



Sulfur-doped ordered mesoporous carbons: A stability-improving sulfur host for lithium-sulfur battery cathodes



Florian Nitze ^{a, b, *}, Kjell Fossum ^a, Shizhao Xiong ^{b, c}, Aleksandar Matic ^b, Anders E.C. Palmqvist ^{a, **}

^a Division of Applied Chemistry, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

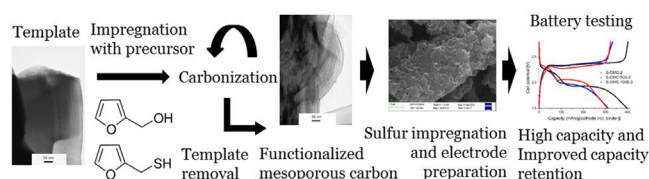
^b Division of Condensed Matter Physics, Department of Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

^c Department of Materials Engineering and Applied Chemistry, College of Aerospace and Material Engineering, National University of Defense Technology, Changsha, Hunan 410073, PR China

HIGHLIGHTS

- Synthesis of sulfur-functionalized ordered mesoporous carbon.
- Sulfur content controlled by the fraction of furfuryl mercaptan in the precursor.
- Very high capacity if used as sulfur-host in lithium sulfur batteries.
- Capacity retention after 50 discharge-charge cycles increased by up to 8%.

GRAPHICAL ABSTRACT



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ABSTRACT

We report on sulfur-functionalized ordered mesoporous carbons aimed for lithium-sulfur battery electrode applications with improved charge capacity retention. The carbons were obtained by a hard-template strategy using a mixture of furfuryl alcohol and furfuryl mercaptan. For the application as electrode material in lithium-sulfur batteries, the carbons were additionally loaded with sulfur following a traditional melt-diffusion approach. It was found that the sulfur interacts stronger with the sulfur-functionalized carbon matrix than with the non-functionalized material. Electrodes showed very high capacity in the second discharge-charge cycle amounting to approximately 1500, 1200 and 1400 mAh/g (sulfur) for carbon materials with no, medium and high degrees of sulfur functionalization, respectively. More importantly, the sulfur-functionalization of the carbon was found to increase the capacity retention after 50 discharge-charge cycles by 8 and 5% for the carbons with medium and high degrees of sulfur-functionalization, respectively, compared to carbon with no sulfur-functionalization. We attribute this significant improvement to the presence of covalently bound sulfur groups at the internal surface of the functionalized carbon providing efficient anchoring sites for catenation to the sulfur loaded into the pores of the carbons and provide experimental support for this in the form of results from cyclic voltammetry and X-ray photoelectron spectroscopy.

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* Corresponding author. Division of Applied Chemistry, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden.

** Corresponding author.

E-mail addresses: florian.nitze@chalmers.se (F. Nitze), anders.palmqvist@chalmers.se (A.E.C. Palmqvist).

1. Introduction

A very promising candidate to replace state-of-the-art Li-ion batteries is the lithium sulfur (Li-S) battery. A Li-S battery has a theoretical charge capacity of 1672 mAh/g and a power density of

2600 mWh/g, thus in theory an improvement of 5–6 times, and in practice up to 3–5 times, the performance of traditional Li-S batteries [1]. The transition from elemental sulfur to Li_2S is what gives Li-S batteries their large capacity. The electrochemical reactions in this transition occur through a series of sub-steps with the creation of various polysulfides and they have to occur in close vicinity to a conducting surface of the electrode to keep an even charge balance.

A big problem for Li-S batteries, limiting the realization of the technology in practice, is capacity fading caused by polysulfides dissolving into the electrolyte and consecutively shuttling to the anode and thereby resulting in a continuous loss of active material in the cathode. This issue has been addressed by covering sulfur with carbon coatings or by trapping it inside porous conducting host materials. A promising strategy in this direction has been the use of mesoporous carbons in which the pores of the host material are filled with sulfur [2–6]. However, the large volume change during the discharge-charge cycle associated with the transition from sulfur to Li_2S often limits the achievable loading of sulfur. Although the use of mesoporous carbons has significantly improved the capacity retention [1], it is still insufficient for commercial applications, in which high sulfur loadings need to be achieved to benefit from the large theoretical capacity and in which long time stability over thousand cycles or more is required.

Recently the use of functionalized mesoporous carbons has been explored with the aim to improve stability. The functionalities introduced by heteroatoms, most often nitrogen, strongly bound to the carbon host, are thought to decrease the dissolution of sulfur and hinder diffusion of poly-sulfides out of the host [7–9]. Studies showed that also sulfur-functionalization of the carbon host improves the affinity of polysulfide to the host structure and increases polysulfide reactivity [10–13] similar to what has previously been found for nitrogen functionalization of mesoporous carbon. However, the sulfur-doping levels achieved were relatively low leaving room for further improvements of this approach.

In the present study, we report on a mesoporous carbon matrix with sufficient sulfur-functionalities to stabilize the cathode and thus efficiently improve the capacity retention. The synthesis of the material is based on a modified version of the silica hard template route for ordered mesoporous carbon (OMC) replicas, reported by Ryoo et al. [14] and further developed by, e.g. Fuertes et al. [15]. By using the sulfur-containing carbon precursor furfuryl mercaptan in varying amounts in the carbon precursor formulation, sulfur functionalities with different carbon/sulfur molar ratios are introduced. A schematic of the synthesis procedure, from precursor to final battery electrode, is shown in Fig. 1. We find that the level of sulfur doping of the carbon matrix significantly influences the behavior of the Li-S cells and that capacity retention is improved. We show by cyclic voltammetry that the electrochemical behavior of the system is significantly changed compared to non-functionalized ordered mesoporous carbon.

2. Experimental section

2.1. Chemicals

Triblock copolymer Pluronic P123 was obtained from BASF, tetraethyl orthosilicate, (TEOS) (98%), furfuryl alcohol (FA) (98%), furfuryl mercaptan (98%) (FM), sulfur (Puriss) and N-methyl-2-pyrrolidone (NMP) all from ACS analytical, polyvinylidene fluoride (PvdF) ($M_w = 534,000$), lithium-bis-(trifluoromethylsulfonyl) imide (LiTFSI) (99.95%) and tetraethylene glycol dimethyl ether (TEGDME) (99.5%) all from Sigma Aldrich, 1-butanol (99%) from Fluka, toluene-*p*-sulfonic acid (>99%) from VWR, and hydrochloric acid (37%) and ethanol from Riedel-de-Haën. All chemicals were

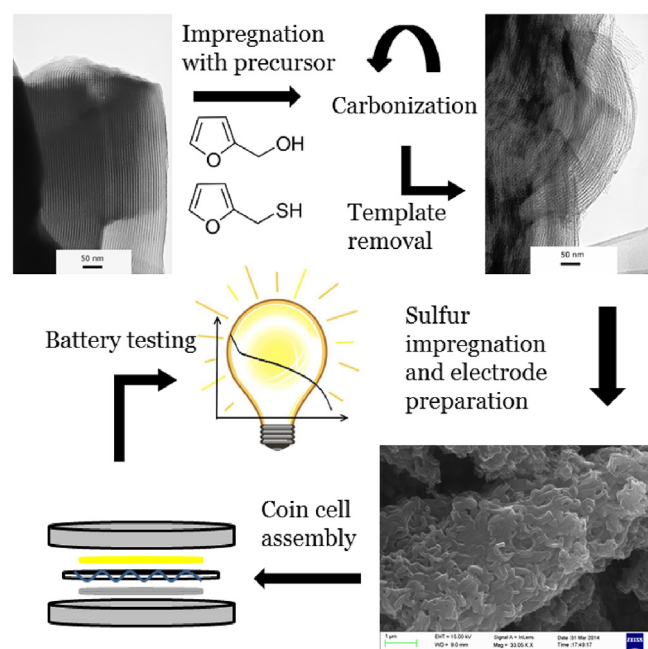


Fig. 1. Schematic of the synthesis process from template to a working battery.

used as received. Deionized water was used throughout the synthesis.

2.2. Synthesis procedures

A well-ordered mesoporous silica template was synthesized following the recipe by Zhao et al. [16]. For details we refer to the Supporting Information. The synthesis of the carbon replicas was performed following a combination of the methods developed by Ryoo et al. and Fuertes et al. [14,15]. First, the silica template was impregnated with 0.5 M toluene-*p*-sulfonic acid in ethanol for 1 h and the silica material was then collected and washed with a small volume of ethanol before allowing the material to dry. A volume of carbon precursor equal to the silica pore volume was then added and let to impregnate the silica pore system while the sample was thoroughly mixed with a spatula. The impregnated sample was kept at 80 °C in air for at least 2 h allowing the carbon precursor to polymerize. The successfulness of the impregnation step was monitored by nitrogen sorption measurements. Subsequently the carbonization of the polymerized carbon precursor in the silica pores was performed in flowing N_2 by a slow (2 °C/min) temperature increase from room temperature (RT) to 800 °C. The pyrolysis process was terminated after 2 h at 800 °C and the material was cooled slowly to RT. The pore volume of the as-prepared silica-carbon composite was subsequently measured. Impregnation, polymerization, BET surface area measurement and carbonization were repeated three times to evaluate the effect of multiple impregnation-pyrolysis cycles. After each impregnation-pyrolysis cycle a silica-carbon fraction was collected and the silica removed by immersing the silica-carbon composite in 48% HF overnight. The resulting carbon material was washed with water and dried at 80 °C before further characterization. Samples are denoted by OMC-xS-y where x is the weight percentage of sulfur source (furfuryl mercaptan) used and y the number of impregnations, e.g. OMC-50S-2 refers to OMC synthesized with 50 wt% FM and employing two impregnation cycles. It was found that two cycles were sufficient in order to obtain full filling of the pores and a high-quality carbon replica, see Table S2 in Supporting Information.

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