



Zinc-salt templating of hierarchical porous carbons for low electrolyte high energy lithium-sulfur batteries (LE-LiS)



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ABSTRACT

Hierarchical porous carbons with small mesopores and distinctive microporosity within the carbon walls are prepared using an efficient zinc-salt based templating approach. The pyrolysis accompanied by carbothermal reduction enables in situ template removal without toxic/reactive gases as byproducts and no further purification steps are required. Since the hierarchical porous carbon offers a specific surface area exceeding $2600 \text{ m}^2 \text{ g}^{-1}$ as well as a high internal pore volume of $2.46 \text{ cm}^3 \text{ g}^{-1}$ the novel material is well suited as sulfur host material to be implemented in cathodes for lithium-sulfur batteries. This leads to an initial discharge capacity of $1225 \text{ mAh g}^{-1}_{\text{sulfur}}$ and, moreover, a stable capacity of over $950 \text{ mAh g}^{-1}_{\text{sulfur}}$ for 100 cycles. Of outstanding importance is the fact, that the synergistic advantage of the hierarchical pore network ensures remarkable sulfur utilizations as well as cycle stabilities at low electrolyte amounts down to $4 \mu\text{l mg}^{-1}_{\text{sulfur}}$ (coin cell). Low electrolyte LiS cell concepts (LE-LiS) are essential for the development of high energy density on cell level.

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1. Introduction

Porous carbon materials are particularly outstanding and versatile due to their unique properties allowing high quality application in catalysis [1,2], gas adsorption [3,4] as well as energy storage [5–7]. Up to date many preparation strategies of porous carbons with tunable pore sizes have been reported [8,9]. On the one hand the most often applied silica hard templating approach allows tuning a wide range of pore sizes but low carbon yields as well as an undesirable expansive and time consuming purification steps are disadvantageous [8,10,11]. More favorable, evaporation induced self-assembly (EISA) approaches (soft templating), developed by Zhao and co-workers [12] allow more efficient processing and upscaling. However, the pore size cannot easily be tailored in a wide range and some purification steps are necessary.

Porous carbons play a crucial role as component for energy storage applications especially as electrodes for high energy lithium-sulfur batteries [5,13,14] representing a very promising

technology for future energy storage systems as a result of the high theoretical capacity of sulfur ($1672 \text{ mAh g}^{-1}_{\text{sulfur}}$). However, several challenges need to be overcome, such as the extensive expansion and shrinking of the active material [15] as well as the repeated dissolution and deposition of insulating sulfur compounds [16,17]. Therefore, initiated by Nazar et al., [18], a huge number of porous carbons with varying pore structures have been explored as conductive host for the active sulfur species [7,19–23]. Particularly of importance for high capacity lithium-sulfur batteries is according to investigations of Li et al. [24] as well as Liang et al. [25] a multimodal pore system with significant differences in pore size especially micro- and mesopores due to the synergistic advantage of both pore systems, which can trigger an improvement of performance under realistic application oriented conditions. In fact, the use of low amounts of electrolyte is crucial to reduce its overall weight share to achieve high energy densities [26,27]. This is in good agreement with the so called “concept of the two lows” [28,29].

Hierarchical porous carbons with high specific surface area (high microporosity) are typically synthesized in a two-step process. First the mesoporous carbon are prepared by the above mentioned hard or soft templating approach followed by chemical or physical activation leading to very low carbon yields [30]. Furthermore nanocasting with carbide-derived carbons (CDCs)

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precursors allows distinctive microporosity with adjustable pore sizes depending on the type of metal in the carbide precursor (e.g. SiC, TiC) [31–33]. The template removal occurs by a selective extraction of the metal atoms through hot halogen treatment. However, besides such complex synthesis to introduce a hierarchical pore system, in particular, suitable and efficient production processes play a crucial role for the final success. For that purpose suitable hard templates such as MgO [34] as well as salt templating strategies [35] have been developed. Nevertheless, a hierarchical porous system cannot be obtained by overcoming the activation process. Recently, our group established a ZnO hard templating approach allowing an efficient in situ template removal without any need of toxic/reactive gases as well as purification steps [36]. Moreover, the carbothermal reduction induced a growth of distinctive microporosity within the carbon walls leading to a hierarchical porous carbon with specific surface areas exceeding $3000 \text{ m}^2 \text{ g}^{-1}$ as well as meso/macropores in range of 20–200 nm with high performance in lithium-sulfur batteries. However, ZnO-NPs synthesis is a prerequisite leading to increased overall material costs. Furthermore, very small ZnO-NP with narrow size distribution are not easy to prepare in large scale due to agglomeration.

Here, we introduce a promising new route with using zinc citrate as template for the synthesis of hierarchical porous carbons (HPC). The important benefit of our approach is (beside the advantages of ZnO hard templating) the in situ formation of ZnO-NP, which is a scalable and an efficient alternative route overcoming the limitations mentioned using previously synthesized ZnO nanoparticles. The obtained HPC (DUT-123, DUT: Dresden University of Technology) provides a unique pore structure and, thus, is highly suited for application as sulfur host material in high energy lithium-sulfur batteries. Especially for systems using very low amounts of electrolyte ($4 \mu\text{l mg}^{-1}_{\text{sulfur}}$) the porous carbon show excellent performance. The low electrolyte concept (LE-LiS) is a hitherto overlooked but essential requirement to achieve high energy density lithium-sulfur batteries.

2. Experimental

2.1. Synthesis of HPC

7.5 g of zinc citrate dihydrate (purchased from Alfa Aesar, reagent grade) were thoroughly mixed in a glass Petri dish with 10 ml aqueous solution consisting of 0.9 g sucrose (Sigma Aldrich; $\geq 99\%$) and 100 mg of a 2.5 M aqueous sodium hydroxide solution (Carl Roth, $\geq 99\%$). The resulting white dispersion was placed in a furnace for 3 h at 100°C and subsequently further 6 h at 160°C . The carbothermal reduction was carried out in a horizontal tubular furnace with an argon flow of 0.5 slm (standard liter per minute) by a heating rate of 5 K min^{-1} to 950°C and tempered there for 2 h.

2.2. Synthesis of reference (ref.)

Since pure zinc citrate dihydrate can be carbonized we used it as reference (ref.) material [37]. The pyrolysis was carried out in a horizontal tubular furnace with an argon flow of 0.5 slm by a heating rate of 5 K min^{-1} to 800°C and tempered there for 2 h. To remove the obtained ZnO, the composite was washed with 1 M HCl solution for 2 h. The template-free carbon was filtered, washed three times with distilled water and finally dried over night at 80°C .

2.3. Composite preparation

After mixing of the porous carbon material (HPC or ref.) and

pristine sulfur (Sigma Aldrich, $\geq 99.5\%$) in a porcelain mortar with a carbon/sulfur weight ratio of 1:2 the sulfur was melt infiltrated (12 h at 155°C).

2.4. Electrode preparation

Cathodes were prepared from the C/S composites following a solvent-free roll-press procedure reported elsewhere [22]. The C/S composite was mixed with carbon nanotubes and PTFE binder in a weight ratio of 85:12:3. The typical active material loading of the punched circular electrodes with a diameter of 12 mm (15 mm for test at $4 \mu\text{l mg}^{-1}_{\text{sulfur}}$) is $2.5 \text{ mg}_{\text{sulfur}} \text{ cm}^{-2}$ with a thickness of 100 μm .

2.5. Structural characterization

Nitrogen physisorption measurements at 77 K were performed on a Rubotherm BELSORP after degassing of the samples overnight under vacuum at 200°C . Multi-point BET equation in the range of 0.05–0.20 relative pressures p/p_0 was used to determine the specific surface area. The micropore volumes were calculated from the cumulative pore volumes at a pore diameter of 2 nm using the Quenched Solid Density Functional Theory (QSDFT) calculation for carbon (slit/cylindrical pores, adsorption branch kernel). The total pore volumes were determined at 0.99 relative pressures p/p_0 . Water adsorption measurements were carried out on a Rubotherm BELSORP at 298 K after degassing of the samples overnight under vacuum at 200°C . The thermal analysis was carried out with a Netzsch STA 409 PC LUXX with a heating rate of 5 K min^{-1} under inert conditions (Ar). The morphology of the samples was characterized by Scanning Electron Microscopy (SEM) on a Stereoscan 260 SEM as well as by Transmission Electron Microscopy (TEM) on a JEOL JEM-2100. Powder X-ray diffraction patterns were collected on a Stoe Stadi-P (Cu-K α_1 radiation).

2.6. Electrochemical characterization

The Carbon/sulfur composite electrode, a porous polyolefin separator and elemental lithium were stacked in a CR2016 coin cell. Before sealing $6.8 \mu\text{l mg}^{-1}_{\text{sulfur}}$ of electrolyte (1 M LiTFSI and 0.25 M LiNO₃ in DME/DOL (1:1 by volume)) was added.

The capacity and long-term stability of the Li–S cells comprising the C/S composite cathodes was characterized by galvanostatic cycling with a BASYTEC CTS cell test system at a constant rate of C/10 ($1\text{C} = 1672 \text{ mA g}^{-1}_{\text{sulfur}}$) in a voltage range of 1.8–2.6 V vs. Li/Li⁺ at room temperature. For rate capability tests (discharge//charge rate: C/10//C/10; C/5//C/5; C/2//C/5; 1C//C/5; 2C//C/5) the voltage window was readjusted to 1.4–2.6 V vs. Li/Li⁺ at high discharge rates (1C–2C) to account for the increased polarization of the cathode. For tests at $4 \mu\text{l mg}^{-1}_{\text{sulfur}}$ the cell was discharge to 1.5 V in the first cycle.

3. Results and discussion

3.1. Structure and porosity of HPC

For hard templating approaches the agglomeration of particles has to be avoided to produce porous carbons with well-defined high internal porosity. In salt derived templating, on the other hand, the in situ formation of pore forming components plays a crucial role as well. To overcome the synthesis issues an elegant way is to use carbonaceous salt templates, which are able to produce a carbon wall around the in situ formed hard template nanoparticles during template decomposition. In the following, zinc citrate is used as beneficial template. The hierarchical porous

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