



Layered carbide-derived carbon with hierarchically porous structure for high rate lithium-sulfur batteries



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ABSTRACT

Practical applications of lithium-sulfur batteries require not only high specific capacities and long cycle life but also high rate performance. Herein, a layered carbide derived carbon (CDC) with hierarchically porous structure is designed and used as sulfur host for high rate lithium-sulfur batteries for the first time. In the layered CDC, sulfur was mainly infiltrated into the micropores and small mesopores, which could efficiently confine sulfur species and suppress polysulfides shuttling. At the same time, the layered structure and large mesopores would further shorten ion diffusion distance and buffer volume expansion. As a result, the layered CDC/sulfur composite with a sulfur loading of 50 wt.% delivered not only a high initial discharge capacity of 1229 mAh g⁻¹ at 0.5C, but also a superior reversible capacity of 621 mAh g⁻¹ at 5C. Especially, the high rate capability could also be achieved even at a higher sulfur loading (68 wt.%). This work suggests that porous carbon combined with layered structure and hierarchical pores could be used as effective matrix to host sulfur for high rate lithium-sulfur batteries.

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1. Introduction

Lithium-sulfur (Li-S) batteries are considered to be a promising energy-storage solution to meet the future demand for higher energy density [1,2]. Currently, sulfur cathodes exhibit some inherent drawbacks [3,4], including the low conductivity of both sulfur and final discharge product (Li₂S), the shuttle of intermediate lithium polysulfides (Li₂S_n, 4 ≤ n ≤ 8) and the large volume expansion, which inevitably lead to fast capacity fading as well as poor rate performance. Encapsulating sulfur in conductive porous carbons has been popular to overcome these issues. Recently, various carbon hosts with respect to their morphology [5–7], pore size [8,9], porosity [10], surface chemistry [11,12] and polymer coating [13] have been widely investigated. Among these porous carbons, the hierarchical micro-mesoporous carbon has been verified as a promising candidate [10,14,15]. This is due to the synergetic effects of multi-scale pores, in which micropores could ensure better confinement of sulfur and strong adsorption of

polysulfides, while mesopores could accommodate high sulfur loading and facilitate Li⁺ transport. With the help of multi-scale pores, the utilization of sulfur and the cycling stability are remarkably improved.

In addition to the pore structure, morphology control of the porous carbon hosts has also been proved to be an effective approach to improve the electrochemical performance of Li-S batteries. Among them, layered porous carbons have received special attentions. Their open nanopores and layered structure could not only ensure good electrolyte accessibility and short ion diffusion distance, but also help to buffer volume expansion [7,16,17]. Thus, the electrochemical performance, especially rate capability, could be significantly enhanced for the resulted sulfur cathodes with layered structure. Various layered carbons with different porous structures and synthetic strategies have been developed recently [18–22]. For example, Zhang et al. [19,20] employed a volatile-metal-induced mesopore construction strategy to prepare hierarchical mesoporous graphene by CVD self-assembly on porous oxide templates. The obtained porous graphene/sulfur composites exhibited excellent cycling stability and rate performance due to the effective confinement of sulfur/polysulfides by large mesopores and the high electronic

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conductivity of the graphene layers. Chen et al. [21] reported a layered graphene/porous carbon-sulfur composite with a thin layer of porous carbon covering both surfaces of the graphene and sulfur highly dispersed in its pores. The as-prepared materials also demonstrated excellent rate performance and cycle stability which was attributed to the high electronic conductivity of graphene matrix and strong polysulfides confinement by mesoporous carbon layer. Huang and Kang et al. [22] prepared nitrogen doped hierarchical porous carbon nanosheets (N-HPCNS) through facile co-pyrolysis of magnesium citrate and potassium citrate mixtures and subsequent NH_3 treatment. The N-HPCNS/S cathodes delivered high discharge capacities of 1209 mAh g^{-1} at 0.2C and outstanding rate performance of 493 mAh g^{-1} at 4C. These studies indicate that the layered porous carbons are ideal sulfur hosts for high rate Li-S batteries, and developing novel layered carbon with hierarchical porosity is urgently demanded.

Carbide derived carbons (CDCs) belong to the porous carbon family, which are produced by selectively etching of carbides upon high temperature treatment (e.g. chlorination) [23–25]. Their pore structures as well as intrinsic carbon structures could be simultaneously controlled by changing the etching conditions such as carbide precursors, chlorination temperature, time and hydrogenation [26]. Compared to traditional porous carbon prepared by carbonization/activation of carbon precursors, the pore size of CDCs can be precisely controlled at the atomic level [27]. With a wide range of physiochemical properties, CDCs have been evaluated for a variety of applications, such as gas adsorption [28], hydrogen storage [24,27], and in particular electrode materials for supercapacitors [29,30]. To date, several CDCs/S composite cathodes have been reported for Li-S batteries with attractive performance. Yushin et al. [31] firstly employed SiC-CDCs as sulfur hosts, which suggested micropores could be favorable for polysulfide retention and small straight mesopores served as channels for uniform sulfur infiltration and rapid Li^+ access. Nevertheless, the specific capacity at higher rate (420 mAh g^{-1} at 1C) is relatively low due to sluggish Li^+ diffusion in small pores. Kaskel's et al. [32,33] employed silica nanospheres and silica foam as templates to prepare hierarchical porous CDCs. The resulted CDCs/sulfur composites delivered high discharge capacity and cycle stability with high sulfur contents. However, additional steps are needed to remove templates, and thus increasing the complexity and cost. Kaskel and Yushin et al. [34] further prepared polymer-based CDCs with combined micro- and mesopores by an advantageous sacrificial templating approach. The cells exhibit good rate performance and stability. These studies suggest that CDCs are highly attractive host materials for Li-S batteries because of their controllable pore structures and graphitization degree. However, all these CDCs are irregular structure and layered CDCs as sulfur hosts have been rarely reported. Besides, optimization of pore size distribution is expected to further enhance the electrochemical performance of CDCs/S cathodes.

In this work, we prepared two types of hierarchically micro-mesoporous CDCs with/without layered structure, and compared their respective CDCs/S cathodes *via* porosity properties, morphology and electrochemical performance. To the best of our knowledge, this is the first report on hierarchical porous CDC with layered structure for sulfur host. It was further concluded that the layered CDC/S composites demonstrated significantly improved rate performance while maintaining a higher specific capacity and longer cycle life. This should be due to the layered CDC having good electrolyte accessibility and short ion diffusion distance to enhance electrode kinetics. In addition, the hierarchical micro-mesoporous structure of the CDC would further promise strong adsorption of polysulfides and uniform sulfur infiltration.

2. Experimental

2.1. Preparation of CDCs

Chlorination of carbides to produce CDCs was well established in the previous reports [35,36]. Here we choose Ti_2AlC to prepare layered CDC, while Mo_2C to obtain non-layered CDC. Typically, 1 g of Ti_2AlC powder was loaded in a tube furnace and purged for 1 h under argon. Then the temperature was ramped to 800°C at $30^\circ\text{C min}^{-1}$ and held for another 1 h. Then chlorine was introduced with a flow rate of 10 sccm and heated at 800°C for 3 h. Next, the furnace was cooled down in the Ar flow to 600°C and switched to hydrogen at 10 sccm for another 2 h. Finally, the furnace was cooled to room temperature under argon flow. The resulting powder was denoted as TAC-CDC. Mo_2C was also chlorinated at similar conditions and denoted as MC-CDC.

2.2. Preparation of CDCs/S composite

The CDCs/S composites were prepared following a conventional melt-diffusion strategy [37]. Typically, the as prepared CDCs and sublimed sulfur were mixed homogeneously. The mixture was sealed in a vacuum vessel, heated at 155°C for 10 h, followed by 300°C for another 2 h to ensure the complete diffusion of melt sulfur into the interior pores of the carbon matrix. In this work, CDCs/S composites with different sulfur loadings were also prepared, and were denoted as CDCs/S- x , where x represents the sulfur content in the composites.

2.3. Materials characterization

Elemental analysis (EA) was carried out with a varioMicro cube elemental analysis instrument using Elemental Vario EL III. The carbon (C), hydrogen (H) contents of the carbons were determined directly using the thermal conductivity detector. The oxygen (O) content was calculated by difference.

The morphologies of the samples were observed on scanning electron microscopy (SEM, JEOL 7100F) and transmission electron microscopy (TEM, JEOL 2100F). Elemental mapping analysis was carried out using a scanning electron microscopy (SEM, FEI Q300).

Nitrogen adsorption-desorption isotherms were performed at 77 K with a Quadrasorb SI analyzer. Before measurements, the CDCs and CDCs/S composites were degassed in vacuum at 473 K and 333 K, respectively, for at least 12 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). The pore size distribution was derived from Quenched Solid Density Functional Theory (QS-DFT) model. The total pore volumes (V_{T}) were estimated using a single point at the maximal relative pressure of 0.995.

X-ray diffraction (XRD) were performed using Cu ($K\alpha$) radiation ($\lambda=1.5406 \text{ \AA}$) with the 2θ -angle recorded from 10 – 80° (Rigaku D/Max 2550). Raman spectra were carried out on a Renishaw system 1000 with an argon-ion laser operating at 514 nm with a charge coupled device detector. The electrical conductivity measurements were obtained at ambient temperature using the four-contact method. The CDCs were filled in a Teflon cylinder with an inner diameter of 16 mm, and two stainless steel plungers were used to deliver 4 MPa pressure through a hydraulic press device. The voltage and current through stainless-steel plungers were recorded by using two Keithley 2000 digital multimeters. The electrical conductivity was calculated on the basis of the powder electrical resistivity. In a control experiment, the electronic conductivity of carbon black (Super C) is measured as 4.25 S cm^{-1} . The sulfur contents in the composites were determined by thermogravimetric analysis (TGA, TA Instrument Q600 Analyser)

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