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Microporous–mesoporous carbons for energy storage synthesized by activation of carbonaceous material by zinc chloride, potassium hydroxide or mixture of them

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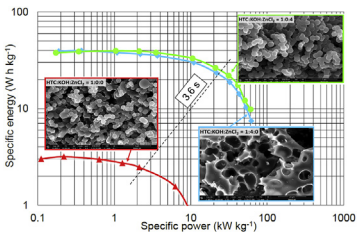
HIGHLIGHTS

- Carbonaceous materials were synthesized by hydrothermal carbonization method.
- The porosity of activated carbon has been fine-tuned by KOH and $ZnCl_2$ activation.
- The energy stored increased with the specific surface area of activated carbon.
- Activated carbons with mixed micro- and mesoporosity deliver very high power.

GRAPHICAL ABSTRACT



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ABSTRACT

Various electrochemical methods have been applied to establish the electrochemical characteristics of the electrical double layer capacitor (EDLC) consisting of the 1 M triethylmethylammonium tetrafluoroborate solution in acetonitrile and activated carbon based electrodes. Activated microporous carbon materials used for the preparation of electrodes have been synthesized from the hydrothermal carbonization product (HTC) prepared via hydrothermal carbonization process of D-(+)-glucose solution in H_2O, followed by activation with $ZnCl_2$, KOH or their mixture. Highest porosity and Brunauer-Emmett-Teller specific surface area ($S_{BET} = 2150\ m^2\ g^{-1}$), micropore surface area ($S_{micro} = 2140\ m^2\ g^{-1}$) and total pore volume ($V_{tot} = 1.01\ cm^3\ g^{-1}$) have been achieved for HTC activated using KOH with a mass ratio of 1:4 at 700 °C. The correlations between S_{BET}, S_{micro}, V_{tot} and electrochemical characteristics have been studied to investigate the reasons for strong dependence of electrochemical characteristics on the synthesis conditions of carbon materials studied. Wide region of ideal polarizability ($\Delta V \leq 3.0$ V), very short characteristic relaxation time (0.66 s), and high specific series capacitance (134 F g^{-1}) have been calculated for the mentioned activated carbon material, demonstrating that this system can be used for completing the EDLC with high energy- and power densities.

1. Introduction

In recent years, environmentally friendly energy storage devices have gained increasing attention due to the growing requirement for sustainable energy. Supercapacitors (electrical double layer capacitors (EDLC) and hybrid capacitors (HC)) are considered as the

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most promising energy storage devices due to their high power capability, short characteristic time constant, good coulombic reversibility (98% or higher) and excellent cyclability (over 10^6 cycles) [1–3], filling the gap between dielectric capacitors and traditional batteries [4–7]. Differently from batteries, EDLCs store energy in the electrical double layer, where the adsorption of ions is based mainly on the electrostatic interactions. The unique characteristics of EDLCs allow them to replace or combine with batteries and fuel cells in applications where the high power pulses are important, such as the different energy recuperation systems and peak power sources, hybrid electric vehicles, wind turbines, digital communication devices, mobile phones, laptops, etc. [8–10].

Porous carbon materials are considered to be the most promising electrode materials for supercapacitors due to the high surface area, good electrical conductivity, good chemical stability and low cost [1–8]. Hydrothermal carbonization is a very attractive process to obtain spherical lyophilic materials from carbon-rich precursors being cheap and "green" since it does not use expensive organic solvents or catalysts and requires only application of the low processing temperature (normally not higher than 300 °C) [11–18]. The pore size distribution, the average pore width and the specific surface area of the carbonized raw powder can be increased by using additional activation methods based on the application of air, carbon dioxide, steam or KOH, NaOH, H_3PO_4, etc. as an activation agent [19,20]. The main advantages applying KOH, NaOH, H_3PO_4, etc. rather than air, carbon dioxide or steam are the higher yield, lower activation temperature, shorter activation time and generally, the higher porosity of carbon prepared. Among the disadvantages, the activating agents are more expensive (KOH and NaOH vs. CO_2 and H_2O) and the additional washing (neutralization) stage is also necessary [21,22].

The electrical charge accumulated in EDLC depends on the electrochemically active surface area and, thus, on the porosity of a carbon material. In addition, porosity and chemical composition also determine the power density of EDLC having a strong effect on the rate of mass transfer (diffusion and migration) and adsorption rate of charge carriers inside porous matrix. Therefore, the characteristics of micro- and mesoporous carbon materials (especially the ratio of micropore and mesopore surface areas and pore volumes) have to be optimized to improve further the specific energy and power density of EDLCs [1,23–26].

Chen et al [27] synthesized series of carbon materials using phenol formaldehyde resin as a carbon precursor and activated the product using the mixture of KOH/$ZnCl_2$ in different ratios. They found that activation with KOH produced highly microporous carbon materials while during activation with $ZnCl_2$ mainly mesoporous carbon materials were formed. When the mixture of KOH and $ZnCl_2$ was used in activation step, carbon materials with a considerable degree of both micro- and mesopores were prepared. As the presence of both micro- and mesopores in carbons used as electrode materials is important for EDLCs with high capacitance and power density, such materials would be well-suited for electrode materials in EDLCs. Thus, in this work, the same activation agents were used to activate the carbonaceous material synthesized via hydrothermal carbonization process of D-(+)-glucose solution in H_2O. For simplicity, carbonaceous material of hydrothermal carbonization process is hereafter noted as HTC. A series of porous carbon materials with variable pore sizes were prepared activating HTC with different ratios of KOH and $ZnCl_2$. Also, carbon materials activating HTC with only KOH or $ZnCl_2$ were prepared for comparison.

Activated carbon materials were used as electrode materials in the two-electrode single cells of EDLC filled with 1 M triethylmethylammonium tetrafluoroborate ($TEMABF_4$) solution in acetonitrile (AN) as an electrolyte. The mixture of $TEMABF_4$ and AN was selected due to good electrochemical stability within a very wide region of potentials [18,23,26,28]. Cyclic voltammetry (CV), constant current charge/discharge (CC), electrochemical impedance spectroscopy (EIS) and constant power discharge (CP) methods were used to study the influence of the physical properties of activated carbon material on the electrochemical performance of EDLC.

2. Experimental

2.1. Chemicals and reagents used

D-(+)-glucose (≥99.5% purity, Sigma), potassium hydroxide (KOH, 30% w/v aqueous solution, Alfa Aesar), $ZnCl_2$ (≥99.99% purity (metals basis) anhydrous, Alfa Aesar) and hydrochloric acid (50% v/v aqueous solution, Alfa Aesar) were used as received. Ultrapure water (Milli-Q^+, 18.2 MΩ cm, Millipore) was used for the preparation of the 1 M D-(+)-glucose solution, for cleaning the resulting solid product formed during hydrothermal carbonization process, and for cleaning the activated carbon from activating agent and by-products. The electrolyte used was prepared from pure acetonitrile (AN, H_2O < 0.003%, Riedel-de Haën, stored over molecular sieves before use) and dry $TEMABF_4$ (Stella Chemifa Corporation).

2.2. Synthesis and physical characterization of activated carbon material

The hydrothermal carbonization of 1 M D-(+)-glucose aqueous solution (100 ml) was carried out in a high-pressure reactor (Büchi limbo, vessel volume 285 ml) at 180 °C for 24 h. Thereafter, the carbonaceous material was collected and washed with Milli-Q^+ water for several times and dried overnight in a vacuum oven (Vaciotem-TV, J.P. Selecta) at 120 °C and 50 mbar.

The following impregnation process of carbonaceous material with $ZnCl_2$, KOH or their mixture was performed for the activation. At first, the carbonaceous material was mixed with activating agents with respective mass ratios of HTC:KOH:$ZnCl_2$ – 1:0:4, 1:3:1, 1:2:2; 1:1:3 and 1:4:0. Then, ultrapure water was added (total volume ca 500 ml) to the mixture and stirred until a homogeneous slurry was obtained. Thereafter, the slurry was placed on a hot plate and stirred until most of the water was evaporated. Final drying of the slurry was carried out overnight in a vacuum oven at 120 °C and 50 mbar. The dry mass was placed in an alumina crucible (Anderman Ceramics) and introduced into an alumina tube (Anderman Ceramics). The alumina tube was then put into the tube furnace (Carbolite CTF 12/65/550) and activation was carried out at 700 °C using heating up rate of 2 °C min^{-1}. During heating up, activation and cooling down steps the reactor was flushed with argon (500 ml min^{-1}). After activation, all samples were washed with the Milli-Q^+ water for several times, then treated with hydrochloric acid (10 ml HCl and 300 ml Milli-Q^+ water) to remove excess of activating agents and the residuals of inorganic matter from the sample and again washed with the Milli-Q^+ water for several times. Finally, activated carbons were dried overnight in a vacuum oven at 120 °C and 50 mbar. For comparison, one carbon sample was synthesized simply by pyrolysis of carbonaceous material in the same condition as the activation was performed. Final treatment of all carbon materials was reducing the surface functional groups with H_2 (purity 99.9999%) at 800 °C for 2 h. Reduced carbon materials demonstrate wider potential region of ideal polarizability [23,26,28].

X-ray diffraction (XRD) patterns were collected by a Bruker D8 diffractometer (Bruker Corporation) with position sensitive LynxEye detector using Cu$K\alpha$ radiation with an angular step 0.01° and counting time 2 s for each angle measured. Diffraction spectra were

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