

Sulfurized solid electrolyte interphases with a rapid Li⁺ diffusion on dendrite-free Li metal anodes



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ABSTRACT

The notorious growth of Li dendrites significantly shortens the longevity and raises safety concerns of high-energy-density Li metal batteries. We proposed a sulfurized solid electrolyte interphase (SEI) to protect Li metal anode in a working Li metal battery. By incorporating Li₂S into the interphase, a polycrystalline and mosaic SEI film with poor crystallinity was achieved. Li₂S, Li₂O, Li₃N, LiNO₃, and LiF nanoparticles were embedded in the sulfurized SEI. A high ionic conductivity of $3.1 \times 10^{-7} \text{ S cm}^{-1}$ was achieved for the sulfurized SEI, around one magnitude higher than that of the routine SEI ($4.2 \times 10^{-8} \text{ S cm}^{-1}$). Therefore, uniform plating/stripping of the Li metal was achieved without Li dendrite formation. The sulfurized SEI enabled stable cycling of Li | Li cells for 500 h at 1.0 mA cm^{-2} and for 150 h at 5.0 mA cm^{-2} . With the protection of a sulfurized SEI film, Li metal anode exhibited a high Coulombic efficiency of 98% during 200 cycles at 1.0 mA cm^{-2} , while the Coulombic efficiency drastically dropped to 70% at the 200th cycle on Li metal anode with routine SEI. The pouch cells exhibited a plating resistance of -331 and -108 mV , a stripping resistance of 67 and 54 mV on Li metal anode with routine and sulfurized SEI films, respectively. The sharply decreased resistance, endowed by the sulfurized SEI, further suggested the rapid Li ion diffusion in working Li-metal batteries. This affords new insights into the SEI structure and its critical role in Li metal protection, and sheds a fresh light on the rational design of electrolyte additives and SEI film in a working Li metal battery.

1. Introduction

Li metal battery has received extensive attentions because of its very high theoretical energy density [1–4]. The strong request on the high-energy-density storage systems renders the revisit of Li metal anodes, which have been sidelined by the commercial application of graphite anode in the 1990s [3,5–8]. Metallic Li is a promising candidate as anode material due to its very high theoretical capacity (3860 mAh g^{-1}) and the lowest electrochemical potential (-3.040 V vs. the standard hydrogen electrode) [9]. When fresh Li metal contacts with the electrolyte, parasitic reactions occur and consequently, a solid electrolyte interphase (SEI) film is formed on the surface of Li metal. As a result of the inhomogeneity of SEI, Li dendrites preferably form and grow during Li plating/stripping at a large current density [10]. The dendritic growth of Li results in low efficiency, short lifespan, and

safety dilemma. All these issues drag Li metal batteries (LMBs) still in infancy [7]. With the rising of advanced material chemistry, new insights into the suppression of dendrite growth and stabilization of Li metal have been substantially explored through strategies of liquid electrolyte additives [11–18], solid/polymer electrolytes [19–27], *ex-situ* coating [28–30], and structured anode [31–42], etc.

An ideal SEI film must have a high mechanical modulus, poor electrical conductivity, and rapid Li-ion diffusion rate to suppress Li dendrite growth [7,43–47]. The SEI can be regarded as an ultrathin solid electrolyte attached to the anode and the ionic conductivity is one of the most important indices of its performance. According to the Sand's time model, dendritic Li starts to grow when Li ions on anode surface are fully depleted, which is easily induced by low ionic conductivities [32]. Lu et al. demonstrated that the highly resistive layer of Li metal anodes caused the escalation of the cell's impedance

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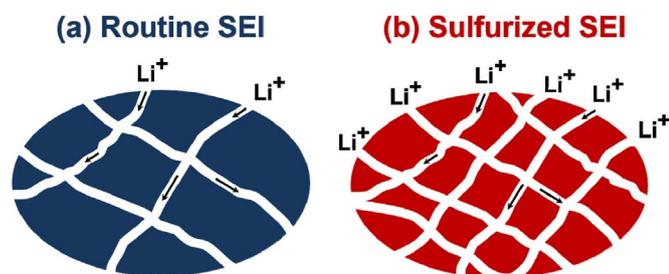


Fig. 1. Schematic diagrams describing the ion diffusion channels in the (a) routine and (b) sulfurized SEI films.

and early termination of the cell's cycle life [48]. A SEI with high Li-ion diffusion rate is therefore highly beneficial to a safe and efficient Li metal anode.

Inspired by the highest ionic conductivity (around 10^{-2} S cm^{-1} at room temperature) of crystalline sulfide solid electrolyte [49,50], we proposed a sulfurized SEI film with high Li-ion diffusion rate to suppress dendrite growth and improve cycling stability of Li metal anode. The sulfurized SEI is achieved by the direct contact of fresh Li metal with a lithium polysulfide (Li_2S_x) – lithium nitrate (LiNO_3) – lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) electrolyte. Compared to the routine SEI formed in Li_2S_x -free electrolyte, the sulfurized SEI possessed enriched grain boundaries and therefore afforded more channels for Li-ion diffusion, leading to a higher ionic conductivity (Fig. 1).

2. Results and discussion

LiNO_3 -containing electrolyte has been considered as an ideal system to protect Li metal in a working Li–S cell [51,52]. A SEI film consisting of both inorganic species (e.g. $\text{Li}_2\text{N}_x\text{O}_y$ and $\text{Li}_2\text{S}_x\text{O}_y$) and organic species (e.g. ROLi and ROCO_2Li) is obtained through the strong oxidation by LiNO_3 [53,54]. However, Li protection through LiNO_3 failed in practical pouch cells when the current density was drastically raised due to the large ion diffusion resistance and continuous consumption of LiNO_3 during long cycling test (Fig. S1) [55]. When polysulfides were added into the electrolyte, except for the well-maintained components produced by LiNO_3 (Fig. 2a and S2), Li_2S was also observed in the sulfurized SEI (Fig. 2a). Though LiTFSI also contained the sulfur element, no Li_2S formation was observed in the polysulfide-free electrolyte. Li_2S was only formed with the presence of polysulfides in the electrolyte [56–60].

To probe the structure of sulfurized SEI, selected area electron diffraction (SAED), high resolution transmission electron microscopy (HRTEM), and time-of-flight secondary ion mass spectrometer (TOF-SIMS) were carried out. Polycrystalline nature of both routine and sulfurized SEI films was clearly validated as SAED patterns illustrated (Fig. 2b and c). The weak diffraction intensity of sulfurized SEI indicated the small grain size in the sulfurized SEI. The HRTEM image of sulfurized SEI confirmed the classical mosaic-like structure of SEI films (Fig. 2d). Various inorganic nanocrystals, including Li_2S , Li_2O , Li_3N , LiNO_3 , LiF were embedded in the sulfurized SEI. The TEM image of the routine SEI was also conducted (Fig. S3). There are two critical difference between the routine and sulfurized SEI films: (1) The crystal size of the routine SEI is much larger than that of the sulfurized SEI, indicating the role of Li_2S in the sulfurized SEI to reduce the crystal size. (2) The images of routine SEI is a little hazy, which is caused by the thick layer of the organic layer of SEI. The increase in the component of the organic layer is not good for the high ionic conductivity of the SEI film [15]. Therefore, the sulfurized SEI film is expected to exhibit a high ionic conductivity.

To characterize the spatial uniformity of the sulfurized SEI, TOF-SIMS elemental surface-mapping and X-ray photoelectron spectro-

scopy (XPS) depth profiles of the Li metal cycled in the polysulfide-containing electrolyte were collected (Fig. S4). Li_2S species were observed not only in the surface but also in the internal layer of sulfurized SEI. Elemental Li, C, O, S, and F exhibited homogeneous distribution in the sulfurized SEI. After the removal of O, C-enriched surface (mainly consisted of less stable organic components) by sputtering, more stable inorganic species (indicated by elemental Li, S, F, and N) were well maintained, exhibiting desirable spatial uniformity in the sulfurized SEI.

The combinatorial results of SAED, HRTEM, XPS, and TOF-SIMS revealed the structure of routine and sulfurized SEI films, respectively (Fig. 2e and f). Li polysulfides in the electrolyte induce the generation of Li_2S nanocrystals during SEI formation. In the resultant sulfurized SEI, Li_2S nanocrystals act as ‘nanopins’ to interrupt the growth of other inorganic crystals. This can be ascribed to the rapid formation of Li_2S and large ionic radius of S^{2-} in Li_2S [61], regulating the rates of parasitic reactions and crystal growths during SEI formation. Therefore, the crystal size of individual SEI components is reduced, resulting in a polycrystalline and mosaic SEI film with poor crystallinity. The enriched grain boundaries are believed to serve as rapid Li-ion diffusion channels.

Poor crystallinity usually leads to superior Li-ion conductivity in solid electrolytes [61]. Li_2S itself is a poor ionic conductor [62]. However, the SEI structure was regulated by Li_2S ‘nanopins’ and the resultant poor crystallinity and enriched grain boundaries improved the Li-ion conductivity synergistically. Such effect was confirmed by quantitative measurements of Li-ion diffusivities in SEI through electrochemical impedance spectra (EIS) (Fig. 2g–i). After Li ion plating and stripping from Cu foil current collector at 1.0 mA cm^{-2} , the cell with sulfurized SEI on lithium anode exhibited much smaller diffusion resistances than those of the cell with routine SEI (Fig. 2g). By adopting the circuit model to interpret the EIS, Li-ion diffusion resistance in the SEI layer (R_{SEI}) was obtained (Fig. S5). R_{SEI} of the sulfurized SEI was smaller than that of the routine SEI (Fig. 2h). If the average thickness of a SEI film was assumed to be 50 nm [45], a high ionic conductivity of $3.1 \times 10^{-7} \text{ S cm}^{-1}$ was achieved for the sulfurized SEI, around one magnitude higher than that of the routine SEI ($4.2 \times 10^{-8} \text{ S cm}^{-1}$) (Fig. 2i). The as-obtained ionic conductivity of the sulfurized SEI is almost among the highest data for the ultrathin solid electrolytes (such as LiPON) [61,63]. Not only the first cycle, Li | Cu cells with the sulfurized SEI indicated a much reduced resistance after 1st, 10th, 50th, and 100th cycles compared to the cells with routine SEI (Fig. S6).

The morphological evolution of Li deposits was firstly investigated by probing the role of sulfurized SEI (Fig. 3a). After 3 h continuous depositing at 0.5 mA cm^{-2} , Li deposits underneath a sulfurized SEI film were compact and uniform, which was preferable for a highly safe and efficient LMB. In contrast, a rugged and inhomogeneous surface was obtained with the routine SEI. The inhomogeneous region served as nucleation sites for dendrite growth after long-term cycling and at high current densities. After the 50th depositing of 1.0 mAh cm^{-2} Li at 1.0 mA cm^{-2} , a large amount of highly resistive porous Li was observed on the electrode surface with a routine SEI, corresponding to the strong ion diffusion resistance. Even worse, Li dendrites formed after 200 cycles (Fig. S7a). On the contrary, the sulfurized SEI rendered the surface of electrode less porous after 50 cycles and maintained dendrite-free morphology even after 200 cycles (Fig. S7b).

The Li metal anode with a sulfurized SEI was then evaluated in a Li | Li symmetric cell for long-term cycling. At 1.0 mA cm^{-2} / 1.0 mAh cm^{-2} , both the routine and sulfurized SEI enabled stable cycling for 500 h with a voltage hysteresis of $\sim 30 \text{ mV}$ (Fig. S8). This was ascribed to the protection by LiNO_3 . However, cycling at higher current densities suggested the inefficiency of LiNO_3 . At 5.0 mA cm^{-2} / 5.0 mAh cm^{-2} , the sulfurized SEI film still maintained a voltage hysteresis of 60 mV constantly for 150 h (Fig. 3b). Whereas for the Li anode with a routine SEI, the voltage hysteresis gradually rose to

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