

文章编号: 1007-8827(2017)04-0319-08

基于硫酸为电解液的超级电容器木基活性炭电极材料的制备

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摘要: 以 NaOH 为活化剂, 采用两步热化学过程制备出木基活性炭。将所制活性炭用作以硫酸为电解液的超级电容器电极材料。探讨了合成条件对活性炭孔结构和电化学性能。结果表明, 在微孔中形成双电层电容, 介孔和大孔则实现离子运输。在高的活化温度或高碱炭比下, 材料被过度活化, 导致高的介孔、大孔孔容, 这增加了电解液的吸收, 从而降低质量比电容。最佳的活性炭合成条件为, 活化温度: 600℃, 碱炭比: 1.25。

关键词: 活性炭; 孔结构; 热化学活化; 碱活化; 超级电容器

中图分类号: TQ127.1⁺1

文献标识码: A

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Wood-based activated carbons for supercapacitor electrodes with a sulfuric acid electrolyte

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Abstract: Wood-based activated carbons were synthesized in a two-stage thermochemical process using sodium hydroxide as an activator, and used as the electrode materials for supercapacitors with a sulfuric acid electrolyte. The dependence of pore structure parameters and the electrochemical properties of the activated carbons on the synthesis conditions was investigated. Results indicate that an electric double layer is formed within micropores while meso and macropores are responsible for ion transport. Excess activation under a high activation temperature and/or a high mass ratio of sodium hydroxide to carbonaceous material leads to high meso and macropore volumes, which increase electrolyte uptake and therefore decrease the specific capacitance based on cell mass. The optimum activated carbon is obtained at an activation temperature of 600 °C with a mass ratio of sodium hydroxide to carbonaceous material of 1.25.

Key words: Activated carbons; Porous structure; Thermochemical activation; Alkali activation; Supercapacitors

Received date: 2017-05-29; Revised date: 2017-08-03

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English edition available online ScienceDirect (<http://www.sciencedirect.com/science/journal/18725805>).

DOI: 10.1016/S1872-5805(17)60125-2

1 Introduction

Electric energy accumulation and transfer is a hot topic and urgent problem nowadays. The existing methods for energy storage do not meet demands of the intensively expanding modern energetic systems, thus it is necessary to create and develop new approaches and solutions.

One of the possible ways to tackle load leveling in the traditional power grids, diesel-generator fluctu-

ations and vehicle breaking energy recuperation is to use electrochemical devices with double electric layer supercapacitors (SCs)^[1-4]. At the current moment carbon materials (CMs) such as activated carbons (ACs) are the main component of SC electrodes since they are stable in various media, have highly developed specific surface, sufficient electric conductivity and relatively low cost^[5-7]. Properties of CMs depend on raw material type and its modification con-

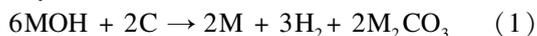
ditions, pretreatment regime and type of activation^[8-20].

Power capacity of carbon electrode is influenced by the AC properties, such as dispersity, elemental composition, micro and mesopores size distribution. Electrode should provide a high capacitance of SCs, minimal energy drop at power increase and stable work in multiple charge-discharge cycles^[21].

The raw materials used for AC production include polymers, pitch, coal, plant biomass (wood and its components, peat, nut shells), etc^[5-7]. The important conditions from the technical and economical standpoints are homogeneity of raw material properties, its low cost and easy availability.

Thermochemical activation of organic raw materials is one of the most widespread methods for the production of ACs with a developed porous structure. The approach is based on mixing of a precursor with an activating agent, for example, H_3PO_4 , $ZnCl_2$, alkali and their salts, and consequent activation in an inert atmosphere^[22]. The activation temperature varies from 400 to 900 °C depending on the activation agents used.

Alkali (KOH, NaOH) activation is the most widespread method for the production of highly effective ACs from various types of raw materials, including wood and its components^[23-26]. At the initial stage biomass-based raw materials usually undergo carbonization at 300-500 °C, with or without a catalyst, and carbonization temperature has a significant influence on AC porous structure^[8,27,28]. In the case of coal this stage is omitted. The carbonized plant biomass or coal are mixed with alkali (in the form of solution or dry) in a mass ratio of alkali/carbon of 1-7 and activated in the inert atmosphere (usually N_2 or Ar) at 600- 900 °C for 30- 180 min. After that the mixture is cooled and washed to remove formed carbonates. Microwave heating of the dry mixtures is effectively used as well^[10,11]. Chemical interaction of alkali with organic raw materials starts already at room temperature^[12]. In the process of heating alkali start to melt (melting temperature of NaOH is 318 °C and of KOH 360 °C) and the reactions rate increases. The reactions in the process can be formulated as follows^[9, 12]:



where M is K or Na. The majority of scientific publications are devoted to application of KOH, but it should be noted that it has been recently demonstrated^[9] that in the case of biomass NaOH is a better activating agent while KOH works best for the precursors with a more developed structure.

For the biomass based AC the most widely ac-

cepted pore model is slit-like^[29,30], where pores are formed by space between carbon layers^[31]. AC particles are represented by more or less ordered three dimensional combinations of graphene structures. Theoretical limit of AC mass specific surface calculated as two-sided area of singular graphene layer is $2\ 630\ m^2 \cdot g^{-1}$ ^[32,33].

In the process of thermochemical alkali activation volume of pores increase at the expense of carbon layer etching via carbon oxidation to form volatile products. These reactions between edge carbon atoms and molten alkali start at the graphene periphery^[12].

The most important processes for the porous structure development are the reduction of alkali metal by carbon and its intercalation into interlayer space of crystallites. Reaction of alkali with carbons in the ratios considerably less than stoichiometric leads to the synthesis of highly porous ACs^[12]. With the increase of alkali/carbon ratio, temperature and time of the processes, porosity and, correspondingly, specific surface of AC increase^[8,9,14,16-20]. Variation of above mentioned synthesis parameters allows reaching high capacities of SCs with electrodes made from ACs, 320- 370 $F \cdot g^{-1}$ in protic^[14,16] and 170- 195 $F \cdot g^{-1}$ in aprotic electrolytes^[20].

Numerous experiments widely available in literature testify that the amount of activator used in the activation process has the highest influence on the AC porous structure formation^[8,9,14,16-20]. The widespread opinion is that to increase electric properties of SCs it is necessary to increase pore volume and specific surface area. For some types of raw materials a linear dependence of specific capacitance ($F \cdot g^{-1}$) on AC specific surface area is found, for others there is a maximum value of capacitance at a definite value of AC specific surface area^[34]. The surface properties of ACs such as presence of surface C—O groups and wetting angle, pore size distribution and other physical-chemical characteristics, also play important role^[14,18,33]. For the ionic liquids based electrolytes pore size distribution is the most crucial characteristic due to their ions size and steric factor^[7,16,35,36]. At the same time in the case of ACs made for aprotic electrolytes with a relatively large ion size, a significant number of mesopores is needed.

The aim of this research is to study the capacity characteristics of SCs with the lowest parasitic mass of electrolyte and internal resistance in relation to the porous structure of alkali activated wood based carbons.

2 Experimental

2.1 Synthesis of activated carbons

AC production is schematically represented in Fig. 1. Thermochemical AC synthesis consists of two stages. At first, raw material (birch sawdust, 0.2–0.4 mm fraction) was carbonized in an argon atmosphere at 400 °C for 150 min (heating rate 4 °C·min⁻¹) and pulverized in a ball mill (particle size 10–50 μm). At the second stage, the carbonaceous material was impregnated with a 50% NaOH aqueous solution. The mass ratio of the activator to carbonaceous material was varied in the range of 1–3.7 (further denoted as K). The obtained mixture was activated under argon flow at 600–850 °C for 120 min (Nabertherm 40 L muffle oven). The activated mixture was washed with deionized water, 10% hydrochloric acid and water until filtrate pH reached 5. The AC obtained was dried overnight at 105 °C. Ash content of AC was 0.05%–0.2%. The main variables in the experiments were activation temperature and mass ratio of activating agent to carbonaceous material (further is denoted as K).

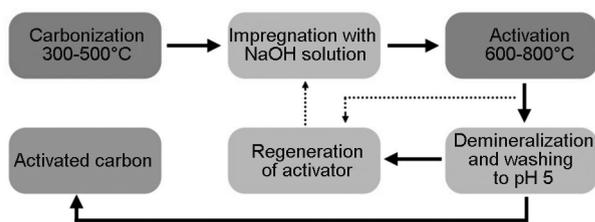


Fig. 1 A schematic representation of activated carbon synthesis.

2.2 Electrode preparation and testing

The test cell was made as follows. AC was mixed with ethanol and then with a PTFE (polytetrafluoroethylene) water suspension as a binder to form a paste, and then pressed with a roller to obtain a film. After that the film was dried and impregnated with 4.9 M sulfuric acid under vacuum. Porous polypropylene membrane was used as a separator and 200 μm thermal expanded graphite foil was used as a current collector. The mass of the cell includes all of the components mentioned above. Thickness of assembled electrode was 400 μm (±10%), active area of electrodes was 4.15 cm², and areal density of active materials was 19–24 mg/cm². It should be noted that electrode thickness was chosen as the most important parameter.

Electrodes separated with an electrolyte impregnated separator were wrapped from both sides with thermal expanded graphite foils and pressed at 1 MPa between gold plated plates connected to a potentiostat

Elins 30-S. Contact resistance between the gold plated plates and the SC cell as well other electrical communications did not exceed 2% of internal resistance of SC (ohmic losses in the solid phase, electrolyte and contact resistances).

After tests each cell was disassembled, the foils and separator were separated and electrodes were weighted. The difference in mass of impregnated, tested and dry electrodes was evaluated as the mass of adsorbed electrolyte. Since the density of sulfuric acid is known, the volume of electrolyte can be calculated. Amount of the electrolyte in the separator was the same for all cells, and amount of electrolyte in electrode depends on porosity of the AC used. Total volume of electrolyte in electrode consists of electrolyte volume adsorbed into micro-, meso- and macropores of AC and also interparticle space formed when AC was mixed with the binder and pressed.

Energy capacity of SC was defined based on a complete discharge after 5 min exposition at 1 V. Internal resistance was calculated by voltage drop at the current step in the beginning of SC discharge.

2.3 Porosity and structure

Porous structure of the AC was evaluated from N₂ sorption. Isotherms were obtained using a Sorptometer KELVIN 1042 (COSTECH Instruments). Degassing temperature was 250 °C, adsorption gas was nitrogen. Brunauer-Emmet-Teller (BET) and Dubinin-Radushkevich (DR) approaches were used to characterize AC porous structure for high (> 0.2) (mesopores) and low (< 0.2) (micropores) relative pressure regions, respectively^[37].

Surface morphology changes of AC were observed using a Vega Tescan scanning electron microscope (SEM).

3 Results and discussion

Highly effective sorbent AC^[38,39], which can be used as electrode materials for SCs with H₂SO₄ electrolyte, was synthesized from wood precursor in two stage thermochemical process with NaOH as an activating agent (Table 1, sample T-0)^[40,41,42]. Sample was synthesized at an activation temperature 700 °C and an activator to carbonaceous material ratio K = 3.7. Specific surface area was 3 300 m²·g⁻¹ and micropore volume was 1 230 mm³·g⁻¹.

SEM pictures of carbon before and after activation at 700 °C and K=3.7 are given in the Fig. 2. It can be seen that in the process of activation particles become smaller, their edges are more rounded and particle size distribution is more uniform. This tendency is the same for all the ACs synthesized.

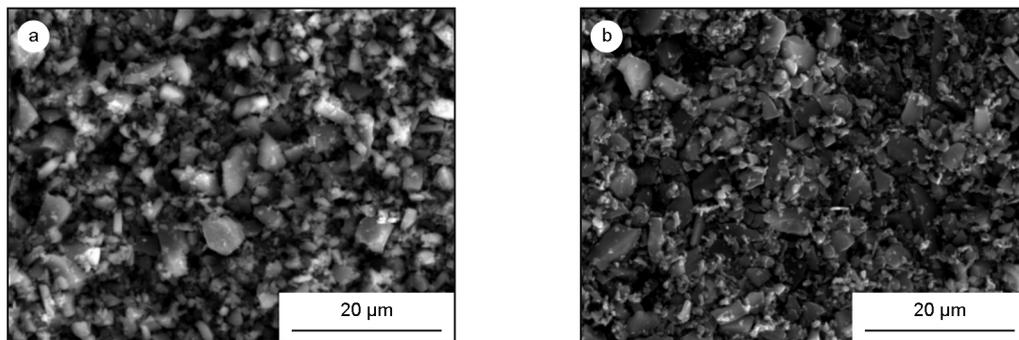


Fig. 2 SEM images of carbon (a) before and (b) after activation at 700 °C and K=3.7.

Tests of SC with electrodes made from T-0 (Table 1) have shown a specific capacity of 310 F·g⁻¹. The electrode using T-0 has a low electrode density and, as a consequence, a high parasitic electrolyte mass due to its high pore volume. In this case positive effect of SC with a high capacity calculated based on dry mass is negated by the increased mass of electrolyte in the electrode pores. Commercial AC Maxsorb-

3^[8] with a high specific capacitance has the same disadvantage. To elucidate this problem, we have tested SC with electrodes made from commercially available AC (Table 1) and have revealed that despite the fact that specific capacitance of T-0 is 1.5 times higher than that of carbon cloth UVIS-AK-T 0.41, its specific power capacity is even lower than that of carbon cloth.

Table 1 A comparison of characteristics of SCs with electrodes made from commercial and experimental AC and carbon fiber cloth. Capacitance and power capacity were tested at a low current density (0.3 A·g⁻¹) in a sulfuric acid electrolyte.

Activated carbon	Specific capacitance (F·g ⁻¹)	Specific resistance (Ohm·cm)	Volume of micropores (mm ³ ·g ⁻¹)	Electrolyte volume (cm ³ ·g ⁻¹)	Specific power capacity of cell (Wh·kg ⁻¹)
YP-50F Kuraray (Japan)	182	4	800	1.35	1.81
V2 EnerG2 (USA)	182	4	800	1.29	1.85
XH-001W Shanxi Xinhui (China)	254	4.4	1000	1.67	2.40
Carbon fabric UVIS-AK -T 0.41 (Russia)	211	7.5	370	1.17	2.35
Maxsorb-3 (Japan)	320	-	-	2.80	-
T-0 (700 °C, K=3.7)	310	4.5	1230	2.30	2.16
T-3 (600 °C, K=1.25)	390	4.6	750	1.4	3.06

To define dependence of SC properties on AC porous structure we tested a number of ACs synthesized at various temperatures and ratios of NaOH to carbonaceous material (K).

Porous structure of AC used for SC electrodes was tested using nitrogen sorption. The isotherms are presented in Fig. 3. Evaluating isotherms of ACs synthesized in the temperature range 600- 800 °C (K=2) (Fig. 3a) it can be concluded that adsorbed gas volume increases with the activation temperature. At the same time for the AC activated at 800 °C, the shape of the isotherm is changed as compared with the isotherms of AC synthesized at lower temperatures. Shape of isotherm of the AC activated at 800 °C illustrates that pore filling is governed by both volume filling and capillary condensation, indicating that mesopores are present.

The same effect is observed in Fig. 3b, where isotherms of AC synthesized at 700 °C with K ranging

from 1 to 3.7 are demonstrated. At K=1 and 2 isotherms correspond to microporous sorbents and the type of isotherms and adsorption mechanism are changed with the increase of K. It should be noted that volume of adsorbed gas does not change with the increase of K from 3 to 3.7.

The isotherms of AC synthesized at activation temperature of 600 °C and a low K (Fig. 3c) similarly illustrate that the volume of adsorbed nitrogen increases with the increase of K from 1 to 2.

Calculations based on isotherms data show that decrease of K from 3.7 to 1.7 at an activation temperature 700 °C leads to a decrease of pore volume (Fig. 4). This is the reason why the total volume of electrolyte (sulfuric acid) adsorbed by electrode decreases. The capacity of SC changes insignificantly and is practically the same for K 1.7 and 3.7 (sample T-0, Table 1) -310 F·g⁻¹.

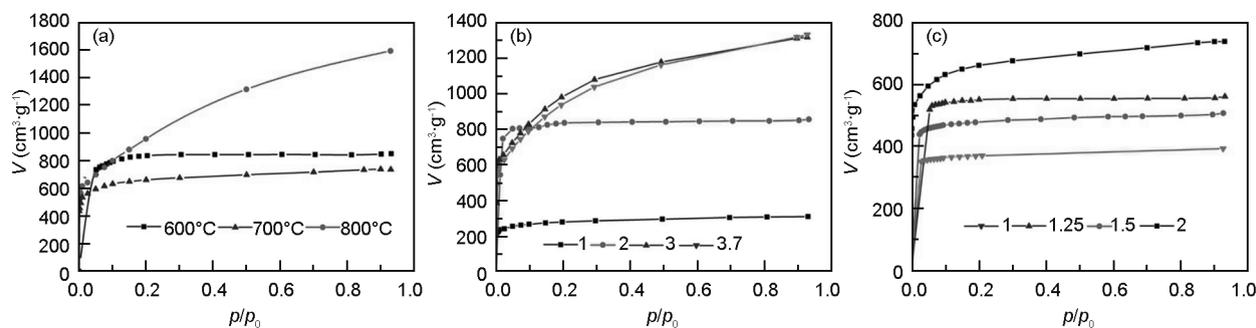


Fig. 3 Nitrogen adsorption isotherms at 77 K. (a) the influence of temperature on specific volume at K of 2; (b) the influence of K on specific volume at an activation temperature of 700 °C; (c) the influence of K on specific volume at an activation temperature of 600 °C.

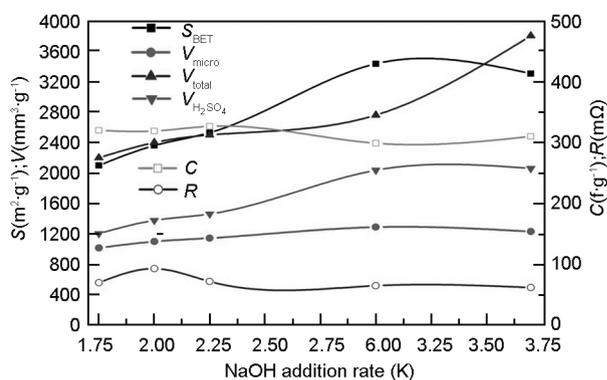


Fig. 4 Dependence of activated carbon porous structure and supercapacitor characteristics on K value at an activation temperature of 700 °C. S_{BET} -specific surface in $\text{m}^2 \cdot \text{g}^{-1}$, V_{micro} -micropores volume, $\text{mm}^3 \cdot \text{g}^{-1}$, V_{total} -total pore volume, $\text{mm}^3 \cdot \text{g}^{-1}$, $V_{\text{H}_2\text{SO}_4}$ -volume of adsorbed electrolyte, $\text{mm}^3 \cdot \text{g}^{-1}$, C -specific capacitance, $\text{F} \cdot \text{g}^{-1}$, R -resistance, milliohm.

Authors of research^[16] also demonstrated that decrease of K from 4 to 2 led to a decrease of pore volume and capacity as well. It was explained by the change of pore size distribution. At low K pore size distribution was unimodal and samples were microporous. With the increase of K pore size distribution shifted to bimodal due to an increase in mesopore volumes. On the base of these results authors^[16] concluded that a high specific area of AC and a highly developed mesoporosity are necessary to achieve a high specific capacitance.

The fact of insignificant change of capacity at the activation temperature of 700 °C regardless K (Fig. 5), can be explained by a minimal pore volume required for the electrical double layer formation. Perhaps in this case there is a factor which negates the positive effect of AC as mesopore volume increases. According to the report in literature^[14] this factor can be represented by a content change of surface oxygen-containing functional groups. These functional groups can contribute to SC capacitance by redox reactions (so called pseudocapacitance effect) and also increase

hydrophilicity of pore surface where electric double layer forms.

Another important parameter in the synthesis of AC is the activation temperature. Characteristics of ACs synthesized in the temperature range of 600-850 °C (K=2) are shown in the Fig. 5.

With the increase of activation temperature total pore volume does not change significantly, but the micropore volume reaches its maximum at 700 °C. The same trend can be observed for SC capacitance. The SC made using the AC synthesized at 600 °C has a capacitance of $330 \text{ F} \cdot \text{g}^{-1}$, but when the AC synthesized at 850 °C is used the capacitance decreases to $180 \text{ F} \cdot \text{g}^{-1}$. Low activation temperature is also economically beneficial for AC costs.

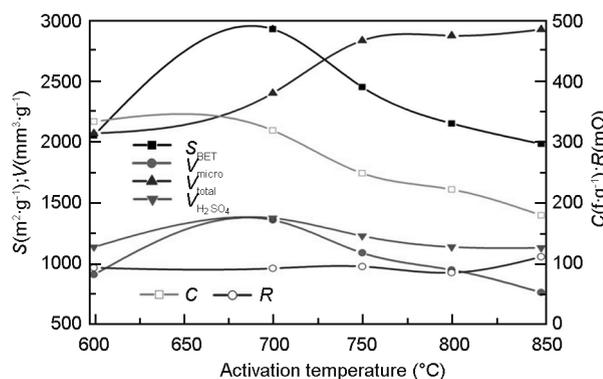


Fig. 5 Dependence of activated carbon porous structure and supercapacitor characteristics on activation temperature at a K value of 2. S_{BET} -specific surface in $\text{m}^2 \cdot \text{g}^{-1}$, V_{micro} -micropores volume, $\text{m}^3 \cdot \text{g}^{-1}$, V_{total} -total pore volume, $\text{mm}^3 \cdot \text{g}^{-1}$, $V_{\text{H}_2\text{SO}_4}$ -volume of adsorbed electrolyte, $\text{mm}^3 \cdot \text{g}^{-1}$, C -specific capacitance, $\text{F} \cdot \text{g}^{-1}$, R -resistance, milliohm

Total volume of electrolyte in the electrode significantly increases with activation temperature, especially in 700-750 °C range. It also should be mentioned that inner resistance practically does not change with the activation temperature and adsorbed electrolyte amount (Fig. 5). The resistance increase at high temperatures should probably be due to a volume in-

crease of large pores. The same trend was observed by other authors^[14]. The decrease of capacitance was explained by the content decrease of C—O groups on the carbon surface with increasing the activation temperature, which influences pseudocapacitance.

Thus, a decrease of activation temperature positively influences specific capacitance of SC, calculated on cell mass. However, it should be noted that activation temperature lower than 600 °C could most probably lead to a decrease of AC porosity since the lowest thermodynamic limit of main structure defining reactions is at 570 °C^[13].

Results of experiments to determine the most beneficial K value at an activation temperature of 600 °C (K varied from 1 to 2) are shown in the Fig. 6.

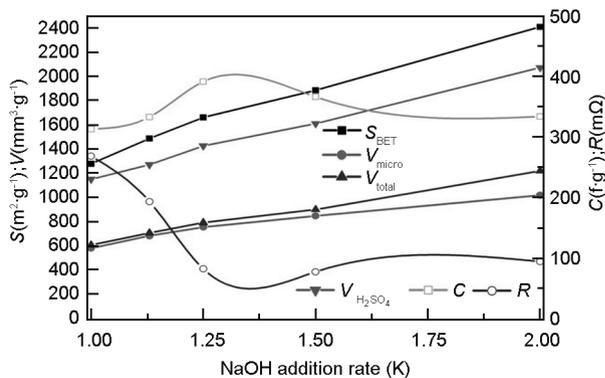


Fig. 6 Dependence of activated carbon porous structure and supercapacitor characteristics on K value (NaOH addition) at an activation temperature of 600 °C. S_{BET} -specific surface in m²·g⁻¹, V_{micro} -micropores volume, m³·g⁻¹, V_{total} -total pore volume, mm³·g⁻¹, $V_{H_2SO_4}$ -volume of adsorbed electrolyte, mm³·g⁻¹, C -specific capacitance, F·g⁻¹, R -resistance, milliohm

An increase of K value leads to an increase of total and micropore volumes, however, the latter takes place to a lesser extent. An increase of porosity leads to an increase of adsorbed electrolyte. With the increase of K value from 1 to 1.25 capacitance of SC increases and its resistance rapidly decreases. The AC sample activated at 600 °C and K=1.25 is denoted as T-3 (Table 1). With a further increase of K from 1.25 to 2 capacitance decreases with a practically constant value of electrode resistance.

Rate performance and cyclic stability of SC with the electrodes made from the AC sample activated at 600 °C and K=1.25 are shown in the Fig. 7 and 8, respectively. SC was tested using cyclic voltammetry at a potential range of 0-1000 mV and a scan rate of 20 mV/s (Fig. 7). First cycle shows the initial stage of device work, and after that it stabilizes i. e. cycles overlap. The more voltammogram resembles rectangle, the lower pseudocapacitance effects and the high-

er the efficiency. Fig. 8 shows stability tests of SC in the galvanostatic mode at a current density of 60 mA/cm². The SC device has no notable loss of its performance after 10 000 cycles.

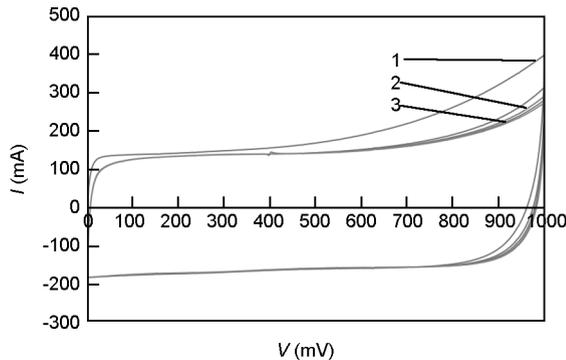


Fig. 7 Rate performance of SC with the electrodes made from the AC (600 °C, K=1.25) at a scan rate of 20 mV/s. Three consequent cycles-1 (initial), 2 and 3 - are shown.

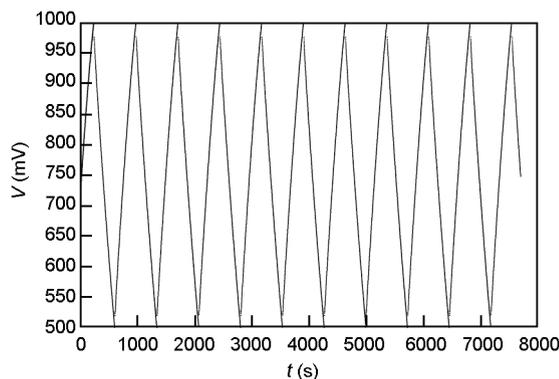


Fig. 8 Cyclic stability of SC with the electrodes made from the AC (600 °C, K=1.25) at a current density of 60 mA/cm².

An increase of activation temperature or/and activator ratio K leads to the formation of additional pores that adsorb electrolyte (Fig. 4 and Fig. 5). With the activation temperature increase pore walls become thinner, which can negatively influence electric double layer formation. This assumption is proven by the authors in literature^[44], where it is postulated that potential distribution in carbon material has the main influence on the system capacitance as compared with the potential distribution in the protic electrolyte. It should be noted that solid phase contribution to the SC internal resistance for the electrolytes with a high and low ionic conductivity is different. For the water-based electrolyte with a high ionic conductivity its effect is more pronounced than that for organic electrolyte.

A decrease of pore wall thickness probably can negatively influence on solid phase coherency which in its turn leads to an increase of ohmic losses due to the loss of contact between carbon particles in the

electrodes. Judged from the dependency of SC characteristics on activation temperature (Fig. 4), the increase of adsorbed electrolyte volume with increasing the activation temperature is not accompanied with a decrease of inner resistance and an increase of specific capacitance. This phenomenon can be explained by two factors. The first one is described in the work in a literature^[44], which showed how the pore deepening can cause difficulties for ion penetration, gating and uneven charge distribution inside micropores. The second one is described in the research in another literature^[45], where it was illustrated that narrowing micropores can have a positive influence on specific capacitance due to ion solvation shells distortion inside carbon nanostructure, which leads to close approaching of the ion center to the electrode surface and improved capacitance.

Electrode pores should provide channels for ion transport in the process of electric double layer formation. The total volume of electrolyte in the micro-, meso- and macropores in our experiment (Fig. 6) is $1\,400\text{ mm}^3 \cdot \text{g}^{-1}$. It is obvious that the minimal micropore volume (in our case $750\text{ mm}^3 \cdot \text{g}^{-1}$, Table 1, T-3) is required for the electric double layer formation. Meso- and macropores of electrode provide transport path for ions. However, their volume exceeding this requirement lead to superfluous electrolyte adsorption. These pores do not contribute to electric double layer formation and excessive electrolyte mass adversely influences specific capacitance of SC calculated on cell under study or whole device.

4 Conclusions

Conditions of formation and characteristics porous structure of wood-based ACs synthesized in alkali activation were defined for use as electrodes in SCs with sulfuric acid electrolyte. It was found that a pore volume of $750\text{ mm}^3 \cdot \text{g}^{-1}$ is sufficient for the effective electric double layer formation in the AC pores. Total volume of electrolyte in pores is $1\,400\text{ mm}^3 \cdot \text{g}^{-1}$, which is sufficient for ion transport and availability. It is demonstrated that change of AC pore structure, specifically reduction of porosity, led to a 30% increase of supercapacitor specific power capacitance calculated on elementary cell mass as compared with the supercapacitor made with AC with a higher pore volume.

Acknowledgements

Authors express gratitude to project ERAF 2OP/2.11.10/14/APIA/VIAA/050.

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