Short communication

Capacitance properties of poly(3,4-ethylenedioxythiophene)/ polypyrrole composites

Youlong Xu *, Jie Wang, Wei Sun, Shihai Wang

Electronic Materials Research Laboratory, Key laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

Abstract

Poly(3,4-ethylenedioxythiophene)/polypyrrole composite electrodes were prepared by electropolymerization of 3,4-ethylenedioxythiophene (EDOT) on the surface of polypyrrole (PPy) modified tantalum electrodes. The electrochemical capacitance properties were investigated with cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) techniques with two- or three-electrode cell configuration. The data showed that the specific capacitance of composite electrodes, due to the synergic effect of poly(3,4-ethylenedioxythiophene) (PEDOT) and PPy, is much higher than the values of either pure PEDOT or pure PPy electrodes. Moreover, the composites prepared on the surface of PPy with horn-like structure allow the specific capacitance up to more than $200\,\mathrm{F\,g^{-1}}$ and have a good cycleability. This implies that PEDOT/PPy composites are promising to be used as electrode material of supercapacitors.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Capacitance; Poly(3,4-ethylenedioxythiophene); Polypyrrole; Supercapacitor

1. Introduction

Supercapacitors are being considered of various applications not only coupling with batteries to provide peak power, but also replacing batteries for memory backup and electric vehicles [1–3].

Many researchers have extensively studied electrically conducting polymers (ECPs), such as polypyrrole (PPy), polythiophene (PTh) and their derivatives, because they are promising electroactive materials for supercapacitors [4–11]. A great interest was recently focused on poly (3,4-ethylenedioxythiophene) (PEDOT), which is a derivative of PTh [6–8]. It is characterized by a good thermal and chemical stability, fast electrochemical switching and a high electrical conductivity in the p-doped state (easily up to $550\,\mathrm{S\,cm^{-1}}$) [12]. What was the most attractive, as a promising electrode material of supercapacitors, PEDOT had wider potential window. However, PEDOT, due to its relatively high molar mass, presented a moderate value of theoretical specific capacitance ($210\,\mathrm{F\,g^{-1}}$) compared to PPy ($620\,\mathrm{F\,g^{-1}}$) did [7]. In order to reach their theoretical specific capacitance, the ECPs composites were often prepared with carbon nanotubes (CNTs) or graphite fiber in the past researches [6–11].

In the present study, PEDOT/PPy composite electrodes were prepared by the galvanostatical electropolymerization of PEDOT on the PPy-modified electrode. Since we were interested in composites serving as active electrode materials in electrochemical supercapacitors, their relevant electrochemical properties were investigated by means of cyclic voltammetry (CV), galvanostatical charge–discharge and electrochemical impedance spectroscopy (EIS) tests.

2. Experimental

2.1. Materials

3,4-ethylenedioxythiophene (EDOT, Bayer, 99%) and pyrrole (Py, Fluka, 99%) were distilled prior to use. All other reagents were obtained from commercial sources and were used as received. Sodium *p*-toluenesulfonate (PTSNa) was used as a surfactant and supporting salt for all the electrochemical polymerizations. LiClO$_4$ was used as a supporting salt in all the electrochemical examinations.

2.2. Electrode preparation and characterization

Pure PPy or PEDOT electrodes were galvanostatically prepared on tantalum electrodes ($10\,\mathrm{mm} \times 10\,\mathrm{mm} \times 0.1\,\mathrm{mm}$) in

---

* Corresponding author.
  E-mail address: ylxu@mail.xjtu.edu.cn (Y. Xu).

a solution containing 0.3 M Py or EDOT and 0.1 M PTSNa. By adjusting the pH of solutions and the current density, PPy films with two kinds of morphology were obtained: cauliflower and horn-like structure. Scanning electron microscope (SEM) observations of samples were carried out on a Hitachi S-2700 apparatus.

PEDOT/PPy composite electrodes were obtained by galvanostatical electropolymerization of EDOT on the PPy-modified electrodes. The appropriate molar ratio (such as 1:5) of the PPy and PEDOT was obtained by controlling the electropolymerization charge of PPy and PEDOT. The mass of PEDOT/PPy composite was determined by the electronic balance (AG 135, Mettler-Toledo).

2.3. Electrochemical test

The electrochemical performance was determined in 1 M $LiClO_4$ solutions using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatical charge/discharge techniques. All electrochemical tests were performed on VMP2 (Princeton applied research) linked with a computer. In three-electrode system, a platinum sheet was used as counter electrode, and saturated calomel electrode (SCE) as reference electrode. Two-electrode systems consisted of two almost identical PEDOT/PPy composite electrodes, serving as the working electrode and the counter electrode, respectively.

The scanning rates of CV tests ranged from 1 to 50 mV s^{-1}. The capacitance could be calculated by integrating the current of a CV curve in half cycle.

The frequency range of EIS tests was 100 kHz–10 mHz. The capacitance could be calculated from the data of EIS by the ZSIMPWIN, an analysis software attached to VMP2.

The current density of charge/discharge ranged from 0.5 to 50 mA cm^{-2}. The discharge capacitance C was calculated from the linear part of discharge curves using the following formula:

$$C = \frac{i\Delta t}{\Delta V} \tag{1}$$

where i is the current and Δt the time interval for the change in voltage ΔV.

3. Results and discussion

Fig. 1(a) shows the CV curves of pure PEDOT electrode. The shapes of CV curves are nearly rectangle, which is characteristic of electrochemical capacitors. The specific capacitance is about 110 F g^{-1} at the scanning rate of 5 mV s^{-1}, and about 90 F g^{-1} at 10 mV s^{-1}. Thinner PEDOT films could supply higher specific capacitance, but such thin films could hardly find any application for energy storage.

Therefore, we adopted two kinds of PPy to modify the PEDOT, cauliflower-like PPy (PPy-c) and horn-like PPy (PPy-h), their SEM as showed in Fig. 2. It is found that the specific
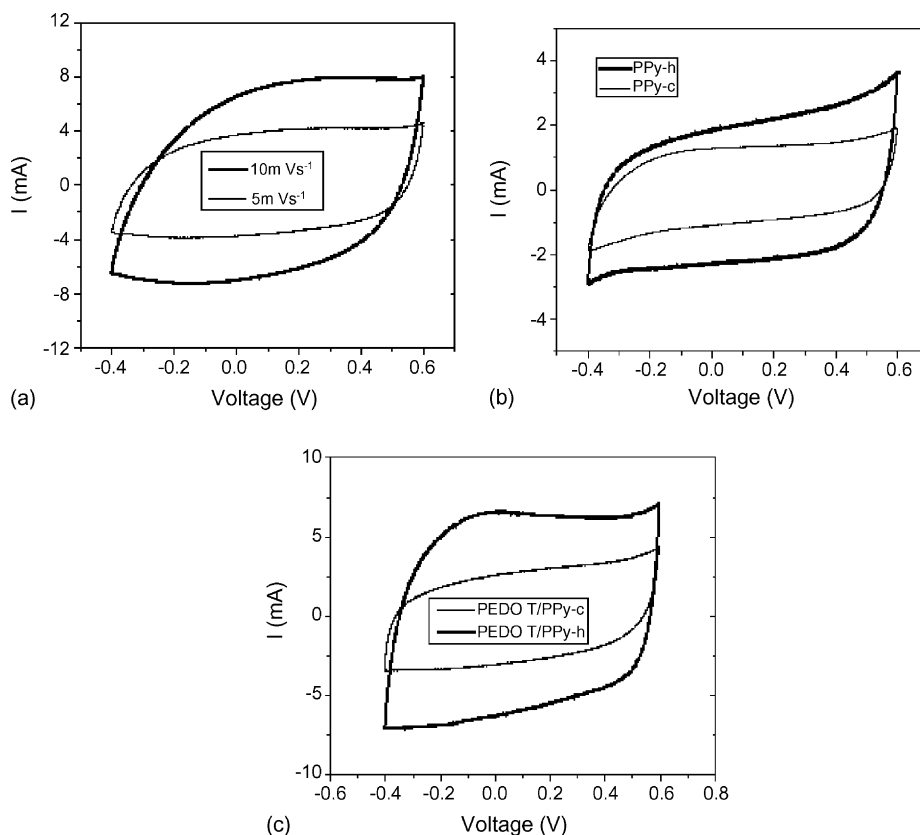

Fig. 1. CV curves of pure PEDOT, mass of 7.5 mg (a); pure PPy films, scanning rate 5 mV s^{-1} (b) and PEDOT/PPy-c and PEDOT/PPy-h composites, scan rate 2 mV s^{-1} (c), three-electrode system.
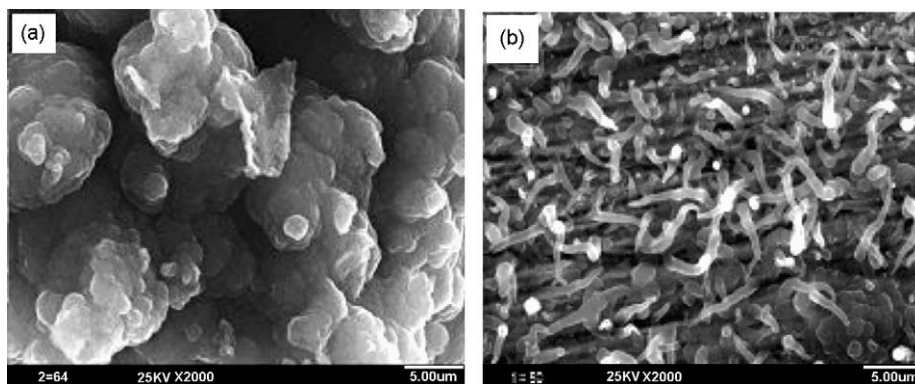
Fig. 2. Scanning electron micrographs of PPy-c (a); PPy-h. (b).

surface area of PPy-h is larger than that of PPy-c. Fig. 1(b) presents their CV curves. It is indicated that PPy-h could present higher specific capacitance ($\sim$130 F g^{-1}) than PPy-c ($\sim$100 F g^{-1}) could.

The CV curves of PEDOT/PPy-c and PEDOT/PPy-h are shown in Fig. 1(c). Their specific capacitances from the data of Fig. 1(c) are about 160 F g^{-1} and about 230 F g^{-1}, respectively. It gives a clear proof that a synergic effect of PPy and PEDOT makes an efficient energy extraction from either pure PEDOT electrode or pure PPy electrode. What is more, the PEDOT/PPy-h composite, due to the higher specific surface area, allows the specific capacitance higher than that of PEDOT/PPy-c.

EIS has been used to study the redox processes of the PEDOT/PPy composites and to evaluate their ionic and electronic conductivity as well as specific capacitance [13,14]. An example (mass of 9.5 mg) of EIS (100 kHz–10 mHz) investigation is shown in Fig. 3. In high-frequency area, a charge transfer-dominated regime is observed, while in low-frequency area, the diffusion of charge in the polymers dominates. The difference in the real part of the impedance between low and high frequencies can be used to evaluate the resistance associated with the transport within the porous structure of the composite. The resistance is about 5 Ω cm^{-2} from Fig. 3. There are two reasons leading to the low resistance. One is that PPy and PEDOT films are characterized with high electronically conductivity.
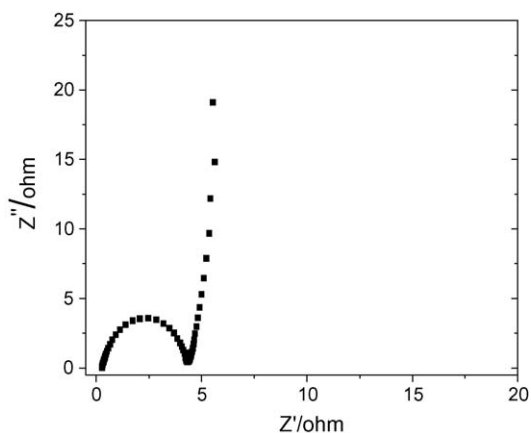
The other lies in that PPy and PEDOT are partly dedoped in the range of all test potential. The imaginary part of the impedance Z'' at low frequencies is almost perpendicular to the real part Z', which proves a good capacitance behavior of the system. The specific capacitance calculated from the Fig. 3 is 200 F g^{-1}, which is slightly smaller than the value computed from its CV curve.

Fig. 4 presents the charge/discharge curves of PEDOT/PPy-h at current load 1 mA cm^{-2} in two-electrode system. The curves are linear in the total range of potential, which signifies an ideal supercapacitor system. The specific capacitance calculated from the Fig. 4 is 225 F g^{-1}. The discharge curves at various current are shown in Fig. 5(a). The specific capacitance calculated from the data in Fig. 5(a) is shown in Fig. 5(b). The specific capacitance decreases slightly when the current increases.

Galvanostatical charge/discharge tests were also used to characterize the cycling behavior. Several samples were examined for up to 1000 cycles. The discharge specific capacitance as a function of cycle number is given in Fig. 6. The specific capacitance (ca. 220 F g^{-1} at the beginning of cycling) maintains stable over 1000 cycles at a current load of 100 mA g^{-1} (a maximum change of only 4 F g^{-1} is observed).

PEDOT is quite an exceptional conducting polymer that can be charge/discharge in a wide potential window in aqueous medium or organic solution. Fig. 7 shows such an electrochemical performance (charging until 1.2 V) of PEDOT/PPy composite (mass of 8.9 mg). It is interesting that the specific capacitance (around 240 F g^{-1}) maintains stable over 100 cycles at a current load 500 mA g^{-1}.
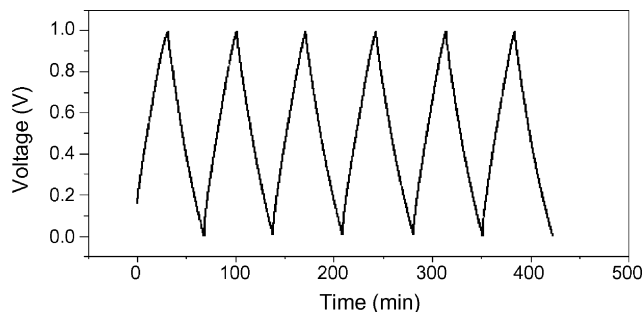

Fig. 3. EIS spectrum of PEDOT/PPy-h, three-electrode system.

Fig. 4. Galvanostatical charge/discharge curves of PEDOT/PPy-h, mass of 10.1 mg, current density 1 mA cm^2, two-electrode system.
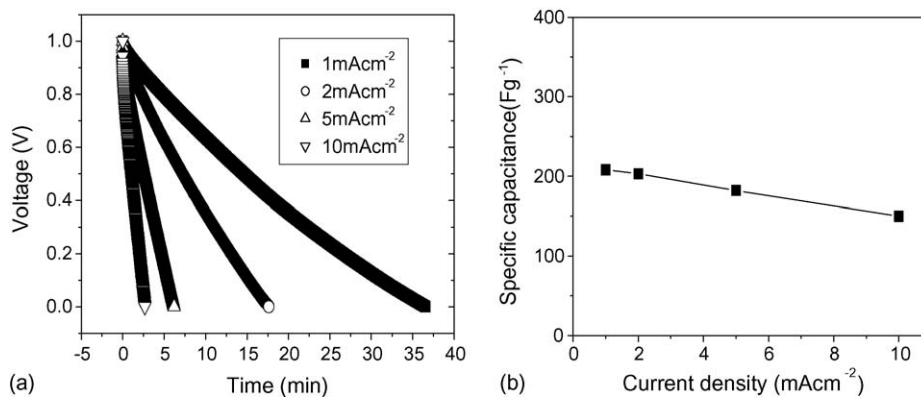
Fig. 5. Galvanostatical discharge curves (a) and discharge capacitance (b) of PEDOT/PPy at various discharge current density, 10.1 mg, two-electrode system.
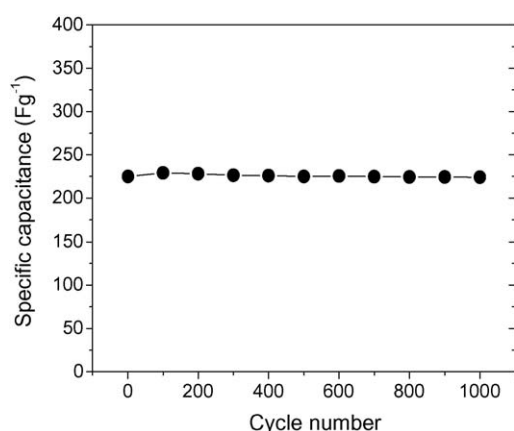

Fig. 6. Variation of capacitance as a function of cycle number at charge/discharge current density of $100 \, \text{mA g}^{-1}$, two electrodes system.
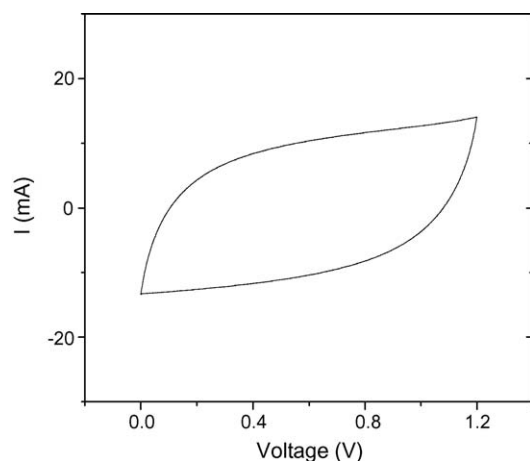

Fig. 7. CV curve of PEDOT/PPy-h composite, scanning rate $5 \, \text{mV s}^{-1}$, two-electrode system.

4. Conclusions

PEDOT/PPy composite electrodes present higher specific capacitance than either pure PEDOT or pure PPy electrodes do.

Especially, PEDOT/PPy-h composite electrodes show a specific capacitance more than $200 \, \text{F g}^{-1}$ and a good cycling performance. This demonstrates that PEDOT/PPy-h composite is a kind of very promising electrode material for supercapacitors with wide potential window.

References

[1] T. Momma, X. Liu, T. Osaka, Y. Ushio, Y. Sawada, J. Power Sources 60 (1996) 249.
[2] B.E. Conway, W. Pell, Proceedings of the Eighth International Seminar on Double-Layer Capacitors and Similar Energy Storage Devices, Florida Educational Seminars, Deerfield Beach, FL 7–9 December, 1998.
[3] M.D. Ingram, H. Staesche, K.S. Ryder, J. Power Sources 129 (2004) 107.
[4] M. Mastragositno, C. Arbizzani, F. Soavi, J. Power Sources 97-98 (2001) 812.
[5] H. Talbi, P.-E. Just, L.H. Dao, J. Appl. Electrochem. 33 (2003) 465.
[6] K. Lota, V. Khomenko, E. Frackoviak, J. Phys. Chem. Solids 65 (2004) 295.
[7] G. Han, J. Yuan, G. Shi, F. Wei, Thin Solid Films 474 (2005) 64–69.
[8] Q. Xiao, X. Zhou, Electrochim. Acta 48 (2003) 575.
[9] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld, J. Power Sources 47 (1994) 89.
[10] V. Khomenko, E. Frackowiak, F. Beguin, Electrochim. Acta 50 (2005) 2499.
[11] J.K. Park, J.M. Ko, O.O. Park, D.-W. Kim, J. Power Sources 105 (2002) 20.
[12] A. Czardybon, M. Lapkowski, Synth. Met. 119 (2001) 161.
[13] E. Karden, S. Buller, R.W. De Doncker, Electrochim. Acta 47 (2002) 2347.
[14] W.-C. Chen, T.-C. Wen, H. Teng, Electrochim. Acta 48 (2003) 641.