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Communication

Utilizing a metal as a sulfur host for high performance Li-S batteries

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ABSTRACT

Molybdenum, for the first time, was used as a new type of sulfur host for lithium-sulfur batteries and exhibited outstanding electrochemical performance, even over traditional porous carbon hosts. A Mo-S composite, with 80 wt% sulfur loading, delivered reversible capacities of 1003 mAh g^{-1} after 130 cycles at 0.1 C, and 786 mAh g^{-1} after 100 cycles at 5.0 C. Further analysis using in situ X-ray diffraction, cyclic voltammetry, and density functional theory calculations demonstrated that the Mo surface can not only effectively trap polysulfides, but also catalytically decompose polysulfides and Li_2S.

1. Introduction

Materials development in lithium-sulfur (Li-S) batteries has been driven by the recognition of favorable traits, such as its higher theoretical energy density compared to current lithium-ion batteries and the natural abundance of sulfur [1–5]. However, their practical applications are limited by a fast capacity decay, caused by the shuttling effect of lithium polysulfides (LiPSs) [5–9]. A sulfur host that can anchor the LiPSs has been proven to be capable of suppressing LiPSs shuttling, and thus enhancing the electrochemical properties. Various polar host materials, which can form strong polar-polar interactions between the LiPSs and the polar host [10], including modified carbon-based compounds [11–15], metal oxides [16–20], metal sulfides [21–23], polymers [24–26], MXenes [27,28], metal organic frameworks [29–31], and covalent organic frameworks [32,33], have been explored as sulfur hosts for Li-S batteries. Metallic powders are a natural choice due to their high conductivity and polarity, but they are rarely reported as sulfur hosts in the literature.

In this study, we are the first to choose molybdenum (Mo) to explore the advantages of a metal powder as a sulfur host. A Mo-S composite, with 60 wt% sulfur loading, delivered a reversible capacity of 1108 mAh g^{-1} after 130 cycles at 0.1 C, exceeding that of a porous carbon-S electrode, 837 mAh g^{-1} under the same condition. In addition, increasing sulfur loading to 80 wt%, a superior capacity of 786 mAh g^{-1} was achieved after 100 cycles at 5.0 C. Further analysis showed that the Mo surface can not only effectively trap LiPSs, but also catalytically decompose the LiPSs and Li_2S.

2. Experimental

2.1. Preparation of Mo-S and carbon-S composites

Mo powder and microporous carbon (Black Pearls 2000, CABOT) were degassed at 120 °C for 12 h, then mixed with sulfur in an Ar-filled glovebox. The mixture was ground for 30 min and sealed in a Pyrex tube. The final materials, Mo-S and carbon-S composites, were obtained by heating at 155 °C for 20 h with a rate of 0.5 °C min^{-1}.

2.2. Characterization

X-ray diffraction (XRD) analysis was carried out on a Smartlab (Rigaku) with filtered Cu Kα radiation (Rigaku D/max-2500, $\lambda = 1.5405$ Å). The morphology of the samples was characterized by a field emission scanning electron microscope (FESEM, Zeiss Ltd.) operated at 20 kV. Thermogravimetric analyses (TGA) were carried out under a N_2

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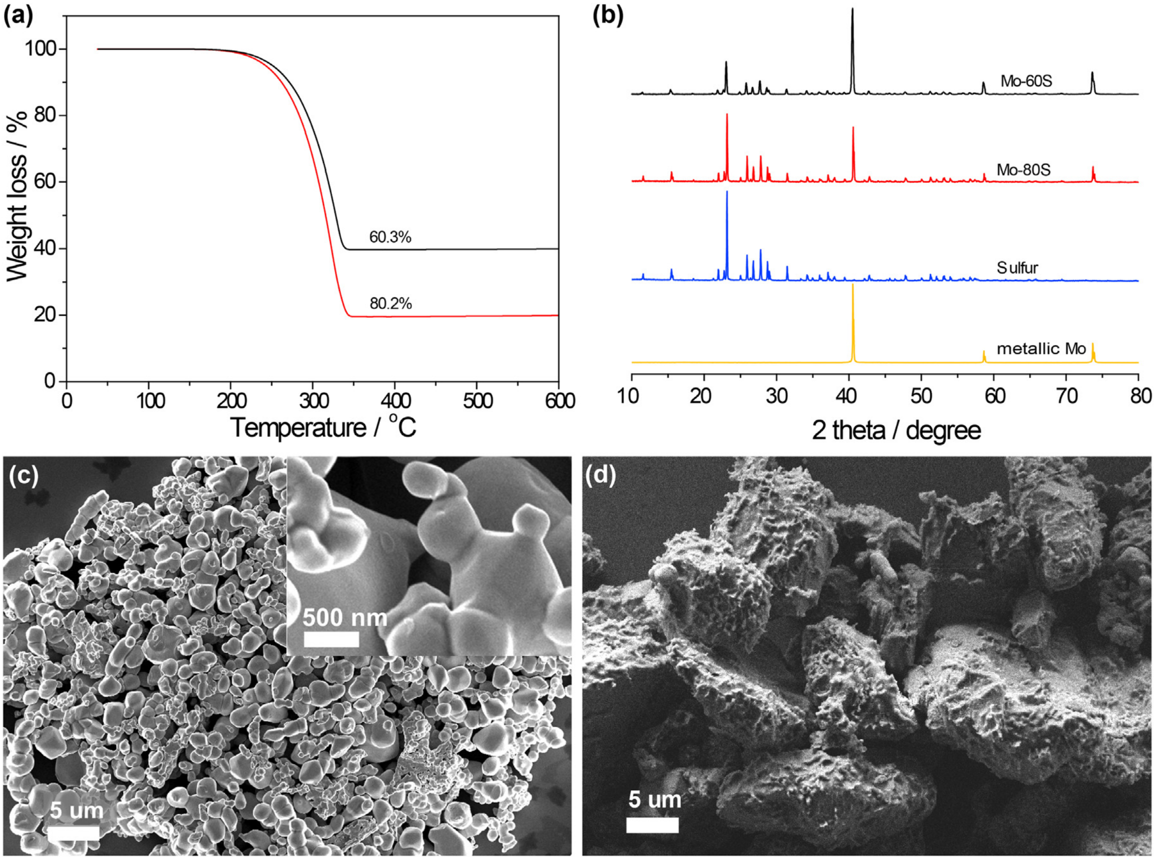

Fig. 1. (a) TGA curves of Mo-S composites in N_2; (b) XRD patterns of metallic Mo, S, and Mo-S composites; SEM images of (c) Mo powder and (d) Mo-S composite. The inserted image is a corresponding high-resolution image.

atmosphere on a TG 209F1 instrument at a heating rate of 10 °C min^{-1} from room temperature to 600 °C to detect the sulfur loading in the composites. X-ray photoelectron spectroscopy (XPS) analysis was carried out with an ECSALAB 250Xi high-performance electron spectrometer (Thermo Fisher Company).

2.3. Electrochemical measurements

The electrochemical performance was measured by assembling CR2016-type coin cells. Mo-S and carbon-S composites were mixed with carbon black and poly(acrylic acid) binder in N-methyl-2-pyrrolidinone (NMP) with a mass ratio of 70:20:10 to form slurries, which were coated onto aluminum foils and dried at 60 °C for 12 h under vacuum. The mass of sulfur loading in the composite electrodes ranged from 1.0 to 1.2 mg cm^{-2}. Microporous interlayers were fabricated by mixing carbon black and polyvinylidene fluoride binder (PVDF) in NMP with a mass ratio of 60:40 to form a slurry [8], coating it onto paper, and drying it at 80 °C for 12 h under vacuum. Coin cells were assembled in an argon filled glove-box using Li foil as the counter electrode and microporous interlayers with Celgard 2400 as the separators. The electrolyte was 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) in a 1:1 ratio (vol%). Cells were galvanostatically cycled on a battery test system (SLAN BT100, Wuhan) between 1.5 and 3.0 V at room temperature. A 1.0 M Li_2S_6 solution was prepared by reacting sulfur and Li_2S in the DOL/DME solvent (1:1, vol%) by stirring the mixture at 70 °C for 12 h in an argon filled glove-box. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were conducted on a VMP3 (bio-logic) electrochemical workstation.

2.4. In situ XRD tests

In situ XRD analysis was conducted with a home-made device, which was assembled in a glove-box. A beryllium (Be) window was used for X-ray beam transmission. The in situ XRD was performed on a Smartlab instrument (Rigaku) with filtered Cu Kα radiation (Rigaku D/max-2500, $\lambda = 1.5405$ Å) and a high power of 9 kW. *In situ* XRD was performed using sequential scans with each scan collected between 22° and 60° at a scanning rate of 20° min^{-1}.

3. Results and discussion

Mechanical mixing and thermal annealing were used to prepare the Mo-S composites in a quantitative manner, and the exact sulfur loadings were analyzed by using TGA. Based on the weight loss between 100 and 600 °C, the sulfur loadings of 60.3% and 80.2% were determined, indicating the Mo-60S and Mo-80S composites matched the designed loadings (Fig. 1a). The XRD patterns of Mo powder, sulfur, and the Mo-S composites are shown in Fig. 1b. Mo powders exhibit a body-center cubic structure. Both Mo and sulfur powders were in the pure phase. Compared to the XRD patterns of Mo and sulfur, the Mo-S composites share the typical peaks of both, indicating that the Mo-S composites consisted of Mo and sulfur that have no interaction. The particle sizes of the Mo powders range from 0.2 to 3.0 μm (Fig. S1) with quasi-spherical morphology, and the smooth surface of Mo particles was evident in the high-resolution FESEM image taken of the Mo powders (Fig. 1c). After sulfur loading, the surface of Mo particles clearly became rough, suggesting that Mo particles were covered by sulfur (Fig. 1d), which was further confirmed by the X-ray energy dispersive spectroscopy (XEDS) for elemental mapping (Fig. S2).

The electrochemical performance of the Mo-S composites was evaluated in the assembled coin cells (Fig. 2 and S3). Fig. 2a presents the cycling performance of the Mo-60S electrode at 0.1 C. The initial discharge and charge capacities were 1265 and 1169 mAh g^{-1}, respectively. After 130 cycles, the reversible capacity was retained at 1108 mAh g^{-1}. It should be mentioned here, the Mo host itself does not contribute to the capacity of the Mo-S electrode as it accounts for a