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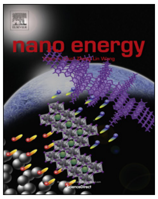

Full paper

# Reduced graphene oxide wrapped MOFs-derived cobalt-doped porous carbon polyhedrons as sulfur immobilizers as cathodes for high performance lithium sulfur batteries

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## ABSTRACT

Reduced graphene oxide (RGO) wrapped metal-organic frameworks (MOFs) derived cobalt doped porous carbon polyhedrons synthesized via a carbonization process, are for the first time used for sulfur immobilizers (RGO/C–Co-S) as cathodes for high performance lithium-sulfur (Li–S) batteries. The RGO/C–Co–S cathode exhibits greatly improved electrochemical performance, showing excellent specific capacity of 949 mAh $g^{-1}$ at 300th cycle at a current density 0.3 A $g^{-1}$, displaying enhanced rate capability with specific capacity of 772, 704 and 606 mAh $g^{-1}$ at current density of 0.5, 1 and 2 A $g^{-1}$, respectively. The synergetic effect of MOFs-derived porous carbon, homogeneously distributed Co nanoparticles and RGO nanosheets simultaneously contributes to the confinement of sulfur species. The presence of abundant mesopores and micropores is conducive to immobilize large amounts of S species. The homogenously inlaid ultrafine Co nanoparticles can further immobilize sulfur by chemical interactions between Co and S/polysulfides. The RGO nanosheets tightly wrapped on carbon hosts act as barrier layers to prevent polysulfides from diffusing out of the matrix, further suppressing shuttle effect. The porous structure and the RGO can effectively alleviate the volume changes resulted from charge–discharge process. This design strategy can be inspiring for MOF-derived materials in energy storage applications.

## 1. Introduction

Lithium sulfur (Li–S) batteries have recently drawn much attention because sulfur cathode can exhibit a theoretical specific capacity of 1672 mAh $g^{-1}$, much higher than that of the commercial cathode materials of lithium ion batteries (LIBs), making it a competitive candidate for the next generation secondary batteries along with the natural abundance, low cost and nontoxicity of elemental sulfur [1–3]. However, several issues needs to be solved before its wide industrial applications for Li–S batteries [4–7]. Firstly, the low electrical conductivity ($5 \times 10^{-28}$ S $m^{-1}$) of sulfur results in limited utilization of active material and poor electrochemical activity. Secondly, the intermediates of lithium polysulfides generated during the electrochemical reaction are soluble in electrolyte, thus leading to a continuous loss of active materials and the subsequent shuttle effect. Furthermore, the dissolved polysulfides may react with lithium metal anode to form insoluble $Li_2S/Li_2S_2$, deposit on the Li anode surface, thus causing the deactivation of lithium anode.

Tremendous efforts have been made to solve these problems in recent years. One of the most popular methods is to build nanohybrids with various carbon materials [8–14]. Carbon materials with a better electrical conductivity not only facilitates charge transfer during electrochemical reactions, but also helps to trap sulfur species through physical adsorption. Various porous carbon materials with large surface area have been used as sulfur hosts to fabricate C-S nanocomposites and exhibit good electrochemical performance when used as cathode materials for Li–S batteries. Small sulfur molecules ($S_{2-4}$) stored in 0.5 nm micropores can avoid the unfavorable transition between $S_8$ and $S_4^{2-}$, thus effectively alleviating the shuttle effect [15–17]. But the sulfur loading content is usually too low for practical use. Mesopores with larger pore volume can store more sulfur. However, owing to the weak interaction of the physical adsorption and the open pore structure, the active materials still show gradually loss during repeated cycles. So it's urgent to take measures to further trap and immobilize sulfur and polysulfides.

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Recently, chemisorption effect between sulfur species and some specific hosts have been proved to efficiently trap and immobilize sulfur species. Several metal oxides, such as $Mg_{0.6}Ni_{0.4}O$ [18], $TiO_2$ [19–20], $MnO_2$ [21–22], $MoO_2$ [23] and $Ti_4O_7$ [24–25] have been used as sulfur hosts, and the possible chemical interactions between sulfur species and metal oxides hosts are responsible for the enhanced electrochemical performance when used as cathode materials for Li–S batteries. For example, $Ti_4O_7$ host with a high surface area fabricated by Nazar and coworkers shows strong ability to retain sulfur species. The demonstrated strong metal oxide-polysulfide interactions indicate that O–Ti–O units can chemically bind LiPSs [25]. Zheng et al. utilizes an electrically conductive $MoO_2$ as the matrix to encapsulate sulfur, and the strong O–S bonding interactions enable firmly confinement of sulfur [23]. Interestingly, transitional metals (such as Cu, Co, Ni, etc.) also show strong chemical interactions between sulfur species and metals. Wang et al. uses Cu-doped microporous carbon to confine S/polysulfides, and Cu nanoparticles anchored in the microporous carbon chemically interact with S/polysulfides through chemically bonding between Cu and S/polysulfides, thus leading to enhanced electrochemical performance when used as cathode for Li–S batteries [26]. Compared with physical absorption ability of traditional porous hosts to retain sulfur, the stronger chemical interactions between sulfur species and hosts may be more efficient to trap S/polysulfides.

Metal organic Frameworks (MOFs) consisting of organic ligands and metal ions can transform into various porous carbons or porous metal oxides [27–31]. MOFs derived porous carbon materials with unique pore structure exhibit excellent ability to trap sulfur and selenium when used as electrodes for lithium secondary batteries [15,30]. Chen et al. reported graphene-wrapped sulfur/MOF-derived microporous carbon composite for Li–S batteries. The introduction of inter-connected graphene network with high electrical conductivity leads to improved charge-transfer kinetics, thus resulting in enhanced capacity [32]. In this paper, cobalt based ZIF-67 with large proportion of organic component is chosen as precursor to fabricate Co-doped carbon with large amount of pores. Then the MOFs-derived Co-doped porous carbon is used to confine sulfur through both the physical adsorption of porous carbon and chemical interaction between cobalt and sulfur. Typically, a porous carbon polyhedrons with ultrafine Co particles homogenously inlaid are first synthesized by carbonization of Co-based MOF (ZIF-67). After reducing graphene oxide (RGO) nanosheets wrapping and then impregnation of sulfur, the RGO/C–Co-S polyhedrons nanohybrids are obtained, showing excellent electrochemical performance when used as cathodes for Li–S batteries. The porous carbon matrix with abundant pores and large surface area can physically adsorb sulfur species, and the ultrafine Co particles further immobilize sulfur species by chemical interactions. The RGO nanosheets tightly wrapping on the surface of polyhedrons serve as barrier layer to further prevent polysulfides from diffusing out of the matrix. The porous carbon matrix, Co particles and RGO nanosheets together play important role to firmly confine the sulfur species, thus leading to greatly suppressed shuttle effect. It's no doubt that the RGO/C–Co-S nanohybrids exhibit excellent electrochemical performance when acted as cathode materials for Li–S batteries.

## 2. Experimental section

### 2.1. Fabrication of C–Co polyhedrons

The cobalt doped carbon polyhedrons C–Co are synthesized via a two-step route, including the preparation of ZIF-67 polyhedrons and then the carbonization process. Typically, 9.96 g $Co(NO_3)_2{\bullet}6H_2O$ and 13.12 g 2-methylimidazole (Aladdin, 98.0%) are respectively dissolved into 1 L methanol to form a homogeneous solution. The 2-methylimidazole solution is slowly poured into the $Co(NO_3)_2$ solution under continuous string to obtain a homogenous system. Then the system is aged at room temperature without stirring for 24 h. After the collected products are washed several times, ZIF-67 polyhedrons are obtained. Then the dried ZIF-67 are annealed in a tube furnace at 600 °C for 3 h Ar flow and then 2 h 10% $H_2-90\%$Ar flow with a heating ramp of 5 °C/min. Then the obtained black C–Co samples are further treated in 2 M $H_2SO_4$ for 12 h to remove part of Co particles, so as to decrease mass density as well as obtain more pores to accommodate more sulfur.

### 2.2. Fabrication of GO/C–Co and RGO/C–Co-S composites

The coating of graphene oxide on C–Co is derived by electrostatic force. Briefly, the C–Co polyhedrons are first functionalized with poly(diallyldimethylammoniumchloride) (PDDA) to gain positive charge surface. Then the negative charged graphene oxide nanosheets can wrap onto the surface of C–Co by the electrostatic force. Typically, C–Co polyhedrons are dispersed into an 150 ml aqueous solution containing 2.149 g PDDA solution (35%), 0.363 g tris and 0.173 g NaCl and the resulting dispersion products are stirred for 120 min. Then free PDDA is removed by 3 times washing. The decorated C–Co samples are then mixed with GO solution and stirred for 6 h. After drying process, the GO-C–Co samples are thoroughly mixed with sulfur with a mass ratio of Ms: Mc=2:1. The mixture is sealed in a glass tube under vacuum and then heated at 155 °C for 24 h. Then the glass tube is broken and the sample is further treated under 210 °C for 2 h to remove the redundant sulfur on the surface. The GO nanosheets are transformed into reduced graphene oxide (RGO) during these heating treatment.

### 2.3. Material characterization

X-ray diffraction (XRD) patterns are collected using Rigaku D/Max-Rb diffractometer equipped with Cu Ka radiation ($\lambda=1.5406$ Å). The morphology and components of the synthesized products are analyzed using SU-70 field emission scanning electron microscopy (FE-SEM) attached with X-ray energy dispersive spectrometry (EDS). The morphology and structure of the synthesized products are analyzed using high-resolution transmission electron microscopy (HR-TEM) of JEM-2100 at an acceleration voltage of 200 kV. Nitrogen adsorption–desorption isotherms are determined at 77 K using a Gold APP V-Sorb 2800 P surface area and porosity 60 analyzer. Raman spectra are measured and collected using a 632.8 nm laser with a JY HR800 under ambient conditions, with a laser spot size of about 1 μm. X-ray photoelectron spectroscopy (XPS) characterization is carried out in an ESCALAB 250 instrument with 150 W Al Ka probe beam.

### 2.4. Electrochemical measurements

The electrochemical measurements are carried out by using 2025 coin-type cells, in which the RGO/C–Co-S composite as working electrode, a lithium metal foil with size of 15.8mm*0.2mm as reference electrode, a celgard 2325 as separator and a solution of 1.0 M LiTFSI in mixed DOL and DME (1:1 by volume) with 0.1 M $LiNO_3$ additives as the electrolyte. The electrode consisted of 85 wt% C – S hybrid, 5 wt% ethylene carbonate, and 10 wt% LA-132 (Indigo, China) binder, with a sulfur loading of 1 mg $cm^{-2}$. Fresh coin cells are assembled in an Ar-filled glove box. The cells are discharged and charged on LAND CT2001A battery test system in the voltage range of 2.6 V to 1.8 V. Cyclic Voltammetry (CV) and electrochemical impedance