



# Narrow-porous pitch-based carbon fibers of superior capacitance properties in aqueous electrolytes



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## ABSTRACT

Two couples of narrow-porous carbons in the form of particulates (PAC) and fibers (ACF) have been prepared by one step carbonization/activation of pitch-based precursors in carbon dioxide or ammonia atmosphere. The activated carbons are assessed as electrode material of EDL capacitor operating in  $6 \text{ mol L}^{-1}$  KOH and  $0.5 \text{ mol L}^{-1}$   $\text{K}_2\text{SO}_4$  aqueous solutions. Electrochemical measurements show distinctly improved charge propagation in pitch-based ACFs compared to corresponding PACs but also to commercial phenolic resin-based FR15 fibers of very similar porosity characteristics, especially in the sulphate medium. Over twice higher capacitance of ACFs than FR15 in  $\text{K}_2\text{SO}_4$  solution (over  $90$  vs  $40 \text{ F g}^{-1}$  at  $1 \text{ F g}^{-1}$ ) is attributed to less distorted basic structural units in pitch-based fibers, and thus facilitating quick penetration of ions along pores. Carbonization/activation treatment in ammonia appears to be a very effective route for enhancing the capacitance without noticeable negative impact of nitrogen and oxygen functionalities with increasing charge rate, current density or frequency. Pitch-based narrow-porous active carbon fibers seem to be a very well adapted candidate for use as electrode material of low-to-moderate power capacitor intended to operate in sulphate electrolyte above water decomposition voltage.

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## 1. Introduction

A variety of porous carbons with high surface area and acceptable electronic conductivity have been considered as active materials of electric double layer capacitors (EDLC) [1–3]. Availability and relatively low cost prefer activated carbons (ACs) produced from common organic precursors by means of thermal or chemical activation. Optimization of porous texture and surface properties of ACs used as electrodes has received enormous attention in the last twenty years [4–9]. It is generally accepted, that the electric capacitance is proportional to the surface area which is accessible to electrolyte ions. However, the electrochemically active surface area can be considerably lower than that derived from gas adsorption, in some cases it is estimated as 20–30% of the measured value [10]. Apparently, there is no linearity in the relationship between surface area and gravimetric capacitance when  $S_{\text{BET}}$  exceeds  $1500\text{--}2000 \text{ m}^2/\text{g}$  [8,11]. Hence, the primary role of pore size distribution (PSD) in the selection of AC for capacitor has been suggested [12,13]. In general, wider pores are required to

improve high power and high frequency capability [14,15]. Several attempts to adapt PSD of activated carbon for a given electrolyte and current load have been reported in the literature [8,16–19]. The pore shape and tortuosity are another features of active material porous texture which are important for application in EDLC. This aspect is hardly reflected in porous texture parameters obtained using the classical sorption technique but it is believed to influence strongly the resistance of electrolyte migration in the pores [17,18,20,21].

Active carbon fibers (ACFs) are known to have a number of advantages over particulate (powdered) activated carbons (PACs) in sorption applications. Narrow diameter ( $10\text{--}20 \mu\text{m}$ ) and opening of micropores directly to the outer surface facilitate access of adsorptive to pores and active sites [22]. The role of porous carbon when used as capacitor electrode is to some extent similar. Indeed, fibrous active carbon, both in the form of powder [13,18,20,23] and fabrics [24–27], applied as electrode material show both the high electric capacity and charge propagation. The improvements are attributed to reduced restriction in electrolyte penetration in less convoluted micropores compared to particulate AC.

Carbon fabrics are very convenient as electrode material because there is no binder required, however drawbacks are low bulk density ( $\sim 0.35 \text{ g cm}^{-3}$  vs  $0.5\text{--}0.7 \text{ g cm}^{-3}$  for particulate ACs

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[28]) resulting in increased need for electrolyte and a high electrical resistance between individual fibers and between cloth and the metal collector [1]. Applying pulverized fibers allows the drawbacks to be minimized whilst benefits attributed to fibrous form are preserved and result in strong improvement in capacitor performance at the enhanced current load [23]. The main barrier in a wide application of fibrous electrode material in capacitor is that ACFs are at least 10 times more expensive than common PACs [22].

Industrial capacitors mostly use organic electrolyte which is able to operate at much higher voltage (up to 2.7 V) than the device with aqueous medium (<1.0 V) and thus to store distinctly more energy. However, aqueous electrolytes have about 10 times higher conductivity and low viscosity, resulting in a good charge propagation and power rates of capacitor. They are also less expensive, environmentally friendly and easier in handling [29]. Increasing operating voltage is therefore the key challenge for making an aqueous capacitor a realistic alternative to that using organic medium. Using asymmetric configuration of electrodes is probably the most explored route to enhance working voltage above 1.2 V, i.e. that of water decomposition, the device with electrodes built of ACs with different properties being one of the considered options [29]. A capacitor with optimized carbons as positive and negative electrodes could reversibly be charged/discharged at 1.6 V in  $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  [30]. Recently, the enhancement of operating voltage of symmetric carbon/carbon capacitor to about 2.0 V by applying neutral electrolytes, mostly sulphates, instead of most widely used sulphuric acid or potassium hydroxide has been reported [31–33].

In the above discussed context our present research has been focused on elucidating the role of active material form, particulates (PACs) and fibers (ACFs), on the performance of symmetric capacitors operating in  $6 \text{ mol L}^{-1} \text{ KOH}$  and  $0.5 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$ . Two couples of narrow-porous electrode materials are used to build electrodes: conventional  $\text{CO}_2$  activated (PACs and ACFs) and those functionalized with nitrogen and oxygen by ammonia treatment (N-PAC and N-ACF). To get reliable comparison, corresponding particulates and fibers are produced from the same precursor and represent very similar porous texture and surface chemistry. We used also identical electrode preparation and cell construction techniques. For the first time, according to our knowledge, we are able to demonstrate so clearly the meaningful effect of active material form and surface functionalization with nitrogen and oxygen on the capacitance behavior in relation to the type of aqueous electrolyte used.

## 2. Materials

The starting material for preparing nanoporous PACs and ACFs was a synthetic anthracene oil-based pitch (AOP) of softening point  $247^\circ\text{C}$  (Mettler) supplied by Industrial Quimica del Nalon S.A. [34]. Anthracene oil is low cost carbon-rich byproduct of coal coking industry. Therefore, the isotropic high softening point pitch derived thereof is a potential precursor of inexpensive general purpose carbon fibers (GPCFs) and active carbon fibers [35,36].

The pitch was used in the form of particulates and fibers. The materials were first subjected to oxidation to cross-link the aromatic molecules by oxygen and change the thermoplastic character into thermosetting. The treatment, called stabilization, is required to preserve the original particulate or fiber shape and to facilitate porosity development during subsequent carbonization/activation. Pitch particulates were prepared by grinding AOP sample to pass the sieve of  $100 \mu\text{m}$ . The oxidation was performed according to the heating program: heating rate of  $1 \text{ K/min}$  with a soak for 1 h at 180, 200, 220,  $240^\circ\text{C}$  and for 2 h at  $270^\circ\text{C}$ . The treatment resulted in the increase in oxygen content in AOPox to 8.8 wt% [37].

Stabilized by air oxidation pitch fibers were provided by the Instituto Nacional del Carbon in Oviedo, Spain. Stabilization of freshly spun pitch fibers was a multi-step process including slow heating in air to  $270^\circ\text{C}$  [35].

One step pyrolysis/activation process was applied for producing nanoporous carbons from stabilized pitch particulates and pulverized fibers. In case of  $\text{CO}_2$  activation, the treatment was performed in a home-made fixed bed tube reactor [38]. A sample was placed in a stainless steel container, which was suspended from an electrobalance to control burn-off. The treatment consisted in heating in carbon dioxide flow at a rate of  $2 \text{ K min}^{-1}$  to the final temperature of  $900^\circ\text{C}$  with soaking time adapted in order to get about 50 wt% burn-off. The reaction with ammonia to produce nitrogen enriched activated particulates N-PAC and fibers N-ACF was performed in a horizontal tube furnace [37]. The stabilized particulates and fibers, placed in a quartz boat, were heated at  $2 \text{ K/min}$  in ammonia gas flow of  $9 \text{ dm}^3 \text{ h}^{-1}$  to the final temperature of  $900^\circ\text{C}$  and  $850^\circ\text{C}$ , respectively, with 0.5 h soak.

Commercial phenolic resin-based active carbon fibers FR15 (Kuraray Chemical Co.; Kuractive Carbon) were used as a reference material.

## 3. Experimental

### 3.1. Characterization of activated carbons and electrodes

The elemental composition (CHNS) was determined using a Vario EL analyzer. The oxygen content was determined directly using a Carlo Erba analyzer.

Particle size distribution was measured in water by Malvern Mastersizer 2000 (laser  $632 \text{ nm}$ ) with a drop of surfactant (Rocafenol N8) added to improve particles wettability.

Scanning electron microscopy (JEOL, JSM 5800 LV) was used to assess the morphology of particles and fibres.

The porous texture of the activated carbons and pressed electrodes was characterized by nitrogen adsorption at  $77 \text{ K}$  (ASAP 2020, Micromeritics). Before the measurement the samples were degassed overnight at  $300^\circ\text{C}$ . Porous texture parameters determined from the  $\text{N}_2$  adsorption isotherms include the total pore volume  $V_T$ , the specific surface area  $S_{\text{BET}}$ , the micropore volume  $V_{\text{DR}}$  and the average micropore width  $L_0$ .  $V_{\text{DR}}$  and  $L_0$  were computed from the application of the Dubinin-Radushkevich and Stoeckli equations [39], respectively. The QSDFT analysis [40] was applied to the  $\text{N}_2$  adsorption isotherms to determine pore size distribution (PSD) and micropore surface area ( $S_{\text{DFT}}$ ).

The electrical conductivity was measured for dry electrodes using the experimental setup similar to that described in [41]. Each electrode was put between two gold current collectors and pressed at 0.8 MPa to ensure electrical contact. The resistance was measured by using milliohm meter (GOM-802) and the electrical conductivity was calculated based on the resistance value and the geometric parameters.

### 3.2. Electrochemical characterization

Electrodes were pressed under 18 MPa in the form of pellets with a geometric surface area of  $0.64 \text{ cm}^2$  and thickness of about  $200 \mu\text{m}$  from a mixture of 85 wt.% of active material, 10 wt.% of polyvinylidene fluoride (PVDF Kynar Flex 2801) and 5 wt.% of acetylene black. Symmetric two-electrode capacitors were assembled in a Swagelok® system with electrodes of comparable mass of 8–11 mg, gold-coated current collectors and glassy fibrous separator. The experiments were performed in  $6 \text{ mol L}^{-1} \text{ KOH}$  and  $0.5 \text{ mol L}^{-1} \text{ K}_2\text{SO}_4$  aqueous electrolytes. All measurements were carried out in a voltage range from 0 to 0.8 V using a potentiostat–galvanostat VMP3 Biologic (France). The capacitance

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