



## Research Paper

# Mechanically activated carbonized rayon fibers as an electrochemical supercapacitor in aqueous solutions



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## ABSTRACT

The activated carbon cloth (ACC), obtained by chemical/physical activation of carbonized rayon fibers, was grinded in a ball mill and studied from the aspect of double layer capacitance. The changes in pore structure, morphology and acid/basic properties caused by ball milling were studied by means of N<sub>2</sub> adsorption/desorption, Fourier-transformed infrared spectrometry, Boehm's titration and Scanning Electron Microscopy. Both potentiodynamic and galvanostatic cycling were used to evaluate the double layer capacitance in three alkaline, acidic and neutral aqueous solutions (KOH, H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>). While double layer capacitance of original ACC was found to be negligible, ball milled material (ACCM) displayed capacitance in the range of supercapacitors. In order to explain this huge capacitance improvement, we found that ball milling substantially increased the concentration of lactone, phenolic and quinone groups on the surface. We suggest that these groups, through improved hydrophilicity, enable faster ion diffusion into carbon micropores. The energy density stored by double layer was highest in neutral sodium sulphate solution. Namely, operational voltage of ~2 V and double layer capacitance of 220 F g<sup>-1</sup> at 1 A g<sup>-1</sup>, enable the energy density of ACCM/Na<sub>2</sub>SO<sub>4</sub>/ACCM capacitor of 31.7 Wh kg<sup>-1</sup> at 2000 W kg<sup>-1</sup>, much higher than that of commercial EDLC carbon capacitors. According to the here presented literature survey in a tabular form, the energy density of the studied sample is also higher from that of numerous thus far published aqueous carbon capacitors.

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## 1. Introduction

The carbon-based supercapacitors in aqueous KOH and H<sub>2</sub>SO<sub>4</sub> solutions may provide extremely high capacitance reaching 150–350 F g<sup>-1</sup> [1–3]. Relatively low voltage window ≤ 1 V available for capacitor charging/discharging processes in aqueous solutions present the main obstacle in their commercialization [3–6]. Ania et al. [4] found that commercial activated carbon as capacitor electrode material underwent the oxidation degradation in the periods of anodic polarization. Both acidic and alkaline aqueous solutions have been preferentially used as electrolytes in aqueous supercapacitors, displaying higher conductivity [7] and slower faradaic processes [8] in comparison to neutral solutions. Namely,

capacitances measured in neutral aqueous electrolytic solutions, ranging 50 to 140 F g<sup>-1</sup>, are generally lower from capacitances measured in either acidic or alkaline solutions [5,7,9–13].

Demarconnay et al. published a pioneering work [14] in which they described a very high voltage window of 2.4 V achievable in Na<sub>2</sub>SO<sub>4</sub> solution with an activated carbon (AC) working electrode in a three-electrode cell. However, voltage interval of only 1.6 V was achievable in a symmetric two-electrode arrangement, with two AC electrodes. In this arrangement capacitance of 125 F g<sup>-1</sup> at the rate of 1 A g<sup>-1</sup> was measured, with displayed very slight fade on cycling. This study incited a rising interest for application of neutral aqueous electrolytes in carbon based capacitors [15–18]. Yang et al. [17] showed that supercapacitors based on hydrated graphene film with neutral electrolyte solution can operate at the voltage of 1.8 V, providing the capacitance of ~200 F g<sup>-1</sup> at a rate of 1 A g<sup>-1</sup>. Fic et al. [6] described a symmetric carbon capacitor operable at voltage close to 2.2 V using 1 mol dm<sup>-3</sup> Li<sub>2</sub>SO<sub>4</sub> solution as the electrolyte.

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For this supercapacitor only a slight capacity decrease from  $140 \text{ F g}^{-1}$  to  $120 \text{ F g}^{-1}$  was evidenced after even 15000 charging/discharging cycles.

Babel and Jurewicz [19] demonstrated that viscose rayon carbon fibers, chemically activated in hot KOH solution, provide very high capacitance of  $340 \text{ F g}^{-1}$  and  $270 \text{ F g}^{-1}$  in  $4 \text{ mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  and  $7 \text{ mol dm}^{-3}$  KOH solutions, respectively. Milczarek et al. [20], for commercial activated carbon fiber cloth, surface enriched by oxygen, measured high capacitance of  $161 \text{ F g}^{-1}$  in sulfuric acidic solution, which even increased to  $172 \text{ F g}^{-1}$  by potentiostatic oxidation.

Ball milling process has been applied to modify the properties of various carbonaceous materials including carbon nanotubes (CNTs) [21–26], graphite [27,28] and activated carbon cloth [29]. For instance, ball milling, transformed CNTs into nanoparticles [21]. Figueiredo et al. [25] developed a simple solvent-free method to obtain N-doped CNTs by ball milling of melamine or urea. The single-walled CNTs [23] and graphite [27], upon ball milling became capable of intercalating high amount of lithium ions. Mechanochemically treated microporous activated carbon cloth, obtained by simultaneous carbonization and  $\text{CO}_2$ -activation of viscose rayon cloth [29], may be used as effective adsorber of As (V) [30] and some other pollutant ions (zinc, cadmium mercury) [31] from aqueous solutions.

Having in mind the successful use of neutral aqueous solutions in carbon supercapacitors [14–18], and the possibility of activation of carbonized rayon fibers by ball milling [19,30], in the present paper, we investigated the applicability of mechanochemically activated carbonised rayon fibers as electrodes of symmetrical supercapacitors with aqueous electrolyte solutions. To the best of our knowledge, this is the first study of mechanochemical modification of this abundant and cheap raw material for the use in the field of supercapacitors. A comparative study was performed in pH-different aqueous solutions,  $\text{KOH}_{\text{aq}}$ ,  $\text{H}_2\text{SO}_{4\text{aq}}$  and  $\text{Na}_2\text{SO}_{4\text{aq}}$ . The results evidenced that mechanochemical modification significantly improved charge storage behavior. Namely, in neutral  $\text{Na}_2\text{SO}_4$  solution, symmetric supercapacitor operable in a wide voltage interval of  $\sim 2 \text{ V}$  is realized, with an energy density being among the highest ones thus far reported for carbon supercapacitors with aqueous electrolyte.

## 2. Experimental section

The commercial rayon cloth (Viskoza, Loznica) impregnated by  $\text{ZnCl}_2$  and  $\text{NH}_4\text{Cl}$  solutions, carbonized and simultaneously activated by  $\text{CO}_2$ , designated as ACC, [30] was used in this study. The cloth was transformed to carbon powder (ACC<sub>m</sub>) by milling in a Turbula Type 2TC mixer under air atmosphere. The milling process was performed in hardened steel vial with BPR fixed at 20:1 and milling time of 20 h. A very fine powder was obtained. Similar procedure has been recently used in ref [29]. However, in this study, before milling, we washed ACC sample with  $0.1 \text{ M HNO}_3$ , to remove Zn-containing impurities used in activation procedure, when the surface was simultaneously subjected to a slight oxidation. The adsorption-desorption isotherms of ACC<sub>m</sub> were measured by nitrogen adsorption at 77 K using a Sorptomat 1990 Thermo Finnigan device. Prior to adsorption, the samples were degassed for 4 h at room temperature under vacuum, additionally 8 h at 383 K and finally 12 h at 523 K at the same residual pressure. Various models [32–35], and appropriate software ADP Version 5.17 CE Instruments were used to analyse the obtained isotherms. The total pore volume ( $V_{\text{tot}}$ ) was calculated applying the Gurevitsch's rule [32] at relative pressure  $p/p_0 = 0.95$  ( $p$  and  $p_0$  represent the equilibrium and saturation pressures of nitrogen at the temperature of adsorption). The specific surface area,  $S_{\text{BET}}$ , was calculated according to the Brunauer, Emmet, Teller method. The interval of  $p/p_0$  for BET plot was selected using procedure proposed by J. Rouquerol et al. [33]. Micropore volumes were obtained using the t-plot method ( $V_{\text{mic-t}}$ ), Dubinin-Radushkevich method ( $V_{\text{mic-DR}}$ ) [34] and Horvath-Kawazoe method ( $V_{\text{mic-HK}}$ ) [35]. Absorbance spectra were measured in the range of  $4000\text{--}400 \text{ cm}^{-1}$ , at  $2 \text{ cm}^{-1}$  resolution, using Nicolet 6700 FTIR spectrometer (Thermo Scientific). The KBr pellet technique was used. In order to disperse ACC in KBr and made pellet, the piece of ACC cloth was grinded by mortar and pestle. Since the fine powder of ACC was very difficult to get in such a way, Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR) was also measured from both ACC and ACC<sub>m</sub> samples in order to check the reliability of all collected data. FTIR-ATR spectra were measured using FTIR-ATR spectrophotometer Nicolet iS10 (Thermo Fisher Scientific). The amounts of acidic and basic surface functional groups were

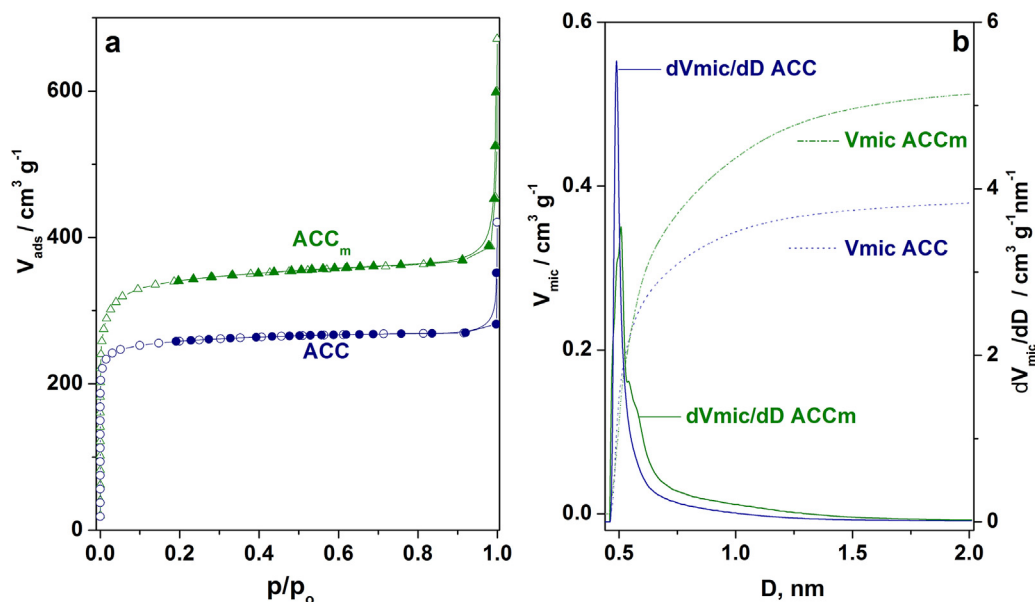


Fig. 1.  $\text{N}_2$  adsorption (colored symbol)/desorption (empty symbol) curves (a) and the pore size distribution (b) of ACC and ACC<sub>m</sub> samples.

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