bias, the actuator motion plateaued for the devices with more IL in the polymer gel electric, where IL/FP ⩾ 1. The actuators with IL/FP < 1 continued to bend further. For operation below 0.5 Hz, the displacement of actuators with low IL concentration (IL/FP < 1) exceeded those with high IL concentration (IL/FP ⩾ 1). Here the actuator motion was enhanced by incorporating *less* ionic liquid in the polymer gel electrolyte. Increasing the IL/FP ratio decreases the weight percentage of the fluoropolymer structural material, and this might affect the bending strain. In addition, the ion distribution in the actuator is investigated in simulations to examine the electrostatics under different ionic liquid concentrations.

The simulations were based on Poisson–Nernst–Planck system of equations [22], and the calculations were done by using the multi-physics, finite-element analysis software COMSOL ("Electrostatics" and "Nernst–Planck Equations" modules). The model geometry was a simple 2D cross-section of the actuator, where the initial ion concentration was estimated to be 0.1 mmol/mm^3 in the electrodes and 0.03, 0.06, or 0.1 mmol/mm^3 in the polymer

gel electrolyte. The values of the simulation constants [23] were as follows: relative dielectric constant = 42, diffusion constant = 2×10^{-12} m^2/s (for anion), 1×10^{-12} m^2/s (for cation). The cation diffusion constant is smaller than anion's, due to their molecular size difference. The model was solved for the stationary case, to determine the equilibrium ion distribution under an applied voltage of +4 V.

The simulation results in Fig. 4 illustrate the cation distribution, and the anion distribution (not shown) followed a similar pattern but with opposite polarity. The simulation results showed that, for a device with 0.3:1 EMIBF$_4$:PVDF-HFP polymer gel electrolyte (Fig. 4(a)), the cations were located in a narrow region close to the electrode edges. In contrast, higher IL concentration (IL/FP = 0.6 and IL/FP = 1, Figs. 4(b and c), respectively) led to a wider spread of the cations in the electrode layers. This widening of concentration gradient was due to charge shielding when more ions were present. The actuator strain may be inferred from the ion distribution, since volume change was caused by ion insertion. In Fig. 4, because the ion gradient was compressed in case (a), the high concentration of ions would generate larger volume change than in case (b) and (c), where the ions were more dispersed and would generate less strain. Moreover, the structure in (c) was the least resistive. The capacitance leakage and high conductivity would reduce the charge storage capacity [12] and may be the reason for why the actuator with high IL concentration (IL/FP ⩾ 1) stopped moving in one second after applying a voltage bias (Fig. 3). Overall, the compact ion-concentration gradient was the physical origin for the increased strain in actuators with less IL in the electrolyte layer. Fig. 5 is an illustration demonstrating that lowering electrolyte IL concentration allows narrow distribution of ions and higher strain in case (a). With high IL concentration in the electrolyte as shown in case (b), the electrodes are saturated with IL, and the swelling in the electrodes are more disperse, leading to smaller difference per unit length and thus lower strain.

For this study, we have concentrated on varying the polymer gel electrolyte composition while keeping the electrode composition the same. Nevertheless, there may be potential advantage to adjust the electrode composition in the future. For example, if the actuator is needed to bend only in one direction, then the electrodes do not need to be symmetric, and the IL concentration in the ground
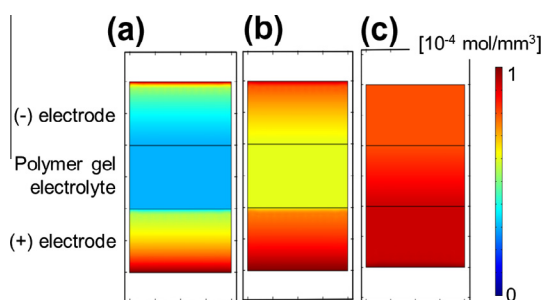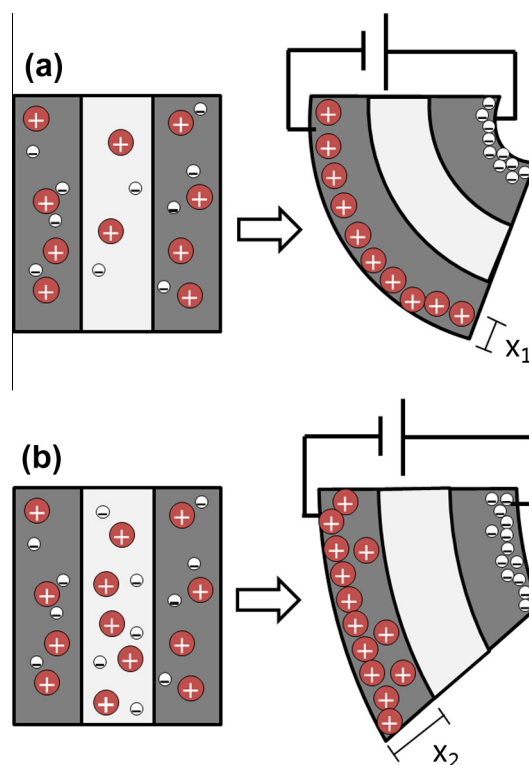
Fig. 5. Illustrations demonstrating the ion distribution for actuator with (a) lower concentration and (b) higher concentration of IL in the gel electrolyte. The arrows indicate the spread of ions, with $X_1 < X_2$. In case (b), the electrodes are saturated with IL, and the swelling in the electrodes are more disperse, leading to smaller difference per unit length and thus lower strain.

electrode may be reduced to enhance actuation asymmetrically. The concentration gradient may be created through layer-by-layer printing technique. The long-term stability of such gradient structures will be studied in the future, and it would be useful to directly image the ion distribution to determine the exact location of the ions.

4. Conclusions

In conclusion, we have fabricated polymer actuators and used an IL blocking layer in our electrode fabrication to enable coating of silver metal and raise the electrode conductivity. As the electrode composition is fixed, we found that the actuator displacement increases with decreasing the amount of ionic liquid in the electrolyte. A maximum strain of 0.48% was observed for an actuator with IL/FP = 0.3 in the electrolyte. This is the limit for our fabrication method, because lowering the IL/FP ratio to below 0.3 results in poor adhesion between structural layers. Simulation results indicate that low IL concentration (IL/FP = 0.3) allowed a compact ion distribution in the electrode layers. With higher IL concentration, charge shielding led to widening of concentration gradient. Since change in the actuator volume was caused by ion insertion, the narrow band of ions would generate larger gradient difference and thus higher strain. Therefore, low IL concentration in

Fig. 4. Distribution of cations in the actuator under +4 V. The EMIBF$_4$:PVDF-HFP ratio is 1:1 in the electrodes, whereas the ratios are (a) 0.3:1, or (b) 0.6:1 and (c) 1:1 in the polymer gel electrolyte.

the polymer gel electrolyte is better for improving actuator strain.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2013.11.026.

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