

PET Fabric/Poly(3,4-ethylenedioxythiophene) Composite as Polymer Electrode in Redox Supercapacitor

Seung Hyun Cho[†]

Polymer Technology Institute, Sungkyunkwan University, Suwon 440-746, Korea

Jin Soo Joo

Department of Physics, Korea University, Seoul 136-701, Korea

Bo Ram Jung, Tae Min Ha, and Jun Young Lee*

School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

Received November 21, 2008; Revised March 6, 2009; Accepted March 10, 2009

Abstract: Poly(ethylene terephthalate) (PET) fabric/poly(3,4-ethylenedioxythiophene) (PEDOT) composite with stable and high electrochemical activity was fabricated by chemical and electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) on a PET fabric in sequence. Effects of polymerization conditions on the following characteristics of the composite were studied: electrical conductivity and surface morphology. The electrochemical properties were also investigated by cyclic voltammetry and cyclic charge/discharge experiments. The specific volume resistivity, electrical conductivity and specific discharge capacitance of the composite were 0.034 Ω -cm and 25 S/cm, and 54.5 F/g, respectively.

Keywords: polymer electrode, PET fabric, poly(3,4-ethylenedioxythiophene), redox supercapacitor.

Introduction

Conducting polymers have been considered as promising pseudo-capacitive materials due to their fast charge-discharge behavior, low fabrication cost and morphology.¹⁻⁴ Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) is a relatively new polymer of the polythiophene class and has drawn much attention due to its good environmental stability, high electrical conductivity and electrochemical activity appropriate for many potential applications.⁵⁻⁸ PEDOT is known to be very stable in its oxidized states with a low band-gap,⁹ showing a little change in conductivity up to 1,000 h at 120 °C under ambient conditions.¹⁰ Since PEDOT has a low redox potential and has been reported to undergo fast redox reactions, where the charging reaction was found to be faster than discharging reaction,¹⁰ some researches have been carried out to apply PEDOT as an electrode material for the supercapacitor in various kinds of electrolyte solutions.¹¹

Textile fabric/PEDOT composites brought about the electrically conducting textiles useful for many applications

since the PEDOT-coated textiles have not only excellent physical properties of the textiles such as mechanical strength and flexibility but also electrical and microwave properties of PEDOT. Polyester (PET) fabric/PEDOT composites with high electrical conductivity have been prepared by chemical and electrochemical polymerization of EDOT on a PET fabric.^{12,13}

In this study, we report a method to fabricate PET fabric/PEDOT composite with extraordinarily high electrical conductivity and energy density for the electrode of the redox-type supercapacitor. We studied the effects of preparation conditions on the characteristics of the composite such as electrical conductivity and surface morphology. Electrochemical activity and stability of the composite were investigated by cyclic voltammetry. The symmetric redox-type supercapacitor was assembled using two PET fabric/PEDOT composite electrodes, whose specific capacitance, stability of capacitance and cut-off voltage were obtained by cyclic charge/discharge experiment.

Experimental

Preparation of PET Fabric/PEDOT Composite. Electrically conducting PET fabric/PEDOT composite was prepared by chemical and electrochemical polymerization of

*Corresponding Author. E-mail: jylee7@skku.edu

[†]Present Address: Department of Organic Materials and Fiber Engineering, Soongsil University, Seoul 156-743, Korea

EDOT on the surface of a PET fabric in sequence. PET fabric was cut into 5 cm × 5 cm and the surface morphology of pristine PET fabric is shown in the previous work.¹³ In the chemical polymerization, we followed the optimized polymerization condition from the previous work.¹³ In the electrochemical polymerization, the kinds of the supporting electrolyte solution were varied.

For chemical polymerization 3,4-ethylenedioxythiophene (EDOT, Bayer) was dissolved in 1-butanol containing 30 wt% poly(vinyl pyrrolidone) (PVP, Mw: 360,000 g/mol, Aldrich) to EDOT monomer as a binder. 40 wt% *N*-dimethylacetamide (DMAc, Aldrich) to EDOT monomer as a reducing agent was also added to the monomer solution. Ferric *p*-toluene sulfonate (FTS) oxidant solution in 1-butanol was purchased from Bayer. Immediately after the monomer and oxidant (mole ratio 1:1.5) solutions were mixed, PET fabric was dipped in the mixed solution and then chemical polymerization was carried out by placing the fabric at 70 °C in the oven for 20 min, followed by washing with methanol and drying at 70 °C for 30 min. Chemical polymerization was repeatedly performed for desired times to obtain an electrical conductivity appropriate for the following electrochemical polymerization.

Electrochemical polymerization was carried out galvanostatically using PET fabric coated with chemically polymerized PEDOT as the working electrode and a stainless steel plate as the counter electrode. Constant current density of 0.3 mA/cm² was applied at 0 °C for 2 h in various kinds of supporting electrolyte solutions (0.1 M) such as tetraethylammonium tetrafluoroborate (Et₄NBF₄, Fluka) in propylene carbonate (PC, Aldrich), tetrabutylammonium hexafluorophosphate (TBAPF₆, Aldrich) or tetrabutylammonium perchlorate (Bu₄NClO₄, Fluka) in acetonitrile (ACN, Aldrich).

Characterization. PEDOT content in the composite was determined from the ratio of the weight of PEDOT in the composite to that of the pristine fabric. Surface resistivity (Ω/□) of PET fabric/PEDOT composite was measured by a two probe method by measuring the resistance between two Pt wire electrodes pressed on the surface of the composite, where the distance between the electrodes and the length of the electrodes were 1 cm. Specific volume resistivity (ρΩ-cm) of the composite was obtained from the measured resistance (*R*) between two ends of the specimen with the following eq. (1):

$$\rho = RA/l \quad (1)$$

where *A* and *l* are the cross-sectional area of the end of specimen and the distance between two ends, respectively.

Surface morphologies of the composites were observed with scanning electron microscopy (SEM, Hitachi).

Electrochemical activity and stability of the composite was investigated by cyclic voltammetry (CV) in a three electrode cell (0.1 M Et₄NBF₄ in PC, Ag/AgCl as a reference electrode) using IM6ex (ZAHNER Elektrik Co. Ltd.,

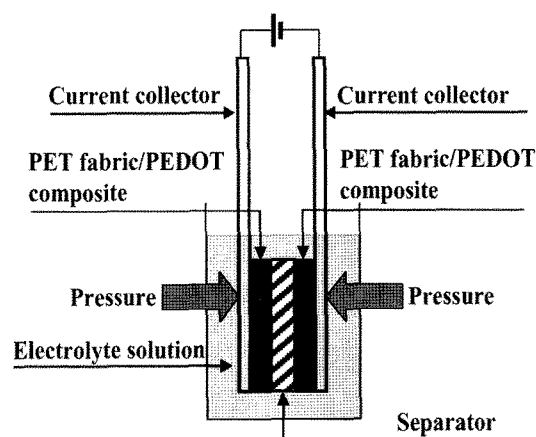


Figure 1. Schematic diagram of the symmetric redox-type supercapacitor using PET fabric/PEDOT composites as electrode.

Germany). Scanning was started from -1.0 V and then performed between -1.2 and 1.3 V at a scan rate of 35 mV/sec and 100 mV/sec, respectively.

In order to measure the specific discharge capacitance and its stability of the composite, the symmetric redox-type supercapacitor was assembled by a simple stack-method with the PET fabric/PEDOT composite as the electrodes and stainless steel plates as the current collectors as shown in Figure 1. The supercapacitor was galvanostatically charged and discharged in different kinds of electrolyte solutions in the voltage range 0-1, 0-1.5 and 0-3 V by using WBCS 3000 (Wonatech, Korea).

The specific discharge capacitance of the supercapacitor was obtained by using the following eq. (2):

$$C_m = (I \cdot \Delta t) / (\Delta V \cdot m) \quad (2)$$

where *C_m* is the specific discharge capacitance (F/g) of the supercapacitor, *I* is the discharge current (A), *t* is the discharge time (s), and ΔV is the voltage difference (V) in discharge and *m* is the weight (g) of the PEDOT coated on fabric, respectively.

Results and Discussion

We found that the resistivity of the PET fabric/PEDOT composite was much further decreased by the electrochemical polymerization since electrochemically polymerized conducting polymer generally has much higher electrical conductivity than chemically polymerized one.^{14,15}

As can be seen in Figure 2, PEDOT was successfully coated on the surface of the PET fabric by chemical and electrochemical polymerization. The composite prepared by chemical polymerization alone shows film-like smooth surface morphology as shown in Figure 2(a), while the composite prepared by chemical and electrochemical polymerization has a random nodular morphology as shown in Fig-

ure 2(b), which apparently increases the surface area of the electrode resulting in the higher conductivity. It has been reported that the surface area of nodular polypyrrole film measured by small angle neutron scattering was 55 times greater than a flat surface with the same dimensions.¹⁶

It was also observed that type of electrolyte solution greatly affected PEDOT content and eventually surface volume resistivity of the resultant composite. The composite prepared with 0.1 M of Et_4NBF_4 in PC showed the highest PEDOT content and lowest specific volume resistivity of $0.034 \Omega\text{-cm}$.

Figure 3 displays the cyclic voltammograms of the composite between -1.2 and 1.3 V at a scan rate of 35 mV/s, confirming that the composite is electrochemically very active. The peak potentials for oxidation and reduction in the first cycle were 0.60 and -0.50 V, respectively. With the scan rate of 100 mV/s, the cyclic voltammograms of the composite showed no differences with those of 35 mV/s.

After 100 cycles, the peak potential for oxidation slightly shifted to 0.58 V. We also figured out the composite possessed relatively good electrochemical stability especially when it is compared to other conducting polymers,¹⁷ which is an essential property for many applications such as secondary battery or supercapacitor. The area of CV curve decreased by 14.9% only even after 100 cycles compared to the area of the first cycle as shown in Figure 3.

Figure 4 shows the specific discharge capacitances of the symmetric redox-type supercapacitor fabricated with the PET fabric/PEDOT composites in three different electrolyte solutions. As shown in the figure, the specific capacitance was greatly influenced by the electrolyte solution used in the supercapacitor, indicating that the electrolyte solution is extremely important to obtain the best performance of the supercapacitor. At the scan voltage range of 0-1 V, the maximum capacitances of the supercapacitors were 54.5 F/g

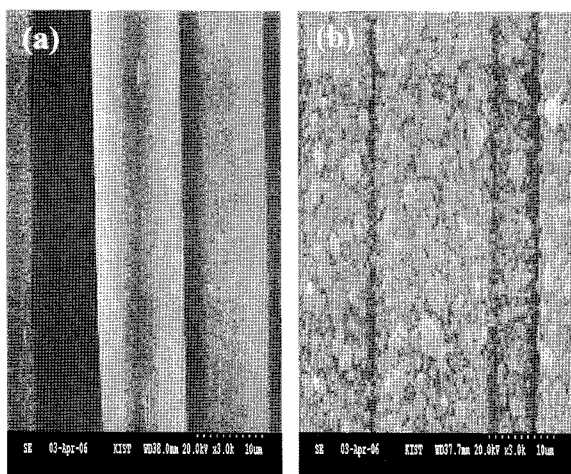


Figure 2. SEM micrographs ($\times 3.00 \text{ K}$) of the surfaces of PET fabric/PEDOT composites prepared by (a) chemical polymerization only and (b) both chemical and electrochemical polymerization.

with Et_4NBF_4 in PC, 50 F/g with TBAPF_6 and 34.4 F/g with Bu_4NClO_4 in ACN, respectively. The specific capacitance values of the composites were comparable or even higher than those of the PEDOT supercapacitors reported earlier.¹⁸ The inset in Figure 4 is the normalized plot which is extrapolated to 1,000 cycles showing that the specific capacitance would drop to only about 85% of initial value when 1,000 cycles are used.

Figure 5 shows the specific capacitances of the capacitor at various charging/discharging voltage range. The specific capacitance in the range of 0-1.5 V was little bit higher at the beginning than that in the range of 0-1 V but decreased rapidly with increasing number of cycles. At 0-3 V range, the specific capacitance drastically dropped in its early stage

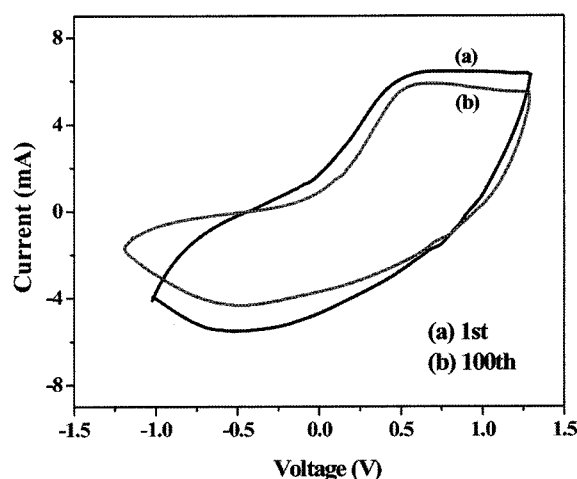


Figure 3. Cyclic voltammograms of PET fabric/PEDOT composite prepared by chemical and electrochemical polymerization. (a) the first cycle and (b) the 100th cycle in 0.1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ solution.

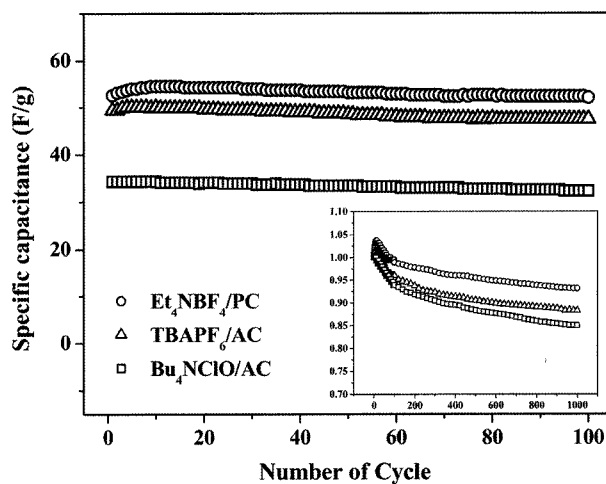


Figure 4. Specific discharge capacitances of the symmetric supercapacitors based on PET fabric/PEDOT composites working in various kinds of 0.1 M electrolyte solutions between the voltage range of 0-1 V. The inset shows the normalized plot.

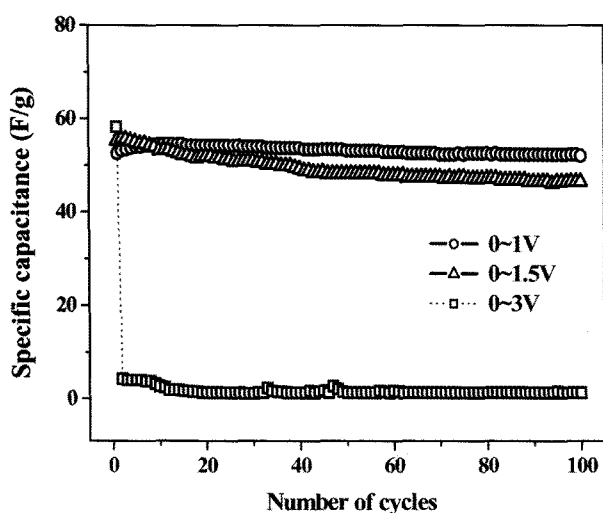


Figure 5. Specific discharge capacitances of the symmetric supercapacitor based on PET fabric/PEDOT composite in 0.1 M $\text{Et}_4\text{NBF}_4/\text{PC}$ with various voltage scanning range.

and showed very low specific capacitance thereof. This must result from the over-oxidation of PEDOT at the higher potentials. The overoxidation is generally considered to bring about considerable loss of conductivity.¹⁹

Conclusions

Electrically conducting PET fabric/PEDOT composite was successfully fabricated by chemical and electrochemical polymerization of EDOT on a PET fabric in sequence. It was found that the specific volume resistivity of the composite was decreased to much lower value after the electrochemical polymerization and was greatly affected by the kind of electrolyte solution used. The composite prepared with 0.1 M of Et_4NBF_4 in PC showed the lowest specific volume resistivity of 0.034 $\Omega\text{-cm}$.

It was also found from cyclic voltammetry and charge/discharge experiment that the composite possessed very stable and high electrochemical activity. The specific discharge capacitance of the composite was very high as 54.5 F/g at the voltage range of 0-1 V and showed little decrease

even after 100 cycles, indicating the composite can be applied as the electrode for flexible supercapacitor.

Acknowledgments. This paper was supported by 63 Research fund, Sungkyunkwan University, 2008.

References

- (1) M. Mastragostino, C. Arbizzani, and F. Soavi, *J. Power Sources*, **97-98**, 812 (2001).
- (2) K. S. Ryu, K. M. Kim, N. Park, Y. J. Park, and S. H. Chang, *J. Power Sources*, **103**, 365 (2002).
- (3) A. M. White and R. C. T. Slade, *Syn. Metals*, **139**, 123 (2003).
- (4) M. Choi, B. Lim, and J. Jang, *Macromol. Res.*, **16**, 200 (2008).
- (5) M. Dietrich, J. Heinze, F. Jonas, and G. Heywang, *Electroanalysis*, **87**, 3369 (1994).
- (6) F. Fusalba, N. E. Mehdi, L. Breau, and D. Belanger, *Chemistry of Materials*, **11**, 2743 (1999).
- (7) Karim *et al.*, *Macromol. Res.*, **16**, 337 (2008).
- (8) Y. Kim *et al.*, *Macromol. Res.*, **16**, 185 (2008).
- (9) F. Jonas and L. Schrader, *Syn. Metals*, **41**, 831 (1991).
- (10) C. Kvarnström, H. Neugebauer, and S. Blomquist, *Electrochim. Acta*, **44**, 2739 (1999).
- (11) J. D. Stenger-Smith, C. K. Webber, N. Anderson, A. P. Chafin, K. Zong, and J. R. Reynolds, *Journal of Electrochemical Society*, **149**, A973 (2002).
- (12) H. K. Kim, M. S. Kim, K. T. Song, Y. H. Park, S. H. Kim, J. S. Joo, and J. Y. Lee, *Syn. Metals*, **135**, 105 (2003).
- (13) B. R. Jung, Y. R. Kwon, J. M. Ko, M. S. Kim, S. H. Cho, J. Y. Lee, and J. Joo, *Mol. Cryst. Liq. Cryst.*, **464**, 109 (2007).
- (14) A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc. Chem. Comm.*, **14**, 635 (1979).
- (15) T. A. Skotheim, Ed., *Handbook of Conducting Polymers*, Marcel Dekker, New York, 1986.
- (16) L. L. Madsen, K. Carneiro, B. N. Zaba, and A. E. Underhill, *Syn. Metals*, **41-43**, 2931 (1991).
- (17) W. S. Shim, Y. H. Lee, I. H. Yoo, J. Y. Lee, and D. S. Lee, *Syn. Metals*, **104**, 119 (1999).
- (18) K. M. Kim, M. G. Kang, N. G. Park, and S. H. Chang, *Electrochim. Acta*, **50**, 843 (2004).
- (19) H. Tang, L. Zhu, Y. Harima, and K. Yamashita, *Syn. Metals*, **110**, 105 (2000).