



# Lithium metal protection through *in-situ* formed solid electrolyte interphase in lithium-sulfur batteries: The role of polysulfides on lithium anode



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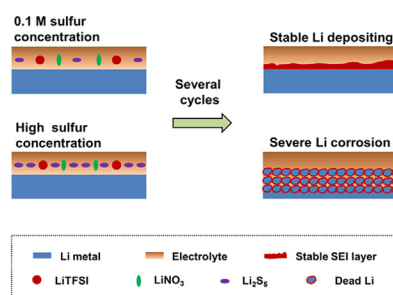
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## HIGHLIGHTS

- The failure mechanism of Li metal etching at a high sulfur loading in a Li-S cell.
- Excellent electrolyte additives for Li metal anode.
- New understanding towards electrolyte additive design used in Li-S batteries.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The dissolution and diffusion of Li polysulfide (LiPS) intermediates are regarded as one of the most serious problems for capacity decay and cell failure of lithium-sulfur (Li-S) batteries. Herein we proposed a failure mechanism of Li metal anode in Li-S cells based on the mechanistic investigation into the complex interactions between LiPSs and Li metal. The LiPSs participate the formation of inorganic layers in the solid electrolyte interphase (SEI) in a LiPS-LiNO<sub>3</sub> containing ether-based electrolyte. Li metal anode is well protected by the stable inorganic layer *in-situ* formed in an electrolyte containing 0.020 M Li<sub>2</sub>S<sub>5</sub> (0.10 M sulfur) and 5.0 wt % LiNO<sub>3</sub>. The metal anode with LiF-Li<sub>2</sub>S<sub>x</sub> riched SEI rendered a stable Coulombic efficiency of 95% after 233 cycles for Li-Cu half cells. A dendrite-free morphology of Li metal anode is observed under the harsh condition. When the LiPS is with a very high concentration of higher than 0.50 M sulfur in the organic electrolyte, the *in-situ* formed SEI cannot well maintain and the Li metal is gradually etched. Therefore, the polysulfide dissolution and diffusion should be delicately regulated to render a practical Li-S cell when the areal sulfur loading is high.

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## 1. Introduction

The steadily increasing attention toward ultralight portable electronics and electric vehicles stimulates an exponential growth of research interest on advanced rechargeable batteries with high energy/power density, superior safety performance, and long life-span. Unfortunately, the existing lithium-ion batteries, which have dominated the consumer device market, remain insufficient for the strong demand of advanced power sources [1]. Therefore, development of energy-storage systems with high energy density is urgently needed. Among various promising battery candidates, lithium-sulfur (Li-S) batteries with a high theoretical energy density of  $2600 \text{ W h kg}^{-1}$  are regarded as an attractive alternative [2]. The Li-S batteries also have the outstanding advantages of high natural abundance, low cost, and nontoxicity of sulfur for bulk applications [3–6].

Despite the considerable superiority of Li-S battery, there are several scientific obstacles hindering their practical applications [7–9]: (1) The intrinsically insulate nature of sulfur and the final discharging product ( $\text{Li}_2\text{S}$ ) induces the low utilization of active materials in electrochemical reactions; (2) The shuttle effect and parasitic reaction of Li polysulfide (LiPS) intermediates between anode and cathode leads to the severe capacity decay and poor lifespan of a full Li-S cell; (3) The formation of Li dendrites causes low energy efficiency and hazardous safety problems. By introducing high conductive nanocarbon and polar scaffolds as the cathode matrix, the conductivity of cathode is significantly improved, which makes the sulfur easy to participate the conversion reactions with  $\text{Li}^+$ . The strategies of physical confinement [10–14] and surface chemical adsorption of LiPSs in the cathode [15–19], interlayers [20–22], electrolyte additives [23,24], LiPS redox mediator [25], polyelectrolyte [26], and ion-selective separator [27,28] have been proposed to regulate the dissolution and diffusion of LiPSs. To inhibit dendrite growth on Li metal anode in a Li-S full cell, several strategies, such as electrolyte additive [29–33], high Li salt concentration [34], artificial protective layer for Li metal [35–38], high transference number electrolytes [39], nanoparticle hybrid electrolyte [40–42], all-carbon anode [43], structured metal anode [44,45], carbon [43,46–48]/silicon [49,50] based metal anode, hybrid anode structure [51,52], gel/solid electrolyte [53–55], and nanostructured framework [27,56,57] have been proposed.

The above-mentioned concepts effectively render a Li-S coin cell to more than 500 cycles with a discharging capacity of  $600\text{--}800 \text{ mAh g}^{-1}$  and a Coulombic efficiency of 92–99%. However, most of tests were achieved with a sulfur loading below 70% and an areal density below  $2.0 \text{ mg cm}^{-2}$  [58,59]. When the sulfur content in the cathode side is increased to  $4.0\text{--}10.0 \text{ mg cm}^{-2}$  for practical cells with high energy density, a large number of LiPS generates, dissolves into the electrolyte, and diffuses to the anode in a working cell [60]. A dramatic increase of LiPS concentration in the electrolyte induces rapid capacity decay and a low Coulombic efficiency even under the protective role of  $\text{LiNO}_3$  additive. The lifespan of the cell is severely limited. When the failed cell is dissembled, the shine Li metal anode becomes dark and the cell is almost dry in most cases. Attributed from the dynamic behavior of LiPSs in the electrolyte and complexity of a working cell based on conversion chemistry of Li and S active materials, the actual degradation mechanism, especially the failure of Li metal anode is a grand challenge.

Relative to the conventional Li metal-based batteries based on intercalation chemistry in conventional metal oxide cathode, dendrite issues in Li-S batteries are more serious and complicated due to the multi-electron conversion chemistry based on LiPS [61].

On one hand, the dissolved and shuttled LiPSs react with Li metal chemically to form  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  in the anode side. The low reactivity of  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  break away from the conductive matrix, resulting in irreversible capacity loss. On the other hand, the shuttled LiPSs participate in the formation of solid electrolyte interphase (SEI) [62–64], which is critically important for even Li depositing and therefore to improve the cycling efficiency. Consequently, LiPS intermediates are regarded as a double-edged sword in Li-S batteries. Exploring the positive role of LiPSs on the Li metal anode is not only critically important to suppress dendrite growth in anode side, but also fundamentally important to understand the shuttle behavior of a working Li-S battery, and thus to improve the discharging capacity, Coulombic efficiency, and long-term stability of practical Li-S cells.

In this contribution, we systematically investigated the role of LiPSs on the Li metal anode in a working Li-S battery. There are always continuous composition and concentration fluctuation of LiPSs in a working Li-S cell during charge/discharge cycle (Fig. 1a). Therefore, the role of polysulfides on the Li metal anode is very difficult to be clearly identified in a real Li-S cell. To mimic the actual composition of working cells and simplify the Li-S system,  $\text{Li}_2\text{S}_5$  was selected as model LiPS in a Li-Cu half-cell to probe the role of LiPS on Li metal anode (Fig. 1b). Herein,  $\text{Li}_2\text{S}_5$  with different concentrations was synthesized in the mostly accepted electrolyte (LiTFSI (1.0 M)-5.0 wt %  $\text{LiNO}_3$ -DOL/DME (1:1, in volume)) for practical Li-S batteries. A high  $\text{Li}_2\text{S}_5$  concentration electrolyte corresponds to a Li-S cell with high areal loading of sulfur in the cathode. The electrochemical performance based on electrolyte

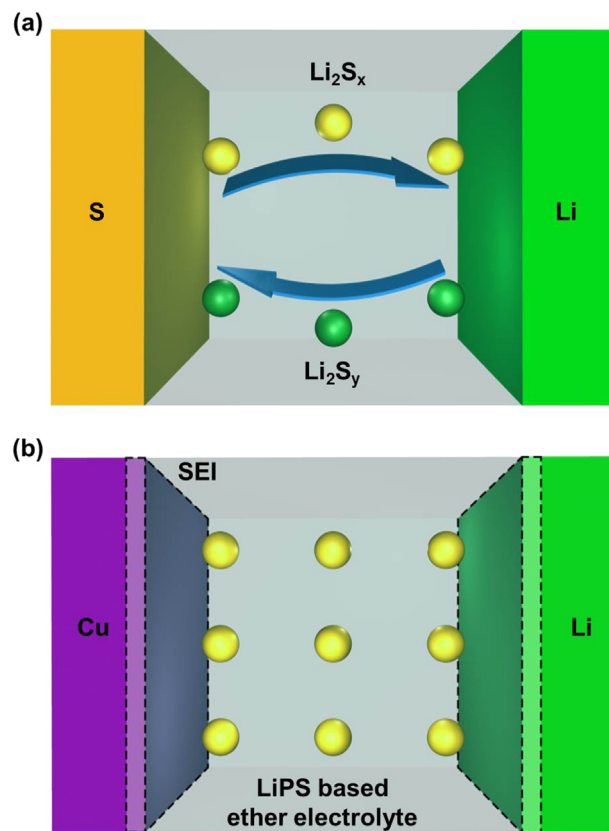


Fig. 1. Proof-of-concept of the role of LiPS on Li metal anode in a Li-S cell: (a) Conventional Li-S full cell, (b) designed Li|Cu half-cell with LiPS electrolyte to clearly discuss the role of LiPS on Li metal anode.

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