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Enhanced performance and anchoring polysulfide mechanism of carbon aerogel/sulfur material with Cr doping and pore tuning for Li-S batteries

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ABSTRACT

The ultrafine Cr_2O_3 modified carbon aerogel (Cr-CA) composites were successfully synthesized through in situ and sol-gel method as cathode material for lithium sulfur battery. The chromium doping remarkably controls structure, decreases carbon sphere size and promotes network interconnect. The nano Cr-CA composites with large pore volume and high specific surface present stronger adsorption ability and effectively immobilize polysulfides. The Cr-CA/S composite cathodes display excellent electrochemical performance with high specific capacity and long cycling stability. Especially, the Cr2-CA/S cathode with 65.9 wt% of sulfur delivers initial specific capacity of 1343 and 987 mAh g^{-1} at the rate of 0.2 C and 2 C, respectively. It exhibits the outstanding long-term cyclic stability with the discharge capacity of 873 mAh g^{-1} at 0.5 C for the 300th cycle. The excellent performance is mainly attributed to special anchoring role of Cr_2O_3 to polysulfides and its catalytic effect for redox reaction process. Furthermore, the adsorb energy between polysulfides and Cr_2O_3 and theoretic analysis by DFT definitely reveals and supports immobilizing and catalytic mechanism.

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1. Introduction

The increasing demand for renewable energy has been leading to the rapid development of energy storage technologies for portable electronic devices and hybrid electric vehicles [1–3]. Among the existing technologies, lithium sulfur (Li–S) battery has attracted increasing interests as a promising candidate for next generation battery for its abundant, inexpensive, nontoxic, high theoretical capacity of 1675 mAh g^{-1} and high energy density of about 2500 Wh kg^{-1} of sulfur cathode [4–6]. Despite these considerable advantages for Li-S battery, there are still several inherent issues to be overcome: (i) the insulating properties of sulfur and lower-order polysulfides (Li_2S_2 and Li_2S) result in low utilization of active substances; (ii) large volumetric expansion from sulfur to lithium sulfide during the reaction process leads to rupture or breakage of the electrode as well as serious deration of capacity during the recession cycle; (iii) the intermediate products of the soluble long chain polysulfides (Li_2S_n, $4 \leq n \leq 8$) into the electrolyte solution during the cycle processes bring about poor cycling life, low Coulombic efficiency and serious capacity decay [7–9].

Much effort has been devoted to address aforementioned problems and significantly improve the electrochemical performance of Li-S battery such as the conducting and highly-flexible carbon materials including hierarchical porous carbon [10–12], 3D graphene/graphene oxide [13–16], carbon nanofiber [17] and carbon nanotube [4,12,18]. These carbon/sulfur composites provided effective pathway as matrix of sulfur in enhancing the electrochemical performance. Recently, the effective method including electrolyte optimization [19], hydrophilic binder [20] and metal-organic framework [3,21] have been proposed to suppress shuttle effect. Furthermore, metal compounds including metal oxides, nitrides and sulfides were used to modify carbon material for sulfur composite electrode. These metal compounds, such as ZrO_2 [22], Sm_2O_3 [23], MnO_2 [24–26], Co_4N [27], CuS [28] and Co_3S_4 [29], improved cathode performance mainly via adjusting their dispersion and changing surface chemistry of carbon framework. Among those investigations, the metal compounds can modify morphology of carbon matrix, but the few can dramatically change morphology and reduce the size. Until now, few reporter of quantum

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mechanical method was employed to describe and calculate electronic structure, in spite of computation chemistry have advantage on comprehending interaction mechanism as a powerful tool. Thus, it is still to develop new strategy by choosing some metal compounds to regulate micro structure and morphology of carbon material. Meanwhile, it is also necessary to understand the anchoring mechanism of the doped and modified composites on lithium polysulfides via quantum chemistry method.

In this work, we devote our efforts to build a comprehensive understanding to interaction mechanism by taking advantages of combining electrochemistry with quantum mechanical method. Considering the special chemical interactions between Cr_2O_3 and lithium polysulfides, we have developed a facile and efficient method synthesizing hybrid micro-mesoporous composites of carbon aerogel, Cr_2O_3 and sulfur. The Scheme 1 illustrates synthesis procedure for Cr-CA/S composites. The Cr-CA/S composites present enhanced electrochemical performance for its 3D interconnected structure, special channels and catalytic role. Especially, the Cr_2O_3 modified CA plays a critical role in promoting surface adsorption of polysulfides and anchoring the intermediates.

2. Experimental section

2.1. Synthesis of carbon aerogel

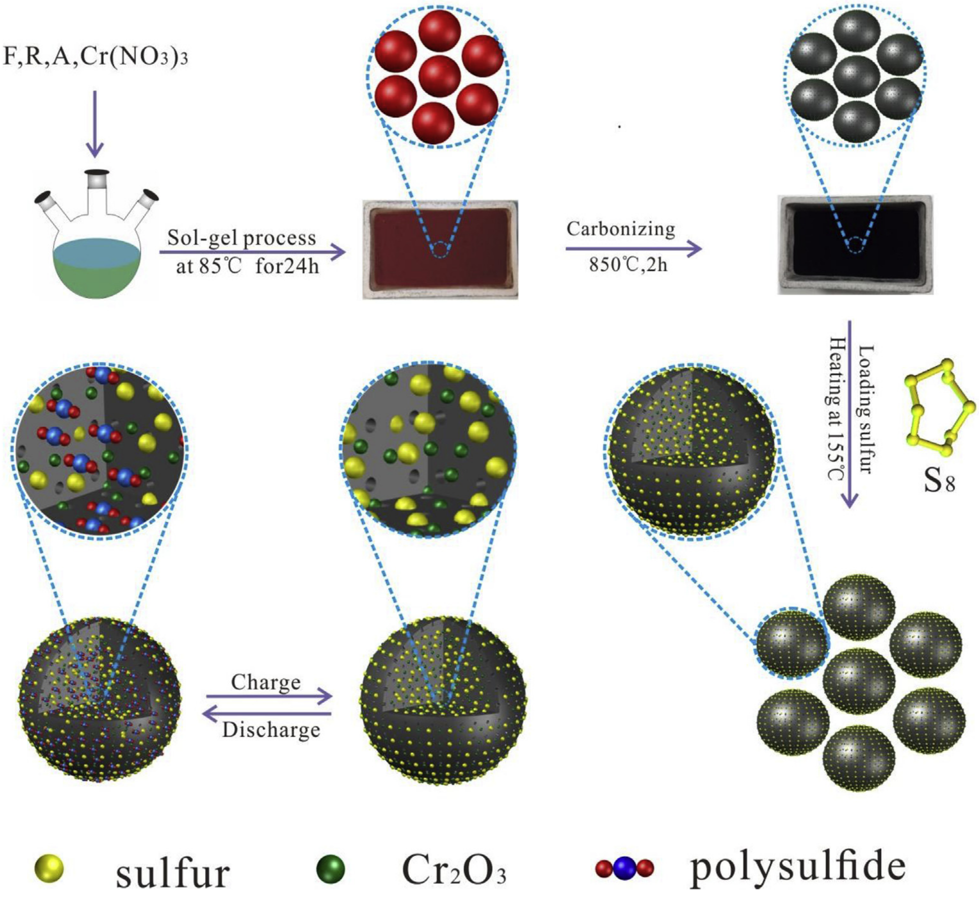
The carbon aerogel (CA) was prepared through sol-gel reaction and a subsequent carbonized process. Typically, resorcinol (R) and ascorbic acid (A) and cetyl trimethyl ammonium bromide (CTAB) were dissolved in redistilled water and stirred for 0.5 h at 85 °C, then formaldehyde (F) was added with constant stirring. The molar ratios for F/R, CTAB/R, A/R and H_2O/R in the system were 2/1, 1/400, 1/300 and 50/1, respectively. After stirring for 0.5 h, the mixture become milky white, then the solution was transferred and sealed in beaker and kept reacting for 36 h at 85 °C. The resulting carbon aerogel precursor was then heated at 850 °C with a heating rate of 5 °C min^{-1} for 2 h under a N_2 atmosphere.

2.2. Synthesis of Cr-CA composites

The Cr_2O_3 modified CA was facilely prepared by in-situ strategy. In a typical synthesis, chromium nitrate, R, A and CTAB were dissolved in redistilled water, and the solution was stirred for 0.5 h at 85 °C. Then liquid formaldehyde was added to the solution and mixture system gradually change its color during reacting process. Once getting cyan, the mixture was sealed in a beaker at 85 °C, the deep brown hydrogel was acquired after 72 h reaction. Further, the intermediate was heated with a rate of 5 °C min^{-1} and carbonized at 850 °C for 2 h under nitrogen atmosphere to form Cr_2O_3-modified carbon aerogel. By adjusting the concentration ratio, the samples with various contents of Cr_2O_3 were acquired. The composites with the Cr/C molar ratios of 0/100, 1/100, 2/100 and 3/100 were denoted as CA, Cr1-CA, Cr2-CA and Cr3-CA, respectively.

2.3. Preparation of CA/S and Crx-CA/S ($x = 1, 2, 3$) materials

The CA/S and Crx-CA/S materials were fabricated using a classical melt-diffusion strategy. Firstly, sublimation sulfur and Cr-CA with the desired mass ration of 7:3 were mixed thoroughly by



Scheme 1. Schematic illustration of synthesis procedure of Cr-CA/S.

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