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Highly conductive microporous carbon fibers by electrospinning of lignin/phosphoric acid/ethanol solutions

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Introduction

Functional carbon fibers are high added-value products with many different applications. Properties such as high surface area, high electrical conductivity, adequate pore size and surface chemistry and elevated oxidation resistance are regarded as more relevant than mechanical ones for functional applications. Most conventional preparation methods use synthetic polymers (mainly polyacrylonitrile) to produce carbon fibers. The use of a low-cost, abundant and greener precursor like lignin would be an interesting alternative from both economic and environmental points of view. In addition, certain functional applications (related to high electrical conductivity and oxidation resistance) requires post-treatments (heat treatment at 1500–3000 ºC) in order to enhance the carbon structural order of the fibers. However, a higher structural ordering is usually related to a lower surface area, what represents a strong disadvantage in some functional applications, such as electrochemical ones. Therefore, the optimization of the post-treatment of the carbon fibers with the goal of increasing both the structural ordering and the porosity development is an important challenge. This contribution reports the preparation of electrospun lignin-based carbon fibers at different carbonization temperatures and the influence of heat treatments at temperatures ranging from 900 to 1600 ºC. The influence of the addition of phosphoric acid in the initial electrospinning solution on the structural ordering, electrical conductivity and porosity development of the final carbon fibers is studied in detail.

Materials and Methods

Alcell lignin fibers were electrospun using a coaxial electrospinning device following the procedure previously reported by our research group [1]. Electrospun H_3PO_4-lignin fibers were prepared in the same device by addition of phosphoric acid to the lignin solution using mass ratios of 0.1 and 0.3. Details about the electrospinning parameters of the latter fibers are given elsewhere [2]. The electrospun fibers were stabilized in air at 200 ºC, using a slow heating rate and carbonized under inert atmosphere at temperatures between 500 and 900 ºC. In addition, the fibers carbonized at 900 ºC were heat treated at temperatures between 1200 and 1600 ºC.

The porosity of the carbonized and heat treated fibers was determined by N_2 adsorption-desorption isotherms at -196 ºC and CO_2 adsorption at 0 ºC. The surface chemistry was analysed by Temperature Programmed Desorption (TPD) and X-Ray photoelectron Spectroscopy (XPS). The microstructure of the carbonized and heat treated fibers has been determined using X-Ray Diffraction (XRD), Raman spectroscopy and High-Resolution Transmission Electron Microscopy (HR-TEM).

Results and Discussion

SEM image in **Figure 1.a** reveals that smooth and continuous carbon fibers with sizes between 500 to 1000 nm were obtained by carbonization of the electrospun lignin fibers. When phosphoric acid is incorporated, the average diameter increases to 2.3 μm (**Figure 1.b**), due to the larger flow rate requested in the electrospinning device. **Table 1** presents the textural perameters and surface chemistry of the carbonized and heat treated fibers. Surface area (S_{BET}), microporosity (V_t^{N2} and V_{DR}^{CO2}) and the average micropore size ($V_t^{N2} > V_{DR}^{CO2}$) increase with the addition of phosphoric acid. The high temperature heat treatment removes most of the heteroatoms (O, P) for both carbon fibers. However, the surface area of the phosphorous containing carbon fibers is mostly preserved after the heat treatment, while a large porosity shrinkage is observed for the pure lignin-derived fibers (see the S_{BET} of 20 m^2/g in pure lignin-derived fibers vs S_{BET} of 840 m^2/g for the fibers prepared using H_3PO_4 ratio of 0.3, **Table 1**). Thus, microporous carbon fibers with large electrical conductivity values have been obtained by heat treatment at 1600 ºC of P-containing electrospun carbon fibers.

Even though Raman and XRD results point out that the microcrystallite size is mostly unaffected by the presence of phosphorus in the heat treated fibers, HR-TEM revealed that these microcrystallites are parallel-oriented in the absence of phosphorus. XPS after argon sputtering confirmed the presence of larger concentration of P in the core of the fibers. These P atoms could be intercalated between the microcrystallites, avoiding the alignment of the microcrystallites during the heat treatment, which originates the porosity shrinkage of P-free carbon fibers.

Table 1. Porosity and surface chemistry of carbonized fibers

H3PO4 ratio	T ºC	S_{BET} m^2/g	V_t^{N2} cm^3/g	V_{DR}^{CO2} cm^3/g	O %	P %
0	900	840	0.33	0.38	4.1	--
0	1600	20	0.00	0.10	1.8	--
0.3	900	1140	0.45	0.34	7.4	2.4
0.3	1600	820	0.33	0.24	1.8	0.3

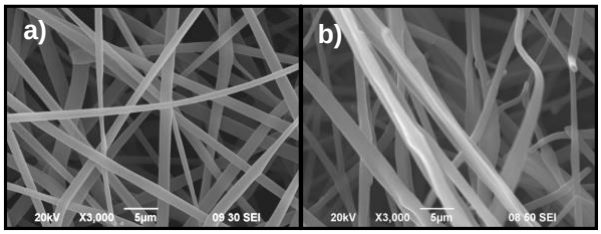

Figure 1. SEM images of carbon fibers prepared at 900 ºC from electrospun lignin solutions with a) no H_3PO_4 and b) H_3PO_4 ratio of 0.3

Conclusions

Microporous carbon fibers with large electrical conductivity can be prepared by electrospinning of H_3PO_4-contaning lignin solutions followed by carbonization at 900 ºC and a heat treatment at 1600 ºC. Phosphorus heteroatoms in the core of the carbon fiber act as pillarlets of the porosity structure, while their presence does not affect negatively to the electrical conductivity of the carbon fibers.

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