Effect of Hot Drawing Process and Carbonization Temperature in Electrochemical Behavior of Electrospun Carbon Nanofibers

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Abstract

Due to the problems that exist on several systems that store energy, such as low energy density, low storage capacity and limited useful life; carbon nanofibers (CNFs) appear as an alternative to remedy such problems, due to their excellent properties, such as high electrical conductivity, high surface area and flexibility. However, there are some alternatives to reinforce their properties and optimize their application in energy storage systems. In this way, in our work, we look for an alternative to increase the capacitive properties of the CNFs. The hot drawing treatment was applied to the CNFs to improve their electrochemical performance for supercapacitor applications. First, non-woven polyacrylonitrile (PAN) membranes were manufactured by electrospinning, and then, the hot-drawing treatment was applied to promote molecular alignment. Prepared and stretched PAN membranes were carbonized at different temperatures to obtain CNFs. According to the applied hot drawing treatment and the increase in temperature, the crystalline structure of the CNFs was improved, which led to an increase in the electrochemical properties of the CNFs. The specific capacitance of the CNFs was increased by 88% when hot drawing process was applied and carbonized at 1000°C, compared to the sample without the application of the stretching treatment. Copyright © VBRI Press.

Keywords: Carbon nanofibers, hot drawing, supercapacitor, carbonization temperature.

Introduction

Energy systems are experienced problems such as: low energy density, low storage capacity and limited useful life, new alternatives that are more environmentally friendly have been sought. The supercapacitors (SCs) have been considered as promising devices for energy storage in different electrical appliances because they have high power density, high charge/discharge capacity and excellent cyclical stability [1-4].

The SCs can be classified into two types according to their energy storage mechanism: (i) electric double layer capacitors (EDLC) and (ii) pseudocapacitors (PC). The EDLCs store and deliver the electrical energy in the double electric layer without the presence of faradic reactions, which allow them to have a great cyclic stability but a low specific capacitance [5, 6]. On the other hand, PCs mechanism is based on an electrochemical reaction in which a reversible faradic type charge transfer occurs, generally due to the presence of metal oxides. PCs are characterized by high energy density, but they lack high power density [5, 6].

Many electrode materials have been developed to improve the electrochemical performance of SCs. This is the case of carbonaceous materials, they have outstanding properties such as good electrical conductivity, chemical stability and they are abundant

[7]. Among the different types of carbonaceous materials, carbon nanofibers (CNFs) have been considered to be a promising SCs because they have a large surface area, good electrical conductivity and due to their 1-D nanostructure, they are also easy to manufacture [8-12]. The most common method to obtain the CNFs is by means of the electrospinning technique from a polymer precursor such as polyacrylonitrile (PAN) because of its high carbon yield [13-14].

To increase the SCs performance of CNFs, different methods have been proposed, such as an increase in the electrical conductivity by improving the surface area and mixing the CNFs with electroactive materials [15]. For example, Kim *et al.* proposed a method in which the collector system rate of electrospinning changed from 250 to 2000 rpm to obtain aligned CNFs. As a result, the authors improved the electrical conductivity, which allowed them to have a better CNFs electrochemical performance [6].

Tian and coworkers [15] reported a great enhancement in the electrochemical performance of CNFs after the addition of 0.3wt. % graphene oxide (GO), specific capacitance increased from 187.8 Fg^{-1} to 279.1 Fg^{-1}. Similarly, Sharma *et al.* [16] adding up to 0.5% of carbon nanotubes (CNTs) to CNFs and the electrical conductivity of CNFs increased from 1.2×10^4

to 3.1×10^6 Sm^{-1}, which could be a good method to obtain a highly capacitive material.

On the other hand, Li *et al.* [**17**] synthesized micro/mesoporous CNFs (MCNF) embedded with ordered carbon by a simple coaxial electrospinning. They obtained an outer mesoporous carbon shell through the carbonization of Fe-containing PAN shell with a subsequent etching process. Due to the catalytic graphitization by Fe, the ordered carbon that was embedded in the nanofibers, could improve the electrical conductivity of the CNFs. The mesopores were obtained after the removal of Fe-species, which could favor the ion diffusion. The novel MCNF structure exhibited a superior capacitive performance of 26%, in contrast with the CNFs [**17**]. Instead, Ra *et al.* [**18**] activated the CNFs applying CO_2 from 700 to 1000 °C in order to generate a porous structure which allowed them to improve the material's capacitive properties. Increasing the carbonization temperature up to 1000 °C and activating with CO_2, they raise the surface area to 705 m^2g^{-1} obtaining a specific capacitance higher than 100 Fg^{-1}. Recently, Rhee *et al.* [**19**] synthesized CNFs based on PAN and subsequently activated at different temperatures (600-1000 °C) with KOH in order to obtain highly porous structures. They found that an increase in activation temperature improves both the porous structure and the electrochemical performance of the CNFs. However, there is an additional method to improve the electrochemical performance of CNFs, which is a process called hot drawing. In this process, the polymer mebranes are held under a certain weight to induce a mechanical stress and later they are placed in an oven at a temperature that lies between the glass transition temperature (Tg) and the melting temperature (Tm), in order to promote molecular movement [**20-21**]. The drawing process aligns long molecules along the nanofibers longitudinal axis [**22**].

In this paper, we evaluate the effect of the hot drawing process and the carbonization temperature on the electrochemical properties of CNFs. Other works used the hot drawing process to increase the mechanical properties of the CNFs. In this case, we decided to test this method to improve capacitive properties. Initially, we expected, that after the CNFs were obtained, a greater electronic transfer that could improve the electrochemical properties of the material. But, after the application of the stretching treatment, a molecular alignment was induced improving the crystalline structure of the CNFs. As a result, after undergoing the hot drawing and being carbonized at 1000 °C, the CNFs showed a better electrochemical behavior due to the enhancement of the electrical properties.

Experimental

Materials

Polyacrylonitrile (PAN) powder with Mw = 150000 gmol^{-1} was selected as the polymer precursor and it was purchased from Scientific Polymer Products. N, N-dimethylformamide (DMF) was acquired from EMD

Millipore Corporation and selected as the solvent to dissolve PAN. The materials were used as received without further purification.

Fabrication of PAN fibers

We prepared a PAN/DMF solution at 12 wt %. This solution was taken to an electrospinning apparatus to fabricate PAN precursor fiber mats. The electrospinning parameters were adjusted to 8 kV, the distance between the tip of the needle and the collector system was 12 cm and the flow rate was 0.5 mlh^{-1}.

Hot drawing treatment

To promote a molecular alignment in the PAN fibers, the electrospun membranes were hot drawing as shown in **Fig. 1 (b)**. The membranes were held with clamps and a suspended weight equivalent to 10 MPa was used. Steel counterweights equivalent to 98.4 g were used and the membranes cross sectional area was calculated in 0.096 mm^2. All this self-made system was placed in an oven at 140 °C for 15 min. Finally, the mats were allowed to cool in the oven to room temperature reaching a draw ratio of 2x.

Stabilization and carbonization

PAN fiber mats were stabilized to avoid their fusion during the carbonization process. This process was done in air at 285 °C at a heating rate of 5 °Cmin^{-1} and holding the temperature for 2h. Then, samples continue with the carbonization process using a tubular furnace with an inert nitrogen atmosphere. The carbonization temperature was evaluated at 700, 800, 900 and 1000°C, with a 1h isotherm at 5 °Cmin^{-1}. Finally, the samples were allowed to cool to room temperature in the oven. **Fig. 1** shows the process used to produce the CNFs.

(a) Electrospinning　　　**(b)** Hot drawing
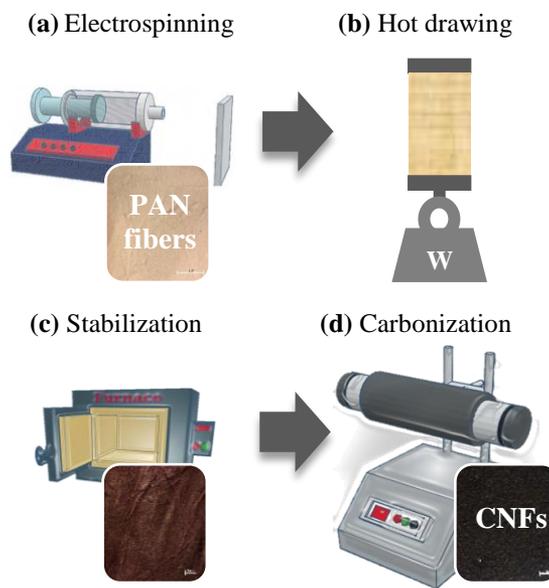
(c) Stabilization　　　**(d)** Carbonization

Fig. 1. Step by step of CNFs manufacturing process: (a) PAN electrospun process, (b) stretching of mats with hot drawing treatment, (c) stabilization process in muffle type oven and (d) carbonization process in tubular furnace.

Characterization

Samples morphology were characterized using scanning electron microscopy (SEM, Phenom World G2 Pro) to evaluate the fiber diameter. The CNFs microstructure was analyzed by Micro Raman (HORIBA Jobin Yvon, model LabRam HR) using a 632 nm laser beam, and by transmission electron microscopy (TEM, Tecnai F20 Super Twin TMP). X-ray photoelectron spectroscopy (NAP, XPS) was used to study the surface chemical composition of CNFs.

The electrochemical performances were measured by the cyclic voltammetry (CV) technique on a potentiostat (Auto Lab) in the potential window of -0.2-0.5 V at scan rate of 10, 20, 30, 40, 50, 80, 100, 200 and 500 mVs⁻¹. The experiments were carried out using a conventional three-electrode system, a platinum mesh as a counter electrode, an Ag/AgCl as reference electrode and 2 mg of CNFs were used directly as the working electrode. They were immersed in 6M KOH electrolyte solution. All experiments were conducted at room temperature The specific capacitance (Cs) was calculated at the discharge stage following the equation (1) [**6**]:

$$C_s = \frac{\int I dV}{\upsilon V} \qquad (1)$$

where, I is the current density at discharge (Ag⁻¹), dV is the potential difference (V) and υ is the scan rate (Vs⁻¹). Galvanostatic charge/discharge curves (GCD) were measured to settle the specific capacitance at 1Ag⁻¹ within the potential window ranged from -0.2V to 0.5V. GCD was calculated following the equation (2) [**6**]:

$$C_s = \frac{I \Delta t}{\Delta V} \qquad (2)$$

where, Δt is the discharge time (s), ΔV is the potential range (V) and I is the discharge current density (Ag⁻¹).

Results and discussion

Morphology characterization

CNFs morphology is presented in **Fig. 2.** They are randomly oriented with uniform diameters and without superficial defects. When the carbonization temperature increased to 800°C, the diameter of the nanofibers was 616 ± 96 nm, representing a diameter decrease of 18.0% with respect to the PAN precursor fibers (751 ± 32 nm); when the temperature reached 900°C, the diameter was 388 ± 41 nm; and at 1000 °C, the diameter was 335 ± 40 nm, yielding a diameter reduction of 48.3 and 55.4% with respect to PAN fibers, respectively. So, when mats were submitted to hot drawing treatment, we noticed that the diameter of the nanofibers decreased to 491 ± 66, 318 ± 44, 310 ± 49 nm at 800, 900 and 1000 °C, respectively.
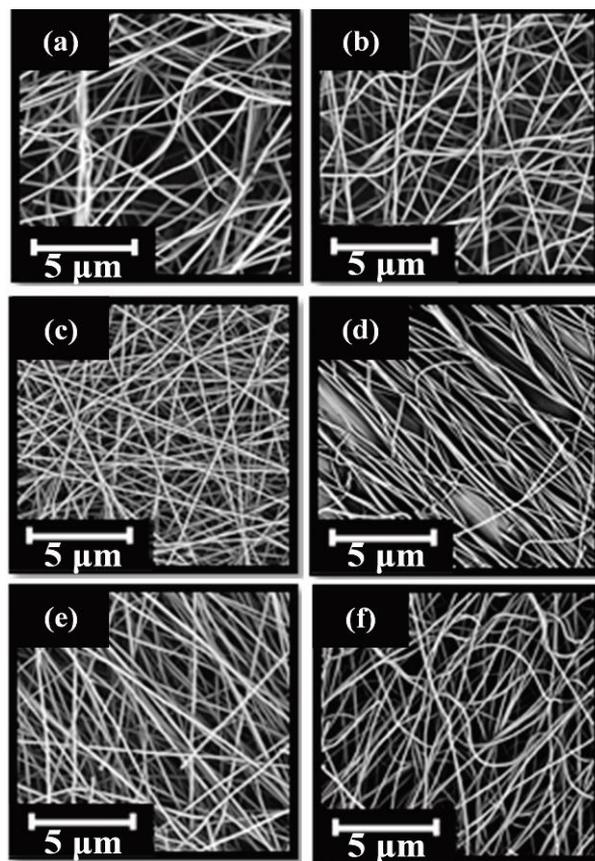

Fig. 2. SEM images of (a) CNFs-800, (b) CNFs-800HD, (c) CNFs-900, (d) CNFs-900HD, (e) CNFs-1000 and (f) CNFs-1000HD.

Microstructure and surface properties

The degree of graphitization was studied by Raman spectrum of CNFs. **Fig. 3** shows two characteristic bands in carbonaceous materials: the D band appears around 1330 cm⁻¹ to 1360 cm⁻¹ and represents the disordered graphitic structure of the CNF and G band, which appears around 1580 cm⁻¹ to 1600 cm⁻¹, indicating the ordered graphitic structure of the samples [**15, 23**]. D and G bands ratio (I_D / I_G) represents the degree of graphitization (R-value) of the material [**24**], a lower R-value represents a higher degree of graphitization, which means that ordered structure predominates in the material [**3**]. For CNFs without the hot drawing treatment (**Fig. 3 (a)**), the R-value was 1.227, 1.095 and 1.058 for carbonization temperatures of 800, 900 and 1000 °C respectively, which suggests an improvement of the graphitic structure after an increase in temperature. Likewise, for CNFs samples with the hot drawing treatment (**Fig. 3 (b)**), the R-value was 1.183, 1.079 and 1.036 for 800, 900 and 1000 °C respectively. It is important to notice that, according to Raman results when applying the hot drawing treatment, there is a decrease in the R-value which indicates that the ordered components were increased. These results are due to the molecular alignment that was induced during the hot drawing treatment. According to this, we expected an increase in the conductivity of the material that facilitate the electron transfer [**25**].
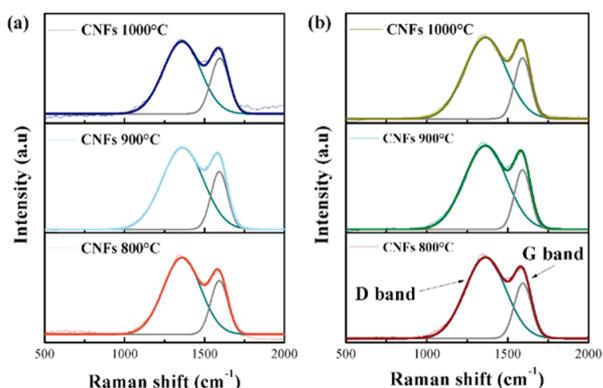
Fig. 3. Deconvoluted Raman spectra of (a) CNFs without hot drawing treatment and (b) CNFs with hot drawing treatment at different temperatures of 800, 900 and 1000 °C.
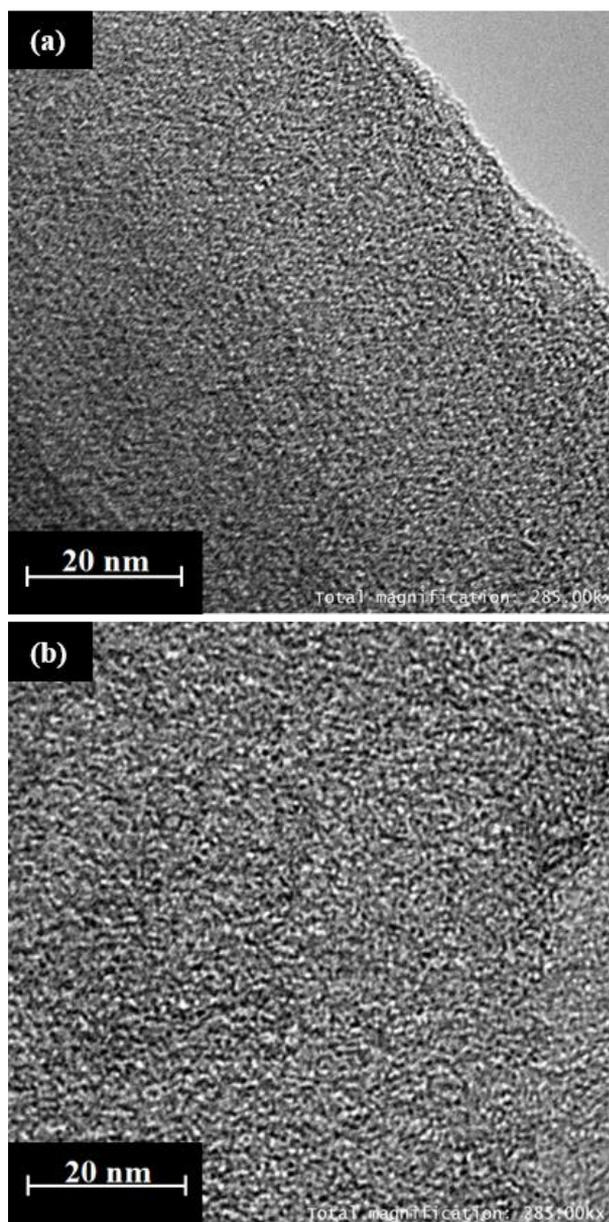

Fig. 4. TEM images of CNFs (a) at 1000 °C without hot drawing treatment with rough-appearance surface and (b) at 1000 °C with hot drawing treatment.

Fig. 4 shows TEM images at 1000°C without and with the hot drawing treatment. CNFs display mainly a turbostatic structure with amorphous carbon. In **Fig. 4 (a)** a rough-appearance structure is exhibit by CNF (see on the borderline). According to Zhu *et al.* [**26**], this appearance favors ionic diffusion and provide sufficient contact area between the active materials and the electrolyte [**26**]. There are not many differences between both treatments, and some crystalline planes were expected to see in the sample with hot drawing treatment (**Fig. 4 (b)**), however, the sample was too thick to see these planes

The chemical surface composition of CNFs by means of XPS analysis is presented in **Fig. 5**, C_{1s}, N_{1s} and O_{1s} signals are marked in the spectrum [**15**]. When temperature increased up to 1000 °C, the N_{1s} signal became weaker, indicating that carbonization was more effective than thermal treatment at 800 °C. **Table 1** shows the elemental chemical composition released from the XPS spectrum. With the increase in the carbonization temperature, the percentage of carbon in the CNFs increased, due to the removal of different non-carbonaceous components, such as, NH_3, H_2O, CO, HCN, N_2 and CO_2. In this way, when the samples were carbonized at 1000 °C, there was an increase of 4.6% of the carbon content with respect to the samples that were carbonized at 800 °C. This increase in carbon in the CNFs could improve the energy storage capacity because there would be an increase in the electrical conductivity of the CNFs.
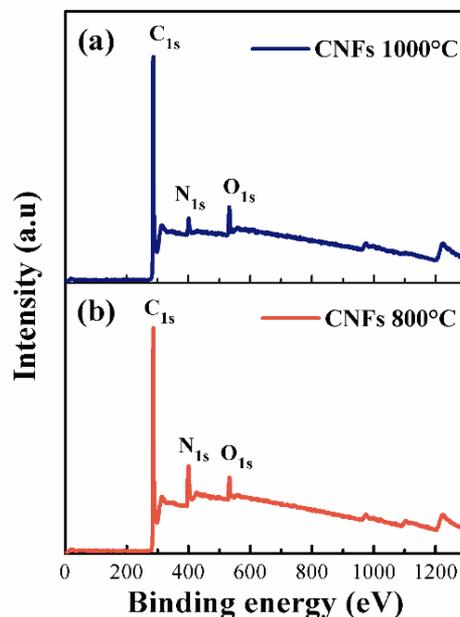

Fig. 5. XPS spectra exhibit the reduction in C_{1S}, N_{1S} and O_{1S} signals from (a) CNFs at 1000 °C without hot drawing and (b) CNFs at 800 °C without hot drawing.

Table 1. Chemical composition of CNFs's surface.

Sample	% C_{1s}	% N_{1s}	% O_{1s}
800 °C	88.17	8.79	3.04
1000 °C	92.21	3.78	4.01

Electrochemical properties

The samples carbonized at different temperatures show a rectangular shape in the CV curves at 10 mVs^{-1}, as indicated in **Fig. 6 (a)**. This behavior corresponds to a typical electric double layer capacitor (EDLC) [**6, 27**].

The Hot drawing treatment effect at 1000 °C at 10 mVs^{-1} is observed in **Fig. 6 (b)**. When the hot drawing treatment was applied, a better capacitive response of the CNFs was obtained. This behavior is related to the molecular alignment of the precursor chains that enhance the material crystallinity, as seen in the Raman results. In the CV curves, small redox peaks appear around -0.35V and -0.25V, associated with the small remaining amounts of nitrogen and oxygen on CNFs surface [**17**], as evidenced by the XPS results.

Fig. 6 (c) shows the specific capacitance at scan rates from 10 to 500 mVs^{-1} calculated according to equation (1). For samples carbonized at 900 and 1000 °C without hot drawing treatment, specific capacitance was 60.66 and 62.29 Fg^{-1} respectively. An increase in carbonization temperature, slightly increased the specific capacitance. However, when hot drawing treatment was applied, the specific capacitance increased up to 93.45 and 117.25 Fg^{-1} in samples carbonized at 900 °C and 1000 °C respectively. An enhance in CNFs crystallinity, increase the specific capacitance by 88% at 1000°C.

Fig. 7 displays the charge-discharge curves of carbonized CNFs at 900 and 1000 °C with and without the hot drawing treatment, at a current density of 1Ag^{-1}. All samples display a typical triangular shape between a potential window of 0.2 and -0.5V, related to EDLC behavior [**6**]. These results are in agreement with CV analysis. From GCD curves, the specific capacitances calculated according to equation (2) at 900 °C were 34.14 (without hot drawing) and 77.50 Fg^{-1} (with hot drawing), and at 1000 °C were 72.98 (without hot drawing) and 98.20 Fg^{-1} (with hot drawing).

All the results follow the same trend as those obtained in CV, and the specific capacitance is improved by the application of the hot drawing process and the increase in carbonization temperature.
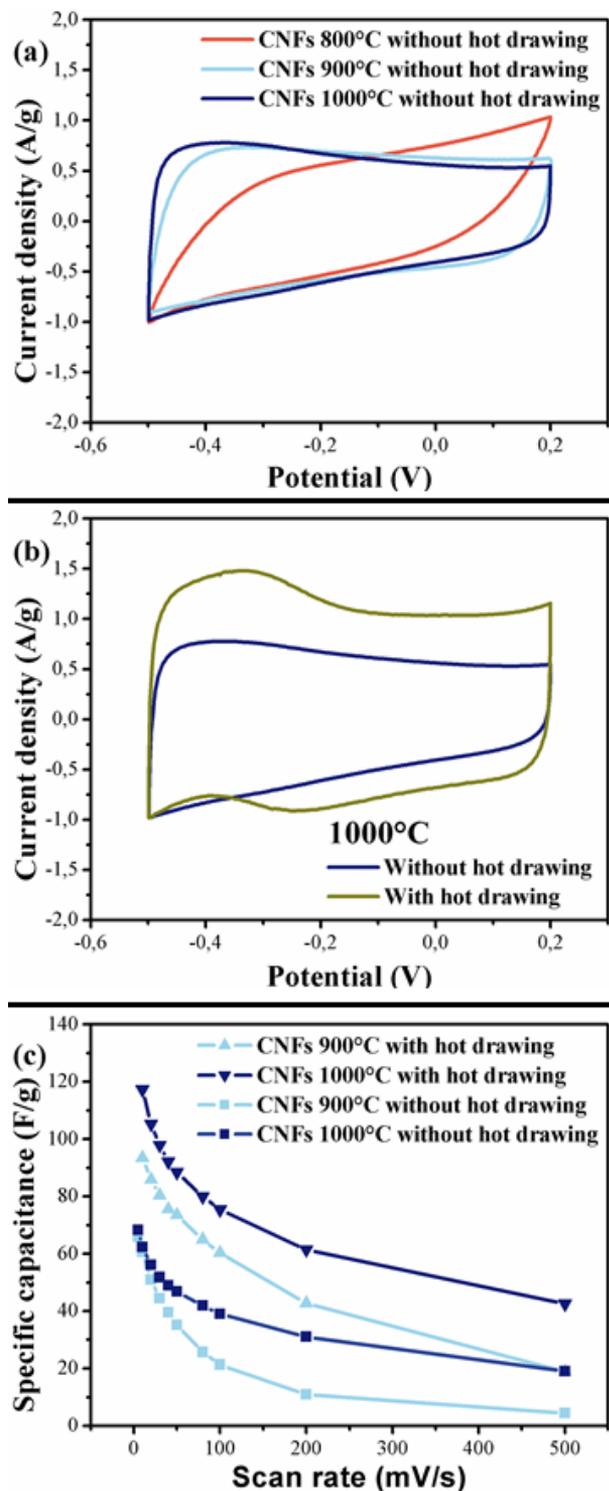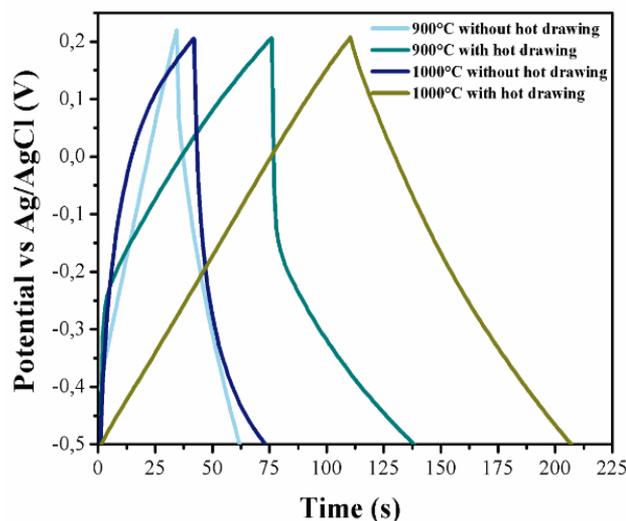

Fig 6. (a) CV curves at 10 mVs^{-1} of CNFs without hot drawing treatment, (b) comparative CV curves of CNFs at 10 mVs^{-1} and carbonized at 1000 °C and (c) specific capacitance curves of CNFs without and with hot drawing treatment.

Fig. 7. GCD curves of carbonized samples at 900 °C and 1000 °C without and with hot drawing treatment.

Conclusions

CNFs were fabricated from electrospun PAN fibers. A hot drawing treatment was applied to the PAN membranes in order to improve the electrochemical properties of the CNFs. According to Raman results, the ordered structure of the CNFs was improved by applying the hot drawing treatment and increasing the temperature up to 1000 °C.

CV and GCD measured the electrochemical properties of the prepared CNFs. The specific capacitance was calculated from the CV curves, showing an increase of 88% for the carbonized CNFs at 1000 °C after the hot drawing treatment, with respect to the 1000 °C sample that did not undergo this treatment. This behavior is justified by the improvement of the crystalline structure of the CNFs after the hot drawing treatment and an increase in the carbonization temperature.

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