Synthesis of carbon nanotubes on carbon felt for supercapacitors

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Abstract:

We made composites of carbon nanotubes grown on carbon felt prepared by 5 different methods to turn them superhydrophilic for application as supercapacitor. The methods were chemical and electrochemical oxidation, O_2 (or N_2) plasma attack and water vapor activation. This study focuses on CNTs morphology after each treatment and their performance as electrodes for supercapacitors. The best electrodes show specific capacitances of hundreds of F/g.

Introduction

Carbon materials have been investigated to develop energy storage devices, mainly supercapacitors. In particular, carbon nanotubes (CNTs) films are good candidates for use as electrochemical capacitors because of their high electrical conductivity, high resistance to acidic electrolytes, and high specific surface area [1-2]. However, as well known, graphitic materials are super-hydrophobic and require surface treatments to improve their wettability, and, as a result, their interaction with the water-based electrolytes [3]. We present here a method to grow CNT on carbon felt (CF) and five ways to get superhydrophilic CF/CNT composites. We submitted the composites to chemical, electrochemical oxidation, O_2 (or N_2) plasma attack and water vapor activation. Characterization shows that the CNTs morphology changed after each treatment, and the electrodes built have different performance as supercapacitors.

Experimental Procedure

To prepare the CNT films, we immersed CF pieces of 15mmx15mmx5mm (~0,100g) in an ethanolic catalyst solution of 0,63% wt. of Fe $(NO_3)_3 \cdot 9H_2$ and 0,25% wt. of $CoCl_2 \cdot 6H_2O$. After drying, CNT growth followed by inserting the pieces into a 2" tubular furnace at 650°C. First, we purged the furnace with argon (200sccm/20min), and then inserted acetylene (30sccm) and the ethanol vapor (0.4 $mL.L^{-1}$/ 140ºC) for 20 min. After growth, we carried out 5 different surface treatment **(a-e)** to change the CF/CNT composites wettability, as summarized in the **Table 1.**

Table1: Treatments to improve the wettability of CF/CNT composites

	Treatment	*Description*
a	Chemical oxidation *CNT_OX*	The CF/CNT composites were dipped in a solution with H_2SO_4 and HNO_3 (3:1) at 60ºC by ~3s, washed until pH back to 7 and dried at 60ºC overnight.
b	Water vapor activation CNT_WV	The water was sprayed (4 $mL.L^{-1}$, 140ºC), and the vapor was inserted to to a furnace at 800ºC, carried by Ar (200sccm) by 1h.
c	Oxygen plasma *CNT_O2*	A DC plasma discharge using Ar/O_2 (10sccm/40sccm), at 100mTorr, 700V, 2 min attached C-O and C=O functional groups to the surface of CF/CNT composites.
d	Nitrogen plasma *CNT_N2*	A DC plasma discharge using Ar/N_2 (10sccm/40sccm), at 100mTorr, 700V, 2 min changed the surface of CF/CNT composites with nitrogen functional groups.
e	Electrochemical oxidation *CNT_EC*	A cyclic voltammogram at 10$mV.s^{-1}$, in H_2SO_4 1M, was run 5 times on CF/CNT composites. This procedure is usual to improve the wettability of electrolyte on electrodes surface before electrochemical measures.

From Scanning Electron Microscopy (SEM) images, we analyzed the morphology changes in the CF/CNT composites after each treatment. Chronopotentiometric curves were performed in a potentiostat (Autolab), in a three-electrode configuration cell with Ag/AgCl reference electrode, a platinum counter-electrode in an electrolytic solution of H_2SO_4 1M. The potential window analyzed ranged from 0 to 0.8V, at a current set at 5.0mA. We calculated specific capacitance, energy and power density [4].

Results and Discussion

The **Fig.1(a-b)** show, respectively, the SEM images of CF before CNT growth, and after CNT growth. Notice that CNT grew with high density and through all CF volume.

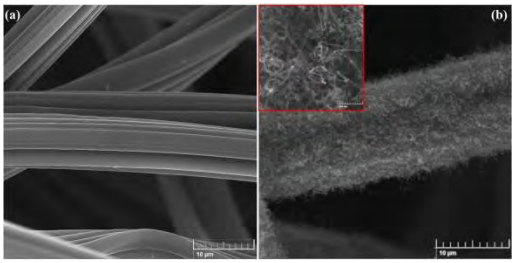

Figure 1: CF (a) before and (b) after growth.

The **Fig.2** shows morphology of CNT/CF composites after each treatment (a-d). Notice that (a-b) treatments are more aggressive than (c-d). We carried out treatment (e) just before electrochemical analysis, in the same electrochemical cell, so we do not show its morphology. The water vapor treatment seems to exfoliate the CNTs and maybe are creating pores in the carbon fiber, since this is a well known method to produce activated carbon [5]. .

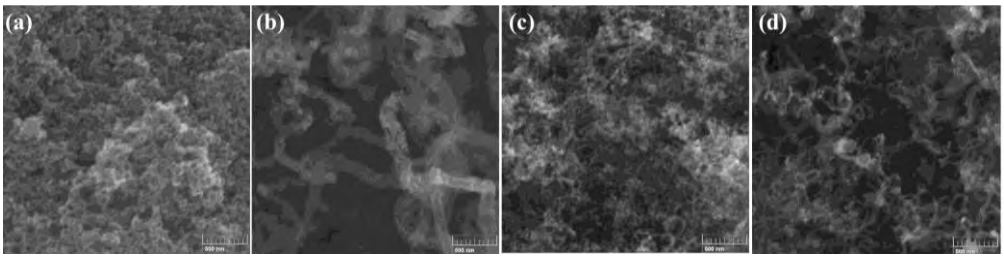

Figure 2: CF/CNT composites after treatments (a-d) stated in *Table 1*.

Figure 3(a) show the chronopotentiometric analysis up to 10 charge/discharge cycles. They showed a very symmetric profile, with some bending in charging curve at the highest potentials. **Table 2** summarizes the calculated value of specific capacitance (SC), energy (SE) and power (SP) from **Fig.3(a**) graphs. In **Fig.3(b),** we inserted our calculated values in a Ragone plot, to compare our values with the range for electrochemical supercapacitors shown in the literature [6].

Water vapor activation (129.2 Fg^{-1}) and chemical oxidation (60.4 Fg^{-1}) show the best results for capacitance. Besides the highest capacitance of the water-vapor treated CF/CNT composites, their energy and power values also fit to batteries range. Further chronoamperometric tests should be provided with shorter times for charge/discharge to test if those values have a strong dependence on the set current, as well, the analyses of surface area should be included.

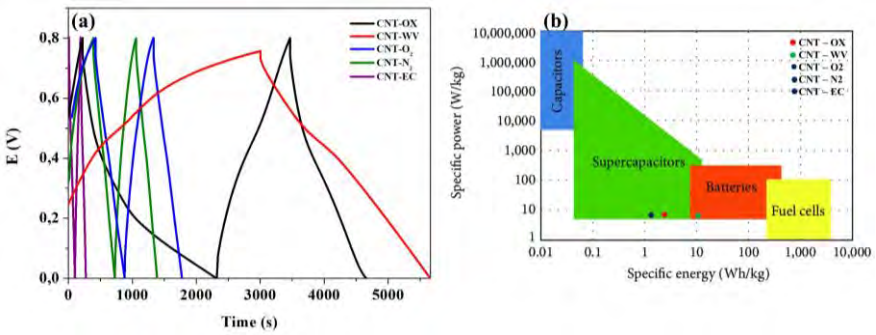

Figure 3: (a) Charge/Discharge curves for treated electrodes, and (b) Ragone plot (adapted from [6])

Table 2: Values calculated from charge-discharge curves of samples after 2 cycles.

Samples	*SC ($F.g^{-1}$)*	*SE ($W.h/Kg^{-1}$)*	*SP ($W.Kg^{-1}$)*
CNT_OX	60,41	5,37	15,88
CNT_WV	129,16	11,48	13,63
CNT_O_2	18,63	1,66	11,93
CNT_N_2	17,49	1,55	12,58
CNT_EC	3,88	0,35	14,81

Conclusions

We show successful CNTs production on CF. All treatments on CF/CNT composites were efficient to produce superhydrophilic surfaces, and, as a result, all of them produced electrode with excellent interaction with the electrolyte. The electrochemical oxidation and plasma treatments revealed just a surface functionalization, while chemical and water vapor showed differences in the electrodes morphology. Perhaps they also activated the carbon fibers by promoting pores formation. From Ragone plot we understand that our electrodes are classified as supercapacitors, still with a low specific power. Further studies need a more detailed electrochemical evaluation, and analysis of specific surface area.

Acknowledgments

The authors are grateful to CAPES/FAPESP by the financial support. Special thanks to Dr. Dalva Almeida, MSc. André Sardinha and Prof. Neidenei Ferreira from Electrochemistry Group (LABAS/INPE), by the training in potentiostats and facilities provided during this work.

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