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Activated carbon fibers prepared directly from stabilized fibers for use as electrodes in supercapacitors

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ABSTRACT

A novel type of carbon fibers, obtained by direct chemical activation of stabilized fibers (non-carbonized), is investigated as active electrode material in supercapacitors (SCs). The main advantage of this novel synthetic method is that it avoids the step of carbonization of the stabilized fibers prior to activation, reducing therefore their cost of production. The as-obtained materials exhibit specific capacitances up to 100 F g^{-1} in aqueous electrolytes (1.0 M H_2SO_4), values that are not only higher than those obtained with conventional fibers but also comparable to the capacitances of SCs based on well-established reference materials such as commercial activated carbons (ACs).

1. Introduction

Carbon-based supercapacitors (CBSCs) have been widely developed as energy storage devices due to their high power density and long cycle life [1]. Activated carbons (ACs) are commonly used as active electrode materials in CBSCs, mainly due to their high specific surface areas, low cost and scalability [2]. As electrode materials with similar characteristics to ACs, activated carbon fibers represent an attractive alternative.

Compared to granular or powdered activated carbons, ACFs show a higher adsorption-desorption kinetics and lower resistance to bulk flows. They can also be woven into matt or fabrics, allowing their incorporation in different designs, as flexible devices, being their main disadvantage their higher manufacturing cost [3–5]. Therefore, any new strategy that would reduce the cost of the production process would be welcomed by manufacturers.

Nowadays, ACFs are commonly prepared by the chemical or physical activation of carbonized carbon fibers. Compared to physical activation, chemical activation with alkaline hydroxides, such as NaOH, provides higher yields and causes less surface damage during the activation of the fibers [6] and so will be the main focus of this study. The overall industrial preparation process (starting from the raw pitch) consists of four consecutive steps: (i) spinning of the parent material (mainly PAN or pitch), (ii) stabilization of the as spun fibers to make them infusible, (iii) carbonization of the stabilized fibers up to 900–1000 °C in order to consolidate their carbonaceous structure and iv) chemical activation (mainly with KOH) of the carbon fibers at temperatures of 700–900 °C [7].

We report herein on the suitability of the direct activation of stabilized (non-carbonized) fibers to produce carbon materials with adequate characteristics for use as electrodes in SCs. This process offers a substantial reduction of energy and time and therefore represents an important contribution to the development of alternative electrode materials for high-performance energy storage devices.

2. Materials and methods

A coal-based pitch, supplied by Nalonchem, S.A. was melt-spun into filaments using a laboratory-scale device (See Supporting information, S.I.) [8]. The fibers were then stabilized at 240 °C under an air flow of 333 ml min^{-1} at a heating rate of 1 °C min^{-1} with isotherm stages of 1 h at 160, 180, 200, 220, 240 and 260 °C, to yield the SFs. These fibers were carbonized under nitrogen at 900 °C for 30 min at a heating rate of 2 °C min^{-1} to yield CFs. The SFs or CFs were chemically activated in a horizontal furnace after impregnation with NaOH (fiber/NaOH ratio of 1/3). The activation temperature used was 900 °C and the holding time was 1 hour. The washed samples (pH∼7) were labeled as ACFs (from CFs) or ASFs (from SFs). The morphology of the fibers was examined by SEM (Evo LS15 Zeiss microscope). The textural parameters of the activated fibers were determined from the N_2 adsorption-desorption isotherms at 77 K (Nova 2200, Quantachrome) [9,10].

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ACFs, ASFs and a commercial activated carbon (ACN; Norit DLC Super 50 - Nederland BV) [11] were used as active electrode materials. Disk-type electrodes (approx. 30 mg and 1.13 cm^2 of geometric area) were prepared by mixing 90% of ACFs, ASFs or ACN with 10% of polytetrafluoroethylene (PTFE) as binder. Cyclic Voltammetry (CV, recorded between 0.0–1.0 V at a scan rate, ν_{scan}, ranging from 1 to 20 mV s^{-1}) and Galvanostatic charge/discharge experiments (GCPL, applying constant current densities, i, of 0.88–88.50 mA cm^{-2} in a voltage range, ΔV, of 0.0–1.0 V) were carried out in a two-electrode Swagelok® type cell using 1.0 M H_2SO_4 as electrolyte. The SCs were constructed using two electrodes of the corresponding ACN, ACFs or ASFs separated by a glassy paper and gold disks as current collectors (See S.I.). The specific electrode capacitances (C_e, F g^{-1}) were calculated from the discharge voltage profiles (See S.I.).

3. Results and discussions

The activated fibers were obtained using as starting material pitch-based carbon fibers (CFs) and also an intermediate material prior to the formation of CFs, i.e., stabilized fibers (SFs) (Fig. 1).

The activated agent used was NaOH (Fiber/NaOH ratio of 1/3) at 900 °C. After activation the materials maintained their characteristic fibrillar shape, as determined by SEM (Fig. 2). The images also confirm the presence of pores in both types of fibers, there being higher presence of pores in ASFs reflecting a greater degree of activation than for the ACFs under the same activation conditions. This would also explain the lower activation yield obtained for the ASFs (17% compared to 33% in the case of ACFs, Table 1). This ACF yield, however, does not take into account the carbonization yield (about 70%). Therefore, the overall activation yield of ACFs derived from the stabilized fibers decreased to $\approx$23%, very similar to the ASF yield. The above results confirm that stabilized fibers can be directly activated to successfully produce activated carbon fibers.

The textural characteristics of the ACFs and ASFs were determined from their N_2 adsorption isotherms (Fig. 2b, e). The results obtained indicate the development of porosity in the fibers during their processing, both samples showing isotherms of Type I, which are characteristics of highly microporous materials. However, the ASFs also exhibited a hysteresis loop indicating the formation of mesopores. The greater N_2 adsorption capacity of ASFs results in a higher BET surface area (2460 and 1101 m^2 g^{-1} for ASFs and ACFs, respectively). This is a consequence of both the higher development of microporosity (0.85 cm^3 g^{-1} for ASFs and 0.41 cm^3 g^{-1} for ACFs) and also of mesoporosity (0.49 cm^3 g^{-1} for ASFs and 0.11 cm^3 g^{-1} for ACFs), also being this latter of larger size (Fig. 2c, f). Since both types of fibers were activated under the same experimental conditions, the higher reactivity of the NaOH with stabilized fibers is evident, which is also evident from the SEM images (Fig. 2a, d). A possible explanation for this could be the higher oxygen content in SFs (8.3%, being negligible in the case

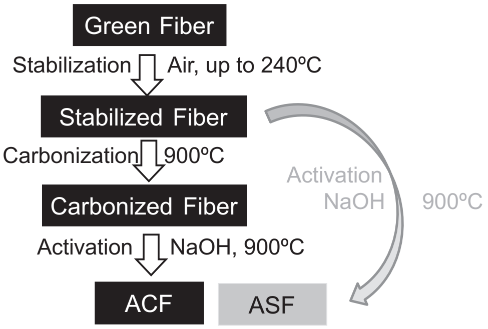

Fig. 1. Scheme of the activation of stabilized (SF) and carbonized (CF) fibers.

Table 1
Activation yield and textural parameters of ASF, ACF and ACN.

	Yield (%)	**S_{BET}** (m^2 g^{-1})	**V_T** (cm^3 g^{-1})	**V_{micro}** (cm^3 g^{-1})	**V_{meso}** (cm^3 g^{-1})	**L_0** (nm)
ACF	33 (23)[a]	1101	0.52	0.41	0.11	1.19
ASF	17	2460	1.34	0.85	0.49	2.02
ACN	–[b]	1749	0.93	0.65	0.31	1.35

[a] Yield in brackets corresponds to the overall yield of ACFs form stabilized fibers.

[b] Not determined. S_{BET}, BET apparent area; V_T, total volume of pores; V_{micro}, micropore volume; V_{meso}, mesopore volume; L_0, average pore width (see Fig. 2 c, f and S.I.).

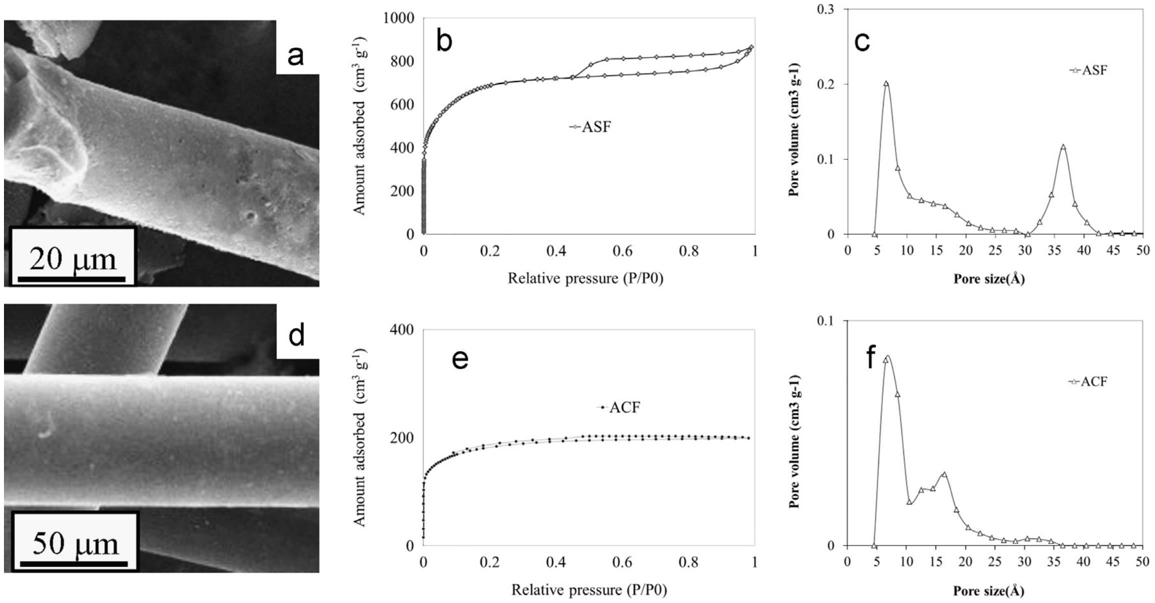

Fig. 2. SEM images (a,d), N_2 adsorption isotherms (b,e) and DFT plots (c,f) of ASFs (a,b,c) and ACFs (d,e,f).