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WOOD BASED ACTIVATED CARBONS FOR SUPERCAPACITORS

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ABSTRACT

Influence of thermocatalytical synthesis on the porous structure formation and properties of microporous carbon wood-based materials is demonstrated. It has been found that increase of activation temperature and alkali activator addition ratio can be used to control not only total pore volume, but also micro- and mesopores proportion. The results of tests of the synthesized carbon materials as electrodes in supercapacitors are shown, as well as properties of carbon materials porous structure influencing on electrodes working characteristics. It was demonstrated that increase of activation temperature from 600°C to 800°C leads to increase of mesopores proportion in the porous structure which negatively influences on supercapacitor cell capacity. It was found that the most feasible way of activated cabons production for use as electrodes in supercapacitors is low-temperature activation.

I. INTRODUCTION

The traditional way of biomass conversion is production of wood chars and carbon materials with developed porous structure, activated carbons (AC), which are used as sorbents in many areas. Nowadays elucidation of AC structure is of scientific and practical interest since areas of these materials application are constantly widening: membrane technologies of rare earth metals separation, metallurgy, electronics, electrochemistry, aerospace technologies, and nuclear energy. This broad spectrum of AC application is justified by diversity of their structures with completely different physical and chemical properties, which can be achieved by certain physical-chemical treatment of carbonaceous precursors. One of distinctive features of plant biomass based AC is the fact that they can be obtained from extremely wide choice of precursors varying conditions of pyrolysis and activation: wood chips, cellulose and lignin, lignocellulosics, nut shells, straw, peat, husks, etc. As the results properties of AC will be different depending of precursor and synthesis conditions.

Wood based carbonizates have low porosity and their structure consists of elementary crystallites divided by multiple slit-like pores [1]. These pores are filled with pyrolysis products – pyrolytic tar. In the process of activation closed pores open up and porous structure forms. Varying carbon materials and activation conditions (temperature, time, atmosphere) it is possible to control total porosity, pore size distribution and nature of inner space.

Chemical activation is a widely used method for production of AC with developed porosity. The most important advantage of chemical activation is a possibility to synthesize carbonaceous materials with very high specific surface which is close to theoretical limits for carbon materials.

Alkali metals hydroxides are one of the most effective activating agents allowing in certain cases to synthesize microporous carbon sorbents with specific surface more than 3000 m^2/g [2].

There are numerous examples of application of AC as electrodes for the perfection of storage and transmission of electrical energy. The main ways of research are aimed at high specific surface and low electric resistance of carbon matrix with low costs of production. AC, synthesized with the use of alkali metals hydroxides, correspond to the above mentioned demands [3-4].

In the development of new systems for the modern electric-power industry one of important problems is the research devoted to application of electric double layer capacitors or supercapacitors (SC) where porous AC are used the main material for electrodes. Development and research of SC is an important subject worldwide. It is known that energy capacity of carbon electrode is influenced by the following AC properties: raw material, its dispersity end elemental composition, modes of carbonization and activation, porous structure characteristics, etc [5].

This work is devoted to the study of influence of wood based carbon material porous structure characteristics for the use in electric double layer capacitors (supercapacitors) with sulfuric acid as electrolyte.

II. EXPERIMENTAL

Materials and methods

***Raw material*:** birch wood chips, 0.2 – 0.4 mm fraction.

AC synthesis is schematically illustrated in the Fig. 1. It consists of two stages of thermal treatment - at the first one raw material was carbonized in the nitrogen atmosphere at 400°C for 150 minutes.

At the second carbonizate was impregnated with NaOH water solution (50 ww %). Ratio of carbonizate to activator was varied from 1:2 to 1:4. The mixture was activated at the temperatures 600-800°C for 120 minutes. Pyrolysis product was washed with deionized water, demineralized with hydrochloric acid and washed with dionized water again up to filtrate pH 5. The obtained AC was dried overnight at 105°C. Ash content in the AC was found to be 0.1-0.4%. The main variables in the experiment were activation temperature and carbonizate/activator ratio.

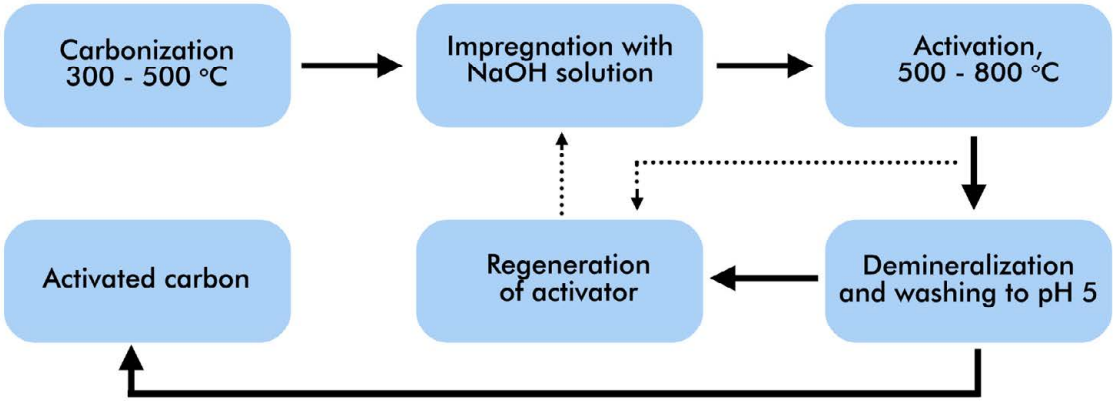

Figure 1. Schematics of microporous carbon materials thermocatalytical synthesis.

Porous structure was evaluated by nitrogen adsorption isotherms at 77 K (Quantachrome Autosorb 6B). Micropores volume was calculated using Dubinin-Radushkevich method [6].

Electrodes were prepared using calandering method, water suspension of PTFE F-4D (5-10% from electrode mass) was used as a binder. Electrodes were dried and impregnated with 4.9 M solution of sulfuric acid under vacuum. Porous PP membrane was used as a separator between electrodes. Thermoexpanded graphite foil was used as substrate-current collector. Energy capacity of supercapacitor was determined at complete discharge with direct current after 10 minute exposure at 1v voltage drop.

II. RESULTS AND DISCUSSION

AC porous structure characteristic for use as electrodes in supercapacitors were evaluated using nitrogen sorption isotherms (Fig. 2).

The samples under study were first carbonized at 400°C and then activated at carbonizate to NaOH ratio 1:2 (Fig. 2, isotherms 2-5) and 1:4 (Fig. 2, isotherm 1) in the isothermal conditions at the temperatures 600, 650, 700 and 800°C. Judging by the shape of isotherms samples obtained at temperatures 600, 650 and 700°C (Fig. 2, isotherms 2-4) are microporous. With increase of activation temperature volume of adsorbed nitrogen increases as well. At activation temperature 800°C (Fig.2, isotherm 5) the shape of isotherm changes. The appearance of hysteresis is indication of capillary condensation of sorbate, which also indicates increase of mesopores number. With the increase of carbonizate/activator ratio to 1:4 (activation temperature 700°C) volume of adsorbed nitrogen, as well as number of mesopores in AC structure, increase (Fig. 2, isotherm 1).

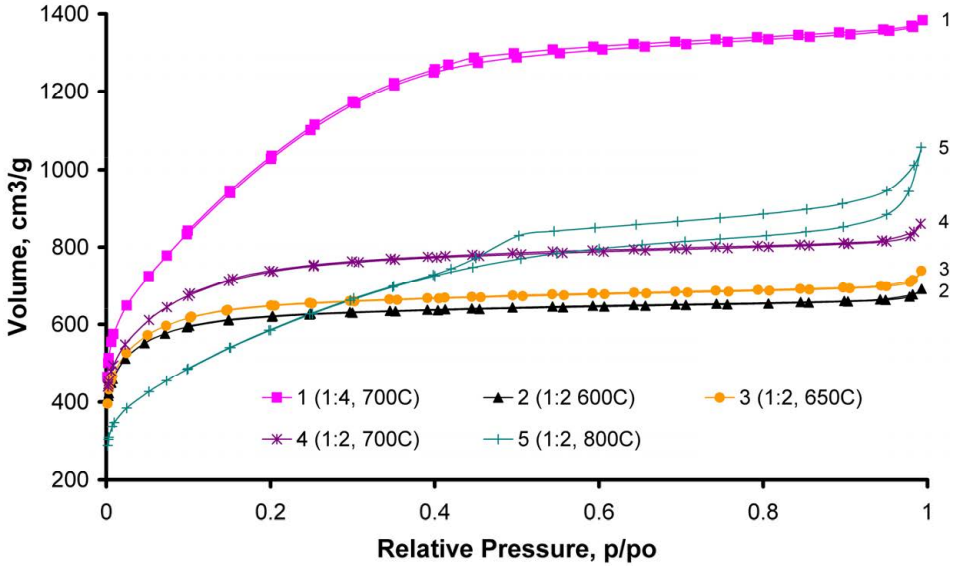

Figure 2. AC nitrogen adsorption isotherms at 77K with alteration of activation temperature and carbonizate/activator ratio.

Volume of micropores increases with the increase of activator ratio and activation temperature in the range 600 – 700°C (Fig. 3). Activation at the temperature 800°C leads to decrease in micropores proportion in the structure of AC, which obviously is explained by elimination of pore walls and combination of smaller pores into the larger ones. Alongside with this proportion of microporosity in the total pore volume decreases with increase of activation temperature and with increase of activator ratio, both (Fig. 3).

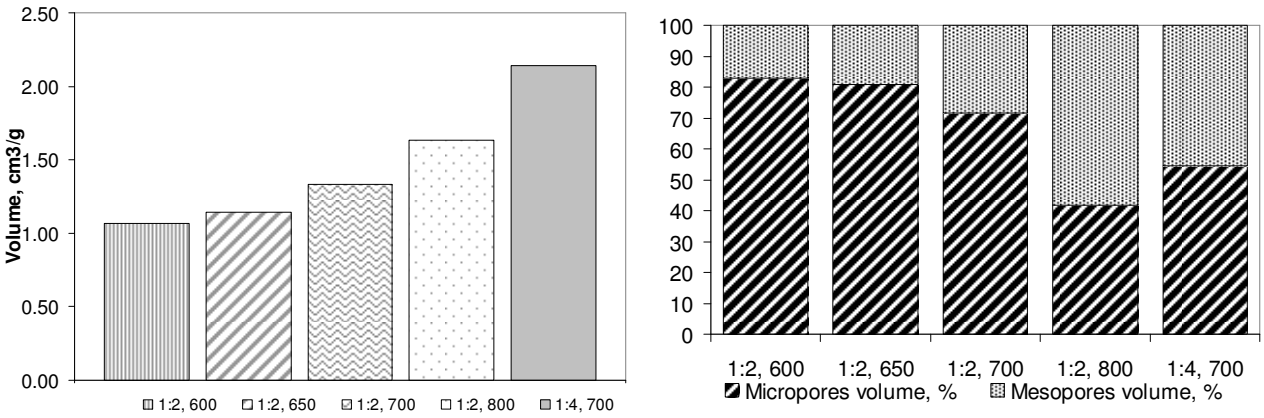

Figure 3. Micropores volume (left) and micropores/mesopores ratio (%) (right) with alteration of activation temperature and carbonizate/activator ratio.

Characteristics of supercapacitor cells made with electrodes from AC prepared at different activation temperatures and carbonizate/activator ratio 1:2 are illustrated in the Figure 4. At the low carbonization temperatures – 600 and 700°C capacitance is 330 and 320 F/g, correspondingly. Increase of carbonization temperature negatively influences on electrochemical properties - at the activation temperature 800°C capacitance decreases to 220 F/g.

As it is shown in the Figure 4 total volume of electrolyte retained by electrode considerably increases with the increase of activation temperature. This parameter is important when evaluating efficiency of the device under development, namely for the calculation of specific characteristics to the mass of elementary capacitor cell.

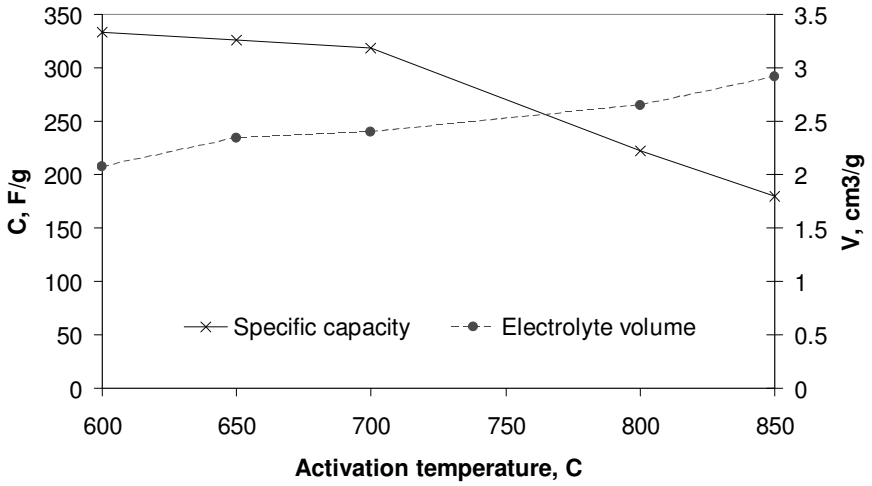

Figure 4. Dependence of supercapacitor cell capacitance and volume of electrolyte retained by AC from the activation temperature (carbonizate/activator ratio 1:2).

Thus the choice of lower activation temperatures positively influences not only on microporous structure of AC, but on electrode quality as well. This makes the described activation process more feasible from the commercial standpoint.

IV. CONCLUSIONS

Microporous wood based carbon materials were obtained using thermocatalytical synthesis, which includes carbonization and consequent alkali activation. The synthesized carbon materials have good electrode characteristics for the capacitors with double electric layer with sulfuric acid as electrolyte. Maximal capacity of supercapacitor – 330 F/g - is achieved at the activation temperature 600^{o}C and carbonizate/activator ratio 1:2. Capacity decreases with temperature increase, which corresponds to decrease of micropores proportion in activated carbons porous structure.

V. ACKNOWLEDGEMENT

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