



ELECTROCHEMICAL PERFORMANCE OF SUPERCAPACITORS BASED ON POLY(PYRROLE)-COBALT SUPPORTED ON CARBON NANOTUBES

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ABSTRACT

Supercapacitors are electrochemical devices that store electrical energy by means of non-faradic and faradic processes, with the advantage of rapid charge/ discharge and high power density. The development of hybrid materials such as carbon nanotubes/polymer/metal, allows increasing the cyclability of the supercapacitor and obtaining higher specific capacitance (Fg^{-1}), through the contribution of faradic processes of polymer and metal.

In this work, electrodes were developed based on intrinsic conductive polymers poly(pyrrole) (PPy), synthesized onto carbon nanotubes (MWCNT) and modified with cobalt. Supercapacitors were fabricated with these electrodes and characterized by cyclic voltammetry and galvanostatic charge/discharge cycles.

The modification of MWCNT with poly(pyrrole) increased capacitance values by increasing the double layer capacitance, up to $12.58 \text{ F}\cdot\text{g}^{-1}$, while charge/discharge times remained unchanged. This sample also contained highest percentage of polymer and showed a decrease of 12% in cyclic stability, compared to the support material and a reduction of 8% compared to devices modified with cobalt.

Keywords: supercapacitors, hybrid materials, conducting polymers, cobalt



1. INTRODUCTION

Supercapacitors are taking an important position as energy storage systems due to fast charge and discharge combined with high power density. Energy storage in the order of farads occurs through two different mechanisms: electrochemical double layer and pseudocapacitance preceded by a double-layer component [1]. The electrochemical double layer exists at the electrode-electrolyte interface due to electrostatic charge and diffusion layers in the electrolyte. The pseudocapacitance relates to charge storage and release during the reversible oxidation and reduction of the electrode material, commonly metal oxides or electroconducting polymers.

At present most of the devices available in the market are double layer capacitors, based on high surface area active carbons. Taking into account that pseudocapacitors can provide capacitance values of the order of $100\text{--}1000\text{ }\mu\text{F}\cdot\text{cm}^{-2}$ [2], much higher than that provided by double layer capacitor devices ($15\text{--}50\text{ }\mu\text{F}\cdot\text{cm}^{-2}$) [2], efforts are made to enhanced the specific capacitance of carbon-based materials such as nanostructured mesoporous carbons [3, 4], by introducing pseudocapacitance for example from redox reactions from conducting polymers (polyaniline, polypyrrole and derivatives of thiophene, etc.) [5-7], transition metal oxides (RuO_2 , IrO_2 , MnO_2 , NiOx y Co_3O_4) [8, 9], and the presence of heteroatoms (nitrogen and oxygen) which can undergo fast redox reactions [10-12].

Intrinsically conducting polymers, as electrode material for supercapacitors, present high conductivity, high storage capacity, good thermal and environmental stability, high redox and capacitive current. However, intrinsically conducting polymers have a disadvantage of lower cycle life as for carbon-based electrodes, due to polymer degradation.

Recent research focuses on using carbons substrate to prepare carbon-polymer composites, such as polypyrrole/carbon aerogel [13, 14], polypyrrole (PPy) on multi-wall carbon nanotubes [14, 15], polypyrrole on single carbon nanotubes [16] and polythiophene and poly(2-methyl thiophene) on carbon fiber [17].

2. EXPERIMENTAL

2.1 Synthesis of composite MWNTC/PPy-Co .

Polypyrrole (PPy) were synthesized and supported onto multiwalled carbon nanotubes (MWCNT) and modified with cobalt (PPy-Co).

Multiwalled carbon nanotubes (by Catalytic Materials) were dispersed by ultrasonic bath in deionizer water and glacial acetic acid (CH_3COOH , Aldrich) for 20 minutes, before adding monomer: pyrrole or 3-methylthiophene (Aldrich). The solution was stirred and H_2O_2 at 30 % (Fluka) was added and stirred for 3 hours. The resulting composite material was filtered at vacuum, successively washed with deionizer water and dried for 48 hours at 50 °C [18].

The modification with cobalt was realized by dispersion of the composite material in deionizer water used a reflux system. A mixed solution of NaBH_4 and NaOH (Sigma-Aldrich) was added until reaching a pH of 11. The modified composite was washed with deionizer water until reaching a pH of 7, and dried for 48 hours at 50°C [18]. The polymer content in the composite was determined by N and S microanalysis, using a LECO CHNS932 equipment. All materials were characterized by SEM and XRD.

The electrochemical performance of the composites was studied in symmetric two-electrode cells by cyclic voltammetry and galvanostatic charge/discharge experiments using a Solartron 1480 potentiostat/galvanostat in a potential window from 0 to 1 V. Supercapacitor electrodes were processed as cylindrical pellets of 12 mm diameter by cold-pressing a mixture of 75 wt% of the hybrid material composite, 20 wt% of polyvinylidene fluoride PVDF (Aldrich) binder (Aldrich) and 5 wt% of carbon black (SuperP, 3M). Each pellet contained between 48-50 mg of active material. The capacitors were prepared from 2 identical electrodes, separated by glassy microfiber paper discs (Whatman BS45) with 1M LiClO_4 as electrolyte. Two stainless steel rods acted as current collectors. All cells were completely discharged before each experiment.

3. RESULTS AND DISCUSSIONS

Data obtained from N and S microanalysis are compiled in Table 1 (average of three tests).

Table 1. Concentration of polymer on multiwall carbon nanotube

Hybrid Material	Support material (% wt)	Polymer concentration (% wt)
MWCNT	100	0
MWCNT-PPy	90.1	9.9

Cobalt modified materials are not presented in this table. The polymer concentration is 9.9 % (see Table 1); The quantification theoretical of the concentration of cobalt was determined from its molecular weight ($\text{Co} = 59 \text{ g mol}^{-1}$) and molecular weight of cobalt nitrate ($(\text{Co}(\text{NO}_3)_2) = 291 \text{ g mol}^{-1}$). For 300 mg of hybrid material of MWCNT-PPy a percent of cobalt was of 10.47%.

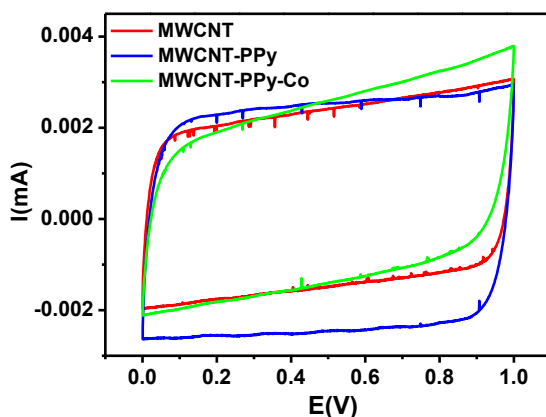


Figure 1: Cyclic voltammetry for MWCNT, MWCNT-PPy and MWCNT-PPy-Co at 10mV/s.

Figure 1 shows the cyclic voltammetry for the electrochemical capacitors under study obtained at a $10 \text{ mV} \cdot \text{s}^{-1}$ potential scan rate. The curves corresponding to the capacitors based on the MWCNT only, MWCNT/PPy and MWCNT/PPy-Co show nearly ideal rectangular shapes. The pseudocapacitance due to the presence of the polymer was not observed in these curves.

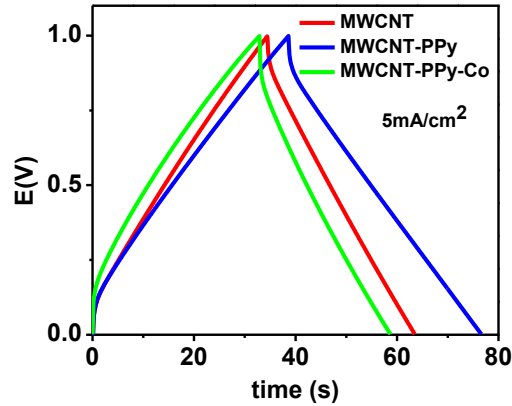


Figure 3: Galvanostatic charge-discharge curves corresponding to MWCNT, MWCNT-PPy, MWCNT-PPy-Co, obtained at a constant current density of $5 \text{ mA} \cdot \text{cm}^{-2}$.

The capacitance of the cell can be determined from the discharge process using:

$$C = \frac{I \cdot t_d}{\Delta V_2} \quad \text{ec (1)}$$

where t_d is the time spent during discharge and ΔV_2 is the voltage range in which the discharge occurs. Since the cell is symmetrical, the specific capacitance of the electrode is calculated as two times the cell capacitance divided by the active mass of one electrode (48 to 50 mg of active material).

The capacitances obtained at $5 \text{ mA} \cdot \text{cm}^{-2}$ are for MWCNT $9.57 \text{ F} \cdot \text{g}^{-1}$; for MWCNT-PPy $12.58 \text{ F} \cdot \text{g}^{-1}$; for MWCNT-PPy-Co $8.96 \text{ F} \cdot \text{g}^{-1}$. From the discharge process, the equivalent series resistance (ESR) of the supercapacitor cell can be estimated according to:

$$\text{ERS} = \frac{\Delta V_1}{2I} \quad \text{ec (2)}$$

where ΔV_1 is a voltage drop, I is the applied current, and 2 is a factor due to the polarity change. The equivalent series resistance (ESR), independently of the applied current density follows the order: MWCNT < MWCNT-PPy < MWCNT-PPy-Co.

The cycling performance of the symmetric electrochemical capacitors was evaluated using galvanostatic charge/discharge over 10000 cycles at a current density of $10 \text{ mA} \cdot \text{cm}^{-2}$. For MWNTC a similar performance was found the low concentration of polymer (see table 1). In the

case of MWCNT-PPy and MWCNT-PPy-Co the addition of cobalt (figure 4), results in a slightly improved cyclability, with 96% of initial capacitance after 10,000 galvanostatic cycles.

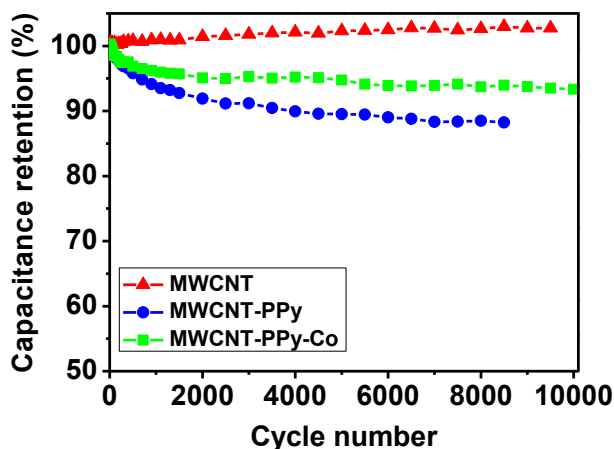


Figure 4: Cyclability for MWCNT, MWCNT-PPy, MWCNT-PPy-Co, obtained at a constant current density of 10 $\text{mA}\cdot\text{cm}^{-2}$.

4. CONCLUSIONS

The highest specific capacity was found for carbon nanotube/PPy composite material. Galvanostatic tests show that the capacitor MWCNT-PPy has best symmetry in the curves of charge/discharge and lower internal resistance. The values of specific capacitance obtained in order of magnitude: MWCNT-PPy, $12.58 \text{ F}\cdot\text{g}^{-1} > \text{MWCNT}, 9.57 \text{ F}\cdot\text{g}^{-1} > \text{MWCNT-PPy-Co}, 8.96 \text{ F}\cdot\text{g}^{-1}$, however show a high resistivity. The addition of cobalt, results in improved cyclability, with 96% of initial capacitance after 10,000 galvanostatic cycles.

5. ACKNOWLEDGEMENTS

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