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Activated Carbon Bio-Xerogels as Electrodes for Super Capacitors Applications

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Abstract

The objectives of this work are to evaluate the use of the lignin as precursor of carbon xerogels and to determinate the effect of porosity and surface functionalities on the electrochemical capacitance of the activated carbon bio-xerogels. Lignin replaced the resorcinol at a mass fraction between 0 and 0.086 (wt%). The organic carbon xerogels are H_3PO_4-activated at H_3PO_4/carbon ratio of 1/1 at 450 ºC to increase pore volume and surface area. Gravimetric capacitance values at 0.125 A/g, in a three-cell configuration, ranged from 138 to 234 F/g. Sample with a 0.086 content of lignin showed the best electrochemical behavior, which was associated with the high BET surface area (1243 m^2/g), high volume ($W_0(N_2)$= 0.518 cm^3/g) and width micropores ($L_0(N_2)$= 1.43 nm) and to the presence of pseudo faradic effects.

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Keywords: Lignin; Activated carbon xerogels;Supercapacitors

1. Introduction

Since their synthesis by Pekala [1], carbon gels have been widely studied due to their interesting properties like high surface area, controlled porous structure, low bulk density, electrical conductivity, etc., that make them suitable for several applications such as catalyst support [2,3], insulator [4], electrode for supercapacitors [5,6], fuel cells [3,7], etc. All carbon xerogels properties can be designed by using different precursors, synthesis conditions, drying methods, thermal treatments and/or activation processes. However, the raw materials and long production process are quite expensive so the resulting products are not yet widely commercially available; currently it has been demonstrated that new and cheaper precursors, as lignin, can be used keeping their textural properties; normal convection drying and chemical activation also help to reduce costs [8].

Lignin is the second most abundant biopolymer after cellulose. It is extremely low cost and of phenolic nature. It has been found that lignin is an excellent precursor of activated carbon and bioadsorbent, thanks to its high molecular weight polymer complex structure and the presence of different high electron density functional groups such carboxylic, carbonyl, hydroxyl and ketone [9].

Although several works synthetize carbon gels with lignin, having good textural properties [10–12], there is no further information about their performance on the multiple applications of carbon gels, mainly electrode for supercapacitors. Supercapacitors are a promising technology that could replace batteries in different areas like load levelling and electrical energy

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storage devices; they also could be used in applications that required rapid charge/discharge, high power, etc. [13].

In this work, lignin carbon xerogels were prepared by chemical activation with phosphoric acid. The main objective is to investigate the effect of lignin incorporation on porosity, surface functionalities and their electrochemical capacitance.

2. Experimental Details

2.1. Preparation of activated carbon bio-xerogels

Lignin was supplied by Propal Company (Cali, Colombia) obtained by extraction of black liquor from alkaline pulping process and was obtained according to the methodology showed in [14]. Soda lignin was precipitated from sugar cane bagasse soda pulping black liquor by acidification with sulfuric acid at 98 % until the pH of the resultant solution was close to 2.The precipitate was washed with water until the pH of the rinse was close to 6, dried in an oven at 105 ºC for 24 h, and a dark-brown powder was recovered.

The organic bio-xerogels, CG, were prepared by the sol-gel polymerization reaction of resorcinol (R) and lignin (L) with formaldehyde (F) in water (W) using sodium hydroxide as catalyst (C). Resorcinol was partially replaced for Lignin at different percentages as showed in Table 1. The (R+L)/F, (R+L)/W and (R+L)/C mass ratios were kept constant at 1.86, 0.62 and 90.3, respectively. The mixtures were cured at 85 ºC for 5 days, cut into 5 mm pellets, washed several times with ethanol and dried at atmospheric pressure at 40 ºC up to constant weight of dry gel. Table1 also are presented the pH of initial dissolutions and the bulk density of the dried organic xerogels.

Portions of organics xerogels were ground and sieved between 0.5 and 1 mm and impregnated with a H_3PO_4 aqueous solution to give H_3PO_4/carbon weight ratio of 1/1. The slurries were heated at 450 ºC for 2 h, washed several times with water and finally dried at 120 ºC. The resultant activated carbon xerogels were termed as CG0A, CG22A and CG27A, according to the percentage of lignin added.

Table 1. Mass fractions, mass ratio and pH of initial dissolutions and bulk density dried organic bio-xerogels.

Sample	L (m.f.)	R (m.f.)	W (m.f.)	F (m.f.)	NaOH (m.f.)	L/(L+R)*100 (*wt/wt*)	R/L (*wt/wt*)	pH	ρ_b (g/*cm*^{3})
CG0	0	0.316	0.511	0.170	0.0044	0	---	7.27	0.967
CG22	0.070	0.246	0.511	0.170	0.0044	22	3.55	6.51	0.595
CG27	0.086	0.230	0.511	0.170	0.0044	27	2.68	5.99	0.552

2.2. Physic-chemical and electrochemical characterization methods

All materials were characterized by N_2 and CO_2 adsorption at -196 °C and 0 ºC, respectively. Adsorption isotherms were measured with an Autosorb 1 from Quantachrome after outgassing samples overnight at 110 ºC under high vacuum (10^{-6} mbar). N_2 adsorption isotherms were analyzed by BET equation, from which the surface area, S_{BET}, was obtained. The Dubinin-Radushkevich (DR) equation was applied to N_2 and CO_2 adsorption isotherms at -196 and 0 ºC, respectively, yielding the micropore volume, W_0, and the characteristic adsorption energy, E_0. The mean micropore width is given by $L_0=24/E_0$, this equation is valid for E_0 values lower than 20 kJ/mol, which correspond to pore widths higher than 1.3 nm [15].

The volume of nitrogen adsorbed at a relative pressure of 0.95, $V_{0.95}$, was considered as the total pore volume measurable obtained from the N_2 adsorption isotherms. The mesopore volume, V_{meso}, was obtained from the difference between $V_{0.95}$ and $W_0(N_2)$ [16]. The pore size distributions (PSDs) were obtained from N_2 isotherms by application of density functional theory (DFT) model [17], considering slit–shaped pores.

Chemical and structural differences between raw lignin and activated carbon xerogels were analyzed by Total Attenuated Reflectance (ATR). All spectra were constructed at the region from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans. For ATR was used a FTIR spectrometer (Nicolet 6700) equipped with an ATR crystal in type IIA diamond mounted on tungsten carbide. Diamond ATR has a sampling area of approximately 0.5 mm^2, which applies a constant pressure to each sample. The weight loss behavior of the samples was measured using a thermobalance Mettler Toledo TGA/SDTA 851 E. Samples were heated to 1000 °C at a heating rate of 10 °C/min under N_2 flow.

The activated carbon xerogels were analyzed by scanning electron microscopy (SEM) by using a microscope Jeol JSM 5910 LV operated at 10 KV equipped with backscattered and secondary electron detectors coupled with Energy Dispersive Spectrometry (EDS). Surface acid groups on activated carbons were determinated by titration with NaOH [18].

Electrochemical measurements were carried out in a multichannel potentiostat Biologic VMP at room temperature using 1 M H_2SO_4 as electrolyte using a typical three- and two-cell configuration. The working electrodes were prepared by using a graphite paper pasted with a homogeneous mixture of the finely ground activated carbon xerogeles, acetylene black, and binder (polytetrafluoroethylene, PTFE) at mass ratio of 80:10:10. Cyclic voltammetry (CV), Chronopotentiometry (CP) and Electrochemical Impedance Spectroscopy (EIS) techniques were applied to estimate the presence or lack of pseudocapacitance effects of the carbon electrode materials [19] and gravimetric capacitance value. The gravimetric capacitance, C_{CP} (F/g), was