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CP-EAPap 생체모방 작동기의 제조 및 성능

CP-EAPap biomimetic actuator fabrication and performance

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Key Words : EAPap, Electro-Active Paper, Ionic movement, CP-EAPap, Polyaniline.

ABSTRACT

Biomimetic actuators composed of cellophane with an electrically conducting polyaniline(PANI) film have been fabricated and tested in air ambience conditions doped with two different counter ions such as perchlorate (ClO_4^-) and tetrafluoroborate (BF_4^-). Fabrication of the trilayer CP//CELLOPHANE//CP substantially enhanced the tip displacement (13.2 mm) compared to the small displacement (8.3 mm) of the bilayer CP//CELLOPHANE. The ion migration among layers is the main factor behind the expansion of cellophane, while the expansion /contraction of PANI are dependent on the redox reaction of the polymer. The displacement of the composite is dominated by the humidity content. This implies that the actuation principle is possibly due to the assistance of water existing.

1. Introduction

Electro-active polymer (EAPap) actuators directly convert electrical energy to mechanical energy with a material response to applied electrical voltage. Due to these characteristics that are similar to biological muscles, these actuators have been dubbed 'artificial muscles'. Applications of these actuators have been found in robotics, optical fiber switches, optical displays, prosthetic devices, microscopic pumps and anti-vibration systems. Ferroelectric and electro-strictive materials have been used as actuator materials owing to their direct energy conversion. Of these materials, shape memory alloys and electroactive ceramics have been the most widely used. However, to realize actuations in these materials a high drive voltage is required.

Electro-active paper actuators operating in air ambience were proposed many years ago [1]. Kim. et.al reported that natural cellulose exhibits large strain under an imposed voltage across their surface electrodes. The ability and possibility of cellulose papers as actuators in a beam structure were well demonstrated [2]. One of the attractive features of the EAPap actuators is a low drive voltage that does not exceed 7V. Even at low voltage, in 95% relative humidity conditions EAP actuators can reach a tip displacement as high as 4.5 mm. Recently, conducting polymers, such as polypyrrole, polyaniline have been demonstrated as an actuator material [3-5]. Based on EAP material, polypyrrole (PPy) was fabricated to form our first conducting polymer electro-active paper (CP-EAPap) actuator, which enhanced the tip displacement [6]. The effect of humidity content during activation process has been experimentally revealed to be an important factor influencing the actuation behavior of materials, where 95% relative humidity provided the best result. The utilization of polyaniline, which is known to be more stable than polypyrrole expects us to give further improvement in CP-EAPap actuators.

The aim of this study is to explore the use of the electro-active paper (EAPap) and electrically conducting PANI composites as an actuator material. The effect of PANI film thickness and layers on surface of cellophane, the ability of actuation in different humidity and doped by different ions will be examined.

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2. Material and experimental details

2.1 Preparation of gold electrodes

The cellophane was commercially available and its thickness is 21 μm. The deposition of gold electrode on both sides was made by an evaporation technique using a physical vapor deposition (PVD) system, proper thickness of gold is found to produce the best actuation. To enhance the adhesion, about 30 nanometers of Titanium layer is added on the surface of gold. And the stiffness of gold layer is negligible compared to the stiffness of cellophane.

2.2 Preparation of PANI film

Electrochemical synthesis of PANI on EAPap matrix was performed potentiostically 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 electrodes on which, polyaniline was deposited composed of cellophane paper coated with gold electrode. The counter electrode is platinum plate. The active area where polyaniline polymerized was

30mm×10mm.

The electrolyte solution from which the polyaniline films were electro-generated contains 0.25M aniline monomer and 0.5 M oxidizing agent in propylene carbonate (PC). The acid we used in the electro-generation was dichloro acetic acid (DCA) to maintain acidity of the electrolyte. The electrolyte was supplied with high concentration of DCA ranging from 1-2 M. The solution in the cell was deoxidized under a stream of nitrogen gas for 15 minutes. Organic solvent is necessary to deposit PANI on gold surface, since cellophane paper gets shrunk in aqueous medium. The thickness of various PANI films obtained was in the range of 10-80 μm. The resulting film was dried in oven, at temperature between 90° C and 100° C.

2.3 Actuation tests

The actuation of the sample was tested in a environmental chamber (as described in [6]) where the temperature and humidity can be controlled. The linear displacement measurement of various sample films was carried out using Laser Vibro-Meter. The best voltage from a Function Generator is chosen to be 7V with frequency changing from 0.5 Hz to 7 Hz.

3. Results

3.1. Characterization of CP-EAP actuator film

The SEM micrograph (Figure 1) is the cross-section view of the bilayer configuration of CP-EAPap actuator. We term the actuator PANI//Cellophane and PANI//Cellophane//PANI as bilayer actuator and trilayer actuator, respectively. The PANI mat is completely attached to gold layer producing a rather featureless surface morphology, while separation between gold and cellophane layers, suggesting the adhesion between PANI and gold layers are qualified enough to form our desired electrode structure.

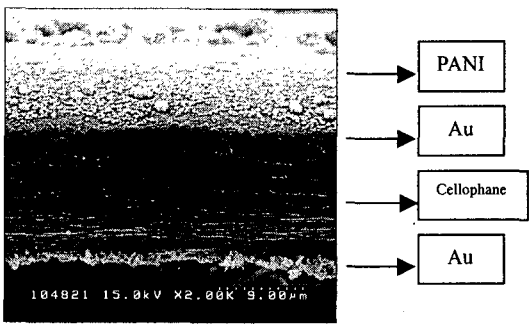

Figure1.SEM cross-section configuration for bilayer

The surface morphologies of PANI doped with different dopants are shown in Figure 2 SEM pictures. Both of them show that electro-synthesized PANI in PC medium in the presence of DCA present a compact structure, similar to that obtained by Yonezawa at. al [7]. Interestingly, comparing with BF_4^- doped structure, the holes exist in PANI ClO_4^- doped films are bigger in the same scanning scale.

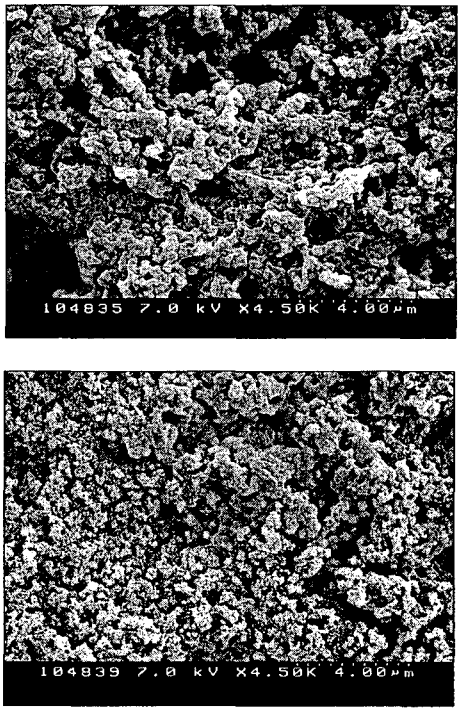

Figure 2. PANI doped by ClO_4^- (above) and PANI doped by BF_4^- (below)

Thickness figure (Figure 3) at different deposition time shows thickness increases almost linearly as deposition time. Obviously, thickness for films doped by ClO_4^- is thicker than ones doped by BF_4^-, due to ionization in the film electro-generation process, where current in ClO_4^- solution cell is much higher than in BF_4^- solution.

3.2. Actuation for different doped ions

CP-EAP actuator's actuations doped by ClO_4^- and BF_4^- ions for trilayers is illustrated in Figure 4. The actuation was investigated in air medium at the same humidity level of 95%, with room temperature 23° C. Actuation test was under 7 AC voltages with the frequency ranging from 0.5 Hz to 7 Hz. It is observed that the acmes of actuation increased to 13.2 mm and 9.7 mm for ClO_4^- and BF_4^- doped samples respectively, both at the deposition time of 30 minutes, while declined rapidly at 45 min and 60 min. The obvious explanation is as the deposition time of conducting polymer on cellophane paper increases the displacement effect associated with ion migration is also increased. While more thickness, on the contrary, increases the actuator's

stiffness causing opposing force for the displacement. Activation of films doped by ClO_4^- is much more than films doped by BF_4^-. More activation obtained in the present comparing can be explained that bigger pores in surface of polymer films allows ions penetrate through out in more freely, observing from the SEM pictures of Figure 2. In a measurement of cellophane deposited gold samples without conducting polymer, the maximum displacement of 4.5 *mm* was observed under identical conditions [2]. This proves that the use of conducting polymer enhances the actuation performance of cellophane paper.

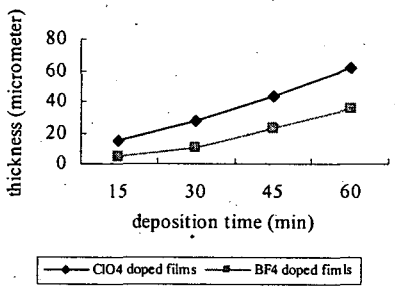

Figure 3. Thickness trends for different dopants

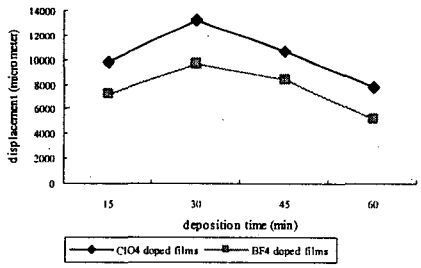

Figure 4. Displacement trends for different dopants

3.3. Actuation for different layers

The results obtained for bilayer and trilayer samples for polyaniline using different dopant ions are depicted in Figure 5, at the same deposition time 30min, where appropriate thickness produced maximum displacement in Figure 4. The measurement was also carried out at the same humidity level of 95%, at room temperature. The results clearly indicated that trilayer actuators perform much better than bilayer actuators. This is due to enhancement of conducting polymer contribution to the activation properties. In all these devices the conducting polymer seems to be playing a dominant role to actuate the samples, though cellophane paper is contributing some effect, comparing with the peak displacements. The dominant effect, associated with migration of counterion of conducting polymer through the interfaces between the polymer films and the cellophane base in high humidity air ambience, is similar to the literature report of PPy//SPE//PPy devices working in air [8]. The maximum displacements occurred around the frequency, 3 Hz, which is the resonance frequency for cellulose and conducting polymer. Besides 3 Hz, activation decreased drastically, until around 0.5 Hz the trends weak down.

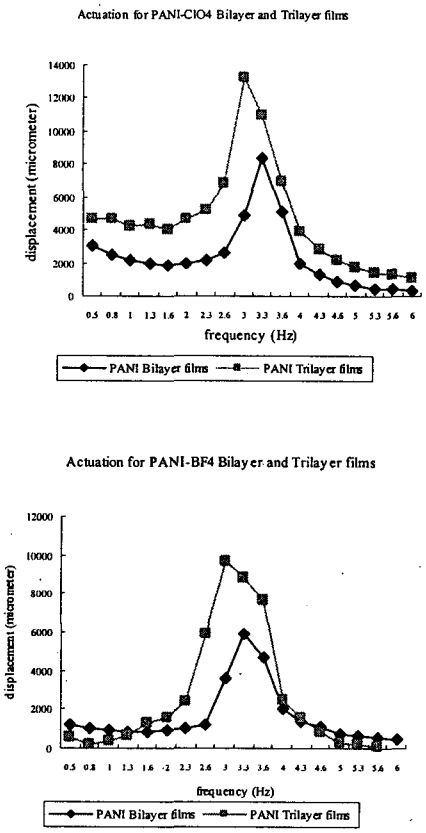

Figure 5. Actuation of CP-EAPap actuators for different CP layers doped with ClO_4^- and BF_4^-

3.4. Actuation for different humidity

Figure 6 shows the effect of humidity on the actuation behavior of Trilayer samples doped by ClO_4^- ion, at the deposition time of 30 min. Of five different humidity levels, the maximum actuation 13.2 μm occurs at humidity of 95% and the peak displacement decreased as humidity levels. It means humidity level plays a crucial effect to the actuator. Water molecule assists the mass transform through cellophane thickness and redox reaction of polyaniline, through electric filed.

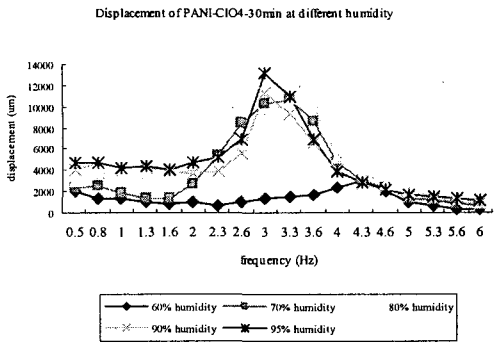

Figure 6. Actuation of CP-EAPap actuator in different humidity

3.5. Working principle of CP-EAPap

In the construction of CP-EAPap, we have used cellophane paper and conducting polyaniline as two components of the device. The base material of cellophane is reported to own piezoelectric properties [9]. Partial orientation of the cells of the paper pulp in the direction of sheet of the paper is primarily the reason for piezoelectric properties of paper [2]. The cellophane paper mainly consists of cellulose in its amorphous state and the hydroxyl groups in it have less restriction in the change of dipole moment. Therefore, the dipole moment of the constituents of the paper, also named ion migration effect, together with electrostrictive effects are combined to the principle for EAPap activation. In this investigation, polyaniline layers are used for the composite devices and its strong oxidation-reduction effect provides major deformations in the film structure. Cellophane paper base and conducting polymer are the two main contributing factors to our activation, to confirm clearly which one is dominant, we need more experiments.

4. Summary and conclusion

In the present investigation, polyaniline films were electro-generated in organic solvent successfully on the surface of cellulose paper. The devices show the good actuation performance, which depend upon three properties: layers of polyaniline film, different dopant ions and different humidity levels. There is prominent effect seen in trilayer devices comparing with bilayer devices. More activation was found in trilayer devices, this is the indicative of role of conducting polymer. The dopant ion effect is seen in trilayer devices where ClO_4^- doped samples are better than BF_4^- doped samples. These investigations presented the primary results of studies on conducting polyaniline deposited on cellophane actuator. The further investigations of effect of temperature, conductivity of polyanline films, force output of the actuator etc. are undergoing in our research center.

Acknowledgement

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References

[1] Y.Bar-Cohen Ed, Electroactive Polymer (EAP) Actuators as Artificial Muscles: Reality, Potential, and Challenges, SPIE Press, 2001.

[2] Jaehwan Kim and Y.B.Seo, Smart Mater. Struct. 11, 355-360 (2002)

[3] A.Mazzoldi, C. Degl'Innocenti, "Actuative properties of polyaniline fibers under electrochemical stimulation," Materials Science and Engineering: C, 6 (1), 65-72, 1998.

[4] J.D. Madden, R.A. Cush, T.S. Kanigan and I.W. Hunter, Synthetic Metals, 113, 185-192(2000)

[5] Bacon, J., Adams, R.N., 1968. J. Am. Chem. Soc. 90. 6596

[6] S.D. Deshpande; Jaehwan Kim and S.R. Yun, Smart Structures and Materials 2004 Proceedings of SPIE Vol. 5385, 260-270 (2004)

[7] S.Yonezawa; K.Nakamura and Z. Takehara, J. Electrochem. Soc. 140, 629 (1993)

[8] Lewis, T.W., Spinks, G.M., Wallace, G.G., De Rossi, D., Pachetti, M., 1997. Polym. Prep. (Am. Chem. Soc., Dive. Polym. Chem.) 38, 520

[9] V. A. Bazhenov, in "Piezoelectric properties of woods" p-119 Consultants Bureau Enterprises, Inc. New York. (1961)