Enhanced Behaviors of Ionic-Polymer Metal Composite (IPMC) Actuator Coupled with Polymeric Anion-doped Polypyrrole Thin Film

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Abstract : In order to overcome the weak actuation and relaxation problems during the deformation of IPMC actuator, polymeric anion (polystyrenesulfonate)-doped polypyrrole(Ppy(PSS)) was electrodeposited onto IPMC actuator. Electrochemical quartz crystal microbalance study showed that hydrated cations were instilled into Ppy(PSS) film and polymeric-anion dopants introduced during polymerization were not expelled. Ppy(PSS)-coated IPMC actuator formed two electrode/electrolyte interfaces, Pt/nafion and Ppy(PSS)/bulk solution, and additive volume expansion phenomena at interfaces induced the large deformation compensating the relaxation of actuation by back diffusion of water.

Key words : Ionic polymer metal composite, Actuator, Conducting polymer, Polypyrrole, Dopant.

1. Introduction

Recently, there have been many demands for highly active sensors, flexible and miniaturized actuators in many fields such as bio-equipments and micro-robots.[1-5] Electro-active polymer (EAP) systems, such as polymer gels, ionic polymer-metal composites (IPMC), and conducting polymers, are considered to be promising candidates for dynamic sensors, robotic actuators, and artificial muscles. IPMC actuator is composed of ion-exchange polymer with metal electrodes and it exhibits large strain capability and fast response at low-voltage operation.[6,7]
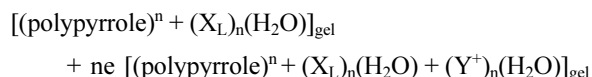
When the electric field is applied to the ion-exchange polymer metal composite (IPMC), the mobility of hydrated ions induces the electro-osmosis resulting in a bending of the film towards the positive electrode.[8,9] Excessive amount of hydrated cations near the cathode induces deformation of the system but, concentration difference inside polymer electrolyte builds up and hydrated cations start to diffuse back to positive electrode. It causes the relaxation of deformation even under the electric field and limits the use of IPMC actuator. Furthermore, IPMC actuator has a limitation in operation because of the solution electrolysis and the resulting loss of solution.

Conducting polymer can be applied to an actuator by its doping and de-doping behaviors, which lead to a change in conductivity, color, and volume.[10-12] When a polypyrrole(Ppy) film is oxidized, the anions are inserted to maintain the electro-neutrality and the swelling is followed, whereas the polypyrrole film of the other side is reduced and the anions are expelled and the shrinkage is followed ;

$$(polypyrrole)_s + (X_s)_{aq} \; [(polypyrrole)^n + (X_s)_n(H_2O)]_{gel} + ne$$

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where s, aq, and X_s are referred to solid film, aqueous solution, and small size anion, respectively.[13]

However, when macromolecular or polymeric anion (e.g. polystyrenesulfonate (PSS$^-$), polyvinylsulfonate, etc) is used as a dopant, Ppy's long chain and PSS$^-$'s chain frame are entangled. Therefore, electroneutrality can be maintained by the insertion of cations because polymeric anions cannot be removed from matrix;

$$[(polypyrrole)^n + (X_L)_n(H_2O)]_{gel}$$
$$+ \; ne \; [(polypyrrole)^n + (X_L)_n(H_2O) + (Y^+)_n(H_2O)]_{gel}$$

where X_L, and Y^+ are referred to large size anion, and cation from aqueous solution, respectively. Recently, polypyrole polymer coating on electro-active paper actuator to enhance the performance of the actuator was reported.[14]

In this work, different actuating behaviors of IPMC and conducting polymer can be combined to enhance the deformation behaviors by controlling each actuation mechanism. PSS$^-$-doped Ppy was electrochemically deposited on metal electrodes of IPMC actuator and the actuation behaviors were investigated to increase the bending performance and reduce the relaxation behaviors.

2. Experimental

Polystyrenesulfonate(PSS$^-$)-doped polypyrrole(Ppy) was electrodeposited onto ionic polymer metal composite (IPMC) which had prepared with electroless deposition. Cation-exchange membrain(Nafion) was used as ionic polymer electrolyte. Before the electroless deposition of Pt on Nafion[TM], Nafion[TM] was pretreated with 2 wt% H_2O_2 for the exchange of Na$^+$ with H$^+$ and then, immersed in 3 M H_2SO_4 for purifi-

cation. Pt thin film was prepared with $Pt(NH_3)_4Cl_2$ and $NaBH_4$ reducing agent by electroless deposition. Polystyrene-sulfonate(PSS^-)-doped polypyrrole(Ppy) film was electrode-posited onto Pt from an aqueous solution of 20 mM pyrrole (F.W 67.09 / 98% / Aldrich, Inc.) and 2 mM Poly(sodium 4-styrene-sulfonate) (Typical M.W 70,000 / Aldrich, Inc.). Pt plate was used as a counter electrode and Ag/AgCl (4 M KCl) electrode was used as a reference electrode. Ppy(PSS) film was formed by applying 0.75 V for 200 seconds. Applied potential or current was modulated with a galvanostat/potentiostat (PAR 273A, EG&G).

Doping/de-doping behaviors of hydrated cations inside Ppy (PSS) film electrode were investigated with the electrochem-ical quartz crystal microbalance (EQCM), which can monitor *in-situ* mass changes during doping/de-doping. The changed Ppy(PSS) films were deposited on 9 MHz Au-coated AT-cut quartz crystals (exposed area, 0.196 cm^2) and the total charge during polymerization was 70 mC. Strain and force of the IPMC actuator, 0.5 cm(W)2 cm(L), were measured with a laser dis-placement (KEYENCE, LK081) and force sensor GSO-30, connected to 12 bit A/D converter for data analysis and 12 bit D/A converter for voltage control.

3. Results and discussion

Thin film of PSS^--doped Ppy (Ppy(PSS)) was anodically polymerized onto Au quartz crystal and Fig. 1 shows the simultaneous current and mass changes during polymerization at a constant potential of 0.75 V. Initially observed high cur-rent density and accompanying fast mass increase indicate the increase in number of nuclei and the following growth of nuclei to form a monolayer. Once the layer is formed, low conductivity of a Ppy works as resistance and the deposition rate, i.e., current, starts to decrease, showing a slow mass increase rate.

Ppy(PSS) electrode was immersed in 0.1 M LiCl and Fig. 2 shows current and mass changes of electrode during 2 suc-cessive cyclic voltammetry. Cyclic voltammograms (CV) are featureless in a potential window of -0.2 to 0.4 V, indicating a typical capacitor behavior of Ppy conducting polymer. The
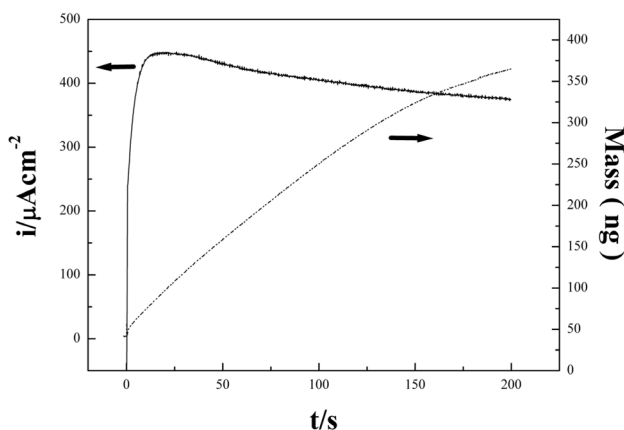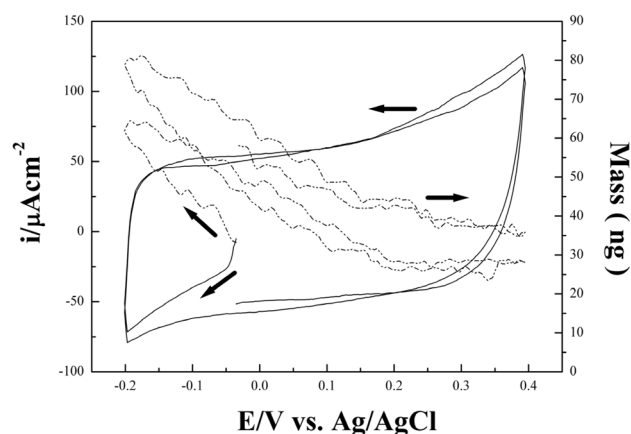

Fig. 2. Current and mass changes during consecutive potential scans in 0.1 M LiCl solution. (scan rate = 20 mV/s)

specific capacitance of Ppy can be calculated from CV by the equation, C=Q/V, where Q is the total charge which is an integrated area of the CV curve. The specific capacitance of Ppy(PSS) remains constant between successive scans. It states the invariable structure of Ppy(PSS) under electric field.

Ppy(PSS) electrode mass increases during cathodic scan. When scan direction is reversed, electrode mass decreases up to 0.15 V and remains constant at more anodic potential. When small anions are doped into Ppy chain, either the expulsion of anions or the intrusion of cations can be simultaneously con-sidered. However, polymeric anion, such as PSS^-, is so big that the entanglement of Ppy chain and PSS^- frame does not allow to move PSS^- freely. Under the electric field, the position of PSS^- is fixed and the mobile species should be only limited to hydrated cations. Therefore, electrode mass variations dur-ing CV are attributed to the mobility of cations inside a Ppy (PSS) matrix. The gain of mass during first cathodic scan is equivalent to the loss of mass during anodic scan. However, in the second cathodic scan, gain of mass is a little higher than the loss of mass during anodic scan, which suggests that inserted materials are not totally expelled from the electrode during CV.

Fig. 3 shows the potential and mass changes when Ppy(PSS) electrode is galvanostatically reduced at -1 mA/cm². The rate
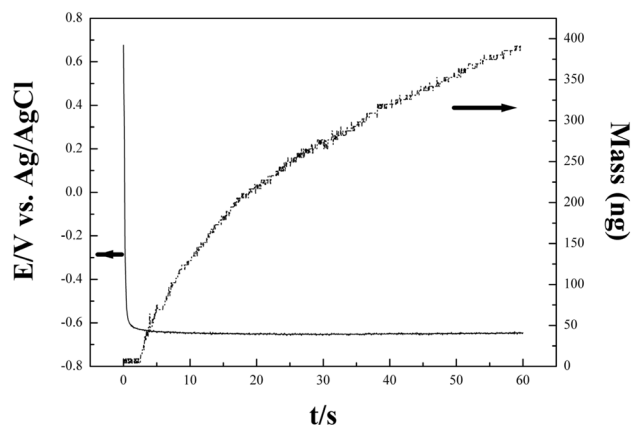

Fig. 1. Current and *in-situ* mass changes during polymerization of PSS-doped Ppy. (20 mM pyrrole monomer and 2 mM NaPSS)

Fig. 3. Potential and mass changes of Ppy(PSS) quartz electrode in 0.1 M LiCl solution. (applied current density = -1 mA/cm²)

of mass increase becomes slow with the continuation of cathodic current. That is, the number of Li$^+$ insertion sites decreases with the gradual occupation of Li$^+$ inside negatively charged Ppy(PSS) film. Deformation of IMPC actuator is caused by the excess amount of water near the cathode and Ppy(PSS) can be swollen with hydrated cations when it is cathodically reduced. Characteristics of IMPC and Ppy(PSS) system can be combined when Ppy(PSS) is electrochemically deposited onto IMPC actuator. In Ppy(PSS) coated IMPC actuator, water inside nafion membrane is accumulated near the Pt cathode and hydrated cations in bulk solution are inserted into Ppy(PSS) cathode. Since two cathodes are contacted together, the deformation of two materials are added and a great deformation can be expected.

Fig. 4 shows the effect of Ppy(PSS)-coating on cyclic voltammogram of IMPC actuator. Ppy(PSS)-coated IMPC actuator has a higher slope in I-E curve, which reflects the ability of the system to store energy that determines the degree of actuation.[15] Fig. 5 shows the current variation when potential is
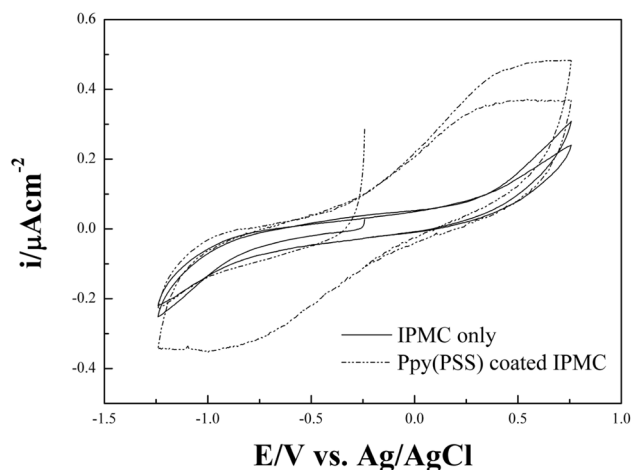
initially stepped up to 2 V for 5 s and then, reduced to -2 V by step. The measured current represents the value of current at the interfaces between electrode and electrolyte. Two interfaces, Pt/nafion and Ppy(PSS)/bulk solution, draw a large capacitive and double-layer charging current and may result in the increase of deformation.

Bending performance of Ppy(PSS)-coated IMPC actuator was measured at 0.1 Hz in the range of ±2 V, as shown in Fig. 6. Since the magnitude of y-axis represents the degree of deformation, it is evident that Ppy(PSS)-coated IPMC actuator has a better bending motion. IPMC actuator shows a fast and large deformation just after potential has a step change but the degree of deformation lessens under the same potential. This observation can be explained that the accumulated water molecules in the cathode start diffusing back to the anode due to the concentration difference of water.[16] That is, relaxation of deformation occurs naturally during actuation at a constant potential. However, bending behaviors of Ppy(PSS)-coated IPMC actuator are much larger than that of IPMC actuator and the relaxation of deformation is significantly retarded. As indicated in Fig. 3, insertion of hydrated cations inside Ppy(PSS) induces a deformation, compensating the relaxation by back diffusion of water.

Fig. 7 shows the schematic of actuation mechanism of

Fig. 4. Comparison of cyclic voltammogram in 0.1 M LiCl solution. (scan rate: 20 mV/s)

Fig. 6. Deformation of IMPC with the change of applied potential. Potential is initially stepped to 2 V and, after 5 s of holding time, reduced to -2 V.
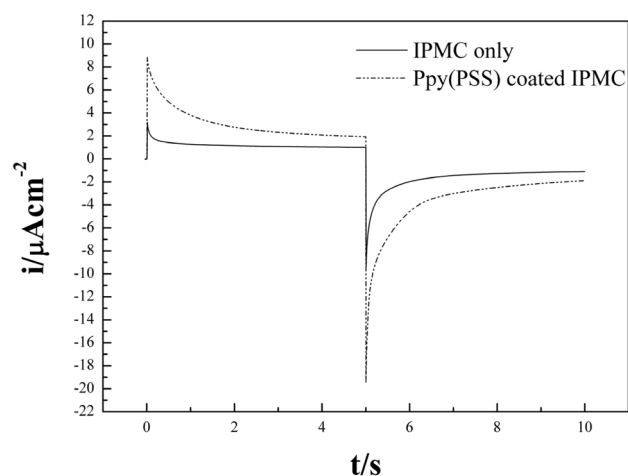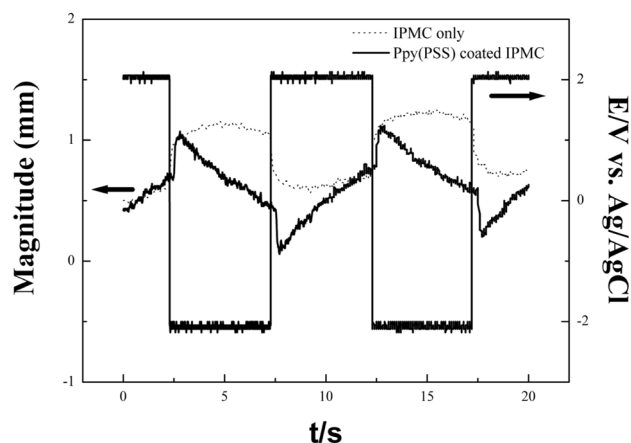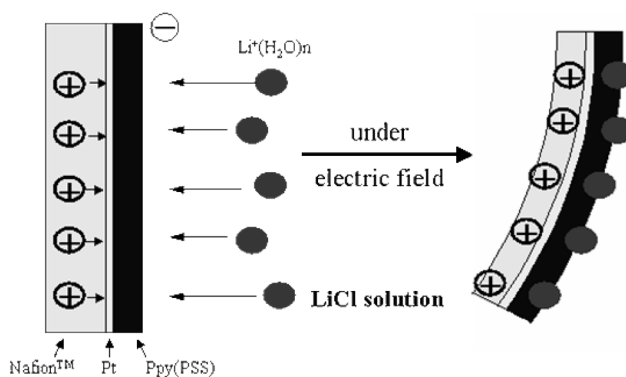

Fig. 5. Current transients when potential square waveform is applied in 0.1 M LiCl solution. Potential is initially stepped to 2 V and, after 5 s of holding time, reduced to -2 V.

Fig. 7. Schematics of Ppy(PSS) coated IPMC actuator.

Ppy(PSS)-coated a IMPC actuator. Large deformation and low relaxation of actuation are ascribed to additive behaviors of IMPC and Ppy(PSS) actuator.

4. Conclusions

Polystyrensulfonate(PSS)-doped polypyrrole(Ppy (PSS)) was electrochemically synthesized and implemented to overcome the limitation of IPMC actuator. When Ppy(PSS) film is negatively charged, EQCM results shows clearly that PSS dopant remains at fixed position inside a film but hydrated cations are instilled to meet electroneutrality.

Ppy(PSS) was electrodeposited onto IPMC actuator and the effect of Ppy(PSS) on the bending of IPMC was investigated. Both swelling of Ppy(PSS) and accumulated water at negatively charged electrode/electrolyte interfaces induce a large deformation and restricted relaxation.

Acknowledgement

References

1. M. Shahinpoor, *Smart Materials and Structures*, **3**, 367 (1994).
2. Y. Osada and D. E. Rossi, *Sensors and Actuators B*, **63**, 1 (2000).
3. Y. Bar-Cohen, T. Xue, M. Shahinpoor, J. O. Simpson, and J. Smith, *Proceedings of SPIE-Smart Structures and Materials*, 3324 (1998).
4. J. W. Gardner and P. N. Battlett, *Sensors and Actuators A*, **51**, 57 (1995).
5. O. Inganas and Q. Pei, *Advanced Materials*, **4**, 277 (1992).
6. W. Kuhn, B. Hargitay, A. Katchalsky, and H. Eisenberg, *Nature*, **165**, 514 (1950).
7. M. Shahinpoor and K. J. Kim, *Smart Materials and Structures*, **10**, 819 (2001).
8. K. J. Kim and M. Shahinpoor, *Smart Materials and Structure*, **12**, 65 (2003).
9. Y. Bar-Cohen and S. Leary, *Proceedings of SPIE*, Newport Beach, CA, March, 2000.
10. R. H. Baughman, *Makromol. Chem., Macromol. Symp.*, **51**, 193 (1991).
11. G. Inzelt, M. Pineri, J. W. Schultze, and M. A. Vorotyntsev, *Electrochim. Acta*, **45**, 2403 (2000).
12. P. Chandrasekhar, *Conducting Polymers: Fundamentals and Applications, A Practical Approach*, Kluwer Academic Publishers, 1999.
13. T. F. Otero, in: H. S. Nalwa (Ed.), *Handbook of Organic Conductive Molecules and Polymers*, Wiley, New York, 1997.
14. J. Kim, S. D. Deshpande, S. Yun, and Q. Li, *Polymer Journal*, **38**, 659 (2006).
15. T. G. Noh, Y. Tak, J. Nam, and H. Choi, *Electrochim. Acta*, **47**, 2341 (2002).
16. S. Tadokoro, S. Yamagani, T. Takamori, and K. Oguro, *Proceedings of SPIE*, Newport Beach, 92 (2002).