Polyfluorene/Carbon Nanocomposite for Electrochemical Capacitors

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Received January 31, 2007 ; Accepted June 6, 2007

A nanocomposite material based on polyfluorene (PF) loaded with a carbon black, namely Ketjen Black (KB), was investigated electrochemically as a cathode material for high-energy electrochemical capacitors. The nanocomposite was prepared by a chemical oxidation of fluorene monomer dissolved in the KB suspension. From TEM observation, thin PF films with 5–15 nm in thickness were loaded onto the surface of the aggregated KB particles. The nanocomposite based capacitor electrode exhibited high specific capacitance of 160 F g^{-1} (260 F g^{-1} per PF mass) in an electrolyte of 1 M tetraethylammonium tetrafluoroborate/propylene carbonate. More importantly, the charge was found to be stored at high potential ranged from 0.4 to 1.0 V vs. Ag/Ag⁺, which is higher than the redox potentials for conventional conducting polymers.

Key Words : Electrochemical Capacitor, Polyfluorene, Nanocomposite, Ketjen Black

1 Introduction

Conducting polymers have been studied widely as electrode material in energy devices and more particularly in electrochemical capacitors.^{1–13)} Charge storage of the conducting polymer based electrochemical capacitors is based on redox reaction of π -conjugated system (p-doping or n-doping) in the conducting polymer, while charge storage of conventional electric double layer capacitors is double layer charging/discharging at the surface of activated carbon electrode. Rudge *et al.*¹⁾ reported electrochemical capacitors based on only one type of conducting polymer, such as polyaniline, that can be reversibly p-doped (Type I capacitors, cell voltage: $\sim 1 \text{ V}$). Also, capacitors based on p- and n-dopable polymer such as polythiophene derivatives have been studied (Type III capacitors, cell voltage: $\sim 3 \text{ V}$).^{1,2,5)}

For higher energy density, hybrid-type electrochemical capacitors (HEC) have been proposed in recent years.^{6,9–12)} For instance, Mastragostino *et al.*⁹⁾ reported a high energy HEC ($\sim 24 \text{ Wh kg}^{-1}$, cell voltage: $\sim 3.6 \text{ V}$) composed of an activated carbon as the anode and poly(3-methylthiophene) [p3MeT] as the cathode. The high energy is attributed to high capacitance ($100 \sim 230 \text{ F g}^{-1}$) and high redox potential ($\sim 0.7 \text{ V}$ vs. Ag/Ag⁺) of the p3MeT cathode. To obtain more high redox potential, other polythiophene derivatives ($\sim 0.9 \text{ V}$ vs. Ag/Ag⁺) were investigated.^{6,10,11)}

The authors have been studying a polyfluorene (PF, Fig. 1) as a cathode material for high energy HEC. The film shows reversible redox reaction at higher redox potential ($\sim 1.2 \text{ V}$ vs. Ag/Ag⁺)^{14,15)} compared with other polymers mentioned above. A first report for electrochemical properties of the PF material for electrochemical capacitors was published in 2006. The report revealed that the pure PF material was found to show low electrochemical capacity because of low electronic conductivity of the bulk PF.¹³⁾ For enhancement of electrochemical activity of the PF, addition of electroconduc-

Fig. 1 Structure of polyfluorene (PF).

tive material with the PF is required.

In this study, a nanocomposite material based on PF loaded with a nanocarbon substrate, namely Ketjen Black (KB) having high specific surface area ($800 \text{ m}^2 \text{ g}^{-1}$), high electronic conductivity ($\sim 10^0 \text{ S cm}^{-1}$) and low cost, was prepared and was investigated for its electrochemical capacitor properties.

2 Experimental

The polyfluorene/Ketjen Black nanocomposite (PF/KB nanocomposite) powder was prepared by following procedures. Firstly, KB powder (Ketjen Black International Co.) was crushed mechanically by use of mixer (general-purpose) for 1 minute. Then, obtained KB powder was dispersed into 10 mmol of fluorene monomer (98%, Wako Chemicals) dissolved in chloroform under ultrasonication for 30 minutes. The KB amounts (W) were 1.0, 3.0, 5.0, 10 and 20 wt% for fluorene mass. Into the suspension, 10 mmol of iron trichloride (98%, Aldrich) as an oxidizing agent was added. After stirring for 72 h, the solution was filtered with a Teflon filter (200 nm of pore size, Millipore). The obtained deposit was washed with chloroform, methanol, and distilled water to remove inactive-oligomer species, monomers, iron ions and chlorides. Thereafter, it was dried under reduced pressure at 60 degree C for 6 hours to obtain a black colored nanocomposite powder. Actual specific content of KB (W_{re}) in the nanocomposite powder was calculated by following equation;

$$W_{\text{re}} = M_{\text{KB}}/Y_{\text{com}} \quad (1)$$

where M_{KB} and Y_{com} are the added KB mass at preparation and the nanocomposite powder mass, respectively. Chemical structure and nanostructure of the nanocomposite powder were characterized by FTIR spectroscopy and TEM observation, respectively.

The PF/KB nanocomposite capacitor electrode was fabricated by mixing 85 wt% PF/KB nanocomposite powder, 10 wt% carboxymethylcellulose and 5 wt% elastomer binder. The mixture was coated onto an Al current collector. Thickness and geometric area of the capacitor electrode were 20 μm and 1 cm^2 , with single electrode mass loading in the range from 0.5 to 0.6 mg (electrode density: 0.25–0.30 g cm^{-3}). Electrochemical characteristics of the capacitor electrode were evaluated by cyclic voltammetry (HZ-3000 system, Hokuto Denko). A three-electrode cell was used, with the PF/KB electrode as the working electrode, an activated carbon sheet (commercially purchased, 6 cm^2 , 150 μm in thickness) as the counter electrode, and Ag/Ag⁺ electrode as the reference electrode (consisting of Ag wire in a solution of 10^{-2} M AgNO₃ in propylene carbonate). The potential of this reference electrode was +0.30 V vs. Ag/Ag⁺ reference electrode using acetonitrile solution with same electrolyte salt. In this study, the potential was expressed as vs. Ag/Ag⁺ using the acetonitrile solution for comparison with other reports. The counter electrode and the working electrode were sandwiched by two glass plates through a cellulose separator (60 μm in thickness). As an electrolyte, 1 M tetraethylammonium tetrafluoroborate dissolved in propylene carbonate (TEABF₄/PC) was used for the electrochemical measurements. The cell assemblies and the electrochemical measurements were carried out in argon atmosphere.

3 Results and Discussion

From FTIR spectra, the nanocomposite powder sam-

Fig. 2 TEM image obtained for PF/KB nanocomposite powder ($W_{\text{re}} = 45$ wt %).

Table 1 Specific contents of KB (W_{re}) in PF/KB nanocomposite powder contrasted with adding KB amount (W) at nanocomposite preparation.

$W/\text{wt}\%$	$W_{\text{re}}/\text{wt}\%$
1.0	7.9
3.0	16
5.0	40
10	45
20	68

ples were found to consist of electroactive PF with main bonding manner of 2,7 position like a structure in Fig. 1, corresponding to the peaks at 820, 760, 730 cm^{-1} assigned to 1,2,4-tri-substituted aromatic ring,¹⁶⁾ as well as the pure PF powder. Specific contents of KB (W_{re}) in the PF/KB nanocomposite powders were summarized in Table 1. The W_{re} values were significantly different from the added KB amounts (W) at the nanocomposite preparation. This indicates that polymerization efficiency (obtained PF mass /added monomer mass) of the PF in the nanocomposite were very low (8~12 %) of all the preparations due to dissolution of soluble oligomer species by the chloroform washing.

Figure 2 shows TEM image of the nanocomposite powder ($W_{\text{re}} = 45$ wt % sample). The certain species perceived as PF films (5–15 nm) formed onto the aggregated KB particles were observed, and also bare KB surfaces were confirmed. At the low W_{re} samples (or high PF content samples), the PF species were increasingly observed in the respective SEM images. In the case of sample of $W_{\text{re}} = 7.9$ wt %, the bulk PF fragments (micrometer size) were observed, leading to low specific capacitance.

Cyclic voltammogram recorded at a scan rate of 5 mV s^{-1} in 1 M TEABF₄/PC for the PF/KB nanocomposite electrode ($W_{\text{re}} = 40$ wt % sample) is depicted in Fig. 3(a) and clearly indicates that the electrochemical redox reaction (p-doping/dedoping) occurred reversibly compared with the voltammogram for pure KB electrode (Fig. 3(b)). The redox potential is ranged from +0.4 to +1.0 V vs. Ag/Ag⁺, which is higher than the conventional polymers such as p3MeT ($\sim +0.7$ V vs. Ag/Ag⁺)⁹⁾ or

Fig. 3 Cyclic voltammograms obtained for (a) PF/KB nanocomposite electrode ($W_{\text{re}} = 40$ wt %), (b) pure KB electrode as a blank.

Fig. 4 Specific capacitance (C_{sp}) obtained for PF/KB nanocomposite electrodes as a function of specific contents of KB (W_{re}) in PF/KB nanocomposites.

Fig. 5 Specific capacitance per PF mass (C_{sp}) obtained for PF/KB nanocomposite electrodes as a function of specific contents of KB (W_{re}) in PF/KB nanocomposites.

other polythiophene derivatives ($\sim + 0.9$ V vs. Ag/Ag^+)^{6,10,11} studied as electrochemical capacitors previously. Specific capacitance (C_{sp}) obtained for the PF/KB nanocomposite electrodes as a function of the W_{re} is shown in Fig. 4. It is revealed the C_{sp} value strongly depends on the W_{re} , and the maximum value of 160 F g^{-1} is obtained for the sample of $W_{re} = 40 \text{ wt \%}$. Figure 5 shows specific capacitance per PF mass (C_{PF}) as a function of W_{re} . The maximum C_{PF} is ca. 260 F g^{-1} (32 mAh g^{-1}), which is 40 % of charge utilization (theoretical value is 80 mAh g^{-1} assuming to 0.5 of maximum doping level). The high C_{PF} is probably attributed to optimized electron pathway and ion transfer in the PF/KB nanocomposite electrode. This will be supported by investigating some additional experiments especially in electrochemical impedance spectroscopy.

4 Conclusion

A nanocomposite based on PF loaded with KB was prepared and was investigated for electrochemical capacitor properties. The nanocomposite electrode was found to be exhibited unprecedented high redox potential, and showed high specific capacitance of 160 F g^{-1} obtained from the nanocomposite sample composed of 40 wt % of KB. These electrochemical characteristics of the PF/KB nanocomposite are promising for the use in high-energy electrochemical capacitors.

Acknowledgement

This work is partial supported by the New Energy and Industrial Technology Development Organization (NEDO) of "Carbon Nanotube Capacitor Project", Japan.

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