



# Effect of pore texture on performance of activated carbon supercapacitor electrodes derived from olive pits



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## ABSTRACT

Activated carbon electrodes for electrochemical capacitors have been prepared by the chemical activation of a natural renewable and by-product material precursor – olive pits – from the olive oil production industry. The careful adjustment of the synthesis conditions has allowed synthesizing a series of microporous carbon electrodes with an optimized microporosity, enabling a gravimetric and volumetric capacitance in basic aqueous medium up to  $260 \text{ F g}^{-1}$  and  $140 \text{ F cm}^{-3}$ , respectively, with good rate capability. A relation amongst capacitance, specific surface area, accessible average pore size and effective dielectric permittivity has been established, demonstrating that there is not just a single parameter decisively impacting the capacitance value. The collective analysis of experimental data suggests that solvation imposes an optimum pore size for each ion with regard to rate capability: moderate solvation contributes to enhancing capacitance in pores slightly exceeding solvated ion size while excessive solvation deteriorates the high-rate response of supercapacitor electrodes having pores much wider than ion size.

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## 1. Introduction

Electrical double-layer capacitors (EDLCs), which are the most widespread type of supercapacitors, are one of the most promising electrochemical power sources, operating by the electrosorption of ions from an electrolyte onto high-surface area electrodes [1]. High capacitance values of a few hundred F per g of active material are attainable with EDLCs because of the high specific surface area (SSA) of electrode materials and the very small charge separation between the surface atoms from the electrode and the ions from the electrolyte (typically below 1 nm) [1]. Unlike batteries, EDLCs can be fully charged in a matter of seconds. They also compare favorably with batteries in discharge time (typically a few seconds) and, most importantly, they feature a much higher cycle life. However, the major drawback of supercapacitors is the lower energy density, in general about  $5 \text{ Wh kg}^{-1}$  [2], although higher-energy systems have recently been offered by hybridizing battery-type and supercapacitor-type electrodes in a single cell (e.g., the Li-ion capacitor). A wide variety of carbon nanomaterials

have been exploited as EDLC electrodes, in particular, template carbons [3], carbon nanoions (e.g., [4]) and graphene (e.g., [5]), but microporous activated carbons (ACs) remain the material of choice owing to their moderate cost and large availability. Although ACs are traditionally produced from petroleum coke, pitch and coals, the scarcity of fossil fuels has recently stimulated an interest in electrode materials originated from inexpensive renewable precursors. Equally to their counterparts derived from fossil sources, they offer a number of attractive attributes such as high SSA, sufficient electrical conductivity, high capacitance values, acceptable cost and high cycle life, but, more advantageously, they can be derived from an abundant organic matter naturally reproducible within a relatively short period of time [6].

This work focuses on microporous carbon electrodes derived from crushed olive pits, which are agricultural olive mill waste byproducts extensively generated by the olive oil milling industry, with estimated production values at a level of 6.8 million tons/year in Europe only [7]. Olive pits have been the subject of thorough studies on the production of ACs by both physical and chemical activation (see, e.g., [7–12]), but do not appear to have been probed as precursors for microporous carbons designed to be used in EDLC electrodes. In this regard, tailoring olive pits-derived carbons for capacitive energy storage can be a good path to a better choice of

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abundant and easily renewable precursors for carbon-based electrode materials.

Apart from the need for renewable sources of electrode materials, the performance requirements of the current and envisioned EDLC market should also be met. In this sense, high volumetric capacitance values are inevitably required [6] since the application areas of supercapacitors are centered on transportation, e.g., on hybrid electric vehicles (HEV) [2]. In this study, the optimization of chemical activation of carbons derived from olive pits has been conducted with the main goal of preparing electrode materials whose textural properties enable high volumetric capacitance values at high charge/discharge rate, *i.e.* on the timescale of supercapacitor applications (typical discharge in less than 10 s). The optimization of carbons derived from olive pits is described with a focus put on the use of carbons for supercapacitors working in basic aqueous electrolyte. We particularly show that minor alterations to textural properties lead to drastic changes in the capacitive response. Finally, we have explored the relation between the textural properties of carbon materials and the rate capability of the corresponding supercapacitor cells.

## 2. Experimental

### 2.1. Preparation of microporous carbons by alkali activation

The activation of carbons was conducted after carbonization of raw olive pits in a tubular furnace by heating under an Ar flow of 100 ml min<sup>-1</sup> at a ramp rate of 5 °C min<sup>-1</sup> to a predefined temperature and further holding the temperature for 2 h (the carbonization yield for olive pits is 25 ± 1% independently of the temperature between 600 °C and 800 °C). After carbonization, the resulting char was physically mixed with potassium hydroxide in variable mass ratios. Physical mixing was chosen as the contacting method because in most cases it has been proven to lead to better porosity development than impregnation [13]. The materials mixed with KOH were placed in an Inconel<sup>®</sup> boat and activated according to the procedures known in the literature by heating up to the maximum temperature under Ar flow (100 ml min<sup>-1</sup>) inside a horizontal stainless steel tube within a tubular furnace [13]. The heating ramp rate was 5 °C min<sup>-1</sup> and the holding time at the maximum temperature was 2 h. The variable parameters were the KOH/carbon ratio (KOH/C ratio) and the maximum temperature. In all cases, preliminary carbonization and subsequent activation were both carried out at the same temperature. After activation, microporous carbons were washed off with a diluted solution of hydrochloric acid and water until neutral pH was reached and then dried at 120 °C under vacuum.

Table S1 details the activation yield as a function of the KOH/C ratio for the activations conducted at 700 °C (the optimum selected temperature as explained below).

### 2.2. Textural and X-ray photoelectron spectroscopy characterization

Nitrogen adsorption isotherms were measured at -195.8 °C using a Micromeritics ASAP 2020 instrument for relative pressure values (P/P<sub>0</sub>) between 10<sup>-8</sup> and 0.995 for samples preliminarily outgassed for 24 h at 200 °C. The SSA values and pore size distribution were calculated by applying the recently-developed 2D Non-Local Density Functional Theory (2D NLDFT) treatment to N<sub>2</sub> adsorption isotherms using the data reduction software SAEIUS [14]. The average pore size ( $L_0$ ) was calculated as a weighted average from the DFT data according to the formula:

$$L_0 = \frac{\int_{V_{\min}}^{V_{\max}} L dV}{V_{\max} - V_{\min}} \quad (1)$$

where  $V_{\max}$  and  $V_{\min}$  are the total pore volume and the pore volume at the minimum pore size, correspondingly.

XPS C1s and O1s spectra were recorded using a PHOIBOS 150 analyzer (SPECS) and monochromated Mg K $\alpha$  X ray source.

### 2.3. Electrode preparation and electrochemical measurements

Electrodes were prepared on the basis of the mixture of a carbon material (95 wt.%) and a polytetrafluoroethylene (PTFE) binder (5 wt.%, from a 60 wt.% aqueous dispersion). The mixture was homogenized by adding a few milliliters of ethanol and then worked out until plasticity. The plastic composite was then rolled to a thickness of ~200  $\mu$ m and dried under vacuum at 120 °C overnight. Disk-shaped electrodes of 11 mm in diameter were then cut out, weighed, and their thickness was measured again. Finally, two-electrode symmetric supercapacitor cells were assembled in a Nylon Swagelok<sup>®</sup> airtight system using two identical carbon electrodes, two titanium current collectors and a porous glass fiber (Whatman GFB) membrane separator. 6 M KOH was used as the electrolyte solution. An Hg/HgO reference electrode was introduced into two-electrode cells for discriminating the potential evolution of each of the two electrodes with the cutoff voltage being imposed between the positive and negative electrodes.

Cyclic voltammetry (CV), Galvanostatic (GA) charge-discharge cycling and electrochemical impedance spectroscopy (EIS) measurements were conducted using a multichannel VMP3 generator (Biologic, France). EIS measurements were conducted by applying a low sinusoidal amplitude alternating voltage of 10 mV at frequencies from 1 MHz to 10 mHz.

The average gravimetric capacitance per electrode was calculated from the data of the GA experiments according to the formula:

$$C = 2 \frac{\int Idt}{\Delta V m_{am}} \quad (2)$$

where  $C$  is the gravimetric capacitance per electrode (F g<sup>-1</sup>),  $Idt$  the differential charge (A s),  $\Delta V$  the cell voltage (V),  $m_{am}$  the mass of active material per electrode (g). The capacitance values are reported for the voltage range between 0 V and the maximum cell voltage, excluding the Ohmic drop.

The gravimetric capacitance per cell was calculated as

$$C_{\text{cell}} = C/4 \quad (3)$$

Additionally, the capacitance of the positive and negative electrodes was separately calculated from the potential variation at the corresponding electrode in the cases where a reference electrode was introduced in a 2-electrode cell. For instance, for the positive electrode

$$C_+ = \frac{\int Idt}{\Delta E_+ m_+} \quad (4)$$

where  $C_+$  is the capacitance (F g<sup>-1</sup>),  $I$  the constant current (A),  $\Delta t$  the discharge time (s),  $\Delta E_+$  the potential evolution (V, excluding the Ohmic drop),  $m_+$  the mass of the positive electrode (g). The corresponding values for the negative electrode are denoted as  $C_-$ ,  $\Delta E_-$ ,  $m_-$ .

The differential gravimetric capacitance per electrode of a two-electrode cell in the CV experiments was calculated according to the formula:

$$C = 2i / [(dV/dt) m_{am}] \quad (5)$$

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