



Full Length Article

Tunable pore structure for confining polysulfides in high performance Li-S battery with coal precursor

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ABSTRACT

The lithium-sulfur (Li-S) battery is a promising technology for next generation energy storage systems due to low cost materials and high theoretical energy capacity. However, the well-known ‘shuttle effect’ of polysulfides, that has significant impact on battery performance, has impeded the commercialization of Li-S batteries with high volumetric energy density and cycle life necessary for economic viability. Herein, we provide a facile method for the fabrication of hierarchical porous carbon with optimal pore structure to support sulfur in the cathode. The specific surface area of the coal-derived hierarchical porous carbon can be as high as 3343 m²/g, with a high distribution of pores between 2 and 5 nm, which is both beneficial to confining the polysulfides and increased sulfur loading (as high as 76 wt%). With most of sulfur confined in small mesopores, the carbon/sulfur composites show a high specific capacity of 1390 mAh/g at 0.05 C with ~85% capacity retention after 100 cycles at 0.5 C.

1. Introduction

Li-S chemistry is a promising technology for next generation energy storage systems with a high theoretical capacity of 1675 mAh g⁻¹ and use of low cost materials such as sulfur [1–7]. However, despite years of research, few companies can provide large Li-S cells or modules. One of several major barriers to Li-S commercialization has been due to the ‘shuttle effect’ of polysulfides [3,8–10]. In this case, long-chain polysulfides generate in the cathode can diffuse to the anode, and after reduction, they return back to the cathode, during which both cathode and anode materials are consumed, leading to a low coulombic efficiency and limited cycle life [3,11].

Recently, carbon supported materials have been shown as an effective way to reduce the ‘shuttle effect’ in the sulfur cathode while providing a conductive network for electron transfer [12–23]. Carbon is a unique material that can have significant electrical conductivity while possessing a highly developed porous structure at both the nano and micro scale. Such properties can lead to increased performance through improved electron and ionic charge transport networks. Mesoporous carbon infused with sulfur can form a stable hybrid carbon/sulfur composite that have shown a reversible capacity of up to 1320 mAh g⁻¹ [11]. Subsequently, carbon nanofibers (CNFs), graphene, carbon nanotube (CNTs) and hierarchical carbons have been applied as carbon matrix for the Li-S cathode and showed significant improvements in

specific capacity, cycle life and rate performance [24–27]. For example, graphene-wrapped sulfur particles demonstrated ~600 mAh/g after 100 cycles [22,28]. Nitrogen-doped graphene with 65.2 wt% sulfur showed a specific capacity of 1167 mAh/g at 0.2 C. After 700 cycles at 1 C, the capacity retention was 52.4% [29]. Carbon nanotubes composed with 50 wt% sulfur showed a specific capacity of 1071 mAh/g at 1 C, and capacity retention as high as 85% after 100 cycles [30].

Hierarchical porous structures were found to be optimal structure for Li-S cathodes, since it combines the advantages of both micropores to confine polysulfides and mesopores to ensure the fast transportation of ions and electrons [14,25,31–35]. Carbon spheres with micropores inside and mesopores outside have shown a high specific capacity of 1412 mAh/g cycling at 0.06 C while demonstrating stable cycling performance with 90% capacity retention after 100 cycles at 0.3 C. However, the sulfur content was limited to 46 wt%, indicating the gains in performance may have been due to the limited sulfur content thereby creating a high utilization rate [25]. High sulfur loading is one of the most important factors to ensure a high specific capacity of the composites. For example, if the content of sulfur in the cathode is less than 60%, the Li-S battery demonstrates a lower specific capacity (volumetric) than current LIB technology [4,5,15,36–39].

Previous results have shown a series of high sulfur loading cathode materials. For example, hierarchical porous carbon rods with sulfur content of 78.9 wt% exhibited a specific capacity of 646 mAh/g at 5 C

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[33]. Graphitized carbon/sulfur composites with 90 wt% sulfur have been fabricated and the composites showed a specific capacity of 1070 mAh/g which reduces to 804 mAh/g after 50 cycles [40]. Although initial results are promising, significant work remains to achieve both high sulfur loading and long term cycling. Here we describe a facile method to obtain both high-sulfur loading and improved cycle life by using coal as a carbon precursor. A simple chemical reaction of KOH with coal can lead to coal derived porous carbons (CDPCs) that show a high specific surface area of up to $3461 \text{ m}^2 \text{ g}^{-1}$, and a pore volume as high as $2.10 \text{ cm}^3 \text{ g}^{-1}$. Moreover, the pore size of CDPCs can be tuned by adjusting the coal precursor with different coalification degrees and volatile contents. By tuning the porous structure of CDPCs, the sulfur infiltrated into the carbon matrix was shown to be as high as 76 wt%, with most of the sulfur confined in small mesopores. When the composites were applied as the cathode material of Li-S battery, the sulfur in the composites contributed to a specific capacity of 1390 mAh g^{-1} , with 84% capacity retention after cycling for 100 times at a rate of 0.5 C.

2. Experimental

2.1. Materials preparation and characterization

Three coal materials with different coal ranks as precursors were used to prepare porous carbons, the coals are named as Coal-1 (anthracite, Pingdingshan, Henan, China), Coal-2 (bitumite, Luoyang, Henan, China) and Coal-3 (Erdos, Inner Mongolia, Chian). The coal particles were mixed with KOH (Sinopharm) with a mass ratio of 1:4 in 15 mL deionized water. After water evaporation, the mixtures were transferred to a tube furnace and heat treated at $750 \text{ }^\circ\text{C}$ for 1 h with heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. This process was conducted in nitrogen atmosphere and the gas flow rate was controlled at 1 L/min. When the furnace cooled down, the product was washed with 5 mol/L HCl (Sinopharm) for 12 h, following by several times of water washing till pH = 7. Then the carbon was dried at $120 \text{ }^\circ\text{C}$ in vacuum. The porous carbons as obtained were named as CDPC-1, CDPC-2 and CDPC-3. The carbon/sulfur composites were prepared by infiltration of the sulfur (Sigma) into the porous structure at $155 \text{ }^\circ\text{C}$ for 12 h. The carbon/sulfur composites were named as CDPC/S-1, CDPC/S-2 and CDPC/S-3.

The morphology and elemental distribution of porous carbon and the composites were characterized by Scanning Electron Microscopy (SEM, FEI Nova NanoSEM 450) and Transmission Electron Microscopy (TEM, JEOL JEM ARM200F). The specific surface area and pore size distribution were characterized by N_2 adsorption-desorption at 77.4 K (Tri-Star, Micromeritic). All the samples were degassed at $300 \text{ }^\circ\text{C}$ for 15 h before test. The relative pressure range was 1.0 E-7 to 0.99. Specific surface area was estimated by Brunauer-Emmett-Teller (BET) method with points between 0.05 and 0.35. The pore size distribution was calculated by Nonlocal Density Functional Theory (NLDFT) with a slit/cylinder model of N_2 at 77 K on carbon and the microporosity was also analyzed by Horvath-Kawazoe (HK) model. Pore volume was calculated by t-plot method with points between 0.20 and 0.50. Thermogravimetry analysis (TGA) was performed on NETZSCH STA 449 F3/QMS 403C with nitrogen atmosphere. Sulfur content was tested by TGA with a temperature range of room temperature to $600 \text{ }^\circ\text{C}$ in nitrogen, with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$. X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer with 2θ ranging from 8° to 90° . X-ray photoelectron spectroscopy (XPS) spectra were recorded on Thermo Scientific Escalab 250Xi.

2.2. Electrochemical tests

The electrochemical performance was tested with CR2025 coin cell. The carbon/sulfur composites were mixed with Ketjen Black and PVDF with a mass ratio of 8:1:1. The mixture was then coated on a alumina foil and dried in vacuum oven at $60 \text{ }^\circ\text{C}$ for 6 h, and the average mass

loading was around 2 mg cm^{-2} . The coated alumina foil was punched into electrode slices with diameter of 11 mm and assembled into coin cells. Celgard was used as the separator and lithium foil as the counter electrode. $60 \mu\text{L}$ of electrolyte (1 mol/L LiTFSI in DOL: DME with volume ratio of 1:1 and 1 wt% LiNO_3 as additive) was used in each cell (electrolyte/sulfur = 30 mL/g) [41]. The galvanostatic charge–discharge test was performed on LAND CT2001A.

3. Results and discussion

Three coals with different coalification degrees (Coal-1 > Coal-2 > Coal-3) were chosen for the experiment. The detailed compositions of the coals are shown in Table S1. Coal-1 is anthracite with the highest fixed carbon and lowest content of volatile (6.94 wt%). Coal-2 and Coal-3 (bitumite) have lower degree of coalification and thus higher content of volatiles (9.90 and 29.48 wt%). Volatile in coal is composed of humic acid, thus coal with high volatile is more likely to have a vigorous reaction with alkali, impacting the pore and overall microstructure formation. Typical activation by KOH reaction involves two steps—pore generation and pore widening. Thus pore generation in high-volatile coal is easier as an increased amount of KOH is able to react, resulting in pore widening and a higher degree of mesopores [42–45]. In this research, pore construction proceeded more efficiently for Coal-2 and Coal-3 compared to Coal-1.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apsusc.2018.07.139>.

The Raman spectra of the coals and the corresponding CDPCs showed the evolution of carbon microstructure during activation (Fig. S1, Table S2). In the Raman spectra, D band at $\sim 1350 \text{ cm}^{-1}$ and G band at 1600 cm^{-1} represent the disordered carbon and quasi-graphitic carbon, respectively. In this specific case, the significant distinction is whether the distribution of D band and G band change after activation. For Coal-1 and CDPC-1, the Raman spectra are almost the same, with the D band and G band of CDPC-1 separated, indicating the integrated structure of Coal-1 was present in CDPC-1 even after reaction with KOH. For CDPC-2 and CDPC-3, the spectra are quite different when compared with Coal-2 and Coal-3. The D band and G bands are merged to some extent, implying the formation of highly developed pores that deconstructs the continuity of the carbon microstructure. The Raman results demonstrate that Coal-2 and Coal-3 are easier to react with KOH when compared with Coal-1. This leads to a higher degree of porosity in CDPC-2 and CDPC-3 as compared to CDPC-1, which is further demonstrated by the higher D/G band ratio (3.71 and 3.51 for CDPC-2 and CDPC-3, and 1.94 for CDPC-1, Table S2).

As shown in Fig. 1 (Fig. S2), all CDPCs exhibit hierarchical porous structure after KOH activation. The huge evolution of surface area and pore volume from coal to CDPCs indicate the effective pore construction by KOH (Table S3). The N_2 adsorption plots show typical IV plots, with gas adsorption at both low and moderate relative pressure. This indicates that both micropores and mesopores exist in the CDPCs. However, the gas adsorption characteristics of CDPCs vary with coal precursors. For CDPC-1, most of the N_2 adsorption occurs at low relative pressure, corresponding to large amount of micropores in the carbon. In contrast, CDPC-2 and CDPC-3 show more gas adsorption at moderate relative pressure, implying more mesopores in carbon matrix [33]. The pore size distributions (Fig. 1b) directly show the mesopores and micropores in CDPCs. Ultra-micropores ($< 1 \text{ nm}$) exist in all samples [46]. There are also considerable micropores with size of 0.5–2 nm in all CDPCs, as shown by the HK model (Fig. S2). For CDPC-2 and CDPC-3, most of pores distribute between 2 and 5 nm, while there are fewer mesopores in CDPC-1. As indicated above, as the coalification degree increases, fewer mesopores are generated during the KOH activation. This could be attributed to the higher activation energy required for KOH to react with the graphitic carbon layer in coal that contains a more ordered arrangement and fewer defects.

Table 1 contains the calculated pore characteristics for the different

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