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Supporting Information

Free-Standing and Binder-Free Highly N-Doped Carbon/Sulfur Cathodes with Tailorable Loading for High-Areal-Capacity Lithium-Sulfur Batteries

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Structure of the glass microfiber filter paper template

Both the morphology and structure of the glass microfiber filter paper (Whatman Grade GF/A) were investigated using SEM. As can be seen from the images below, the filter paper has a non-uniform structure and consists of fibers of diameter between 150 nm and 1.5 μm.

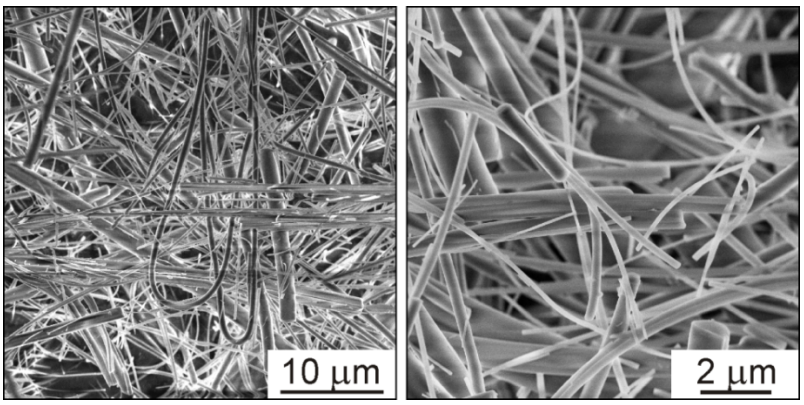

Fig. S1 SEM images at different magnifications of the glass microfiber filter paper used as hard template in this work.

Rate performance of the free-standing sulfur composite cathodes

The capacity retention of batteries using the hierarchical N-doped carbon/sulfur cathode with a loading of 4.6 mg_{sulfur} cm^{-2} was tested for different rates up to C/5. They delivered specific capacities of about 440 mAh g_{sulfur}^{-1} (2.0 mAh cm^{-2}), 500 mAh g_{sulfur}^{-1} (2.3 mAh cm^{-2}) and 610 mAh g_{sulfur}^{-1} (2.8 mAh cm^{-2}) at C/5, C/10 and C/20, respectively.

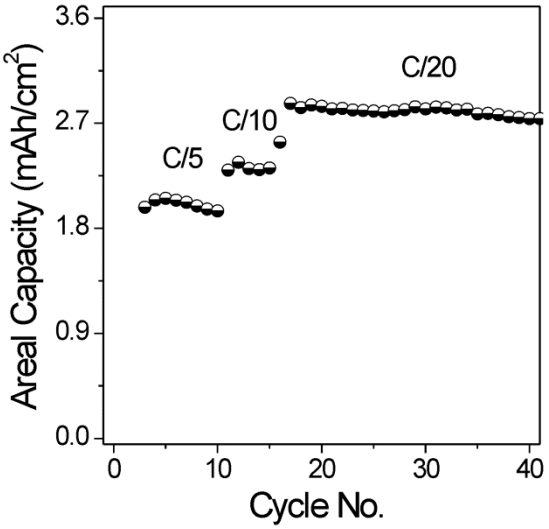

Fig. S2 Rate capability of the hierarchical N-doped carbon/sulfur cathode with 4.6 mg_{sulfur} cm^{-2}. The first cycle was performed at C/50 (1090 mAh g_{sulfur}^{-1}, 5.0 mAh cm^{-2}). Only the discharge capacities are shown for clarity.

Adsorption ability of the nitrogen-doped and nitrogen-free carbon

We show that the hierarchical N-doped carbon is able to adsorb more than twice as much lithium polysulfide (LiPS) from solution than nitrogen-free carbon (prepared under otherwise identical conditions). Given that the structure and porosity are similar, these data provide clear evidence that the presence of nitrogen dopants considerably alters the adsorption ability. Specific chemical interactions between the surface functional groups of the carbon and the LiPS species hinder them from leaving the cathode architecture, thus improving the cycling performance.

The adsorption capacity was calculated as follows:

$$\text{adsorption capacity } (g_{LiPS}/g_{carbon}) = ([LiPS]_0 - [LiPS]) \times V_{solution} \times M_{LiPS} / m_{carbon}$$

where $[LiPS]_0$ is the lithium polysulfide (Li_2S_6) concentration before adsorption, [LiPS] is the concentration after adsorption, $V_{solution}$ is the volume of the lithium polysulfide solution, M is the molar mass of the lithium polysulfide species (solute), and m represents the mass of the carbon (adsorbent). From this analysis we obtain values of 0.012 and 0.005 g_{LiPS}/g_{carbon} for the EMIM-DCA- and furfuryl alcohol-derived carbon, respectively. The former value is notable considering the comparably low BET surface area of the N-doped carbon utilized as cathode host.

For calibration, a stock solution of known concentration was diluted followed by measuring the absorption at 415 nm through UV-Vis spectroscopy. According to Song et al. (*Angew. Chem. Int. Ed.*, 2015, **54**, 4325), the absorption follows Lambert-Beer`s law up to a concentration of about 1 mM.

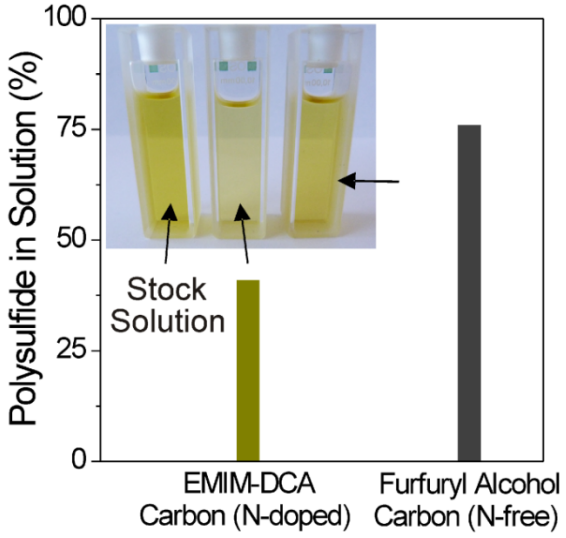

Fig. S3 Comparison of the amount of remaining lithium polysulfide after adsorption (*i.e.*, exposure to the carbon adsorbent). The inset shows a photograph of cuvettes containing the lithium polysulfide solution (here Li_2S_6) after separation from the carbon. Left to right: stock solution, EMIM-DCA-derived carbon and furfuryl alcohol-derived carbon.