

Electromechanical Actuation of Highly Conductive PEDOT/PSS-coated Cellulose Papers

Jian Zhou^{*1} and Mutsumi Kimura^{*1,*2}

^{*1} Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan

^{*2} Collaborative Innovation Center of Nanotech Fiber, Shinshu University, Ueda 386-8567, Japan

Abstract: The electromechanical properties of poly (3, 4-ethylenedioxythiophene)/poly (styrene sulfonate), (PEDOT/PSS)-coated cellulose paper are investigated by varying the weight of PEDOT/PSS and frequencies of applied voltages. Through simple conformal coating, different weight of conductive PEDOT/PSS papers were fabricated and exhibited electromechanical actuation with stress generation controlled by low alternating applied voltage in ambient air. The dependence of electromechanical actuation on the weight of PEDOT/PSS and the frequency of the applied voltage are determined. The repeatability of the actuation is confirmed by generation of a stable stress more than 2000 times under ambient conditions. Furthermore, the PEDOT/PSS paper underwent intensive bending/unbending motion and showed a dependence on relative humidity. The present study suggests that PEDOT/PSS papers can be highly scalable for high-performance electromechanical devices in ambient air.

(Received 11 February, 2011 ; Accepted 25 February, 2011)

1. Introduction

Electromechanical actuators that show reversible changes in volume or length under electrical stimulus have attracted considerable attention for their biomimetic capability. High performance actuators are especially sought for biomedical applications and biomimetic robotics.¹⁻⁶ Conjugated polymers have lots of desirable features like large stress generated, high reversibility and low operating voltages (0-10 V) which make them attractive for the use as actuators.⁷⁻¹⁰ To date, many conjugated polymers have been investigated as candidates for actuators, including polypyrroles,^{7,8,11-13} polyanilines^{14,15} and polythiophenes.¹⁶ These conjugated polymers undergo changes in volume caused by the movement of ions in and out of the polymer. Recently, the actuation of solid-state conjugated polymers under ambient conditions has received attention because such actuators would further expand the range of applications, and can be operated without immersion in a liquid.^{8,17,18}

Poly (3, 4-ethylenedioxythiophene)/poly (styrene sulfonate), (PEDOT/PSS), which consists of a conducting polythiophene derivative (PEDOT) that is electrostatically bound to a PSS polyanion, has attracted great attention.¹⁹⁻²¹ PEDOT/PSS offers characteristics such as high transparency, excellent thermal stability, and good film forming properties. The low conductivity of as-prepared PEDOT/PSS films or fibers can be enhanced by several reported methods from 10^{-1} to 10^2 S·cm⁻¹.²²⁻²⁴

These methods provide the possibility to realize the actuation of PEDOT/PSS under a low applied electric field. Moreover, the hygroscopic properties of PEDOT/PSS from its PSS groups allow uses, such as a humidity sensor, which was fabricated by inkjet printing PEDOT/PSS on a flexible polyimide substrate.²⁵ The humidity sensor shows not only fully reversible and repeatable capacity but also has a good sensitivity with an accuracy of 1% relative humidity (RH). The combination of electrical and hygroscopic properties of PEDOT/PSS lends itself to the production of novel actuators that operate under ambient conditions. Recently, Okuzaki and coworkers reported a PEDOT/PSS film actuator that exhibits large contraction strain under an applied electric field in ambient conditions.^{26,27} The mechanism of the PEDOT/PSS film actuator lies in the desorption of water vapor sorbed in the film through Joule heating, where the equilibrium of water vapor sorption can be controlled by an applied electrical field. The applications of free-standing conductive polymer films are very limited because they tend to be brittle. However, by coating cellulose papers with conductive polymers, their desirable electromechanical properties can be combined with the mechanical strength and flexibility of cellulose papers to produce conductive papers.

In our earlier work, we used a mechanically robust cellulose paper as a substrate for PEDOT/PSS actuators that exhibited anisotropic mot.²⁸ The PEDOT/PSS-coated paper takes advantages of intrinsic properties of cellulose

paper, such as good mechanical properties, high solvent absorption and strong binding with the conductive polymer, allowing a simple and controllable coating process. The PEDOT/PSS-coated paper exhibited actuation by controlling the equilibrium of the sorption of water vapor in response to an applied electric field. However, the desired advantages of an actuator depend on the final applications. Some applications benefit from an actuator with a rapid response, while others require a high actuation stress. For instance, to produce a PEDOT/PSS paper actuator that exhibits a rapid response, the cellulose paper should maintain a porous structure to improve the sorption of water vapor.

In this study, we demonstrate the amount of PEDOT/PSS in cellulose matrix can be easily controlled by the coating process and we show the weight of PEDOT/PSS influences the electromechanical property in the cellulose matrix. In particular, the amplitude of the generated stress and actuation response time can be adjusted by varying the weight of PEDOT/PSS. The bending motion of the PEDOT/PSS paper is also investigated by changing the RH and applied voltage. Our results provide a foundation for the design and fabrication of paper-based composite actuators with tunable electromechanical properties.

2. Experimental

2.1 Materials

An aqueous dispersion of PEDOT/PSS (Clevios P AG) was purchased from H. C. Starck, Inc (USA). Cellulose paper with a basis weight of 15.6 g/m² (thickness : 25 μm) was used as a substrate for the paper actuators. Ethylene glycol (EG) was purchased from Wako Chemicals (Japan) in analytical grade.

2.2 Preparation of PEDOT/PSS papers

The aqueous dispersion of PEDOT/PSS was evaporated at 120 °C for 3 hours to increase its viscosity. The solid content of the concentrated solution of PEDOT/PSS was ca. 3.1% estimated from the change in weight, and its absolute viscosity was 170 mPa·s at 25 °C, as measured by a viscometer (VA-10A, CBC Co. Ltd., Japan). Coating and drying processes were carried out in a labcoater/drier (LTE-S E-06, Werner Mathis AG, Switzerland). PEDOT/PSS papers were obtained by bar-coating the concentrated PEDOT/PSS solution onto cellulose paper with dimensions of 21 × 27 cm with a doctor blade and then the coated papers were dried at 120 °C. Five different thicknesses of PEDOT/PSS-coated paper were obtained by controlling the distance between the doctor blade and the paper at 0.04, 0.06, 0.08, 0.1 and

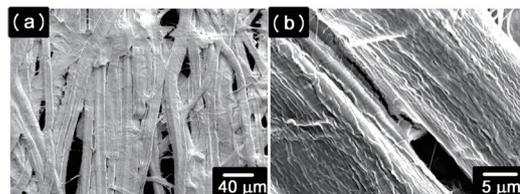


Fig. 1 SEM images of cellulose paper.

0.13 mm. The coated papers were immersed in EG (100 ml) for 20 min and then dried at 100 °C for 60 min in air.

2.3 Measurement

The sheet resistance and electromechanical actuation of the PEDOT/PSS papers were investigated according to the method described previously.²⁸ Actuation specimen for butterfly demonstration was prepared in size of 140 × 5 mm, the distance between the electrodes was 100 mm. “Butterfly wings” made from cellulose paper were adhered to the edges of the PEDOT/PSS papers using double-sided tape. The bending/unbending motion of the “butterfly” was recorded by a digital video camera.

3. Results and discussion

3.1 Fabrication of conductive PEDOT/PSS papers of different thicknesses

Cellulose paper was used as a substrate to fabricate paper-based actuators. Fig. 1 shows that the cellulose paper is composed of long belt-like cellulose fibers with an average width of $15.6 \pm 3.7 \mu\text{m}$ and an average thickness of $3.5 \pm 0.7 \mu\text{m}$. Each cellulose fiber is comprised of multiple individual fibrils that are rich in hydroxyl groups. This hierarchical structure has high porosity, which allows the cellulose paper to absorb large amounts of water or other polar solvents.^{29, 30} As a result, cellulose papers can be coated with conductive polymers effectively.^{31–33} Cellulose fibers have an excellent ability of adsorbing PEDOT/PSS dispersion, the strong interaction between PEDOT/PSS and cellulose implied a broad molecular distribution of PEDOT/PSS.

The paper became dark blue once the PEDOT/PSS ink had been applied onto cellulose paper by conformal coating. Five different thicknesses of PEDOT/PSS coated paper were obtained by controlling the distance between the doctor blade and the paper to 0.04, 0.06, 0.08, 0.1 and 0.13 mm. The PEDOT/PSS coated papers were baked at 100 °C for 60 min in air. The density of the PEDOT/PSS layer in the coated papers was determined to be 0.21, 0.56, 0.97, 1.21 and 1.42 mg/cm², respectively, from the change in weight after coating. SEM images (Fig. 2a–e.) show the morphology of the coated side of PEDOT/PSS papers.

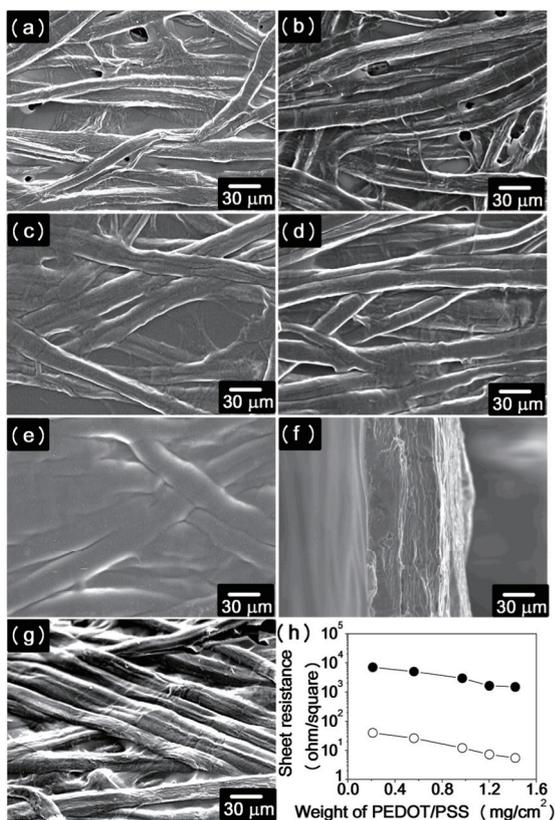


Fig. 2 SEM images of PEDOT/PSS papers containing different weights of PEDOT/PSS: (a) 0.21 mg/cm², (b) 0.56 mg/cm², (c) 0.97 mg/cm², (d) 1.21 mg/cm², (e) 1.42 mg/cm², (f) cross-section of (e), (g) uncoated side of (e) and (h) sheet resistance of PEDOT/PSS papers containing different weights of PEDOT/PSS : (●) as-prepared PEDOT/PSS paper, (○) EG-treated PEDOT/PSS paper.

For the thinnest PEDOT/PSS paper (Fig. 2a), some parts of the cellulose fibers and microfibrils can still be clearly seen. However, as the distance between the doctor blade and paper increased, the fibers in the paper and the interspace between fibers gradually became well coated with PEDOT/PSS. For the sample with a weight of 1.42 mg/cm², the PEDOT/PSS coatings are continuous and possess good homogeneity on the coated side (Fig. 2e). No obvious cellulose fiber structure is observed in the cross section which indicated the PEDOT/PSS penetrated to the uncoated side (Fig. 2f-g). Mechanical adhesion tests to assess the strength of the interaction between PEDOT/PSS and the cellulose paper were performed by immersion in water. The PEDOT/PSS papers were immersed in water for 60 min, and then baked at 100 °C for 60 min. After this process, there was no PEDOT/PSS present in the water, so PEDOT/PSS adhered well to the cellulose paper without peeling or dissociation in water. These results suggest that PEDOT/PSS adheres very strongly to the cellulose fibers, which is critical for electronic paper devices. Such strong binding

may be caused by large capillary forces, as well as, hydrogen bonding between PEDOT/PSS and the cellulose fibers. Fig. 2h shows that the sheet resistance (R_s) of the as-prepared PEDOT/PSS papers decreases as the weight of PEDOT/PSS increases. Immersing the PEDOT/PSS papers in EG for 20 min followed by drying decreased their R_s by approximately three orders of magnitude. The R_s of the EG-treated PEDOT/PSS papers were as low as 5.5 Ω/\square , corresponding to a conductivity of 150 S/cm in the PEDOT/PSS layer. The enhancement in conductivity was caused by the benzoid structure of PEDOT transforming into a quinoid structure.²²⁻²⁴ Thus, PEDOT/PSS papers with a large range of R_s could be obtained by tuning the weight of PEDOT/PSS and treatment with EG. These methods may allow the actuation of PEDOT/PSS papers to be realized at low electrical field.

3.2 Electromechanical actuation of PEDOT/PSS papers

Fig. 3a shows time profiles of the stress generated in two PEDOT/PSS papers at 50% RH and 25 °C. The PEDOT/PSS papers generated stress in response to the application of a voltage (8 V) for 100s. Fig. 3b shows the effect of the weight of PEDOT/PSS on the electromechanical properties of the paper. To clarify the effect of the electrical potential on the electroactive behavior of the conductive papers in more detail, each sample was measured at five voltages (3, 5, 8, 10, and 12 V) at 25 °C and 50% RH. For each of the five different applied voltages, the stress generated increased linearly with the weight of the PEDOT/PSS paper. For the thickest PEDOT/PSS paper, the stress reaches 3.5 and 4.5 MPa under an applied voltage of 10 and 12 V, respectively. These stresses are more than 10 times that produced in the skeletal muscle of animals (about 0.3 MPa).³⁴ When a voltage of 8 V was applied to the samples, a clear indication of the importance of the weight of PEDOT/PSS on the papers on the change in response time was observed (Fig. 3c). The 95% full stroke time is the time that it takes the PEDOT/PSS paper to reach 95% of the maximum stress after applying a voltage. The 95% full stroke time increases with the weight of PEDOT/PSS coated on the cellulose paper, as did the recovery time after turning off the applied voltage. This is because the thickness of the conductive paper increased with the weight of PEDOT/PSS coated on paper, as shown in the inset in Fig. 3b. For the thinner samples, the surfaces of the cellulose paper were not completely coated with PEDOT/PSS. The resulting porous structures in the paper allow water vapor to be absorbed readily by PEDOT/PSS inside the paper. For the

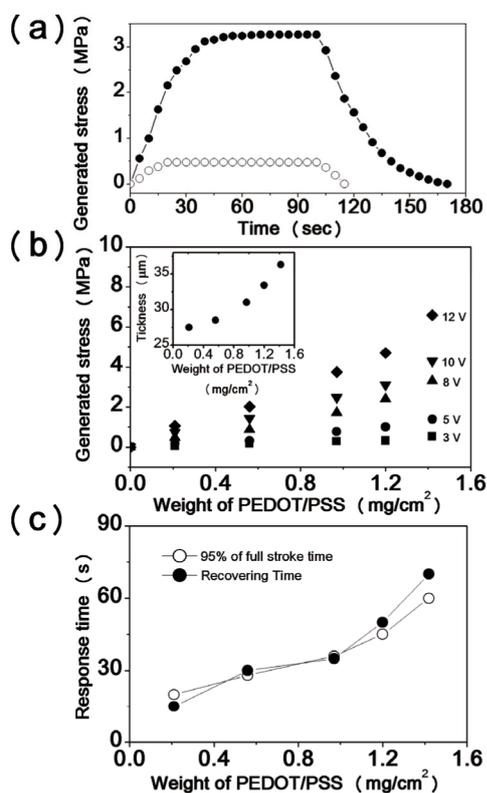


Fig. 3 (a) Time profiles of stress generated in two PEDOT/PSS papers : (●) 1.42 mg/cm², (○) 0.21 mg/cm². (b) The dependence of the weight of PEDOT/PSS on stress generated under different applied voltages at 50% RH and 25 °C : (■) 3 V, (●) 5 V, (▲) 8 V, (▼) 10 V, (◆) 12 V. Inset : dependence of the thickness of the PEDOT/PSS paper on the weight of PEDOT/PSS. (c) The dependence of response time on the weight of PEDOT/PSS : (○) 95% full stroke time after applying a voltage, (●) recovery time after turning off the voltage.

thicker samples, both desorption and absorption is more difficult for the PEDOT/PSS inside the paper. Meanwhile, the charge density increases more rapidly in the thinner film than in the thicker film, which results in faster actuation in the thinner film. Thus, the weight of PEDOT/PSS influences the actuation properties of the cellulose paper. The electromechanical properties of the PEDOT/PSS papers can therefore be adjusted simply by tuning the weight of PEDOT/PSS in the paper.

The electromechanical actuation of the PEDOT/PSS papers under square voltages (0-8 V) with different frequencies is shown in Fig. 4a. The duty of all square wave signals was 50%. The amplitude of the stress generated was calculated from the highest peak and lowest peak as shown in Fig. 4a (inset). It can be seen that at the same applied voltage frequency, the amplitude of stress generated increased with the weight of PEDOT/PSS. However, as the voltage frequencies increased, the

amplitude of stress generated decreased significantly. For the sample with a higher weight of PEDOT/PSS (1.42 mg/cm²), a response was not detected when the frequency was higher than 10 Hz. For the lighter sample (weight of PEDOT/PSS of 0.56 mg/cm²), an electromechanical response was not detected when the

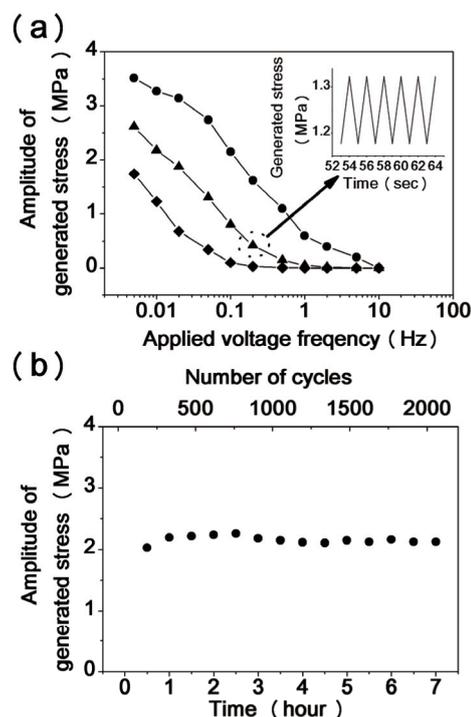


Fig. 4 (a) The amplitude of stress generated in PEDOT/PSS papers under applied square voltages (0-8V) with different frequencies : weight of PEDOT/PSS of (●) 1.42 mg/cm², (▲) 0.97 mg/cm², (◆) 0.56 mg/cm². Inset : The dependence of stress generated on time under an applied voltage frequency of 0.5 Hz. (b) Cycle life of PEDOT/PSS paper with a weight of 1.42 mg/cm² and dimensions of 2 mm × 100 mm × 36 μm under a square wave voltage of (0-8V) with a frequency of 0.1 Hz. Measurements were obtained at 50% RH and 25 °C.

frequency was higher than 0.5 Hz.

The repeatability and reliability of the actuation of the PEDOT/PSS papers were examined by applying a continuous alternating square wave voltage (0.1 Hz, 0-8 V). After more than 2000 cycles, no significant degradation in performance was found, as shown in Fig. 4b. These results indicate that the actuation of PEDOT/PSS papers is both repeatable and reliable. They also show that the amplitude of the stress generated can be controlled by the weight of PEDOT/PSS in the paper and the application of different voltage frequencies.

3.3 Butterfly-like motion based on PEDOT/PSS papers

Both edges of the PEDOT/PSS paper (100 mm long between two copper electrodes and 5 mm wide) bend towards the middle upon applying a voltage at 50% RH (Fig. 5a). The edges of the paper bent and the width of the paper changed from 5 to 2 mm within 25 seconds of applying a voltage of 8 V. When the voltage was turned off, the curled PEDOT/PSS paper reverted to its original straight shape after 50 seconds, and this motion was reversible. The PEDOT/PSS paper bent on the coated side, in which PEDOT/PSS was embedded within the cellulose fiber network in high density. We propose that the difference in the density of PEDOT/PSS on the two sides of the cellulose paper results in the preferred bending direction of PEDOT/PSS paper. The PEDOT/PSS particles containing water will shrink under an applied electrical potential because of Joule heating, and the cellulose paper moves as a result of the shrinking of the PEDOT/PSS layer. The shrinking of the layer on the coated side significantly influences the bending of the paper compared to the uncoated side. Noted that the cellulose paper did not show obvious bending motions when the RH was reduced from 90% to 35% (Fig. 5b). Thus, the bending/unbending motion of the PEDOT/PSS paper mainly results from the shrinking or expansion of the PEDOT/PSS film. Fig. 5c shows a schematic illustration of the bending movement of the PEDOT/PSS paper. The cross-section of bilayer AB will bend into an arc A_1B_1 by applying electrical field. If C is the midpoint of AB, and supposing that arc A_1C equals line A_1C , the bending angle (θ) of the PEDOT/PSS paper can be estimated from the equation (1);

$$\cos \theta = A_1B_1/AB \quad (1)$$

where $AB=5$ mm, and A_1B_1 can be measured using a camera recorder. Fig. 5d shows the dependence of the bending angle of the PEDOT/PSS paper on the response time under applied square voltages (0-8V). The bending was recorded when the PEDOT/PSS paper started to bend. After applying an electrical field, it took 25 s for the paper to reach a θ of 68.4° . When the electrical field was turned off at 40 s, it took another 50 s for the paper to unbend from $\theta = 68.4^\circ$ to 0° at RH = 50%. A lower RH of 35% results in a slower unbending movement, while a higher RH of 60% results increases the rate of unbending. Furthermore, θ can be adjusted by applying different voltages, as shown in Fig. 5e. Thus, the bending/unbending movements of the PEDOT/PSS papers can be

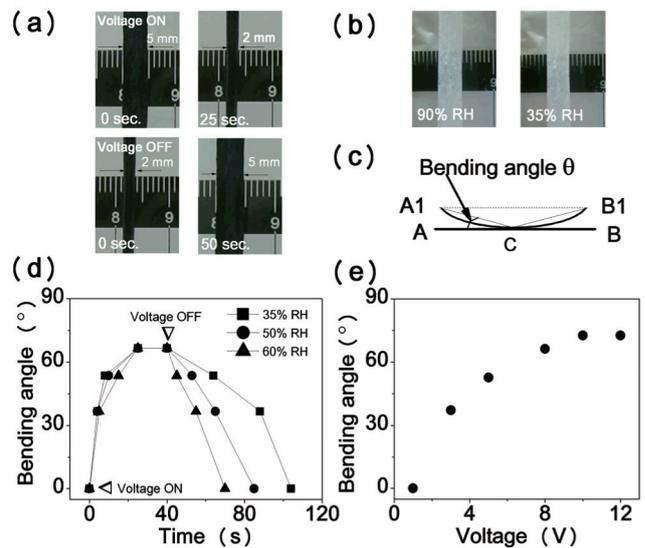


Fig. 5 (a) Bending/unbending motion of PEDOT/PSS paper with dimensions of 5 mm × 100 mm × 36 μm upon switching a voltage on and off at 50% RH and 25 °C. (b) Configuration of cellulose paper at 90% and 35% RH (c) Schematic illustration of the bending/unbending movement of a PEDOT/PSS paper. (d) Time-dependent bending angles of PEDOT/PSS paper at different RH at 8 V and 25 °C : (■) 35% RH, (●) 50% RH, (▲) 60% RH. (e) Voltage-dependent bending angles of PEDOT/PSS paper at 50% RH and 25 °C.

controlled by adjusting the applied voltage and the RH around the paper.

The intensive bending/unbending movement of the PEDOT/PSS paper gave us the inspiration to mimic the motion of a butterfly.³⁵ Wings made of cellulose paper were stuck to the edge of the PEDOT/PSS paper and the

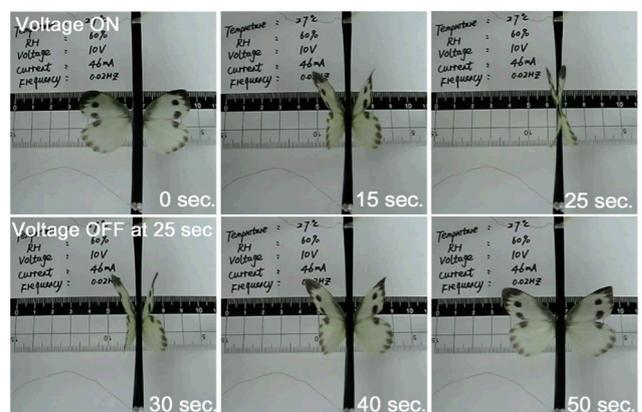


Fig. 6 Time profiles of butterfly-like motion based on PEDOT/PSS paper at 60% RH and 27 °C. The applied voltage (10 V) is switched on and off with a frequency of 0.02 Hz (that is, a voltage of 10 V was turned on for 25 s and turned off for 25 s repeatedly).

resulting “butterfly” moves reversibly when a voltage was switched on and off with a frequency of 0.02 Hz, as shown in Fig. 6.

4. Conclusions

In conclusion, PEDOT/PSS papers were fabricated by coating PEDOT/PSS onto cellulose paper. The PEDOT/PSS papers displayed electromechanical properties that could be tuned by varying the weight of PEDOT/PSS and the frequency of the applied voltage. The PEDOT/PSS papers can undergo intensive bending/unbending motions when the voltage is switched on and off. These bending/unbending motions can also be controlled by changing the RH and applied voltage. Based on this electromechanical response, butterfly-like motion of the PEDOT/PSS paper was demonstrated. The unique actuation performance of this PEDOT/PSS/cellulose paper composite system, coupled with the ease of conformal coating, and its mechanical robustness, low driving voltage, and good cycling ability, provides the potential to further expand the range of applications of artificial muscles that operate under ambient conditions.

Acknowledgment

This work was partially supported by the Global COE Program for the “International Center of Excellence on Fiber Engineering” and the Knowledge Cluster Initiative Program (Second Stage) “Shinshu Smart Devices Cluster” from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References

1. J. D. Madden, *Science*, **318**, 1094 (2007).
2. M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.*, **8**, 621 (2009).
3. T. Mirfakhrai, J. D. Madden, R. H. Baughman, *Mater.Today.*, **10**, 30 (2007).
4. Y. Hu, W. Chen, L. H. Lu, J. H. Liu, C. R. Chang, *ACS Nano*, **4**, 3498 (2010).
5. F. Carpi, E. Smela, “*Biomedical Applications of Electroactive Polymer Actuators*”, John Wiley and Sons Ltd Publishers, Chichester, p.279 (2009).
6. B. C. Yoseph, “*Biomimetics : Biologically Inspired Technologies*”, CRC Press, Boca Raton, London, New York, p.267 (2006).
7. W. H. Jager, E. Smela, O. Inganas, *Science*, **290**, 1540 (2000).
8. E. Smela, *Adv. Mater.*, **15**, 481 (2003).
9. R. H. Baughman, *Science*, **308**, 63 (2005).
10. T. A. Skotheim, J. R. Reynolds, “*Handbook of Conducting Polymers*”, Vol. 2, CRC Press, Boca Raton, London, New York, p.1649 (2007).
11. M. J. Higgins, S. T. McGovern, G. G. Wallace, *Langmuir*, **25**, 3627 (2009).
12. X. Z. Wang, E. Smela, *J. Phys. Chem. C*, **113**, 359 (2009).
13. R. Z. Pytel, E. L. Thomas, Y. Chen, I. W. Hunter, *Polymer*, **49**, 1338 (2008).
14. W. Lu, A. G. Fadeev, B. H. Qi, E. Smela, B. Mattes, J. Ding, G. M. Spinks, J. Mazurkiewicz, D. Z. Zhou, G. G. Wallace, D. R. MacFarlane, S. A. Forsyth, M. Forsyth, *Science*, **297**, 983 (2002).
15. G. M. Spinks, B. B. Xi, V. T. Truong, G. G. Wallace, *Synth. Met.*, **151**, 85 (2005).
16. P. A. Anquetil, H. H. Yub, J. D. Madden, P. G. Madden, T. M. Swager, I. W. Hunter, *Proc.SPIE Smart Structures and Materials Symposium, EAPAD Conference*, San Diego, CA, March 18-21, 2002.
17. H. Okuzaki, K. Funasaka, *Macromolecules*, **33**, 8307 (2000).
18. U. L. Zainudeen, M. A. Careem, S. Skaarup, *Sens. Actuators. B*, **134**, 467 (2007).
19. B. H. Fan, X. G. Mei, J. Y. Ouyang, *Macromolecules*, **41**, 5971 (2008).
20. S. Kirchmeyer, K. Reuter, *J. Mater. Chem.*, **15**, 2077 (2005).
21. P. Tehrani, L. O. Hennerdal, A. L. Dyer, Reynolds, J. R. Berggren, *M. J. Mater. Chem.*, **19**, 1799 (2009).
22. J. Huang, P. F. Miller, J. S. Wilson, J. C. De Mello, A. J. De Mello, D. C. Bradley, *Adv. Funct. Mater.*, **15**, 290 (2005).
23. Y. S. Hsiao, W. T. Whang, C. P. Chen, Y. C. Chen, *J. Mater. Chem.*, **18**, 5948 (2008).
24. Y. J. Xia, J. Y. Ouyang, *Macromolecules*, **42**, 4141 (2009).
25. H. C. Lim, Y. F. Hor, Y. L. Hor, J. L. Zunino III, J. F. Fedefice, *Sens. Trans. J.*, **101**, 52 (2009).
26. H. Okuzaki, H. Suzuki, T. Ito, *Synth. Met.*, **159**, 2233 (2009).
27. Okuzaki, H. Suzuki, H. Ito, *T. J. Phys. Chem. B*, **113**, 11378 (2009).
28. J. Zhou, T. Fukawa, H. Shirai, M. Kimura, *Macromol. Mater. Eng.*, **295**, 671(2010).
29. L. B. Hu, J. M. Choi, Y. Yang, S. M. Jeong, F. L. Mantia, L. F. Cui, Y. Cui, *Proc. Natl. Acad. Sci. U.S.A.*, **106**, 21490 (2009).
30. L. B. Hu, M. Pasta, F. L. Mantia, L. F. Cui, S. M.

- Jeong, H. D. Deshazer, J. M. Choi, S. M. Han, Y. Cui, *Nano Lett*, **10**, 708 (2010).
31. G. Nyhølm, A. Razaq, M. Strömme, L. Nyholm, A. Mihranyan, *Nano Lett*, **9**, 3635 (2009).
32. M. Elson, J. Lars, L. Magnus, *Cellulose*, **16**, 807 (2009).
33. F. M. Kelly, J. H. Johnston, T. Borrmann, J. Richardson, *Eur. J. Inorg. Chem.*, 5571 (2007).
34. R. M. Alexander, *Exploring Biomimetics : Animals in Motion* W. H. Freeman and Company Publish, New York, p.260 (1992).
35. Y. Ma, J. Q. Sun, *Chem. Mater.*, **21**, 898 (2009).