Electronic supplementary information

A high performance lithium-ion sulfur battery based on a Li₂S cathode using a dual-phase electrolyte

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Fig. S1 Illustration of lithium polysulfides serve as redox mediators.

In the cell, Li_2S is electrochemically oxidized into soluble polysulfides (Li_2S_x , $4 \le x \le 8$) with higher conductivity at the beginning of charge [electrochemical reaction: $xLi_2S \rightarrow Li_2S_x + (2x-2)Li^+ + (2x-2)e^-$]. It can be assumed that the further charge of Li_2S after formation of liquid polysulfides includes both electrochemical and chemical reactions.

For instance, the Li_2S was initially electrochemically oxidized to Li_2S_4 , and then to Li_2S_8 (polysulifes-I), as equation (1,2) shows,

 $4Li_2S \rightarrow Li_2S_4 + 2Li^+ + 2e^-$ (equation 1)

 $2\text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_8 + 2\text{Li}^+ + 2e^-$ (equation 2)

The oxidized products of polysulfides can in turn chemically react with Li_2S to form Li_2S_4/Li_2S_6 (polysulfes-II), as equation (3,4) shows,

 $Li_2S_8 + 2Li_2S \rightarrow 2Li_2S_2 + Li_2S_6$ (equation 3)

 $2Li_2S_2 + Li_2S_8 \rightarrow 3Li_2S_4$ (equation 4)

The chemically formed products can be further electrochemically oxidized to high-order lithium polysulfides, as equation (5,6) shows,

 $2\text{Li}_2\text{S}_4 \rightarrow \text{Li}_2\text{S}_8 + 2\text{Li}^+ + 2e^- (equation 5)$

 $4\text{Li}_2\text{S}_6 \rightarrow 3\text{Li}_2\text{S}_8 + 2\text{Li}^+ + 2e^- (equation 6)$

In conclusion, the polysulfides intermediates serving as redox mediators to facilitate the direct electrochemical oxidization of Li_2S .



Fig. S2 SEM images of commercially available pristine Li_2S with different magnification. $\times 500(left)$, $\times 2000(right)$.



Fig. S3 (a) Representative galvanostatic charge-discharge profiles of the first cycle at current rate of 1/20 C (black) and 1/40 C (red) at room temperature of 25 °C. (b) Representative galvanostatic charge-discharge profiles of the first cycle at current rate of 1/20 C at 25 °C (black) and 50 °C (blue).



Fig. S4 Electrochemical performance of the Li–S battery at 1/30 C (56 mA g⁻¹, 1 C = 1672 mA g⁻¹S) of current rate. (a) 100-times cycled charge-discharge profiles. (b) Cyclic performance presenting Coulombic efficiency and specific capacity upon charge-discharge cycles.



Fig. S5 Electrochemical performance of the Li–S battery at 1/10 C of current rate. (a) The representative 10th charge-discharge profile. (b) Cyclic performance presenting Coulombic efficiency and specific capacity upon charge-discharge cycles.



Fig. S6 Digital pictures of the cathodic suspension without (left) and with (right) in situ-formed lithium polysulfides. 0.2 M Li₂S added to 1 M LiClO₄ dissolved THF solution (left). 0.2 M Li₂S and 0.02 M sulfur added to 1 M LiClO₄ dissolved THF solution (right). Li₂S can be chemically oxidized into soluble polysulfides (Li₂S_x, $4 \le x \le 8$) by in situ reacting with sulfur additive (chemical reaction: Li₂S + (x-1)S \rightarrow Li₂S_x, $4 \le x \le 8$).



Fig. S7 Electrochemical impedance spectra (EIS) of as-prepared Li–S cells with (red) and without (black) in situ-formed lithium polysulfide additives.



Fig. S8 Self-discharge behaviour of cells with different configurations. Rest time-driven Li–S cell performance with a conventionally used coin cell configuration (a) and with the new cell architecture (b). The cells were rest for different times from 1 h to 12 h after different depth of charge from 100% to 45% (from left to right), and then discharge. For Li–S coin cell assembly, electrochemical tests were conducted using CR2016-type coin cell, consisting of positive and negative electrodes separated by one sheet of microporous membrane (Celgard 2500) and one sheet of glassy fibre (GF/C, Whatman). Coin cells were (LiTFSI) assembled with 1M bis(triflouromethanesulfonyl)imide dissolved 1,3-dioxolane (DOL)/dimethoxyethane (DME) (1:1, v:v) electrolyte. In preparing the electrode, commercial sulfur (99.98%, Aldrich) was mixed Super P carbon additive and PVdF in a 50:35:15 mass ratio. The loading mass of sulfur is ~1mg.

Fig. S9 Initial three charge/discharge profiles of a Li–Al half cell consists of Al foil cathode, Li metal anode, 1 M LiPF₆ dissolved ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by volume) electrolyte and one sheet of Celgard 2500 separator.

Fig. S10 Electrochemical performance of Al–Li₂S battery with Li₂S cathode and Al foil anode. (a) The first charge profiles with (red) and without (black) in situ-formed lithium polysulfides at 1/20 C. (b) The subsequent 10-times cycled charge-discharge profiles at 1/10 C of current rate with in situ-formed lithium polysulfide additives.

Fig. S11 Cyclic performance of a Li–graphite half cell with graphite cathode, Li metal anode, 1 M LiPF₆ dissolved ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by volume) electrolyte and one sheet of Celgard 2500 separator. Inset is the representative charge-discharge profiles.

The operating current density of the cell is 0.5 C (1 C = 370 mA g⁻¹). The first discharge and charge capacity is 315 and 278 mAh g⁻¹, resulting in a low Coulombic efficiency of 88%. The initial discharge capacity arises from both the Li-intercalation and the decomposition of electrolyte (i.e. the formation of the solid electrolyte interface (SEI). A stable SEI would protect the structure of graphite from collapse and thus facilitate the cyclic performance of the battery. Upon the formation of a stable SEI, 100% Coulombic efficiency can be achieved in following cycles. It should be noted that the initial charge capacity of 278 mAh g⁻¹ is much lower than the theoretical capacity of 370 mA g⁻¹, indicating that the graphite composite electrolyte is not well wetted by electrolyte. In the following cycles, the graphite electrode is further wetted, and thus utilization of graphite is increased gradually to reach a stable value of 316 mAh g⁻¹ at 15th cycle. After repeated cycles, the achieved capacity reduces at a very slow rate. The capacity increase process over 1–15 cycles is a typical activation process of electrode. If lower discharge/charge rate is applied, the activation process would be finished within several cycles. Herein, we only briefly demonstrate the cycle ability of the graphite with a rate of 0.5 C.

Fig. S12 Electrochemical performance of $G-Li_2S$ battery with Li_2S as cathode and graphite as anode at 1/20 C of current rate in voltage range of 1.0–3.5 V. (a) The initial charge-discharge profiles of the G-Li₂S cell (blue) compared with that a Li–S cell (black). Inset is the enlargement of the initial potential barrier at the beginning of charge. (b) The initial charge profiles of the G-Li₂S cells with (red) and without (blue) in situ-formed lithium polysulfide additives.

Fig. S13 Charge-discharge profiles of G–Li₂S battery with Li₂S cathode and graphite anode. The cell was cycled at 1.0-3.5 V at a 1/20 C rate.

Fig. S14 Initial charge-discharge profiles of the physically mixed Li₂S/C cathodes at 1/40 C (blue) or at 1/20С (black) current with a conventional coin cell configuration. rate (a) 1M bis(triflouromethanesulfonyl)imide (LiTFSI) dissolved 1,3-dioxolane (DOL)/ dimethoxyethane (DME) (1:1, v:v) as electrolyte. (b) 1M LiClO₄ dissolved THF as electrolyte. In preparing the electrodes for the coin cells, the same commercial Li₂S was mixed with Super P carbon additive and PVdF in a 60:30:10 mass ratio in NMP, casted onto the carbon-coated Al foil and dried in vacuum oven. Li metal as anode. A polymer Celgard 2500 used as separator. The electrolyte is either 1 M LiTFSI dissolved DOL/DME or 1M LiClO₄ dissolved THF. The former is the most popular electrolyte for current Li–S battery research, and the latter is the same as the cathodic electrolyte used in this work.

Fig. S15 The optical images for the permeation behavior of polysulfides across the LATP. (a) Before storage. (b) After storage for one week.

To visibly show permeation behavior of polysulfides across the LATP, the THF solution with in-situ formed lithium polysulfides was prepared. The red solution was deliberately injected into the left chamber of a "V" shape glass tube. The right chamber was full of colourless EC/DMC/ DEC solution with LiPF₆ dissolved in. The two solutions were separated by one sheet of LATP. After storage for one week, the change of the colour in the right chamber cannot be observed. Whereas, in the case of cells with the routine membrane couldn't effectively to limit polysulfides, as previously reported.¹

Fig. S16 XRD patterns of LATP communicating with cathode (red) and anode (blue) electrolytes for 100 cycles accompany with the pristine one (black).

Fig. S17 (a) Digital pictures of the equivalent Li_2S_6 dissolved in THF (left), Li_2S suspended THF (middle) and the mixed solution (right). UV-visible absorption spectra of equivalent Li_2S_6 dissolved in THF (b) and the mixture (c).

To confirm the possible chemical reaction of lithium polysulfides and Li_2S , individual Li_2S_6 as a representative high-order lithium polysulfide was prepared using the appropriate ratio of elemental sulfur and Li_2S as a reducing agent in THF at room temperature. It is reported that chemically preparation of Li_2S_8 is not possible for the rapid disproportionation of S_8^{2-} in solution.² Thus the more stable Li_2S_6 is prepared.

It is expected that the following chemical reactions is possible: $Li_2S_6 + Li_2S \rightarrow Li_2S4 + Li_2S_3$

Herein, appropriate ratio of equivalent Li_2S_6 dissolved THF solution and Li_2S suspended THF was mixed together (Fig. S17a). UV–visible absorption spectroscopy was chosen to characterize the dissolved lithium polysulfides, as are well known to strongly absorb the UV–visible radiation. It can be detected in Fig. S17b that the different UV bands are attributed to the S_6^{2-} species, i.e., the 218, 262, and 360 nm bands. The spectrum of the mixed solution is shown in Fig. S17c, there is still obvious absorption bands ascribed to S_6^{2-} . However, an absorption band at 420 nm was detected, which should be attributed to S_4^{2-} . On the other hand, as Li_2S is insoluble in ether solvents, no UV response could be obtained, in agreement with previous report.³ The absorption band of S_3^{2-} , which was reported at 340 nm in a tetraethylene glycol dimethylether (TEGDME) solution³ couldn't clearly identified. The broad band of S_6^{2-} in the range of 320~380 nm has made the identification difficult.

Fig. S18 Charge-discharge profiles of the Li–S cell with Li₂S concentration of 1 M at 1/20 C of current rate (0.02 M sulfur additive was added to in situ form lithium polysulfides). To increase the mass loading of Li₂S five times higher (1.0 M Li₂S), the cathodic suspension have a total volume of 150 μ L. Therefore, the Li₂S loading is almost 7 mg. The dried Super P carbon has an averaged loading amount of 1 mg cm⁻². The geometric area of the cast carbon was 9 mm in diameter, thus the carbon loading is approximately 0.6 mg. The mass ratio of Super P:Li₂S = 0.6 mg:7 mg. 0.02 M sulfur additives was further added to in situ form lithium polysulfides by chemical react with Li₂S, i.e., the total sulfur concentration is 1.02 M. The specific capacity of the initial charge is 1593 mAh g⁻¹, indicating ~95% utilization of Li₂S still can be maintained at the first charge.

If the measurement of energy is adopted from the reported method by Zhao et al.⁴, the energy density for an electrode couple are calculated from

$$W_{cell} = \frac{E_{cell} \cdot Q \cdot m_{Li2S}}{M_{anode+cathode}} = \frac{E_{cell} \cdot Q \cdot m_{Li2S}}{(m_{Li})_{anode} + (m_{Li2S})_{cathode}} \approx \frac{2.2 \, V \cdot 1166 \,\mathrm{mAh} \,\mathrm{g}^{-1} \cdot 7mg}{(4.2 \, mg)_{anode} + (7 \, mg)_{cathode}} = 1.60 \,\mathrm{kWh} \,\mathrm{kg}^{-1}$$

Where W_{cell} is the energy density (kWh kg⁻¹), E_{cell} is the average reversible potential (2.2 V vs. Li⁺/Li), Q is the specific capacity of Li₂S (1166 mAh g⁻¹), and $M_{anode+cathode}$ (kg) is the total mass of Li metal anode and Li₂S. Here the lithium anode applied with a practical mass two times higher than theoretical need. When 7 mg Li₂S was used at the active material, the calculated energy density of the cell is 1.60 kWh kg⁻¹. The lithium super ionic conductor glass film (LISICON) of Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂ (LTAP) has a mass density of 46 mg cm⁻². In this work, 36 mg LATP is necessary for the system with an area 0.79 cm² (10 mm in diameter). If the mass of LATP is included, the energy density dramatically decreases to 0.38 kWh

 kg^{-1} . However, the value is still higher than the current practical Li-ion systems, having energy density always below 0.25 kWh kg^{-1} .

Reference

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