KOH-Treated Single-Walled Carbon Nanotubes as Electrodes for Supercapacitors

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Abstract

Electric-arc-obtained single-walled carbon nanotubes (SWNTs) have been chemically activated by treatment with KOH. It results in a development of porosity without destroying the SWNTs entangled structure. The chemically activated sample shows a specific capacitance of ca. 100 F·g^{-1}, maximum energy density of 4 Wh·kg^{-1} and maximum power density of 300 W·kg^{-1}. The electrochemical response of the chemically activated sample is compared with the response found in the raw sample and in a physically activated sample.

Introduction

Carbon materials with high surface area are, in principle, appropriate as electrode materials for electrochemical double layer (ECDL) capacitors. In fact, it is well known that the capacitance is associated with the electrical charge at the electrode-electrolyte interface and thus that magnitude depends on the extent of the surface area. In accordance with this, activated carbons seem to be suitable electrode materials for ECDL capacitors because of their high surface area, (BET surface values can be higher than 2500 m^2·g^{-1}). Most of the commercially available supercapacitors contain activated carbons as electrodes.

On the other hand, carbon nanotubes were soon probed as active electrode materials for ECDL capacitors with initial promising results [1]. Good behavior can be expected from multi walled (MWNTs) and single walled (SWNTs) nanotubes due to their low mass density, morphology, mechanical properties [2] and porous structure. Moreover, values of specific capacitance that are comparable to those exhibited by high area activated carbons can be strikingly reached with carbon nanotubes, although these present lower BET surface areas. This effect is observable at moderately high current drains and it is probably due to the SWNTs structure in form of entangled network and to the mesoporosity that is usually present in the samples [3].

Conventional activation methods for carbons can be applied to develop surface in carbon nanotubes. Chemical activation methods using KOH as reagent are known to lead to very high BET surface areas. MWNTs obtained by means of chemical vapor deposition (CVD) have been previously activated with KOH treatment and an enhancement of specific capacitance has been observed, the increase being up to six times the original value (from 15 to 90 F·g^{-1}) [4]. On the other hand, previous studies in mineral activated carbons [5] and carbon fabrics [6] indicate that the enhancement of specific capacitance after KOH activation is mainly due to surface development but also to the introduction of oxygen containing groups that improve the wettability of the material and can produce some pseudocapacitance contribution.

In the preset work, SWNTs have been chemically activated with KOH and the effect of this activation on the electrochemical behavior has been studied. Specific capacitance, energy density and power density have been measured and compared with those obtained in raw SWNTs and in air oxidized SWNTs. The entangled structure of the SWNTs, which probably favors the electrolyte diffusion, remains after KOH activation. The chemically treated SWNTs show better electrochemical performance compared to the other two samples.

Experimental

SWNTs were produced by the electric-arc method with graphite rods as electrodes and using Ni and Y as catalysts [7], in proportions of 2 and 0.5 atomic % respectively. The raw soot obtained from such experiments is denoted hereafter S. This material was modified through two different activation processes:

i) One consists in a physical activation by means of thermal treatment in air. S was introduced in a furnace at 350 ^{o}C for one hour in air atmosphere without any flux. This sample will be named PAS (physically activated sample).

ii) The other treatment is a chemical activation with KOH similar to that described in reference [8]. S was stirred in a KOH solution (KOH / S weight ratio of 4/1) at 60ª C for two hours. After drying the excess water, the material was pyrolized at 700ª C for one hour (heating ramp 5ª C/min) under nitrogen flux (800 ml/min). It resulted in a 10.66 wt% burnt off. Then the sample was washed with 5M HCl and finally washed with water in a Soxhlet extractor for seven days. This sample will be denoted as CAS (chemically activated sample).

The effect of the activation processes in the structure and porosity was examined by means of transmission electron microscopy (TEM) and gas adsorption (N_2 at 77 K and CO_2 at 273 K), respectively.

S, PAS and CAS were the electrode materials used to assemble ECDL capacitors in two-equal electrode Swagelock type cells. A 6M KOH aqueous solution was used as electrolyte in the three cases. The electrodes were processed as composites, containing 5 wt% PVDF and 95 wt% of the mentioned samples. SWNTs and PVDF were mixed and ground in a mortar. Then, pellets of 13 mm diameter and ca. 0.5 mm thick were compacted by cold pressing at 38 MPa.

Results and discussion

PAS and CAS have the typical entangled microstructure that is characteristic of SWNTs. After the activation processes, SWNTs can be still seen in TEM micrographs as grouped into railway-like bundles (Figure 1).

Porosity data about the samples are included in Table 1 and Figure 2. The BET surface area increases with the activation treatments and is the highest for the CAS. Porosity of S is characterized by the presence of mesopores. The mesopore volume increases after the activation but the mesoporous character of PAS and CAS is not so marked as in S because of the increase in the micropore volume. Moreover, an increase in the amount of the widest micropores related to the narrowest micropores seems to occur through the activation process, as deduced from the increase in the difference between the N_2 micropore volume and the CO_2 micropore volume.

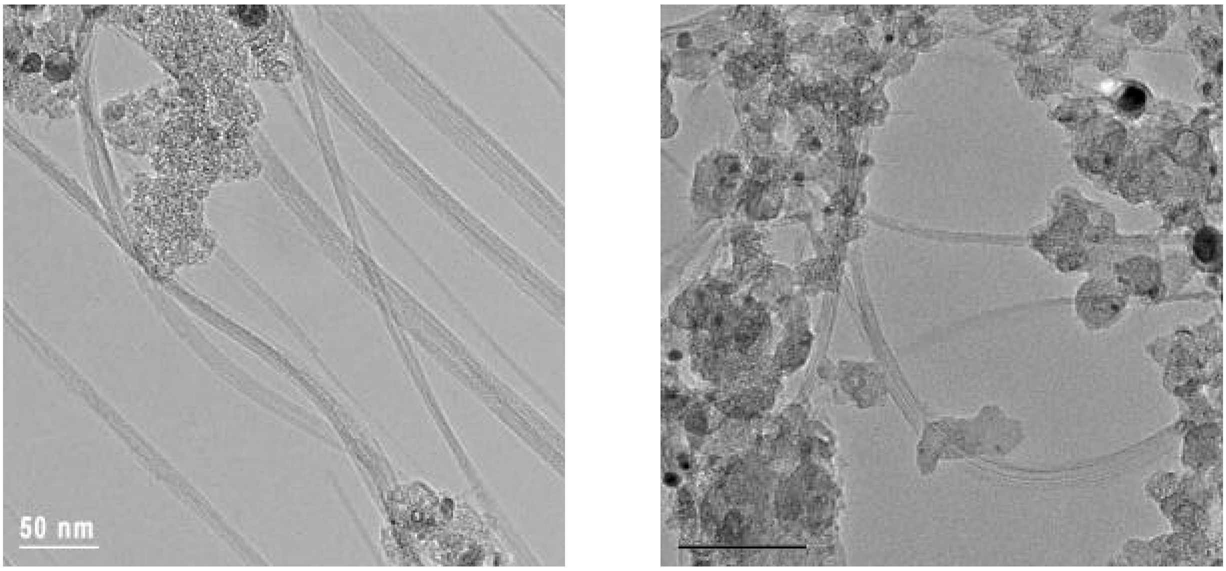

Figure 1. TEM images of PAS (left) and CAS (right).

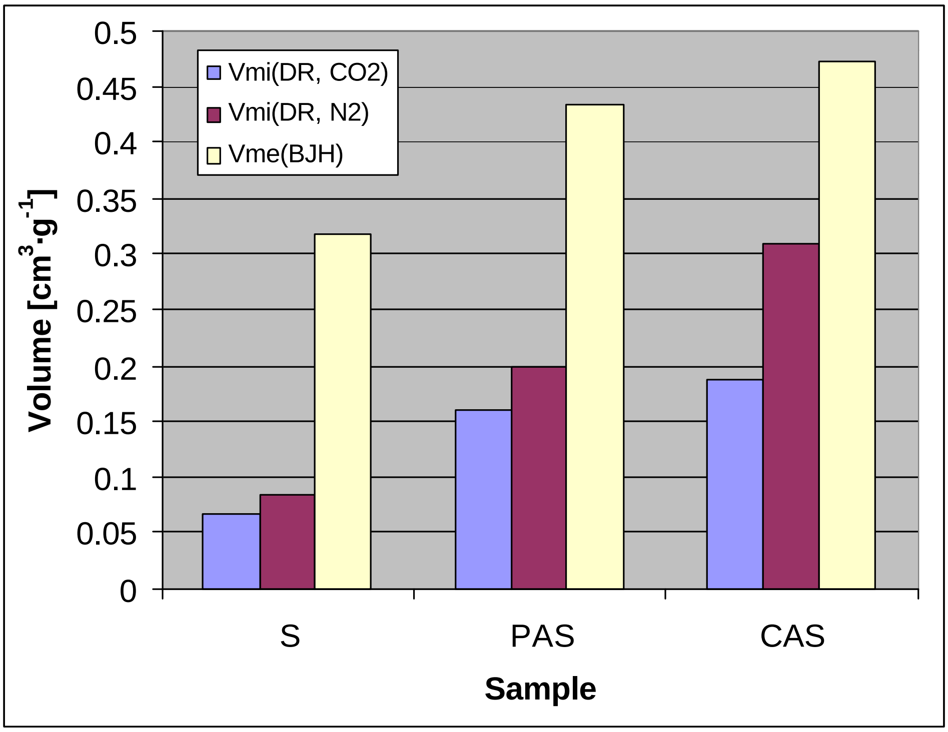

Figure 2. CO_2 Dubinin-Radushkevich micropore volume, N_2 Dubinin-Radushkevich micropore volume and Barrett-Joyner-Halenda mesopore volume for the three samples.

Figure 3 shows a galvanostatic charge-discharge for the capacitor made with CAS as electrode material. From the galvanostatic curves the specific capacitance, energy density and power density have been calculated as usual.

Table 1. Porosity data for the three samples. Pore volume is given in $cm^3 \cdot g^{-1}$ and the BET surface area in $m^2 \cdot g^{-1}$.

	$V_{DR}(CO_2)$	$V_{DR}(N_2)$	$V_{DR}(N_2)$-$V_{DR}(CO_2)$	V_{Me}(BJH)	S_{BET}
S205	0.0666	0.0830	0.016	0.3186	262
S205+350	0.1604	0.1995	0.039	0.4344	552
S205 +KOH	0.1873	0.3103	0.123	0.4717	882

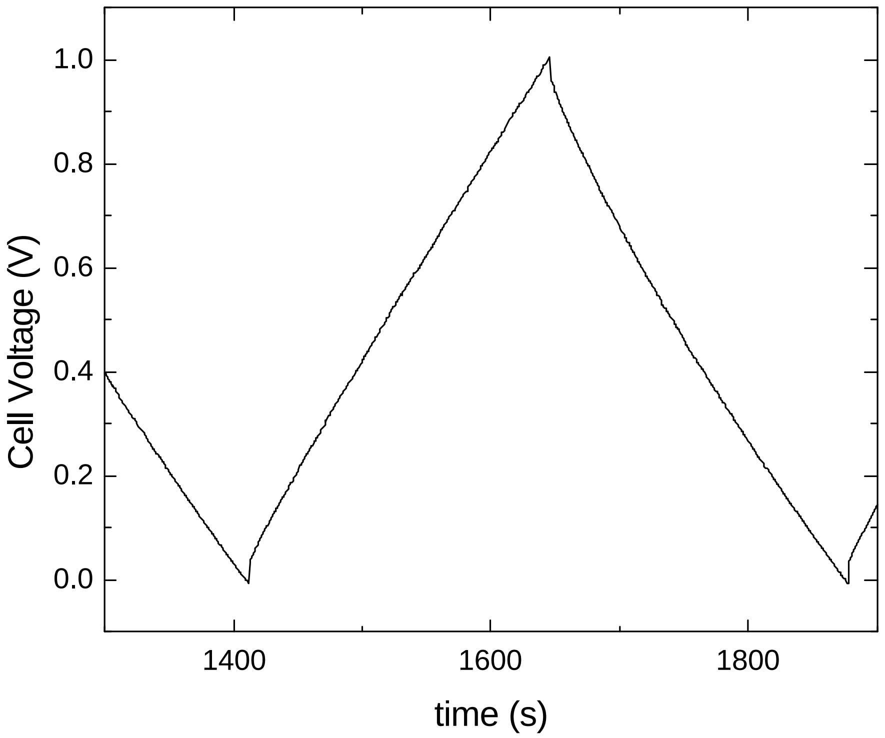

Figure 3. Charge-discharge cycle recorded at 10 mA for the ECDL capacitor containing CAS as electrode material. Aqueous 6M KOH solution was the electrolyte.

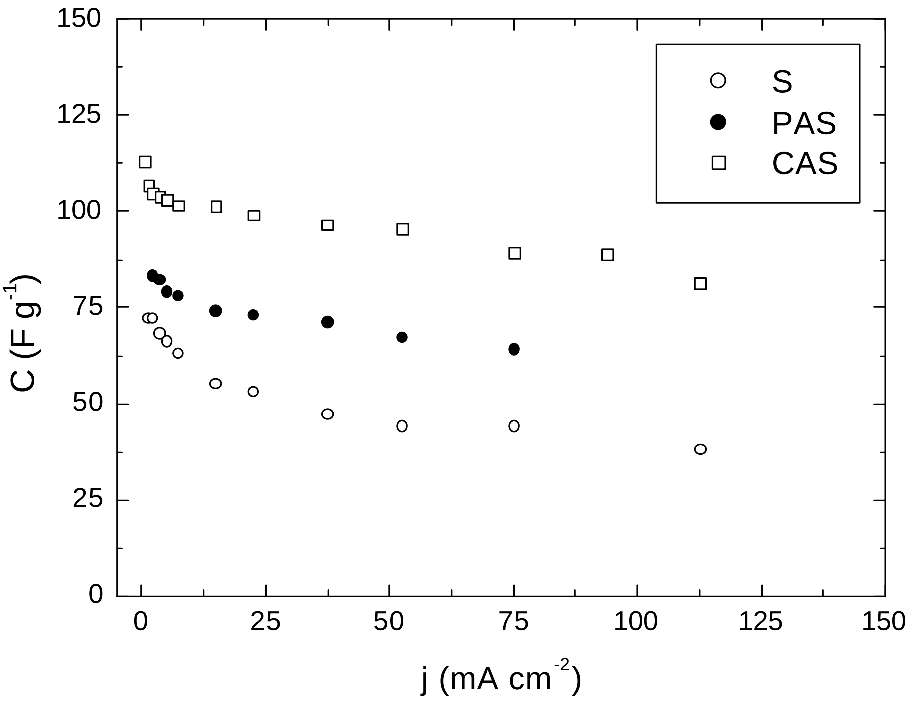

Figure 4. Specific capacitance vs. current density for the three samples of SWNTs.

In Figure 4, the specific capacitance for the three samples of SWNTs is plotted versus the current density (j). The specific capacitance is higher for CAS than for PAS and S. The shape of the specific capacitance curve is similar in the three cases.

Figure 5 shows a plot of power density versus energy density for the three samples. Power density and energy density are higher for CAS compared to the other two samples. The maximum power density is similar for PAS and S. The maximum energy density is higher for PAS than for S.

Conclusions

SWNTs have been physically activated by oxidation in air at moderate temperature and chemically activated in KOH. The entangled structure of the raw SWNTs remains in some extent after the activation. Raw and activated materials have been used as electrodes in ECDL capacitors. We have found that the specific capacitance is higher for the activated materials. The highest specific capacitance of the chemically activated sample agrees with the highest BET area, mesopore volume, micropore volume and the largest amount of wide micropores found in that sample. Moreover, energy density and power density are higher for the chemically activated sample.

Acknowledgements

A Ansón and F Picó thank the CSIC Fuel Cell Network for their respective fellowships.

A Ansón would like to acknowledge D Lozano and JB Parra for fruitful discussions.

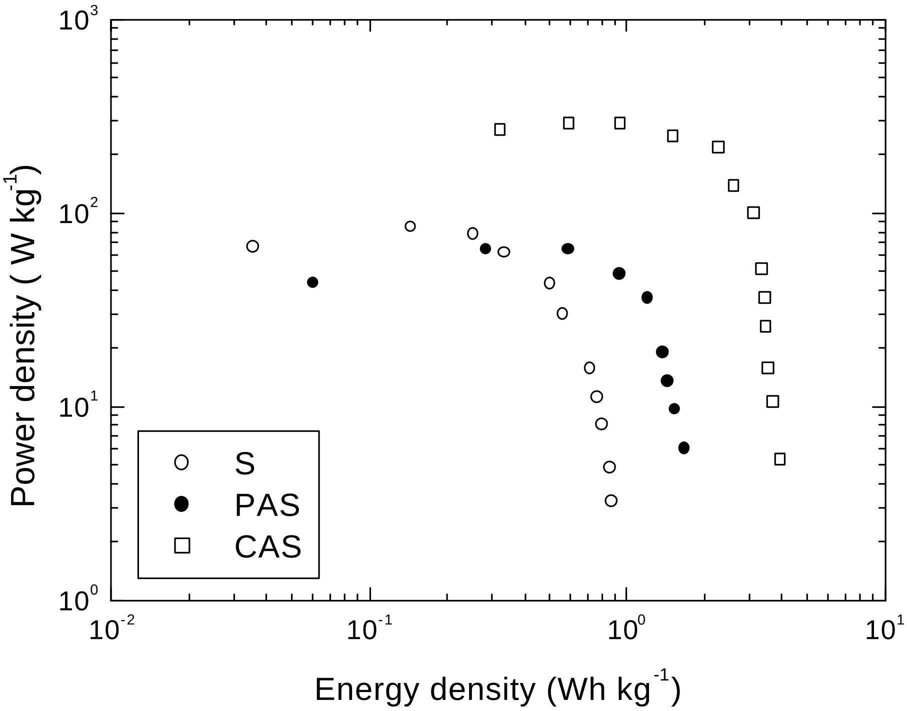

Figure 5. Ragone plots for the three samples of SWNTs.

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