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HIGH TEMPERATURE TREATMENTS OF POROUS ACTIVATED CARBON

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Introduction

The use of biomass waste for the preparation of activated carbon is of great industrial interest for reducing costs and increasing the sustainability, specifically in the field of energy storage. A high temperature treatment is required to obtain a more ordered carbon material, thus increasing its electrical conductivity. However, this high temperature treatment entails as disadvantage significant porosity shrinkage. Therefore, the development of new methods to prepare activated carbons with high conductivity while preserving their porosity development could be of great interest for many applications.

Chemical activation of biomassic waste with H_3PO_4 is a well-known method for the preparation of porous carbon materials. This method allows that, under certain conditions, high amounts of phosphorus to remain stably on the carbon surface, even after a strong washing step. The aim of this work is to analyse the influence of these phosphorus compounds on the physico-chemical properties of different carbon materials thermally treated at relatively high temperatures (1600 ºC).

Materials and Methods

Porous activated carbons were prepared from different carbon precursors (olive stone, lignin and hemp) and conformations (powder, fibers and monoliths). Lignin fibers were prepared by electrospinning of Alcell lignin/ethanol (1/1) and H_3PO_4/Alcell lignin/ethanol (0.3/1/1) solutions[1]. Lignin fibers were stabilized in air at 200 ºC and then activated at 900 ºC (CF900 and PCF900 for pure and phosphorus carbon fibers, respectively). Activated carbon monolith from biomass waste (hemp) and powder activated carbon (from olive stone) were chemically activated at 800 ºC with a weight impregnation ratio of 2 (OS2800 and H2800, respectively). Subsequently, these carbon materials were thermally treated (TT) at 1600 ºC under inert atmosphere. The different samples were characterized by N_2 and CO_2 adsorption at -196 and 0 ºC, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectroscopy. The oxidation resistance of these samples was also evaluated in a thermogravimetric balance. The electrical conductivity of these carbon materials has been assessed using a 2-probe DC system at constant pressure of 1 MPa.

Results and Discussion

Figure 1 shows the SEM micrographs of the carbon materials obtained at high temperature in different conformations. **Table 1** compiles the textural parameters of prepared activated carbons. As can be seen, high temperature treatments of carbon fibers without the presence of P surface groups produced an important contraction of the porosity (from 900 to 150 m^2/g). However, the presence of P-surface groups avoids the collapse of the porous texture during the thermal treatments, allowing the preparation of carbon materials with a well-developed porosity (c.a. 900 m^2/g). Similar trends are observed when the thermal treatments are performed on activated carbons obtained from olive stone and hemp residue (**Table 1)**. It is known that the use of high H_3PO_4 impregnation ratio in the preparation of activated carbons from biomass waste produces carbon materials with large development of wide micro- and mesoporosity, along with surface phosphorus groups. These groups seem to be probably responsible for the low porosity shrinkage after the heat treatment.

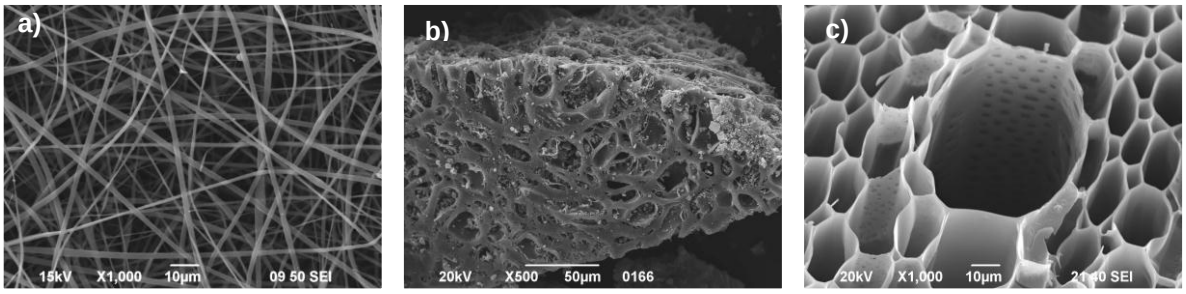

Figure 1. SEM micrographs of activated carbon prepared at 1600 ºC. a) Carbon fibers from lignin, b) powder activated carbon from olive stone and c) activated carbon monoliths from hemp.

Table 1. Textural parameters of carbon materials. Effect of heat treatment at 1600 ºC

	N_2 adsorption					CO_2 adsorption	
Activated Carbon	**A_{BET} (m^2/g)**	**A_t (m^2/g)**	**V_t (cm^3/g)**	**$V_{0.995}$ (cm^3/g)**	**V_{meso} (cm^3/g)**	**A_{DR} (m^2/g)**	**V_{DR} (cm^3/g)**
CF900	840	7	0.33	0.34	0.01	951	0.38
CF900-TT	150	7	0.06	0.07	0.01	506	0.20
PCF900	1143	16	0.45	0.47	0.02	859	0.34
PCF900-TT	822	15	0.33	0.34	0.01	599	0.24
OS2800	1259	362	0.46	1.05	0.59	467	0.19
OS2800-TT	1072	305	0.40	0.90	0.50	392	0.16
H2800	1302	291	0.51	0.91	0.40	495	0.20
H2800-TT	1172	289	0.46	0.85	0.39	217	0.09

An increase of the treatment temperature produces an increase of the structural order (observed by Raman and XRD measurements), a higher oxidation resistance and an enhancement in the electrical conductivity (from 2-5 to ca. 15 S/m) of the final carbon materials. We have previously demonstrated the importance of high electrical conductivity in the use of binderless carbon fibers as electrodes for capacitors with an ultrafast energy storage[2] and that high oxidation resistance correlates with high electrochemical resistance[3]. It is then expected that the increase of electrical conductivity of porous carbon material observed in this work would improve its electrochemical behaviour, especially for support of electrocatalysts and power-hungry applications.

Conclusions

Carbon materials were prepared from different biomass wastes at 1600 ºC. A proper porosity development, structural order and electrical conductivity for the carbon were obtained. Phosphorus surface groups generated during the H_3PO_4 chemical activation process seem to be responsible for avoiding the porous texture contraction during the thermal treatment.

Acknowledgment

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