Role of different nitrogen functionalities on the electrochemical performance of activated carbons

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ABSTRACT

Different oxidation, reduction and thermal methods are used for selectively obtaining each of the most common surface nitrogen groups (almost isolated) on the surface of a phosphorus-containing activated carbon (ACP), and their electrochemical performances are analyzed. Nitro- and amino-containing activated carbons show defined pseudocapacitive peaks, characteristic of redox processes, which can be associated to the formation of hydroxylamino groups (observed by means of XPS). Condensed structures of nitrogen, such as pyridinic and pyrrolic, additionally improve the ionic diffusion on the carbonaceous structure, increasing the specific capacitance of the carbon electrode up to 317 F g^{-1}. The formation of poly (amido-amine) chains on ACP surface leads to an activated carbon with poor textural properties (A_{BET} = 43 m^2 g^{-1}) but surprisingly high surface capacitances (ca. 3256 mF m^{-2}) attributed to an enhancement of the carbon conductivity. Some of the activated carbons are submitted to a severe thermal treatment at 900 °C, yielding carbons with a developed porous texture, stable surface phosphorus groups and an increased proportion of quaternary nitrogen surface species. These activated carbons exhibit a faster development of the electric double layer, due to the more ordered carbon planes and the presence of charged functional groups.

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1. Introduction

Activated carbons are usually prepared from waste or lignocellulosic raw materials in an environmentally attractive process [1,2]. They are traditionally used as adsorbent or catalyst support due to their surface properties, with elevated surface areas and pore volumes (mainly micropores) [3,4]. The recent advances in electrochemistry and the increasing knowledge on carbons at micro and nanoscale have generated important innovations in the energy storage field [5]. Because of the cost-effectiveness [6,7], the sustainability of the production and the surface properties, activated carbons are one of the main studied materials for electrochemical double-layer supercapacitors [7–9].

The electric double-layer (EDL) development directly depends on the surface area of the carbon material. However, the optimal pore size required is controversial. Some authors defend the importance of micropores contribution in the EDL formation [10], and others highlight the ion diffusional problem of the electrolyte in narrow micropores and, thus, the better behavior of mesopores [11]. On the other hand, the surface functional groups of carbonaceous materials play a key role in the pseudocapacitive reactions on the surface of the electrodes, what improves their capacitances [12–14]. Activated carbons offer the possibility of modifying and controlling the porous texture by varying the preparation conditions. Besides, they can be submitted to thermal and chemical processes to enlarge the porosity or enhance the surface chemistry. Chemical activation with H_3PO_4 allows for obtaining activated carbons with a high development of the porosity [15], generating narrow mesopores [16]. This should avoid the ion diffusional problem in the thinner micropores, enhancing the carbon capacitor performance [17].

The influence of heteroatoms like P or N on the electrochemical activity of the carbonaceous materials has been widely studied, as well as the pseudocapacitive redox reaction of surface groups containing these atoms [18,19]. In fact, some phosphorus functional groups remain fixed on the carbon surface during the activation process, which is beneficial for the electrochemical carbon behavior [20]. On the other hand, nitrogen surface groups, along with

oxygenated groups, are the most investigated surface heteroatoms in the literature due to: (i) the presence of these atoms in biomass precursors [21,22]; (ii) the better electric conductivity due to the conjugation of the nitrogen lone-pair electron and the carbon π-system [23,24]; and (iii) the electrochemical synergy of N-chained groups with oxygenated or P-surface groups [13,18]. Apart from this N-P synergy, it has been proved that P-groups (remaining after chemical activation with phosphoric acid) play a key role in the nitrogen functionalization of the carbon surface [25]. This strategy allows for obtaining N-enriched activated carbons from a N-free lignocellulosic raw material, which considerably opens the possibilities of producing functionalized activated carbons.

Different nitrogen oxidation states and forms have been reported, and the importance of some of them (pyridinic nitrogen, quaternary nitrogen …) on the pseudocapacitance of an activated carbon electrode has been described [26−28]. Although the positive influence of nitrogen on carbon electrodes are extendedly accepted, nitrogen-enriched carbons usually present more than one structure of nitrogen, hindering the possibility of studying the contribution of each one or the inert character of some of them [13,23,26−29]. In this line, our research group has developed different methods to selectively obtain each of the most common surface nitrogen groups studied (almost isolated) by chemical or thermal treatments of a phosphorus-containing activated carbon [25,30]. In this work, different nitrogen surface functionalities have been selectively prepared on a phosphorus-containing activated carbon and their electrochemical performances have been studied in order to elucidate the electrochemical contribution of each nitrogen surface group.

2. Experimental

2.1. Activated carbon preparation

Olive stone (OS), as lignicellulosic raw material, was chemically activated to obtain phosphorus-containing activated carbons [31]. The precursor was impregnated with H_3PO_4 (85 wt%), with an impregnation ratio (wt. H_3PO_4/wt. OS) of 3, and was dried at 60 °C for 24 h in a vacuum dryer. Then, the substrate was submitted to a carbonization treatment at 500 °C under a continuous N_2 flow (150 cm^3 min^{-1}), the final temperature was maintained for 2 h. The activated carbon was then washed with distilled water at 60 °C to remove H_3PO_4. The obtained activated carbon, named ACP, presented a yield of 44.8 wt%.

2.2. Activated carbon functionalization

ACP was functionalized by a nitric acid treatment [25]. ACP was contacted with a 5 M HNO_3 solution (1 g of ACP in 50 cm^3) with a continuous stirring at 80 °C for 3 h. The surface-oxidized activated carbon was washed until constant pH in the eluate and was used as the nitrogen-enriched activated carbon precursor for obtaining the rest of the functional groups. The nomenclature used for this sample was ACP-N [25].

ACP-N was submitted to different chemical and thermal reduction processes to modify the nitrogen oxidation state [30]. Chemical reduction was carried out by mixing 50 cm^3 of an ACP-N solution in ethanol with 50 cm^3 of a $NaBH_4$ (reducing agent) solution in ethanol. $NaBH_4$ solution was slowly dripped over the carbon solution, and was maintained for 24 h with continuous stirring. The final activated carbon was washed with distilled water at 60 °C. Activated carbons yielded by this method were named by adding −B to the nomenclature (i.e. ACP-NB). On the other hand, a mild or a severe thermal reduction of the nitrogen-functionalized activated carbon were carried out by thermal

treatments under inert atmosphere at 300 or 930 °C, respectively. Activated carbons obtained were named by adding −Δ or −HT, for the mild or severe thermal reduction process, respectively. A detailed description of the reduction treatments can be found elsewhere [30].

Amido-amino groups were incorporated to the carbon through a sequential treatment for acyl chloride formation and amidation reaction. Firstly, ACP-N was contacted with thionyl chloride (1 g of ACP-N in 37.5 cm^3) under continuous stirring, at 70 °C for 5 h, in order to transform carboxyl groups into acyl chlorides ones. Once washed with isopropyl alcohol and oven-dried, this intermediate activated carbon was treated with ethylendiamine, under continuous stirring at 90 °C for 24 h. The corresponding (amido-amine)-containing activated carbon (ACP-E) was yielded after washing with methanol, and then with distilled water until constant pH.

Propagation of poly (amido-amine) dendrimers (PAMAM) on ACP-E was performed by sequential alkylation and amidation treatments. Firstly, Michael addition was carried out in a stirred tank at 50 °C for 24 h. Methyl acrylate and methanol were mixed in 1:4 (cm^3:cm^3) ratio with ACP-E. Subsequently, amidation was carried out under the same conditions mixing the resulting activated carbon with ethylendiamine and methanol with a ratio of 1:2 (cm^3:cm^3) to obtain the first poly (amido-amine) generation (ACP-E1). The second generation of poly (amido-amine)-fuctionalized activated carbon (ACP-E2) was prepared from ACP-E1 by using a double proportion of methyl acrylate (ratio 1:2) in the Michael addition reaction and of ethylendiamine (ratio 1:1) in the amidation reaction.

2.3. Activated carbon characterization

The porous texture of the activated carbons was characterized by N_2 adsorption-desorption at −196 °C and CO_2 adsorption at 0 °C, using a Micromeritics ASAP2020 apparatus. Samples were previously outgassed for 8 h at 150 °C under vacuum. The apparent surface area (A_{BET}) was calculated using the BET equation from the N_2 adsorption-desorption isotherm. Micropore volumes were estimated with the Dubinin-Radushkevich equation from N_2 adsorption-desorption isotherms and CO_2 adsorption isotherms, obtaining information about the adsorption in the range of micropores $\left(V_{DR}^{N_2}\right)$ and narrow micropores $\left(V_{DR}^{CO_2}\right)$, respectively.

The surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS) analyses and by temperature-programmed desorption (TPD) experiments. XPS analyses were carried out in a 5700 C model Physical Electronics apparatus with MgKα radiation (1253.6 eV). The C1s peak position was set at 284.5 eV [16] and used as reference to locate the other peaks. TPD experiments were carried out in a customized quartz fixed-bed reactor placed inside an electrical furnace. CO and CO_2, as output gases, were measured by a non-dispersive infrared (NDIR) gas analyzer, Siemens ULTRAMAT 22. 80 mg of the carbon sample was heated from room temperature to 930 °C at a heating rate of 10 °C min^{-1} under N_2 flow (200 cm^3 min^{-1}).

Ninhydrin test was carried out in order to analyze the presence of primary amino groups fixed on the activated carbon surface. A 10 mg cm^{-3} solution of Ninhydrin in ethanol (96%) was added to the activated carbon in a stirred tank microreactor at 85 °C for 45 min. At these conditions, ninhydrin reacts with the primary amino groups forming a condensed molecule from ninhydrin, ammonia and the intermediate hydrindatin, thus yielding a blue-colored solution. Detailed information of this test that we have adapted from the classical ninhydrin method [32], can be found elsewhere [30].

Activated carbon particles morphology was studied by scanning