

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

Aleksandrs Volperts^{1*}, Galina Dobeļe¹, Aivars Zhurīnsh¹, Darya Vervikishko², Evgeny Shkolnikov², Jurijs Ozoliņš³

¹Latvian State Institute of Wood Chemistry, 27 Dzerbenes St., LV-1006, Riga, Latvia;

²Scientific Association for High Temperatures, Russian Academy of Sciences, 13/2 Izorskaya St., 125412 Moscow, Russia;

³Riga Technical University, Faculty of Material Science and Applied Chemistry 14/24, Āzenes Street, LV-1048, Riga, Latvia

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

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 fluctuations 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 conditions, 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), et al [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

Received date: 09 May. 2017; Revised date: 03 Aug. 2017

*Corresponding author. E-mail: volperts@edi.lv

Copyright©2017, Institute of Coal Chemistry, Chinese Academy of Sciences. Published by Elsevier Limited. All rights reserved.

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

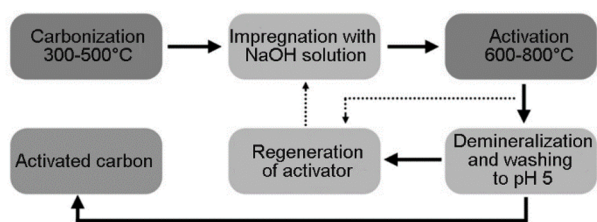
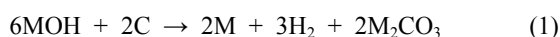


Fig. 1 A schematic representation of activated carbon synthesis.

(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 accepted 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 2630 m² g⁻¹^[32,33].

In the process of thermochemical alkali activation volume of pores increase at the expense of carbon layer etching via carbon oxidization 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 g⁻¹ in protic^[14,16] and 170-195 F 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 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 40L 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).

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 N_2 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 H_2SO_4 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 $m^2 g^{-1}$ and micropore volume was 1 230 $mm^3 g^{-1}$.

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.

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.

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} .

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

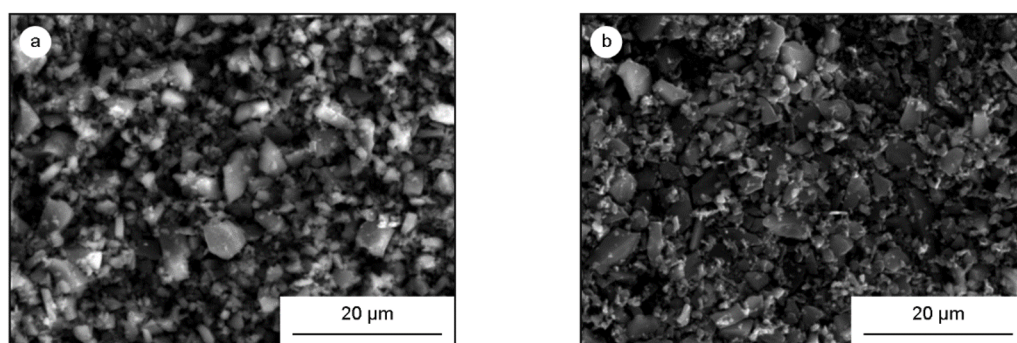
Fig. 2 SEM images of carbon (a) before and (b) after activation at 700 °C and $K=3.7$

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

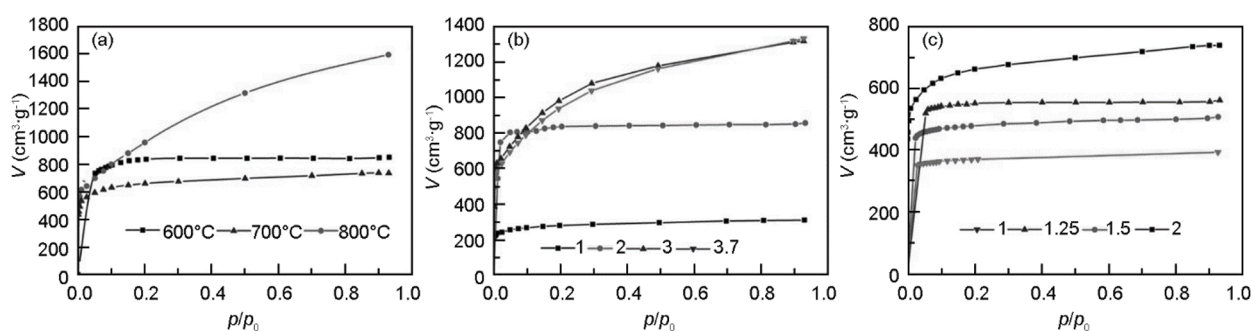


Fig. 3 Nitrogen adsorption isotherms at 77 K. (a) the influence of temperature on specific volume at K of 2; (b) the influence of K on specific volume at an activation temperature of 700 °C; (c) the influence of K on specific volume at an activation temperature of 600 °C.

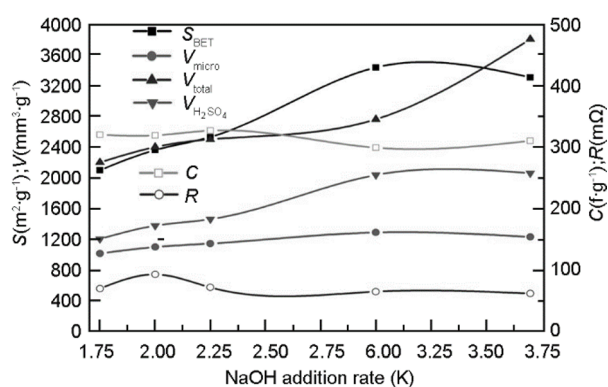


Fig. 4 Dependence of activated carbon porous structure and supercapacitor characteristics on K value at an activation temperature of 700 °C. S_{BET} -specific surface in $\text{m}^2 \text{g}^{-1}$, V_{micro} -micropores volume, $\text{m}^3 \text{g}^{-1}$, V_{total} -total pore volume, $\text{mm}^3 \text{g}^{-1}$,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

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 F g^{-1} , but when the AC synthesized at 850 °C is used the capacitance decreases to 180 F g^{-1} . Low activation temperature is also economically beneficial for AC costs.

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 increase 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

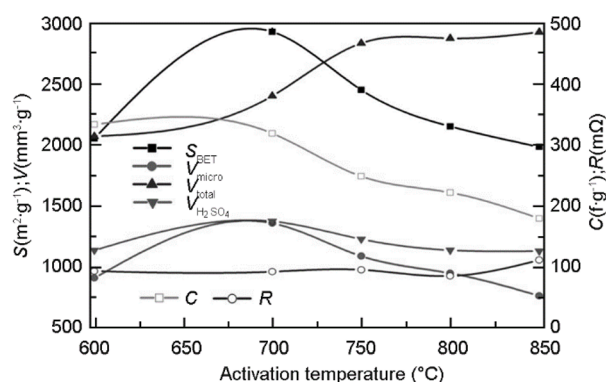


Fig. 5 Dependence of activated carbon porous structure and supercapacitor characteristics on activation temperature at a K value of 2. S_{BET} -specific surface in $\text{m}^2 \text{g}^{-1}$, V_{micro} -micropores volume, $\text{m}^3 \text{g}^{-1}$, V_{total} -total pore volume, $\text{mm}^3 \text{g}^{-1}$,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

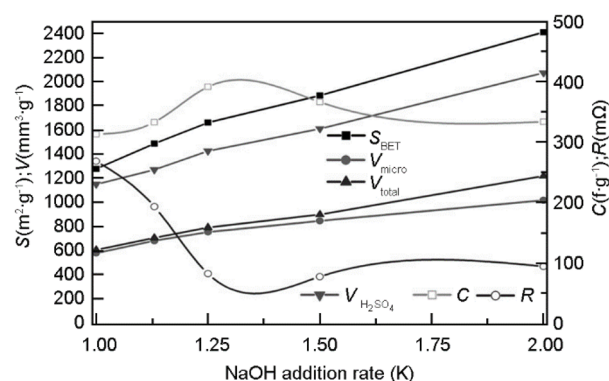


Fig. 6 Dependence of activated carbon porous structure and supercapacitor characteristics on K value (NaOH addition) at an activation temperature of 600 °C. S_{BET} – specific surface in $\text{m}^2 \text{g}^{-1}$, V_{micro} -micropores volume, $\text{m}^3 \text{g}^{-1}$, V_{total} -total pore volume, $\text{mm}^3 \text{g}^{-1}$, $V_{\text{H}_2\text{SO}_4}$ -volume of adsorbed electrolyte, $\text{mm}^3 \text{g}^{-1}$, C -specific capacitance, F g^{-1} , R -resistance, milliohm

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].

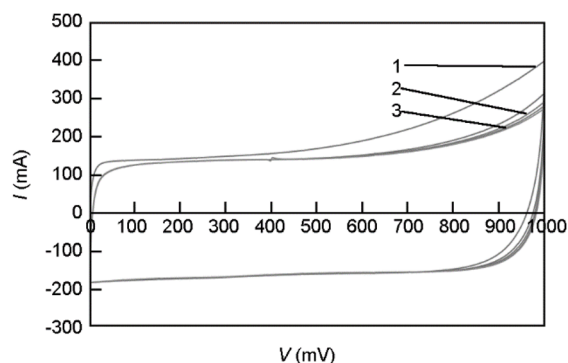


Fig. 7 Rate performance of SC with the electrodes made from the AC (600 °C, $K=1.25$) at a scan rate of 20 mV/s. Three consequent cycles 1 (initial), 2 and 3 are shown.

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.

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 higher 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.

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

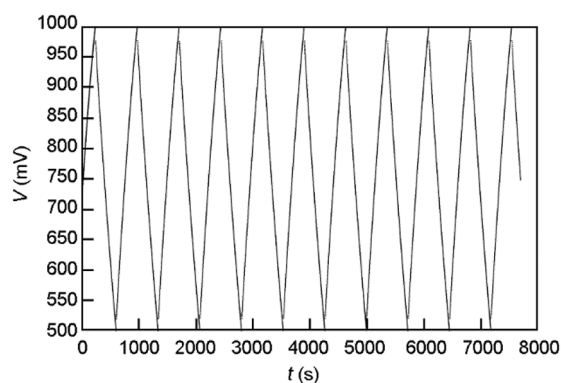


Fig. 8 Cyclic stability of SC with the electrodes made from the AC (600 °C, $K=1.25$) at a current density of 60 mA/cm².

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 mm³ g⁻¹. It is obvious that the minimal micropore volume (in our case 750 mm³ 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 $750 \text{ mm}^3 \text{ g}^{-1}$ is sufficient for the effective electric double layer formation in the AC pores. Total volume of electrolyte in pores is $1400 \text{ mm}^3 \text{ g}^{-1}$, 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.

Acknowledgments

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

References

- [1] Yu Chabot AV, Zhang J. Electrochemical Supercapacitors for Energy Storage and Delivery: Fundamentals and Applications [M]. Boca Raton: Taylor & Francis Group; 2013.
- [2] Ariyanayagam Kumarappa D. Advanced Electrode Materials for Electrochemical Supercapacitors[D]. Open Access Dissertations and Theses; 2012.
- [3] Jayalakshmi M, Balasubramanian K. Simple capacitors to supercapacitors - An overview[J]. Int J Electrochim Sci, 2008, 3: 1196-1217.
- [4] Burke A. R&D considerations for the performance and application of electrochemical capacitors[J]. Electrochim Acta, 2007, 53: 1083–1091.
- [5] Lipka S M, Swartz C R. Electrochemical capacitor carbons[Z]. Energeia, 2007, 18(5): 1-4.
- [6] Frackowiak E. Supercapacitors based on carbon materials and ionic liquids[J]. J Braz Chem Soc, 2006, 17(6): 1074-1082.
- [7] Simon P, Gogotsi Y. Materials for electrochemical capacitors[J]. Nat Mater, 2008, 7: 845-854.
- [8] Xu B, Chen Y, Wei G, et al. Activated carbon with high capacitance prepared by NaOH activation for supercapacitors[J]. Mater Chem Phys, 2010, 124: 504-509.
- [9] Linares-Solano A, Lillo-Rodenas MA, Marko-Lozar JP, et al. NaOH and KOH for preparing activated carbons used in energy an environmental applications[J]. Int J Energ Environ Econ, 2012, 20(4): 59-91.
- [10] He X, Geng Y, Qiu J, Zheng S, et al. Effect of activation time on the properties of activated carbons prepared by microwave-assisted activation for electric double layer capacitors[J]. Carbon, 2010, 48: 1662-1669.
- [11] He X, Li R, Qiu J, et al. Synthesis of mesoporous carbons for supercapacitors from coal tar pitch by coupling microwave-assisted KOH activation with a MgO template[J]. Carbon, 2012, 50: 4911-4921.
- [12] Tamarkina YV. Thermo-induced reactions of coal with alkali metal hydroxides[J]. Chem Chem Tech, 2010;162: 70-80 (in Russian).
- [13] Lillo-Rodenas MA, Cazorla-Amoros D, Linares-Solano A. Understanding chemical reactions between carbons and NaOH and KOH. An insight into the chemical activation mechanism[J]. Carbon, 2003, 41: 267-275.
- [14] Bleda-Martinez MJ, Macia-Agullo JA, Lozano-Castello D, et al. Role of surface chemistry on electric double layer capacitance of carbon materials[J]. Carbon, 2005, 43(13): 2677-2684.
- [15] Tamarkina YV, Shendrik TG, Kucherenko VA, et al. Conversion of alexandriya brown coal into microporous carbons under alkali activation[J]. Journal of Siberian Federal University Chemistry, 2012, 5(1): 24-36 (in Russian).
- [16] Xu B, Wu F, Chen R, et al. Highly mesoporous and high surface area carbon: A high capacitance electrode material for EDLCs with various electrolytes[J]. Electrochim Commun, 2008, 10: 795-797.
- [17] Zhang Z, Cui M, Lai Y, et al. Preparation and electrochemical characterization of activated carbons by chemical-physical activation[J]. J Cent South Univ Technol, 2009, 16: 91-95.
- [18] Lota G, Centeno TA, Frackowiak E, et al. Improvement of the structural and chemical properties of a commercial activated carbon for its application in electrochemical capacitors[J]. Electrochim Acta, 2008, 53: 2210-2216.
- [19] Cuhadaroglu D, Uygun OA. Production and characterization of activated carbon from a bituminous coal by chemical activation[J]. Afr J Biotechnol, 2008, 7(20): 3703-3710.
- [20] Liao WC, Liao FS, Tsai CT, et al. Preparation of activated carbon for electric double layer capacitors[J]. China Steel Tec, 2012, 25: 36-41.
- [21] Conway BE. Electrochemical Supercapacitors – Scientific Fundamentals and Technological Applications[M]. New York: Kluwer Acad., Plenum; 1999.
- [22] Marsh H, Rodriguez-Reinoso F. Activated Carbon[M]. Amsterdam: Elsevier, 2006.
- [23] Ioannidou O, Zabaniotou A. Agricultural residues as precursors for activated carbon production, a review[J]. Renew Sustain Energ Rev, 2007, 11: 1966-2005.
- [24] Rodriguez-Reinoso F. Production and Applications of Activated Carbons[M]. In: Schuth F, Sing KSW, Weitkamp J, editors. Handbook of porous solids, Weinheim: Wiley-VCH; 2002, p. 1766-1782.
- [25] Kalinicheva OA., Bogdanovich NI, Dobelev GV. Pretreatment of wood raw materials in the synthesis of NaOH activated carbons[J]. Forest J, 2008, 2: 117-122 (in Russian).
- [26] Lillo-Rodenas MA, Marco-Lozar JP, Cazorla-Amoros D, et al. Activated carbons prepared by pyrolysis of mixtures of carbon precursor/alkaline hydroxide[J]. J Anal Appl Pyrol, 2007, 80: 166-174.
- [27] Mikova NM, Ivanov IP, Parfenov VA, et al. Influence of thermal and chemical modification conditions on properties of birchwood based carbon materials[J]. Siberian federal University J Chem, 2011, 4: 356-368 (in Russian).

- [28] Dobe G, Jakab E, Zoltan S, et al. Formation of nanoporous carbon materials in thermocatalytic synthesis conditions[J]. *J Anal Appl Pyrol*, 2013, 103: 173-180.
- [29] Fryer JR. The micropore structure of disordered carbons determined by high-resolution electron-microscopy[J]. *Carbon*, 1981, 19: 431-439.
- [30] Dubinin M. Microporous structures of carbon sorbents. General characteristics of micro- and supermicro pores of slit-like model[Z]. *News of USSR Science Academy Chem*, 1979, 8: 1691-1696 (in Russian).
- [31] Guryanov VV, Petuhova GA, Polyakov NS. Forecasting of microporous structure parameters and adsorption properties of activated carbons[Z]. *News of Russian Science Academy Chem*, 2001, 6: 933-939 (in Russian).
- [32] Kaneko K, Ishii C, Ruike M, et al. Origin of superhigh surface area and microcrystalline graphitic structures of activated carbons[J]. *Carbon*, 1992, 30(7): 1075-1088.
- [33] Lewandowski A, Galinski M. Practical and theoretical limits for electrochemical double-layer capacitors[J]. *J Power Sources*, 2007, 173: 822-828.
- [34] Lozano-Castello D, Marko-Lozar J.P, Bleda-Martinez MJ, et al. Relevance of porosity and surface chemistry of superactivated carbons in capacitors[J]. *Tanso*, 2013, 256: 41-47.
- [35] Izmailova MY, Rychagov AY, Denshikov KK, et al. Electrochemical capacitor with ionic liquid as electrolyte[J]. *Electrochemistry*, 2009, 45(8): 1014-1015.
- [36] Izmailova MY. Development of supercapacitor with ionic liquid 1-methyl-3-butylimideazolium tetraboronfluoroborate[D]. PhD dissertation, Russian D.I Mendeleev Chemical-Technological University. Moscow, Russia, 2010 (in Russian).
- [37] Bansal R, Goyal M. *Activated Carbons Adsorption*[M]. Boca Raton: CRP Press Taylor & Francis Group; 2005.
- [38] Dobe G, Telyseva G, Dizhbite T, et al. Method for obtaining carbon-based sorbent[P]. Patent LV14683 2013.
- [39] Dobe G, Dizhbite T, Gil MV, et al. Production of nanoporous carbons from wood processing wastes and their use in supercapacitors and CO₂ capture[J]. *Biomass Bioenerg*, 2012, 46: 145-154.
- [40] Volperts A, Mironova-Ulmane N, Sildos I, et al. Structure of nanoporous carbon materials for supercapacitors[J]. *IOP Conf Ser: Mater Sci Eng*, 2012, 38: 1-5.
- [41] Atamanyuk IN, Vervykishko DE, Grigorenko AV, et al. Influence of technological aspects of electrodes production on electrochemical characteristics of supercapacitors with protic electrolyte[J]. *Electrochem Energ J*, 2014.
- [42] Shkolnikov E, Sidorova E, Malakhov A, et al. Estimation of pore size distribution in MCM-41-type silica using a simple desorption technique[J]. *Adsorption*, 2011, 17(6): 911-918.
- [43] Lankin AV, Norman GE, Stegailov VV. Atomistic simulation of the interaction of an electrolyte with graphite nanostructures in perspective supercapacitors[J]. *High Temp*, 2010, 48(6): 837-845.
- [44] Kowal J, Avaroglu E, Chamekh F, et al. Detailed analysis of the self-discharge of supercapacitors[J]. *J Power Sources*, 2011, 196: 573-579.
- [45] Chmiola J, Yushin G, Gogotsi Y, et al. Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer[J]. *Science*, 2006, 313: 1760-1763.