Polym. Bull. (2012) 68:1395–1404
DOI 10.1007/s00289-011-0649-y

ORIGINAL PAPER

Development of supercapacitor active composites by electrochemical deposition of polypyrrole on carbon nanofibres

Ahu Gümrah Dumanlı · Ayca Erden · Yuda Yürüm

Received: 23 February 2011 / Revised: 6 September 2011 / Accepted: 7 October 2011 /
Published online: 20 October 2011
© Springer-Verlag 2011

Abstract In this study, pyrrole monomer is polymerized on carbon nanofibres (CNFs) via electropolymerization. This is a new technique to produce a chemically bonded CNF–polypyrrole composite. Deposition of the polypyrrole (PPy) on the nanofibres was optimized by varying the degree of deposition and deposition speed. Optimization studies have proven that the high deposition amounts result in blocks of polymers, which can be overcome through tuning the degree of polymerization by means number of cycles of electropolymerization and the scan rate of the electropolymerization.

Keywords Supercapacitor active material · Conductive polymer · Polypyrrole–carbon nanofiber composite

Introduction

Supercapacitors [1–3] are devices that store electrical energy on the basis that interfacial capacity increases with increasing surface area of the electrode of interest. Conjugated polymers have been intensively studied in this field because of their reversible doping/de-doping ability, light weight, flexibility, improved

---

A. G. Dumanlı (✉) · A. Erden · Y. Yürüm
Faculty of Engineering and Natural Sciences, Sabanci University,
Orhanli, Tuzla, Istanbul 34956, Turkey
e-mail: agd33@cam.ac.uk

Y. Yürüm
e-mail: yyurum@sabanciuniv.edu

stability, and price [4]. On the other hand, electrodes made of carbon materials are highly polarizable, and the amphoteric character of carbon allows use of the rich electrochemical properties of this element from donor to acceptor state. To achieve a high volumetric efficiency, the super capacitor must have extremely high surface area electrodes. At this point of time, because of their small size, carbon nanomaterials seem like a good choice for this purpose. The naturally occurring double-layer created at the interface between the carbon and the liquid electrolyte when a voltage is applied establishes a thin dielectric layer. This allows very thin plate separations [5]. Carbon containing capacitors which have an effective contact surface area of 2000 m^2 g^{-1} have already achieved capacitance densities of 30 Fg^{-1} or more [6]. Recently, various carbon materials including carbon nanotubes (CNTs) and carbon nanofibres (CNFs) have been considered for supercapacitor electrodes and great attention was also focused on conducting polymers [7–10]. In many of the reports, it is observed that the conducting polymers formed globular clusters around the CNTs or CNFs [9, 11]. In addition, conductive polymers (CPs) have been of interest in recent years and they are promising materials for the realization of high performance supercapacitors, as they are characterized by high specific capacitances, high conductivities in the charged states, and fast charge–discharge processes. The charge processes pertain to the whole polymer mass and not only to the surface [12]. These features suggest the possibility of developing devices with low internal resistance, or in other words the equivalent series resistance and high specific energy and power. However, the long-term stability during cycling is a major demand for an industrial application of CPs. Swelling and shrinkage of CPs, caused by the insertion/de-insertion of counter ions required for doping the polymer, is well known and may lead to degradation of the electrode during cycling. This obstacle can be solved to some level using composite materials made of carbon materials such as CNTs or activated carbons with conductive polymers. Carbon material in the bulk both ensures a good electrical conductivity and improves the mechanical properties of the electrodes.

In this article, we report an efficient, novel, and simple technique to produce a composite electrode material, PPy is chosen in this study since it is easy to prepare in the form of extended surface thin films, it can store the charge throughout its entire volume and it is environmental stability in the oxidized state [13, 14]. Although it is a very promising energy source, PPy lacks the flexibility for insertion/de-insertion of the dopant ions resulting in shorter recycling life times than desired and so CNF is needed to improve the flexibility and the surface area. Therefore, the objective of this study is to develop a new method to produce polypyrrole/CNF composites by depositing a conducting polymer, PPy, on to carbon nanomaterials via electropolymerization. The electrochemical synthesis technique has two important advantages. First, it is a straightforward and simple process. Second, it allows the production of polymer coatings with high levels of conductivity and chemical stability. Using this method we aim to achieve high levels of bulk charging. Since the coating thickness is in magnitudes of nanometers, we believe that only surface charging will be achieved, which is very important and desirable for supercapacitor applications.

Experimental

Materials

All reagents used were analytical grade without further purification. All the electrochemical reactions were performed under an argon atmosphere.

Synthesis of carbon nanoproducts

Carbon nanostructures were produced using a conventional tube furnace chemical vapor deposition (CVD) set-up. The catalyst system based on NaCl supported 5% nickel tartrate [15] was placed into the quartz tube reactor which had a diameter, $\Phi = 30$ mm and a length, $L = 90$ cm. For 30 min the system was kept at 500 °C under Ar flow for the stabilization of the catalysts following this step. Then, prior to the hydrocarbon source flow, hydrogen gas was passed through the tubular reactor for 15 min to reduce the catalyst into the metallic form at the same temperature. After the catalyst system was prepared for the production of carbonaceous material, high-purity acetylene was flowed through at 550 °C for 30 min with a rate of 2 L min^{-1} for the formation of the carbon nanostructures [15]. The carbon nanostructures were separated from the NaCl support by washing with deionized water.

Deposition of PPy on carbon nanomaterials

Electropolymerization was carried out with an Epsilon EC potentiostat/galvanostat, employing a three electrode system: a working electrode, a counter electrode, and a reference electrode. The potentiostat keeps the voltage difference between the working electrode and the reference electrode at a constant value despite the changes in the current passing through the electrolytic cell, the concentration of the electroactive substance, and the solution resistance. The current supplied by the potentiostat can be determined by measuring the voltage drop across a resistance connected to the counter electrode in series. To compensate the changes in potential of the working electrode the potentiostat continuously checks the potential of the working electrode measured with respect to the reference electrode, and changes the potential difference in between to maintain the desired potential value. A schematic representation of the electrolysis cell is represented in Fig. 1. In the deposition process of PPy on to CNFs, a complex sandwich electrode is employed where the working electrode was an ITO-coated glass slide ($7 \times 50 \times 0.6$ mm^3, Rs $\leq 10\Omega$, Delta Technologies Inc.), the counter electrode was a platinum wire and a Ag wire was used as the pseudo-reference electrode. The pseudo-reference was calibrated externally using a 5 mM solution of ferrocene ($\mathrm{Fc/Fc^+}$) in the electrolyte ($E_{1/2}(\mathrm{Fc/Fc^+}) = +0.130$ V versus Ag wire and $+0.080$ V versus $\mathrm{Ag/Ag^+}$ in 0.1 M $\mathrm{Bu_4NPF_6}$/MeCN). The potentials are reported versus $\mathrm{Ag/Ag^+}$. A two-sided sticky copper plated was fixed onto the conducting side of the ITO slide. Then, while weighing, 50 mg CNF is put on to the sticky copper plate carefully and distributed evenly so as to cover the plate completely. The deposition of PPy onto CNF is carried out in 0.1 M $\mathrm{LiClO_4}$ dissolved in methylene cyanide (MeCN). A three-

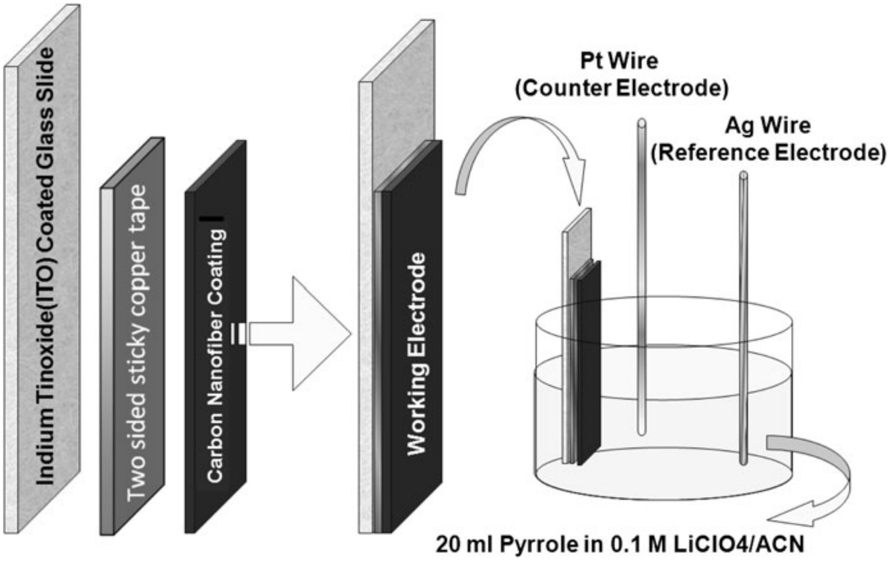

Fig. 1 A schematic representation of the electrolysis cell

electrode electrolysis configuration is set in a one compartment UV cell. The working electrode is prepared as described above; a Pt wire is used as counter electrode and an Ag wire is employed as the reference electrode. The electrodeposition was performed from a 0.1 M solution of the monomer in the electrolyte potentiodynamically at a scan rate of 25 mV s^{-1}. The cell has gas inlets to pass N_2 gas through the solution to achieve an inert medium and to prevent oxidation during the electrolysis .

Characterization methods

The microstructure of the catalyst systems and the CNF products were examined with a Leo G34-Supra 35VP scanning electron microscope (SEM) coupled with energy dispersive spectrometer (EDS) software. Surface area measurements of the materials were done using a Quanta Chrome NOVA 2200e instrument. The adsorption isotherms were obtained at 77 K. Before the experiments the samples were degassed under vacuum at 350 °C for 4 h. The surface areas of the samples were determined using the Brunauer, Emmett, and Teller (BET) method [16] in the relative pressure range between 0.005 and 0.25 bar, scanned over 12 adsorption points. The specific capacitance value for each sample was calculated from the area under the CV curve.

Results and discussion

The CNFs obtained in the CVD were herringbone-type nanocoils with an average diameter of 100 nm, Fig. 2. The fibrous carbon materials have a significantly high

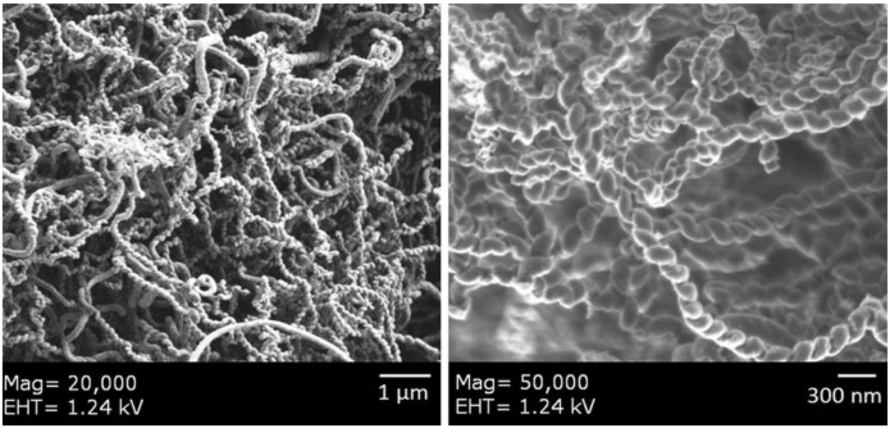

Fig. 2 SEM images of uncoated CNFs used as a template for PPy

specific surface area of 250 m^2 g^{-1}. The surface area of the polymer-coated samples with their 220 to 300 m^2 g^{-1} surface area did not show a big change compared to the starting material. This may be due to the thickness of the coating, the porosity of the polymer structure or the homogeneity of the starting carbon materials.

The coiled carbon nanostructures made it possible to observe the PPy coating through an electron microscope. In order for a material to be a desirable candidate for supercapacitor applications, charge deposition should take place at the surface of the active material rather than in the bulk. Therefore, direct observation of the PPy coating using SEM images provides a clear measure of how successfully the CNFs are coated after polymerization.

Since the charge deposition takes place at the surface of the active material rather than in the bulk, a thinner layer should be formed to enhance the surface charge deposition in the bulk of the conductive polymer. On the other hand, high specific capacitance values can be achieved by increasing the amount of deposition of the conducting polymer. Hence, it is necessary to optimize the amount of deposition of the conducting polymer on to the CNFs.

During the optimization process the dependency of the capacitance on the number of deposition cycles (i.e., the thickness of the PPy deposition) was tested. Initially, two different batches, one with 5 times cycling and the other with 10 times cycling, were selected. Figure 3 shows the voltammograms of CNF-templated PPy samples that are 5 times cycled (a), and 10 times cycled (b) and the corresponding SEM images showing them magnified 50,000 times. The specific capacitance of the samples were calculated by integrating the area of the outermost cycle in the voltammogram and it was found as 12.9 C cm^{-2} for the first one and 22.7 C cm^{-2} for the latter one. From this result it can be stated that the specific capacitance of the sample increases by increasing the amount of deposition. However, from SEM images, it is obvious that as the number of cycles is increased, not only the surface of the CNFs was coated but also there was some block deposition of PPy in between the fibers. This is not desirable for supercapacitor applications since it decreases the

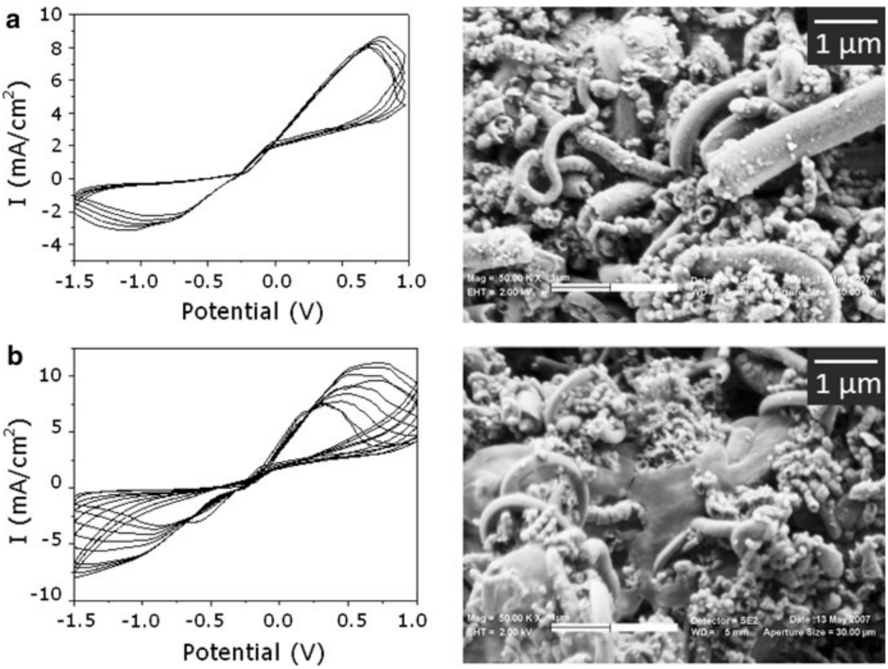

Fig. 3 Voltammograms of CNF templated PPy with different amounts of deposition and their consequent SEM images: **a** 5 times cycled at 100 mV s^{-1} and **b** 10 times cycled at 100 mV s^{-1}

Table 1 PPy coating optimization summary—number of cycles of the polymer deposition

Number of cycles	5	6	7	8	9	10
Q_d C cm^{-2}	12.9	13.3	14.7	17.2	20.8	22.7

surface area and the capacitance accumulated in the bulk. Therefore, as the next step, the deposition profile in between 5 and 10 times cycling was observed. The specific capacitance values of these entire test groups are summarized in Table 1; the voltammograms (at the same scan rate; 100 m Vs^{-1}) suggest that the specific capacitance values of the samples increase with the increasing amount of deposition as before. On the other hand, the SEM images of these samples showed that increasing the number of deposition cycles of PPy increases the deposition of blocks through the CNF network. The SEM images also show that samples free from blocks of polymer can be produced only until the 6th cycle. The block polymerization starts at the 7th cycle and increases as the cycling continues. In fact the block polymerization gets so high by the 9th cycle that it is not only in between the PPy-coated CNFs, but is also on them making the surface area even smaller.

In the second stage of the optimization, the goal to be accomplished was to increase the deposition amount without having blocks of polymers in the sample.

Since it is known from the former experiments that the blocking starts right after the 6th cycle, there were two possible solutions:

i. Increase the extent of deposition per cycle using a slower scan rates while cycling 6 times.
ii. Decrease the extent of deposition per cycle using a faster scan rate while cycling 7 times.

The 6 times cycled PPy deposition was performed at 25, 50, and 75 mV s^{-1} scan rates while the 7 times cycled PPy deposition was performed at 150 and 200 mV s^{-1} scan rate. The scan rate dependence of these samples is summarized in Table 2. The most successful deposition was achieved via scanning at 25 mV s^{-1} over 6 cycles and the corresponding voltammogram and SEM images are given in Fig. 4a and Fig. 5a. With this sample, the specific capacitance value has shown a drastic increase and was found to be 27.6 C cm^{-2}. Comparing the SEM images of the two scanning rates at 25 and 100 mV s^{-1}, it can be clearly seen that there are fewer uncoated CNFs at a deposition rate of 25 mV s^{-1} which reflects in the best

Table 2 PPy coating optimization summary—scan rate of the polymer deposition

Number of cycles/scan rate	6/25	6/50	6/75	6/100	7/100	7/150	7/200
Q_d C/cm^{-2}	27.6	16.6	15.1	13.3	14.7	20.8	16.7

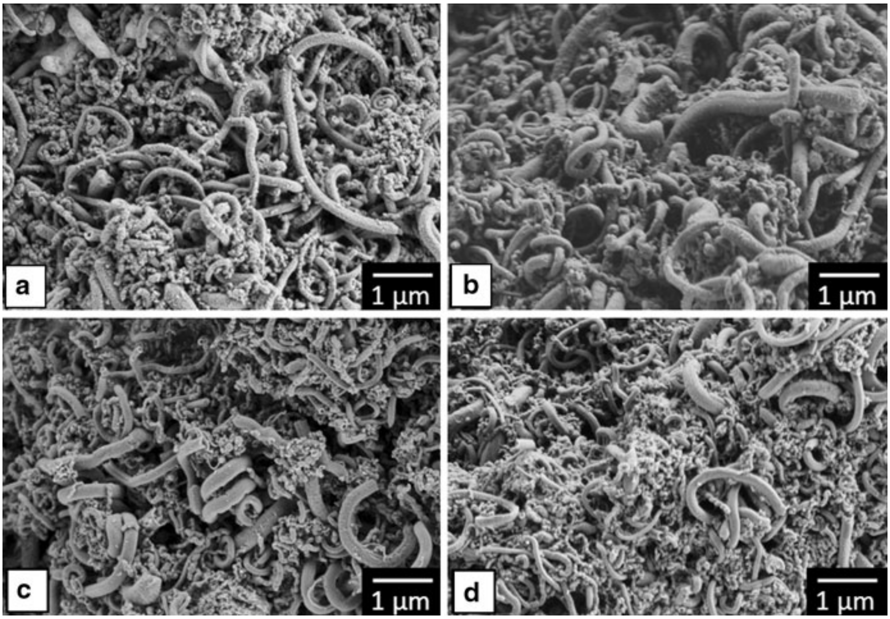

Fig. 4 The SEM images of PPy-deposited CNFs. **a** 6 times cycling at a scan rate of 25 mV s^{-1}, **b** 6 times cycling at a scan rate of 75 mV s^{-1}, **c** 7 times cycling at a scan rate of 100 mV s^{-1}, and **d** 7 times cycling at a scan rate of 200 mV s^{-1}

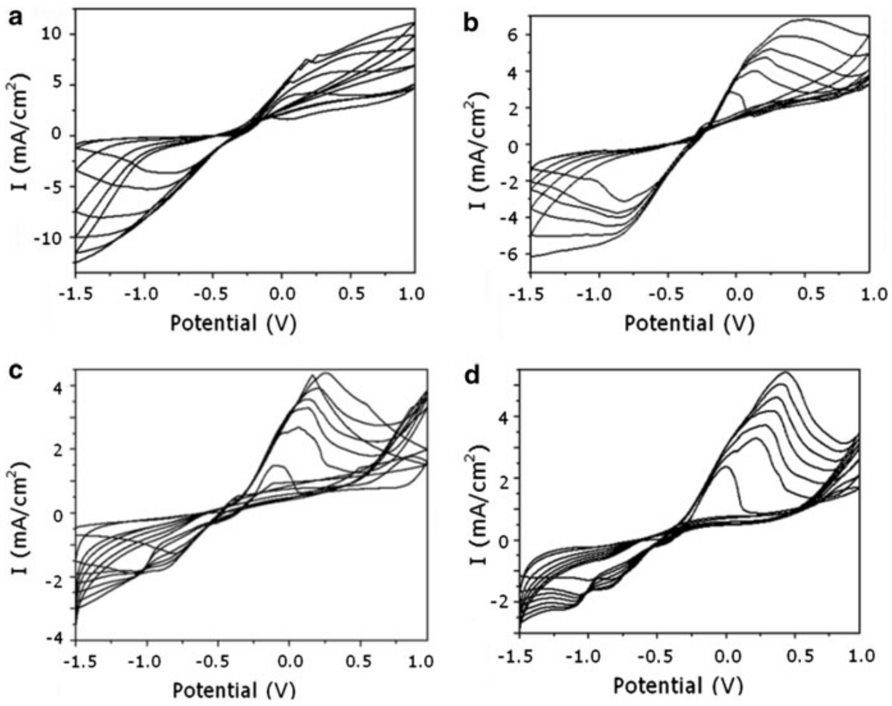

Fig. 5 Voltammograms of PPy-deposited CNFs. **a** 6 times cycling at a scan rate of 25 mV s^{-1}, **b** 6 times cycling at a scan rate of 75 mV s^{-1}, **c** 7 times cycling at a scan rate of 100 mV s^{-1}, and **d** 7 times cycling at a scan rate of 200 mV s^{-1}

capacitance measurement. The deposited PPy thickness varies between 300 and 400 nm, implies a successful surface for charge deposition but not for bulk deposition, which is desired for supercapacitor active materials. A decrease in the capacitance values was observed as the deposition rate increased from 25 mV s^{-1} (Table 2). Parallel to this, SEM images show that the homogeneity and the thickness of the deposition at 25 mV s^{-1} scan rate is the best, Fig. 4.

For the 7 times cycled samples, two additional scan rates were analyzed. Initially, at a scanning rate of 150 mV s^{-1}, the specific capacitance of the sample, calculated by integrating the area of the last full scan of the cyclic voltammogram, is found as 20.8 C cm^{-2} which is higher than the 7 times cycled sample at 100 mV s^{-1} scan rate. This sudden increase is most likely the result of not having blocks of PPy unlike the sample scanned at 100 mV s^{-1}. Therefore, it is clear that the presumption that was made at the beginning of the optimization is proven correct. When the scan rate is increased, the block polymerization is prevented resulting in the increase of specific capacitance. However, the specific capacitance of the sample deposited by 7 times cycling at 150 mV s^{-1} scan rate is not as high as the sample which was deposited by 6 times cycling at 25 mV s^{-1} scan rate. The SEM image and the voltammogram of the sample scanned at 200 mV s^{-1} scan rate are given in Figs. 4

and 5. As can be clearly seen, the homogeneity of the thickness of the PPy-coated CNFs is completely lost and there are many CNFs which remained uncoated, resulting in decreasing of the specific capacitance of the sample.

Mass transport basically depends on three main issues: convection, migration, and diffusion. Convection results from the action of a force on the solution. This can be a pump, a flow of gas, or even gravity and can be controlled by not giving any disturbance to the reaction cell during the reaction. Migration is essentially an electrostatic effect which arises due the application of a voltage on the electrodes. This effectively creates a charged interface (the electrodes). Any charged species near that interface will either be attracted or repelled from it by electrostatic forces. Also migration can be eliminated, or more realistically reduced to its minimum by increasing the amount of the electrolyte. Diffusion occurs in all solutions and arises from local uneven concentrations of reagents. Entropic forces act to smooth out these uneven distributions of concentration and are therefore the main driving force for this process. Diffusion is particularly significant in an electrolysis experiment since the conversion reaction only occurs at the electrode surface. Consequently, there will be a lower reactant concentration at the electrode than in the bulk solution. Similarly, a higher concentration of product will exist near the electrode than further out into the solution. For the diffusion, on the other hand, since the transfer rate of an electron is much higher than its diffusion rate we simply should always have the same amount of electrons in the diffusion layer of the electrode not to be dependent on diffusion. By observing the polymer growth at different scan rates, we can establish if the electrochemical reaction is affected by diffusion or not. Normally, the polymerization rate of pyrrole does not depend on the scan rate. When we compare the 7 times cycling samples given in Fig. 5c, d, current densities of the PPy increase as the scan rate is increased. This means that as the polymer is scanned faster, we have more electrons in the diffusion layer although the concentration is always kept constant, proving the cell reaction is diffusion independent. However, this is not the case for the CNF-templated PPy samples. This situation may arise from the fact that the infinitesimally small distance from the electrode is not smooth, therefore, the electron concentration around the surface may differ with different scan rates.

Conclusions

In this study, pyrrole monomer is polymerized on CNFs via electropolymerization. The deposition of the polymer was optimized by varying the deposition amount and the deposition speed. In this study, CNFs with coiled morphology and high specific surface area were produced successfully. Subsequently, a new technique was developed to have chemically bonded CNF–PPy active material which is different from the composites used for supercapacitor technology. This new technique can be used with different types of CNFs, CNTs, and CPs to produce a superior active material with higher surface area and higher specific capacitance. Our optimization studies showed that the final capacitance values are highly dependent on the number of deposition cycles and deposition rates. The best result for our coiled CNF/PPy composite system is found to be 27.6 C cm^{-2} at 6 times cycling using 25 mV s^{-1} voltage, which is considered a slow scan rate.

Acknowledgments The authors would like to acknowledge The Scientific and Technological Research Council of Turkey (TUBITAK) supported the study through Project No: 104T552.

References

1. Conway BE (1999) Electrochemical supercapacitors—scientific fundamentals and technological applications. Kluwer Academic/Plenum, New York
2. Frackowiack E, Béguin F (2001) Carbon materials for the electrochemical storage of energy in capacitors. Carbon 39(6):937–950
3. Kötz R, Carlen M (2000) Principles and applications of electrochemical capacitors. Electrochim Acta 45(15–16):2483–2498
4. Kim J-H, Sharma AK, Lee Y-S (2006) Synthesis of polypyrrole and carbon nano-fiber composite for the electrode of electrochemical capacitors. Materials Letters 60(13–14):1697–1701
5. Roth S, Carroll D (2004) One-dimensional metals: conjugated polymers, organic crystals, carbon nanotubes. Wiley-VCH, New York
6. Shi H (1996) Activated carbons and double layer capacitance. Electrochim Acta 41(10):1633–1639
7. Frackowiak E, Béguin F (2002) Electrochemical storage of energy in carbon nanotubes and nanostructured carbons. Carbon 40:1775–1787
8. Frackowiak E et al (2001) Nanotubular materials for supercapacitors. J Power Sour 97–98:822–825
9. Peña R (2002) Electrochemical synthesis of conducting polymers on carbon nanotube films and its effect on electrochemical capacitance 2002, Welch Summer Scholar Program, The University of Texas at Austin
10. Khomenkoa V, Frackowiak E, Béguin F (2005) Determination of the specific capacitance of conducting polymer/nanotubes composite electrodes using different cell configurations. Electrochim Acta 50(12):2499–2506
11. Dumanli AG, Erden A, Yürüm Y (2008) Production of CNTs and CNFs and utilization in the manufacture of super-capacitors, in German-Turkish symposium: development and technology of carbons, Istanbul
12. Mastragostino M, Arbizzani C, Soavi F (2002) Conducting polymers as electrode materials in supercapacitors. Solid State Ionics 148(3):493–498
13. Rudge A et al (1994) Conducting polymers as active materials in electrochemical capacitors. J Power Sour 47(1–2):89–107
14. Açık M, Barıştıran C, Sönmez G (2006) Highly surfaced polypyrrole nanonetworks and nanofibers. J Mater Sci 41(14):4678–4683
15. Dumanli AG, Yürüm Y (2011) Carbon nanotube and nanofiber growth on Zn-based catalysts. Fuller Nanotubes Carbon Nanostruct 19(3):155–165
16. Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. J Am Chem Soc 60(1):309–319