

Highly Porous Wood Based Carbon Materials for Supercapacitors

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Abstract: Wood based activated carbons synthesized by two-stage thermocatalytical synthesis with NaOH activator were studied and used as supercapacitor electrodes (sulphuric acid electrolyte). Porous structure and electrochemical properties of carbons vs synthesis conditions were assessed. It was found that there are correlations between carbons synthesis variables, their porosity and supercapacitors functional characteristics. At the temperature 600°C and activator/precursor ratio 1.25 porosity decreased, however energy capacitance of supercapacitor increased calculating on elementary cell mass.

1. Introduction

The existing methods of energy storage lag behind the intensity of modern power systems development, thus it is of high importance to provide the solutions meeting these demands. One of the possible solutions to level peak loads in the grid, to suppress fluctuation in Diesel-generators and to recuperate breaking energy for vehicles is the application of electrochemical capacitors with double electric layer – so called supercapacitors (SC) [1-4]. Activated carbons (AC) are universally accepted as a main component of SC electrodes since they are stable in various media, have highly developed porosity, sufficient conductivity and are relatively cheap [5-7]. AC properties depend on precursor type, its modification as well as activation conditions [8-10].

Power capacitance of carbon electrode is mainly influenced by dispersity, elemental composition and micro- and mesopores size distribution of AC. Electrodes should provide high capacitance, minimal energy drop with power increase and stable operation at high number of charges-discharges cycles [11].

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Alkali thermochemical activation (KOH, NaOH) is the most widespread method for production of highly effective AC from various precursors including wood and its components [12-17]. For the biomass based AC the universally accepted pore model is slit-like [18,19], where primary pores are represented by the gaps between carbon layers [20]. AC particles are the more or less structured 3D graphene structures combinations. Sorption methods and Raman spectroscopy are the most popular non-destructive technique for the characterization of carbon-containing materials [21, 22]

In the process of charcoal alkali activation size and volume of pores increase on the expense of carbon layer thickness decrease due to carbon oxidation and volatile products formation. These reactions start on the graphenes periphery, between boundary carbon atoms and molten alkali [12]. With the increase of alkali/carbon ratio, treatment temperature and time, porosity and, accordingly, specific surface of AC increase. Variations of these parameters let to SC with high capacitance - 320-370 F g⁻¹ [23,24] in water and 170-195 F g⁻¹ [25] in aprotic electrolytes.

Numerous literature sources testify that activator amount is the deciding factor for the porous structure formation [26-28]. There is a widespread opinion that AC pore volume and specific surface increase is the necessary prerequisite for SC electrical characteristics increase. For some types of precursors this dependency exists indeed, however for others there is a maximum capacitance value at the some definite AC specific surface value [29].

Our research is devoted to study of capacitance characteristics of SC, providing the minimum parasitic electrolyte mass, altering porous structure of wood based alkali activated carbons.

2. Experimental

2.1. Activated carbons synthesis

AC samples were synthesized by two stage thermal treatment. At the first stage wood chips (birch, 0.2-0.4 mm fraction) were pretreated in nitrogen atmosphere at 600°C for 150 min (4°C min⁻¹ rate). At the second stage the obtained charcoal was impregnated with 50 w% NaOH water solution, ratio of alkali/charcoal was varied from 1 to 3.7. The mixture was activated at 600-800°C in the stream of argon for 120 min, washed with dionised water, HCl, and water again up to pH 5, and then dried overnight at 105°C. Ash content of the synthesized AC was 0.1-0.4%. The main variables in the experiment were activation temperature and activator/charcoal ratio (further denoted as K).

2.2. SC 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 calandered in rollers. Electrodes were dried and then impregnated with 4.9M water solution of H₂SO₄. Cellulosic separator NKK TF 4030 (10 μm) was used to make a suprecapacitor (SC). The electrode area was 4.15 cm². 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 capacitance was assessed using potentiostate ELLINS 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.

2.3. Porous structure assessment

Porous structure was assessed by N₂ adsorption at 77 K (Kelvin 1042, Costech Instruments). Pores volumes were calculated using Dubinin-Radushkevich and Brunauer–Emmet–Teller (BET) theories using N₂ sorption isotherms [21].

2.4. Raman scattering

Raman spectra of carbon material were measured 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 P_{ex}=10 mW). The spectral signal was dispersed by the 2400 grooves/mm grating onto Peltier-cooled (-60 C) CCD detector. Frequency shifts in the Raman spectra were calibrated using CaWO₄ as a reference.

3. Results and discussion

Raman spectroscopy was used to compare structures of charcoal and activated carbon (AC) synthesized at 700°C and K=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 sp² 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 [30]. 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 sp² – bonded carbon atoms [22]. 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 [31]. We can see this phenomenon: after activation of carbon intensity of Raman scattering D band increases with decreasing particle size of carbon (figure 1 and figure 2). Stretch vibrations of N₂ in the ambient might cause the sharp (narrow) peak at about 2325 cm⁻¹ [31].

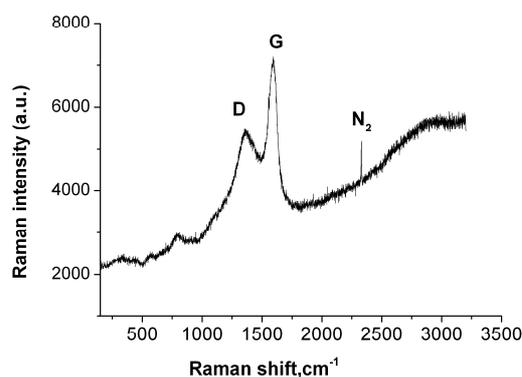


Figure 1. Micro-Raman scattering spectrum of wood charcoal

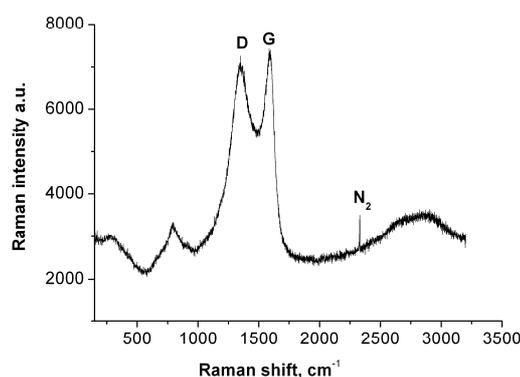


Figure 2. Micro-Raman scattering spectrum of activated carbon after activation (activation temperature 700°C, K=2)

Structural characteristics of AC synthesized at activation temperature 700°C and K variation from 1.7 to 3.7 were calculated using N₂ sorption isotherms. With increase of alkali addition total specific area and pore volume increase as well, however micropores volume changes negligibly (figure 3).

When these AC were used for electrodes in SC alkali addition rate variation manifested itself in increase of total volume of adsorbed electrolyte and specific capacitance (310 F g⁻¹) practically stays the same. Probably the minimal micropores volume is required to form double electric layer. There can be another factor negating positive effect of total porosity increase – it was reported [28] that change of surface groups' content can be such a factor, since they take part in redox reactions and lead to pseudocapacitance effect.

Activation temperature is another important parameter in AC synthesis. Characteristics of activated carbons synthesized in temperature range 600–850°C and K=2 are shown in figure 4. Specific surface area and pore volume reach maximum at activation temperature 700°C and diminish after that. The same trend can be observed for SC specific capacitance – 330 F g⁻¹ at 600°C and 180 F g⁻¹ at 850°C.

Total adsorbed electrolyte volume significantly increases with the increase of activation temperature. It should be noted that inner resistance practically does not change with the increase of activation temperature up to 800°C and corresponding volume of adsorbed electrolyte (figure 4). At higher temperature resistance somewhat increases, probably this can be explained by the increase of

larger pores volume. The same trend was observed in the work [23], where decrease of capacitance was attributed to decrease of surface C-O groups, which influences pseudocapacitance (reversible faradaic redox reactions).

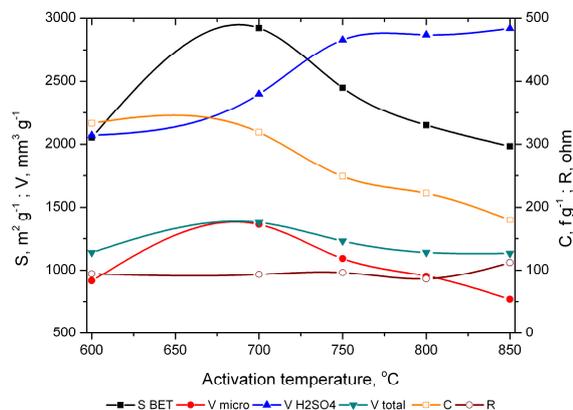
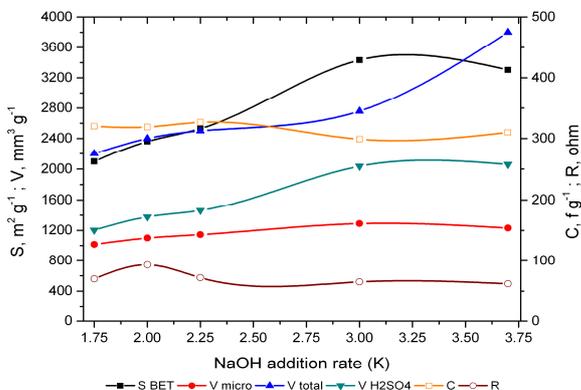


Figure 3. Dependence of activated carbons porous structure and supercapacitor characteristics from NaOH addition rate at activation temperature 700°C

Figure 4. Dependence of activated carbons porous structure and supercapacitor characteristics from activation temperature at NaOH addition rate K=2

S_{BET} – specific surface in $m^2 g^{-1}$, V_{micro} – micropores volume, $mm^3 g^{-1}$, V_{total} – total pore volume, $mm^3 g^{-1}$, $V_{H_2SO_4}$ – volume of adsorbed electrolyte, $mm^3 g^{-1}$, C – specific capacitance, $F g^{-1}$, R – resistance, $ohm \cdot 10^{-3}$

Thus in our case lower activation temperature positively influences specific capacitance of SC, however it should be noted that activation temperature lower than 600°C is not feasible since thermodynamical boundary of the main reactions is 580°C [33].

Results of the experiments devoted to assessment of the lowest beneficial K value for AC synthesis at 600°C are shown in figure 5.

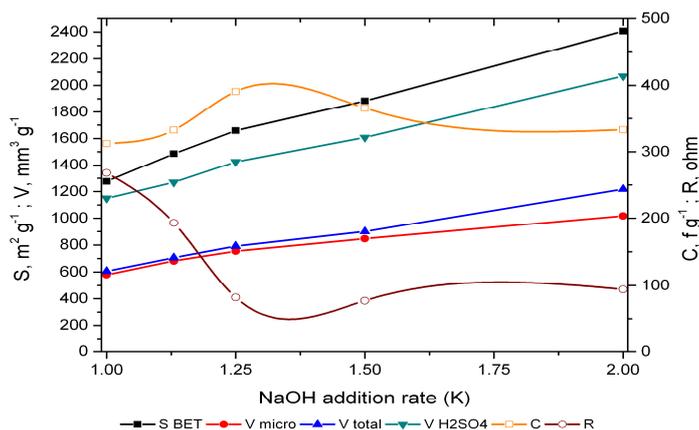


Figure 5. Dependence of activated carbons porous structure and supercapacitor characteristics from NaOH addition rate at activation temperature 600 °C

S_{BET} – specific surface in $m^2 g^{-1}$, V_{micro} – micropores volume, $mm^3 g^{-1}$, V_{total} – total pore volume, $mm^3 g^{-1}$, $V_{H_2SO_4}$ – volume of adsorbed electrolyte, $mm^3 g^{-1}$, C – specific capacitance, $F g^{-1}$, R – resistance, milliohm

Increase of activator addition rate from 1 to 2 leads to increase of total and micropore volume, though the latter is pronounced to the lesser extent. At K=1.25 SC specific capacitance reaches its maximum, which is accompanied with significant decrease of resistance. This value of resistance, which is the sum of ohmic losses in solid phase, electrolyte resistance and contact resistances, does not

change with the subsequent increase of K from 1.25 to 2. In or case decrease of charcoal activation temperature and activator addition rate led to 30% increase of SC specific capacitance calculating on elementary cell mass.

Thus electrode pores should provide transport and availability of ions in the process of double electric layer charge and discharge. The total volume of electrolyte adsorbed in macro-, meso- and micropores in our experiment (figure 5) is $1400 \text{ mm}^3 \text{ g}^{-1}$. Obviously there is a minimal micropores volume (in this case around $750 \text{ mm}^3 \text{ g}^{-1}$) required to form double electric layer, and 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.

4. Conclusions

Porous structure and electrochemical properties of hardwood based activated carbons obtained by thermocatalytical NaOH activation were assessed. It was found that the effective double layer in the supercapacitor cell electrodes (sulfuric acid electrolyte) and maximum capacitance 330 F g^{-1} can be achieved at micropores volume $750 \text{ mm}^3 \text{ g}^{-1}$ and specific surface area $1600 \text{ m}^2 \text{ g}^{-1}$. These parameters can be achieved at activation temperature 600°C and activator/charcoal ratio 1.25 and with the increase of carbon porosity electrical capacitance decreases.

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