IOP PUBLISHING SMART MATERIALS AND STRUCTURES

Smart Mater. Struct. **16** (2007) S214–S219 doi:10.1088/0964-1726/16/2/S03

A Flemion-based actuator with ionic liquid as solvent

Jin Wang[1], **Chunye Xu**[1], **Minoru Taya**[1] **and Yasuo Kuga**[2]

[1] Center for Intelligent Materials and Systems, Department of Mechanical Engineering, University of Washington, Seattle, WA 98195, USA
[2] Department of Electrical Engineering, University of Washington, Seattle, WA 98195, USA

E-mail: chunye@u.washington.edu

Received 16 June 2006, in final form 18 July 2006
Published 9 March 2007
Online at stacks.iop.org/SMS/16/S214

Abstract
A perfluorinated carboxylic acid membrane, i.e. Flemion, shows improved performance as actuator material compared with Nafion (perfluorinated sulfonic acid). Flemion has a higher ion exchange capacity and good mechanical strength. In particular, Flemion will deform with no back relaxation under applied electrical stimulus. However, with water as solvent, the operation of Flemion in air has serious problems, since water would evaporate quickly in air. Moreover, the electrochemical stability for use in water is around 1 V at room temperature. In previous work, investigations on Nafion with ionic liquid as solvents have been carried out by some researchers and good results have been obtained. In this work, we explore the use of highly stable ionic liquid instead of water as solvent in Flemion. Experimental results indicate that Flemion-based actuators with ionic liquid as solvent have improved stability as compared to the water samples. Although the forces exhibited by Flemion-based actuators with the use of ionic liquid decreased dramatically compared to water, these preliminary results suggest good potential for the use of Flemion with ionic liquid in future applications.

1. Introduction

Electroactive polymers (EAPs) have many attractive characteristics for applications, especially for actuators and sensors. Numbers of types of polymer such as conducting polymers [1–4], PVDF-based ferroelectric polymers [5, 6], elastomers [7], non-ionic polymers [8], ionic polymers, etc, are commonly used EAPs. Ionic polymer–metal composites (IPMC) have attracted a great deal of attention in the past years due to their large strain. Several polyelectrolytes have been found to show actuation properties. The most popular polyelectrolyte is Nafion, commercially available from Dupont. Many investigations have focused on this polymer, studied the effects of cations on mechanical properties, optimization of metal electrodes' morphology and stability of mechanical properties [9–17]. The results of these studies show that Nafion has very good dynamic properties as an IPMC actuator but not so good as a quasi-static actuator. However, there is another ionic polymer candidate, Flemion, which also plays a significant role in this field. Flemion has been developed by Asahi Glass and has been studied as an IPMC mainly by Oguro's group in Japan, which has achieved excellent results in Flemion-based IPMC actuation amplitude [18–21]. The major difference in the actuation between Flemion and Nafion is the back relaxation, namely the deformation is stable or even increases as long as the voltage is applied quasi-statically. Interestingly, a recent report by Bennett and Leo shows that Nafion with ionic liquids EMI-Tf and EMI-Im as solvents shows no back relaxation in the cesium ion form [22]. This newly found results still need more investigations and characterization on output force. Flemion, which has been demonstrated to show no back relaxation, is the major candidate in our work. We consider the use of Flemion in the switching application, where two stable positions are required. The switch application includes microwave antennas for satellite based internet connections. In fact, these antennas use magnetic mechanical switches to switch connections on and off. Therefore, a switch based on IPMC would be very simple, compact and easily controlled. It consumes very low power and may exhibit similar properties as the current mechanical switches driven by electromagnets [23], but not interfering with incoming and outgoing electromagnetic waves.

0964-1726/07/020214+06$30.00

Table 1. The content of ionic liquids in Flemion-based IPMC.

	Density of ionic liquid (mg mm^{-3})	Mass after hydration (mg)	Mass with ionic liquids (mg)	Dry volume (mm^3)	Ionic liquid content (vol%)
(1) BMI-BF$_4$	1.21	19.4	22.3	9.350 88	25.63
(2) BMI-PF$_6$	1.38	19.8	20.4	8.798 976	4.94
(3) EMI-Tf	1.39	23.0	41.6	10.220 69	130.92
(4) EMI-Im	1.52	21.9	22.2	10.213 63	1.93

In a previous report, Le Guilly and co-workers have developed a Flemion-based actuator for a mechanically controlled microwave switch [23]. However, long-term operation of the Flemion based on water as a solvent could not be achieved, i.e. it could only operate for several cycles in air. According to a previous report [24], Nemat-Nasser *et al* has demonstrated that Nafion- and Flemion-based IPMC with ethylene glycol as solvent could be actuated at higher potentials and operated in the open air. However, to obtain a long lifetime of actuation in dry conditions, IPMC with other solvents, which could provide higher stability, need to be developed. A plating recipe to create gold electrodes on Flemion is developed based on the impregnation reduction technique for thin Flemion by Le Guilly [23]. In this paper, we present IPMC samples based on a Flemion membrane, which are fabricated with ionic liquids as solvents. The actuation displacement and output force of the prepared Flemion composite are measured and compared. The effects of different ionic liquids on IPMC mechanical properties and lifetime are investigated. The possible application in switches is also discussed.

2. Experiment

2.1. Preparation of IPMC based on Flemion

Deposition of a gold electrode is done according to the impregnation–reduction technique following a recipe developed by Fujiwara *et al* and Le Guilly *et al* [23, 25]. In this technique, a gold complex $[Au(Phen)Cl_2]^+$ is introduced into the Flemion membrane with K^+ as counterions by ion exchange. This process will fully take place if the amount of gold complex in the exchange solution is sufficient to drive the exchange and if the affinity of the membrane for its present cation is not too high [23]. Then, the Flemion membrane with gold complex is soaked in de-ionized water for reduction. A small amount of 5 wt% sodium sulfite solution is gradually added to the reducing bath and the temperature is slowly increased. For a thin Flemion membrane, the reduction process will finish after six hours, followed by rinsing in acid and de-ionized water for cleaning. Finally, all the samples were immersed in 1 mol l^{-1} KOH solution for ion exchange of H^+. According to the work done by previous researchers in our group [26], Flemion with sodium and tetrabutylammonium (TBA) were characterized and compared. Here, potassium was selected as the counterion to get some supplementary results on Flemion-based IPMC. Moreover, potassium has been widely used as the counterion in Nafion-based IPMC, so that the performance of Flemion-based IPMC with K^+ could be compared to the similar Nafion-based IPMC.

2.2. Incorporation of ionic liquid as solvent

Recently, Bennett and Leo demonstrated that ionic liquids could be used to replace water in ionic polymer transducers [8]. Ionic liquids are non-volatile and have greater electrochemical stability than water. Therefore, IPMC with ionic liquids as solvent are expected to be able to operate for a long time in dry conditions with higher applied voltages. Here, four types of ionic liquids were incorporated into Flemion-based IPMC. They are 1-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF$_4$), 1-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF$_6$), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf), and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imidate (EMI-Im). The electrochemical windows of BMI-BF$_4$ and BMI-PF$_6$ are -2.5 to $+2.5$ versus Ag/Ag^+ [27]. The electrochemical stability window of EMI-Tf and EMI-Im is around 4 V [28].

Before introducing these ionic liquids into samples, all the samples were dehydrated in an oven at 120 °C overnight, and then they were immersed in the respective ionic liquid bath at 100 °C for one week. To characterize the ionic liquid content in the membranes, the volume of ionic liquid in the membranes as a percentage of the dry volume of the membrane was calculated by measuring the membrane volume and weight before soaking in the ionic liquid and the membrane weight after soaking in the ionic liquid.

The four different volumes of ionic liquid in the membrane as a percentage of the dry volume of the membrane are shown in table 1. Table 1 indicates that the third sample with EMI-Tf has an exceedingly large content of ionic liquid, which will cause significant distortion of the sample strips and affect the mechanical properties.

2.3. Mechanical performance

Flemion-based IPMC is prepared according to the method discussed above. To characterize its mechanical properties, strips (25 mm × 3.5 mm) of the membranes with different ionic liquids are set in a cantilever beam configuration horizontally in air connected to an electrochemical analyzer (CH Instruments). A square wave voltage is applied with different frequencies. The strips bend in response to the voltage. The displacement is measured by laser displacement equipment by Keyence Inc. and the tip force is measured by a load cell from Transducer Tech. Inc. The analyzer software plots the current through the Flemion gold composite and the signal from the laser displacement equipment and load cell in real time.

3. Results and discussion

3.1. Curvature response

Curvature response of Flemion-based IPMC with different ionic liquids in a cantilever configuration at ±3 V as a function of time is shown in figure 1, where (a), (b), (c), (d) and (e) correspond to the lowest to the highest frequencies.

From the displacement (Δ) measured by the laser equipment, the curvature response $1/R - 1/R_0$ is calculated by applying the following equations

$$\frac{1}{R} - \frac{1}{R_0} = \frac{2\Delta}{l^2 + \Delta^2} \cong \frac{2\Delta}{l^2} \qquad \text{since } l \gg \Delta \qquad (1)$$

where $l = 20$ mm is the length of the free testing point to the fixed end, and R_0 and R are the radii of the specimen in the initial and current configuration.

Figure 1 shows that Flemion has a continuous deformation to a maximum displacement without back relaxation. Among the samples with different ionic liquids, the sample with BMI-BF_4 shows the largest displacement. Compared with the previously reported Nafion with EMI-Tf and EMI-Im [8], Flemion-based IPMC also exhibited a relatively small displacement, one order of magnitude lower than the one with EMI-BF_4, if the factor of different thickness was neglected.

Among the samples with different ionic liquids, the one with BMI-BF_4 shows the best performance. The reason might be due to the interaction of charged groups in the ionic liquid and the fixed group COO^- of the Flemion sample. Furthermore, the response of the IPMC also depends on the level of hydration. According to table 1, the content of ionic liquid appears to be very different in the samples. For the sample with EMI-Tf, the content is so high that it caused severe shape deformation of the sample, resulting in performance degradation. For the sample with BMI-PF_6 and EMI-Im, both the contents are less than 5 vol%, which are relatively small. The content of BMI-BF_4 in the sample is 25.63 vol%, which is a reasonable level to benefit IPMC performance. Further investigation of ionic liquid influence on IPMC performance will be done.

Here, we observe asymmetric displacement when a symmetric excitation by a $+3/-3$ V square wave is applied. This indicated different results to previous results on Flemion-based IPMC with water. This could be mostly due to the larger viscosity of the ionic liquid. At the starting position, the solvent distribution in the IPMC sample was homogeneous. After the applied +3 V, volumetric swelling due to solvent redistribution occurred, leading to the shrinkage of the anode side and swelling of the cathode side. For Flemion-based IPMC with water, as the applied voltage was reversed, the response time for the displacement changing from positive to negative is really small. However, due to the large viscosity of the ionic liquid, this solvent redistribution process required relatively a much longer time. When the applied voltage was reversed, a negative potential was necessary to overcome the large inertia of the ionic liquid, reverse the solvent distribution and bring it back to the original starting position rather than directly leading to negative displacement. Overall, the large viscosity of the ionic liquid caused slow solvent redistribution and resulted in asymmetric displacement under symmetric applied voltage. The mechanism involved in detail will be the next step in our work.

Figure 2 shows the maximum curvatures varying with frequency and voltage. With ±3 V applied voltage, all samples show the decreasing trend of displacement as frequency increased. This could be explained by the slow process of ion redistribution due to the larger viscosity of the ionic liquid. At low frequency, a larger voltage is necessary to enhance the actuation of all the samples. Due to the larger electrical stability window of ionic liquids, a voltage as large as 5 V could be applied to the Flemion samples to achieve larger displacement.

According to figure 2, the sample with EMI-Tf with 130 vol% ionic liquid uptake shows similar performance as the samples with EMI-PF6 and EMI-Im, both of which have less than 5 vol% ionic liquid uptake. This result indicates that extremely large or small content of solvent uptake has a negative influence on the transducer's performance, and a reasonable level of content in a sample with 25 vol% EMI-BF4 will benefit the mechanical properties.

3.2. Force response

To characterize the force response of Flemion-based IPMC, a large voltage of 5 V is necessary to actuate the samples to obtain a force reading. However, the samples with BMI-PF_6, EMI-Tf and EMI-Im exhibited too small a displacement to get force data: only the Flemion with BMI-BF_4 exhibited a measurable force.

The results plotted in real time are shown in figure 3. Flemion continuously deforms to a maximum force. However, the actuation process could be divided into two parts. The actuation is fast in the first 5 s and then slows down to saturation. Meanwhile, no back relaxation was observed in the current test. However, due to the slower response of Flemion-based IPMC with ionic liquid, a longer test duration should be applied to characterize the relaxation behavior.

However, the force of Flemion is relatively small compared with that of Nafion. According to the work done by Nemat-Nasser [29], the internal forces created within the anode and cathode boundary layers result from the ion redistribution. Due to the different polarity and viscosity of BMI-BF4 and water, the process of ion redistribution will be quite different, leading to a different maximum tip force. Another possible factor is the sample stiffness, which will be different corresponding to the different solvents. All these factors will be evaluated carefully in future work on modeling. This relatively small force could be enhanced by the densified electrode microstructure with fractal geometry. To avoid large noise, a load cell with compatible measurement range is necessary. In addition, a data processing program would be helpful for eliminating the unwanted noise.

3.3. Environmental stability

To evaluate the environmental stability of Flemion-based samples with ionic liquids, the time history of the curvature response of Flemion-based IPMC with BMI-BF_4 in air was measured and compared with the one with water. The applied voltage is ±5 V, 0.025 Hz for the case of Flemion with BMI-BF_4.

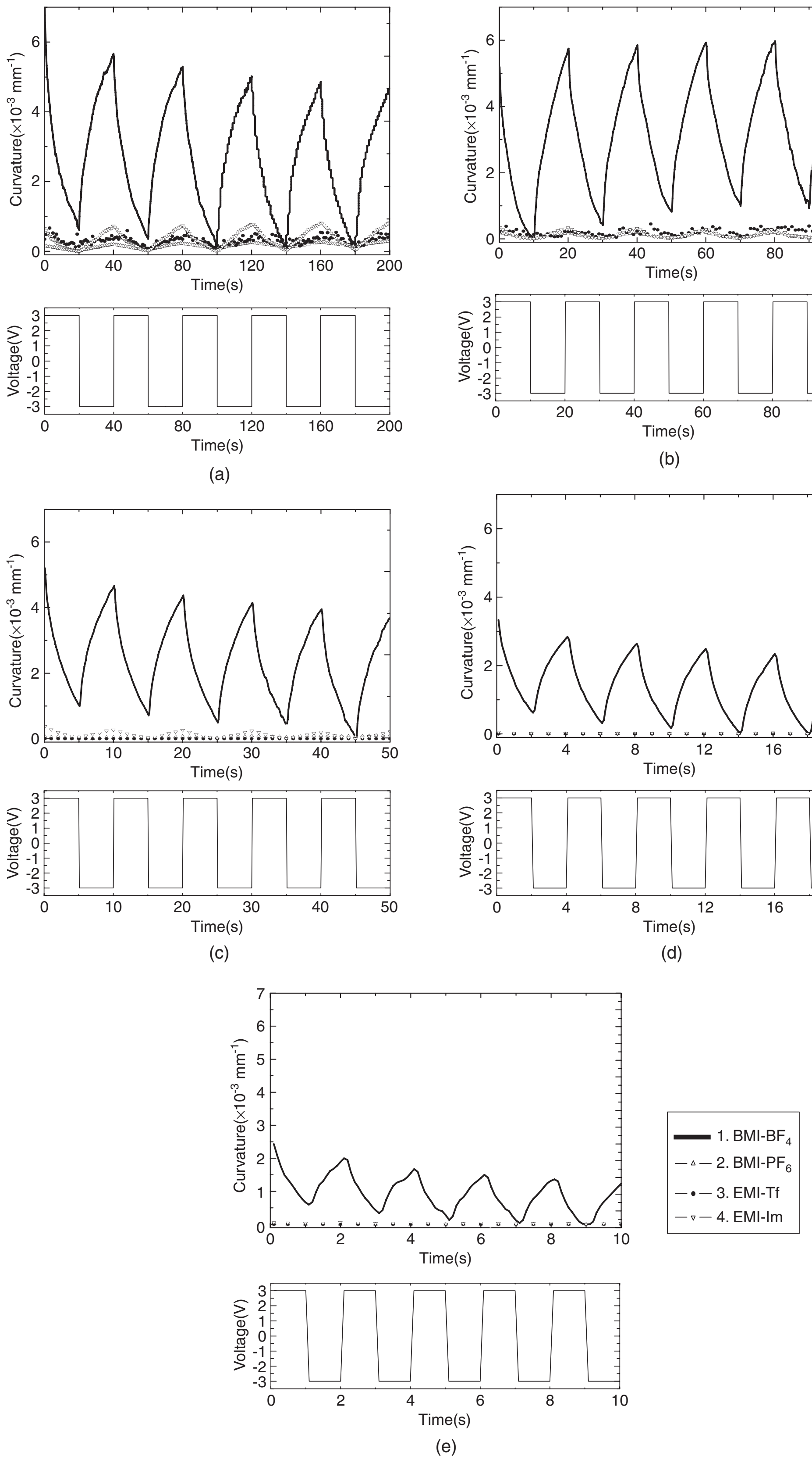
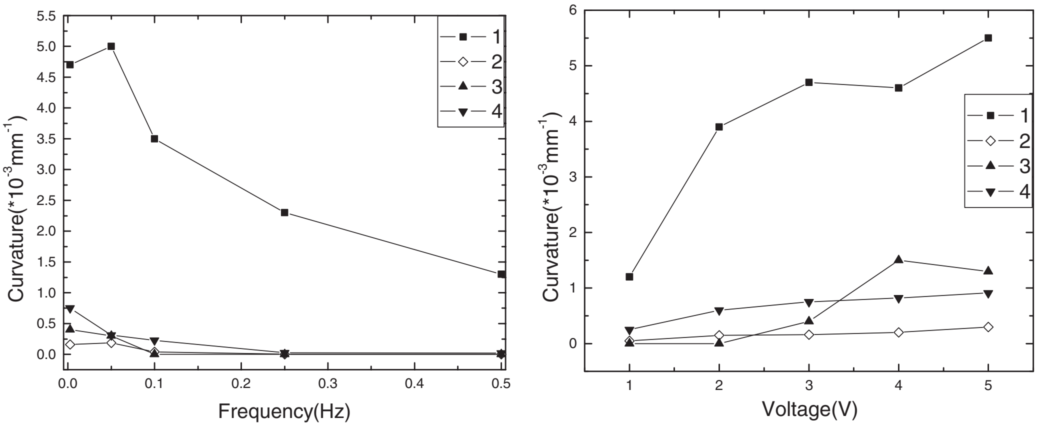


Figure 1. Curvature response of Flemion-based IPMC in a cantilever configuration at ±3 V with different frequencies: (a) 0.025 Hz, (b) 0.05 Hz, (c) 0.1 Hz, (d) 0.25 Hz and (e) 0.5 Hz.

Figure 4(a) shows the curvature response during a 10 000 s test. It suggested that ionic liquids could improve Flemion-based IPMC actuation stability compared with water. For IPMC with BMI-BF$_4$, the lifetime could be improved to



(a) (b)

Figure 2. Curvature response of Flemion-based IPMC in cantilever configuration with (a) different frequencies at ±3 V and (b) different voltages with 0.025 Hz, where the symbols with 1, 2, 3 and 4 correspond to Flemion with the ionic liquid of (1) BMI-BF$_4$, (2) BMI-PF$_6$, (3) EMI-Tf and (4) EMI-Im.

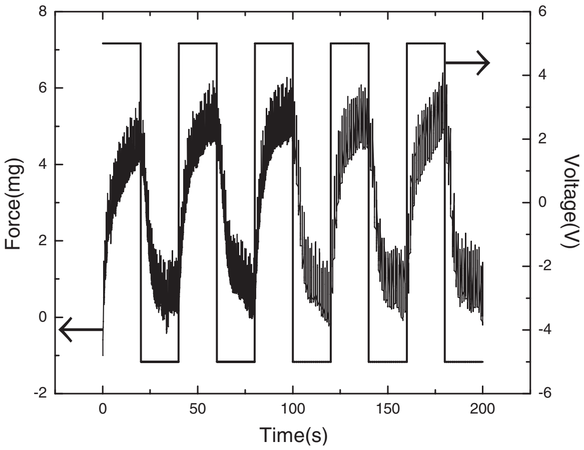


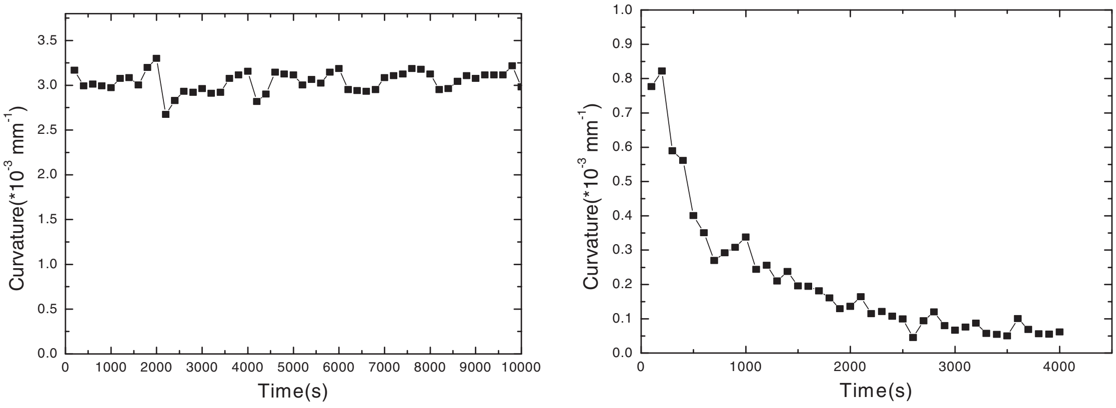
Figure 3. Force response of Flemion-based IPMC with BMI-BF$_4$ in a cantilever configuration at ±5 V with 0.025 Hz.

10 000 s, which lasts one day, whereas IPMC with water could only operate in water for several hundred seconds and then the curvature response decreased dramatically. However, more effort should be made to optimize Flemion-based IPMC actuation in long range.

Finally, we would like to discuss the possible application of Flemion-based IPMC with ionic liquids as microwave switches. Here, the Flemion-based IPMC with ionic liquids exhibited the key advantages of stable deformation (no back relaxation) and longer durability. Therefore, they are suitable for switch applications. However, the output force should be further improved.

According to our latest results on Flemion-based IPMC with glycerol as solvent [30], the lifetime in air could be improved dramatically up to six days, keeping a reasonably stable displacement even compared to that of a sample with BMI-BF$_4$.

The average curvature response for each day is shown in figure 5. It shows that the operational stability increased remarkably, as well as the curvature being one order of magnitude higher than that of samples with BMI-BF$_4$. This result indicated that the mechanical performance of Flemion-based IPMC could be enhanced by a properly selected solvent.



(a) (b)

Figure 4. Time history of the curvature response of Flemion-based IPMC with (a) BMI-BF$_4$, and (b) water. The applied voltage is ±5 V and ±1.5 V with $f = 0.025$ Hz, respectively.

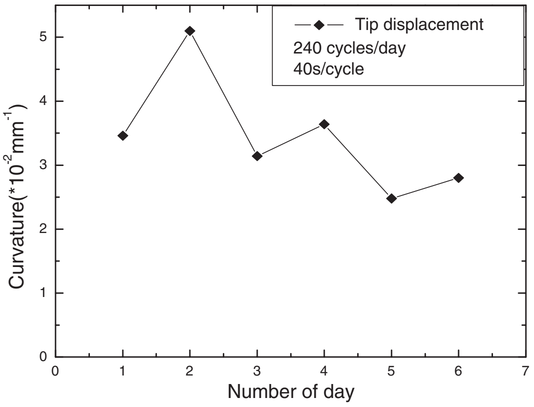


Figure 5. Durability measurement of Flemion-based IPMC curvature response for 6 days. The applied voltage is ±5 V with $f = 0.025$ Hz.

4. Conclusion

Flemion-based IPMC was fabricated based on a Flemion membrane with a thickness of 145 μm. A gold plating recipe based on an impregnation reduction method is applied and yields flexible, highly conductive electrodes on Flemion. Ionic liquids as solvents were introduced into Flemion-based IPMC to improve the stability of their mechanical properties. The results show that a sample with BMI-BF$_4$ exhibited the largest deformation among different samples. As for Flemion, a larger applied voltage and lower frequency was necessary to get larger actuation. However, the forces that Flemion-based IPMC with ionic liquids generate tend to be small compared to water. The environmental stability characterization indicated that Flemion-based IPMC could operate in air with good stability for 10 000 s. These initial results suggest good potential for this approach in future work.

Acknowledgments

This work is supported by the National Science Foundation Grant No ECS-0424414. The authors would like to thank Asahi Glass Corporation Japan for providing the Flemion samples.

References

[1] Okabayashi K, Goto F, Abe K and Yoshida T 1987 *Synth. Met.* **18** 365

[2] Smela E 2003 Conjugated polymer actuators for biomedical applications *Adv. Mater.* **15** 481–94

[3] Bay L, West K, Sommer-Larsen P, Skaarup S and Benslimane M 2003 A conducting polymer artificial muscle with 12% linear strain *Adv. Mater.* **15** 310–3

[4] Madden J D, Cush R A, Kanigan T S and Hunter I W 2000 Fast-contracting conducting polymer-based actuators *Synth. Met.* **113** 185–92

[5] Davis G T, Furukawa T, Lovinger A J and Broadhurst M G 1982 Structural and dielectric investigation on the nature of the transition in a copolymer of vinylidene fluoride and trifluoroethylene (52/48 mol%) *Macromolecules* **15** 329

[6] Cheng Z Y, Xu T B, Bharti V, Wang S and Zhang Q M 1999 Transverse strain responses in the electrostrictive poly(vinylidene fluoride-trifluoroethylene) copolymer *Appl. Phys. Lett.* **74** 1901–3

[7] Pelrine R, Kornbluh R, Pei Q and Joseph J 2000 High-speed electrically actuated elastomers with strain greater than 100% *Science* **287** 836–9

[8] Zheng J M, Watanabe M, Shirai H and Hirai T 2000 Electrically induced rapid deformation of nonionic gels *Chem. Lett.* **5** 500–1

[9] Sadeghipour K, Salomon R and Neogi S 1992 Development of a novel electrochemically active membrane and ‘smart’ material based vibration sensor/damper *Smart Mater. Struct.* **1** 172–9

[10] Oguro K 1993 Actuator element *US Patent* 5268,082

[11] Kim K J and Shahinpoor M 2002 Novel ionic polymer–metal composites equipped with physically loaded particulate electrodes as biomimetic sensors, actuators and artificial muscles *Sensors Actuators* A **96** 123–32

[12] Kim K J and Shahinpoor M 2003 Ionic polymer–metal composites: II. Manufacturing techniques *Smart Mater. Struct.* **12** 65–79

[13] Millet P, Andolfatto F and Durand R 1995 Preparation of solid polymer electrolyte composites: investigation of the ion-exchange process *J. Appl. Electrochem.* **25** 227–32

[14] Millet P, Andolfatto F and Durand R 1995 Preparation of solid polymer electrolyte composites: investigation of the precipitation process *J. Appl. Electrochem.* **25** 233–9

[15] Akle B, Leo D J, Hickner M A and McGrath J E 2005 Correlation of capacitance and actuation in ionomeric polymer transducers *J. Mater. Sci.* **40** 3715–24

[16] Nemat-Nasser S and Wu Y 2003 Comparative experimental study of ionic polymer–metal composites with different backbone ionomers and in various cation forms *J. Appl. Phys.* **93** 5255

[17] Bennett M and Leo D J 2004 Ionic liquids as stable solvents for ionic polymer transducers *Sensors Actuators* A **115** 79–90

[18] Fujiwara N, Asaka K, Nishimura Y, Oguro K and Torikai E 2000 Preparation of gold–solid polymer electrolyte composites as electric stimuli-responsive materials *Chem. Mater.* **12** 1750–4

[19] Onishi K, Sewa S, Asaka K, Fujiwara N and Oguro K 2000 Morphology of electrodes and bending response of the polymer electrolyte actuator *Electrochim. Acta* **46** 737–43

[20] Onishi K, Sewa S, Asaka K, Fujiwara N and Oguro K 2001 The effect of counter ions on characterization and performance of a solid polymer electrolyte actuator *Electrochim. Acta* **46** 1233–41

[21] Asaka K, Fujiwara N, Oguro K, Onishi K and Sewa S 2001 State of water and ionic conductivity of solid polymer electrolyte membranes in relation to polymer actuators *J. Electroanal. Chem.* **505** 24–32

[22] Bennett M and Leo D J 2005 Morphological and electromechanical characterization of ionic liquid/Nafion polymer composites *Proc. SPIE—Int. Soc. for Optical Engineering* **5759** 506–17

[23] Le Guilly M, Xu C, Cheng V, Taya M, Opperman L and Kuga Y 2003 Flemion based actuator for mechanically controlled microwave switch *Proc. SPIE—Int. Soc. for Optical Engineering* **5051** 362–71

[24] Nemat-Nasser S and Zamani S 2003 Experimental study of Nafion-and Flemion-based ionic polymer metal composites (IPMCs) with ethylene glycol as solvent *Proc. SPIE* **5051** 233–44

[25] Fujiwara N, Asaka K, Nishimura Y, Oguro K and Torikai E 2000 Preparation of gold–solid polymer electrolyte composites as electric stimuli-responsive materials *Chem. Mater.* **12** 1750–4

[26] Le Guilly M 2004 Flemion actuator array *PhD Dissertation* University of Washington Ch.4

[27] Lu W *et al* 2002 Use of ionic liquids for π-conjugated polymer electrochemical devices *Science* **297** 983–7

[28] Bonhôte P, Dias A, Papageorgiou N, Kalyanasundaram K and Grätzel M 1996 Hydrophobic, highly conductive ambient-temperature molten salts *Inorg. Chem.* **35** 1168–78

[29] Nemat Nasser S 2002 Micromechanics of actuation of ionic polymer–metal composite *J. Appl. Phys.* **92** 2899–915

[30] Wang J, Xu C, Taya M and Kuga Y 2006 Mechanical stability optimization of flemion-based composite artificial muscles by use of proper solvent *J. Mater. Res.* **21** 2018–22