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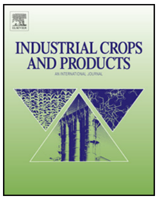

Electrochemical performances of hydrothermal tannin-based carbons doped with nitrogen

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ABSTRACT

Six porous carbon materials, produced by hydrothermal treatment of flavonoid tannin and subsequent carbonization at 1173 K, were tested as electrodes of supercapacitors. Four of these carbons were doped with nitrogen by putting tannin in contact with ammonia before or during the hydrothermal treatment. The pyrolyzed hydrothermal carbons had moderate surface areas, within the range 442–684 $m^2\,g^{-1}$, and nitrogen contents ranging from 0.7 to 8.0 wt.%. Specific capacitances as high as 320 $F\,g^{-1}$ and normalized capacitances as high as 58 $\mu F\,cm^{-2}$ were measured at 2 $mV\,s^{-1}$. These performances are comparable with those obtained with high surface area-activated carbons, whereas, normalized capacitances values are among the highest ever reported. Mesostructuration, within the range 3–13 nm, of these materials appears to be a good strategy to improve their electrochemical performances at higher scan rates. We confirmed the beneficial role of oxygen up to 18 wt.%, while an optimum in nitrogen content exists from 3 to 6 wt.%.

1. Introduction

Supercapacitors are the basis of reversible electrochemical systems able to rapidly charge and discharge energy at high specific powers (Conway and Pell, 2003; Obreja, 2008). There are two kinds of supercapacitors: (i) electric double-layer capacitors (EDLCs), in which energy storage is made by the electrostatic adsorption of electrolyte ions on the surface of porous electrodes; and (ii) pseudocapacitors, in which energy is stored by redox reactions (Du et al., 2013; Pandolfo and Hollenkamp, 2006; Shukla et al., 2012). Activated carbons, carbon aerogels, and carbon xerogels have been widely tested as capacitor electrodes mainly because of their high surface area and appropriate pore size distribution, wettability, and electrical conductivity (Candelaria et al., 2012; Chang et al., 2013; Liu et al., 2013; Su and Centi, 2013; Xie et al., 2010). Adsorption characteristics are indeed very important for such kind of materials, and the addition of some heteroatoms, such as oxygen and nitrogen can improve the wettability and the electronic conductivity, respectively (Hsieh and Teng, 2002; Wei et al., 2011). Hydrothermal carbons doped with nitrogen have been already tested as electrode capacitors. For example, carbons were produced from hydrothermal treatment (HT) of D-glucosamine and activated with potassium hydroxide (KOH), and the resultant microporous carbon materials presented a BET surface area around 600 $m^2\,g^{-1}$ and capacitance values of 300 $F\,g^{-1}$ at 0.1 $A\,g^{-1}$ in an acid electrolyte (Zhao et al., 2010). Rice husk activated with phosphoric acid produced micro/mesoporous texture with BET surface area value of 2530 $m^2\,g^{-1}$ and capacitance of 130 $F\,g^{-1}$ (Wang et al., 2011a). Eucalyptus wood saw dust submitted to HT and KOH activation produced supermicroporous materials having surface areas as high as 3000 $m^2\,g^{-1}$ and capacitance values of 236 $F\,g^{-1}$ at 1 $mV\,s^{-1}$ (Wei et al., 2011). In order to obtain carbon with nitrogen, Chinese human hair together with glucose were submitted to HT at 453 K overnight and the materials were further activated using KOH; surface areas and capacitance values were found to be around 600 $m^2\,g^{-1}$ and 264 $F\,g^{-1}$, respectively (Si et al., 2013). N-doped graphene presents also better electrochemical performances than undopped graphene. Capacitances values for N–graphene based supercapacitors lie in the range of 150–370 $F\,g^{-1}$ (Jeong et al., 2011; Lai et al., 2012; Lee et al., 2012; Sun et al., 2012; Wen et al., 2012; Hassan et al., 2013; Lu et al., 2013; Wang et al., 2013, 2014).

Tannins are used in leather process (Sreeram and Ramasami, 2003), medicine (Shahat and Marzouk, 2013), wine (Harbertson et al., 2012), and dye industries (Sánchez-Martín et al., 2010),

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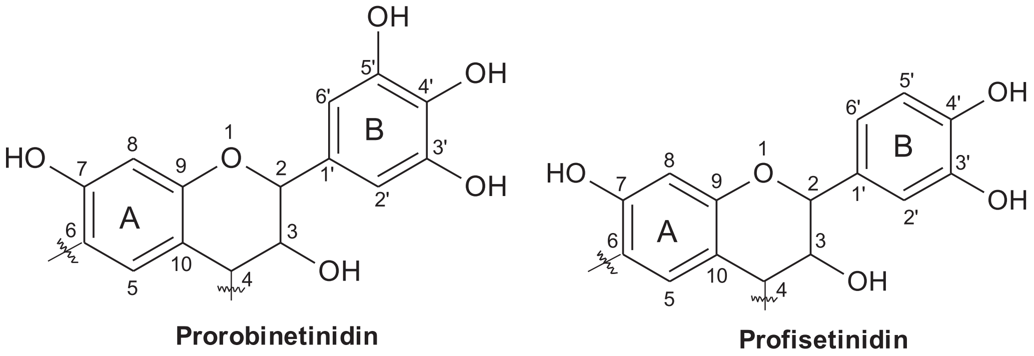

Fig. 1. The main two flavonoid units contained in Mimosa tannin: prorobinetinidin and profisetinidin.

among others. Moreover, tannins are also used as the main precursor of resins (Pizzi, 1983; Pizzi and Mittal, 2003), gels (Amaral-Labat et al., 2012a), foams (Szczurek et al., 2013), mesostructured carbons (Schlienger et al., 2012), and more recently hydrothermal carbons (Braghiroli et al., 2012, 2015). Braghiroli et al., 2015 showed that high surface area and high N content, 500 $m^2 g^{-1}$ and 8 wt.%, respectively, carbons were obtained after submitted tannin to HTC and further carbonization. No other natural precursor submitted to HTC reached so high N content and so high surface area at the same time. Braghiroli et al., 2015 concluded that such carbon materials should be very promising in electrochemical energy storage. The amination of tannin with ammonia proceeds by replacement of a great proportion of phenolic hydroxyl ($-OH$ groups) by $-NH_2$ groups. The possible formation of $-N=$ bridges connecting the flavonoid units during the crosslinking process has been demonstrated (Braghiroli et al., 2013). Fig. 1 shows the two main flavonoid structures that are present in Mimosa tannin, the natural precursor used in this work. Prorobinetinidin and profisetinidin are polyphenolic molecules which are present in condensed Mimosa tannin in proportions of around 70% and 25%, respectively (Pizzi, 2008).

In the present study, we tested the electrochemical properties of N-doped carbon materials prepared by hydrothermal carbonization (HTC) followed by carbonization at 1173 K. The performances of these materials were compared with available data from the open literature. The superior electrochemical performances of our N-doped carbon materials were correlated to their porous texture and, to their oxygen and nitrogen contents.

2. Materials and methods

2.1. Materials synthesis

2.1.1. Tannin

Commercial Mimosa bark extract, known as FINTAN OP on the market, was used in this work and was kindly supplied by the company SilvaTeam (San Michele Mondovi, Italy). The way it has been extracted from barks of *Acacia Mearnsii* (de Wild) and its composition have been detailed elsewhere (Braghiroli et al., 2012). This raw material is a light-brown powder that contains generally 80–82% of phenolic flavonoid materials, 4–6% of water, 1% of amino and imino acids, the remainder being monomeric and oligomeric carbohydrates, in general broken hemicelluloses.

2.1.2. Synthesis of hydrothermal carbons

Two kinds of aminated materials were prepared using two different amination methods described elsewhere (Braghiroli et al., 2012). Briefly, evaporated aminated tannin (EAT) was prepared with 2 g of tannin mixed with 40 cm^3 of 28% aqueous ammonia in air in room conditions. The mixture was placed in a closed vessel for preventing evaporation and was stirred for 1 h at room temperature. Then, the solution was poured in a Petri dish and left for complete evaporation in a fume hood during 2 days at room temperature. The obtained solid was then mixed with 16 g of bi-distilled water at room temperature. Aminated tannin (AT) was prepared by mixing 2 g of tannin with 16 cm^3 of 28% aqueous ammonia in a glass vial until total dissolution. Two grams of tannin (T) dissolved in 16 cm^3 of bi-distilled water was also used as precursor of a reference material. EAT, AT, or T solutions were placed in a Teflon-lined autoclave of 50 cm^3 for HT treatment in an oven for 24 h. After HTC, the samples were labeled H-EAT, H-AT, and H-T, respectively. The HTC was carried out either at T1 = 453 or at T2 = 483 K, and depending on such temperature, the number 1 or 2, respectively, was added to sample's label, e.g., H-EAT1 or H-EAT2 for H-EAT materials.

2.1.3. Pyrolysis

Pyrolysis of hydrothermal carbons was performed in a flow of high-purity nitrogen up to 1173 K at a heating rate of 3 K min^{-1}, and the final temperature was maintained for 3 h. The letter C for "carbonized" was thus, added to samples' labels, e.g., CH-EAT1 and CH-EAT2 are the resultant materials after pyrolysis of H-EAT1 and H-EAT2, respectively.

2.2. Materials characterization

2.2.1. Materials morphology and pore texture analysis

Scanning electron microscopy (SEM) observations were carried out with a FEI-Philips CM200 apparatus for investigating the morphology of the samples, which were metalized beforehand. Pore texture parameters were obtained by nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 automatic apparatus. Carbon samples were degassed for 48 h under vacuum at 543 K before nitrogen adsorption. The following parameters were determined: surface area S_{BET}, from the BET (Brunauer–Emmet–Teller) calculation method (Brunauer et al., 1938); micropore volume V_μ (Dubinin, 1989); total pore volume $V_{0.97}$ (Gregg and Sing, 1991); and mesopore volume V_m calculated as the difference $V_{0.97} - V_\mu$. The pore size distribution was determined by application of density functional theory (DFT) (Tarazona, 1995).

2.2.2. Elemental analysis

Ultimate analyses of all samples submitted to pyrolysis at 1173 K were carried out in a ThermoFlash 1112 apparatus to determine carbon, hydrogen, nitrogen, and sulfur contents. Oxygen content was obtained by difference.

2.3. Electrochemical experiments

Porous electrodes were prepared by pressing together a mixture of 75 wt.% of finely ground pyrolyzed hydrothermal carbon,