

ACTIVATED MESOPOROUS CARBONS DERIVED FROM TANNIN AS ELECTRODES FOR SUPERCAPACITORS

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Introduction

The limited fossil fuels reserves and the increasing global warming make necessary a transition to sustainable energy production and environment-friendly technologies. However, renewable sources of energy have an intermittent nature, so the improvement of energy storage devices together with a better energy management are needed. Supercapacitors (SC) are already in use in many car models for brake energy regeneration, in Start-Stop systems (not only in electric vehicles) and in hybrid systems along with batteries.¹ Activated mesoporous carbons are valuable materials to be used as electrodes for SCs due to their high surface area and hierarchical pore structure that facilitates the diffusion of electroactive species.²

Herein, an easy and green one-pot synthesis method was developed to produce mesoporous carbons through ball milling of mimosa tannin as carbon precursor, with Pluronic® F127 and water.³ CO₂ activation carried out on selected ordered and disordered mesoporous carbons (OMCs and DMCs, respectively) allowed improving their textural properties. Activated OMCs and DMCs were tested as electrodes for SCs.

Materials and Methods

Mimosa tannin (T), Pluronic® F127 (P) and water (W) were ball-milled for 60 min in a single step; the retrieved paste-like materials were directly submitted to pyrolysis at 900°C under N₂ atmosphere. Afterwards, CO₂ activation was carried out on an OMC and a DMC obtained with T:P:W weight ratios of 2:0.75:1.75 and 2:2:2, respectively. CO₂ activation was performed at 900°C during times ranging from 15 to 120 min.

The textural characterization was performed by N₂ and CO₂ adsorption at -196 and 0°C, respectively and XPS analysis was used to study the surface chemistry. The electrochemical performance of the assembled SCs was tested through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) in aqueous and organic electrolytes (1 mol L⁻¹ H₂SO₄ and 1 mol L⁻¹ TEABF₄/ACN, respectively).

Results and Discussion

The two materials selected for CO₂ activation, OMC and DMC, presented similar microporosities and surface oxygen contents before activation; however the activation process was more effective

on the DMC as shorter activation times were needed to achieve similar porosity properties as those of their ordered counterparts, see **Figure 1**. The easier development of textural properties observed for the DMC might be due to a higher residence time of CO₂ in the materials, caused by the disordered structure that imposes a longer path to go for the gas. However, when surface areas (**Figure 1b**) or volumes (**Figure 1b**) were represented as a function of burn-off (BO), materials' textural properties were only dependent on the BO and not on the ordered or disordered nature of the mesoporosity.

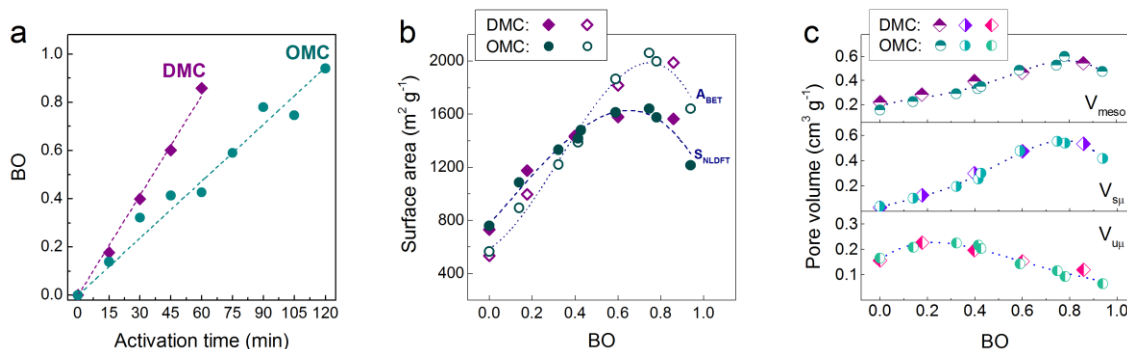


Figure 1. (a) Burn-off (BO) as a function of activation time for the DMC and OMC series of activated carbons. Porosity properties as a function of BO for the activated DMCs and OMCs: (b) surface area and (c) pore volume in the ultramicro-, supermicro- and mesopore ranges.

Two activated carbons (ACs) with similar textural properties were chosen out of each serie of OMC and DMC materials: the A75-OMC and the A45-DMC, respectively. These two materials exhibited similar contents of oxygen surface functionalities and surface areas, and only differed in their pore size distribution (PSD) in the mesoporous range as well as in the order of these mesopores. **Figure 2a** shows that A75-OMC has a narrow PSD centred on 5 nm while A45-DMC has a wider PSD, from 2 to 15 nm and centred on 7 nm. This factor allowed assessing the impact of the mesoporous ordering on the SCs performances. Both types of ACs presented a similar SC behaviour and high-rate capabilities as seen in **Figure 2b-e**. As for the effect of the order, A75-OMC had a slightly better response than A45-DMC in aqueous electrolyte, which could be due to a better ion diffusion within the channels of the first. Contrary to what was expected, in organic electrolyte A45-DMC outperformed A75-OMC; this could be explained by the fact that ions in TEABF₄/ACN are of larger size than those in H₂SO₄ and that most of the mesopores in A75-OMC are only accessible through narrower pores, the latter being revealed by scanning experiments of the adsorption-desorption isotherms. The pores of A45-DMC are more accessible to the larger TEABF₄/ACN ions; hence, this material exhibited a better performance when compared to A75-OMC.

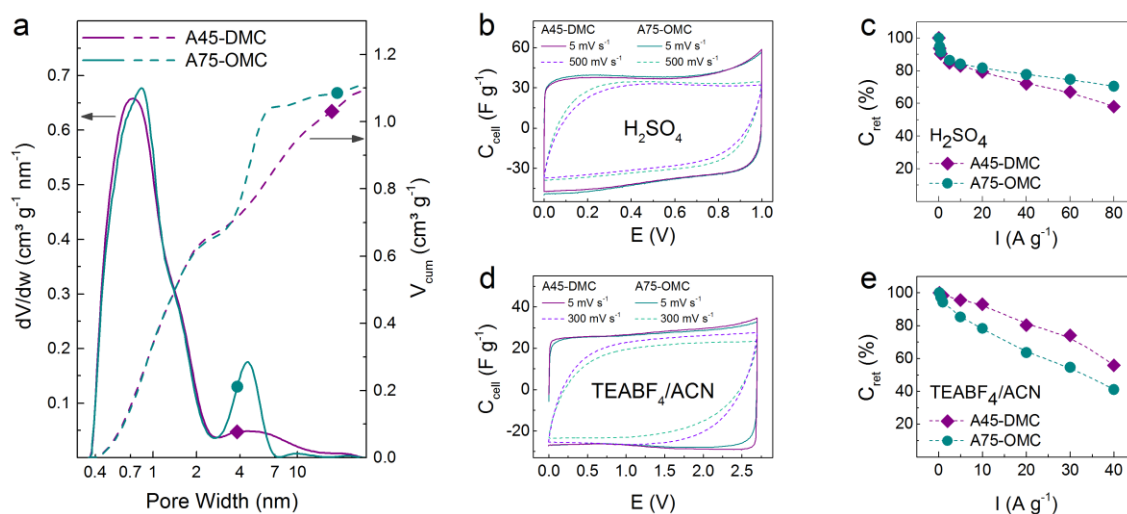


Figure 2. (a) Pore size distribution of A45-DMC and A75-OMC, chosen for electrochemical characterization. Electrochemical performance of selected samples in aqueous and organic electrolyte (H₂SO₄ and TEABF₄/ACN, respectively): (b, d) CV curves and (c, e) capacitance retention calculated from GCD tests.

Conclusion

Mechanosynthesis based on tannin, water and a non-hazardous surfactant constitutes a simple and green method to produce mesoporous carbons with either ordered or disordered structures. After activation, selected materials were tested as electrodes for SCs and they exhibited good supercapacitor behaviour, high-rate capabilities and long-term stabilities over time and after continuous cycling. Although further studies must be carried out, it was possible to gain insight on the effect of the ordered structure on the electrochemical performance of the materials.

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