

# SYNTHESIS OF HIERARCHICAL MACRO- / MESOPOROUS CARBON BY SPINODAL DECOMPOSITION

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## INTRODUCTION

The major shares of porous carbon materials that are used in applications are activated carbons, e.g. for filtration purposes. Activated carbons are highly microporous (pore size < 2nm) exhibiting large surface areas (up to 3000 m<sup>2</sup> g<sup>-1</sup>) due to slit-like shaped pores. Recently, growing interest emerged in the synthesis of mesoporous materials (2 - 50 nm) since they are better suited for applications involving the uptake of bigger molecules or nanocrystals, e.g. adsorption of dyes or as catalyst support for oxidic nanoparticles.

Carbon materials are also used as anode material in lithium ion batteries and it could be recently shown that a mesoporous carbon material (also exhibiting macroporosity to improve the diffusion of electrolyte) gives rise to an excellent charge capacity and rate performance [1].

Most of the mesoporous carbon materials are synthesized via the nanocasting route using (mesoporous) silica as hard template. Usually, sucrose (in solution) or furfuryl alcohol are used as carbon precursors since they are a liquid that allows easy infiltration of the porous silica template. After infiltration, the hybrid material is carbonized, and the carbon replica is then obtained by dissolution of the template (e.g. by HF). However, these precursors give rise to a carbon microstructure that can exhibit substantial amounts of microporosity that is often undesired, particularly in electrochemical applications. More suitable carbon precursors such as mesophase pitch were used instead and some mesoporous carbon materials with low micropore content could be successfully synthesized [1]. However, hard templating is a multi-step procedure and the sacrificial use of the mesoporous silica template makes the whole synthesis time consuming and expensive.

Hence, soft-templating seems a much more cost effective way of synthesizing porous materials. Here, the (organic) template is simply burned off, making the template removal an easy step. However, soft-templating of (meso-) porous carbon materials so far faces some difficulties:

(1) Since the carbonization happens under reductive atmosphere, the organic template cannot be simply burned off. Instead, the template has to decompose completely under reductive atmosphere. (2) The carbon precursor has to carbonize (or at least forms a stable configuration) before the template decomposes. Otherwise the huge structural changes that occur during the carbonization disrupt the mesopores. (3) The resulting carbon should not only contain mesopores, but also macropores (which are connected through the smaller mesopores), because macropores are helpful to facilitate the transport of liquids/electrolytes, while a high surface area is achieved by the

Considering these problems, only little progress has been achieved recently. For example, Zhao et al. reported the formation of ordered carbonaceous mesoporous structures by condensation of phenolic resin around micelles [2].

Here, we present a novel soft-templating-based technique to synthesize a hierarchical macro- / mesoporous carbon material taking advantage of phase-separation between mesophase-pitch as carbon precursor and poly styrene as hard template. Hereby, we were inspired by the Nakanishi process that allows the generation of hierarchical porous silica materials [3].

MP was chosen as carbon precursor because it already consists of extended, condensed poly-aromatic moieties, giving rise to a better carbonization behaviour compared to e.g. sugar-based carbon precursors. PS was chosen because it almost completely decomposes under reductive atmosphere, even in the presence of a catalyst.

## RESULTS AND DISCUSSION

The principle of the synthesis and the proposed mechanism is shown in Figure 1. The synthesis starts by generating a homogeneous solution of mesophase pitch (MP), poly styrene (PS) and THF as a solvent. FeCl<sub>3</sub> is added to spur the carbonization process. The solution is then poured into crucibles and the THF is slowly evaporated. During evaporation, the mixture enters the miscibility gap, inducing a continuously increasing incompatibility between MP and PS and the system starts to phase separate. In the spinodal case, the microphase-separation leads to the formation of a bicontinuous, sponge-like structure. Similar to the Nakanishi process, the phase separation is then further controlled by a suitable heat treatment. Two main processes happen during the first heat treatment at around 300 °C. (1) The carbonization process of the mesophase pitch is initiated, resulting into further incompatibility between MP and PS and thus further phase separation occurs. The resulting system then consists of MP rich and PS rich domains on the macro- and nanometer scale. The heat treatment is maintained for 10 h. This ensures that (2) the MP molecules slowly start to cross-link and transform into a more and more stable carbon matrix.

After this stabilization step, the temperature is increased towards higher temperatures (600 – 800 °C) for final carbonization and template removal. Due to the stabilization, the structural changes within the carbon material remain small and closure of the mesopores is prevented.

The total porosity of the synthesized samples can be adjusted by variation of the template content. Samples were denoted as “MPPS-x-y” with “x” as the weight fraction of template and “y” as the carbonization temperature.

Thermogravimetric (TGA) measurements were made to examine the decomposition of PS and carbonization of MP under the presence of FeCl<sub>3</sub> as catalyst (Fig. 2a). Clearly, the carbonization of MP starts already at temperatures well below the decomposition temperature of the PS, which is crucial for a successful templating. Furthermore, PS decomposes almost completely. A residual weight of around 5 - 10 wt% was found mainly due to iron species. The weight loss at lower temperatures can be explained by evaporation of residual THF (the solvent was used to homogeneously distribute the catalyst in the samples).

Small angle x-ray scattering (SAXS) was used to examine the phase separation behaviour during the synthesis. Already the comparison of the SAXS data of the sample after evaporation with the scattering of pure PS and pure MP shows pronounced differences (Fig. 2b). An almost ideal Porod law was observed, indicating the presence of a well-defined microphase-separated two-phase system (MP-PS) on the nanometer scale. The Porod law was also observed after carbonization at 600 °C, proving the presence of a two-phase system between, in this case, carbon matrix and pores (Fig. 2c).

Nitrogen sorption was used for further evaluation of the porosity. Figure 2d shows the isotherms of samples synthesized with different template concentrations. The isotherms are clearly from type IV and show distinct

hysteresis. Lower polymer content produced accordingly lower mesoporosity, thus proving that the mesoporosity originated indeed from a templating process and not from inherent porosity of the components. A BET surface area of  $170 \text{ m}^2 \text{ g}^{-1}$  was found for the sample templated with 66wt % PS whereas only 90 and  $20 \text{ m}^2 \text{ g}^{-1}$  were measured for the samples templated with 50 wt% and 33 wt%. The total pore volumes determined from the last point of the adsorption branch were  $0.45$ ,  $0.21$  and  $0.07 \text{ cm}^3 \text{ g}^{-1}$ , respectively.

The pore size distribution was calculated from the isotherms using a non-local density functional theory (NLDFT) model (Fig. 3a). Figure 3a shows the cumulative pore volume as a function of the pore diameter for the different samples. As an important finding, the micropore content of all samples is quite low, due to the use of mesophase pitch as carbon precursor. The pore volume increases constantly in the mesopore range, proving for a very broad pore size distribution.

Transmission electron microscopy (TEM) also showed the presence of mesopores and small macropores ( $> 50 \text{ nm}$ ) of different sizes and shapes (Fig. 3b). The darker spots in the image can be attributed to Fe residues in the sample.

Scanning electron microscopy (SEM) revealed the presence of a continuous macropore network with diameters between  $2\text{-}4 \text{ }\mu\text{m}$  (Fig. 4a). Such a pore system can be useful, since the macroporous network can act as a transport system for a gas or liquid (e.g. electrolyte) that creates accessibility towards the mesopores.

The different phases present in the samples were determined using wide-angle x-ray scattering (WAXS). The WAXS pattern of a sample carbonized at  $600 \text{ }^\circ\text{C}$  (Fig. 4b) shows the presence of  $\text{Fe}_3\text{C}$  and  $\alpha\text{-Fe}$  as side products after carbonization. The well defined maximum at around  $2\theta = 26^\circ$  reveals the good carbonization behaviour of the mesophase pitch.

## CONCLUSION

In conclusion, it could be successfully shown that hierarchical macro- / mesoporous carbon materials can be synthesized by a novel soft-templating approach using spinodal decomposition between mesophase pitch and polystyrene. The macropores form a 3D network that enhances the accessibility towards the mesopores. Due to the carbon precursor, the micropore content of the synthesized material is very small, even at low carbonization temperatures.

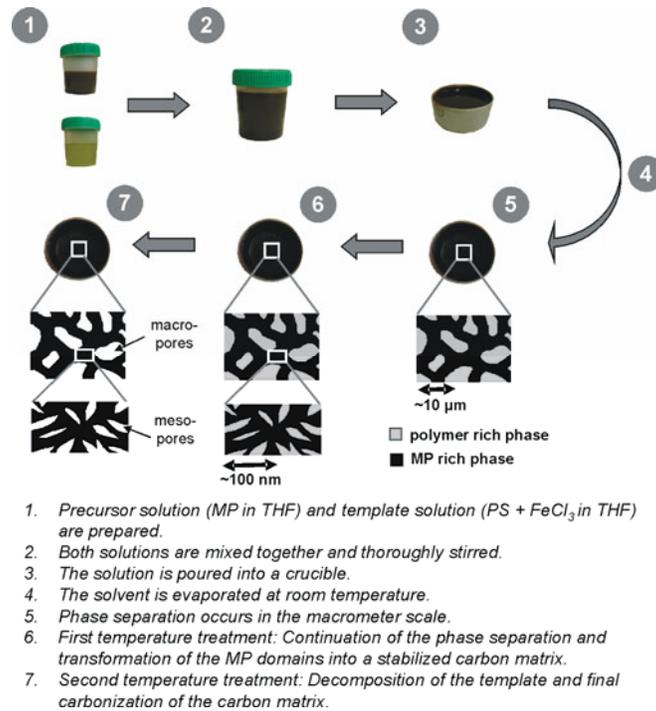
Such a material is in particular interesting when micropores are undesired, i.e. lithium insertion / extraction. Cheap chemicals were chosen in order to demonstrate that such porous materials can be produced at lower costs compared to hard templated systems. Thus, the simple synthesis could open a new pathway of producing cheap carbon electrode materials with improved porosity.

## REFERENCES

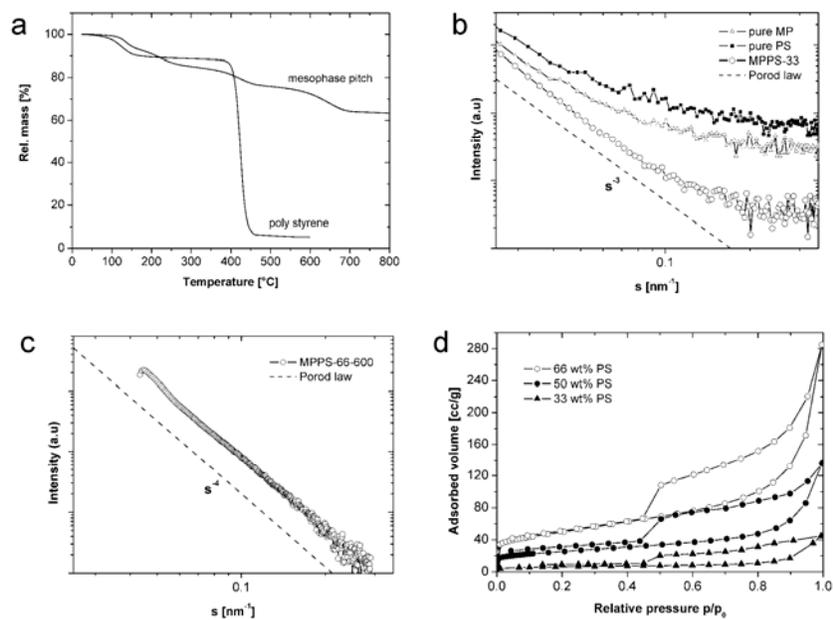
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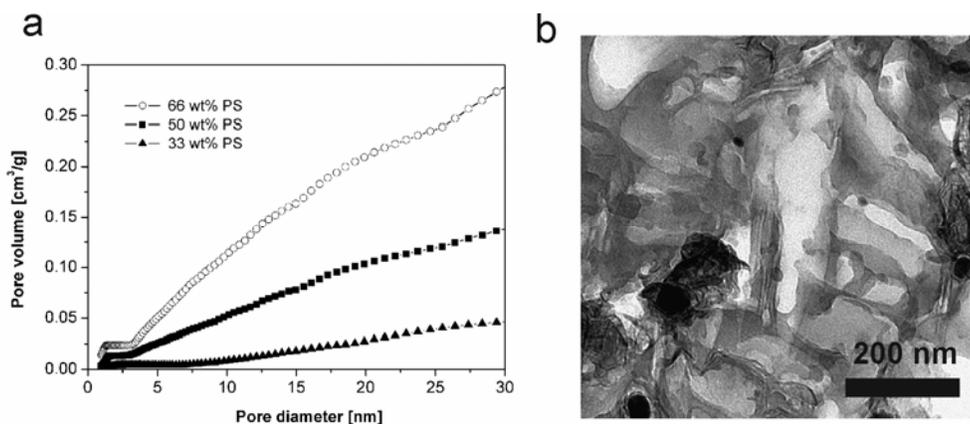


**Figure 1.** New synthesis approach and proposed mechanism for the generation of hierarchical macro- / mesoporous carbon via soft-templating.

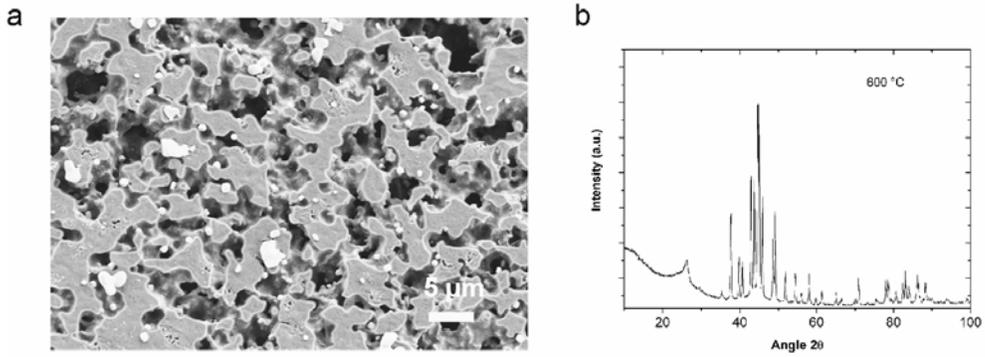


**Figure 2.** (a) Thermogravimetric measurements of the carbonization of mesophase pitch and decomposition of poly styrene (under nitrogen flow and the presence of 10 wt% FeCl<sub>3</sub> as catalyst). (b) SAXS of the pure compounds and the phase separated sample after evaporation of the solvent. (c) SAXS of the phase separated sample after carbonization at 600 °C.

*Note:* A Kratky camera with slit smearing was used for the samples shown in (b), therefore  $s^{-3}$  is found for the Porod law.



**Figure 3.** (a) Cumulative pore volume determined from nitrogen sorption using NLDFT model. (b) TEM image of MPPS-66-600



**Figure 4.** (a) SEM image and (b) WAXS pattern of MPPS-66-600