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Fabrication and electromechanical performance of a novel high modulus ionogel micro-actuator

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Abstract

In this work, a novel, high modulus sulfonated polymer is utilized as an ionomer for ionic liquid containing micro-ionic actuators (ionogel) is presented. The ionic polymer is composed of one-to-one ratio 4,6-bis(4-hydroxyphenyl)-N,N-diphenyl-1,3,5-triazin-2-amine and 4,4′-biphenol with bis(4-fluorophenyl) sulfone (DPA-PS:BP). The ionogel maintains a relatively higher modulus (700 MPa for 120 wt% of ionic liquid) compared to other widely used ionomers. High modulus of ionogel enables to realize thin films through solution casting. As an initial demonstration of a micro-ionic actuator, an ionic micro cantilever (200 μm x 33 μm x 5 μm) has been micromachined by using focused ion beam (FIB) milling on the substrate. The micro cantilever performance under DC actuation is tested using optical profilometer and a maximum tip displacement is 42 μm at 1.6V was obtained.

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Keywords: Ionic electroactive polymers; ionic liquids; ionomer; micro ionic actuators, ionogel, DPA-PS:BP

1. Introduction

Electroactive polymers (EAPs) are smart materials, which exhibit large mechanical strain (displacements) in response to electrical stimulation. Ionic electroactive polymers (i-EAPs) are a subclass of EAPs where the bending actuation is achieved through the movement of cation and anion pairs inside the polymer matrix as a result of electrical stimulation. The cation-anion pairs are introduced into the polymer matrix through ionic liquids (ILs). ILs are molten organic salts. Due to their high ionic conductivity and large electrochemical potential window (up to 5.7 V between platinium electrodes) [1],

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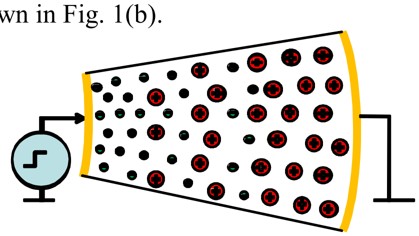
ILs are widely used in applications such as lithium batteries [2], dye synthesized solar cells [3], actuators [4] and electric double layer capacitors [5]. Melting point of ILs may range from -96 °C to 800 °C [6]. Most research fields emphasized above require room temperature operation. Therefore, room temperature ionic liquids (RTILs) are generally desired. For this research, 1-methyl-3-butylimidazolium tetrafluoroborate ([BMIm][BF_4]), an imidazolium based RTIL, has been utilized.

ILs act as electrolytes within the ionomer membranes and enhance the electrochemical response of the actuators. For example, the ionic conductivity is increased within the ionomer membrane, which may improve the bending strain and response time [7]. The polymer matrix endows the IL with dimensional and mechanical stability while preserving the electrical conductivity of the IL and any loss of the material due to the outflow of IL. These kind of hybrid materials where ILs are confined within an ionomer membrane are defined as ionogels [8]. Ionogels can be configured as soft sensors and actuators, which are promising for applications such as artificial muscles [9], soft robotics [10], and energy harvesting [11]. They require low voltages, typically 1-5 V, which is limited by the electrochemical potential window of the IL and electrode type. The ionogel actuator configuration is achieved via placing ionogel between two electrode layers. In this work, 50 nm gold layers are embossed on top and bottom surfaces of the ionogel membranes to act as electrodes.

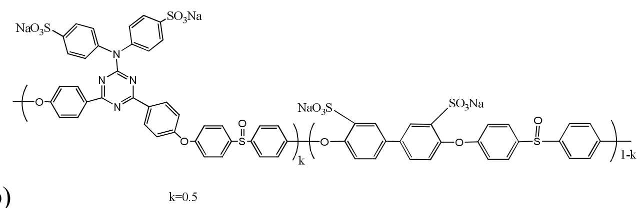
When an electric field is applied through the electrodes, cations drift and diffuse towards cathode, whereas anions drift and diffuse towards anode. For RTIL, there is generally a molecular volume difference between the cation and anion. For [BMIm][BF_4], the $BMIm^+$ molecular volume is larger than BF_4^- The accumulation of cation and anions at cathode and anode respectively causes a net volume difference, which in turn causes bending of the ionogel. Figure 1(a) schematically illustrates the bending mechanism in ionogels.

Despite the fact that ILs enhance the actuator performance acting as electrolytes within the ionomer, endowing high amounts of IL within the membrane dramatically decreases the elastic modulus of the films. Using solution casting methods, it is very challenging to realize sufficiently thin films out of these ionogels that can be used for the development of microelectromechanical systems (MEMS) scale sensors and actuators. Nafion^{TM} is one of the most widely used ionomer in literature that is manufactured by DuPont. For Nafion^{TM}, the elastic modulus versus IL uptake has been investigated experimentally and theoretically by Davidson [12]. The theoretical relation between elastic modulus and IL uptake can be mathematically expressed with $E = a_1/w + a_2$ relation, where E is the elastic modulus in MPa, w is the ionic liquid uptake in weight percent and a_1, a_2 are coefficients for slope and intercept respectively. For example, the elastic modulus of Nafion^{TM} is around 40 MPa for 60 weight % of uptake.

In this work, we have developed a novel ionomer [13], which is composed of one-to-one ratio 4,6-bis(4-hydroxyphenyl)-N,N-diphenyl-1,3,5-triazin-2-amine and 4,4′-biphenol with bis(4-fluorophenyl) sulfone (DPA-PS:BP). The elastic modulus of DPA-PS:BP:[BMIm][BF_4] ionogel is measured as 700 MPa for 120 weight % of endowed [BMIm][BF_4]. When compared to Nafion^{TM}, this ionomer can form robust thin films due to its higher elastic modulus with endowed ionic liquid. Thin films of 5–7 μm have been realized via solution casting DPA-PS:BP with [BMIm][BF_4]. The chemical structure of DPA-PS:BP is shown in Fig. 1(b).



a)



b)

Figure 1: (a) The bending due to molecular volume difference between anion and cation, which accumulate at anode and cathode side. [7] (b) The chemical structure of DPA-PS:BP [13]

Another challenge related to i-EAPs is fabricating micro-structures using these hybrid materials. Most of the traditional MEMS manufacturing techniques such as lithography and wet etching are not applicable with ionogels since the endowed IL within the ionomer tends to outflow when dipped into another solution. To overcome this manufacturability issue, focused ion beam (FIB) milling, was used to fabricate a 200 μm x 33 μm cantilever on 5 μm thick DPA PS:BP containing 150 wt % [BMIm][BF_4]. The FIB milling is discussed in the next section. This work demonstrates a free standing cantilever utilizing IL containing i-EAP as a microactuator and should be viewed as an initial work towards more widespread application i-EAPs as new materials for polymer based MEMS.

2. Manufacturing of micro-ionic cantilever via Focused Ion Beam milling

FIB milling is a top-down fabrication method, where finely focused, high energy (momentum) Gallium ions (Ga^+) strike on substrate surface and mill out the material in the region of impact. For milling, FEI Quanta 200 3D FEG Dual Beam Electron Microscope has been used. This model gives the ability to observe the cutting during milling since it has dual beam. For [BMIm][BF_4] containing DPA-PS:BP, the critical parameters are redeposition and cutting time. Redeposition is the deposition of the removed material on the milled region as shown in Fig. 2(a). The redeposition depends on dwell time (0.1 μs – 4.8 ms) and the ion beam current (3 – 20 nA). These two parameters have to be finely tuned in order to obtain a cleanly cut cantilever while keeping reasonable cutting time and cost. If these parameters are slightly changed, a redeposition run (cutting time: 15 mins, dwell time: 2.4 μs, ion current: 20 nA) or a damaged run (cutting time: 20 mins, dwell time: 4.8 μs, ion current: 20 nA) are observed as shown in Fig. 2 (a) and (b) respectively. Figure 2(c) shows the cleanly cut cantilever. The overall cutting time is 50 mins with 2.4 μs of dwell time and 7 nA of ion beam current. These are finely tuned parameters for this ionomer-IL combination. The obtained cantilever dimensions are a 200 x 33 x 5 μm. This fabrication method with FIB is also feasible to fabricate arrays and different shaped actuators on the thin film of ionogels.

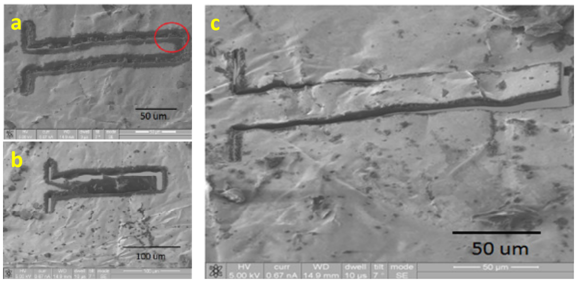


Figure 2:(a) High deposition run (b) High current run, and (c) The cleanly cut and released cantilever.

3. Electromechanical Characterization

After the fabrication of the micro-ionic cantilever, the electromechanical performance is tested. The film with the cantilever pattern on is mounted between two conductive plates. After careful wire bonding, the cantilever is released at the edge of two plates. A potential difference is applied incrementally between the two electrodes of the ionogel. The tip deflection is measured using a white light interferometer (Zygo 100 New View profilometer). Figure 3(a) shows the Zygo image at 1.6 V applied voltage. Figure 3(b) shows the deflection of the cantilever along its length for 3 actuation voltages. The solid lines are smooth fit to the deflection data obtained. Unlike high modulus materials, ionogels are very soft and upon release are very difficult to obtain as cantilevers with smooth surface. This explains some of the observed discrepancy between the smooth fits and the measured data. The maximum tip deflection is measured as 42 μm at 1.6 Volts.

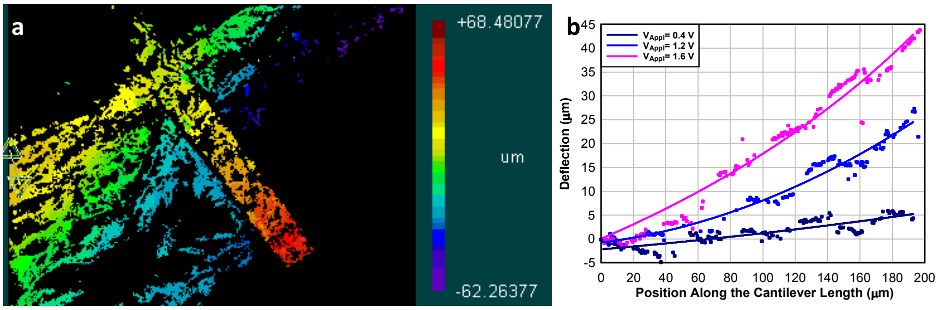


Figure 3.(a) Optical profilometer image of the ionogel cantilever actuated at 1.6 V (b) Deflection profile along the length of the cantilever for 3 different actuation voltages. The experimental data (dots) are fitted to a smooth mathematical function (solid lines) to show the curvature of the cantilever.

4. Conclusion

A high modulus ionomer, DPA-PS:BP, has been investigated as a novel ionomer for IL containing i-EAPs. The higher modulus enables to realize thin film actuators, which can be used for micro sensors and actuators applications. An ionogel microcantilever has been fabricated using FIB etching and is shown as a viable method for micromachining IL containing i-EAPs. Electromechanical characterization of the cantilever showed a maximum tip deflection of 42 μm at 1.6 Volts. The ionomer performance is promising for further investigation.

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