

# Li-INSERTION IN HIERARCHICAL MESO-MACRO-POROUS CARBON MONOLITHS

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## INTRODUCTION

Carbon materials are widely used as anode material in lithium ion batteries. In current batteries, usually graphite is used. The theoretical capacity of graphite is  $372 \text{ mA h g}^{-1}$  and it is well known that non-graphitic carbon materials exceed this value by far. However, their application is limited due to a bad overall battery performance (cycability, rate performance, high loss during first cycle), but a designed porosity of the electrode material could help to solve this problem.

A non-graphitic carbon material exhibiting mesopores (2-50 nm) would increase the interface for ion exchange and therefore would allow better battery performance. At the same time, the micropore content ( $d < 2 \text{ nm}$ ) should be as small as possible to prevent irreversible trapping of the Li ions.

A hierarchical porous carbon material also exhibiting macropores ( $> 50 \text{ nm}$ ) would allow easy access to the mesopores and could further improve the transport through the material. In particular, a continuous macropore network could facilitate the migration of lithium ions.

Mesoporous carbon materials can be synthesized by a nanocasting method introduced in 1999 by Ryoo et al. in which a porous template (usually silica) is infiltrated with a carbon precursor. After carbonization of the hybrid material, the porous carbon replica is obtained by dissolution of the template. During the last years, various mesoporous carbon materials could be synthesized that way. The carbon precursors usually used were sucrose and furfuryl alcohol. However, these precursors give rise to a disordered carbon microstructure, i.e. small average dimensions of the graphene stacks, and thus exhibit inherent microporosity. In contrast, mesophase pitch (MP) carbonizes very well and ensures a low micropore content of the carbon matrix compared to other carbon precursors. However, it remained a challenge to use this precursor for the replication of monolithic hard templates, due to its poor solubility and high viscosity.

Here, we present the synthesis of a porous carbon material that combines for the first time the advantages of a defined hierarchical macro- / mesoporous structure with a well developed carbon microstructure by choosing mesophase pitch (MP) as carbon precursor. Also, the excellent performance of the synthesized material as anode material in lithium ion batteries is shown.

## EXPERIMENTAL

Figure 1 shows the principle of the synthesis procedure. First, the hierarchical porous silica monolith is placed into an opened glass vessel. Mesophase pitch (AR, Mitsubishi Chemical Company) is dissolved in THF to obtain a solution (10 wt% MP) of low viscosity. The solution is then poured into the vessel and the porous silica monolith is infiltrated under

horizontal agitation. The agitation and slow evaporation of the solvent allows a continuous accumulation of the mesophase pitch molecules in the porous template. After evaporation of the solvent, the infiltrated silica / MP hybrid material is taken out of the vessel and dried in a quartz tube. This ensures a slow drying process that prevents cracking and also helps to retain the macroscopic shape of the monolith. The hybrid material is then heat treated under nitrogen flow between 700 - 1000 °C. The carbon replica is then obtained by dissolving the silica template in a solution of ammonium hydrogen difluoride. The synthesized monoliths are mechanically stable and usually crack-free.

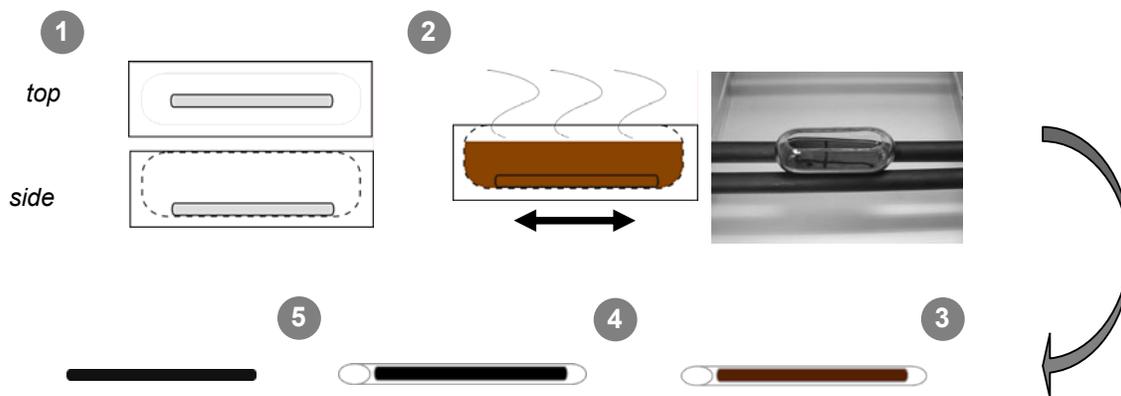
The macroporous structure of template and carbon replica is shown in Figure 2a. It can be seen that the carbon replica exhibits a continuous macroporous network with pores between 1 – 3  $\mu\text{m}$ . The cumulative pore volume and the pore size distribution determined by Hg porosimetry are shown Figure 2b. The graph shows that the synthesized carbon material exhibits a well defined hierarchical (bimodal) porosity with narrow pore size distributions for meso- and macropores. Hg-porosimetry stated a mesopores size between 6 - 8 nm and macropores in the range of 2  $\mu\text{m}$ . Nitrogen sorption revealed a surface area of around 300  $\text{m}^2 \text{g}^{-1}$ . Micropore analysis and krypton sorption confirmed the low micropore content. The presence of a well developed carbon microstructure could be approved using wide angle x-ray scattering (WAXS) measurements.

Li insertion / extraction measurements showed that the structure of the synthesized material is highly advantageous when used as anode material in lithium ion batteries. As can be seen from Figure 3a., the first reversible capacity was as high as 900  $\text{mA h g}^{-1}$ . The capacity stabilized after around 15 cycles at values around 500  $\text{mA h g}^{-1}$ , significantly higher than the theoretical capacity of graphite (372  $\text{mA h g}^{-1}$ ).

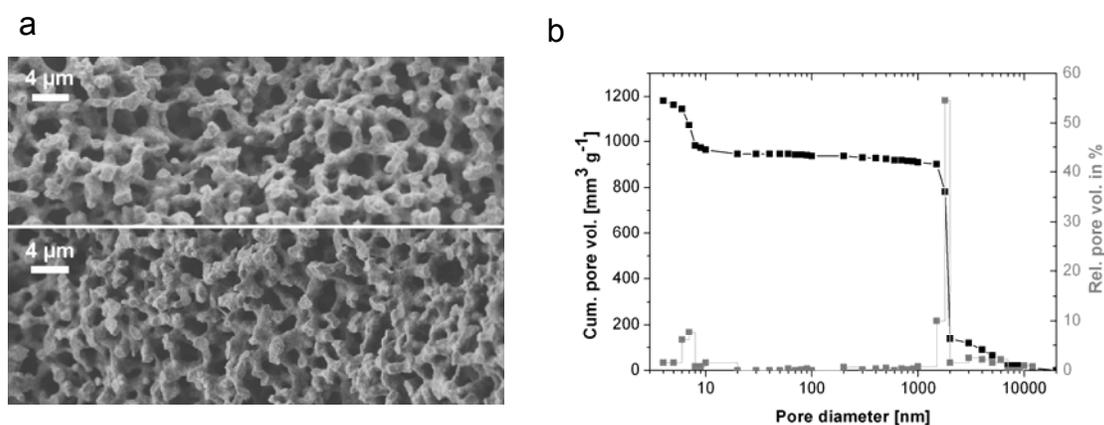
The advantage of the hierarchical pore structure takes effect at higher C-rates, giving rise to a unique rate performance at much higher currents. Figure 3b shows the rate performance for samples carbonized at different temperatures. The sample carbonized at 700 °C showed the best performance, with reversible capacities of around 540  $\text{mA h g}^{-1}$  at 1C, 260  $\text{mA h g}^{-1}$  at 10C and 145  $\text{mA h g}^{-1}$  at 30C. Even at rate of 60C, a capacity as high as 70  $\text{mA h g}^{-1}$  was found. For comparison, only 25  $\text{mA h g}^{-1}$  were measured for graphite when rated at 10C. As can be seen, also the cycability of the material was excellent.

## CONCLUSION

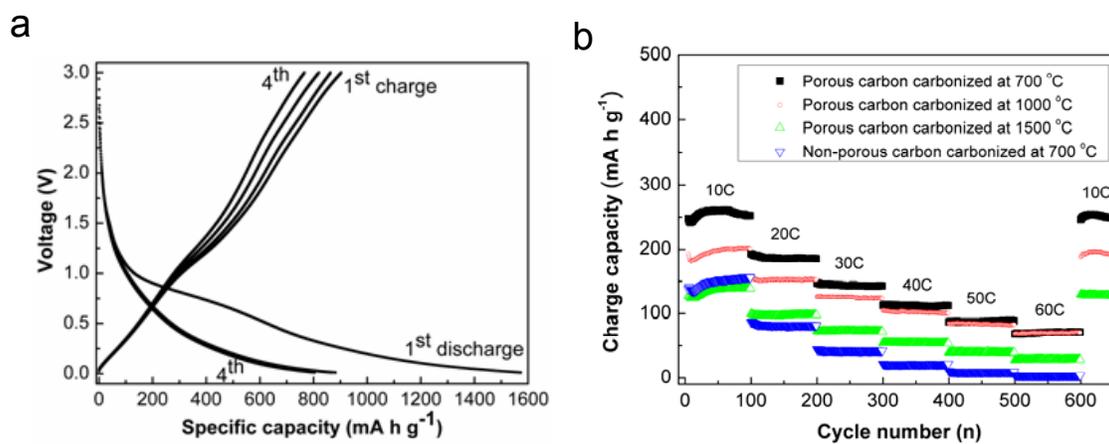
It could be demonstrated that the performance of carbon materials as anode material in lithium batteries can be strongly improved by introducing a hierarchical pore system. For the present samples, the 3D macroporous network and the mesopores allow fast diffusion of lithium ions into and out of the carbon matrix, giving rise to an excellent cycability and rate performance. Also, the use of mesophase pitch as carbon precursor allows for a very high reversible charge capacity. The overall performance of the material could facilitate the development of future high performance battery systems.



**Fig. 1.** Synthesis of hierarchical porous carbon monoliths using mesophase pitch as carbon precursor.



**Fig. 2.** a) SEM image of silica template (upper image) and carbon replica (lower image). b) Mercury porosimetry of the synthesized carbon monolith.



**Fig. 3.** a) Galvanostatic discharge (Li insertion, voltage decreases) / charge (Li extraction, voltage increases) curves for a sample carbonized at 700 °C and a C-rate of C/5. b) Rate performance of carbon samples carbonized at different temperatures. The given C-rate was applied for the charging and discharging process. The non-porous carbon is mesophase pitch carbonized as a bulk without template. (Note: Due to the experimental setup, the samples had to be grinded for the measurements. However the hierarchical structure was maintained)