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Nitric acid functionalization of carbon monoliths for supercapacitors: Effect on the electrochemical properties

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ABSTRACT

Activated carbon monoliths and oxidized carbon monoliths are prepared from *Eucalyptus grandis* wood by pyrolysis and subsequent activation under CO₂ (aCMs) and further functionalization using nitric acid (ox-aCMs). Their textural and chemical properties are compared and the electrochemical characteristics as supercapacitor electrodes are tested. The nitric acid treatment does not produce substantial changes in the textural properties of the monolith obtained. Elemental analysis and X-ray photoelectron spectroscopy (XPS) reveal that the oxidized monolith presents a high content of oxygenated functional groups that can participate in pseudocapacitive reactions. This determines that the oxidized monoliths have higher electrical capacitance (80 F cm⁻³) at low current densities and higher energy density (up to $W_v = 2.7 \text{ W h L}^{-1}$) than the non-oxidized ones. The supercapacitor cell containing the oxidized monoliths presents higher total resistance values and response time compared to the non-oxidized monolith. The non-oxidized monolith showed the highest power density (up to $P_v = 94.5 \text{ W L}^{-1}$).

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Introduction

Electrochemical capacitors also called supercapacitors, have the potential to become the most important devices for electrical energy storage in the future [1–4]. Electrical double-layer capacitor (EDLC) is based on the physical adsorption/

desorption of electrolyte ions onto the surface of electrodes [1,2]. Activated carbons are the most widely used materials for EDLC electrodes due to its high surface area, electrochemical stability and high electrical conductivity [1,2,5,6]. Furthermore, carbon materials may have different types of oxygenated and/or nitrogenated surface functional groups. These functional groups can also be introduced through different chemical

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treatments such as nitric acid functionalization [7]. Some functional groups are electrochemically active in acidic electrolyte and can contribute to the total capacitance by reversible redox reactions, phenomenon known as pseudocapacitance [1,2,5,8–11]. Even though the positive impact of these functional groups in the total capacitance is well known, issues related to the effect of these groups on other important parameters associated with the supercapacitor application must still be clarified [12].

Activated carbons are currently prepared from a precursor, such as a polymer, mineral carbon or some kind of biomass wastes [13]. Regarding the latter, biomass wastes are a renewable source, available in large amounts, and still at low cost [14]. The use of biomass derived carbons as active electrode materials for supercapacitors has been reported in the last years [15–17]. On the other hand, carbon monoliths are pieces of carbon without binders or other additives. They have been tested as supercapacitor electrodes and they show higher electrical conductivity and better structural integrity than the electrodes processed with binders [18–21]. Also, some type of carbon monoliths may have higher mass per geometric area, allowing the direct assembly of monolithic electrodes of several milligrams into the supercapacitor cell [20]. Carbon monoliths can be prepared from various precursors and by using different procedures: block-copolymer assisted synthesis [21], fiberboard [22], biomass materials [23,24], and others [20,25–27]. Recently, we have reported that carbon monoliths obtained from *Eucalyptus grandis* wood, with high consistency, large porosity and very good electrical conductivity, exhibited excellent electrochemical performance as compared with conventional electrodes made from powdered activated carbon [28].

In this work, activated carbon monoliths (aCMs) were prepared from *E. grandis* wood by pyrolysis and subsequent activation under CO_2 . In order to increase the content of oxygenated functional groups of the monoliths, oxidized carbon monoliths (ox-aCMs) were prepared from aCMs by nitric acid treatment. These two types of carbon monoliths were compared considering textural and chemical properties and their different electrochemical parameters associated with the supercapacitor application.

Experimental

Samples preparation

Activated carbon monoliths (aCMs) and oxidized activated carbon monolith (ox-aCMs) were prepared from parallelepiped pieces of *E. grandis* wood (WMs). The pieces were cut in the transversal direction of the wood tree trunk as described by Cuña et al. [28]. Carbon monoliths (CMs) were obtained by pyrolysis of WMs at $900\text{ }^\circ\text{C}$ for 2 h under N_2 (99.998%) flow (200 mL min^{-1}). Subsequent activation under CO_2 flow (200 mL min^{-1}) at $800\text{ }^\circ\text{C}$ for 2 h allowed obtaining the activated carbon monoliths (aCMs). All the thermal treatments were carried out in a horizontal Carbolite (CTF 12/75) furnace and the heating rate was $2\text{ }^\circ\text{C min}^{-1}$. ox-aCMs were obtained by nitric acid oxidation of the some aCMs samples at $100\text{ }^\circ\text{C}$ for

8 h in 8 M HNO_3 solution. These conditions were selected considering the results obtained by Liu et al. [29].

Textural characterization

Textural parameters were obtained from N_2 adsorption–desorption isotherms at 77 K on the unmilled monoliths using a Beckman Coulter SA 3100 apparatus. Before the experiments, degasification of monoliths was performed at $200\text{ }^\circ\text{C}$ and 10^{-2} Pa for 20 h.

The analysis by the Dubinin–Radushkevich equation led to the volume of the micropores, W_0 , the average micropore width, L_0 , and the micropore surface area, S_{mic} [30] (listed in Table 1).

Chemical characterization

Elemental analysis

Carbon monoliths were characterized by elemental analysis using a Termo Scientific Flash 2000 instrument. Ash content was determined as in ASTM D2866 norm.

XPS

X-ray photoelectron spectroscopy (XPS) was performed in an Omicron-SPHERA station using Al $K\alpha$ radiation (1486.6 eV). The anode was operated at 225 W (15 kV, 15 mA). Survey spectra were recorded with a 50 eV pass energy. The C 1s region was recorded with a higher resolution (pass energy of 10 eV). The detection angle of the photoelectrons (Θ) with respect to the sample surface (take-off angle) was fixed at 53° for all measurements. The C 1s signal from adventitious carbon at 285 eV was used as an internal energy reference.

Electrochemical analysis

Two-electrode Swagelok®-type cells having two tantalum rods as current collectors were used for galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) measurements. A glassy microfibre paper (Whatman 934 AH) was chosen as separator. aCM and ox-aCM with a cross-section area of $0.40\text{--}0.48\text{ cm}^2$ and thickness of 0.20 cm were utilized as electrodes. The weight of the electrodes was between 41 mg and 47 mg. A 2 M H_2SO_4 solution was used as electrolyte. Before the cell assembly, the electrodes were soaked in the electrolyte under vacuum ($\approx 3 \cdot 10^3\text{ Pa}$) for 24 h.

The specific and volumetric capacitances were determined from galvanostatic charge/discharge measurements in the voltage range of 0–1 V at current densities in the range $1\text{--}70\text{ mA cm}^{-2}$. The specific capacitance C_s was determined at each current according to the equation: $C_s = 2 I t_d / E_2 m_e$, where I is the current applied, t_d is the discharge time, E_2 is the voltage range during the discharge, and m_e is the mass of one

Table 1 – Textural properties and bulk density (ρ).

Sample	W_0 ($\text{cm}^3\text{ g}^{-1}$)	S_{mic} ($\text{m}^2\text{ g}^{-1}$)	L_0 (nm)	ρ (g cm^{-3})
CM	0.16	406	0.80	0.53
aCM	0.22	603	0.75	0.50
ox-aCM	0.23	643	0.73	0.43

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