Supercapacitor electrodes from activated wood charcoal

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Influence of main stages of wood thermochemical activation parameters on activated carbons porous structure formation were elucidated with for sodium hydroxide as activating agent. The main factors governing the properties of carbon materials, such as specific surface area, volume and pore size distribution, surface oxygen content, as well as their influence on capacitance and working properties of supercapacitor electrodes are demonstrated.

Keywords: wood, activated carbon, alkali activation, porous structure, supercapacitors

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 for 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 various physical-chemical treatment of carbonaceous precursors. One of distinctive features of plant biomass based AC is the fact that they can be obtained in various conditions of pyrolysis and activation from extremely wide choice of precursors: wood chips, cellulose and lignin, lignocellulosics, nut shells, straw, peat, husks, etc. As the result properties of AC will be different depending on 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 the porous structure is being formed. 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 metal hydroxides are one of the most effective activating agents allowing in certain cases to synthesize microporous carbon sorbents with specific surface more than 3000 m² g^{-1} [2].

There are numerous examples of application of AC as electrodes for storage and transmission of electrical energy. The main goals of ongoing researches are high specific surface and low electric resistance of carbon matrix with low costs of production. AC synthesized with the use of alkali metals hydroxides meet the above mentioned demands [3-4].

Sorption methods and Raman spectroscopy are the most popular non-destructive techniques for the characterization of carbon-containing materials. The intensity ratio of the G and D bands as well as their wavenumbers and widths are useful quantitative criteria for comparing the degree of structural order of different carbon forms [5, 6].

In the development of new systems for the modern electric-power industry one of the important problems is the research devoted to application of electric double layer capacitors or supercapacitors (SC) where porous AC are used as the main material for electrodes. It is known that energy capacity of carbon electrode is influenced by the following AC properties: precursor origin, dispersity and elemental composition, conditions of

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carbonization and activation, porous structure characteristics, etc. [8].

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.

MATERIALS AND METHODS

Birch wood chips (0.2 – 0.4 mm fraction) were used as a raw material. It was carbonized in the argon atmosphere at $400^{o}C$ for 150 minutes. Then the carbonizate was impregnated with NaOH water solution (50 wt%). Ratio of carbonizate to activator was varied from 1:2 to 1:4. The mixture was activated at the temperatures $600-800^{o}C$ for 120 minutes in Nabertherm L-40 muffle oven in argon flow ($150\ l\ h^{-1}$). Pyrolysis product was washed with deionized water, demineralized with hydrochloric acid and washed with deionized water again up to filtrate pH 5. The obtained AC was dried overnight at $105^{o}C$. 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.

Porous structure was assessed by N_2 sorption at 77 K (Nova – 4200e, Quantachrome). Pores volumes were calculated using, Brunauer–Emmet–Teller(BET) and in case of micropores Dubinin-Radushkevich theories from N_2 sorption isotherms [9].

Raman spectra of carbon material were taken in back-scattering geometry at room temperature through 50 x microscope objective using micro-Raman spectrometer equipped with argon laser (514.5 nm, max cw power Pex=10 mW). The spectral signal was dispersed by the 2400 grooves/mm grating onto Peltier-cooled ($-60^{o}C$) CCD detector. Frequency shifts in the Raman spectra were calibrated using $CaWO_4$ as a reference.

Immersion calorimtery was performed using Setaram C-80 device in water and benzene. Samples were outgassed at $300^{o}C$ and sealed under vacuum in glass ampules.

For supercapacitor assembly AC was first mixed with ethanol, then a binder - water suspension of PTFE F-4D (10 wt% on dry electrode mass) was added, and the resulting mixture was treated in calender press. Electrodes were dried and then impregnated with 4.9M water solution of H_2SO_4. Cellulosic separator NKK TF 4030 (10 μm) was used to make a supercapacitor (SC). The electrode area was 4.15 cm^2. Foil from thermally expanded

graphite (200 μm) was used as a current collector. Assembled SC were pressed under 10 atm in a dry box. SC capacity was assessed using potentiostate Elins 30-S at 1 V for 5 minutes. Inner resistance was calculated by voltage drop at current transient in the beginning of SC discharge. Capacities shown are calculated on a dry mass of electrode, without electrolyte.

RESULTS

Raman spectroscopy was used to compare structures of charcoal and activated carbon (AC) synthesized at $700^{o}C$ and carbonizate to activator ratio 2.
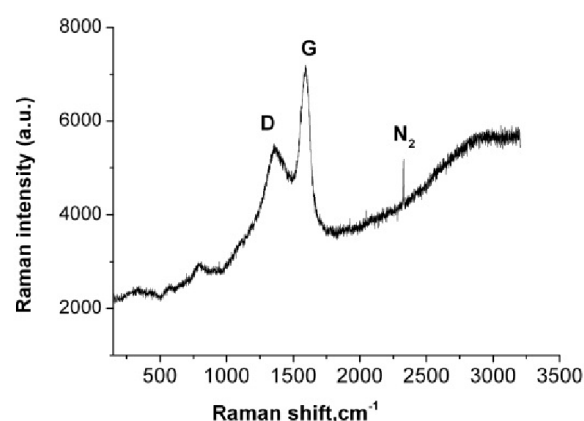

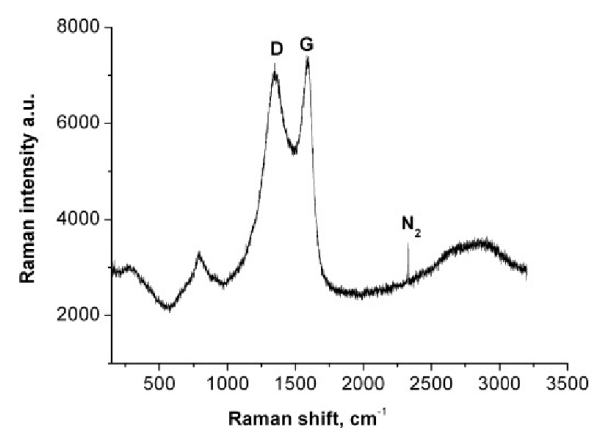**Fig.1.** Micro-Raman scattering spectrum of wood charcoal

Fig.2. Micro-Raman scattering spectrum of activated carbon (activation temperature $700^{o}C$, carbonizate to activator ratio 1:2)

The Raman-active vibration numbering for natural single-crystal graphite exhibits a single Raman peak at around 1580 cm^{-1}, called the G peak.

This peak is associated with the in-plane C−C stretching mode of the sp^2 hybridized carbon atoms. For polycrystalline graphite, depending on the size of the crystallites, a second peak at 1350 cm^{-1}

appears namely the disorder or D peak. If the long-range order of the crystalline material is lost and the carbon phase becomes glassy, both the G and the D peaks broaden [7]. Three Raman scattering peaks at around 1364, 1596 and 2325 cm^{-1} are observed. The peak at 1580 cm^{-1} (G band) is attributed to an E_{2g} mode of graphite and is related to the vibration of sp^2 – bonded carbon atoms. For polycrystalline graphite, depending on the size of the crystallites a second peak at 1350 cm^{-1} appears, namely the disorder or D peak [10]. Note that in a perfect graphite crystal the first-order vibrational mode of the D band is forbidden because of the selection rules. Decreasing particle size or bending of the lattice fringes may activate this band [11]. We can see this phenomenon: after carbon activation the intensity of Raman scattering D band increases with decreasing of particle size of carbon (Fig.1 and Fig.2.). Stretch vibrations of N_2 in the ambient might have caused sharp (narrow) peak at 2325cm^{-1} [10].
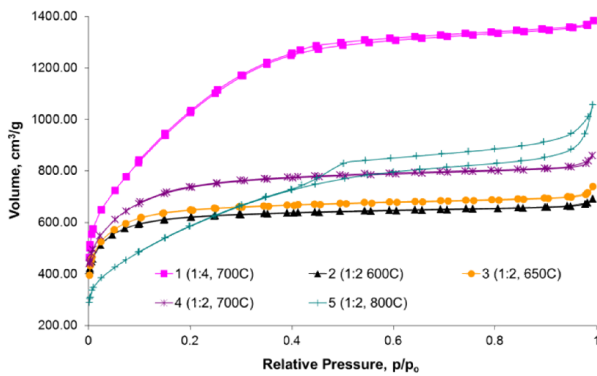

Fig.3. AC nitrogen adsorption isotherms at 77K with alteration of carbonizate to activator ratio and activation temperature

AC porous structure characteristic for use as electrodes in supercapacitors were evaluated using nitrogen sorption isotherms (Fig.3). The samples under study were first carbonized at 400°C and then activated at carbonizate to NaOH ratio 1:2 (Fig.3, isotherms 2-5) and 1:4 (Fig.3, 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.4, isotherms 2-4) are microporous. With increase of activation temperature volume of adsorbed nitrogen increases as well. At the activation temperature 800°C (Fig.3, isotherm 5) the shape of isotherm changes. The appearance of hysteresis is an indication of capillary condensation of sorbate, which also points at increase of mesopores number. With the increase of carbonizate to activator ratio to 1:4 (activation

temperature 700°C) volumes of adsorbed nitrogen, as well as number of mesopores in AC structure, increase (Fig.3, isotherm 1).

Total pore volume increases with the increase of carbonizate to activator ratio (1:2 and 1:3) and activation temperature in the range 600 – 750°C, but micropores (0.8 – 1.5 nm) volumes were increasing only until 700° (Fig.4). At the same time specific surface area increased with increase of NaOH addition ratio and activation temperature in the whole range (Fig.5).
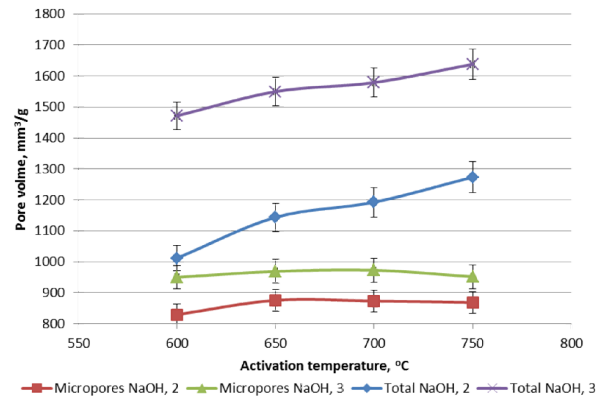

Fig.4. Dependence of total and micropores (Dubinin-Radushkevich) volumes from activation temperature and NaOH addition ratio
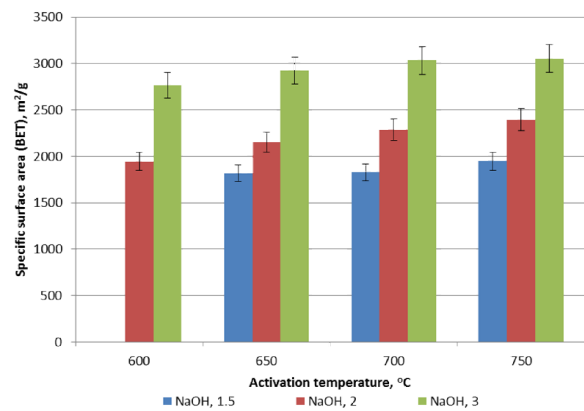

Fig.5. Dependence of specific surface from activation temperature and NaOH addition ratio

Immersion calorimetry can be used to determine content of oxygen-containing surface groups in the carbonaceous materials by immersion into polar (water) and nonpolar (benzene) liquids [12]. This method allowed establishing correlation between heats of immersion, specific surface area and surface oxygen content which are important parameters for supercapacitor stability in charge-discharge cycles and double electric layer formation.

It was shown that the lowest oxygen content was found for the samples obtained at 650-700°C

(Fig.6). For these samples the highest specific capacitance (~330 F/g) and electric resistance (~250 mOhm) was found. This proves that comparison of porosity and immersion enthalpies allows forecasting supercapacitor electrical properties.
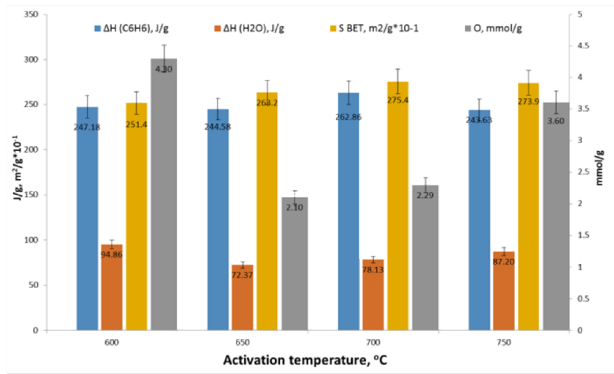

Fig.6. Influence of activation temperature on surface oxygen content (carbonizate to NaOH 1:2)

Characteristics of supercapacitor cells made with electrodes from AC prepared at different activation temperatures and carbonizate/activator ratio 1:2 are illustrated in the Fig.7. At the lower carbonization temperatures – 600 to 700°C capacitance was around ~330 F g^{-1}. Increase of carbonization temperature negatively influences on electrochemical properties - at the activation temperature 800°C capacitance decreased to 220 F g^{-1}.
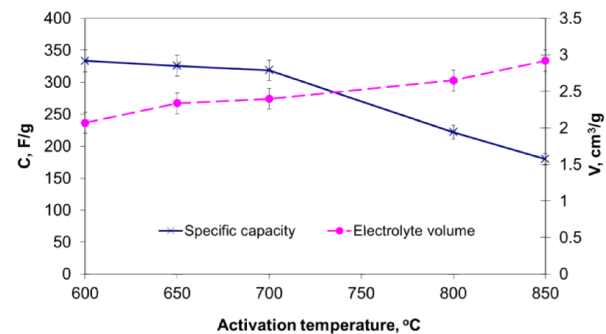

Fig.7. Dependence of supercapacitor cell capacitance and volume of electrolyte retained by AC from the activation temperature (carbonizate to activator ratio 1:2)

As it is shown in the Fig.7 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. This behavior can be explained basing on

literature data [13]. Decreasing the pore size to a value approaching the crystallographic diameter of the ion leads to a 100% increase in normalized capacitance. It was shown that under a potential, there is substantial ion motion and diminished dielectric permittivity in pores less than the size of their solvation shells. The solvation shell becomes highly distorted as the ion is squeezed through the pore in much the same way a balloon distorts when squeezed through an opening smaller than its equilibrium size.

The distortion of solvation shells in small pores of carbon nanostructures was also reported recently. Such distortion would allow closer approach of the ion center to the electrode surface which leads to improved capacitance [13].

Thus electrode pores should provide transport and availability of ions in the process of double electric layer charge and discharge. Obviously there are an optimal micropores volume and size required to effectively form double electric layer, while meso- and macropores provide transport function for electrolyte ions. These pores do not contribute into electric double layer formation, and additional electrolyte mass negatively influences on the SC specific characteristics calculating on cell or whole device.
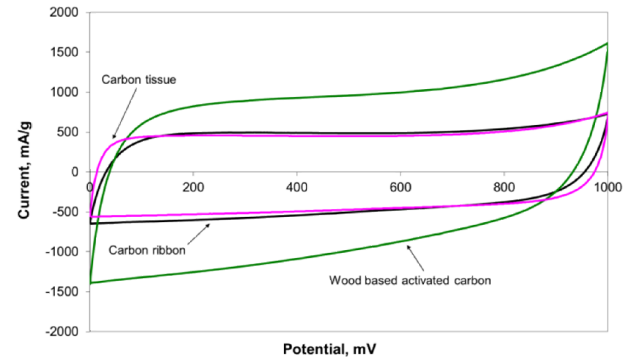

Fig.8. Cyclic voltammograms (two electrode cells) of the capacitors with electrodes built from wood based activated carbons (carbonizate to activator ratio 1:2, activation temperature 600 °C), commercial carbon tissue electrodes and commercial carbon ribbon electrodes (H2SO4 aqueous solution)

To illustrate properties of the obtained nanoporous activated carbons they were tested in two electrode system. Charge/discharge cyclic voltammograms were recorded and compared to vomtammograms obtained for electrodes based on commercial carbon materials (Fig.8). All three materials exhibit a regular box-like shape with a steep current change at the switching potential, which is a characteristic of the behavior of an ideal

capacitor. It is clear that nanoporous activated carbons show higher specific capacitance. The other benefit of disperse carbon material is the ability to control thickness of carbon layer.

Further research of the carbon porous structure and synthesis of materials with optimal volume of pores with sizes tailored for the specific electrolyte may allow both energy and power characteristics of supercapacitors to be improved.

CONCLUSIONS

Microporous wood based carbon materials were obtained using thermochemical synthesis, which includes carbonization and consequent alkali activation. The synthesized carbon materials have good electrode characteristics for the capacitors with double electric layer. Maximal capacity of supercapacitor ~330 F g^{-1} is achieved at the activation temperatures 650°C and carbonizate to activator ratio 1:2 for sulphuric acid electrolyte. Capacity decreases with activation temperature increase, which corresponds to decrease of micropores proportion in activated carbons porous structure.

ACKNOWLEDGEMENTS

REFERENCES

1 Tsyganova, S., Korolkova, I., Bondarenko, G., Chesnokov, N., Kuznetsov, B. Synthesis of Active Carbons from Birch Wood modified by phosphoric Acid and Potassium Hydroxide. J. Siberian Fed University Chemistry, 2009, vol. 2, N 3, p. 275-281.

2 Torne-Fernandez, V., Mateo-Sanz, J.M., Montane, D., Fierro, V. Statistical Optimization of the Synthesis of Highly Microporus Carbons by Chemical Activation of Kraft Lignin with NaOH. J. Chem. Eng. Data. 2009, N 54, p. 2216–2221.

3 Marsh, H., Rodriguez-Reinoso, F. Activated Carbon. Amsterdam : Elsevier, 2006, 536 p.

4 Dobele, G., Dizhbite, T., Gil, M.,V., Volperts, A..Centeno,T.,A. Production of Nanoporous Carbons from Wood Processing Wastes and their use in Supercapacitors and CO2 Capture. Biomass and Bioenergy, 2012, N 46, p. 145-154.

5 Bansal, R, Goyal, M. Activated carbons Adsorption, Boca Raton : CRP Press, 2005. 472 p.

6 Cheng, Y. H., Tay, B.K., Lau, S.P., Shi, X., Qiao, X.L., Chen J.G., Wu, Y.P., Xie, C.S. Raman spectroscopy of carbon nitride films deposited using the filtered cathodic vacuum-arc combined with a radio-frequency nitrogen-ion beam. Appl. Phys. 2001, A 73, p. 341–34.

7 Zickler, G. A., Smarsly, B, Gierlinger, N., Peterlik, H., Paris, O. A reconsideration of the relationship between the crystallite size of carbons determined by X-ray diffraction and Raman spectroscopy. Carbon, 2006, N 44, p. 3239–3246.

8 Inagaki, M., Konno, H., Tanaike, O. Carbon Materials for Electrochemical Capacitors. J. Power Sources, 2010, N 195, p. 7880-7903.

9 Rouquerol, J., Rouquerol, F., Sing K. Adsorption by Powders and Porous Solids Principles, Methodology and Applications. San Diego : Academic Press, 1998. 467 p.

10 Ferrari A. C., Meyer J.C., Scardaci, V., Casiraghi, C., Lazzeri, S., Mauri, F., Piscanec, S., Jiang, D., Novoselov, A. K., Roth, S., Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. Phys. Rev. Lett., 2006, N 97, p. 187401.

11 Klinke, C., Kurt, R., Bonard, J.M. Raman Spectroscopy and Field Emission Measurements on Catalytically Grown Carbon Nanotubes. J. Phys. Chem. B, 2002, N 106, p. 11191-11195.

12 Centeno, T.A., Fernandez, J.A.,. Stoeckli F. Correlation between heats of immersion and limiting capacitances in porous carbons. Carbon 46, 2008, p. 1025-1030.

13 Chmiola, J., Yushin, G., Gogotsi, Y., Portet, C., Simon, P., Taberna P.L. Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer. Science, 2006, N 313, p.1760-1763.