HIGH POWER SUPERCAPACITORS BASED ON BIOPOLYMER/MWCNTs COMPOSITES

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Introduction

One-step carbonization of oxygen-rich biopolymers extracted from seaweeds and seaweeds themselves has been shown to provide very interesting materials for supercapacitor electrodes (Béguin et al. 2006; Raymundo et al. 2006). Due to the high oxygen content of the resulting carbons, e.g., 10-15 wt%, quick pseudofaradaic charge transfer reactions are involved. Capacitance reaches values as high as 260 F/g in aqueous medium, despite the poorly developed specific surface area (200-700 m^2/g). These weakly porous materials present a high density, which makes them more interesting than activated carbons (AC) in term of volumetric capacitance. Additionally, the incorporated oxygen may provoke a potential shift of both electrodes, allowing the operating voltage to be enhanced. The maximum cell voltage for charging reversibly the capacitor can reach 1.0 to 1.4 V whereas only 0.7-0.8 V can be applied with activated carbons. As a consequence, the volumetric energy which can be accumulated with the biopolymer based carbon capacitors is higher than with activated carbons. Moreover, a low capacitance fading was observed after 10000 cycles. In the present work we will show that the power density of such high energy density materials can be improved if a given amount of multi-walled carbon nanotubes (MWCNTs) is introduced before the carbonization step in order to obtain a nanocomposite.

Experimental

MWCNTs obtained by decomposition of acetylene over a Co based catalyst (Delpeux et al. 2002) were dispersed into sodium alginate (Aldrich) or milled seaweeds before carbonization at 600°C during 3 hours under N_2 flow. The final weight percentage of the MWCNTs was fixed to 5wt% and 10wt% considering the carbonization yield of the biopolymers/seaweeds determined before.

The porous texture was analyzed by N_2 adsorption at 77 K or CO_2 adsorption at 273 K (Autosorb-1MP, Quantachrome). The char texture was observed by transmission electron microscopy (Philips CM20). Surface functionality was analysed by using X-ray photo-electron spectroscopy (XPS) with a VG ESCALAB 250 spectrometer (Al Kα monochromatic source).

The electrodes were 1 cm^2 pellets obtained by pressing a mixture of the (alginate char)/(MWCNTs) composite or (seaweed char)/(MWCNTs) composite (90 wt%) together with a binder (PVDF, 10 wt%). For comparison purposes, electrodes were prepared by pressing carbonized alginate or carbonized seaweed (85 wt%) together with 5 wt% carbon black and 10 wt% binder or by pressing carbonized alginate or carbonized seaweed (90 wt%) together with 10 wt% binder. The electrochemical characteristics were determined in 1 mol.L^{-1} H_2SO_4 electrolytic medium, either in two or three-electrode cells, using the galvanostatic, voltammetric and impedance spectroscopy techniques (VMP multichannel potentiostat-galvanostat, Biologic, France).

Results and discussion

Porous Texture and Surface Functionality Characterization

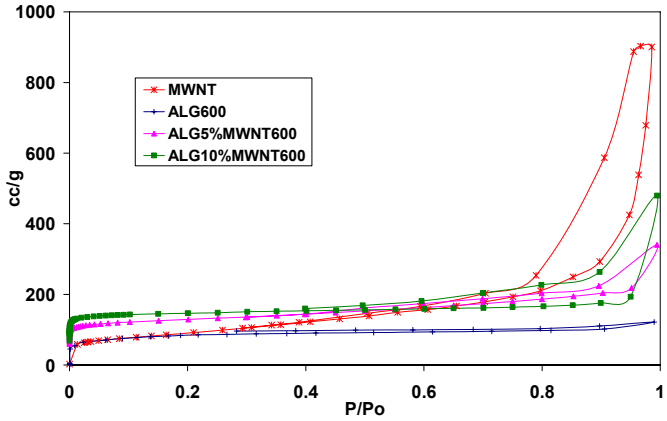

Figure 1. N_2 adsorption isotherms at 77 K for the MWCNTs, the ALG600 char and its composites.

Figure 1 shows the N_2 adsorption isotherms for the sodium alginate-based carbon obtained at 600°C (ALG600) and its composites containing 5wt% and 10wt% of MWCNTs (ALG-5wt%MWCNT600 and ALG-10wt%MWCNT600) in comparison with the MWCNTs. It can be observed that the addition of MWCNTs to the alginate-based carbon gives as result a slight increase of the N_2 adsorption in the range of microporosity and an important increase in the range of mesoporosity. These results, also observed in the case of the carbonized seaweed (SW600), are in concordance with the SEM and TEM analysis. It was clearly seen that the carbonized polymer/seaweed is spread over the MWCNTs and covers them. Thus, a clear templating effect of MWCNTs is produced on the texture of the nanocomposites which adopt the mesoporous texture of the nanotubes. On the other hand, the surface functionality of the carbonized biopolymers is not modified by their carbonization in the presence of MWCNTs and as a result high oxygen content materials are obtained (ALG600: 15 at% O; LN600: 9.6 at% O).

Electrochemical Characterization

Two electrode supercapacitors were built with the different materials in 1 mol.L^{-1} H_2SO_4. Table 1 presents the values of the equivalent series resistance (ESR), related with the resistances of the electrode material, contacts and electrolyte, and the equivalent distributed resistance (EDR), related with the diffusion of ions into the charge storing material, obtained from the impedance spectroscopy experiments. It can be observed that the addition of carbon black does not significantly reduce the resistance of the cell. By contrast, in the nanocomposites realized with MWCNTS, due to the excellent conductivity of MWCNTs and the good propagation of ions favored by the presence of opened mesopores, the resistance of the cells is reduced. In particular, the EDR values related with the diffusion of ions are dramatically diminished.

Table 1. ESR and EDR values obtained by impedance spectroscopy.

Sample	*ESR(10Kz)* *Ω*	*EDR* *Ω*
ALG600	0.48	1.22
ALG600-5wt%Carbon Black	0.46	1.09
ALG-5wt%MWCNT600	0.34	0.57
ALG-10wt%MWCNT600	0.31	0.48
SW600	0.38	1.40
SW600-5wt%Carbon Black	0.39	1.35
SW-5wt%MWCNT600	0.42	0.72
SW-10wt%MWCNT600	0.31	0.52

As a consequence, the SW600 composites with MWCNTs present very interesting performance at high current density (Figure 2). Specific capacitance values as high as 180 F/g can be obtained for the composites containing 10 wt% of MWCNTs at a current density of 50 A/g, whereas the addition of carbon black does not give any benefit. These results confirm that there is an improvement of the charge propagation due to the open mesoporosity given by the nanotubes, which favors the accessibility of ions to the active mass.

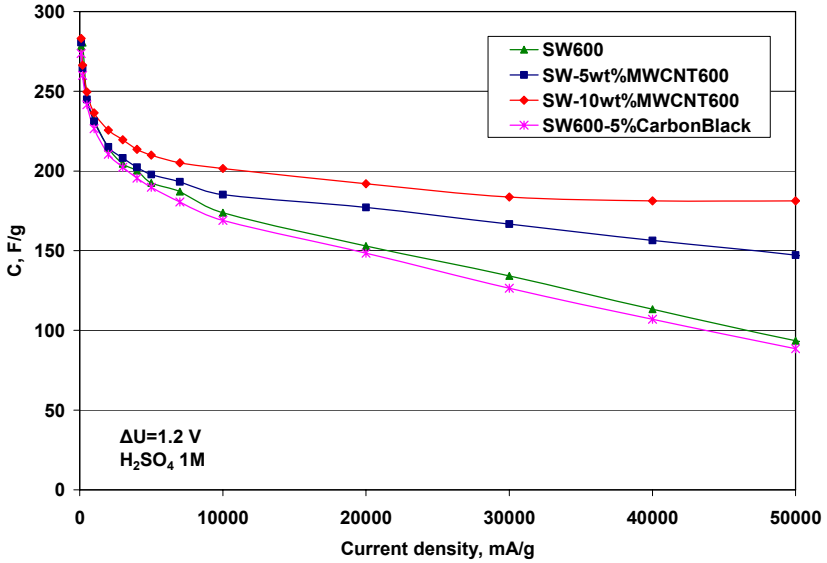

Figure 2. Specific Capacitance vs Current Density for SW600 char and its composites.

This improvement is further reflected in the Ragone plot (Figure 3) showing the available volumetric energy density as a function of the volumetric power density for the same materials as those presented in Figure 2 (SW600 and its composites). The energy extractable from the capacitor at high power density is higher for the electrodes containing the MWCNTs than for the electrodes with only carbonized polymer or with added carbon black. Additionally, in figure 3 the results for two commercial activated carbons, Maxsorb (S_{BET}=3487 m^2/g; 5.0 at% O) and Norit Super 50 (S_{BET}=1402 m^2/g; 4.6 at% O), have been included for enlightening the advantages of the biopolymer based materials as electrodes for supercapacitors in aqueous medium.

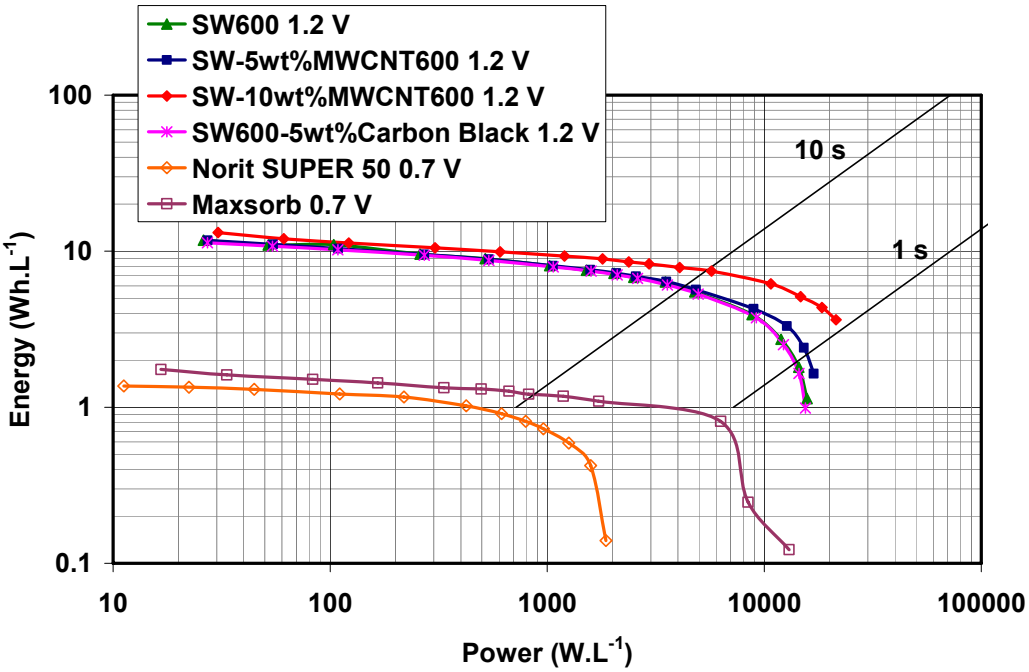

Figure 3. Volumetric Ragone plot for SW600 char and its composites in comparison with ACs.

Finally, another advantage related with the presence of MWCNTs in the carbonized biopolymers is a better cycle life of the systems. After charging/discharging the capacitors with a charge density of 1 A/g between 0 V and 1.4 V during 15 000 cycles, the capacitance lost was reduced from 35 % to 17 % in the presence of MWCNTs for the SW600 material. The composite electrodes are resilient during the charge/discharge of the capacitors, i.e., they can perfectly accommodate the dimension changes produced in the active material without mechanical damages.

Conclusions

The low temperature carbonization of oxygen-rich biopolymers gives materials for supercapacitor electrodes which are more performing than activated carbons in aqueous medium. The carbonisation of such biopolymers in the presence of multi-walled carbon nanotubes adds several advantages in the electrochemical performance of the carbon based electrodes. The MWCNTs have a templating effect, and the texture of the biopolymer char becomes mesoporous. Moreover, the presence of MWCNTs drastically increases the conductivity of the materials. Due to the open mesoporosity and to the high conductivity of MWCNTs, the accessibility of ions to the active mass and the charge propagation are improved. As a consequence, more energy can be extracted at high powers for the composites which contain MWCNTs. In addition, cyclability is improved due to the resilient properties introduced by the MWCNTs in the composites.

References

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