ACS Sustainable Chemistry & Engineering
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Carbohydrate-Derived Nanoarchitectures: On a Synergistic Effect Toward an Improved Performance in Lithium–Sulfur Batteries

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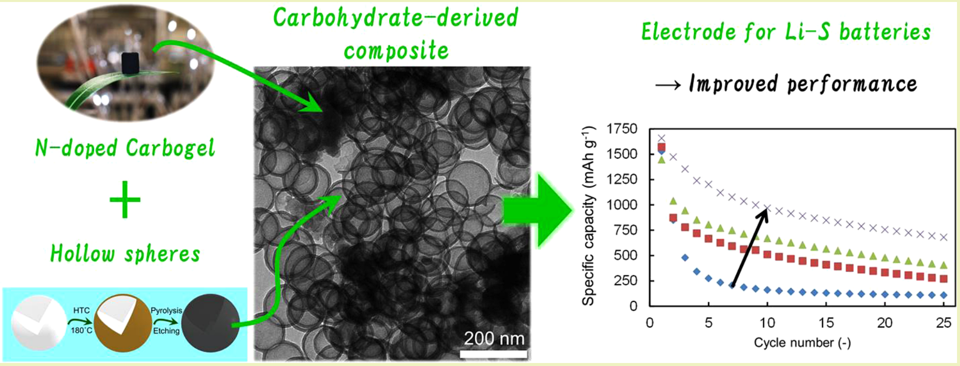
Supporting Information



ABSTRACT: We combined the good cycle ability and rate performance of carbon-nanostructured hollow spheres with the high specific capacity at first discharge of nitrogen-doped carbon aerogels. Beneficial contributions of each constituent material, i.e., N-doped carbogel and carbon hollow spheres, led to a promising synergistic effect. A high specific capacity of more than 700 mA h g^{-1} was reached with a limited fading over 25 cycles.

KEYWORDS: *Hydrothermal carbonization, Biosourced carbons, Nanocomposites, Nanostructures, Lithium–sulfur batteries*

Nanoarchitectures have been shown to be of great interest in catalysis,[1] electrocatalysis,[2] and as electrodes in energy storage devices.[3−5] Reducing materials size to nanodimensions can lead to higher electrode/electrolyte interface areas together with shorter diffusion length, while generating new intrinsic properties related to particular nanomorphologies. For the past decade, moving from bulk to nanostructured architectures offered the opportunity to design cutting-edge materials with improved electrochemical performances, particularly in the major field of lithium-ion (Li-ion) rechargeable batteries.[6−11] Nevertheless, the development of novel nanostructured electrodes for Li-ion batteries did not allow overcoming the major drawbacks related to high cost and limited specific capacity (heavy-weight transition metals are usually employed at the cathode side). More recently, lithium–sulfur (Li–S) batteries have been the center of attention and go beyond the limited perspective provided by the Li-ion technology. Because of a higher theoretical specific energy density than traditional Li-ion batteries together with the natural abundance and relative low cost of sulfur, the Li–S technology may represent a leading candidate for electronic vehicles and large scale applications.[12,13] However, some electrochemical limitations related to the insulating nature of sulfur together with the rapid capacity fading on cycling, induced by the dissolution of intermediate polysulfides into the electrolyte, represent main challenging drawbacks.[12,13] Overcoming these challenges requested the design of functional binders[14] and original composite nanoarchitectures allowing for increasing the overall electronic transport properties while trapping the soluble polysulfides.[15−22] In this context, nanostructured porous carbons/sulfur composites were seen to largely improve both charge/discharge cycling properties and specific capacities.[12,13,23,24] In particular, carbon-based hollow sphere electrodes for Li–S batteries recently allowed high specific energy density and power cumulated with a good cycling performance.[25−27] For example, sustainable glucose-derived hollow spheres obtained via the hydrothermal carbon coating of premade Stöber silica nanoparticles showed a Coulombic efficiency of almost 100% over 20 cycles, maintaining a discharge capacity of more than 600 mA h g^{-1}.[27]

Received: August 14, 2013
Revised: October 21, 2013
Published: October 30, 2013

dx.doi.org/10.1021/sc4002966 | *ACS Sustainable Chem. Eng.* 2014, 2, 126−129

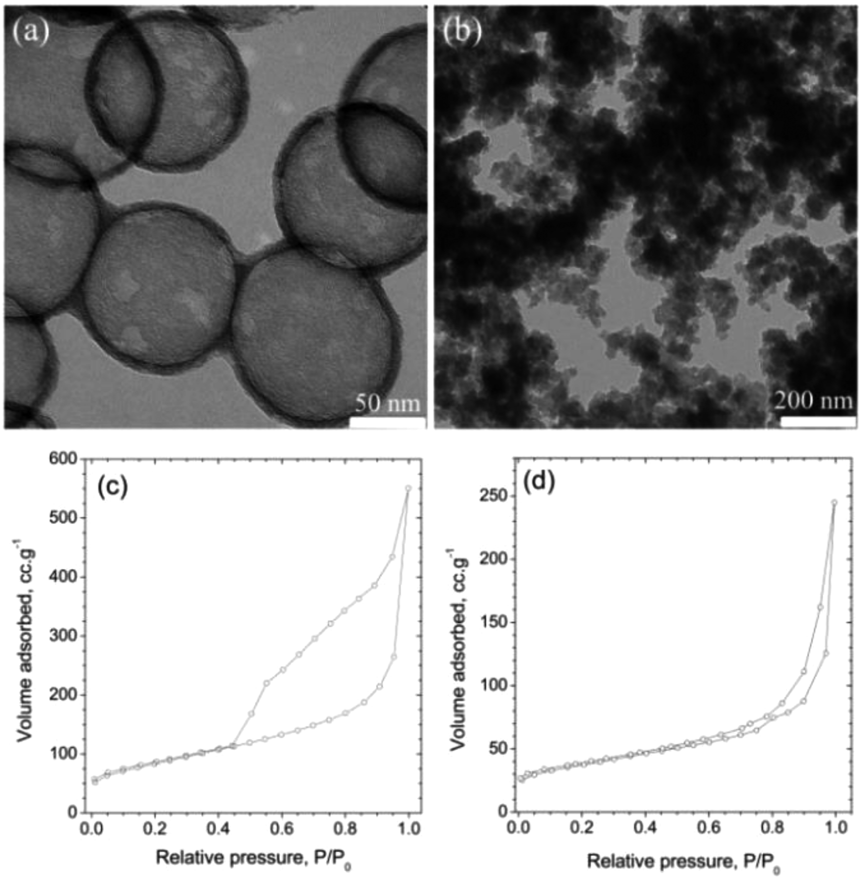


Figure 1. Micrographs obtained by transmission electron microscopy (TEM) and nitrogen sorption isotherms of hydrothermal glucose-derived (a–c) hollow spheres (HSs) and (b–d) nitrogen-doped carbon aerogels (NdCAs).

Herein, a synergistic effect toward improved electrochemical performances is reported for the first time by combining the good cycle ability and rate performance of the glucose-derived hollow spheres (referred as to HSs) mentioned earlier[27] with the high specific capacity at first discharge of nitrogen-doped carbogels (carbogels for carbon aerogels; referred as to NdCAs).[28] As shown in Figure 1, the two materials selected for our study have different nanostructured morphologies. While the HSs have homogeneous carbon shells of about 7–8 nm thick (Figure 1a), the NdCAs are made of a continuous structure composed of aggregated nanoparticles of about 20 nm diameters (Figure 1b). Both of these carbonaceous nano-architectures depict type IV isotherms (Figure 1c,d), typical of mainly mesoporous materials. The nitrogen sorption profile observed for HSs shows a higher hysteresis loop area as compared with NdCAs, indicative of ink-bottle type pores.[29,30] Moreover, both show decent intrinsic electrical conductivities (about 10 S m^{-1}) and relatively high porosities (i.e., BET surface areas of 130 and 296 m^2 g^{-1} for NdCAs and HSs, respectively),[27,28] making them good candidates as sulfur hosts for Li–S batteries.

As showed in our previous study,[27] the HSs used herein present a good cycling ability but a first discharge capacity restricted to 1250 mA h g^{-1} (at a current density of 0.1 C; Supporting Information). With the aim of increasing this specific capacity, mixing the hollow spheres with nitrogen-doped carbogels appears as a rational strategy because the NdCAs display a first discharge capacity as high as 1550 mA h g^{-1} (at a current density of 0.1 C; Figure 2a).

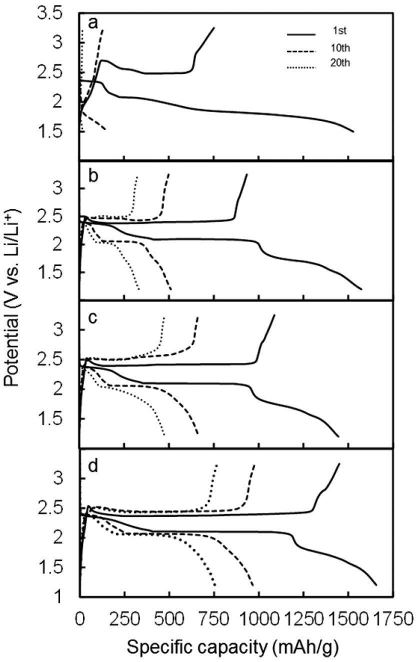


Figure 2. Charge–discharge curves at a current density of 0.1 C (i.e., 167.5 mA g^{-1}) for the carbon/sulfur electrodes using (a) NdCAs alone and composites with NdCA:HS mass ratios of (b) 4:1, (c) 1:1; and (d) 1:4.

Interestingly, as compared with nitrogen-free related carbogels,[31] NdCAs distinctly showed a different electrochemical behavior (Supporting Information). As the total pore volume and surface area are largely higher for the nitrogen-free carbogels (700 m^2 g^{-1} and 0.75 cc g^{-1} versus 130 m^2 g^{-1} and 0.23 cc g^{-1}),[28,31] one may assume that their divergences toward electrochemical properties are closely related to their respective porous structures. A rise in mesoporosity and microporosity should significantly increase the sulfur–electrolyte interface. Concomitantly, both the first discharge capacity (i.e., first lithium loading) and the dissolution of the intermediate polysulfides should be favored.[27] However, we could observe herein an opposite behavior because the nitrogen-free carbogels present the lowest initial capacity and the less dramatic polysulfide shuttle effect (Supporting Information). Consequently, the presence of nitrogen (about 5 wt %) seems to significantly increase the first discharge capacity while drastically accelerating the capacity fading on cycling. One may presume that the nitrogen-doping could enhance the electrical conductivity, as reported previously,[32−35] leading to a higher first capacity. Nevertheless, and probably due to a low nitrogen loading (i.e., 5 wt %), we did not notice any significant difference in electrical conductivity among the nitrogen-free and -doped samples (*c.a.* 10 S m^{-1}). Another explanation could be related to the nitrogen-doping itself, which is known to significantly increase the basic character of carbonaceous materials. This aspect could favor the adsorption and subsequent chemical reaction of lithium ions with sulfur during the first discharge, in good agreement with the study reported by Sun et al. showing that nitrogen-doped carbons are more active toward sulfur reduction.[36] Conversely, the basic character of NdCAs could greatly intensify the release into the electrolyte of the polysulfides anions (PS, S_{4-8}^{2-}) generated during the delithiation of sulfur causing a dramatic capacity fading. This bilateral effect seems to be further emphasized through the larger hysteresis recorded on the charge–discharge curve at first cycle of NdCAs alone as compared with the related composites (Figure 2). Supporting these hypotheses would require further characterizations providing a deeper insight into the effective role of nitrogen with regard to Li–S electrochemical properties. Such studies are currently under investigation.

After having selected NdCAs as a propitious additive to HSs, different composites were evaluated as Li–S cathode materials. As shown in Figure 2, by mixing HSs and NdCAs at different mass ratios the first discharge capacity of the related composites was nicely kept above 1500 mA h g^{-1}, while both the cycle ability and the Coulombic efficiency could be greatly enhanced. The former feature was seen to be closely dependent on the mass ratio NdCA:HS. Decreasing this ratio induced improved cycling performances, particularly for a ratio of 1:4 (Figure 2d) for which the electrochemical properties over 25 cycles were better than HSs and NdCAs alone (Figure 3). On one hand, one may assume that the overall basic character of the composite would decrease while decreasing the NdCA:HS mass ratio, leading to a concomitant drop of the initial discharge capacity. Surprisingly, as shown in Figure 3, the composite made of the lowest mass ratio (i.e., 1:4) depicts a slightly higher specific capacity at the first cycle than all the other materials reported herein.

On the other hand, as mentioned in our previous article,[27] the presence of residual silica within the carbon hollow spheres seems to noticeably counterbalance the dramatic shuttle effect observed for the nitrogen-doped carbogels. While the NdCAs alone showed a 50% drop of their specific capacity from the first to the second cycle, the composite made of the lowest NdCA:HS mass ratio conserved a specific capacity of about 1500 mA h g^{-1} at the second discharge (Figure 3). Such a cooperative and beneficial interaction can be clearly seen as a synergistic effect leading in fine to unique electrochemical properties with regard to cathode materials for Li–S batteries.

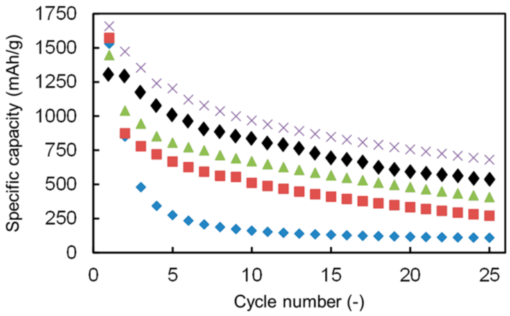


Figure 3. Cycling performances at 0.1 C for NdCAs alone (blue diamonds), HSs alone (black diamonds), and composites with NdCA:HS mass ratios of 4:1 (red square); 1:1 (green triangle); and 1:4 (×).

In conclusion, we reported herein on the use of carbohydrate-derived carbonaceous nanoarchitectures depicting antagonistic electrochemical properties for the design of competitive nanocomposite electrodes. Beside an advantageous sustainable aspect related to the use of biomass-derived precursors, beneficial contributions of each constituent material led to a promising synergistic effect. An unexpected high specific capacity of more than 700 mA h g^{-1} was reached with a limited fading over 25 cycles. Moreover, the potential of nitrogen-doped carbons as cathode materials for Li–S batteries was reported for the first time, opening exciting prospects. We believe that this study offers new perspectives for the design of carbon–carbon composites or even multi-functional carbon-based electrode materials for Li–S batteries.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

N.B. is grateful to the Max Planck Society for financial support. K.S. was financially supported by DAAD (A/09/74990).

Notes

The authors declare no competing financial interest.

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