High-rate lithium–sulfur batteries enabled by hierarchical porous carbons synthesized via ice templation

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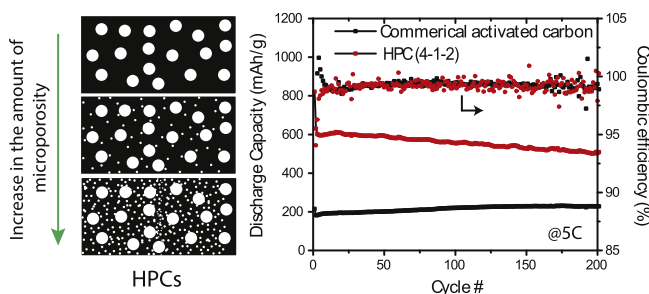
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HIGHLIGHTS

- Porous carbons synthesized via ice templation were tested as sulfur hosts.
- Extremely high surface area and pore volume led to good high C-rate performance.
- Studied capacity decay in the presence of LiNO₃ electrolyte additive.
- Demonstrated independence of pore size and capacity decay in the above study.

GRAPHICAL ABSTRACT

ABSTRACT

We report the performance of a series of hierarchical porous carbons (HPCs) with extremely high surface areas of up to 2340 $m^2\,g^{-1}$ with total pore volume of up to 3.8 $cm^3\,g^{-1}$ as supports for sulfur for Li–S batteries. The hierarchical structure of the carbon originating from interconnected large mesopores (10–50 nm), small mesopores (2–10 nm) and micropores (<2 nm) makes the total available surface area highly accessible, resulting in excellent electrode kinetics. At high C-rates of 2 C and 5 C, large specific capacities of 647 $mA\,h\,g^{-1}$ and 503 $mA\,h\,g^{-1}$, respectively, were obtained after 200 cycles. In addition, we also systematically show that the cyclic stability is independent of the size of the pores sulfur is initially confined in, when LiNO₃ is used as the electrolyte additive, indicating that capacity fade due to polysulfide shuttle is effectively eliminated and that it is not related to pore size anymore.

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1. Introduction

Several issues with the present cathode materials involved in the current rechargeable lithium-ion battery technology have led to a vast new research area in search of new rechargeable battery systems which incorporate inexpensive, light weight active materials and most importantly have much higher theoretical specific capacities and energy densities [1]. Lithium-sulfur is one such system that has a theoretical specific capacity of 1672 $mA\,h\,g^{-1}$ and theoretical specific energy of 2567 $W\,h\,kg^{-1}$, which are almost an order of magnitude higher than the current lithium-ion batteries, due to the light weight of sulfur and a high charge storage of 2e⁻ per S atom [2,3]. Sulfur is also non-toxic, highly abundant and cheap. Yet, there are many problems associated with this system, primarily, lower than theoretical specific

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capacities and poor cycle life. Both of these problems have been linked with the insulating nature of sulfur and with the high solubility of the electrochemical reaction intermediates called "polysulfides" in the electrolyte. The former makes sulfur that is not very close to the carbon surface (more than a few tens of nanometers) essentially electrochemically inactive and the later causes the loss of active material as the polysulfides dissolve and diffuse towards the lithium metal anode and react with the Li to irreversibly form insoluble and electrically insulating Li_2S_2 or Li_2S [4–8].

Among the various candidate materials, porous carbons have received great attention since they provide a high surface area, electrically-conductive framework on which insulating sulfur can be made electrochemically active when properly dispersed [9–17]. Besides, the sorption effect of polysulfides on the carbon surface is known to impede their diffusion into the electrolyte [9]. But the kind of porosity in these carbons is very crucial in their overall battery performance including specific capacity values, cycle life, and rate capability. Mesopores (2–50 nm) have been shown to be the most effective in getting close to theoretical specific capacities at high rates due to fast transport of Li^+ ions in and out of the electrode. For example, a bimodal mesoporous (3.1 nm and 6 nm) carbon support in the form of 300 nm diameter spherical particles was shown to give high specific capacity of up to 1200 mA h g^{-1} at a high C-rate of 1 C [18]. Micropores (<2 nm), on the other hand, due to their smaller size are the most effective in trapping polysulfides [19–23]. Completely microporous carbons have been shown to have excellent long cycle life even in the reportedly polysulfide-incompatible carbonate-based electrolytes [24]. But limiting the size of the pores leads to poor Li^+ ion kinetics and the specific capacities drop significantly at high C-rates. Hence, to achieve higher specific capacities at fast charge/discharge rates, a framework which is open, but still has large surface area seems the most desirable. In fact, nanocarbons like CNTs and stacked graphene, which generally have low surface area, showed greatly improved performance with cycling at rates up to 10 C upon incorporating mesopores or micro-/meso-hierarchical porosity [25].

Here, we report the high C-rate performance of a series of hierarchical porous carbons (HPCs) with extremely large surface areas up to 2340 m^2 g^{-1} and pore volumes up to 3.8 cm^3 g^{-1}, which is among the highest for similar systems reported previously for this application [22,23,26–29]. The carbons are prepared via a two-step process of hard templation followed by physical activation for different time durations. The detailed synthesis of similar carbons was reported earlier by our group [30]. Since the highly open nature of the carbon framework facilitates the Li^+ ion diffusion in and out of the electrode, it also makes the out diffusion of the polysulfides easier. To prevent active material loss via diffusion and its reaction with lithium anode, $LiNO_3$ salt was used as an electrolyte additive, which has been shown to make a stable and Li^+ ion conducting solid–electrolyte interface (SEI) on the lithium metal surface inhibiting the shuttle mechanism that limits the cycle life [31–36]. We systematically show that in the presence of $LiNO_3$ additive, cyclic stability while improved is rather independent of the size of the pores where the sulfur is initially confined in, indicating effective suppression of capacity loss due to polysulfide shuttle or the presence of other capacity loss mechanisms to cause a gradual decay in capacity over cycling. Lastly, the performance of the HPCs is compared and contrasted with cathodes prepared using a commercially available microporous carbon. We show that the HPCs consistently outperform the commercially available carbon signifying that the intricate network of hierarchical porosity is critical for good performance.

When tested as supports for sulfur at a ~50 wt. % S loading using ether based DOL/DME electrolyte with $LiNO_3$ additive, these HPCs showed excellent high rate performance with exceptionally high capacities of up to 647 mA h g^{-1} and 503 mA h g^{-1} (per gram of sulfur) at 2C, and 5 C rates respectively after 200 cycles, with ~99% coulombic efficiencies. In contrast, a commercial microporous carbon gave a much lower initial capacity of 345 mA h g^{-1} @1 C under similar sulfur loading indicating much slower Li^+ transport kinetics in the cathode. Moreover, @1 C similar capacity retention values of 80–85% from the 10th to 100th cycle were observed for all the carbons despite their different textural characteristics confirming our result that cyclic stability is independent of the size of pores sulfur is initially confined in.

2. Experimental section

2.1. Preparation of mesoporous and activated mesoporous carbons

HPCs were synthesized using a slight modification of our previously reported procedure [30]. The nomenclature of HPCs is in the following format: A-x-y, where A is the size of the colloidal silica template used (as provided by the supplier), x is the weight ratio of colloidal silica to sucrose, and y is the time of CO_2 activation. To synthesize 4-1-0 carbon, 6 g sucrose was dissolved in 40 g of a 15 wt. % colloidal silica suspension in so as to achieve 1:1 weight ratio of sucrose to silica content. The solution was frozen by plunging the container in liquid nitrogen and then immediately transferred to a freeze dryer to sublime away the ice. The sublimation time was approximately 48 h to ensure complete removal of the ice. The melting point of the freeze dried composite remains above room temperature under the vacuum conditions of 0.014 mBar inside the freeze drier jar, which prevents its melting during dying. After that, the sucrose-silica composite was carbonized in an inert atmosphere of argon gas while heating with a ramp rate of 180 C h^{-1} to1000 °C for 3 h. To remove the silica, the carbonized material was etched using a stirred 3 M NaOH solution at 80 °C for 24 h. Finally, the sample was washed with deionized water until a neutral pH solution is obtained and then kept in a vacuum oven at 80 °C for at least 24 h for drying. CO_2 activation of the carbon was carried out in a tube furnace at 950 °C by flowing CO_2 gas over the carbon at 50 cm^3 min^{-1} for various times from 0 to 2 h. The sample was never exposed to air during the activation cycle. 4-0.5-0 carbon was synthesized using the same procedure as above, except the silica to sucrose weight ratio was changed to 0.5.

2.2. Preparation of carbon–sulfur composites

Carbon-sulfur composites were prepared via melt infusion. Typically, carbon and sulfur powders were taken in a 1:1 weight ratio and mixed well in a mortar and pestle to ensure uniform dispersion on the micron scale of sulfur particles in the carbon. The mixture was then transferred to a stainless steel Parr reactor and placed in an oven heated at 160 °C for 18 h to obtain the C–S composites.

Structural characterization: Nitrogen adsorption and desorption isotherms were obtained at 77 K using a Micromeritics ASAP2020 instrument. Specific surface areas and pore volumes were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models, respectively, applied on the adsorption branches of the adsorption–desorption isotherms. TG/DTA analysis was performed using EXSTAR TG/DTA6200, where the samples were heated at a rate of 10 °C/min from room temperature to 500°. XRD traces were obtained using a Scintag Theta–Theta X-Ray Diffractometer with Cu Kα radiation.

2.3. Electrochemical testing

The cathode was prepared by making a slurry of the carbon-