

# Pre-modified $\text{Li}_3\text{PS}_4$ based interphase for lithium anode towards high-performance Li-S battery

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## ABSTRACT

Due to the high theoretical specific capacity and energy density, lithium sulfur battery is regarded as a potential candidate for next generation energy storage devices. However, severe corrosion reaction between polysulfides and lithium anode causes the poor cycling stability and low coulombic efficiency. Herein, we demonstrate the construction of protective layer on lithium anodes by a spontaneous and rapid reaction between Li metal and the mixture solution of  $\text{P}_2\text{S}_5$  and S in THF. The main constituents of the protective layer are confirmed as a sulfide lithium ion solid electrolyte  $\text{Li}_3\text{PS}_4$  and its derivatives, which effectively stabilize the interphase of lithium anode and suppress the shuttle effect in the Li-S batteries, enabling the greatly enhanced cycling stability and Coulombic efficiency. With modification of lithium anode, the lithium sulfur batteries exhibit a specific capacity of  $840 \text{ mA h g}^{-1}$  after 200 cycles at 0.3 C with average Coulombic efficiency of 90.1% without  $\text{LiNO}_3$  additives in the electrolyte. Moreover, by applying  $\text{Li}_3\text{PS}_4$  modified Li anode, Li-S pouch cells with sulfur loading of  $3.8\text{--}4.2 \text{ mg cm}^{-2}$  deliver good cycling performance of  $803 \text{ mA h g}^{-1}$  with average Coulombic efficiency of 90% after 20 cycles. Hence, introducing sulfide solid electrolyte as protective layer of Li anode provides a new strategy for the improvement of lithium sulfur batteries.

## 1. Introduction

Since conventional lithium ion batteries can't satisfy the increasing demands for high power application, scientists have paid more attention to the improvement of the next generation energy storage [1]. Sulfur cathode possesses a high theoretical energy density ( $2600 \text{ Wh kg}^{-1}$ ) and specific capacity ( $1675 \text{ mA h g}^{-1}$ ). Besides, because of the cost effective, abundant and eco-friendly of sulfur, metal-sulfur system possesses bright future in enlarged commercialization of portable energy storage [2]. In order to achieve a higher energy density, Li metal anode which possesses low electrode potential ( $-3.04 \text{ V}$  vs standard  $\text{H}^+/\text{H}_2$  electrode) and high capacity ( $3860 \text{ mA h g}^{-1}$ ) is recommended and essential [3]. Unfortunately, more challenges will be introduced by the direct usage of lithium metal anode, including the dendrite growth, pulverization, and corrosion reaction [3–7]. Dendrite growth will trigger short circuit and cause latent danger of Li-metal based batteries. Due to the large volume change of Li anode during the plating and stripping process, Li would pulverize and broke away from

the current collector, which significantly shortened the life of the batteries [6]. Moreover, the corrosion reaction towards Li anode will lead to low Coulombic efficiency and excessive consuming of Li [3,6,8,9]. In order to overcome the drawbacks of the lithium anode, considerable efforts have concentrated on nanostructure design of lithium anode, optimization of electrolyte additives and ex-situ lithium anode protection [3,6,8,10–13]. Nanostructure designs, including 3D current collectors and various kinds of porous hosts, were widely applied and significantly suppressed the dendrite growth by reducing the current densities of lithium anode [10,14–17]. However, contrary to other battery systems, as the dissolved polysulfide may help to suppress the growth of dendrite on the lithium, corrosion and pulverization of lithium anode are more specific and ubiquitous in the lithium sulfur system [9]. Therefore, constructing stable and protective solid electrolyte interphase (SEI) film on the lithium anode have been proved as a more concise and efficient strategy for the practical application of lithium anode in Li-S batteries. Electrolyte additives, such as  $\text{LiNO}_3$ , were contributed to form in-situ passivation

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layers on the surface of lithium anode, which helped to hinder the subsequent corrosion reaction [18,19]. Nevertheless, the electrolyte additives still cannot satisfy the demands for practical application. Not only  $\text{LiNO}_3$  will produce gas during the cycling, which is a fatal phenomenon for the assembling of pouch battery, but strong oxidation of  $\text{LiNO}_3$  may introduce safety issues [20]. Ex-situ protection of lithium anode is another feasible approach in lithium sulfur battery. The protective layer, working as an artificial SEI on lithium anode, can hinder the side corrosion reactions with electrolyte and dissolved polysulfide [12,21–24]. Besides, the protective layer will impede the unsafe stripping and deposition of lithium anode [25,26]. According to the latest reports on the lithium sulfur batteries, inorganic compounds (eg.  $\text{Li}_3\text{N}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{LiIO}_3$ ), various kinds of polymer (PEDOT-PEG) and carbon based matrices (graphite) have been verified to be effective protective materials for lithium anode in the lithium sulfur batteries [12,21,27–30].

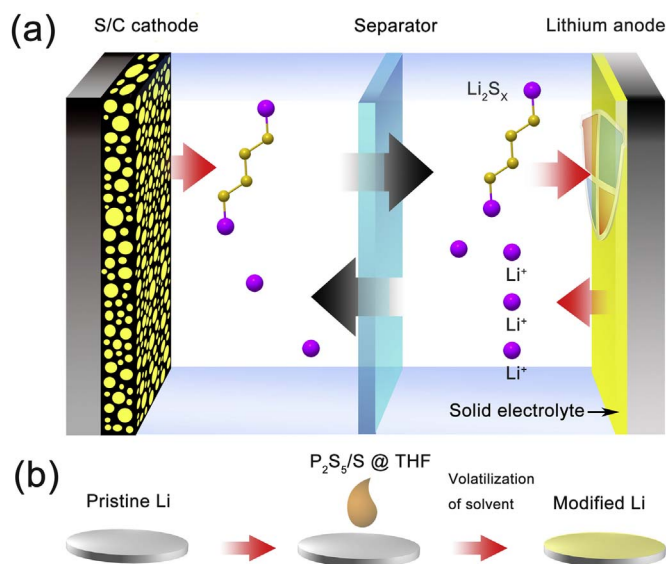
In order to improve the stability of the SEI without sacrificing the lithium ionic transfer, selecting an appropriate chemical substance is of great concern in constructing protective layer on the lithium anode [31]. Inorganic lithium ion conductors are good candidates as anode protective layers in lithium sulfur batteries. In particular, sulfide lithium conductors possess high lithium ion transfer conductivity, some of which with simple chemical constitution (e.g.  $\text{Li}_3\text{PS}_4$ ) could be easily synthesized via wet chemical method [13,32]. Hence a smart incorporation of the sulfide lithium ion conductors with the lithium anode would further create plenty of opportunities.

In this work, we discovered spontaneous and rapid reaction between Li metal and the THF solution of  $\text{P}_2\text{S}_5$  and S which was utilized to construct  $\text{Li}_3\text{PS}_4$  based protective layer on Li metal (Scheme 1). Compared to the metallic sulfides,  $\text{Li}_3\text{PS}_4$  possesses better stabilization and compatibilities against Li metal [33]. With the protected Li anode by this ex-situ reaction, Li-S batteries delivers the specific capacity of  $840 \text{ mA h g}^{-1}$  at 0.3 C, with average Coulombic efficiency of more than 90%. Furthermore, the rate capabilities and the suppression of self-discharge phenomenon are also greatly developed with the modified Li anode.

## 2. Experimental section

### 2.1. Pre-treatment for the lithium metal anode

15 mg  $\text{P}_2\text{S}_5$  and 4 mg sulfur were added into 4 mL tetrahydrofuran



**Scheme 1.** (a) Schematic model of the lithium anode modification in lithium sulfur batteries and (b) schematic process of the modification to Li anode.

(THF) and the mixture was fully stirred before using. 50  $\mu\text{L}$  of the mixture solution was dropwise added on one side of the lithium anode, and the process was repeated twice. After the reaction, the modified anodes were dried under room temperature in vacuum for 48 h to completely evaporate the solvent. To optimize the modification, the amount of mixture solution was adjusted among 50, 100, 150 and 200  $\mu\text{L}$  mixture solution, respectively. Then the modified anode by different amount of mixture solution were assembled into coin cells. 100  $\mu\text{L}$  is an optimized amount which is demonstrated in Fig. S1. The following experiments are carried out by using the optimized amount of mixture solution.

### 2.2. Preparing of the sulfur electrode

The sulfur/carbon composite was prepared by the following steps: sulfur and Ketjen Black was mixed in the weight ratio of 2:1. After the ball milling for 4 h, the mixture was heated at  $155^\circ\text{C}$  for 24 h. The slurry with sulfur/carbon composites, super P carbon, and styrene-butadiene rubber (SBR) and carboxyl methyl cellulose (CMC) in weight ratio of 80%, 10%, 5%, 5%, respectively, was prepared by ball milling, then was coated on the aluminum foils. After fully drying in vacuum, the electrode was cut into 12 mm diameter disks. The sulfur loading amount of the electrode was  $1.5\text{--}2 \text{ mg cm}^{-2}$  in the coin cells and the mass loading of sulfur in pouch cell reached  $3.8\text{--}4.2 \text{ mg cm}^{-2}$ . The electrolyte was the solution composed of 1 M  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (LiTFSI) solved in the mixed solution of dimethyl ether (DME) and 1,3-dioxolane (DOL) in an equal volume ratio without  $\text{LiNO}_3$  additives. CR2025 coin cells and pouch cells were assembled in an argon filled glove box with the contents of water and oxygen below 0.1 ppm.

### 2.3. Characterization

SEM images were obtained by scanning electron microscope (SEM, Hitachi JSM 6700). Electrochemical analysis including cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were carried out on an Autolab electrochemical workstation (ECO CHEMIE B.V, Netherlands) with the Frequency Response Analyzer. The charge and discharge profiles for the cells were measured a LAND CT2001A battery test system (China) in voltage range from 2.6 to 1.5 V. Fourier transform infrared spectra (FTIR Nicolt IS10 FTIR analyzer) were tested in argon filled glove box to prevent the influence of moisture and oxygen. X-ray photoelectron microscopy (XPS Thermo scientific ESCALAB 250) was applied to analyze the chemical state of various elements on the lithium surface. All the samples for XPS examination were prepared in an argon filled glove box.

### 2.4. Theoretical calculation

Calculations of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy of DME, DOL, LiTFSI and  $\text{Li}_3\text{PS}_4$  was adopted for the anticipation of the interfacial stability between the protective layer and the electrolyte components by Gaussian 09 programs based on Density Functional Theory (DFT) [34,35]. The calculation processes were performed by B3LYP 6-311G+ + (d,p) function [34].

## 3. Results and discussion

### 3.1. The characterization of modified lithium anode

The preparation of the protective layer is based on the treatment of lithium metal in  $\text{P}_2\text{S}_5/\text{S}$  solution. The action of constituent of the mixture solution on lithium metal surface is confirmed separately. As shown in Fig. 1a, it is easy to be discovered that the combinatorial  $\text{P}_2\text{S}_5$  and S in THF react with lithium metal spontaneously and quickly. After adding the mixture solution to lithium anode, the surface of lithium

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