



Confine sulfur in mesoporous metal–organic framework @ reduced graphene oxide for lithium sulfur battery



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ABSTRACT

Mesoporous metal organic framework @ reduced graphene oxide (MIL-101(Cr)@rGO) materials have been used as a host material to prepare the multi-composite sulfur cathode through a facile and effective two-step liquid phase method successfully, which is different from the simple MIL-101(Cr)/S mixed preparation method. The successful reduced graphene oxide coating in the MIL-101(Cr)@rGO improve the electronic conductivity of meso-MOFs effectively. The discharge capacity and capacity retention rate of MIL-101(Cr)@rGO/S composite sulfur cathode are as high as 650 mAh g⁻¹ and 66.6% at the 50th cycle at the current density of 335 mA g⁻¹. While the discharge capacity and capacity retention rate of MIL-101(Cr)/S mixed sulfur cathode is 458 mAh g⁻¹ and 37.3%. Test results indicate that the MIL-101(Cr)@rGO is a promising host material for the sulfur cathode in the lithium–sulfur battery applications.

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1. Introduction

With the rapid development of portable electronic equipment, electric vehicles and intelligent power grid and other areas, a higher demand for batteries with high power and energy density and longer cycling life has been put forward, and developing a new generation of battery system is becoming more and more urgent [1]. Lithium–sulfur battery is one of the most promising candidates for high energy density rechargeable batteries due to its high theoretical specific capacity of 1672 mAh g⁻¹ and theoretical energy density of 2600 Wh kg⁻¹ based on sulfur active material [2]. Meanwhile, utilization of sulfur as a cathode material has the advantages of low cost, natural abundance and nontoxicity. Nevertheless, studies on the Li–S system were initiated back to the early 1960s, the system has yet to conquer the marketplace, as a few scientific hurdles remain to be cleared. Among them are: (i) the poor electrode cyclability, owing to the high solubility of lithium polysulphides in organic electrolytes and redox shuttle mechanisms from excessive dissolution and migration of polysulphides, (ii) the use of a Li metal anode which brings safety problems, and (iii) the low active material utilization due to the insulating nature of both the sulfur itself and the polysulfide species resulting from its reduction [3,4].

Many approaches, such as optimization of the electrolyte, replacing binder and modifying the cathode material have been investigated to solve above problems [5–8]. Most of strategies have been

considered to design cathode architecture via a precise control of its porosity to trap polysulphide, recently. A few studies successfully confined sulfur in a porous matrix based on conductive carbonaceous materials or insulating powders which have high microporosity such as metal–organic framework or porous silica [3,9,10].

However, to the best of our knowledge, mesoporous metal–organic frameworks (meso-MOFs) have even richer pore structure and larger specific surface area than the porous carbon [11]. Depending on the metal and organic-ligand selected, networks with various pore shape, size, volume, chemistry can be synthesized and thus adapted to the specific needs of lithium–sulfur battery. Sulfur powder is encapsulated in the micropores of meso-MOFs uniformly. The high dispersion of sulfur inside the micropores of mesoporous metal–organic frameworks is beneficial to the high discharge capability of the sulfur cathode. Especially, the mesopores of meso-MOF can stably trap sulfur and subsequent polysulfide ions during cycling due to such a strong adsorption, avoiding the shuttle reaction [12].

Recently, there has been growing research interest for the application of metal organic framework in lithium sulfur battery. Cakan et al. present a strategy based on the use of a metal organic frameworks (MOFs) as host material for sulfur cathode [10]. However, due to the poor conductivity of the MOFs and sulfur particle themselves, the sulfur cathode need to add a large amount of conductive carbon to ensure the normal charge and discharge of the lithium–sulfur battery. Furthermore, since the volume expansion of the sulfur cathode during the charge–discharge process [13], the pore structure stability of metal–organic frameworks (MOFs) is very fragile, and then it impacted the cycle stability of lithium–sulfur

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battery seriously. Xi et al. present a method of carbonized MOFs for sulfur loading to fabricate cathode structures for lithium–sulfur batteries [14]. Xu et al. synthesized a porous carbon via one-step pyrolysis of MOF-5 using in lithium sulfur battery [12]. Their research strategies focus on the same aspects of carbon material carbonized by MOFs, the interesting application of MOFs for lithium–sulfur battery needs to be further explored.

Graphene, as a single-atom-thick carbon material, inherently holds many favorable advantages such as excellent electronic conductivity, flexibility, mechanical strength, light weight and high surface area [15–17], which can improve the conductivity of the meso-MOFs effectively. Inspired by these previous studies, we demonstrate combining the advantages of mesoporous metal–organic frameworks (meso-MOF) materials and the reduced graphene oxide material (rGO) to yield the hierarchical architecture of meso-MOF@rGO hybrid nanocomposites with rich pore structure and good electronic conductivity, might serve as a high performance matrix for lithium–sulfur battery.

Herein, we report the preparation of meso-MOF@rGO/S multi-composites through the facile and effective two-step liquid phase method by using meso-MOF@rGO materials as a host material (Fig. 1). We choose MIL-101(Cr) as the representation of the Mesoporous Metal–organic frameworks (meso-MOF), which can exhibit open channels or cavities from microsize (pore size ~ 1.4 nm) to mesosize (pore diameter ~ 3.0 nm). [11,18] Graphene sheets are deposited by the in situ chemical oxidation polymerization on the surface of the Mesoporous Metal–organic frameworks to prepare MIL-101(Cr)@rGO multi-composite materials. Subsequently, sulfur is loaded by a two-step liquid method to fabricate MOF@rGO/S multi-composites. The two steps include in situ compound of graphene and mesoporous metal–organic frameworks + the sulfur liquid phase infiltration. This new method is not only form the effective conductive network but also obtain a uniform dispersion, high electrical conductivity, high nano-sulfur content of the composite at low temperatures without extra high temperature treatment. Compared with the MIL-101(Cr)/S composite, the MOF@rGO/S multi-composites with the same sulfur loading shows an obviously improved electrochemical performance, including discharge capacity and high capacity retention.

2. Experimental

2.1. Preparation of graphite oxide (GO)

Graphite oxide (GO) was prepared using a conventional Hummers method [19]. In a typical reaction, 0.5 g of graphite, 0.5 g of NaNO_3 , and 23 mL of H_2SO_4 were stirred in an ice bath for 15 min. Following, 4 g of KMnO_4 was slowly titrated. The solution was transferred to a $35 (\pm 5)^\circ\text{C}$ water bath and stirred for about 2 h to form a thick green paste. Then, 40 mL of water was added very slowly followed

with stirring for 1 h while the temperature was raised to $90 (\pm 5)^\circ\text{C}$. Finally, 100 mL of water was added followed by the slow addition of 3 mL of H_2O_2 (30 wt%), turning the color solution from dark brown to pale brown yellowish. The warm solution was then filtered and washed with 100 mL water. The final product was stored under vacuum for drying.

2.2. Preparation of mesoporous metal–organic framework (MIL-101(Cr))

The synthesis of MIL-101(Cr) consists in the hydrothermal reaction of H_2BDC (1.162 g) with $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.8 g), fluorhydric acid (1.4 mL), and H_2O (33.6 mL) in a 60 mL Teflon-lined stainless steel autoclave. The reaction mixture was heated in an oven at 220°C for 8 h. The synthesized large cubic crystals were collected by filtration and repeatedly washed several times with DMF and de-ionized H_2O [18].

2.3. Preparation of meso-MOF@rGO (MIL-101(Cr)@rGO)

The composite material was prepared as following. GO (100 mg) was loaded in a 250-mL round-bottom flask and water (100 mL) was then added, yielding an inhomogeneous yellow–brown dispersion. This dispersion was sonicated until it became clear with no visible particulate matter to obtain grapheme oxide suspensions. The MIL-101(Cr) green powder is dispersed in the well-dispersed GO suspensions by the mass ratio of 1:1. The resulting suspensions were subsequently stirred. Hydrazine hydrate (1.00 mL, 32.1 mmol) was then added and the solution heated in an oil bath at 95°C under a water-cooled condenser for 12 h over which the reduced graphene oxide gradually precipitated out as a black solid.

2.4. Preparation of meso-MOF@rGO/sulfur multi-composites (MIL-101(Cr)@rGO/S)

The detailed synthetic procedures are shown in Fig. 1. Typically, meso-MOF@rGO is dispersed with the oil-phase containing sulfur in carbon disulfide (CS_2) under stirring. Following complete evaporation of CS_2 from the mixture at 50°C . After stirring for 2 h at 25°C , the MIL-101(Cr)@rGO/S multi-composites is collected by water-washing cycles as well as dried under vacuum at 60°C . The MIL-101(Cr)@rGO/S multi-composites have 50 wt% sulfur, according to thermogravimetric analysis (TGA). For comparison, the simple MIL-101(Cr)/S composite is prepared by simple ball milling with the same sulfur content, adding an amount of carbon black in accordance with the proportion of the reduced graphene oxide.

2.5. Electrode preparation

The cathode slurry was prepared by mixing 80 wt% MIL-101(Cr)@rGO/S multi-composites, 10 wt% carbon black (Super P, Timcal) and 10 wt% PVDF (6020, Solef). For comparison, the slurry using simple mixture of MIL-101(Cr)/S composite was prepared by a similar route. Then, the slurry was spread onto aluminum foil current collector ($20 \mu\text{m}$ thickness) by a doctor blade. The electrode was dried under vacuum at 60°C for 24 h. The sulfur loading density of the cathode is 1.5 mg cm^{-2} , and the total thickness of electrode layer was approximately $30 \mu\text{m}$. The MIL-101(Cr)@rGO/S composite cathode and MIL-101(Cr)/S mixed cathode were obtained using MIL-101(Cr)@rGO/sulfure and MIL-101(Cr)/sulfure, respectively.

2.6. Cell assembly and characterization

Coin-type (CR2025) cells were assembled in an argon-filled glove box (Universal 2440/750) in which oxygen and water contents were less than 1 ppm. Sulfur-containing electrode was used as the cathode, lithium foil as the counter and reference electrode, microporous polypropylene membrane as the separator, and

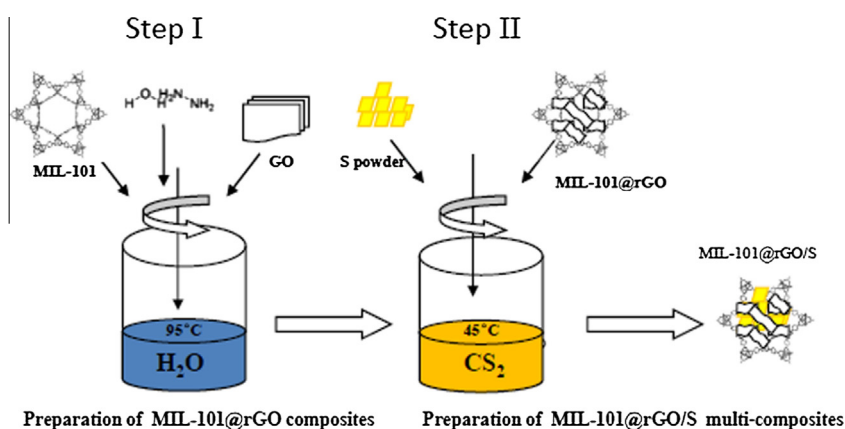


Fig. 1. Synthesis procedure of the MIL-101(Cr)@rGO/S multi-composites.

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