



Hydrothermal functionalization of ordered mesoporous carbons: The effect of boron on supercapacitor performance



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ABSTRACT

Hierarchical carbons with different boron contents (from 0.42 to 2.37 wt.%) were prepared by combination of soft-templating and hydrothermal approaches. This newly developed strategy enables adequate control of the chemical state of the boron functionalities in carbon materials since the self-generated pressures favour B–C bond formation. The total content of oxygen increases simultaneously with the boron content, and its speciation is also influenced by the boron chemical state distribution: the presence of C–B–C (BC₃ and BC₂O) species induces the oxidation of phenols to carbonyls. The electrochemical performance of the prepared carbons was tested in a three-electrode cell configuration (1 M H₂SO₄) showing good specific capacitances per BET specific surface area (20–36 μF/cm²). The presence of boron on the carbon backbone improves both the charge propagation and the pseudocapacitive properties. Nevertheless, the electrochemical properties are only enhanced up to some level of boron doping (around 1.8 wt.%). A two-electrode supercapacitor built with a carbon prepared by a mild hydrothermal synthesis (50 °C during 28 h) delivered energy densities similar to those of commercial activated carbons. This could lead to high volumetric capacitance, since the boron doped carbons present much higher density.

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1. Introduction

Electric double layer capacitors (EDLCs) are energy storage devices presenting fast charging rate and quick energy-release. However, low energy density constitutes their main limitation, and consequently much effort is focused on increasing their capacity. The storage mechanism consists in electrostatic adsorption of electrolyte ions on the electrode surface, which means that the capacity increases with the electrode specific surface area. The electrochemically active surface may be limited by diffusion problems [1]. Ordered mesoporous carbons (OMC) present an adjustable and interconnected ordered porous network, which enhances the diffusion of molecules from the bulk to the electrode surface by providing a well-defined mesoporous systems [2–5]. The capacity can also be enhanced by reversible redox reactions developed at the electrode surface [6–8]. This so called pseudocapacitance is

introduced by enriching the carbon surface with electroactive species containing nitrogen [9], oxygen [10], boron [11], phosphorus [12], or sulphur [13]. During the last decade, carbons doped with oxygen and nitrogen have been extensively studied as EDLCs electrodes [14–18]. As a result, quinone, pyrrolic and pyridinic groups have been identified as the most active groups in pseudocapacitors [17]. On the other hand, it has been stressed that nitrogen can replace carbon atoms within the matrix, modifying the conductive properties of the electrodes [14]. The boron atom has not been so thoroughly studied, but it presents an interesting electronic situation. It has one electron less than carbon in the valence layer and lower electronegativity, which induces changes both on the conductive properties and the oxidation behaviour of the carbon materials [19–22], respectively. On the other hand, the formation of borates (BC_xO_y or B₂O₃) on the carbon surface induces pseudocapacitive charge storage. Boron doped carbons with well defined mesoporosity can be prepared by hard-templating [23–25] or by soft-templating methods. The former is a multistep procedure requiring; i) preparation of a silica template, ii) infiltration of the template with a carbon and/or heteroatom precursors iii)

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carbonization of the obtained composite and iv) removal of the template with HF or concentrated base. In contrast, OMCs can be directly obtained by soft-templating approaches avoiding the use of corrosive reactants. Several works preparing boron containing OMCs using block copolymers as templates and polymerizable carbon/boron precursors in solution can be found in the literature [26–30]. Nevertheless, some of them involve the use of silica in solution (tri-constituent co-assembly method) [26,27] or the evaporation of large amounts of organic solvents (EISA method) [11,28]. On the other hand, Wickramaratne et al. investigated the preparation of boron doped OMCs by macroscopic phase separation [29]. They obtained carbon materials with 1.8 w/w % of boron (measured by XPS) and well defined porosity by a “one-pot” procedure. However, and similarly with other previous works, the study is mainly focused on adjusting the total boron content but not on controlling the boron speciation. Bearing this in mind, the development of new synthesis strategies to directly obtain ordered mesoporous carbons with tunable surface chemistry is highly attractive. In addition to the total content, it is expected that the nature of the different boron functionalities will also affect the carbon properties. The main drawback of soft-templating approaches is the low participation of the precursors in the polymerization process, which generally leads to amorphous materials (with no defined nanostructure) or to low doping levels. In that regard, hydrothermal treatments (HT) have demonstrated to be advantageous [30–32] because the generated high pressures favour the aggregation of molecules. Therefore, the main goal is to achieve a controlled hydrothermal synthesis allowing not only to adjust the boron content, but also to define the chemical state of boron functionalities in ordered mesoporous carbons. A detailed analysis of both the pore structure and the surface chemistry is presented for different hydrothermal treatments. The relationship between the different surface features and the electrochemical behaviour of the prepared carbons is discussed. Hence, this work not only presents a new synthetic procedure to prepare boron doped ordered mesoporous carbons with tailored surface chemistry but also provides new insights into the rational design of supercapacitor electrodes.

2. Experimental

2.1. Chemicals

Resorcinol (Acros Organics, 98%), Pluronic (Sigma–Aldrich, F127 powder), ethanol (98%), ethanol absolute (PS, Panreac), HCl (Sigma–Aldrich, 37%), boric acid (Fluka, 99%), formaldehyde (Sigma–Aldrich, 37%), polytetrafluoroethylene (PTFE, Sigma Aldrich 60%), Printex 200 (Degussa) and DLC Supra 50 (Norit).

2.2. Materials synthesis

Boron doped ordered mesoporous carbons were prepared by a slight modification of the phase separation soft-templating method [33]. Namely, 3 g of resorcinol and 2.5 g of Pluronic® F127 were dissolved under stirring in 20 mL of a 10:9 (w/w) ethanol/water solution. After complete dissolution of the surfactant, the pH was adjusted to 1.0 with 0.2 mL of HCl 37% and kept under stirring for an additional hour. In order to study the influence of the doping agent proportion, different quantities of boric acid (1.0, 1.5 and 2.0 g) were added to the reaction mixture. Finally, 2.3 g of formaldehyde were added dropwise to the solution. The temperature was raised to 50 °C to promote polymerization and, a phase separation occurs approximately after 2 h (Fig. 1Sa). The aqueous phase was discarded and the organic phase was cured. Two additional carbon series were prepared to study the possible effects of a hydrothermal

treatment (HT) during the polymerization process. To this end, the proportion of boric acid to resorcinol was set to 33% (1 g of boric acid) and, after the addition of formaldehyde, the reaction mixture (24 cm³) was transferred to an autoclave (120 cm³). Samples were hydrothermally treated at 50 or 100 °C during 2, 8 or 28 h, the phases were separated, and the organic phase was kept for curing. All the as-prepared organic resins were cured according to the following temperature profile: 50 °C/12 h, 80 °C/12 h and 100 °C/12 h. The resulting resin monoliths (Fig. 1Sb) were placed in a vertical furnace and heated up under N₂ flow (100 cm³/min) to 550 °C at 2 °C/min during 1 h to remove the template. Then, the temperature was raised to 800 °C at 5 °C/min and kept during 2 h to perform the monoliths carbonization (Fig. 1Sc). The carbons prepared in the absence of a hydrothermal treatment were denoted as CX series, where X stands for the boric acid/resorcinol ratio (% w/w) and C is the un-doped carbon. On the other hand, the carbons prepared using the HT method were designated as C33_T_t series, where T is the temperature and t the duration. As example, C33_50_28 is a carbon prepared with a boric acid/resorcinol ratio of 33% and hydrothermally treated at 50 °C during 28 h.

2.3. Materials characterization

An IQ2 volumetric adsorption analyser (Quantachrome) was used to measure N₂ and CO₂ adsorption–desorption isotherms, respectively at –196 °C in the relative pressure range 10^{–7}–0.99, and at 0 °C in the relative pressure range 10^{–5}–0.03. Samples were degassed at 150 °C during 12 h under vacuum. The BET specific surface area (*S*_{BET}) was calculated according to the BET model [34] from the nitrogen isotherms in the relative pressure range of 0.05–0.25. The micropore volume (*V*_{DR} (N₂)) and ultramicropore volume (*V*_{DR} (CO₂)) were calculated by applying the Dubinin–Radushkevich (DR) method [34] in the relative pressure ranges of 10^{–6}–0.1 and 10^{–5}–0.03, respectively, for the N₂ and CO₂ isotherms. The total pore volume (*V*_T) was calculated as the amount of N₂ adsorbed at the relative pressure of 0.95. The mesopore volume (*V*_{mesop}) was obtained as the difference between *V*_T and *V*_{DR} (N₂). The QSDFT [35] method (slit-cylindrical pores, equilibrium) was used to obtain the pore size distributions (PSDs).

The low-angle X-ray diffraction (XRD) measurements were carried out in a Siemens D5000 diffractometer using Cu K α radiation, a scanning range of 2 θ = 0.5–5°, with a step width of 0.01° and time per step of 1 s. The XPS analysis was performed using a Kratos AXIS Ultra HSA, with VISION software for data acquisition. The analysis was carried out with a monochromatic Al K α X-ray source (1486.7 eV), operating at 15 kV (90 W), in Fixed Analyser Transmission (FAT) mode, with a pass energy of 40 eV for regions ROI and 80 eV for survey. Data acquisition was performed with a pressure lower than 10^{–6} Pa, and with a charge neutralization system. The binding energies were calibrated by referencing the C1s peak (284.6 eV) to reduce the sample charge effect. The deconvolution of spectra was performed using the XPS Peak program and peaks were fitted to a Gaussian–Lorentzian function (80/20) and using a Shirley type background subtraction. The compositions (expressed as wt.%) were determined from the survey spectra by considering the integrated areas of the main XPS peaks assigned to the different elements (C1s, B1s and O1s) and their respective sensitivity factors.

2.4. Electrochemical measurements

2.4.1. Electrodes preparation

The carbon monoliths were crushed and ball-milled to obtain a particle size below 100 μ m. A paste was prepared by mixing 80% of the carbon sample, 10% PTFE and 10% Printex 200 in absolute

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