Ionic Polymer-Metal Composite Actuators with Increased Air-Operating Stability by Using Ionic Liquids

*Jang-Yeol Lee, Man-Jae Han, Sung-Won Lee, Sun-Jin Park, Bye-Ri Yoon, and Jae Young Jho**

School of Chemical and Biological Engineering,
Seoul National University, Seoul 151-744, Korea
jyjho@snu.ac.kr*

Introduction

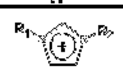
There have been considerable attentions for biomimetic actuators including electro-active polymers (EAPs). Ionic polymer-metal composite (IPMC), an ionic EAP, is one of the most promising actuator because of its large bending displacement with low applied voltage. Its unique characteristics can be made use of in a number of applications such as robotics and artificial muscles [1]. The bending deformation is attributed to water drag associated with the unidirectional migration of the counter cations in the ion-exchange membrane (IEM) [1]. It consequently requires that IPMC should be operated in some humid conditions or in the bulk water to function constantly, since water would be easily evaporated in the dry condition. Also, water electrolysis in IPMC is known to progress when applied voltage exceeds approximately 1.3 V [2]. Water loss in IPMC is surely one of the most serious problems related to the actuation capability, and results in short air-operating life time. In order to prevent solvent loss in the IPMC, water has been substituted with ionic liquids as solvent and electrolyte owing to their high ion conductivity, non-volatility, non-flammability, and the large electrochemical stability windows [3]. However, almost all the normal IPMCs based on commercial IEM like Nafion® or Flemion® soaked with ionic liquids are not efficiently actuated, since ion conductivity of ionic liquids in commercial IEM is relatively low compared with that of water.

The present study is intended to prepare the effective IPMC with increased air-operating stability by using ionic liquids. The IEM containing sufficiently larger amount of anionic group than commercial IEM was necessary for adequate ionic conductivity of ionic liquids in IEM. IPMC employing the prepared IEM soaked with ionic liquids is expected to have proper actuation capability and high air-operating stability.

Experimental

The ionic liquids were purchased from C-TRI. The other materials including Nafion® 117 membrane were purchased from Aldrich. The IEMs were synthesized by radiation-grafting and sulfonation process. Poly(vinylidene-*co*-hexafluoropropylene) (P(VDF-*co*-HFP), Mw 400K) films of 200 μm thickness were irradiated at room temperature under N_2 with γ-ray (0.7 kGy/h dose rate; 10, 30, and 50 kGy) using a ^{60}Co source (KAERI, Korea). Irradiated films were immersed in N_2-purged styrene at 70 °C and grafted for 16 h, and then sulfonated with 1.5 vol % chlorosulfonic acid in 1,2-dichloroethane. The amount of sulfonic acid group was evaluated from ion-exchange capacity, which was determined by traditional titration method. Pt electrode was chemically deposited on both surfaces of IEM by using effective plating method, known as impregnation-reduction with $Pt(NH_3)_4Cl_2$ and $NaBH_4$ [1]. In order to effectively imbibe the ionic liquids into IEMs, the dehydrated IPMCs were immersed in methanol/ionic liquids mixture (50/50 by weight) [3]. The properties of the ionic liquids and prepared IEMs are given in **Table 1** and **Table 2**. Ionic conductivity was determined by using AC impedance method.

Table 1. Structure and properties of the ionic liquids.

Ionic liquid(1)	Cation type(2)	Anion type	Melting temp. (°C)	Ionic conductivity (ms/cm)
[E][B]		BF_4^-	-15	14
[B][B]			-71	3.1
[H][B]	R1= -CH3, R2= -(CH2)nCH3		-82	1.15

* (1) The former abbreviation; [E] = 1-ethyl-3-methylimidazolium ion, [B] = 1-*n*-bthyl-3-methylimidazolium ion, [H] = 1-*n*-hexyl-3-methyl-imidazolium ion, the later abbreviation; [B] = tetrafluoro borate anion, (2) n=1 ; [E], n=3 ; [B], n=5 ; [H]

Table 2. Properties of PSSA-grafted PVDF-*co*-HFP membranes.

Membranes	Ion exchange capacity (meq./g)	Uptake of water & ionic liquid (%)	Ionic conductivity with water & ionic liquid (mS/cm)
IEM 1.21	1.21	0.97, 0.85	44.31, 0.34
IEM 2.68	2.68	1.46, 1.12	23.73, 1.16
IEM 3.11	3.11	1.96, 1.25	75.50, 4.29

Bending actuation of the prepared IPMC was measured by laser displacement meter (**Figure 1**). The detection position of IPMC strips (30 mm free length and 5 mm width) was 20 mm apart from the tip. Air-operating stability was quantified by actuation cycling.

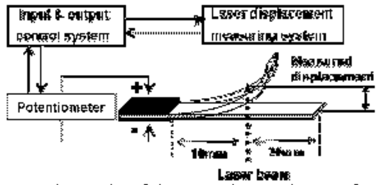


Figure 1. A schematic of the experimental setup for the actuation analysis.

Results and discussion

Figure 2 shows the bending displacement and response of the prepared IPMCs by applying a direct current to the electrode at 2 V for 50 s. The bending performance of the IPMCs, which made from each of IEMs and soaked with each of ionic liquids differs from each other in the maximum displacement and the response time. And the actuation capability of the prepared IPMCs is similar to or higher than that of Nafion IPMC with waters. We demonstrate that the difference in the bending capability can be caused by the difference in the various properties of IEMs and ionic liquids. The higher concentration of hydrophilic sulfonyl group enables the IEM to possess more ionic liquids. The maximum displacement of the IPMCs is considered to be affected by the amount of soaked content of ionic liquids in IEMs. The higher conductivity causes the fast transportation of mobile cations accompanying ionic liquids, and consequently, the response time of the IPMCs is dependant upon the ionic conductivity. And air-operating stability of the IPMCs with improved actuation behavior is appreciably governed by various physical and electrochemical properties of soaked solvents in IEMs.

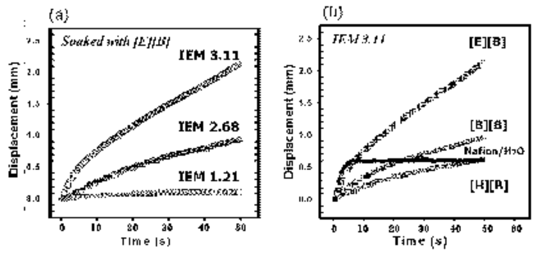


Figure 2. Actuation capability of IPMCs employing (a) different IEMs with [E][B] and (b) IEM 3.11 with different ionic liquids.

Conclusions

The prepared IPMCs employing the IEMs soaked with ionic liquids were effectively deformed three times larger and actuated for 300 times longer than those of Nafion with water at the same applied conditions owing to improved properties of the IEMs and ionic liquids.

Acknowledgements

This work was supported by Korea Ministry of Health and Welfare through Advanced Motion Recovery Research Center (02-PJ3-PG6-EV03-0004).

References

[1]Y. Bar-Cohen, Electroactive Polymer (EAP) Actuators as Artificial Muscles, : SPIE Press, Washington **2001**; Chapter 6
[2] Paquette, J. W.; Kim, K. J.; Kim, D. *Sensors Actuators A*. **2005**, *118*, 135.
[3] M. D. Bennett, and D. J. Leo, *Sensors Actuators A*. **2004**, *115*, 79.