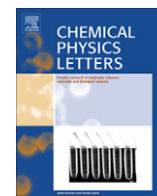


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# Influence of the PANi morphology deposited on the carbon fiber: An analysis of the capacitive behavior of this hybrid composite

Carla Polo Fonseca\*, Dalva A.L. Almeida, Mauricio R. Baldan, Neidenei G. Ferreira

Laboratório Associado de Sensores e Materiais, Instituto Nacional de Pesquisas Espaciais – INPE, Av., dos Astronautas 1758, 12245-970 S. J. Campos, SP, Brazil

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## ABSTRACT

CF/PAni composites were synthesized using the polymerization chemistry. Three different deposition times were used in the synthesis, such as: 30, 60 and 90 min. The morphology and the structure of composites were analyzed by SEM and Raman spectroscopy, respectively. The influence of the mass of polymer deposited on the carbon fiber, with respect to the values of specific capacitance ( $C_{sp}$ ) was analyzed by electrochemical experiments. The optimum value of the  $C_{sp}$  was obtained for CF/PAni-30 min ( $C_{sp} = 188 \text{ Fg}^{-1}$ ). This fact is related to the lower charge transfer resistance, due to its more homogeneous morphology and thin layer polyaniline.

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## 1. Introduction

The growing demand for portable electronic systems, digital communication devices, load-leveling for renewable power generation and power grid interfacing and electric vehicles have motivated considerable interest in supercapacitors. Supercapacitors or electrochemical capacitors are energy storage devices characterized by high power densities, and cycle lives of  $>10^6$  [1–4]. Even more, the specific energies of these devices are greater than found in the electrolytic capacitors, and their specific power levels are superior to the secondary batteries. Thus, the electrochemical characters of supercapacitors are located between the electrolytic capacitors and batteries. Besides, this device can be used when high power is required in a short time.

The materials usually used in the assembly of these electrochemical devices are active species, such as: metal oxides [4] or conducting polymers [5,6], where they can be reversibly oxidized/reduced over the potential range of operation.

Conducting polymers represent an interesting class of electrode materials for supercapacitors, due to their high kinetics of the electrochemical charge–discharge processes. Besides, the charge is stored throughout the volume of the polymer material. Furthermore, it can be produced at lower cost than noble metal oxides. The conducting polymers can exist in either two or three general states. As-formed polymers tend to be an oxidized or ‘p-doped’ state, being positively charged with a high electronic conductivity. When the p-doped polymer is reduced, the ‘undoped’ state is formed. Usually, this state is insulating or semi-insulating, depending on the degree of completion of the undoping process [5–9].

Among the conductive polymers, polyaniline (PAni) is considered the most promising electrode material for supercapacitors, due to its excellent capacity for energy storage, easy synthesis, and high conductivity, the low price of aniline monomers and ease of manipulation. In addition, the PAni has a better accessibility of the ions to the electrochemically active surface. This can be seen as being responsible by higher values of capacitance [4,6]. However, the main disadvantage in the use of the conducting polymer as the base to make supercapacitors is the poor cycle life, due to the volume change during the doping and undoping process. Therefore, it is necessary support adequately the electrochemically active sites of conducting polymers and this can be made by the addition of conducting material with a large surface area, such as: carbon fiber or carbon nanotubes (CNTs).

CNTs have many attractive properties, such as: large surface area, high conductivity, temperature stability and percolated pore structure. Moreover, the CNT can be easily functionalized targeting different applications [10–15]. CNT/conducting polymers have been extensively studied due to their superior performance resulted from the significant synergy of them [16–21].

Porous carbons as carbon fiber are extremely attractive as electrode materials due to their large specific surface area, high pore accessibility, excellent thermal and chemical stability, as well as a relatively low cost. The storage of electric charges in these materials is a purely non-Faradaic and the accumulation of ionic charges occurs on the double-layer at the electrode/electrolyte interface [22]. The capacitive behavior of carbon materials can be further improved by the presence of active species as conducting polymer, that contribute to the total specific capacitance [23–26].

In this work, the Polyaniline (PAni) was deposited on the carbon fibre (CF) with the aim of to design a hybrid composite, CF/PAni. The polymer deposition occurs at several times, in the view to

\* Corresponding author. Fax: +55 12 3208 6675.

E-mail address: [carla.polo@yahoo.com.br](mailto:carla.polo@yahoo.com.br) (C.P. Fonseca).

produce various composites with different mass of the conducting polymers.

## 2. Experimental parts

The carbon fibers were cut in size  $2 \times 1$  cm and weighed. For each synthesis were produced six samples, simultaneously. The fibers were fixed in a platinum wire and placed in a solution containing distilled aniline ( $12.6 \text{ mmol L}^{-1}$ ) and  $1.0 \text{ mol L}^{-1}$  HCl,  $3.0 \text{ mol L}^{-1}$  NaCl at  $-10^\circ\text{C}$ . Another solution containing  $1.0 \text{ mol L}^{-1}$  HCl,  $3.0 \text{ mol L}^{-1}$  NaCl and  $0.03 \text{ mol L}^{-1}$  ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , was added to the aniline solution at different deposition times of the 30, 60 and 90 min at  $-10^\circ\text{C}$  with vigorous stirring. CF/PAni composites were synthesized by oxidative polymerization. The composite was washed with  $1.0 \text{ mol L}^{-1}$  HCl, obtaining the conducting state of the polyaniline (esmeraldine).

The morphology of the CF/PAni composites was evaluated by SEM analyses using a JEOL JSM-5310 microscope system. Raman's spectra were recorded using a micro – Raman scattering spectroscopy (Renishaw microscope system 2000) with an excitation of Ar, 514.5 nm laser with a  $500\times$  objective.

The CF/PAni composites were electrochemically characterized by chronopotentiometry and electrochemical impedance spectroscopy. The charge–discharge curves were obtained by applying constant  $i \pm 1.0 \text{ mA}$  ( $E_{\text{cut-off}} = -0.1$  and  $0.8 \text{ V}$ ). All impedance spectra were recorded at open circuit potential, where an ac amplitude of 10 mV was applied in the frequency range of  $10^5$  to  $10^{-3}$  Hz. The impedance data were analyzed using Boukamp's fitting program.

All measurements have been performed in  $1.0 \text{ mol/L H}_2\text{SO}_4$  solution deaerated by 30 min.

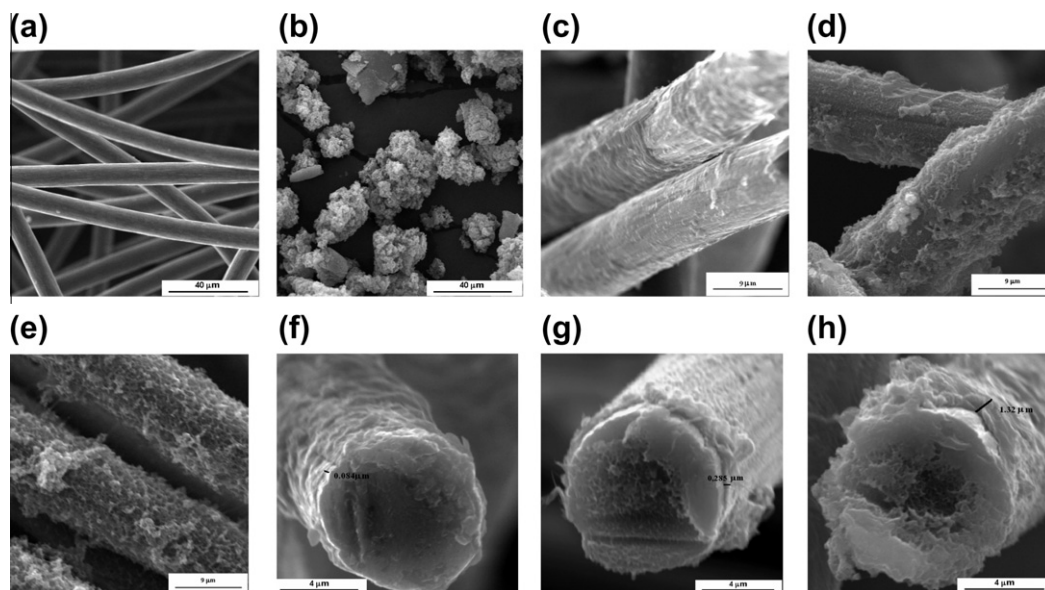
## 3. Results and discussion

The SEM images of the bare CFs, PAni powder and various CF/PAni composites are shown in Figure 1. The average diameter of the CF (Figure 1a) was measured to be about  $9 \mu\text{m}$  with a surface very clean before polyaniline deposition. The polyaniline powder morphology showed the presence of the fine particles agglomerated, Figure 1b.

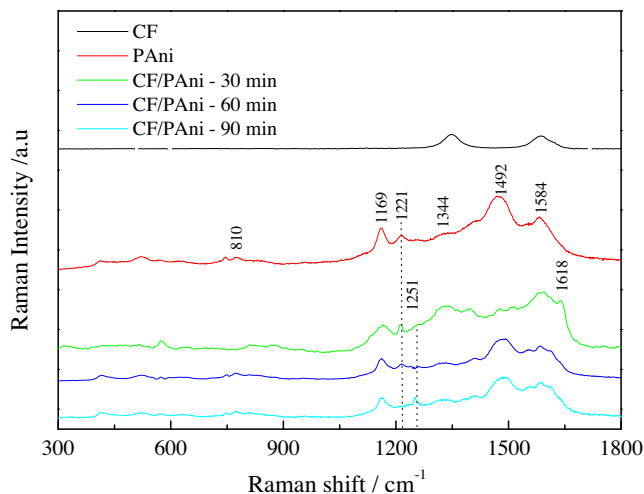
SEM images in Figure 1c–h exhibit the carbon fibers well dispersed and enwrapped uniformly with PAni. This suggests that the interaction between polymer molecules and CFs overcomes the Van der Waals interaction between CFs, with the effective interaction between the  $\pi$ - bonds in the aromatic ring of the polyaniline and the CF should strongly facilitate the charge-transfer reaction between the two components. In these composites, CFs can offer a good mechanical support to PAni and also ensure the electronic conduction in the composite electrode.

A gradual increase in the PAni layer thickness over fibres is clearly observed with the increase deposition time. The carbon fiber is uniformly and completely coated with polyaniline in, Figure 1c–e. The PAni coating thickness was estimated to be 0.084, 0.285,  $1.32 \mu\text{m}$  for the CF/PAni 30, 60 and 90 min, respectively (Figure 1f–h). To CF/PAni – 60 and 90 min composite showed an irregular morphology (Figure 1d and e). In the case of CF/PAni – 90 min composites showed also big particles between the CF, on the other hand, the CF/PAni 30 min exhibited a uniform coating.

The FC/PAni composites were studied by Raman spectroscopy, Figure 2. The vibrational frequency provides detailed information about polymer composition. The spectra of CF/PAni composites are shown in Figure 2 and they are typically corresponded to poly-emeraldine [27]. Figure 2 illustrates the bands at  $1584$  and  $1492 \text{ cm}^{-1}$ , which represents the C=C stretch of quinoid and benzenoid rings, in PAni molecules, respectively. The band located at  $1344 \text{ cm}^{-1}$  was assigned to C–N<sup>+</sup> stretching of radical cations, cyclised structures. The FC/PAni – 30 min Raman spectrum is quite different of the others spectrum composites. We can see variations in the peak intensity of the Raman spectrum and the strong presence of the band at ca.  $1344 \text{ cm}^{-1}$  in the CF/PAni – 30 min Raman spectrum. The bands at ca.  $1330/1370 \text{ cm}^{-1}$ , are dependent on the degree of delocalization of  $\pi$ -electrons along the polymeric chain due to radical cations [28–30], indicating a highly conductivity material. Furthermore, the difference in polyemeraldine doping (protonation) state can be seen from bands at  $1221$  and  $1251 \text{ cm}^{-1}$ , which it represents the CN stretching in polaronic units. The shift of the band from  $1221$  to  $1251 \text{ cm}^{-1}$  observed in the 30–90 min CF/PAni composites results from the doping process. The single band  $1251 \text{ cm}^{-1}$  states observed in CF/PAni – 90 min means the complete doping of PAni [31].



**Figure 1.** SEM images of carbon fibre (a), PAni powder (b), FC/PAni composite lateral view 30 min (c), 60 min (d) and 90 min (e) and frontal view 30 min (f), 60 min (g) and 90 min (h).



**Figure 2.** Raman spectra at 632.8 nm at several time depositions to CF/PAni synthesis.

The electrochemical characterization of the composites, the bare FC and powder PAni was evaluated by galvanostatic curves and electrochemical impedance spectroscopy. The specific capacitance values, **Figure 3**, were evaluated by the galvanostatic measurements (figure in closed). The potential range was chosen considering the CV curves, where the degradation of the conducting polymer and their insulated state were determined at positive and negative potential, respectively.

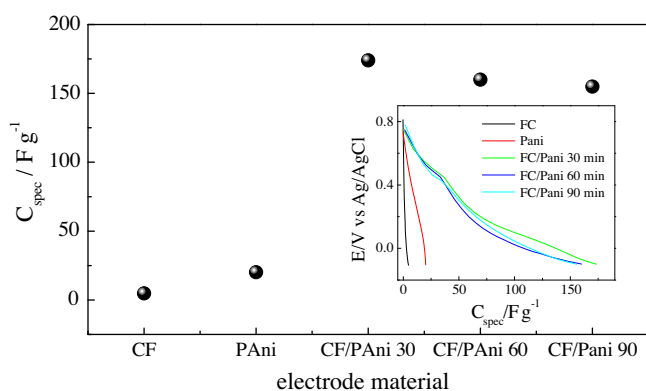
Specific capacitance values (**Figure 3**) can be calculated by the following relationship:

$$C_{\text{spec}} = 1/(m \times (dV/dt))$$

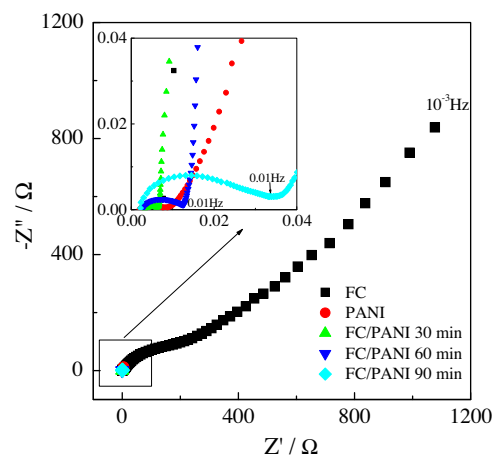
where  $dV/dt$  is obtained from the slope of the discharge curve and  $m$  is the active electrode mass. The CF and PAni electrodes have a lower specific capacitance than composite electrodes ( $C_{\text{spCF}} = 4.77$  and  $C_{\text{spPAni}} = 20.14 \text{ Fg}^{-1}$ ). The optimum condition of the specific capacitance ( $C_{\text{sp}} = 188 \text{ Fg}^{-1}$ ) was accomplished for the 30 min deposition time to composite synthesis.

It seems this fact may be related to the CF/PAni composite thickness. Apparently, smaller thickness but with a more homogeneous coating is more effective in the charge/discharge process. The granular morphology observed at 90 min deposition time apparently can cause difficulties in the charge transport.

To elucidate the effect of the amount of polymer deposited on the carbon fibers in the charge/discharge process were performed



**Figure 3.** Discharge curves at 1.0 mA current CF, PAni and CF/PAni composite electrodes.



**Figure 4.** Nyquist diagrams for CF, PAni and CF/PAni composite electrodes the at open circuit potentials.

EIE measurements, **Figure 4**. The spectra were recorded at an open circuit voltage of approximately 0.5 V vs. Ag/AgCl. The high frequency region is related to the electrolyte properties, while at the mid-frequency region, the impedance response is associated with the electrode/electrolyte interface. The corresponding relaxation effect is represented by a semicircle and the intersections with the real axis ( $Z'$ ) at high and mid frequencies correspond to the electrolyte and charge transfer resistances ( $R_e$  and  $R_{ct}$ ), respectively. The time constant is the product of charge transfer resistance and double layer capacitance ( $C_{dl}$ ). In the low frequency region, the impedance is controlled by the diffusion of counterions inside the composite electrode. The impedance response ideally to this process is a  $45^\circ$  straight line (Warburg impedance), represents the mass transfer parameters of the electrochemical doping process. At very low frequency, when the diffusion layer involves the entire electrode thickness, the response resembles that of a pure capacitance (ideally a  $90^\circ$  straight line). Variations on this slope have been related to the morphology of the material.

The impedance spectra analyses showed that the CF electrodes have a higher charge transfer resistances than the composite and PAni electrodes. This may be related to increasing formation of the charge-transfer complex. However, the lower charge transfer resistance was obtained for the composite with 30 min of deposition time, and therefore, with the smaller mass of conductive polymer. Above 30 min of deposition, polyaniline is also synthesized as irregular grains between the covered fibers by PAni. These grains have fewer active sites to faradic reaction, and it does not facilitate the charge-transfer in the electrode materials. A uniform morphology of the PAni on the carbon fiber is desired because it reduces the charge transfer resistance and therefore, increases the ionic conductivity of the composite material promoting a fast load/discharge rates, and larger specific faradic capacitance, so that the performances of composite electrodes are enhanced.

#### 4. Conclusion

CF composite electrodes/PAni were synthesized by chemical polymerization. With increasing of the deposition time, the composite showed a less uniform morphology and with a higher doping. The highest specific capacitance was obtained for the composite formed with 30 min deposition. This material presented a more homogeneous morphology than the other composites, with the carbon fiber covered by a thin layer of polyaniline. Electrochemical impedance spectroscopy experiments showed that a more homogeneous morphology with a thin layer of conducting polymer

resulted in a lower charge transfer resistance easing the process of charge and discharge. In sum, the electrochemical processes of CF/PAni composite electrodes depended on the formation of the charge-transfer complex, of the microstructure, as well as mass PAni content.

### Acknowledgments

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