



Glucose derived ionothermal carbons with tailor-made porosity



Jonas Pampel, Caleb Denton, Tim-Patrick Fellinginger*

Department of Colloid Chemistry, Max-Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany

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ABSTRACT

An ionothermal synthesis strategy to obtain a set of glucose derived carbons with tailored pore system is demonstrated. The biomass derived materials possess high surface areas and large total pore volumes with values up to $2160 \text{ m}^2 \text{ g}^{-1}$ and $1.74 \text{ cm}^3 \text{ g}^{-1}$, respectively. The tailoring of the pore system is realized by simply changing the molar composition of the KCl/ZnCl_2 mixture which serves as combined solvent-porogen. Increasing KCl contents result in a continuous pore opening and rising pore volume leading to enhanced mass transport porosity. Those effects are accompanied by a linear decrease of the specific surface area which allows for the preparation of porous carbons of high and predictable surface areas between 2160 and $960 \text{ m}^2 \text{ g}^{-1}$. Experiments exemplarily shown for the application as supercapacitor electrodes, the different materials show a decreased gravimetric capacity, but enhanced capacity retention as well as improved areal capacity with increased KCl content nicely supporting the improved mass transport properties.

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1. Introduction

Highly porous carbon materials play an important role in numerous applications, such as adsorption, catalysis, energy conversion, and energy storage [1–7]. The main reasons for the widespread usage of carbon are not only its abundance, outstanding mechanical, chemical and thermal stability, but also its low specific weight [8]. Certain applications require specifically optimized porosity and three main parameters derived from nitrogen physisorption measurements are often used as descriptor. In surface related applications such as adsorption or catalysis, the specific surface area (SSA) can be easily related to the performance-to-price ratio. High total pore volumes (TPV) are very important for adsorption related applications, but can also limit the performance per volume. The pore size distribution (PSD) and the resulting pore structure specify the accessibility of the surface sites and thus the transport properties of the material. Obviously, the importance of each factor and their interplay strongly depends on the aimed application. Therefore, the development of preparation methods for porous materials with defined tailor-made pore system and SSA is of great interest.

There are numerous approaches to obtain porous carbons such as hard and soft templating or chemical and physical activation

methods [2,9–15]. Activation methods like KOH or CO_2 activation are widely employed at industrial scale, however, bring along drawbacks such as low yields and the mainly microporous character of the resulting carbon. Templating methods can overcome those drawbacks and lead to well defined, highly ordered and even hierarchically structured pore systems combining micro- ($d < 2 \text{ nm}$), meso- ($2 \text{ nm} < d < 50 \text{ nm}$) and macropores ($d > 50 \text{ nm}$) [9,14,16–18]. Nevertheless, these strategies often comprise a two-step procedure with a low temperature reaction and a successive post heat treatment to achieve high SSAs which is the case for soft templating. The often used hard templating requires the utilization of harsh chemicals such as hydrofluoric acid or strong bases leading to restricted scalability. Different activation strategies are used to generate porosity in a top-down fashion [19,20]. Zinc chloride activation is a classical (also industrial) approach, which shows surprisingly high carbon yields. However, because expensive technical requirements outweigh the higher yields for the current low price product, production sites vanish continuously. As previously described by Cesano et al. ZnCl_2 activation can only in parts be considered a classical activation [21]. Besides the leaching of carbon atoms at elevated temperatures (due to carbothermal reduction of Zn^{2+}), the generation of pores (herein called porogenesis) can largely be explained by the formation of nanodroplets of the molten salt, which act as a fluidic template, inside the carbon (or inside the carbonizing precursor). In addition to the catalytic effect of Zn^{2+} ions for e.g. sugar dehydration, the relatively high yield can be explained this way. In this light, the use of low melting salts

* Corresponding author.

E-mail address: Fellinginger@mpikg.mpg.de (T.-P. Fellinginger).

including ZnCl_2 may be increasingly relevant especially if larger amounts of salt porogen can be dispersed inside the carbon as compared to classic ZnCl_2 protocols. Such processes can be called ionothermal carbonization and in an extreme case the carbon precursor occasionally is completely dissolved within an inorganic salt melt. The ionothermal process combines facility and scalability with the possibility to obtain highly porous carbon materials containing hierarchical pore systems in high yields. We previously investigated an obviously soluble precursor using carbonizable ionic liquids as precursors and eutectic inorganic salt mixtures as combined porogen/solvent [22]. The successful pore formation requires the compatibility of the organic (precursor) phase and the inorganic molten salt phase during the decomposition/carbonization process at high temperatures under inert gas resulting in a nanoseparation of salt phase and the final carbon material. This one-pot reaction towards highly porous nitrogen doped carbons only requires aqueous washing for removal of the inorganic salt. In recent years, various precursor-salt combinations were investigated to achieve highly porous (heteroatom doped) carbon materials for topical applications in the energy storage and conversion field [23–34]. The more recent research focused on the application of cheap and sustainable carbon sources, such as human hair, water hyacinth, bio-imidazoliums, glucose, glucosamine, modified lignin or adenine, but even common organic solvents could be carbonized via hot-injection. [29,35–41] However, for some precursors, especially sulfur containing compounds acidic work-up may be required to remove side products such as zinc sulfide or zinc oxide.

Biomass derived ionothermal carbons were obtained with hierarchical pore structure (and different heteroatom doping) supporting their widespread high-end application, for example as cathode host material in lithium sulfur batteries, as electrodes for the capacitive deionization, as supercapacitor (SC) electrodes and as electrocatalysts for the oxygen reduction reaction. Each application has a more or less obvious performance-porosity relation, with different priority towards SSA, TPV and PSD. In SCs, besides the general need of high SSA and sufficient TPV, different pore types can be linked to a certain function [42,43]. Micropores supply high SSA to reach high double-layer capacities. Ultramicropores were shown to increase the capacity even more by a desolvation/intercalation mechanism and meso-/macropores support the ion supply. The pore size distribution directs the ion diffusion kinetics and therefore influences the maximum power density of the devices [7,44–47]. Consequently, the development of facile, cheap and scalable approaches for preparation of highly porous carbons with tailor-made pore system is still a major challenge. Among other synthesis strategies, the ionothermal approach delivers two straight forward parameters for a facile pore tuning. The compatibility/miscibility of precursor phase and molten salt depends on the type of eutectic and the precursor chosen. As previously reported varied pore systems can be obtained by using different eutectic salt mixtures, such as LiCl-ZnCl_2 , NaCl-ZnCl_2 , or KCl-ZnCl_2 [22]. In certain limits the porosity can be enhanced simply by increasing the salt to precursor ratio, a characteristic of a sol-gel process. However, the special character of salt phases can also lead to sheet-like carbons of unusual porosity [48]. Our latest study comprised the variation of the NaCl content in NaCl-ZnCl_2 mixtures employing adenine as carbon precursor. A defined and continuous (meso)pore tuning was achieved with additional characteristics of hard templating in the macropore range at high NaCl contents [38].

Herein we adopt the procedure to prove the widespread applicability of the developed (meso)pore tuning method. Glucose was selected as model molecule for biomass derived carbohydrate precursors and KCl-ZnCl_2 as the salt system. An additional isothermal heating step was necessary to reach a homogenous liquid phase during the run of reaction. The KCl content inside the

salt mixture has a large impact on the obtained SSA and pore structure. Higher KCl contents lead to an increase of the pore size accompanied by an enhanced mesopore volume and an almost linear decrease of the SSA. The carbon materials show high SSAs and TPVs with maximum values of $2160 \text{ m}^2 \text{ g}^{-1}$ and $1.74 \text{ cm}^3 \text{ g}^{-1}$, respectively. The obtained carbons were tested as supercapacitor electrodes to exemplarily show the potential for porosity optimization. In case of slow charge/discharge the specific capacitance rises with increasing SSA whereas the materials with an open pore system perform better at fast charge/discharge albeit the SSA is relatively lower. The carbons prepared with high KCl content within the salt melt give rise to increased capacity retention and a clear enhancement of the areal capacity owing to an improved pore system.

2. Experimentals

2.1. Synthesis

Prior to the experiments the salt mixtures with varied potassium chloride (>99.5%, Roth) and zinc chloride (98+%, Alfa Aesar) ratios were freshly prepared by thorough grinding. Typically, 4000 mg of the salt mixture was mixed with 800 mg of D-glucose (>99.5%, Roth) which served as biomass based precursor. After transferring the resulting mixture in a ceramic crucible (50 ml, VWR), the heat treatment was conducted in a chamber furnace under nitrogen atmosphere. The heating rate was always kept at 2.5 K min^{-1} . Typically, the samples were heated from room temperature to $350 \text{ }^\circ\text{C}$ and annealed at this temperature for 2 h. Then, the temperature was increased to $900 \text{ }^\circ\text{C}$ and kept for 1 h. The cooled down, mostly black, monolithic structures were thoroughly grinded, washed twice with 1 l of deionized water and dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ for 24 h.

2.2. Characterization

The samples were analyzed by scanning electron microscopy (SEM, Zeiss Gemini 1550) and transmission electron microscopy (TEM, Zeiss 912 Omega). N_2 -physisorption measurements were conducted at a Quantachrome Quadrasorb SI porosimeter. The SSAs were determined according to the multipoint Brunauer-Emmett-Teller (BET) model using the data points suggested by the *micropore BET assistant* of the software (however, not exceeding the range between 0.05 and 0.30 p p_0^{-1}). The quenched solid density functional theory (QSDFT) model for slit shaped, spherical and cylindrical pores, provided by Quantachrome data reduction software QuadraWin Version 5.11, served for the calculation of the pore size distributions (PSDs) using the adsorption branch. The TPV was calculated at $\text{p p}_0^{-1} = 0.99$. Mercury intrusion was conducted on a Micromeritics AutoPore IV 9500 in a mercury pressure range between 0.035 and 227 MPa reflecting a pore radius between 335 and $0.0055 \text{ }\mu\text{m}$. Elemental analysis was obtained by combustion analysis on a Vario Micro device. A Bruker D8 Advance device was used for X-ray diffraction (XRD) measurements between 3.0° and $70.0^\circ 2\theta$ using a step of 0.05° and a measurement time of 2 s per step under $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Light microscopy studies were conducted on an Olympus BX41TF combined with a Linkam THMS600 temperature controlled stage under N_2 -atmosphere.

2.3. Electrochemical analysis

The electrochemical characterization of the samples was carried out in a two electrode Swagelok-cell and recorded on a Bio-Logic VMP3. Therefore, two electrodes for one measurement were prepared in a typical fabrication procedure. Accordingly, a freshly

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