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폴리아닐린이 코팅된 Electro-Active Paper 작동기 성능평가

Performance Characterization of Polyaniline Coated Electro-Active Paper Actuator

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Bending actuators composed of cellulose with an electrically conducting polymer (CP) are fabricated and their performance is characterized in the air. Two different counter ions, perchlorate and tetrafluoroborate are used as dopant ions in the polyaniline CP processing. CP-cellulose-CP trilayer and CP-cellulose bilayer samples are fabricated with different dopant ions, and their actuation performance is evaluated in terms of tip displacement, blocked force and electrical power consumption along with the humidity level and actuation frequency. The trilayer samples substantially enhanced the tip displacement compared to the bilayer ones. The actuation performance of the trilayer actuator is three times better than that of original cellulose electro-active paper (EAPap) actuator. The displacement and blocked force of CP-EAPap actuators are dependent on the humidity and frequency.

Key Words: Electro-Active Paper, Conducting Polymer, Polyaniline, Biomimetic actuator, Blocked force

1. Introduction

Conducting polymers with electron conjugated system such as polyacetylene, polypyrrole, polythiophene and their analogies take three stages such as neutral, oxidized and reduced states.[1-5] The reduced and oxidized states are conductive with the conductivity range from 10^2 to 10^3S·cm-1, while the neutral state is intrinsically insulating.[5] The neutral conducting polymer is either electrochemically oxidized by ejecting electrons accompanied with doping of anions, viz., p-type doping, or electrochemically reduced by injecting electron with doping of cations, viz., n-type doping. The oxidized and reduced conducting polymer can be electrochemically reduced and oxidized to the neutral state releasing the dopants, respectively. Electrochemical actuators using conducting polymers have been proposed by Baughman.[6] A polymer gel actuator was shown by Osada et al.[7] However, electrochemical actuators generally require an auxiliary counter electrode and an electrolyte solution. Nevertheless, one of the attractive features of the conducing polymer actuators is a low actuation voltage, comparing to either piezoelectric or electrostrictive materials, which operates at high voltages. Many attempts have been made to construct a fully polymeric actuators using solid polymeric electrolyte working in air using polypyrrole (PPy),[8,9] polyaniline (PANi)[10,11] and few composites using carbon nanotubes (CNT) and conducting polymer[12] had been demonstrated as an actuator material, where substantial changes in the length of individual nanotube and redox of conducing polymer by charging and discharging improve the performance of

actuator devices.

Electro-active paper (EAPap) actuator operating in an air has been proposed recently.[13,14] Kim et al. have reported that natural cellulose paper exhibits a large strain under an imposed voltage across surface electrodes. The possibility of cellulose papers as biomimetic actuators has been well demonstrated. Attractive features of the EAPap actuators are low activation voltage, large displacement output, dryness, lightweight, high Young's modulus, low price and biodegradable. Even at low voltage, the cellulose based EAP actuators can reach a tip displacement up to 10% of its length. The effect of humidity, however, is an important factor influencing actuator performance. To enhance the performance of EAPap actuator, PPy and PANi conducting polymers have been coated on EAPap.[15-17] The PANi conducting polymer coated EAPap (CP-EAPap) actuator enhanced the tip displacement to 10 mm.[16]

This study aims at exploring the mechanical performance of PANi coated EAPap actuators. The effect of PANi layer thickness, different dopants and the configuration of CP-EAPap are evaluated in terms of tip deflection and blocked force with different humidity levels.

2. Material and experimental details

2.1 Preparation cellulose based EAPap

Cellulose EAPap is made by coating thin electrode on regenerated cellulose. Detail procedure of cellulose EAPap has been reported[18] and this is a brief summary. Cotton pulp (Buckeye, USA) with degree of polymerization, 4500 is torn in small pieces. The cotton pulp and LiCl (Junsei Chemical) is heated in oven at 100°C to evaporate water. The cotton pulp is mixed with LiCl/anhydrous DMAc (N,N-dimethylacetamide) (Aldrich) in proportion of cotton cellulose pulp/LiCl/ DMAc to 2/8/90. The cellulose is dissolved in the solvent by heating at 155°C with mechanical stirring according to the solvent exchange technique. The cellulose solution is cast on a glass using a doctor blade and washed with deionized water to regenerate cellulose, followed by drying and stretching. The deposition of gold electrode on both sides is made by using a physical vapor deposition system. The thickness of regenerated cellulose and the gold layer are about 20 m and 100nm, respectively. To enhance the adhesion of PANi, about 30 nm of Titanium layer is added on the surface of gold layer.

2.2 Preparation of PANi film

Electrochemical synthesis of PANi on EAPap matrix is performed using a Solartron Electrochemical Interface unit [Model SI 1287] at 0.9V. vs. SCE for varying time intervals such as 15, 30, 45 and 60 minutes. The working electrode on which PPy deposited is composed of regenerated cellulose film coated with gold layers and the counter electrode is platinum plate. The active area where PANi is polymerized is 30 ×10 mm.

The electrolyte solution for the PANi films contains 0.25M aniline monomer and 0.5 M oxidizing agent in propylene carbonate (PC). The acid used in the electro-generation is dichloro acetic acid (DCA) to maintain acidity of the electrolyte. The electrolyte is supplied with high concentration of DCA ranging from 1-2 M. The solution in the cell is deoxidized under a stream of nitrogen gas for 15 minutes. Organic solvent is necessary to deposit PANi on gold surface since cellulose gets shrunk in aqueous medium. Thickness of PANi films is in the range of 10-80 m. The produced sample is dried in an oven, at temperature between 90°C and 100°C.

2.3 Tip displacement measurement

The actuation of the samples is tested in an environmental chamber where the temperature and humidity can be controlled.[14] The CP-EAPap sample is hung on a vertical mount (Fig. 1). A function generator is used to activate the CP-EAPap actuators. The actuation voltage is 7 AC Volt and the frequency range is from 0.5Hz to 7Hz. The tip displacement of the sample is measured using a laser doppler vibrometer (LDV). The current is measured using a current probe (AM 503B, Tektronix).

2.4 Blocked force measurement

To evaluate the performance of CP-EAPap, the blocked force of the actuators is measured using microbalance (Precias XT220A) as reported previously (Fig. 2).[19] While the sample is hung on the vertical mount, the end tip is inserted into the groove of a very light

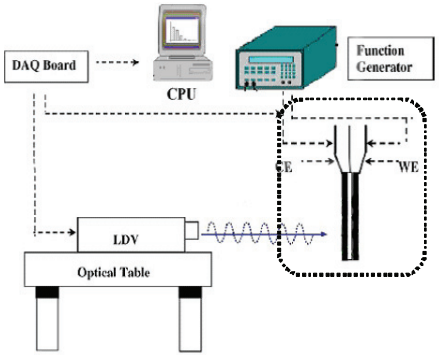

Fig. 1 Scheme of tip displacement measurement

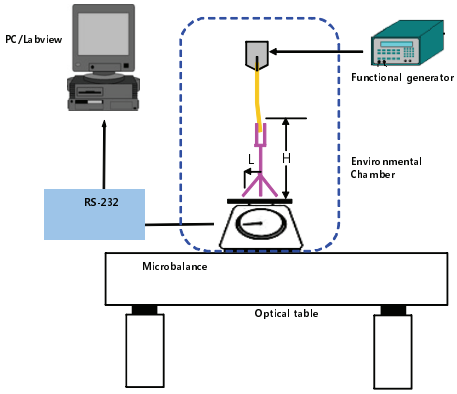

Fig. 2 Diagram of blocked force measurement setup

fixture. The weight change can be marked out with the help of microbalance. The blocked force, F, at the tip due to the activation is calculated using

$$F = N \times \frac{L}{H} \quad (1)$$

where H is the height between sample's top and the surface of microbalance, L is the half length, N is weight change exhibited from the microbalance.

3. Results and Discussion

3.1 Characterization of CP-EAP samples

We termed the CP-EAPap actuators of PANi// Cellulose and PANi//Cellulose//PANi as bilayer and trilayer actuators, respectively. Fig. 3 shows the cross-section SEM image of the bilayer actuator. The PANi layer was completely attached to the gold layer producing

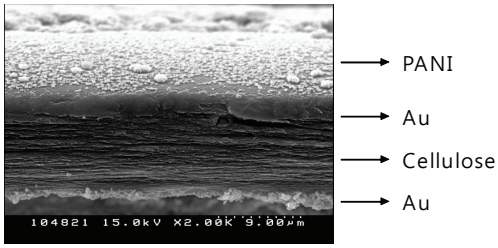

Fig. 3 SEM cross-sectional image of bilayer CP-EAPap actuator

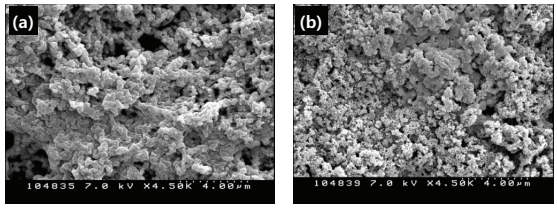

Fig. 4 SEM images of PANi doped by (a) ClO_4^- and (b) BF_4^-

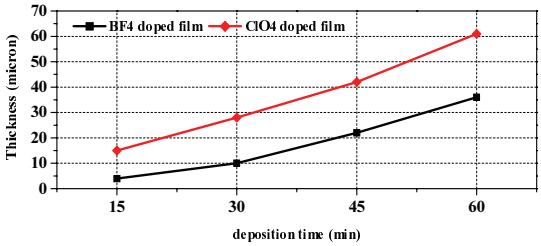

Fig. 5 hickness trends with deposition time and different dopants[16]

a rather featureless surface morphology, while the gold and cellulose layers were easily separated. This suggests that the adhesion between PANi and gold layers is good.

SEM images of PANi doped with different dopants are shown in Fig. 4. Left shows the ClO_4^- doped one and right is the BF_4^- doped one. Both show that electro-synthesized PANi in PC medium in the presence of DCA is a compact structure, similar to that obtained by Yonezawa at al.[20] Interestingly, the BF_4^- doped structure shows more compact structure than the ClO_4^- doped films.

Fig. 5 shows the thickness of PANi layer with the deposition time.[16] The thickness was increased almost linearly with the deposition time. Obviously, the film thickness doped by ClO_4^- was thicker than the BF_4^- doped case. This may be due to the ionization in the film

electro-generation process, since the electric current in ClO_4^- solution cell was much higher than the current in the BF_4^- solution.

3.2 Actuator performance with different dopants

The actuation test for dopant effect was investigated in air medium at 95% relative humidity (RH) level with room temperature 23°C. The test was made with 7 AC Volt and the frequency range from 0.5Hz to 7Hz. The tip displacement of CP-EAPap trilayer actuators doped by ClO_4^- and BF_4^- ions is illustrated in Fig. 6. The tip displacement increased to 13.2mm and 9.7mm for ClO_4^- and BF_4^- doped samples, respectively, when the deposition time was 30 minutes. Notice that the displacement output decreases after 30 min deposition time. Obvious explanation on this phenomenon is that as the deposition time of conducting polymer increased, the ion migration effect associated with the displacement output is also increased. The redox process taking place in PANi layer is associated with anion movement through the thickness direction. Under certain conditions, however, especially for thick layers of PANi, the anion movement can limit the kinetics of electrochemical redox process. Furthermore, when the thickness of PANi layer is increased the actuator is so stiffened that the displacement can be decreased. Thus, there is an optimal thickness of PANi layer for the best performance of actuator. Actuation phenomenon of ClO_4^- doped sample is better than the BF_4^- doped one. This is due to the fact that bigger pores in the surface of ClO_4^- doped film allow ions penetrate throughout the film more freely. The cellulose EAPap exhibited its maximum displacement of 4.5mm under identical conditions.[14] This proves that the use of conducting polymer enhances the actuation performance of EAPap actuator.

3.3 Actuation performance of bilayer and trilayer actuators

The results obtained for bilayer and trilayer actuators for PANi using different dopant ions are depicted in Fig. 7 when the deposition time is 30 min. The measurement was also carried out at the same humidity level and temperature. The result clearly indicates that the trilayer actuator is better than the bilayer actuator. The maximum displacements occurred near 3Hz, which is the first

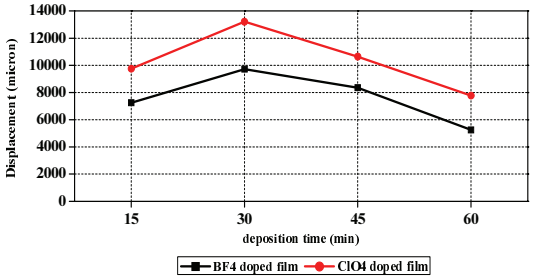

Fig. 6 Tip displacement for different dopants

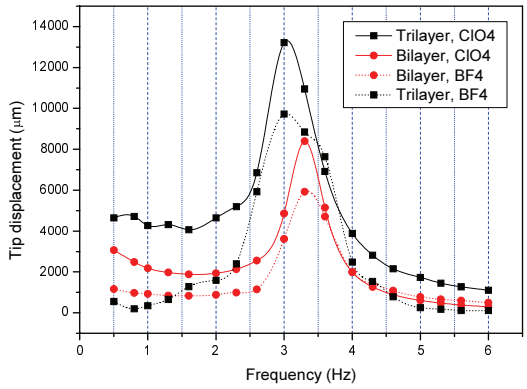

Fig. 7 Actuation of CP-EAPap actuators for different CP layers doped with ClO_4^- and BF_4^-

resonance frequency of sample. In all these devices the conducting polymer layer seems to be playing an important role in actuation performance, though cellulose film is contributing some effect. The dominant effect associated with migration of counter ion of conducting polymer through the interfaces between the polymer films and the cellulose film in high humidity air ambience is similar to the literature report of trilayer conducting polymer devices working in air.[21]

3.4 Humidity effect on the performance

Fig. 8 shows the effect of humidity on the actuation performance of trilayer samples doped by ClO_4^- ion. Five different relative humidity levels were made from 60% to 95%. The maximum tip displacement of 13.2mm was occurred at 95% RH. It is evident that the humidity has some effect. This is due to the fact that water molecules can be easily absorbed in cellulose film and the absorbed water can assist the redox reaction of PANi through electric filed. Nevertheless, a remarkable result is that

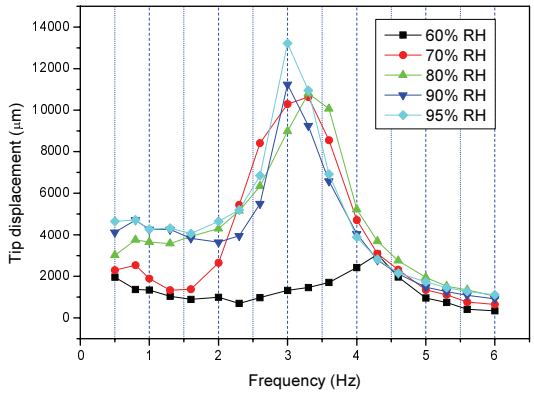

Fig. 8 Actuation of CP-EAPap actuator with humidity

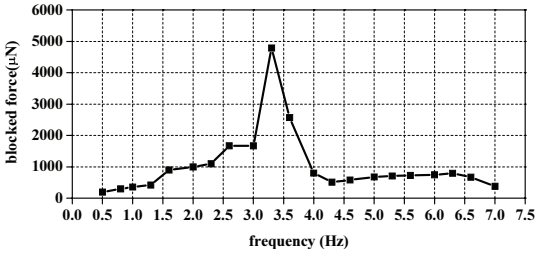

Fig. 9 Blocked force varying with different frequency

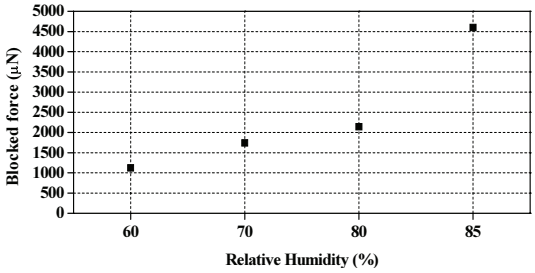

Fig. 10 Blocked force at different humidity

when the relative humidity is 70%, the actuation performance is nearly 85% of the maximum performance. Note that 70RH% is a threshold humidity level that produces large displacement.

3.5 Blocked force and electrical power at different humidity

The blocked force of CP-EAPap actuator doped with ClO_4^- ion was measured at 85% RH with 7 AC Volt. Fig. 9 shows the blocked force with actuation frequency. The trend is similar to the tip displacement output, whereas

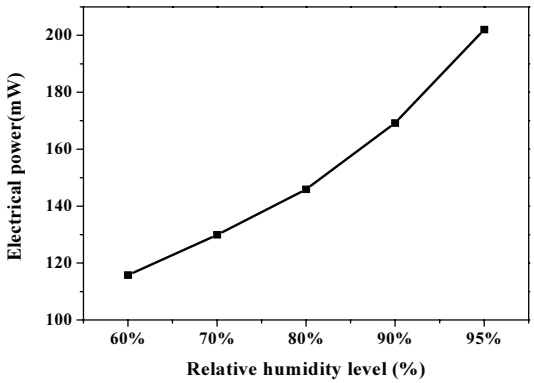

Fig. 11 Electrical power at different humidity

the maximum blocked force was 4.6 mN at 3.3Hz. Fig. 10 shows the humidity effect on the blocked force. As the humidity is increased the force is increased.

The electrical power consumption was found by measuring the current for the trilayer CP-EAPap doped with ClO_4^- ion and 30 minute deposition time. Fig. 11 shows the averaged power along with relative humidity at 3.3Hz. The maximum averaged electrical power is 202 mW.

The actuation principle of CP-EAPap is associated with three factors: the structural changes in conducting PANi due to applied current causing adsorption and extrusion of water in the film structure, the piezoelectric effect of cellulose and the third factor is ion migration effect of CP-EAPap itself.[16]

4. Summary

Bending actuators composed of cellulose with PANi layers were fabricated and their performance was tested in the air depending on humidity level and frequency. The comparative study between bilayer and trilayer actuators indicated that the performance of trilayer actuators is superior to bilayer ones. There is an optimal thickness ratio between the conducting polymer and cellulose layer. The dopant effect was seen in both bilayer and trilayer actuators where ClO_4^- dopant better than BF_4^- dopant. The maximum tip displacement and blocked force of CP-EAPap were found to be 13.2mm and 4.6mN, respectively from the trilayer actuator with ClO_4- dopant ion.

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