

Short communication

Carbon nanofiber and PEDOT-PSS bilayer systems as electrodes for symmetric and asymmetric electrochemical capacitor cells

Ana Karina Cuentas Gallegos*, Marina E. Rincón

Centro de Investigación en Energía-UNAM, Priv. Xochicalco S/N Col. Centro, Temixco 62580, Morelos, Mexico

Received 25 May 2006; received in revised form 27 June 2006; accepted 28 June 2006

Available online 14 August 2006

Abstract

In this work, we describe the fabrication of electrodes based on carbon nanofibers (NFC), bilayer systems of NFC and a commercial polythiophene (PEDOT-PSS), and NFC/PEDOT-PSS composites, for symmetric and asymmetric electrochemical capacitor (EC) cells. The basic electrochemical characterization was carried out for each electrode material by cyclic voltammetry (CV) using a three-electrode cell and a non-aqueous electrolyte (1 M LiClO₄ in acetonitrile). We assembled two-electrode cells using Swagelok cells with filter paper as the electrode separator with only the best electrode materials (NFC, and bilayer electrodes), and they were electrochemically characterized by CV to determine the working voltage window, and galvanostatic cycling to evaluate the cycle-life of the symmetric (NFC–NFC, NFPC–NFPC) and asymmetric (NFC–NFPC) cell assemblies. Capacitance values were normalized by electrode area and calculated from galvanostatic cycling experiments. We discuss the influence of PEDOT-PSS as a dispersing agent for NFCs and as an electrical conductivity enhancer. Also, we found that the asymmetric cell configuration doubled the capacity in comparison to NFCs symmetric cells, and the cycle-life was compared to the symmetric cell assembled with bilayered electrodes.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Carbon nanofibers; Polythiophene; PEDOT-PSS; Supercapacitor; Assymmetric cells

1. Introduction

Electrochemical capacitors (EC) are also known as ultracapacitors, and are devices that have the ability to store energy. The components of ECs are similar to those of a battery (two electrodes and an electrolyte), where the main structural difference is that in most double layer capacitors both the positive and negative electrodes are made of the same material. EC have more power density than ordinary batteries, and a long charge–discharge cycle-life. Because of these characteristics ECs have attracted much interest for applications where high power is required. Hybrid systems of batteries or fuel cells and ECs are needed for electric vehicle propulsion. These hybrid systems are of great interest for the automobile industry (Ford, General Motors, Chrysler, Toyota, Honda, Nissan, Renault, etc.), where ECs give peak power during acceleration and are recharged during braking, and the batteries or fuel cells give the necessary energy for the vehicle's range. It is important

to underline the complementary nature of these energy storage devices, and that they must be developed in parallel [1].

High surface carbon materials have been considered as electrode materials for electrochemical capacitor cells. The great diversity of carbon (as powders, fibers, paper, nanotubes, nanofibers, aerogels, and nanocomposites) gives way to the whole field of research. Furthermore, carbon has a relatively low cost, no toxicity, high chemical stability in various solutions and a high thermal stability [1]. Based on these materials, different methodologies have been applied to increase their specific area and the performance for nanostructured carbon [2–4]. In this way, introduction of electroactive metallic particles or conducting polymers has been carried out to modify the pore size distribution, and asymmetric cells have been fabricated to enhance their performance. The capacitance of these materials is given basically by the double layer storage mechanism. Therefore, the specific surface area is a major determinant of the total device capacitance. Thus, larger specific surface area gives greater specific capacitance C and a greater specific energy W ($W = CV^2/2$, where V is the potential). On the other hand, the resistance due to the carbon materials porosity is associated with

* Corresponding author. Tel.: +52 5556229729; fax: +52 5556229742.
E-mail address: akcg@cie.unam.mx (A.K. Cuentas Gallegos).

the power density P ($P = W/\Delta t$, Δt is the discharge time, and $P = V/4R$, R is the resistance). Materials characterized by a high conductivity and large pores demonstrate a high specific power.

Carbon nanofibers (NFC) are fibers of submicron size (50–500 nm of diameter and 50–100 μm length) that have a graphitic structure [4,5]. Unlike carbon nanotubes (CNT), NFCs do not have a hollow center and they have exterior walls with many edges. The presence of a wide pore size distribution is possible due to these edges, resulting in a greater surface area and high capacitances [1,4]. On the other hand, conducting organic polymers such as polyacetylene, polypyrrole, polyaniline, and polythiophenes, can improve the energy density of ECs through redox processes that contribute a pseudocapacitive storage mechanism in addition to the capacitance of the carbon material. Although, this storage mechanism contributes more to the total capacitance than the double layer of carbon materials, the dynamic characteristics are poor. This can be observed when successive charge–discharge cycles are carried out. Conducting polymers suffer volumetric changes on intercalation/deintercalation of ions through cycling, causing their degradation. Hence, in the last few years research in composite materials based on conducting polymers and carbon materials with high surface area and good mesopores distribution like NFCs and CNTs are being developed [3,4,6–8]. The carbon mesoporous structure gives mechanical stability to the composite in a way that adapts to the polymer volumetric changes, resulting in a more stable capacitance in successive charge–discharge cycles. Therefore, in this work, we describe the electrode fabrication process based on carbon nanofibers with a commercial polythiophene (PEDOT-PSS). Furthermore, bilayer and composite electrodes were electrochemically characterized in a three-electrode cell configuration, and in a symmetric and asymmetric electrochemical capacitor cell with a two-electrode configuration. We have selected a polythiophene derivative because of its stability in air and humidity [6], and specifically PEDOT-PSS due to high electric conductivity on its p-dope stage and fast redox kinetics. Finally, we electrochemically evaluated the electrode fabrication method as well as the effect of a small amount of conducting polymer on the capacitance values.

2. Experimental

2.1. Reagents

BAYTRON P (PEDOT-PSS) from Bayer, Triton X-100 and propylene glycol from Aldrich, were used according to supplier specifications. For the electrolyte preparation we used acetonitrile and LiClO_4 from Aldrich, which were used according to shipment specifications. Carbon nanofibers were provided by Columbian Chemicals, Co.

2.2. Electrode fabrication

NFCs were used to fabricate electrodes by a screen-printing technique. A soft paste made of NFCs, propyleneglycol and Triton X-100 was used to screen print over stainless steel substrates

using a T62 mesh. Rectangular electrodes, $2.5\text{ cm} \times 1.2\text{ cm}$ ($A = 3\text{ cm}^2$) were used for three-electrode cyclic voltammetry studies and circular electrodes (diameter 1 cm, $A = 0.7854\text{ cm}^2$) for two-electrode studies. Screen-printed electrode was thermally treated using a heating rate of 100°C h^{-1} up to 400°C and maintain during 1 h. The thickness of the electrodes could not be measured by profilometer due to its powdery aspect. Nevertheless, by weight difference we obtained 5 mg of NFCs in rectangular substrates, which corresponds to a mass density of 1.66 mg cm^{-2} . Some of these electrodes were used for the deposition of PEDOT-PSS by a dip-coating technique to obtain a bilayer electrode. The dip-coating technique was carried out by immersing NFC electrodes in concentrated PEDOT-PSS (Baytron P) solutions during 1 h, followed by 24 h of air-drying. These bilayered electrodes were thermally treated at 80°C for 1 h to eliminate loosely bond water, preventing polymer degradation. The amount of adsorbed PEDOT-PSS on rectangular electrodes of 0.6 mg was calculated by weight difference and corresponded to 0.2 mg cm^{-2} of polymer film. On the other hand, the electrode composite fabrication was carried out as follows: 10 mg of NFCs and 0.092 mL of PEDOT-PSS were immersed in an ultrasound bath for 10 min, then 0.5 mL of acetone was added to enhance dispersion and an additional 10 min ultrasound treatment was carried out. This suspension was then added drop wise to a rectangular substrate obtaining a weight of 5.6 mg, equivalent to the bilayer electrode composition elaborated by screen-printing and dip-coating techniques, and was treated at 100°C for 4 h. We have assigned the nomenclature of NFCP for the bilayered configuration, and CNFCP for the composites electrodes formed from NFCs and conducting polymer emulsion.

2.3. Electrode characterization

We used a SEM JEOL model JMS-5400LVTM to verify the nanofiber integrity over the stainless steel substrates after the thermal treatment. The electrochemical characterization of the bilayered and composite electrodes in a three-electrode cell was carried out by cyclic voltammetry, using a Pt mesh as counter electrode and a Ag/AgCl as reference electrode in a potentiostat/galvanostat ZRA Gamry model PCI4/750. After the voltage window was determined by cyclic voltammetry, two-electrode Swagelok cells were assembled using a filter paper as separator and a Solartron potentiostat model SI 1287 applying a galvanostatic cyclic technique, where the capacitance was calculated by multiplying the applied current intensity (I) by the charge or discharge time (t) of the electrochemical capacitor, divided by the used voltage window (2.4 V), $C = It/V$. In all electrochemical experiments we used 1 M LiClO_4 in acetonitrile as electrolyte.

3. Results and discussion

In Fig. 1, we show a SEM image of NFC electrodes thermally treated at 400°C where the scale bar corresponds to 5 μm , resulting in fibers with diameters less than 50 nm. In addition, the surface roughness of the electrode is evident, as well as a wide pore size distribution, and the small carbon clusters of the bright areas.

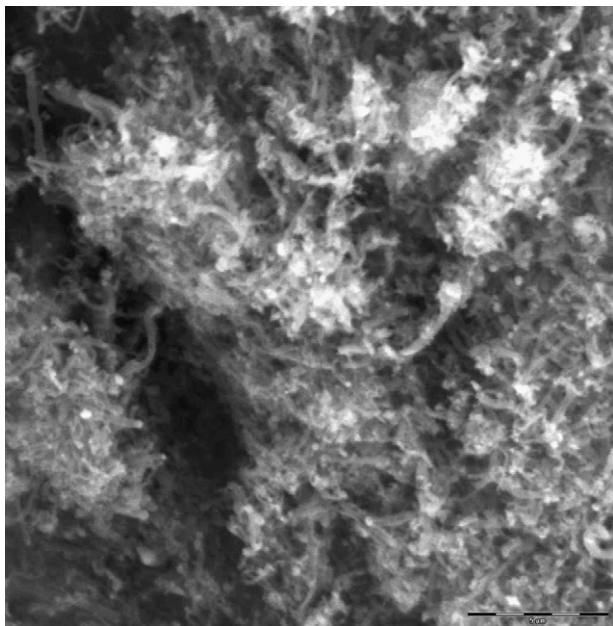


Fig. 1. SEM image of CNFs over stainless steel substrates thermally treated at 400 °C.

In Fig. 2, we show the cyclic voltammograms carried out at 50 mV s^{-1} for all electrode materials in the optimum voltage window. NFC electrode as well as NFCP bilayered electrode presented a profile that resembled a good capacitive behavior characteristic of a double layered mechanism, where the bilayered system showed a more rectangular profile suggesting less ohmic loss (greater conductivity) and higher reversibility. On the other hand, the profile of the composite system (CNFCP) showed lower currents and clearer Faradaic processes (≈ -0.75 and 0.75 V). The greater currents obtained for electrodes fabricated by the screen-printing technique (NFC and NFCP), were probably due to the thermal elimination of the used surfactants (propylene glycol and Triton X-100) that could induce a greater porosity in the electrodes giving way to more exposed electroactive area. In contrast, in the composite electrode (CNFCP), both

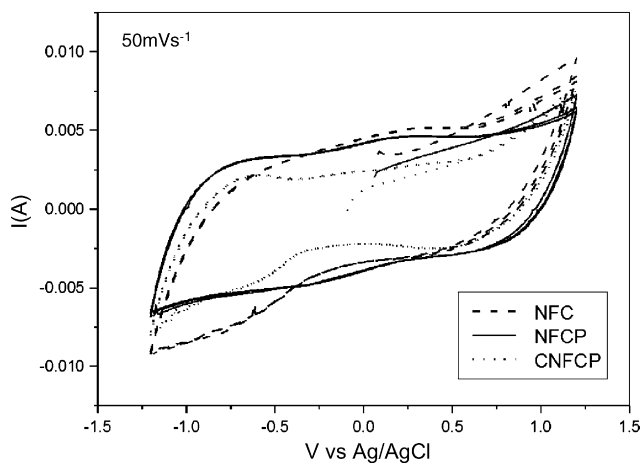


Fig. 2. Cyclic voltammetry of the three types of electrodes fabricated (NFC, NFCP, CNFCP), using 1 M LiClO_4 in acetonitrile as the electrolyte, and a Pt mesh as counter electrode.

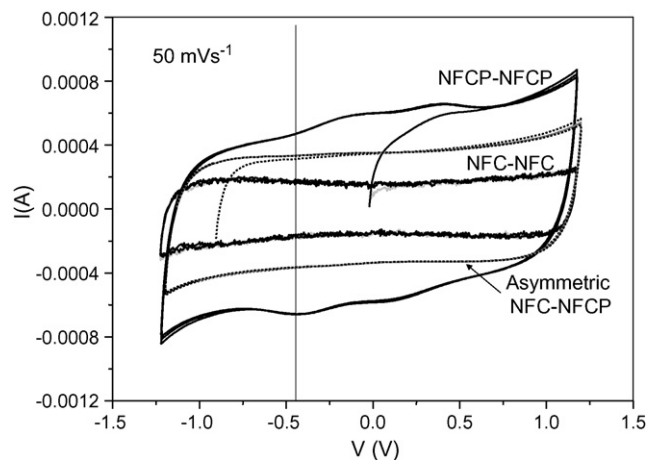


Fig. 3. Cyclic voltammetry at 50 mV s^{-1} in two-electrode Swagelok cells. Symmetric and asymmetric electrochemical capacitor cells, using a non-aqueous electrolyte (1 M LiClO_4 in acetonitrile).

components are dispersed but are more compacted since no surfactants were used.

We assembled two-electrode cells using circular electrodes made by a screen-printing technique over stainless steel substrates. Only NFC and NFCP electrodes were used to assemble symmetric and asymmetric cells, since the composite electrode showed poorer results. In Fig. 3, we show the cyclic voltammograms of symmetric and asymmetric two-electrode cells. Symmetric cells were assembled with the same material in both electrodes (NFC–NFC and NFCP–NFCP), while in the case of asymmetric cells were assembled with different electrodes (NFC–NFCP). These voltammograms were carried out to determine the voltage window in which the electrochemical capacitor cells should be cycled, aside from their profiles differences. The optimum voltage window for these cells was $\pm 1.25 \text{ V}$ ($\Delta V = 2.5 \text{ V}$) were no electrolyte decomposition was observed and a good reversibility was observed. NFC–NFC (symmetric) and NFC–NFCP (asymmetric) cells presented a rectangular profile, where the symmetric cell (NFC–NFC) resulted in lower current values ($\pm 0.2 \text{ mA}$) and the asymmetric cell (NFC–NFCP) in current values intermediate compared to the other two cells. On the other hand, NFCP–NFCP symmetric cell assembled with bilayered electrodes showed higher current values ($\pm 0.8 \text{ mA}$), and its rectangular voltammogram profile revealed additional peaks at $-0.45/-0.14 \text{ V}$ and $0.10/0.40 \text{ V}$ most probably due to the polymer presence. Since the voltammograms profiles of Fig. 2 (three-electrode) were similar for NFC and NFCP electrodes, we assume that the additional peaks observed in Fig. 3 for NFCP–NFCP symmetric cell are related with a higher carbon surface area exposed and to a higher electric conductivity due to the polymer as already mention in Fig. 2. Also, we assume that when we use the two-electrode sandwich configuration the electrodes are nearer, and the materials under study substitute the Pt counter electrode. Therefore, these could be factors to consider, particularly because in the two-electrode device the ohmic drop is smaller (the rectangular form of the cyclic voltammogram is clearer).

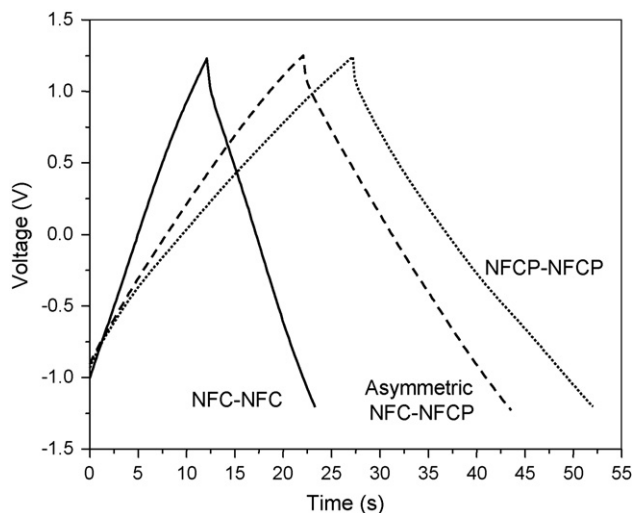


Fig. 4. Comparison of one charge–discharge cycle at 0.5 mA cm^{-2} for all symmetric and asymmetric electrochemical capacitor cells assembled with NFC and NFCP electrodes.

The same two-electrode Swagelok cells were evaluated using a galvanostatic cycling technique in the voltage window determined by cyclic voltammetry ($\pm 1.25 \text{ V}$), in order to calculate capacitance values for each cell and study the behavior in successive charge–discharge cycles. In Fig. 4, we show the charge–discharge profiles measured at 0.5 mA cm^{-2} for the different two-electrode electrochemical capacitor cells, where it was evident the enhancing effect of the polymer addition in the electrodes of the asymmetric and NFCP–NFCP symmetric cells with bilayered electrodes. This enhancing effect is observed in the higher time value required to carry out one charge–discharge cycle (Fig. 4).

In Fig. 5, we show the dependence of the current density applied (mA cm^{-2}) with the calculated capacitance per unit area (mF cm^{-2} , fill symbols), and per unit mass (F g^{-1} , hollow symbols). In the case of the symmetric cell with NFC electrodes

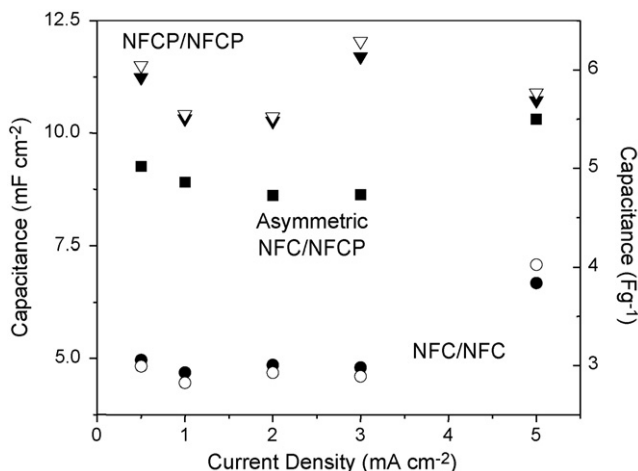


Fig. 5. Dependence of the capacitance values of symmetric (NFC/NFC and NFCP/NFCP) and asymmetric (NFC/NFCP) electrochemical capacitor cells with current density in a voltage window of $\pm 1.25 \text{ V}$. The filled symbols correspond to the capacitance normalized per geometric area (mF cm^{-2}), and the hollow to the capacitance per mass (F g^{-1}).

we observed a small increment of the capacitance values as the current density increased, suggesting the accessibility of the surface area for the generation of the double layer. NFCs seemed to present an open mesoporous matrix [3] exposing a higher surface area, and since the formation of the double layer is immediately, shows an independent behavior in the range of current densities applied. On the other hand, the symmetric cell with bilayer electrodes (NFCP–NFCP) showed higher capacitance values for all current densities applied due to the polymer addition in good agreement with Figs. 2 and 3, but we could not detect a clear trend in capacitance values with the increase of the current density. The synergic effect between NFC and PEDOT-PSS is similar to other publications [3], where they suggest that the tubular compounds form a volumetric electrode and the charge is distributed in three directions due to an open mesoporous matrix of these kinds of materials. On the other hand, from the obtained values it is clear that the contribution of the 10 wt% of conducting polymer as dispersant agent and electric conductivity enhancer was the main reason for the increase. The conducting polymer revealed a dispersant effect over the nanofibers at the interface level increasing the charge storage in the double layer. It has been previously observed that higher content of polymer in the electrodes of this type of cells, results in increased capacitance values due to a pseudocapacitance contribution [9]. For the case of the asymmetric cell (NFC–NFCP), the capacitance values were doubled compared to NFC–NFC and were slightly lower than NFCP–NFCP symmetric cells.

In Fig. 6, we show the capacitance evolution in 500 successive charge–discharge cycles for all cells (NFC–NFC, NFCP–NFCP, and NFC–NFCP) using an $I = 1 \text{ mA cm}^{-2}$ and the same working voltage window. The capacitance evolution for the symmetric cell with NFC electrodes remained constant at $4.5\text{--}5.5 \text{ mF cm}^{-2}$ ($2.75\text{--}3.5 \text{ F g}^{-1}$), inferior to the capacitance values for the other cells. On the other hand, the symmetric cells with NFCP bilayered electrodes showed the highest capacitance values, but were not maintained during cycling. The capacitance values for this

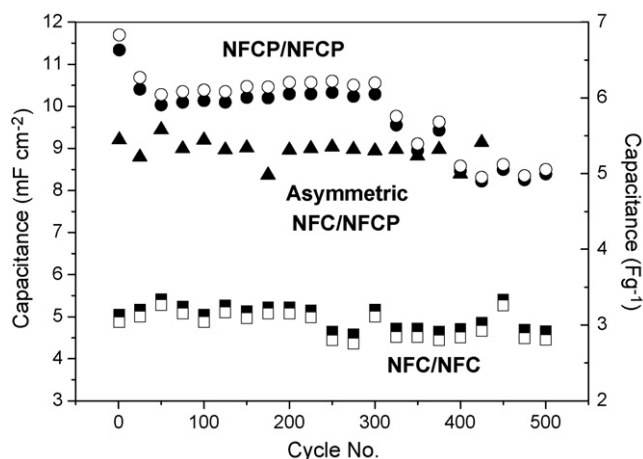


Fig. 6. Evolution of the capacitance during 500 charge–discharge cycles of the different electrochemical supercapacitor cells using a $I = 1 \text{ mA cm}^{-2}$. The filled symbols represent the capacitance per geometric unit area (mF cm^{-2}), and the hollow the capacitance per electrode unit mass (F g^{-1}). Non-aqueous electrolyte was used (1 M LiClO_4 in acetonitrile) and a working voltage window of $\pm 1.25 \text{ V}$.

cell decreased from 11.5 to 10 mF cm⁻² in the first 50 cycles (13% loss), and remained stable during the next 300 cycles (at 10 mF cm⁻² or 6.25 F g⁻¹). Nevertheless, after the cycles 300–500 a greater capacitance loss of 15–20% was observed. This capacitance loss suggests the conducting polymer degradation as has been previously proposed [10]. It is important to point out that the values of the last 100 cycles (cycles 400–500) were the same as for the asymmetric cell, where the conducting polymer was only used in one electrode. This suggests the degradation/deactivation of the polymer only in the amount equal to one electrode. In this sense, Lota et al. [6] suggested that for the electrochemical capacitor durability is important that the conducting polymer is used as the positive electrode, since in this case the oxidized state remains with good electric conductivity. In contrast, the conducting polymer loses its p-type conductivity (dedopage) and converts to its insulator state. The combination of two different electrodes, one of NFC as negative electrode and the other of NFC/PEDOT-PPS (NFCP) as positive electrode, permits the improvement of the cyclability in the same voltage window without a noticeable influence on the capacitance values. This effect can be observed in Fig. 6, where the capacitance values for the asymmetric cell remain constant (8.5–9.5 mF cm⁻²; 5–5.5 F g⁻¹) in the successive 500 charge–discharge cycles, in good agreement with previous work [11].

4. Conclusions

We fabricated carbon nanofiber electrodes (NFC) by a screen-printing technique modified by means of conducting polymer impregnation by dip-coating (NFCP), or a dispersion method (CNFCP). The bilayered systems (NFCP) and composites were characterized using a three-electrode cell and a two-electrode EC cell. Cyclic voltammograms from three-electrode cells gave higher currents for screen-printed electrodes, suggesting that the thermal treatment at 400 °C gave way to an increase in electrochemical active area, while the composite electrode fabricated by dispersion of NFC in PEDOT-PSS resulted in compact systems. Symmetric cells assembled with NFC electrodes resulted in capacitance values of 4.5–5.5 mF cm⁻² (2.75–3.5 F g⁻¹), which were maintained during successive 500 charge–discharge cycles at 1 mA cm⁻². The effect of a small amount of PEDOT-PSS adsorbed (10% by dip-coating) over the NFC electrodes resulted in a higher electric conductivity and a dispersion effect that provided more accessible area of the NFCs matrix for the generation of a double layer giving higher values of capacitance (doubled), particularly for the symmetric cells (NFCP/NFCP). Nevertheless, a 15–20% capacity loss was observed for this sym-

metric cell with bilayered electrodes, due to conductivity loss due to degradation. On the other hand, the asymmetric electrochemical capacitor cell (NFC/NFCP) gave capacitance values slightly lower (8.5–9.5 mF cm⁻²; 5–5.5 F g⁻¹), but with an enhanced cycle life during 500 charge–discharge cycles. Future work on the capacitance improvement of Colombian Chemicals, Co., carbon nanofibers is underway, based on the study of other electrolytes such as alkalis and acids [6]. Also, other fabrication techniques for the composite electrodes are being studied for comparison with the screen-printing technique.

Acknowledgements

We would like to thank German Orozco from CIDETEQ for SEM assistance, CONACYT-México, and UNAM-MEXICO through the projects PUNTA and IN111106-3.

References

- [1] P.V. Adhyapak, T. Maddanimath, S. Pethkar, A.J. Chandwadkar, Y.S. Negi, K. Vijayamohan, Application of electrochemically prepared carbon nanofibers in supercapacitors, *J. Power Sources* 109 (1) (2002) 105–110.
- [2] C. Kim, Electrochemical characterization of electrospun activated carbon nanofibres as an electrode in supercapacitors, *J. Power Sources* 142 (1–2) (2005) 382–388.
- [3] E. Frackowiak, F. Béguin, Electrochemical storage of energy in carbon nanotubes and nanostructured carbons, *Carbon* 40 (10) (2002) 1775–1787.
- [4] S.U. Kim, K.H. Lee, Carbon nanofiber composites for the electrodes of electrochemical capacitors, *Chem. Phys. Lett.* 400 (2004) 253–257.
- [5] C. Merino, P. Soto, E. Vilaplana-Ortego, J.M. Gomez de Salazar, F. Pico, J.M. Rojo, Carbon nanofibres and activated carbon nanofibres as electrodes in supercapacitors, *Carbon* 43 (2005) 551–557.
- [6] K. Lota, V. Khomeiko, E. Frackowiak, Capacitance properties of poly(3,4-ethylenedioxythiophene)/carbon nanotubes composites, *J. Phys. Chem. Solids* 65 (2004) 295–301.
- [7] Q. Xiao, X. Zhou, The study of multiwalled carbon nanotube deposited with conducting polymer for supercapacitor, *Electrochim. Acta* 48 (2003) 575–580.
- [8] J.M. Ko, R.Y. Song, H.J. Yu, J.W. Yoon, B.G. Min, D.W. Kim, Capacitive performance of the composite electrodes consisted of polyaniline and activated carbons powder in a solid-like acid gel electrolyte, *Electrochim. Acta* 50 (2004) 873–876.
- [9] E. Frackowiak, V. Khomeiko, K. Jurewicz, K. Lota, F. Béguin, Supercapacitors based on conducting polymers/nanotubes composites, *J. Power Sources* 153 (2006) 413–418.
- [10] A.K. Cuentas-Gallegos, M. Lira-Cantú, N. Casañ-Pastor, P. Gómez-Romero, Nanocomposite hybrid molecular materials for application in solid-state electrochemical supercapacitors, *Adv. Funct. Mater.* 15 (2005) 1125–1133.
- [11] W.G. Pell, B.E. Conway, Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes, *J. Power Sources* 136 (2004) 334–345.