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Complex insight into the charge storage behavior of active carbons obtained by carbonization of the plane tree seed

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ABSTRACT

Activated carbon was prepared using plane tree seed as a cheap and renewable raw material. The samples were prepared by carbonization under N_2 atmosphere up to 850 °C, and activation in CO_2 atmosphere at different both temperatures (750 and 850 °C) and times of activation (0.3, 1 and 2 h). The influence of activation parameters on physicochemical properties was studied by XRPD, Raman spectroscopy, FTIR, N_2 physisorption, SEM and electrochemical methods. The pore structure was correlated to the specific capacitance and the amount of hydrogen stored, in alkaline, neutral and acidic electrolyte solution. The relationship of asymmetrical shape of CV curves with the porosity of samples has served to better understand some unclear issues related to the complex mechanism of charge storage. The sample activated at 850 °C for 2 h displayed the best behavior. At a high scan rate of 300 mV s^{-1}, its capacitance, amounted to $\sim$26.8 $\mu F\,cm^{-2}$ $\sim$19.69 $\mu F\,cm^{-2}$ and $\sim$25.8 $\mu F\,cm^{-2}$ in KOH, Na_2SO_4, and H_2SO_4 solutions, respectively.

1. INTRODUCTION

Powdery carbon materials were extensively studied as electric double–layer capacitors, hydrogen storage materials, highly efficient catalysts, catalyst support for fuel cells, *etc.* Their performances, as well as the area of application, are mainly determined by texture properties and surface chemistry, which depend on synthesis conditions [1–4].

The charge storage without any charge transfer through the electrode/electrolyte interface is characteristic for pure double layer capacitors. If surface charge storage involves charge transfer (faradaic reaction), one deals with the participation of pseudocapacitance. The last one is usually slower, since, according to the theory of rate processes, requires the energy of activation. The relative contribution of these two ways of surface charge storage depends strongly on the pore structure and surface chemistry of carbon material, as well as on the nature of the electrolyte [5–11].

In order to obtain a high–power and durable carbon capacitor, the investigations were focused mainly on the development of carbon materials with high specific surface area. However, proportionality between the surface area and the specific capacitance, although often observed, cannot be generalized. Some authors reported that the specific capacitance increases with the increase of the surface area [12–14], while some others reported the opposite behavior [13,15,16]. Depending on the type of carbon [13,17], both viewpoints can be accepted. Actually, beside the high specific surface area, other parameters including pore size distribution, electric conductivity and presence of surface heteroatoms [15,17–20] can be detrimental in the achievement of the high–rate performance of carbon capacitors. Many studies [7,9,21–28] revealed the importance of micro- and mesopores in surface charge storage. Some authors claimed that the detraction of pore radii provides higher capacitance values [7,9,25]. The pivotal role of micropores in the effective charge storage was clearly demonstrated by Gogotsi et al. [21,22] and confirmed afterwards by other

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researchers [12,23]. However, well-balanced ratio of micro and mesopores was found to lead to the highest capacitance values [24,26–29].

The complexity of charge accumulation at the porous carbon electrode/electrolyte interface manifests itself by deviation of cyclovoltammograms from the rectangular shape [30–36], has not been solved yet. The kinetics of both ions penetration into pores [30,31,36] and pseudocapacitance processes [32–35] are suspected as responsible for such behavior.

Activated carbon (AC) is commonly used as electrode material of double layer capacitors. To save fossil raw materials in AC production, a broad variety of natural and synthetic precursors was studied, such as nutshells, wood, starch, sucrose, cellulose, sugar cane bagasse, corn grain and banana fibers [7,4,26]. Wei et al. [7] obtained microporous carbon by pyrolysis of sucrose followed by CO_2 activation, where the activation helped to improve the capacity from 4 to 160 $F g^{-1}$ (measured in H_2SO_4 solution at rate 1 $mV s^{-1}$). Subramanian et al. [37] obtained carbon from banana fibers and activated it with pore-forming substances such as $ZnCl_2$ and KOH. The capacitance of this material in neutral aqueous Na_2SO_4 aqueous solution amounting to 86 $F g^{-1}$ was rather insensitive to charging/discharging rate, and this behavior was attributed to the presence of mesopores.

Formerly we studied the role of porosity in charge storage behavior of variety of activated carbon materials (Carbonized PANI, Carbonized PANI 3,5-dinitrosallcylate and Carbonized PANI 5-sulfosalicylate), synthesized by carbonization of polyaniline salt precursors [26]. The outstanding charge storage behavior of Carbonized PANI 5-sulfosalicylate in 6 M KOH was attributed to a well-balanced ratio of micro and mesopores [26].

In the present study, we selected cheap, environmentally renewable, fiber- structured product, plane-tree seed, to obtain AC material in various regimes of CO_2 activation. The activation was carried out at temperature 750 °C during 2 h, and at temperature 850 °C during three time periods: 0.3, 1 and 2 h. A detailed cyclovoltammetric investigation evidenced that a proper activation procedure of the carbonized material may provide high specific capacitance rather insensitive to charging/discharging rate. Special attention was paid to the correlation of textural and electrochemical behavior. In order to provide deeper insight into the mechanism of charge storage, the capacitance was examined in alkaline, neutral and acidic aqueous solutions.

2. EXPERIMENTAL

2.1. Materials

Carbonization of the plane tree seed was carried out in the tube furnace (Protherm Furnaces, model PTF 16/38/250, Turkey), with gas inlet and outlet tubes under N_2 flow (0.5 $L min^{-1}$). The heating rate was 4 $°C min^{-1}$ up to the temperature of 850 °C. Thereafter spontaneous cooling to room temperature was performed keeping nitrogen flow. The yield of carbonization was 31%. The activation of carbonized samples was carried out in the same horizontal furnace at 750 °C for 2 h and 850 °C for 0.3, 1 and 2 h, under CO_2 flow (0.5 $L min^{-1}$). Active carbons obtained in such a way were denoted as AC@T–t, where T means temperatures of activation, and t represents time of activation.

2.2. Characterization methods

For the purposes of this study, elemental analysis was performed on a Vario EL III C, H, N, S/O Elemental Analyzer (Elementar). Simultaneous thermogravimetric and differential thermal analysis (TG/DTA) was performed in the Thermobalance TA STD Model 2090.

The adsorption/desorption isotherms based on adsorption/desorption of N_2 at 77 K were determined using a Sorptomatic 1990 Thermo Finnigan device. Before measurement, the samples were degassed for 12 h at 110 °C and for 24 h at 350 °C under vacuum. The values of pore size distribution, mesopore surface and micropore volume were calculated from the obtained isotherms using the Software ADP Version 5.13 CE Instruments. The Dollimore and Heal method [38] was applied to obtain mesopore size distribution, mesopore volume (V_{meso}–DH) and mesopore surface area (S_{meso}–DH). The micropore volume (V_{mic}–DR) was calculated according to the Dubinin–Radushkevich (DR) equation [39], while the Dubinin's method modified by Kaganer [40] was used to calculate the specific surface area of micropores. The pore–size distribution, as well as the mean pore–size in the microporous region and micropore surface area (S_{mic}–HK) [41] were obtained by the Horvathh–Kowazoe method. Total specific surface area (S_{tot}) was estimated as the sum of S_{mic}–HK and S_{meso}–DH.

The samples of active carbons were characterized at room temperature by X–ray Powder Diffraction (XRPD) analysis using Ultima IV Rigaku diffractometer, equipped with Cu Kα1,2 radiation source (a generator voltage of 40.0 kV and a generator current of 40.0 mA). All samples were recorded in the range of 10–90°2θ, with a scanning step size of 0.02° and at a scan rate 2°/min.

Raman spectra of investigated active carbons were collected on a DXR Raman microscope (Thermo Scientific, USA) equipped with an Olympus optical microscope and a CCD detector, with a diode pumped solid state high–brightness laser (532 nm) and a 10 x objective. The powdered sample was placed on X–Y motorized sample stage. The analysis of the scattered light was carried out by the spectrograph with a grating 900 lines mm^{-1}. The laser power was 1 mW.

Fourier transform infra–red (FTIR) spectra of the investigated active carbons were collected using a PerkinElmer Spectrum Two FTIR spectrometer, in the transmission mode. The samples were made by pressed KBr pellets (1:100) technique. The spectra were recorded in the range from 4000 to 400 cm^{-1} with the resolution of 4 cm^{-1}.

The morphology was studied by scanning electron microscope (SEM) JEOL JSM–5800. The chemical composition of the ash residue, obtained after burning the active carbon samples, was determined using the energy dispersive X–Ray spectrometry (EDS).

2.3. Electrode preparation and electrochemical measurements of active carbons

The electrode materials were prepared by mixing the active carbon materials (85 wt.%), carbon black (10 wt.%) and poly (vinylidenefluoride) (PVDF) binder (5%) in N–methyl 2–pyrrolidone. As the carbon black additive, Vulcan XC 72R was used, which ensures good electronic conductivity, but contributes negligibly to the overall capacity. After the treatment in an ultrasonic bath, the suspension was deposited on the electrical conductive support. As–prepared electrodes were dried at 130 °C under vacuum, and then were tested in 6 $mol dm^{-3}$ KOH, 0.5 $mol dm^{-3}$ Na_2SO_4 and 0.5 $mol dm^{-3}$ H_2SO_4 aqueous solutions. The Cyclic Voltammetric and Impedance measurements were performed by Gamry PCI4/300 Potentciostat/Galvanostat, using classical three–electrode cell with wide Pt foil as a counter electrode, and saturated calomel (SCE) as a reference electrode. The impedance diagrams were collected at different potentials, by using AC voltage amplitude of 5 mV in the frequency range from 10 mHz to 100 kHz.

The specific capacitances ($F g^{-1}$) were evaluated from the surface area under charge/discharge CV curves, according to the equation: