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Asymmetric capacitors using lignin-based hierarchical porous carbons

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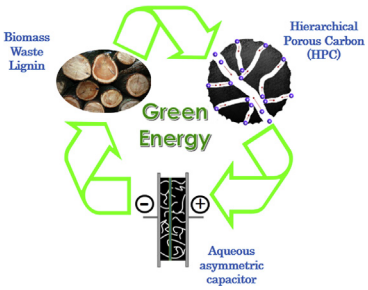
HIGHLIGHTS

- Green supercapacitors constructed with lignin-based HPC in aqueous electrolyte.
- Asymmetric design allowed to safely expand the voltage to 1.4 V.
- Performance comparable to commercial activated carbon in spite of its lower porosity.
- Higher power densities can be achieved with the HPC compared to commercial AC.

GRAPHICAL ABSTRACT



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ABSTRACT

Hierarchical porous carbons (HPC) were fabricated from lignin by hard template method using Beta and Y zeolites as templates. Textural properties were dictated by the hard template, obtaining a bi-modal pore size distribution with similar micropore sizes but different mesopore sizes. These HPCs provide a well-connected and developed porosity that show capacitance values near to 140 F g^{-1} in 1 M H_2SO_4 at 1 A g^{-1} and a capacitance retention of ca. 50% and 40% when the specific current is increased from 1 to 64 A g^{-1} for the Y and the Beta-based carbons, respectively. A symmetric capacitor working at 1.2 V with energy densities of 4.2 Wh kg^{-1} at 1.3 kW kg^{-1} has been obtained using the Beta-based HPC. Asymmetric in mass design allowed to operate the capacitor safely at 1.4 V, yielding an energy density of 6.3 Wh kg^{-1} at 1.3 kW kg^{-1}, an increase of 50% with respect to the symmetric configuration, while keeping a maximum power near to 50 kW kg^{-1}. This capacitor has an energy density comparable to that of a symmetric supercapacitor built using a commercial activated carbon of much higher porosity development, outperforming it in terms of energy, coulombic efficiencies and maximum power.

1. Introduction

The ever increasing energy demand along with the environmental concerns of our society have generated a need for new and more sustainable techniques, devices and materials for the production and storage of energy. In the field of supercapacitors, carbon materials have taken the role as electrode materials due to the combination of excellent performance (high electrical conductivity, high surface area and pore volume) and electrochemical stability with a reduced production cost.

Supercapacitors are of high interest since their features

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complement other energy production and storage devices, such as batteries and fuel cells. Their most relevant parameter is the power density, which allows them to serve in power-demanding applications where other devices cannot be employed, such as consumer electronics, electric vehicles and power management [1]. The high power density of supercapacitor arises from their energy storage mechanism, which is based in the electrostatic interaction between the polarized surface of the porous carbon electrode and the ions of the electrical double layer formed in the electrode-liquid interface [2]. When increasing the sustainability and safety and reducing the toxicity of supercapacitors by using greener materials for electrodes (as sustainable carbon materials) and electrolytes (i.e. aqueous-based electrolytes), it is mandatory to preserve the power characteristics of these devices, while increasing as much as possible the energy density of the novel systems.

For keeping a high power density, it is necessary to combine a carbon material of high electrical conductivity and good ion transport through the pore network with an electrolyte of high ionic conductivity. Aqueous-based electrolytes are the best suited in this sense, although their small stability potential window have traditionally hampered their use, since it reduces the energy density of the cell. Recently, it has been shown that the stability of the potential window of aqueous electrolytes can be expanded by modifying the surface chemistry of the porous carbon electrodes [3–8]. Another strategy for increasing the voltage of aqueous-based electrolytes is the use of asymmetric configuration in mass electrodes [9], being optimized from the balance of charge by using the maximum allowable potential window of each electrode [10]. Its implementation has allowed to reach cell voltages as high as 1.9 V in aqueous-based electrolyte [11], being highly helpful for the development of more sustainable supercapacitor devices based on greener electrolytes and carbon materials.

On the material side, the power characteristic of the materials is also connected to the electrical conductivity and the ion mobility in the pore network [1,12,13]. The use of zeolite templated carbons, which are hard templated carbon materials obtained as the negative replica of a parent zeolite infiltrated with a carbon precursor [14,15], has proven that an ordered arrangement of highly interconnected pores leads to enhanced capacitance retention under high power demanding conditions [16]. A direct comparison between the electrochemical performance of the highly microporous Maxsorb and activated ordered mesoporous carbon demonstrated that the presence of mesopores in the pore size distribution also contributes to promote the capacitance retention of the electrodes, since it facilitates the use of the surface of the micropores [17]. As for the arrangement of porosity, hierarchical porous carbons, where pores with different sizes are spatially ordered in the structure of the carbon material, have demonstrated that the presence of mesopore reservoirs connected to the micropores allow fast and smooth ion diffusion between micropores and mesopores, delivering an improved capacitance retention compared to other carbon materials with meso and micropores that are disordered [18].

Finally, the production of carbon materials from green, renewable and sustainable sources is of high interest [19]. In this sense, the use of lignocellulosic raw materials or processed fractions for the synthesis of porous carbon materials is straightforward, and lignin is one of the better placed materials for fulfilling that purpose [20]. Thanks to its low cost, high carbon content and high aromaticity, the use of lignin as raw material for the preparation of advanced carbon materials has been in the focus of the scientific community for a long time, and since the rise of the wood-to-ethanol bio-refineries, where lignin is also obtained as a by-product in large amounts, the development of novel value-added products from lignin has been invigorated [21]. It has been profited in the past for the production of activated carbons [22,23], high temperature carbons [24], carbon fibers [25,26], electrospun carbon fibers [27,28] and porous carbon electrodes [29]. In the supercapacitor field, lignin-based porous carbons [30–34] and electrospun fibers [35–37] have already been utilized as sustainable carbon electrodes.

We have recently reported that hierarchical porous carbons (HPCs) can be obtained through a hard template method upon carbonization of organosolv lignin-zeolite mixtures [38,39]. To our knowledge, there are only two studies in the literature dealing with the production of HPCs from lignin for supercapacitor applications, and both of them relies on the use of KOH as activating agent in order to promote porosity [33,34]. Contrarily, our lignin-based HPCs were produced by direct carbonization of the lignin-zeolite mixtures, without requiring any other activating agent than the hard template. Moreover, these materials showed interesting electrochemical behavior in 1 M H_2SO_4, obtaining in some cases capacitances over 250 F g^{-1} at 50 mA g^{-1}. Thanks to the presence of mesopores connected to the micropore network, these capacitance values were well retained when the current density was increased up to 20 A g^{-1} (capacitance retention higher than 50% without discounting the ohmic drop). In this work, we propose to combine the use of lignin-based HPCs with the asymmetric in mass design in order to build more sustainable supercapacitor cells in an aqueous-based electrolyte with superior performance. The performance and durability of the obtained supercapacitors is reported. Further comparison with a symmetric supercapacitor assembled with a commercial activated carbon used for capacitors preparation has been also detailed.

2. Experimental

2.1. Materials and preparation of lignin-based HPCs

Alcell Lignin, provided by Repar Technologies Inc., has been used as the carbon precursor. The Alcell process is one of the most utilized of the organosolv category, and allows the recovery of a high purity lignin, which only contains a small amount of inorganic compounds, through the use of a more environmental friendly pulping process [20]. Zeolite Y (CBV 300) and Zeolite β (CP 814 E) in ammonium form have been acquired from Zeolyst International Company (PA, USA) and used as received as the hard templates. The preparation process of the HPCs has been carried out following the protocol derived by Valero-Romero et al. [38]. Briefly, it implies three steps. First, lignin has been solved in ethanol, and the zeolite has been added to the solution using a 1:1 lignin to zeolite weight ratio. The mixture has been stirred for 1 h and dried at 60 °C for one day. Secondly, carbonization of the mixture was carried out at 900 °C for 2 h under continuous N_2 flow (150 cm^3 STP/min). Finally, the zeolite template has been removed by refluxing the carbonized mixture in sodium hydroxide 1 M for 6–24 h, washed with distilled water and dried at 120 °C overnight. Samples were manually milled and sieved under 50 μm size. The obtained HPCs have been named L-Y-900 (HPC obtained using Y-zeolite as hard template) and L-B-900 (HPC obtained using β zeolite as hard template). The preparation yields are 45% and 35% for Y and β-based hierarchical porous carbons, respectively. Ash content lower than 0.5% has been found in these materials. The main elements found by XPS over the surface of these materials were carbon and oxygen with mass surface concentrations of around 84–86% and 12–15%, respectively, followed by small amounts of nitrogen, 1–2%. Aluminum and silicon were detected in quantities lower than 0.5%.

A commercial activated carbon was used in the construction of supercapacitor cells for comparison purposes (sample ACJM).

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