

Supercapacitors using carbon nanotubes films by electrophoretic deposition

Chunsheng Du, Ning Pan*

Nanomaterials in the Environment, Agriculture and Technology (NEAT), University of California, Davis, CA 95616, USA

Received 31 January 2006; received in revised form 21 February 2006; accepted 24 February 2006

Available online 18 April 2006

Abstract

Multi-walled carbon nanotube (MWNT) thin films have been fabricated by electrophoretic deposition technique in this study. The supercapacitors built from such thin film electrodes have exhibited near-ideal rectangular cyclic voltammograms even at a scan rate as high as 1000 mV s^{-1} and a high specific power density over 20 kW kg^{-1} . More importantly, the supercapacitors showed superior frequency response, with a frequency ‘knee’ at about 7560 Hz, which is more than 70 times higher than the highest ‘knee’ frequency (100 Hz) so far reported for such supercapacitors. Our study also demonstrated that these carbon nanotube thin films can serve as a coating layer over ordinary current collectors to drastically enhance the electrode performance, indicating the huge potential in supercapacitor and battery manufacturing. Finally, it is clear that electrophoretic deposition is a promising technique for massive fabrication of carbon nanotube electrodes for various electronic devices.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Carbon nanotubes; Thin film; Supercapacitor; Electrophoretic deposition

1. Introduction

Carbon nanotubes (CNTs) have been demonstrated to be exciting new material for electrodes of electrochemical energy storage and conversion devices, owing to their unique internal structures, high surface area, remarkable chemical stability and electronic conductivity as well as light weight. Consequently a wide range of their potential applications to electrochemical energy storage and conversion systems have been proposed in recent years, for example, as electrodes for supercapacitors [1–12], for Li-ion secondary batteries [13–17] and for hydrogen storage in fuel cells [18].

As unique energy storage devices, supercapacitors are able to provide huge amount of energy in a short period of time, making them indispensable for surge-power delivery [19]. It is worth noting that, in the conventional supercapacitors made of activated carbon or carbon fibers, most of the surface area resides in the micropores of the carbons and thus is unlikely to contribute significantly to the charge storage, especially at high rate. This results in a poor frequency response, with the energy stored in those carbon electrode materials can be released only

at slow rate. Recent efforts have been focused on the development of supercapacitors that have high power density and improved frequency response [2,20] for better performance and more demanding applications.

The key factors limiting the power density and frequency response of a supercapacitor include the internal resistivity of the electrode itself, the resistivity between the electrode and current collector and the resistivity of the electrolyte within the porous structure of the electrode [1,20]. There have been several successful attempts in improving the power density of supercapacitors. For example, An [1,4] obtained high power density with single-walled carbon nanotubes by using polished nickel foil with lower contact resistivity and then conducting a heat-treatment at high temperature so as to reduce the internal resistance of carbon nanotube electrode. Yoon [10] lowered the contact resistivity by directly growing carbon nanotubes on metal current collectors. Niu et al. [20] reported that higher power density $>8 \text{ kW kg}^{-1}$ and better frequency response of about 100 Hz were obtained by using free-standing mats of entangled multi-walled carbon nanotubes (MWNTs) as electrodes. In our previous work, we have lowered the equivalent series resistance (ESR) of electrodes significantly, by adopting thin films fabricated using highly concentrated colloidal suspension of carbon nanotubes [21]. While devoting to improve the performance of the supercapacitors made of CNTs, another more

* Corresponding author. Tel.: +1 530 752 6232; fax: +1 530 752 7584.
E-mail address: npan@ucdavis.edu (N. Pan).

practical but just as important issue is the fabrication efficiency of such supercapacitors. So far there is still no viable method reported to prepare CNT-based electrodes with controlled quality in large scale and massive quantity.

We report here an electrode coated with MWNT thin-film prepared by the electrophoretic deposition (EPD) technique [22–24], which has the advantages of short formation time, simple apparatus and suitability for mass production. In addition, the technique allows for flexibility in shape and size of the substrates on which the thin film is formed. The supercapacitors built from such electrodes have exhibited an near-ideal rectangular cyclic voltammograms even at a high scan rate of 1000 mV s^{-1} , an indication of an extremely small ESR, and a very high specific power density of about 20 kW kg^{-1} . More importantly, the supercapacitors showed superior frequency response, with a knee frequency about 7560 Hz , more than 70 times higher than the highest knee frequency (100 Hz) so far reported for supercapacitors. All of these make EPD a highly attractive route in fabricating CNT electrodes for high performance supercapacitors and other similar devices.

2. Experimental

The multi-walled carbon nanotubes (MWNTs) used for this study were made via chemical vapor deposition (CVD), which was described elsewhere [21]. Purified nanotubes were refluxed with concentrated nitric acid (10.8N) for 10 h, and then washed with distilled water by filtration followed by rinsing with absolute ethanol and drying at 60°C . In a typical EPD experiment, 6 mg of refluxed MWNTs were dispersed in 60 ml of absolute ethanol by ultrasonication. In order to charge the carbon nanotubes, 10^{-5} to 10^{-4} mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added into the suspension as electrolyte for EPD. Two 5 cm-diameter nickel foils were used as electrophoretic deposition (EPD) electrodes, and were put into the suspension and kept parallel (see Fig. 1). A dc voltage of 40–50 V (GoldTool DC power supply, model DSP-5050) was applied on the EPD electrodes and thus the charged carbon nanotubes were attracted towards the cathode.

After EPD, the deposition electrode was cut into small pieces of samples with a dimension of 0.8 cm by 0.8 cm for further test. The small samples were heated in tube furnace at 500°C for 30 min under either argon or hydrogen.

The microstructures of the electrodes were investigated by high resolution scanning electron microscopy (FEI XL30-SFEG). Elemental analyses were carried out on FEI XL30-SFEG equipped with energy dispersive X-ray spectroscopy (EDS) system. For electrochemical measurement, a test cell of capacitor was fabricated with a 6N KOH used as electrolyte. A cellulose fiber filter paper (Fisherbrand) immersed in the electrolyte was used as a separator placed between the two electrodes. The electrochemical behavior of the supercapacitor was analyzed using cyclic voltammetry (CV) and galvanostatic charge/discharge on a potentiostat/galvanostat (EG&G Princeton Applied Research, Model 263A), and electrochemical impedance spectroscopy (EIS) on a frequency response detector driving the EG&G 263A.

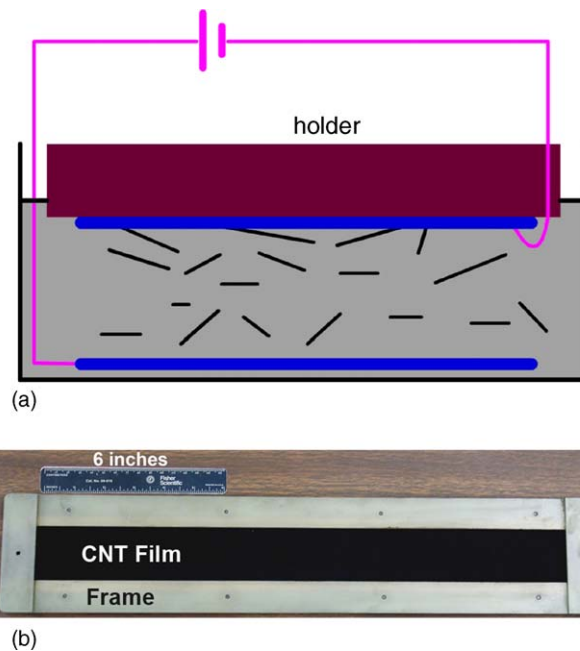


Fig. 1. (a) Schematic diagram of the electrophoresis process for the deposition of carbon nanotubes. (b) Photograph of the carbon nanotube thin film on a nickel foil that is held in a frame. Note that the scale of the ruler in the photograph is 6 in.

3. Results and discussion

3.1. Electrochemical behavior of the supercapacitor

The electrophoresis process that we used to fabricate the carbon nanotube thin films is illustrated schematically in Fig. 1(a). Upward deposition separates EPD from sedimentation [25]. Early research [26,27] has demonstrated that oxidation treatment of carbon nanotubes in concentrated acid created a negatively charged surface through the ionization of such functional groups as $-\text{COOH}$, $-\text{OH}$, and $>\text{C}=\text{O}$, and thus provided hydrophilic sites on the tube surface to impart cation-exchange properties. The resulting electrostatic repulsion among the nanotubes makes the

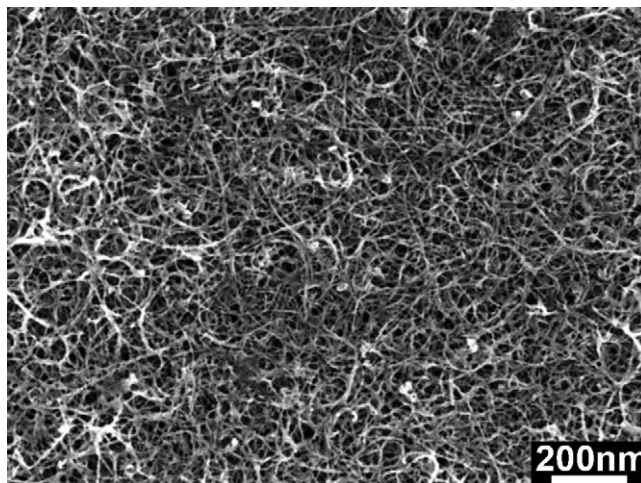


Fig. 2. SEM image showing the porous structure of the EPD film.

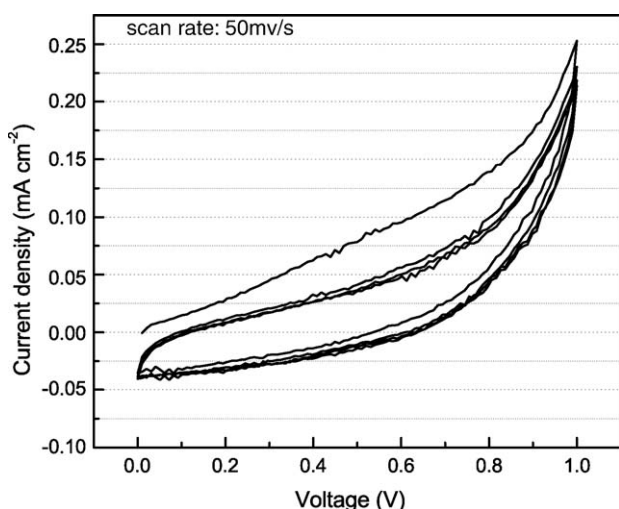


Fig. 3. CV of a supercapacitor using the as-received EPD films as electrodes at a scan rate of 50 mV s^{-1} .

dispersion of CNT much easier and leads to dramatic increase in the stability of the colloidal suspension. When $\text{Mg}(\text{NO}_3)_2$ was added into the suspension of the carbon nanotubes, the carbon nanotubes became positively charged as a result of the adsorption of Mg^{2+} , hence under an electrical field moved towards the negative deposition electrode and deposited there to form a thin film. Fig. 1(b) shows a photograph of the carbon nanotube thin film thus prepared on a large rectangular nickel foil by EPD. Note that the scale of the ruler in the photograph is 6 in. therefore this technique is very easy to scale up.

The SEM image of the nanotubes thin film is shown in Fig. 2. It can be seen that the film has a uniform pore structure formed by the open spaces between entangled nanotubes. Such an open porous structure with a highly accessible surface area is unobtainable with other carbon materials, and enables easy access of the solvated ions to the electrode/electrolyte interface, which is crucial for charging the electric double layer. In addition, because the charged carbon nanotubes in the suspension during EPD process were driven by a uniform dc electric field, the film formed on EPD electrode (the nickel foil in this case, also serving as the current collector in the supercapacitor) is

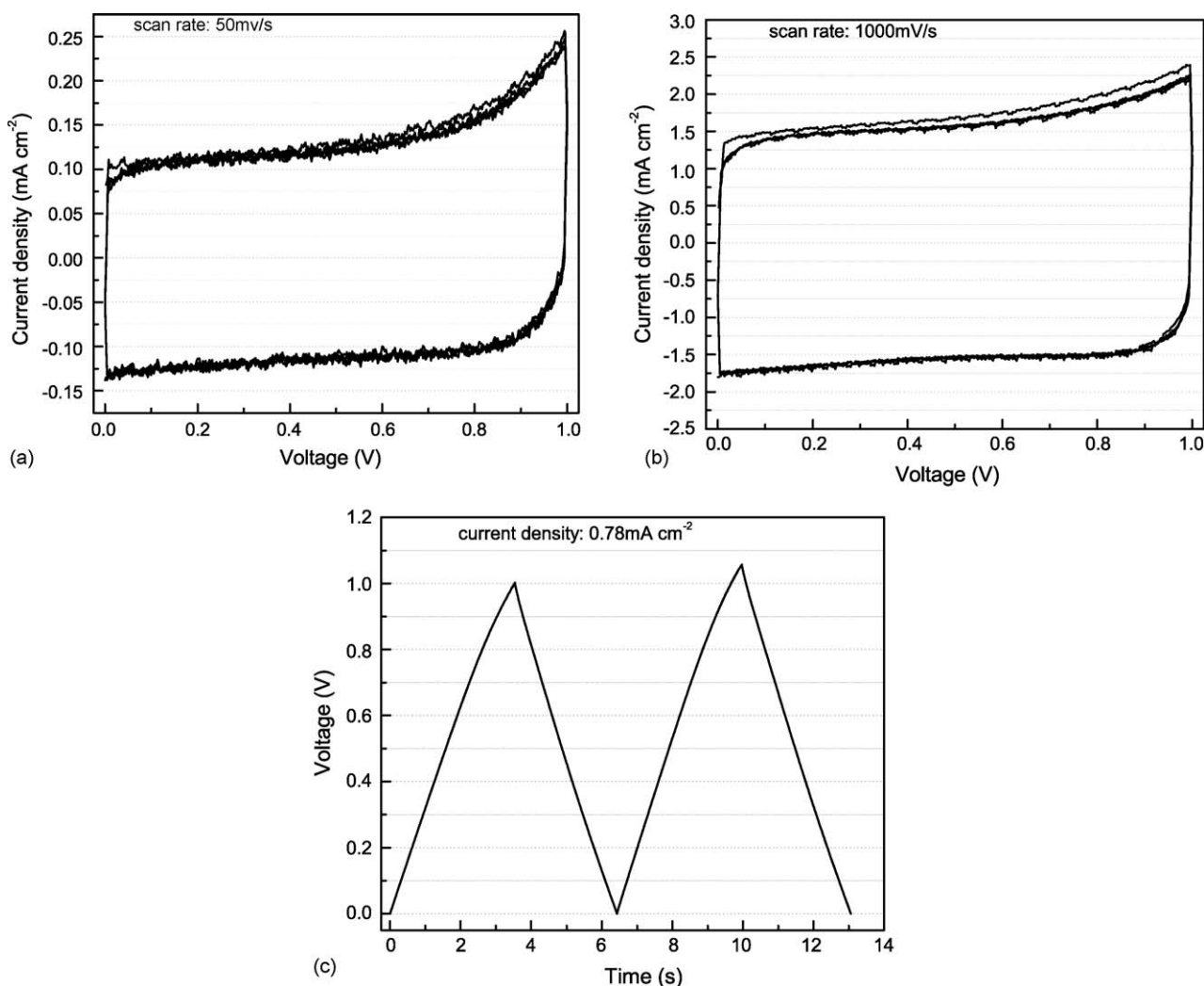


Fig. 4. (a, b) CVs at different scan rates of 50 and 1000 mV s^{-1} , and (c) charge/discharge curves (current density: 0.78 mA cm^{-2}) of a supercapacitor using the electrodes made of the hydrogen-treated EPD films.

dense and uniform with a very strong adhesion to the nickel foil.

The electrical resistance of the just-made EPD film has been measured to be in the range of kilo-ohms (10-mm separation between the contacts), which is very large considering the high conductivity of multi-walled carbon nanotubes. Due to such a large resistance, the cyclic voltammetry (CV) of a capacitor made of EPD film shows narrower loops with a large oblique

angle (Fig. 3), which is typical of a highly resistive electrode. It should also be noted that there is a large non-capacitive current response between 0.7 and 1.0 V.

To improve the performance, the EPD films were annealed in hydrogen atmosphere at 500 °C for 30 min, and the resistance of the films decreased remarkably, as evidenced by the greatly improved electrochemical performance of the supercapacitor built from the hydrogen-treated EPD films as shown in

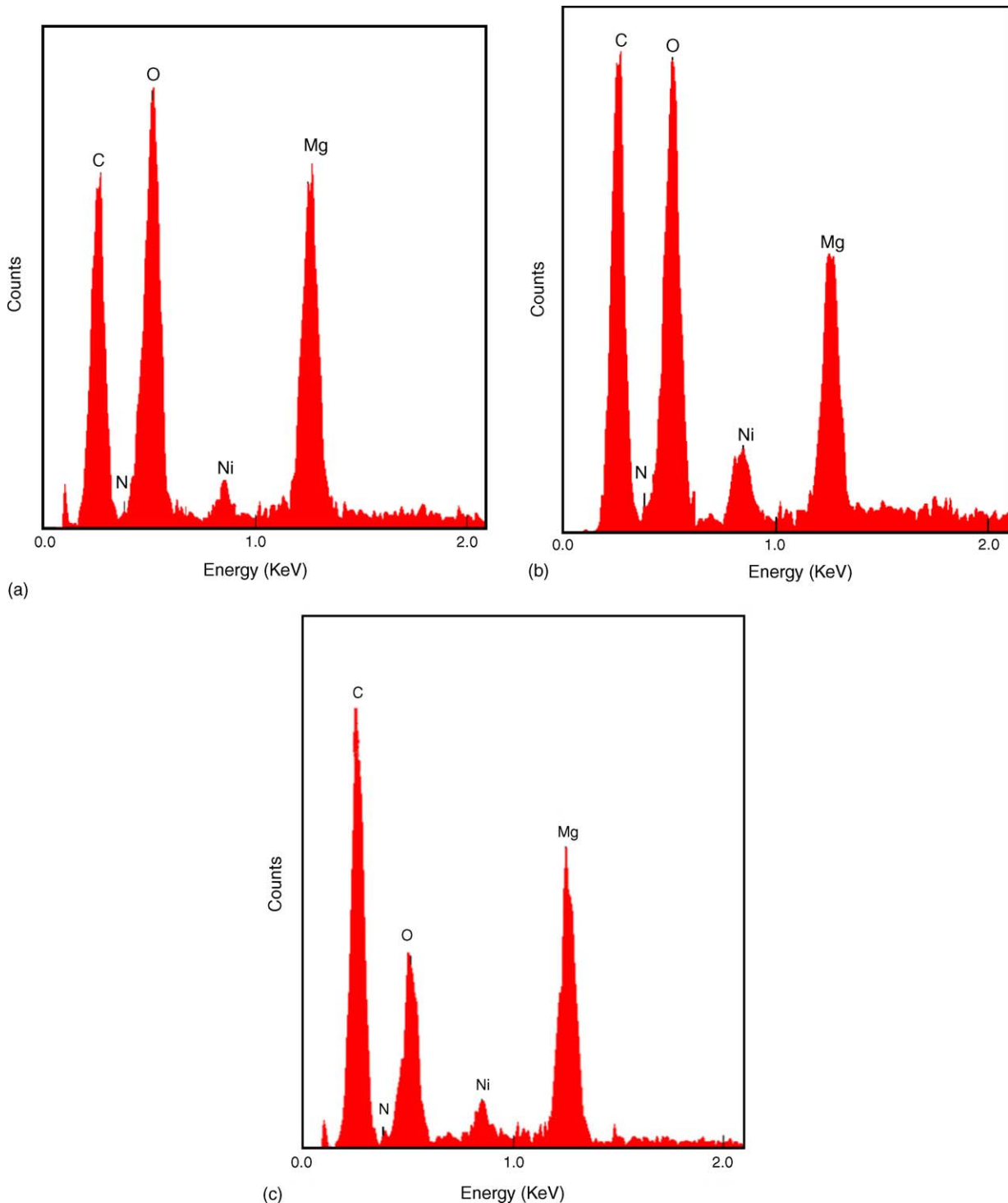


Fig. 5. EDS patterns of the EPD films: (a) without heat treatment, (b) heated in argon and (c) heated in hydrogen at 500 °C for 30 min.

Fig. 4. The CV curves at scan rate of 50 mV s^{-1} show almost the mirror images with respect to the zero-current line, except the peaks at 0.9–1.0 V, attributable to the redox reactions caused by the residual functional groups remained on the nanotubes [8]. It should be noted that this peak gradually diminished after several tens of cycling due to the removal of those functional groups. Nevertheless, the CV curve generally presents a nearly rectangular shape, a clear proof of well-developed capacitance properties. Even at a very high scan rate of 1000 mV s^{-1} , the CVs of the capacitor still remain the rectangular shape (Fig. 4(b)). The excellent CV shapes at such a high scan rate reveal a very rapid current response on voltage reversal at each end potential, and the straight rectangular sides represents a very small ESR of the electrodes and also the fast diffusion of electrolyte in the films [28]. The capacitor was cycled for several hundreds of cycles and no degradation was observed.

Typical constant current charge/discharge curves for the supercapacitor from hydrogen-treated EPD thin film electrodes are provided in Fig. 4(c). As can be seen, the $E-t$ responses of the charge process again show almost the mirror images of their corresponding discharge counterparts, and no IR drop was observed, reflecting a very small ESR of the electrodes. The capacitance calculated from the CVs is 21 F g^{-1} , and a power density of 20 kW kg^{-1} based on the active materials is easily obtained here. It should be noted that all of the data presented here were obtained from a real two-electrode system, and not from a half cell or single electrode. This is important to note because most data in the literature are from the three-electrode system, which quadruples the numbers shown here [29,30], and sometimes are overestimated [31].

3.2. Study of the hydrogen treatment effect

The effect of hydrogen treatment on reducing the resistance of EPD film was further investigated. In our previous study [21], we have found that nitric acid treatment did not reduce the conductivity of the MWNTs themselves much, and the electrodes made of nitric acid-treated carbon nanotube films exhibited very good electrochemical performance. Therefore the remarkable increase of resistance of EPD films in this study must be attributed to the deposition process.

We speculate that some electrochemical oxidation occurred on the MWNT surface via an intermediate stage when H_2O was converted to oxygen [32] during the EPD process. The sources of water include that from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and absorbed from the atmosphere. The presence of small amount of water is beneficial to enhancing the adhesion strength of EPD film by forming $\text{Mg}(\text{OH})_2$ binder material [33,34]. Taking into account the fact that the acid-treated MWNTs have many defects on the surfaces, electrochemical oxidation can proceed much easier during EPD and therefore created large amount of functional groups in such an overwhelming way that it caused the rehybridization from sp^2 to sp^3 of carbon atoms on the nanotubes, resulting in the reduction of the $\text{p}\pi$ -derived density of states (DOS) and hence increasing the resistance of the carbon nanotubes. Particularly, this kind of electrochemical oxidation at high potential is very efficient and usually irreversible [35].

In comparison, functional groups created by acid treatment can be easily removed by annealing the nanotubes at high temperature [36]. Indeed, no change of resistance of the EPD films was found after heating in argon, and the resistance of the EPD film was still in the range of kilo-ohms. As a result, the CV of the capacitor using argon-treated electrodes showed a similar shape as that of capacitor using just-made thin films as electrodes. Yet, the resistance of the films decreased remarkably after hydrogen treatment. Fig. 5 shows the energy dispersive X-ray spectroscopy (EDS) spectra of just-made EPD film, and of EPD films treated in argon and in hydrogen, respectively. The EDS quantitative analysis showed that the atomic ratio of carbon to oxygen for these three samples are 1.89, 2.46 and 3.70, correspondingly. Clearly, considerable amount of oxygen-containing species on the nanotubes were removed after hydrogen treatment. There have been reports that hydrogen treatment can effectively purify carbon nanotubes by converting amorphous carbon to CH_4 [37]. Therefore, it is highly possible that the functional groups on the MWNTs in EPD films were eliminated in the similar way.

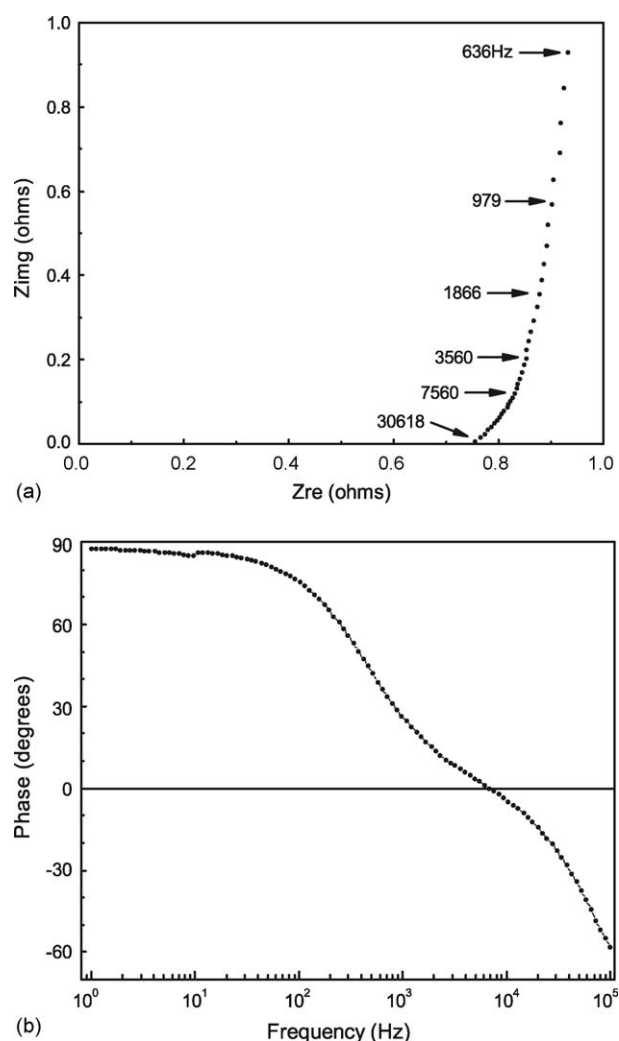


Fig. 6. (a) Complex-plane impedance, and (b) Bode angle plot, of the supercapacitor made of EDP thin CNT film electrodes.

3.3. Frequency response of the EPD thin film electrodes

In addition to the excellent electrochemical performance, supercapacitors built from the hydrogen-treated EPD thin film electrodes also displayed superior frequency response. Fig. 6(a) shows a complex-plane plot of the impedance of the supercapacitor. The impedance curve intersects the real axis at a 45° angle, which is consistent with the porous nature of the electrodes when saturated with electrolyte. The impedance plots can be divided into a high-frequency component (inclined at 45°) and a low-frequency component (near vertical) with the transition point between the two regions being referred to as the ‘knee’ [2,20]. The increased electrical and ionic conductivity of the EPD film is reflected in the frequency of the ‘knee’. The knee frequency denotes the maximum frequency at which capacitive behaviors is dominant, and is an indication of the power capability of a supercapacitor. An electrode with a higher knee frequency can be more rapidly charged and discharged. Note that the frequency ‘knee’ in the impedance plot shown in Fig. 6(a) is about 7560 Hz, which suggests that most of its

stored energy is still accessible at the frequencies as high as 7560 Hz.

To the best of our knowledge, the highest reported knee frequency in other capacitors from CNT electrodes is 100 Hz [2,20]; while the knee frequency for most commercially available supercapacitors, including those specially designed for high power applications, is lower than 1 Hz [38]. This great improvement in frequency response of the nanotube EPD thin film electrodes constitutes a substantial advance in the rate of charge and discharge of the supercapacitor.

From physical aspect, this superior frequency response is due to small ESR and the excellent electrolyte access to the film through its unique pore network formed by EPD. As mentioned earlier, the key factors determining the power density and frequency response of a supercapacitor are the internal resistivity of the electrode itself, the resistivity between the electrode and current collector and the resistivity of the electrolyte within the porous structure of the electrodes [1,20]. In the thin film electrodes, the carbon nanotubes form a highly conductive network and thus the internal resistance of the electrode itself is small; on

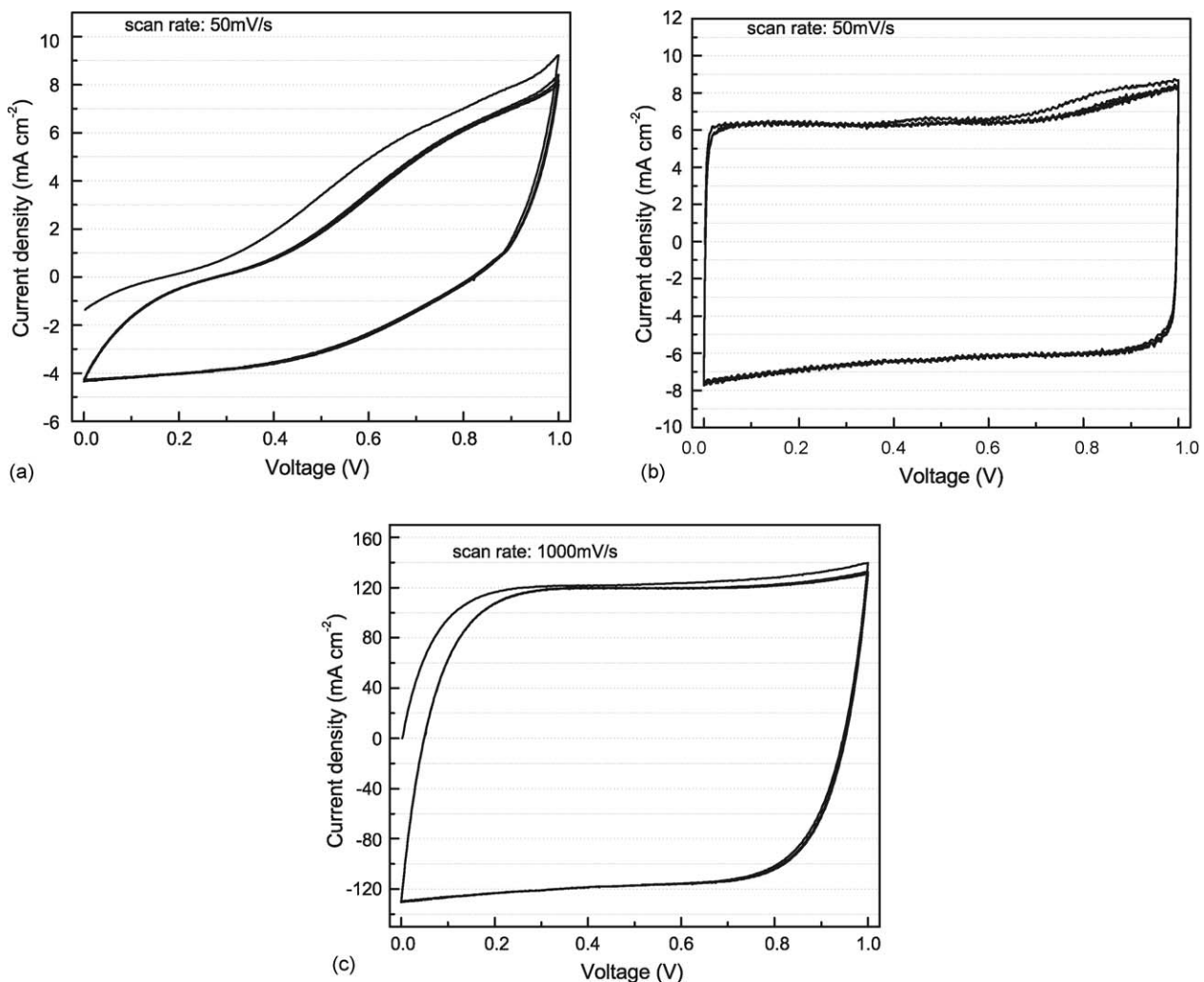


Fig. 7. CVs of the supercapacitors using filtered carbon nanotubes mats as electrodes: (a) plain nickel foils as current collectors (scan rate: 50 mV s^{-1}). (b and c) Nickel foils coated with carbon nanotubes as current collectors (scan rate were 50 mV s^{-1} and 1000 mV s^{-1} , respectively). All measurements were carried out with 6N KOH as electrolyte.

the other hand, all the nanotubes were driven by electrical field during EPD and deposited on the nickel foil, forming a direct conductive path between electrode and current collector, therefore the contact resistance is also reduced. Most importantly, the EPD film is characterized as porous structures with significant volume of mesopores, thus enabling the excellent electrolyte access to the porous network in the film and a low resistance of electrolyte within the porous structure of the electrodes.

Fig. 6(b) shows a Bode angle plot for the EPD supercapacitor. For frequencies up to 100 Hz, the phase angle is very close to 90° , which again indicates that the device functions close to ideal capacitors.

3.4. EPD thin film as coatings for ordinary current collectors

In addition to being used directly as supercapacitor electrodes, the EPD films can also be used as a coating over other

current collectors to reduce the contact resistance between the active materials and the current collectors. To demonstrate this concept, we prepared carbon nanotube mats by simply filtrating suspension of purified MWNTs (without acid oxidation). These free-standing mats are much thicker compared to the EPD films and therefore are capable of outputting a much higher current.

Fig. 7(a) shows the CVs of the supercapacitors using the filtered mats as electrodes while plain nickel foils served as the current collectors. As can be seen, the CV curves at a scan rate of 50 mV s^{-1} are highly distorted. Clearly, there is a big contact resistance between the nanotube mats and the current collectors, as also evidenced by a noticeable IR drop in the constant current density (1.56 mA cm^{-2}) charge/discharge curves in Fig. 8(a). However, when nickel foils coated with a very thin layer of carbon nanotubes were used as the current collectors, the CV curves show very nice rectangular shape, even at a very high scan rate of 1000 mV s^{-1} , as shown in Fig. 7(b) and (c). No IR drop was detected even at a much higher discharge current density of 15.6 mA cm^{-2} (Fig. 8(b)), indicating a very low ESR. Since the electrodes used in this test were the same mats, the improved performance has to be attributed to the coated carbon nanotube layer on the nickel foils, which increased the contact surface area between the current collectors and the mats and also lowered the contact resistance due to the extremely strong bonding and direct conductive paths between nanotubes and the nickel foils.

4. Summary

In conclusion, we have fabricated MWNT thin film electrodes via the electrophoretic deposition technique. The supercapacitors built from these electrodes have exhibited an ideally rectangular cyclic voltammograms even at a high scan rate of 1000 mV s^{-1} , an indication of a significantly small ESR leading to a very high specific power density of 20 kW kg^{-1} . Furthermore, the supercapacitors showed superior frequency response, with a frequency ‘knee’ at about 7560 Hz, more than 70 times higher than the highest reported knee frequency (100 Hz) for supercapacitors. Moreover, our carbon nanotubes thin films can also act as coatings over ordinary current collector to decrease the contact resistance between the active materials and the current collector for improved performance.

Finally, owing to the nature and versatility of the EPD process, the current approach may provide a promising technique for massive fabrication of such CNT electrodes for various energy storage devices.

Acknowledgements

Financial support from EISG program (03-28) and UC Discovery Grant (ele03-10175) are gratefully acknowledged.

References

- [1] K.H. An, W.S. Kim, Y.S. Park, Y.C. Choi, S.M. Lee, D.C. Chung, D.J. Bae, S.C. Lim, Y.H. Lee, *Adv. Mater.* 13 (2001) 497–500.

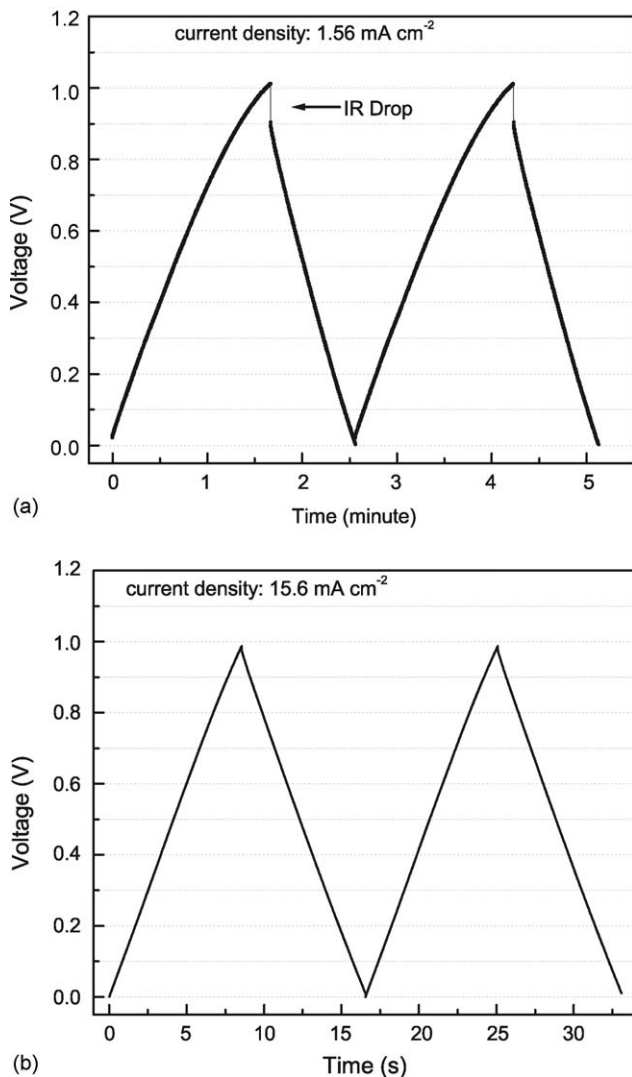


Fig. 8. Charge/discharge curve of supercapacitors using filtered carbon nanotubes mats as electrodes: (a) plain nickel foils as current collectors (current density: 1.56 mA cm^{-2}). (b) Nickel foils coated with carbon nanotubes as current collectors (current density: 15.6 mA cm^{-2}).

- [2] M. Hughes, M.S.P. Shaffer, A.C. Renouf, C. Singh, G.Z. Chen, J. Fray, A.H. Windle, *Adv. Mater.* 14 (2002) 382–385.
- [3] M. Hughes, G.Z. Chen, M.S.P. Shaffer, D.J. Fray, A.H. Windle, *Chem. Mater.* 14 (2002) 1610–1613.
- [4] K.H. An, W.S. Kim, Y.S. Park, J.M. Moon, D.J. Bae, S.C. Lim, Y.S. Lee, Y.H. Lee, *Adv. Function. Mater.* 11 (2001) 387–392.
- [5] C.Y. Liu, A.J. Bard, F. Wudl, I. Weitz, J.R. Heath, *Electrochem. Solid State Lett.* 2 (1999) 577–578.
- [6] J.N. Barisci, G.G. Wallace, R.H. Baughman, *J. Electroanal. Chem.* 488 (2000) 92–98.
- [7] L. Diederich, E. Barborini, P. Piseri, A. Podesta, P. Milani, A. Schneuwly, R. Gallay, *Appl. Phys. Lett.* 75 (1999) 2662–2664.
- [8] E. Frackowiak, K. Metenier, V. Bertagna, F. Beguin, *Appl. Phys. Lett.* 77 (2000) 2421–2423.
- [9] E. Frackowiak, K. Jurewicz, S. Delpeux, F. Beguin, *J. Power Sources* 97–98 (2001) 822–825.
- [10] B.J. Yoon, S.H. Jeong, K.H. Lee, H.S. Kim, C.G. Park, J.H. Han, *Chem. Phys. Lett.* 388 (2004) 170–174.
- [11] E. Frackowiak, K. Jurewicz, K. Szostak, S. Delpeux, F. Beguin, *Fuel Process. Technol.* 77 (2002) 213–219.
- [12] K.H. An, K.K. Jeon, J.K. Heo, S.C. Lim, D.J. Bae, Y.H. Lee, *J. Electrochem. Soc.* 149 (2002) A1058–A1062.
- [13] A.S. Claye, J.E. Fischer, C.B. Huffman, A.G. Rinzler, R.E. Smalley, *J. Electrochem. Soc.* 147 (2000) 2845–2852.
- [14] E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy, F. Beguin, *Carbon* 37 (1999) 61–69.
- [15] B. Gao, A. Kleinhammes, X.P. Tang, C. Bower, L. Fleming, Y. Wu, O. Zhou, *Chem. Phys. Lett.* 307 (1999) 153–157.
- [16] H.C. Shin, M.L. Liu, B. Sadanadan, A.M. Rao, *J. Power Sources* 112 (2002) 216–221.
- [17] G. Maurin, C. Bousquet, F. Henn, P. Bernier, R. Almairac, B. Simon, *Chem. Phys. Lett.* 312 (1999) 14–18.
- [18] C. Nutzenadel, A. Zuttel, D. Chartouni, L. Schlapbach, *Electrochem. Solid State Lett.* 2 (1999) 30–32.
- [19] R. Kotz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483–2498.
- [20] C.M. Niu, E.K. Sichel, R. Hoch, D. Moy, H. Tennent, *Appl. Phys. Lett.* 70 (1997) 1480–1482.
- [21] C.S. Du, J. Yeh, N. Pan, *Nanotechnology* 16 (2005) 350–353.
- [22] A.R. Boccacini, I. Zhitomirsky, *Curr. Opin. Solid State Mater. Sci.* 6 (2002) 251–260.
- [23] P. Sarkar, P.S. Nicholson, *J. Am. Ceram. Soc.* 79 (1996) 1987–2002.
- [24] O.O. Van der Biest, L.J. Vandeperre, *Ann. Rev. Mater. Sci.* 29 (1999) 327–352.
- [25] J. van Tassel, C.A. Randall, *J. Mater. Sci.* 39 (2004) 867–879.
- [26] K. Esumi, M. Ishigami, A. Nakajima, K. Sawada, H. Honda, *Carbon* 34 (1996) 279–281.
- [27] R.Z. Ma, J. Liang, B.Q. Wei, B. Zhang, C.L. Xu, D.H. Wu, *J. Power Sources* 84 (1999) 126–129.
- [28] B.E. Conway, *Electrochemical Supercapacitor: Scientific Fundamentals and Technological Application*, Kluwer Academic/Plenum Publisher, New York, 1999.
- [29] S.T. Mayer, R.W. Pekala, J.L. Kaschmitter, *J. Electrochem. Soc.* 140 (1993) 446–451.
- [30] D.Y. Qu, H. Shi, *J. Power Sources* 74 (1998) 99–107.
- [31] E. Raymundo-Pinero, V. Khomenko, E. Frackowiak, F. Beguin, *J. Electrochem. Soc.* 152 (2005) A229–A235.
- [32] T. Ito, L. Sun, R.M. Crooks, *Electrochem. Solid State Lett.* 6 (2003) C4–C7.
- [33] B.E. Russ, J.B. Talbot, *J. Electrochem. Soc.* 145 (1998) 1245–1252.
- [34] B.E. Russ, J.B. Talbot, *J. Electrochem. Soc.* 145 (1998) 1253–1256.
- [35] H.S. Ye, X. Liu, H.F. Cui, W.D. Zhang, F.S. Sheu, T.M. Lim, *Electrochem. Commun.* 7 (2005) 249–255.
- [36] C.S. Li, D.Z. Wang, X.F. Wang, J. Liang, *Carbon* 43 (2005) 1557–1560.
- [37] S.R.C. Vivechand, A. Govindaraj, M.M. Seikh, C.N.R. Rao, *J. Phys. Chem. B* 108 (2004) 6935–6937.
- [38] J.R. Miller, *Proceedings of the Electrochemical Society Meeting, Chicago, October, 1995*, pp. 246.