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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 highenergy-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 3.1×10^{-7} S cm⁻¹ was achieved for the sulfurized SEI, around one magnitude higher than that of the routine SEI (4.2×10^{-8} 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 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], *exsitu* 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 (Li₂S_x) – lithium nitrate (LiNO₃) – lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) electrolyte. Compared to the routine SEI formed in Li₂S_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

LiNO₃-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.* Li₂N_xO_y and Li₂S_xO_y) and organic species (*e.g.* ROLi and ROCO₂Li) is obtained through the strong oxidation by LiNO₃ [53,54]. However, Li protection through LiNO₃ failed in practical pouch cells when the current density was drastically raised due to the large ion diffusion resistance and continuous consumption of LiNO₃ during long cycling test (Fig. S1) [55]. When polysulfides were added into the electrolyte, except for the well-maintained components produced by LiNO₃ (Fig. 2a and S2), Li₂S was also observed in the sulfurized SEI (Fig. 2a). Though LiTFSI also contained the sulfur element, no Li₂S formation was observed in the polysulfide-free electrolyte. Li₂S 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 Li₂S, Li₂O, Li₃N, LiNO₃, 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 Li2S 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 spectroscopy (XPS) depth profiles of the Li metal cycled in the polysulfidecontaining electrolyte were collected (Fig. S4). Li₂S 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 Li₂S nanocrystals during SEI formation. In the resultant sulfurized SEI, Li₂S nanocrystals act as 'nanopins' to interrupt the growth of other inorganic crystals. This can be ascribed to the rapid formation of Li₂S and large ionic radius of S²⁻ in Li₂S [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 Liion diffusion channels.

Poor crystallinity usually leads to superior Li-ion conductivity in solid electrolytes [61]. Li₂S itself is a poor ionic conductor [62]. However, the SEI structure was regulated by Li2S '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 3.1×10^{-7} 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 ~30 mV (Fig. S8). This was ascribed to the protection by LiNO₃. However, cycling at higher current densities suggested the inefficiency of LiNO₃. 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



Fig. 2. Component and structure of sulfurized SEI. (a) XPS spectra of S 2p species in the routine and sulfurized SEI. SAED patterns of the (b) routine and (c) sulfurized SEI. (d) A HRTEM image of the sulfurized SEI. Mosaic models of the (e) routine and (f) sulfurized SEI (The green patches present the incorporated Li₂S components). (g) EIS of Li | Cu cells with different SEI films. The calculated (b) Li-ion diffusion resistance and (c) ionic conductivity of SEI films based on the EIS data in (g).

120 mV after 50 h, which was ascribed to the highly resistive layer of routine SEI. The superb and persistent Li-ion diffusion behaviours within sulfurized SEI was thereafter validated.

Li utilization during repeated depositing/stripping was indicated by the Coulombic efficiency of Li | Cu cells. At $1.0 \text{ mA cm}^{-2}/1.0 \text{ mAh cm}^{-2}$, the sulfurized SEI enabled coin cells with a Coulombic efficiency (CE) of ~98% during 200 cycles (Fig. 3c). Stable cycling during the first 120 cycles with a CE of 97% was initially realized by the routine SEI. Nevertheless, the CE drastically dropped to 70% at the 200th cycle. Because of the highly resistive layer, Li-ion flux became highly inhomogeneous, inducing dendrite growth. The Li dendrites pierced the routine SEI and were further exposed to the electrolyte. Progressive consumption of Li and electrolyte finally lowered the CE after long-term cycling [55].

To demonstrate the feasibility of sulfurized SEI in practical applications, Li | Cu cells were tested in pouch-cell configuration with high loading of active materials and high areal current density. Compare with coin cell, Li deposition in pouch cell is much more challenging to overcome the inhomogeneous distribution of local currents, to suppress the Li dendrite growth, and to realize high utilization of Li. The pouch cell with a routine SEI on the Li metal failed after 80 cycles (Fig. 3d). In contrast, the sulfurized SEI enabled a



Fig. 3. Morphological evolution and cycling performance of Li metal anodes. (a) SEM images of Li deposits with the routine and sulfurized SEI after the 1st continuous Li platting for 3 h at 0.5 mA cm⁻² and the 50th platting of 1.0 mA cm⁻². (b) Voltage-time curves of Li | Li symmetrical coin cells cycled at 5.0 mA cm⁻²/5.0 mAh cm⁻². Coulombic efficiency of Li | Cu (c) coin and (d) pouch cells at 1.0 mA cm⁻²/1.0 mAh cm⁻².

relatively stable CE of *ca.* 90% and extended longevity of over 200 cycles.

The polarization induced by Li-ion diffusion through the SEI was further probed (Fig. 4). The charge-discharge curves of Li | Cu coin (Fig. 4a) and pouch cells (Fig. 4d) illustrated the combinatorial effects of the Li-ion diffusion in the SEI and the barrier of Li nucleation/ dissolution in the phase transition between Li ions and Li metal. In a typical discharging curve, a large voltage dip firstly emerged at the beginning of Li platting, followed by a flat voltage plateau (left part in Fig. 4b and e). Correspondingly, the voltage bumps in the charging curves corresponded to the resistance of Li stripping (right part in Fig. 4b and e). In a coin cell, routine and vulcanized SEI films indicate a plating restance of -86 and -60 mV, stripping resistance of 62 and 34 mV, respectively (Fig. 4b). Therefore, sulfuration of SEI film can effectively reduce the restance for Li depositing and stripping. The difference in resistance of routine and sulfurized SEI films was much magnified in pouch cells with high loading of active materials. Routine and vulcanized SEI films in pouch cells indicate a plating restance of -331 and -108 mV, stripping resistance of 67 and 54 mV, respectively (Fig. 4e). The sharply decreased resistance, endowed by the sulfurized SEI, futher suggested the rapid Li-ion diffusion.

Long-term voltage hysteresis calculated by the difference value between charging and discharging voltage plateau was recorded. For the coin cell, routine SEI indicates the largest voltage hysteresis of 156 mV in 1st cycle (81 mV for vulcanized SEI) (Fig. 4c). After 190 cycles, the hysteresis of routine SEI is still nearly two times larger than that of vulcanized SEI (51 and 29 mV for routine and vulcanized SEI). Li ion diffusion behavior of Li | Cu pouch cells was also recorded (Fig. 4f). The sulfurized SEI realized a small and stable hysteresis in 200 cycles, while the hysteresis of routine SEI, was dramatically increased. More importantly, a sharp increase in the hysteresis at 80th cycle was observed, which was perfectly consistent with the moment when the CE dropped steeply (Fig. 3d). This was a critical evidence to denote the failure of Li anodes with a routine SEI that the drastic increase in Li-ion diffusion resistance accounted for. Hence, the poor crystallinity and rich grain boundaries are the key of the sulfurized SEI as the two desired merits significantly promote the Li-ion conductivity within SEI. Stable cycling, high Li utilization, and small polarization are thereby ensured.

As with solid electrolyte, ionic conductivity is one of the most important indicators for a robust SEI. Li_2S_5 in the electrolyte renders Li_2S 'nanopins' in the SEI, which generates a sulfurized SEI with a polycrystalline mosaic-like structure and rapid Li ion diffusion rate.



Fig. 4. Voltage polarization in the Li | Cu cells. (a) 1st charging/discharging curves, (b) enlarged views of marked areas in (a), (c) voltage hysteresis of Li | Cu coin cells. (d) 1st charging/discharging curves, (e) enlarged views of marked areas in (d), (f) voltage hysteresis of Li | Cu pouch cells.

LiNO₃ is habitually believed to be effective in protecting Li metal anode by forming a stable SEI film (routine SEI herein). It fails in pouch cells due to the ever-increasing voltage polarization [55]. This is a totally new perspective to elucidate the failure mechanism of LiNO₃ electrolyte. Even so, Li₂S₅ alone cannot maintain a stable cycling of Li metal anode (Fig. S9). Though Li₂S content is still in the SEI film, the other contents caused by LiNO₃ exist no more (Fig. S10). The highly reactive nature between Li₂S₅ and Li metal can account for the failure of Li₂S₅ additive. The new perspectives shed herein can be summarized below:

- (1) A sulfurized SEI is constructed. By incorporating Li₂S 'nanopins' into the polycrystalline mosaic-like SEI film, the crystallinity is reduced and ionic conductivity is vastly improved from 4.2×10^{-8} to 3.1×10^{-7} S cm⁻¹.
- (2) The cognition on SEI is critically reinforced. Though SEI plays a vitally important role in Li plating /stripping process, understanding on SEI component, structure, and its influence on cell performance are still limited. By firstly clearly characterizing the mosaic structure of SEI film and the acquisition of its ionic conductivity, the cognition on SEI is greatly enriched, which can promote the understanding of SEI and cell performance.

- (3) New failure mechanism of LiNO₃ electrolyte and solution are proposed. By clear investigation of EIS data and voltage polarization in long-term cycling, a conclusion can be easily reach that the ever-increasing Li ion diffusion resistance contributes to the failure of LiNO₃ electrolyte. More channels presented by sulfurized SEI can solve the issue effectively.
- (4) New philosophy to design a robust SEI film is proposed. An ideal SEI is expected to have a high modulus to block the penetration of dendrites and high ionic conductivity to realize a superior long-term cycling performance [64–66]. However, these two characteristics seem conflicting, because blocking the penetration of dendrites needs compactness, while high ionic conductivity requires more channels. The dilemma can be perfectly handled if the role to suppress Li dendrite is vacated to the efficiently designed anode and the SEI film only function to facilitate Li ion diffusion and protect Li metal from the corrosion of electrolyte.

3. Conclusions

We proposed a sulfurized SEI for highly stable, safe, and efficient dendrite-free Li metal anodes by incorporating Li_2S 'nanopins'. Li_2S

nanocrystals rendered a polycrystalline mosaic-like SEI film with poor crystallinity and rich grain boundaries. The Li-ion diffusion rate was therefore enhanced to suppress Li dendrite growth and improve the CE of Li metal anodes. Sulfurized SEI withstood harsh Li plating/stripping at a very high current density of 5.0 mA cm^{-2} and a high capacity of 5.0 mA cm^{-2} for long-term cycling, and even in pouch cells. These results provide new insights into the SEI structure and its role in the stability of Li metal anode, shedding fresh lights on the designing principles of electrolyte additives and SEI film in a working LMB.

4. Experimental section

4.1. Materials

Li metal is commercially available from China Energy Lithium Co., Ltd. The ether based electrolyte composed of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (1.0 M) dissolving in 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) with a volumetric ratio of 1:1 was purchased from Beijing Chemical Industry Group Corporation. S, Li₂S, and LiNO₃ powders were purchased from Alfa Aesar. Li₂S₅ was obtained by the stoichiometric reaction between S and Li₂S. The routine electrolyte was obtained by dissolving 5.0 wt% LiNO₃ into the LiTFSI-DOL/DME electrolyte. The Li₂S₅ electrolyte was obtained by dissolving 0.02 M Li₂S₅ into the LiTFSI-DOL/DME electrolyte with 5.0 wt% LiNO₃.

4.2. Electrochemical measurements

The Li | electrolyte | Cu and Li | electrolyte | Li cells were employed to investigate the plating/stripping processes which assembled in the 2025-type coin cells (MTI Corporation). All cells were assembled in an Ar-filled glove box with O2 and H2O content below 1.0 ppm. The Li | Cu cells were tested in a galvanostatic mode at a density of 1.0 mA cm⁻²/ 1.0 mAh $\rm cm^{-2}$ within a voltage range of $-0.5-0.5\,\rm V$ with a Neware multichannel battery cycler. The discharge process is time-controlled (1.0 h), while the charge process is voltage-controlled (0.5 V). The pouch cells was constructed with 2×3 configuration, meaning two pieces of Li metal and three pieces of Cu foil in pouch cells. The cells have two pieces of Li metal as the anodes and three pieces of Cu foil as the cathodes to assemble into four parallel circuits (Fig. S11). The Li | Li coin cells were tested in a galvanostatic mode at a density of $1.0~\mathrm{mA~cm^{-2}/1.0~mAh~cm^{-2}}$ and $5.0~\mathrm{mA~cm^{-2}/5.0~mAh~cm^{-2}}$ within a voltage range of -0.5-0.5 V with Neware multichannel battery cycler. The discharge and charge processes are controlled by the time (1 h). The interfacial resistance is tested *via* EIS measurement $(0.1-10^5 \text{ Hz})$ with Solartron 1470E electrochemical workstation. The Voltage hysteresises in Figs. 3b, 4c and f were obtained by the difference value of charge and discharge voltage at midpoint capacity.

4.3. Characterization

The morphology of Li deposits was characterized by a JSM 7401F SEM operated at 3.0 kV and a JEM 2100 TEM operated at 120.0 kV. Al-KR radiation (72 W, 12 kV) at a pressure of 109 Torr was used to obtain the X-ray photoelectron spectra. The diameter of the analyzed area was 400 mm. An argon ion beam (accelerating voltage 2.0 keV, ion beam current 6.0 mA) was employed to perform the etching process. A time-of-flight secondary ion mass spectrometer (TOF-SIMS 5 by ION-TOF GmbH, 2015) at a pressure below 10^{-9} Torr was used for surface mapping analysis of Li metal anodes. The sample was prepared in a glove box with a home-made container to avoid oxidation and parasitical reactions before they were transferred to the test chamber.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2017.03.008.

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