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RESEARCH PAPER

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 ^{o}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 ^{o}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 ^{o}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 ^{o}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

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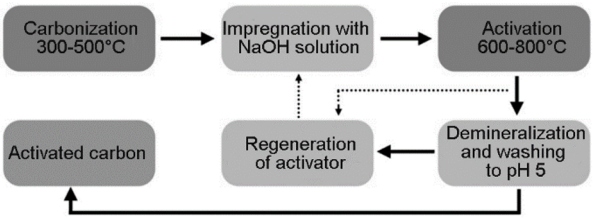

Fig. 1 A schematic representation of activated carbon synthesis.

(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]:

$$6MOH + 2C \rightarrow 2M + 3H_2 + 2M_2CO_3 \quad (1)$$

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 $m^2 g^{-1}$ [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 cm^2, and areal density of active materials was 19-24 mg/cm^2. 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 potentiostate Elins 30-S. Contact resistance between the gold plated plates and the SC cell as