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The capacitance properties of activated carbon obtained from chitosan as the electrode material for electrochemical capacitors

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ABSTRACT

Porous carbon was prepared through KOH activation of a chitosan – a nitrogen rich precursor. The porosity and surface area strongly depend on the temperature of activation. Different electrolytes were tested to select the most suitable one for electrochemical capacitors with obtained activated carbon as electrode material, and the acidic medium, i.e. 1 M H_2SO_4 was chosen. The activated carbon prepared with the temperature of activation standing at 750 °C exhibits the largest specific surface area and capacitance of 295 F g^{-1} at a current density of 0.1 A g^{-1} in the acidic medium. Moreover, the activated carbon from chitosan shows good rate capability and excellent cycling stability (almost 99% capacitance retention over 5000 cycles).

1. Introduction

Electrochemical capacitors are attractive power sources because of their high power density, long cycle-life and moderate energy compared to conventional dielectric capacitors and batteries [1]. Electric double layer capacitors mainly use activated carbons with a high specific surface area as electrode materials, which enhances the efficient use of the electrode surface. Efforts are being made to develop new materials for capacitor electrodes and suitable electrolytes which should be characterized by a large capacitance, cyclic stability and low cost.

Chitosan is a macromolecular copolymer, obtained as a derivative of chitin, which can come from shells of shrimps, crabs, krill etc. and which is the second most popular natural polymer after cellulose [2]. The process of chitosan carbonization leads to creating a microporous carbon with a high amount of nitrogen – above 6% atomic [3].

In the literature there is some information about capacitance properties of electrode material containing chitosan. I.V. Sheveleva et al. [4] used chitosan as a binder with the aim of improving the mechanical properties of carbon fiber material. The capacitance of prepared electrode material did not exceed 75 F g^{-1}. Q. Ji et al. prepared chitosan based porous carbons, yet without any process of activation. Carbons differed in terms of surface areas and capacitance properties (which did not exceed 154 F g^{-1} at a current density of 0.05 A g^{-1}) and strictly depended on the temperature of carbonization [5]. However, there is no information about capacitance properties of carbonized chitosan as electrode material for supercapacitors after chemical activation (using KOH).

2. Materials and methods

In the paper the active carbons based on carbonized (at 650 °C in N_2 atmosphere) chitosan (Aldrich®) (CH) were prepared. Chemical activation of a carbonized chitosan (CRCH) was carried out in the ambient atmosphere in the temperature range of 750–850 °C, with a C:KOH ratio of 1:4. The structure, morphology and physicochemical properties of active carbon (ACRCH) were estimated using: Scanning Electron Microscopy (SEM EVO®40 ZEISS), nitrogen adsorption/desorption measurements (ASAP 2010 M (Micromeritics)) and elemental analysis (Vario MICRO CUBE Elementar Analysen Systeme GmbH). The capacitor electrodes were formed as pellets consisting of 85% active material, 10% binder (PVDF, Kynar Flex 2801) and 5% acetylene black. The activated carbons were tested in three aqueous electrolytes: 1 M H_2SO_4, 6 M KOH and 1 M Na_2SO_4 electrolyte, and one aprotic electrolyte: 1 M $TEABF_4$ in PC, using two-electrode Swagelok® system. The specific capacitances of electrode materials were obtained using three techniques: cycling voltammetry (CV) 1–100 mV s^{-1}, galvanostatic charge/discharge (100 mA g^{-1}–10 A g^{-1}) and

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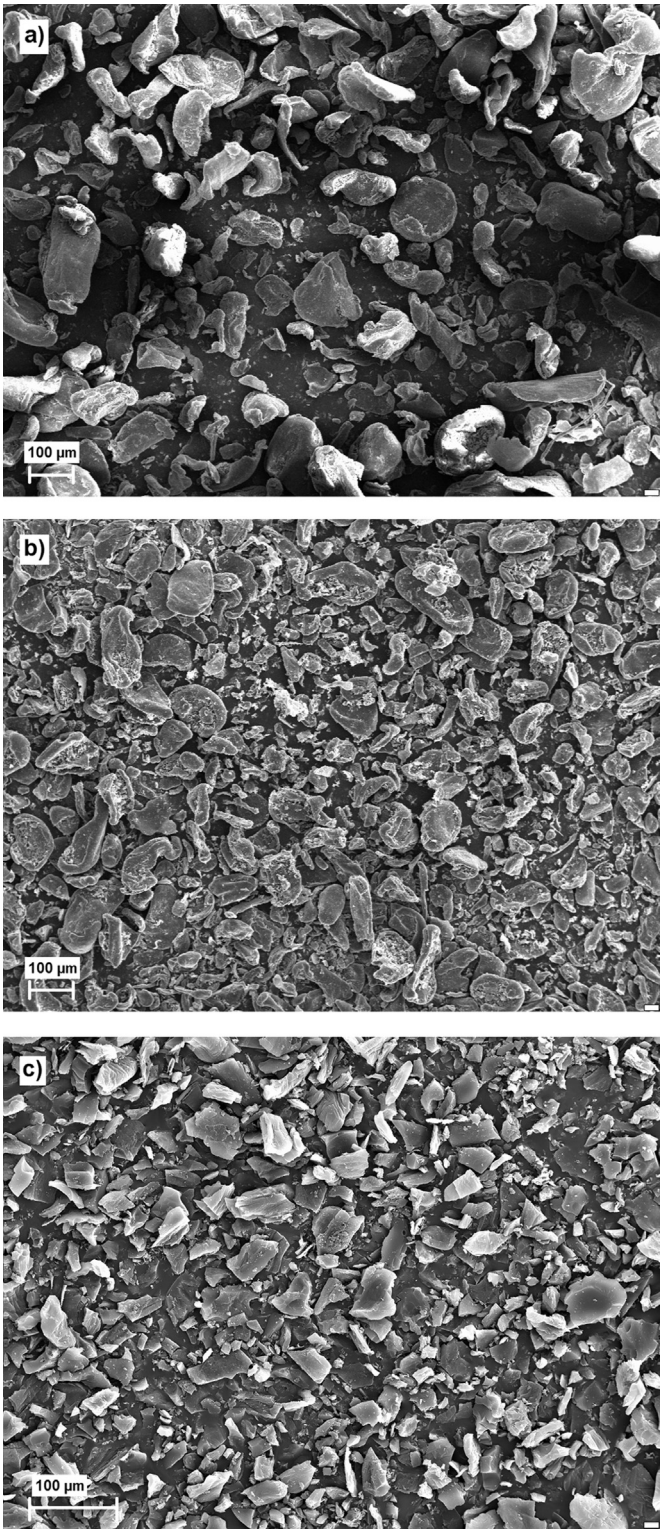

Fig. 1. SEM images of (a) chitosan, (b) carbonized chitosan, (c) carbonized and then activated chitosan.

electrochemical impedance spectroscopy (100 kHz–1 mHz) using potentiostat - galvanostat VMP3/Z (Biologic, France). The capacitance values were expressed per active mass of one electrode. The activated carbon was subjected to cycle stability (5000 cycles) with current regime 2 A g^{-1}.

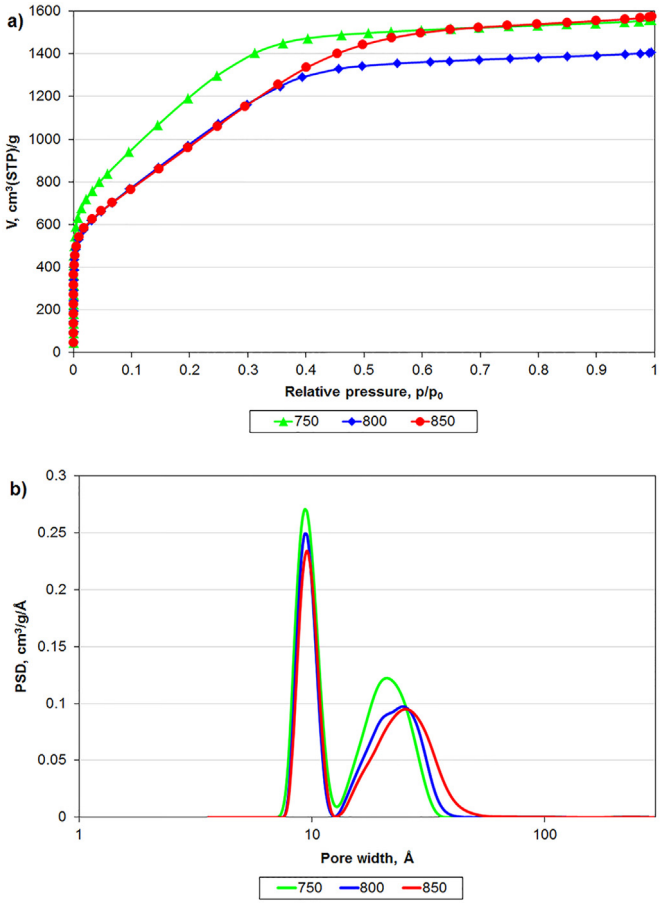

Fig. 2. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of activated carbons from chitosan (different temperatures).

3. Results and discussion

Surface morphology of the initial chitosan and after it had been carbonized and activated was characterized using scanning electron microscopy. SEM images of materials are shown in Fig. 1.

The commercial chitosan (Fig. 1a) has particles with a rather rounded shape. Carbon prepared by carbonization of chitosan demonstrated similar morphology with visible fragmentation (Fig. 1b), while in activated carbon image particles with a destroyed, irregular shape were well visible (Fig. 1c).

The adsorption model of Brunauer-Emmett-Teller (BET) was used to calculate the specific surface area. Fig. 2a presents the nitrogen adsorption-desorption isotherms of activated carbons from chitosan, prepared at different temperatures (750 °C, 800 °C, 850 °C).

The main nanotextural parameters and the carbon, hydrogen and nitrogen contents in the samples are given in Table 1. The activated carbons contain heteroatoms and functional groups and the percentage of carbon increases as the temperature of activation grows. Process of KOH activation significantly reduces hydrogen and nitrogen contents in samples (from more than 1.5% (H) and more than 9% (N) after carbonization process to less than 0.2% (H) and less than 0.1% (N) after chemical activation in 850 °C).

The pore size distribution of carbons (PSD, calculated by NLDFT method with heterogeneous surface model using SAIEUS Program, ver. 1.02 by J. Jagiello) [6] as well as $V_{mi}/(V_{mi}+V_{me})$ confirmed unimodal PSD profile with the highest contribution of micropores, which is shown in Fig. 2b (ACRCH 750 °C). Higher temperature of