

The capacitive characteristics of supercapacitors consisting of activated carbon fabric–polyaniline composites in NaNO_3

Chi-Chang Hu*, Wen-Yar Li, Jeng-Yan Lin

Department of Chemical Engineering, National Chung Cheng University, Chia-Yi 621, Taiwan

Received 7 April 2004; received in revised form 14 May 2004; accepted 21 May 2004

Available online 31 July 2004

Abstract

A sandwich-type supercapacitor consisting of two similar activated carbon fabric–polyaniline (ACF–PANI) composite electrodes was demonstrated to exhibit excellent performance (i.e., highly reversibility and good stability) in NaNO_3 . Polyaniline with the charge density of polymerization less than or equal to 9 C cm^{-2} synthesized by means of a potentiostatic method showed a high specific capacitance of 300 F g^{-1} . Influences of the polymerization charge density (i.e., the polymer loading) on the capacitive characteristics of ACF–PANI composites were compared systematically. The capacity of an ACF–PANI electrode reach ca. 3.4 F cm^{-2} (a 100% increase in total capacity) when the charge density of polymerization is equal to 9 C cm^{-2} . The surface morphology of these ACF–PANI composites was examined by a scanning electron microscope (SEM).

© 2004 Elsevier B.V. All rights reserved.

Keywords: Supercapacitor; Activated carbon fabric–polyaniline composite; Cyclic voltammetry; Pseudocapacitance

1. Introduction

Activated carbon-based materials with high specific surface areas are widely recognized as the electrode materials for electric double-layer capacitors (EDLCs) [1–4] because the double-layer capacitance is directly proportional to the accessible surface area of an electrode [1,2,5]. In addition, based on the cost consideration, activated carbon (AC) and activated carbon fabrics (ACFs) are more commercially attractive in comparison with carbon nanotubes (CNTs) although the equivalent series resistance (ESR) of the latter materials with better frequency responses is definitely smaller than that of the formers [6]. Moreover, the energy densities of carbon-based supercapacitors are generally lower than that of redox supercapacitors [1,2]. Therefore, modifications of AC-based materials by adding electroactive redox species [7,8] or by introducing electroactive functional groups [4,9,10] were widely used to promote their capacities.

The modification of carbon-based materials with permanent electroactive species providing fast Faradaic redox currents seems to be a more powerful rout to enhance the capacity of supercapacitors because some functional groups

formed on the surface of carbons are not very stable during the repeated charge–discharge cycles [11]. Moreover, due to the Faradaic reactions, the energy density of a supercapacitor consisting of electroactive materials with several oxidation states or structures (e.g., transition metal oxides and conducting polymers) is expected to be higher than that of an EDLC [1,2,12–14]. Hence, composites consisting of electroactive species and carbon materials with highly specific surface areas are considered to significantly promote the energy density of supercapacitors [15,16].

Conducting polymers, such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), and their derivatives with a large degree of π -orbital conjugation and various oxidation structures have been recognized as the electrode materials for the supercapacitor application [1,2,13,15–19]. Moreover, PANI and its derivatives show a lot of advantages for practical applications, such as ease of polymerization in aqueous media [20], good stability in air [21], simplicity in doping/dedoping [22], etc. In addition, these polymers are relatively cheap and the preparation costs are competitive for commercialization without considering the high specific capacitance (capacitance per gram of polymers) and the excellent redox reversibility of these polymers [13,17,18].

Polyaniline was found to show ideally capacitive responses in a neutral NaNO_3 solution in our recent work [23]. In addition, ACFs are more preferable for the supercapacitor

* Corresponding author. Tel.: +886 5 2720411x33411;

fax: +886 5 2721206.

E-mail address: chmhcc@ccu.edu.tw (C.-C. Hu).

applications in comparing with AC powders because a higher ESR should result from the electron hopping between AC powders during charge/discharge processes although the electronic conductivity of conventional carbons in various forms is good. Accordingly, ACF–PANI composites are expected to possess a synergistic effect on the capacitive performance for the application of supercapacitors. In this communication, effects of the charge density of polymerization on the capacitive performance of ACF–PANI composites in a neutral NaNO_3 solution are systematically investigated. In addition, a sandwich-type cell consisting of a pair of similar ACF–PANI electrodes is employed to show its applicability in supercapacitors. Finally, the morphology of ACF–PANI composites with different charge densities of polymerization was examined by a scanning electron microscope (SEM).

2. Experimental

Polyacrylonitrile (PAN)-derived activated carbon fabrics (ACFs) were served as the basic electrode materials for the electrochemical polymerization of polyaniline. The mean thickness of these fabrics is ca. 0.48 mm, which were bound onto 10 mm \times 10 mm \times 3 mm graphite substrates (Nippon Carbon EG-NPL, N.C.K., Japan) with a conductive graphite-powder paste. These substrates before binding with ACFs were first abraded with ultrafine SiC paper, rinsed in an ultrasonic bath of water for 10 min, then, etched in a 0.5 M H_2SO_4 solution at room temperature for 10 min, and finally rinsed in the ultrasonic bath of water for 30 min.

The weight of each ACF was measured through a microbalance with an accuracy of 10 μg (Sartorius BP 211D, Germany) before binding with the substrate. The graphite paste slurries ground for 30 min were composed of fine graphite powders (60 wt.%) with a low specific surface area (2.8 m² g⁻¹) and PVDF powders (40 wt.%) with some *N*-methyl-2-pyrrolidone. The total amount of the binding paste on each electrode was kept approximately constant (ca. 0.01 g cm⁻²) to avoid any unexpected influences. These ACF-coated electrodes were dried in a vacuum oven at 85 °C overnight. The exposed geometric area of these ACF-coated electrodes is equal to 1 cm² and the other surface areas were coated with polytetrafluorene ethylene (PTFE) films. The electrochemical polymerization of PANI was carried out by a potentiostatic method at 0.75 V with different charge densities of polymerization in a solution containing 1 M HNO_3 (Merck GR) and 0.2 M aniline (Fluka GR). In order to avoid the interference due to the change in the aniline concentration and the presence of aniline radicals on the polymerization rate, every electrode was polymerized in a freshly prepared solution. The aniline monomers were purified by distillation before usage. After polymerization, the PTFE films were removed from the electrodes and these electrodes were doubly rinsed with water and then dried in a vacuum oven at room temperature overnight (≥ 12 h). The

loading of PANI is the weight difference of the electrode without PTFE coating before and after the application of polymerization through a microbalance. The surface morphology of all composite electrodes was examined by a scanning electron microscope (SEM JEOL JSM 35).

The electrochemical analyzer system, CHI 633A (CH Instrument, USA) was employed to perform the electrochemical and charge/discharge measurements for the polymerization and characterization of composite electrodes. An Ag/AgCl electrode (Argenthal, 3 M KCl, 207 mV versus SHE at 25 °C) was used as the reference, and a piece of platinum gauze with an exposed area of 4 cm² was employed as the counter electrode for the three-electrode measurements. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of the working electrode, was used to minimize errors due to *iR* drop in the electrolytes. For the sandwich-type cells, Manila paper was served as the separator between a pair of identical ACF–PANI/G (or ACF/G) electrodes.

All solutions used in this work were prepared with 18 M Ω cm water produced by a reagent water system (MILLI-Q SP, Japan) and all reagents not otherwise specified in this work were Merck, GR. The electrolyte, containing 1 M NaNO_3 , used to evaluate the capacitive behavior of various ACF–PANI composites was degassed with purified nitrogen gas before measurements and nitrogen was passed over the solutions during the measurements. The solution temperature was maintained at 25 °C by means of a water thermostat (HAAKE DC3 and K20).

3. Results and discussion

In our previous work [9], the capacitive performance of activated carbon fabrics (ACFs) was definitively improved by the employment of a graphite current collector (i.e., ACF/G electrodes). In addition, the performance of ACF/G electrodes was optimized when ACFs were bound onto the graphite substrates with the conducting binders consisting of 60 wt.% fine graphite powders and 40 wt.% PVDF powders. Accordingly, this ACF/G electrode is used as the bare electrode in this work and the ACF-bound graphite electrode coated with PANI is denoted as ACF–PANI/G. Typical results of ACF/G and ACF–PANI/G electrodes with a charge density of polymerization = 9 C cm⁻² measured by means of cyclic voltammetry at 5 mV s⁻¹ in 1 M NaNO_3 are shown in Fig. 1a as curves 1 and 2, respectively. In addition, the results measured through means of chronopotentiometry at 10 mA cm⁻² in the same medium are shown in Fig. 1b as curves 1 and 2, respectively. Note in Fig. 1a that curve 1 shows the typical *i*–*E* responses of ACF/G in aqueous media, indicating the fact that currents of double-layer charge/discharge are typically capacitive since no obvious redox peaks can be found on this CV curve. In addition, currents rapidly reach the steady state value when the sweep direction is changed, indicating that the equivalent circuit

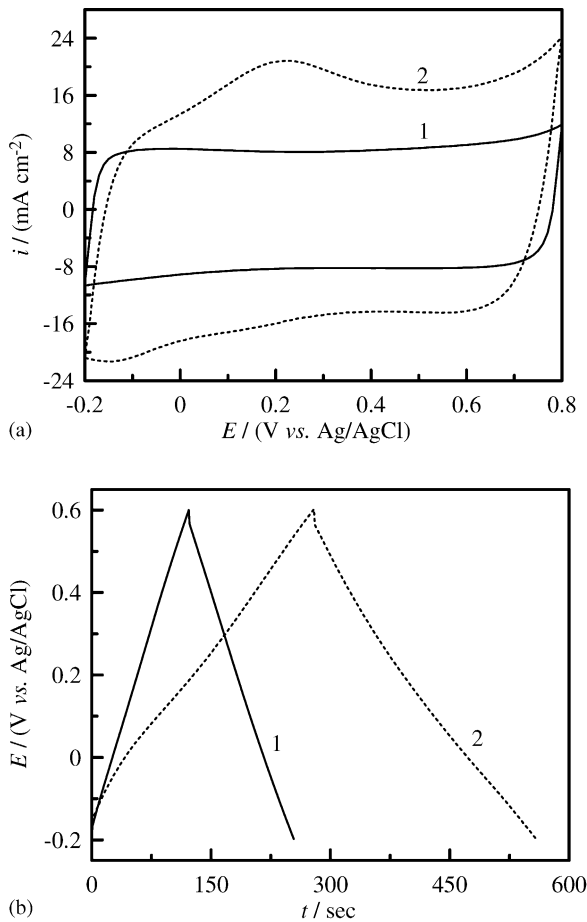


Fig. 1. (a) Cyclic voltammograms and (b) chronopotentiograms of (1) ACF/G and (2) ACF-PANI/G electrodes in 1 M NaNO₃ at 5 mV s⁻¹. PANI was polymerized at 0.75 V in 1 M HNO₃ and 0.2 M aniline at 25 °C with a charge density of 9 C cm⁻².

resistance (ESR) on this electrode should be low and acceptable. Thus, graphite is a good current collector and the ACF is a suitable electrode material for the application of EDLCs. On curve 2, much higher voltammetric currents are clearly found on both positive and negative sweeps, revealing the significant contribution of the redox currents of PANI. In addition, a broad peak is clearly found on the positive sweep, which was not found for a PANI-coated graphite electrode [23]. On the other hand, the charges on the positive sweep are approximately equal to that on the corresponding negative sweep, revealing the good electrochemical reversibility of redox transitions of PANI in this neutral medium. Moreover, the absence of redox peaks as well as the capacitive-like responses of PANI in NaNO₃ has been attributed to the doping/de-doping nature and electronic conductivity from the pH-potential phase diagram of PANI [23,24].

In Fig. 1b, the $E-t$ responses in the cathodic discharge process show the mirror image of their corresponding anodic charge counterparts on both curves. In addition, the iR drop is approximately independent of the PANI coating when the sign of applied currents was changed from anodic to cathodic. This is attributed to the good conductivity of

PANI prepared by means of potentiostatic polymerization [23]. Therefore, ACF-PANI/G electrodes show the ideally capacitive characteristics in 1 M NaNO₃. Based on Eq. (1), the average specific capacitance of these ACF-PANI composites can be deduced from their discharge curves [14]:

$$C_{S,T} = \frac{i}{|(dE/dt) \times m|} \approx \frac{i}{[(\Delta E/\Delta t) \times m]} \quad (1)$$

where m indicates the total mass of ACF-PANI composites. The slope of chronopotentiograms (dE/dt) is very close to its mean value ($\Delta E/\Delta t$) since all CP curves are linear and highly symmetric. From a comparison of curves 1 and 2, a 100% increase in the capacity was obtained when PANI (with 9 C cm⁻²) was deposited onto this ACF (reaching a high capacity of 3.4 F cm⁻²).

Due to the good electrochemical reversibility and the capacitive-like behavior of this ACF-PANI composite in NaNO₃, the energy density (ED) and power density (PD) of this electrode can be calculated on the basis of following equations:

$$ED = \frac{C_{S,T} \Delta E^2}{2m} \quad (2)$$

$$PD = \frac{ED}{\Delta t} = \frac{C_{S,T} \Delta E^2}{2m \Delta t} \quad (3)$$

Accordingly, ED and PD of the ACF-PANI composite shown in Fig. 1a are equal to ca. 18.3 and 340 W/kg, respectively, revealing its good performance. In addition, the power density of this electrode should be doubled when the scan rate is 10 mV s⁻¹ (see Figs. 3 and 4).

Fig. 2 shows the dependence of PANI loading, specific capacitance of composites ($C_{S,T}$), and specific capacitance of PANI (C_S) on the charge density of polymerization. The specific capacitance of PANI can be estimated on the basis of Eq. (4):

$$C_S = \frac{C_{S,T} - C_{ACF}}{w} \quad (4)$$

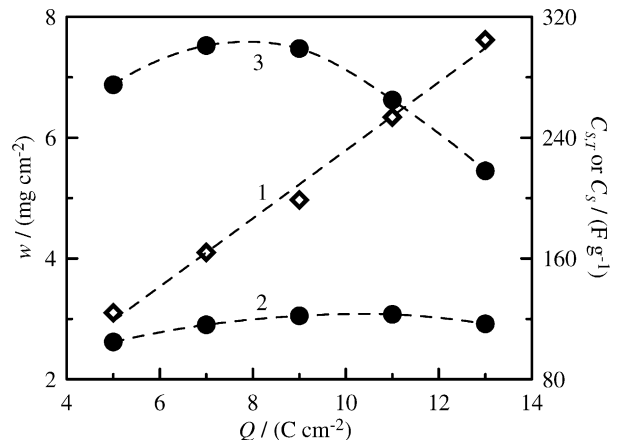


Fig. 2. Dependence of (1) loading and (2) total capacitance ($C_{S,T}$) of ACF-PANI/G electrodes; and (3) specific capacitance (C_S) of PANI measured in 1 M NaNO₃ on the charge density of PANI polymerization.

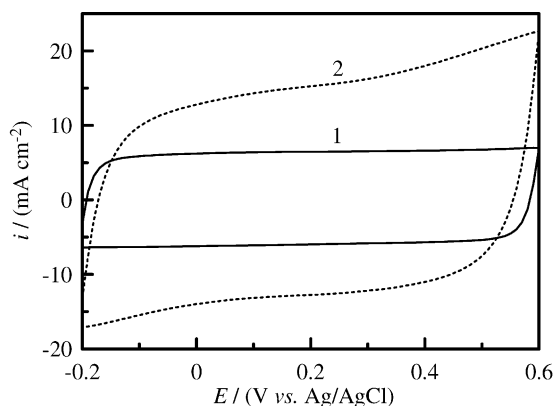
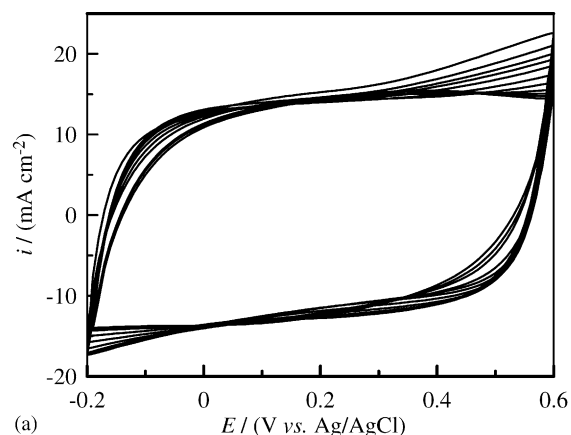


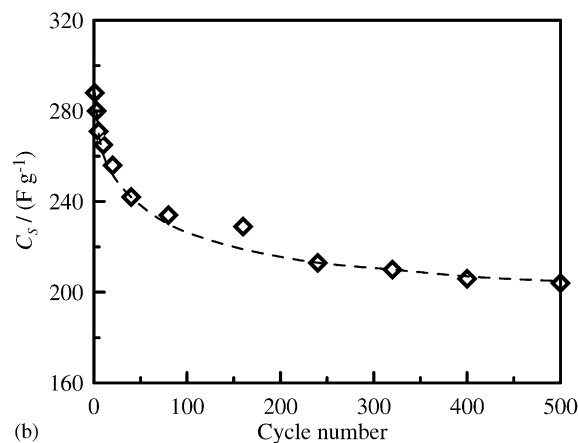
Fig. 3. Cyclic voltammograms of sandwich-type cells consisting of two similar (1) ACF/G and (2) ACF-PANI/G electrodes in 1 M NaNO_3 at 10 mV s^{-1} . PANI was polymerized at 0.75 V in 1 M HNO_3 and 0.2 M aniline at 25°C with a charge density of 9 C cm^{-2} .

where $C_{S,T}$, C_{ACF} and w are indicative of the total capacitance of a bare ACF-PANI composite, the total capacitance of an ACF/G electrode, and the mass of PANI ($m - w_{ACF}$; w_{ACF} is the mass of bare ACFs). Line 1 shows that the mass of PANI is approximately linearly proportional to the passed charges of polymerization, indicating that the loading of PANI can be controlled by the charge density of polymerization. On curve 2, the specific capacitance of composites, however, reaches a maximum value (ca. 125 F g^{-1}) as the charge density is set between 9 and 11 C cm^{-2} , which is about 1.67 times of that of a bare ACF (ca. 75 F g^{-1}). The obvious difference between $C_{S,T}$ of all ACF-PANI composites and $C_{S,ACF}$ of a bare ACF is attributable to the significant contribution of pseudocapacitance coming from PANI since the PANI loading is relatively low ($< 8 \text{ mg cm}^{-2}$). In addition, the high C_S ($\approx 300 \text{ F g}^{-1}$) becomes lower when the charge density of polymerization is above 9 C cm^{-2} (see curve 3), indicating a relatively poorer utilization of PANI. Accordingly, the ACF-PANI composite with the charge density of polymerization equal to 9 C cm^{-2} is considered to be the most suitable electrode of supercapacitors.

Curves 1 and 2 in Fig. 3 show the typical cyclic voltammograms of two sandwich-type supercapacitors consisting of two similar ACF/G and ACF-PANI/G electrodes (charge density of polymerization = 9 C cm^{-2}), respectively. These CV curves were measured in 1 M NaNO_3 at 10 mV s^{-1} . On curve 1, $i-E$ responses on the positive sweep are completely symmetric to that on the following negative sweep, demonstrating the typical behavior of a supercapacitor, which further supports the promising applicability of ACFs to EDLCs. On curve 2, a slight increase in anodic currents with the positive shift of potentials on the positive sweep as well as a slight increase in cathodic currents with the negative movement in potentials on the negative sweep is found while the $i-E$ behavior is smooth and featureless. The above phenomena support the applicability of ACF-PANI composites to supercapacitors.



(a)



(b)

Fig. 4. (a) Cyclic voltammograms of a sandwich-type cell consisting of two similar ACF-PANI/G electrodes against the cycle number of CV in 1 M NaNO_3 at 10 mV s^{-1} . (b) The capacitance loss of PANI polymerized at 0.75 V in 1 M HNO_3 and 0.2 M aniline at 25°C with a charge density of 9 C cm^{-2} against the cycle number of CV.

Since degradation of conducting polymers is usually found when they are potential cycled in aqueous media [23,25–27], the stability of ACF-PANI/G electrodes has to be examined in order to evaluate their practical applicability. Typical potential cycling results of a sandwich-type supercapacitor consisting of two freshly prepared ACF-PANI/G electrodes with the charge density of polymerization = 9 C cm^{-2} measured at 10 mV s^{-1} in the potential ranges of -0.2 to 0.6 V for 500 cycles are shown in Fig. 4a. In addition, the decay in C_S with the cycle number is shown in Fig. 4b. Note that the decay in $C_{S,T}$ is presumably due to the degradation of PANI only in the calculation of C_S for Fig. 4b. In Fig. 4a, with increasing the cycle number of CV, the voltammetric behavior becomes similar in shape to that of a capacitor consisting of a pair of ACF/G electrodes (i.e., curve 1 in Fig. 3) while the high background currents do not decay in the whole potential region of investigation. Accordingly, the charge/discharge behavior of this supercapacitor becomes more ideal during the repeated applications of CV between -0.2 and 0.6 V although a decay in C_S from ca. 290 to 220 F g^{-1} is found after 500 cycles of CV

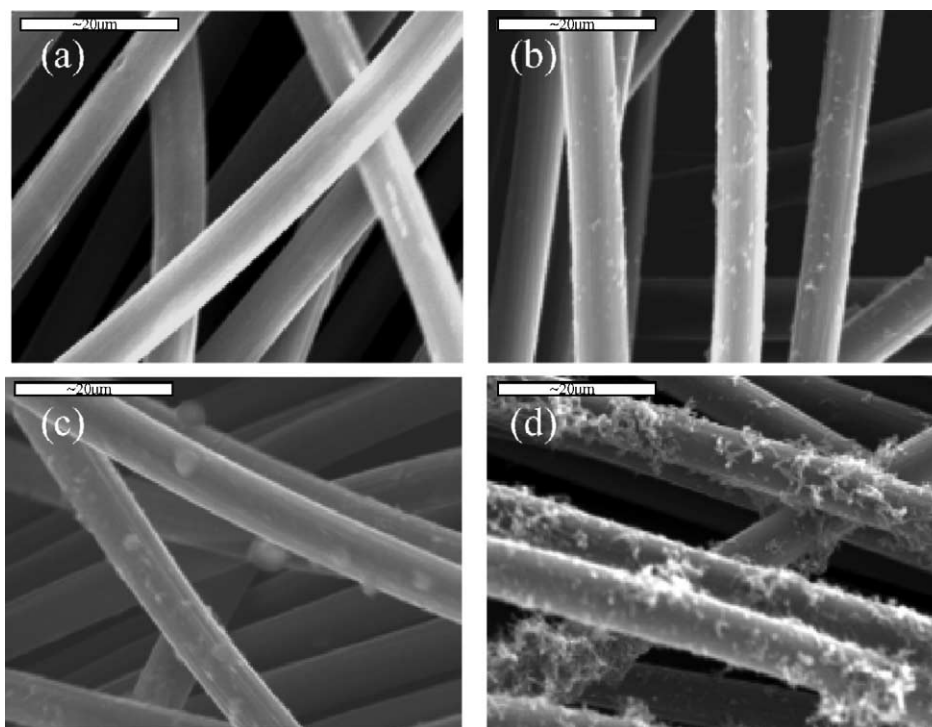


Fig. 5. SEM photographs of ACF-PANI composites with PANI polymerized at 0.75 V with the charge density of polymerization: (a) 0 C cm^{-2} ; (b) 5 C cm^{-2} ; (c) 9 C cm^{-2} ; (d) 13 C cm^{-2} .

(see Fig. 4b). Also note that the loss of C_S is relatively fast during the initial 100 cycles. However, C_S is approximately independent of the CV cycle number when it is above 240 cycles since the corresponding $i-E$ curves in Fig. 4a are overlapped completely. Hence, ACF-PANI composites are considered to be stable in the potential region of investigation. This is attributable to the fact that degradation of PANI usually occurs at potentials positive than 0.6 V in aqueous media. Based on the capacitive characteristics and the good stability of a supercapacitor consisting of two ACF-PANI/G electrodes in NaNO_3 , ACF-PANI composites should be excellent electrode materials for electrochemical supercapacitors.

The effect of polymerization charge density on the coverage of PANI at the surface of ACFs was examined from the SEM photographs. Typical SEM photographs for an ACF/G electrode and the ACF-PANI/G electrodes with the charge density of polymerization equal to 5, 9, and 13 C cm^{-2} are shown as Fig. 5a–d, respectively. In Fig. 5a, activated carbon fibers with a smooth surface morphology are clearly found, indicative of the microporous nature of activated carbon fibers. These activated carbon fibers are partially coated with PANI when the charge density of polymerization is equal to 5 C cm^{-2} (see Fig. 5b). The surface of activated carbon fibers should be completely coated with PANI with some large polymer particles when the charge density of polymerization is about 9 C cm^{-2} (see Fig. 5c). When the charge density of polymerization is equal to 13 C cm^{-2} , PANI fibers, aggregates, and particles are formed on the

surface of activated carbon fibers (see Fig. 5d). The above results support the statement that the loading of PANI on ACFs can be controlled by the passed charges of polymerization. In addition, the specific capacitance of PANI remains high (ca. 300 F g^{-1}) when the surface of activated carbon fibers is partially/completely covered with thin PANI films without the presence of PANI fibers or aggregates (i.e., the charge density of polymerization $\leq 9 \text{ C cm}^{-2}$).

4. Conclusions

Activated carbon fabric-polyaniline (ACF-PANI) composites with the charge density of polymerization equal to 9 C cm^{-2} showed the promising applicability to electrochemical supercapacitors between -0.2 and 0.6 V in 1 M NaNO_3 . The specific capacitance of PANI reached 300 F g^{-1} when the charge density of polymerization was equal to or less than 9 C cm^{-2} . A sandwich-type supercapacitor consisting of a pair of similar ACF-PANI composite electrodes exhibited the ideally capacitive behavior and a good stability for 500 cycles of CV. The loading of PANI on ACFs could be controlled by the passed charges of polymerization and PANI remained the high specific capacitance when the surface of activated carbon fibers was partially or completely covered with thin PANI films without the presence of polymer fibers or aggregates (i.e., the charge density of polymerization $\leq 9 \text{ C cm}^{-2}$). The capacity of electrodes was doubled and reached about 3.4 F cm^{-2}

(i.e., a 100% increase in total capacity) when PANI with 9 C cm^{-2} was deposited onto ACFs, further extending the supercapacitor application.

Acknowledgements

The financial support of this work, by the National Science Council of the Republic of China under contract no. NSC 92-2214-E-194-005, is gratefully acknowledged.

References

- [1] B.E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic Publishers, New York, 1999.
- [2] A. Burke, *J. Power Sources* 91 (2000) 37.
- [3] D. Qu, H. Shi, *J. Power Sources* 74 (1998) 99.
- [4] Y.-R. Nian, H. Teng, *J. Electrochem. Soc.* 149 (2002) A1008.
- [5] A.J. Bard, L.R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, Singapore, 1980.
- [6] C. Niu, E.K. Sichel, R. Hoch, D. Moy, H. Tennent, *Appl. Phys. Lett.* 70 (1997) 1480.
- [7] C. Lin, J.A. Ritter, B.N. Popov, *J. Electrochem. Soc.* 145 (1998) 4097.
- [8] C.-C. Hu, C.-C. Wang, *Electrochem. Commun.* 4 (2002) 554.
- [9] C.-C. Hu, C.-C. Wang, *J. Power Sources* 125 (2004) 299.
- [10] H. Yang, M. Yoshio, K. Isono, R. Kuramoto, *Electrochem. Solid-State Lett.* 5 (2002) A141.
- [11] P.-Z. Cheng, H. Teng, *Carbon* 41 (2003) 2057.
- [12] J.P. Zheng, P.-J. Cygon, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699.
- [13] C.-C. Hu, C.-H. Chu, *Mater. Chem. Phys.* 65 (2000) 329; C.-C. Hu, C.-H. Chu, *J. Electroanal. Chem.* 503 (2001) 105.
- [14] C.-C. Hu, T.-W. Tsou, *Electrochem. Commun.* 4 (2002) 105; C.-C. Hu, T.-W. Tsou, *Electrochim. Acta* 47 (2002) 3523; C.-C. Hu, T.-W. Tsou, *J. Power Sources* 115 (2003) 179.
- [15] E. Frackowiak, F. Beguin, *Carbon* 39 (2001) 937.
- [16] Y.-R. Lin, H. Teng, *Carbon* 41 (2003) 2865.
- [17] A. Laforgue, P. Simon, C. Sarrazin, J.-F. Fauvarque, *J. Power Sources* 80 (1999) 142.
- [18] C.-C. Hu, X.-X. Lin, *J. Electrochem. Soc.* 149 (2002) A1049.
- [19] J.H. Park, O.O. Park, *J. Power Sources* 111 (2002) 185.
- [20] B.Y. Choi, I.J. Chung, J.H. Chun, J.M. Ko, *Synth. Met.* 99 (1999) 253.
- [21] J.-Ch. LaCroix, A.F. Diaz, *J. Electrochem. Soc.* 135 (1988) 1457.
- [22] E.N. Paul, A.J. Ricco, M.S. Wrighton, *J. Phys. Chem.* 89 (1985) 1441.
- [23] C.-C. Hu, J.-Y. Lin, *Electrochim. Acta* 47 (2002) 4055.
- [24] C.M. Lampert, C.G. Granqvist, *Large-Area Chromogenics: Materials and Devices for Transmittance Control*, SPIE Optical Engineering Press, Washington, USA, 1990.
- [25] C.-H. Yang, T.-C. Wen, *J. Appl. Electrochem.* 24 (1994) 166.
- [26] E.M. Genies, M. Lapkowski, J.F. Penneau, *J. Electroanal. Chem.* 249 (1988) 97.
- [27] C.-C. Hu, E. Chen, C.-Y. Lin, *Electrochim. Acta* 47 (2002) 2741.