A lithium-sulfur battery with a solution-mediated pathway operating under lean electrolyte conditions

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**ABSTRACT**

Lithium-sulfur (Li–S) battery is one of the most promising candidates for the next generation energy storage systems. However, several barriers, including polysulfide shuttle effect, the slow solid-solid surface reaction pathway in the lower discharge plateau, and corrosion of Li anode still limit its practical applications, especially under the lean electrolyte condition required for high energy density. Here, we propose a solution-mediated sulfur reduction pathway to improve the capacity and reversibility of the sulfur cathode. With this method, a high coulombic efficiency (99\%) and stable cycle life over 100 cycles were achieved under application-relevant conditions (S loading: 6.2 mg cm\textsuperscript{-2}; electrolyte to sulfur ratio: 3 mL g\textsuperscript{-1}; sulfur weight ratio: 72 wt%). This result is enabled by a specially designed Li\textsubscript{2}S\textsubscript{4}-rich electrolyte, in which Li\textsubscript{2}S is formed through a chemical disproportionation reaction instead of electrochemical routes. A single diglyme solvent was used to obtain electrolytes with the optimum range of Li\textsubscript{2}S\textsubscript{4} concentration. Operando X-ray absorption spectroscopy confirms the solution pathway in a practical Li–S cell. This solution pathway not only introduces a new electrolyte regime for practical Li–S batteries, but also provides a new perspective for bypassing the inefficient surface pathway for other electrochemical processes.

**1. Introduction**

The development of rechargeable lithium-sulfur (Li–S) batteries based on conversion reactions is driven by their higher theoretical specific energy at reduced cost compared to those of Li-ion batteries based on intercalation reactions [1–6]. However, Li–S batteries still suffer from their limited cycle life and low specific energy under flooded electrolyte conditions. These challenges are related to the continuous irreversible passivation of electrode by insulating Li\textsubscript{2}S and the deteriorating solid-electrolyte interphases on the Li metal anode upon cycling under high sulfur loadings [7–11]. To overcome these challenges and reach the full potentials of Li–S chemistry, it is essential to tune electrolyte formulations to enable a robust interface and a new reversible pathway for Li–S reactions [12–17].

Full sulfur-utilization has rarely been reported in solvent-flooded Li–S cells, where the traditional binary ether solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) are used [18,19]. Most of the reported specific capacity of sulfur cathode is less than 1200 mAh g\textsuperscript{-1} (i.e., 71.6\% of sulfur utilization based on its theoretical capacity of 1672 mAh g\textsuperscript{-1}), limited by a surface pathway in the lower discharge plateau because the active surface area is decreasing during discharge [20]. Recently, a new strategy of sparingly solvating electrolytes has been proposed to render a significant increase in the sulfur utilization at elevated temperature owing to the increased concentration of S\textsubscript{2} radical.

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in a high dielectric constant (DC) solvent of acetonitrile, where a chemical/electrochemical redox pathway involving $S_{2\text{-}}$ was proposed to take place simultaneously [21,22]. In other words, the full sulfur utilization enabled by this pathway strongly relies on the concentration of $S_{2\text{-}}$ [23,24]. However, the poor compatibility of high DC solvents against Li metal has been an unsettled hurdle and the aggressive nucleophilic attack of DOL and carbonate solvents by $S_{2\text{-}}$ has been extensively studied [25–27]. Fortunately, the Li-benign linear ether solvents, except for DME, have been experimentally confirmed to be resistant to $S_{2\text{-}}$ attack [28,29]. Linear ethers with a higher number of solvating oxygen atoms are found to enhance the stability of the solvent-Li$^+$ solvating complex and thus the stability of $S_{2\text{-}}$.

Li salts with different anions have been reported to greatly affect the solubility of low-order Li polysulfides (LiPS) and thus the concentration of $S_{2\text{-}}$, since the latter is a product of the disproportionation reaction equilibrium of LiPS [30,31]. Higher ionic-association-strength (i.e., high Lewis basicity) of anion X$^-$ ($X^- = NO_3^-, CF_3SO_3^-, Br^-$, etc.) has been demonstrated to render a higher concentration of low-order LiPS due to a stronger interaction between Li$^+$ from LiPS and X$^-$. Compared to the low ionic-association-strength of the base anion of NC[(CF_3SO_2)$_3$] (bis(trifluoromethanesulfonyl)imide [TFSI$^-$]), one can thus expect that tuning electrolyte formulations, especially through highly solvating Li-benign linear ether solvents [12] and high ionic-association-strength anions, can steer a synergetic chemical/electrochemical sulfur redox pathway in the lower discharge plateau by the presence of stabilized $S_{2\text{-}}$.

2. Results and discussion

2.1. A new Li$_2$S$_x$-dictated pathway under lean electrolyte conditions

In a Li–S cell with a critical electrolyte-to-sulfur (E/S) ratio (i.e., $<$4.0 mL g$^{-1}$ when the maximum solubility of LiPS reaches 8 M [3]); where mL$^{-1}_E$ and g$^{-1}_S$ represent volume of electrolyte and weight of sulfur in Li–S cell, respectively, Supplementary Fig. 1), sulfur is first reduced at the cathode during discharge to form quasi-solid Li$_2$S$_x$ by reactions [1-2] as shown below [32]. In the subsequent reaction represented by the lower border of the discharge plateau [3], nucleation and growth barriers of insoluble solid Li$_2$S present a tremendous hurdle due to slow Li$^+$ diffusion and solid-state solid-support transfer process.

\[ S_4 (s) + 2Li^+ + 2e^- \rightarrow Li_2S_2 (s or l) \]

(1)

\[ Li_2S_2 (s or l) + 2Li^+ + 2e^- \rightarrow 2Li_2S_4 (s) \]

(2)

\[ Li_2S_4 (s) + 6Li^+ + 6e^- \rightarrow 4Li_2S (s) \]

(3)

\[ E^{\text{charge}} = 2.1 \text{ V} \]

In order to investigate electrolyte dependence of sulfur utilization in the lower discharge plateau under lean electrolyte conditions, a carbonaceous model matrix is important to eliminate effects of the diffusion/migration of high-order LiPS in the bulk electrolytes from cathodes. A microporous sulfur-loading matrix of activated carbon fiber cloth (ACFC) was used as a model substrate (Supplementary Fig. 2) because it can confine high-order LiPS in micropores [13]. Despite different electrolytes and sulfur sources, no diffusion/migration of high-order LiPS from micropores of ACFC was observed in cyclic voltammograms (Supplementary Fig. 2). Moreover, the relatively high pore volume of ACFC allows high sulfur loadings in micropores with limited solvent permeation [13], akin to where the Li–S redox reactions would take place in practical applications.

A Li–S cell was assembled with a sulfur containing electrolyte E$_{G2}$: 0.5 M Li$_2$S$_4$ (E$_G2$ represents 1 M LiTFSI:0.3 M LiNO$_3$ in G2) as the sulfur source and ACFC as the carbon matrix. Sulfur loading is 1.58 mg cm$^{-2}$ calculated by total amount of sulfur in the electrolyte divided by the geometrical area of ACFC electrode. A typical discharge/charge curve is shown in Fig. 1a, which shows a discharge capacity of 1590 mAh g$^{-1}$ and a coulombic efficiency (CE) of 99.1%, suggesting that 95.1% of the sulfur is reduced to solid Li$_2$S. To determine the sulfur reduction mechanism in E$_{G2}$: 0.5 M Li$_2$S$_4$, potentiodynamic cycling with galvanostatic accumulation (PCGA) was performed in the Li$_2$E$_{G2}$: 0.5 M Li$_2$S$_4$/ACFC; results are shown in Fig. 1b. PCGA is a quasi-equilibrium technique that can provide very useful detailed information on electrochemical processes by analyzing the integral of the current during the step time (60s) versus the potential in the same step. The reversibility of solid Li$_2$S$_4$ reduction at 2.06 V and oxidation at 2.22 V is high, as indicated by the observed comparable SO$_4$ and the narrow potential difference of 0.16 V between the two reactions, which further supports ACFC as a model material. Interestingly, there is an additional broad reduction peak below the major reduction. To reveal the origin of the broad reduction peak in the 1.98–1.99 V, the dependence of PCGA traces for the discharge of Li–S cell on Li$_2$S$_4$ concentrations and stepwise potentials was then investigated and the results are shown in Supplementary Fig. 3. A broad peak between 1.9 and 2 V was observed for the sample using a Li$_2$S$_4$ containing electrolyte (E$_{G2}$: 0.5 M Li$_2$S$_4$). In contrast, no broad reduction peak was observed for the cell without Li$_2$S$_4$ (E$_G2$), indicating the strong dependence of this broad reduction peak on the electroactive species of Li$_2$S$_4$ (see Supplementary Fig. 3a). On the other hand, a sharp reduction peak, corresponding to the major electrochemical reduction of Li$_2$S$_4$ from bulk electrolyte, is observed at $\sim$2.04 V and increases with increasing concentration of Li$_2$S$_4$. However, the subsequent broad reduction peak between 1.9 and 2 V is weakened, which is consistent with the stepwise potential dependence of PCGA measurement results using the same cell shown in Supplementary Fig. 3b. The size of this broad reduction peak is thus closely related to the Li$_2$S$_4$-retaining in the bulk electrolytes, suggesting a new reduction pathway for sulfur in micropores.

The cell using E$_{G2}$: 0.5 M Li$_2$S$_4$ was cycled at the much lower rate of 0.075C; results are shown in Fig. 1c. A gradual increase in the discharge capacity was observed in the initial cycles probably due to the improved wetting ability of ACFC [33,34]. After the 10th cycle, both the maximum deliverable discharge capacity (i.e. 1590 mAh g$^{-1}$) and CE of the cell continuously decay upon further cycling, suggesting the sulfur redox environment significantly evolves within ACFC as soon as most sulfur from Li$_2$S$_4$ in bulk electrolytes migrates into ACFC and only sparse Li$_2$S$_4$ is remained outside ACFC. An identical cell discharged at 0.3 C showed an increasing discharge capacity from 825 to 979 mAh g$^{-1}$ and an ultras high average CE of 99.7% for 100 cycles (Fig. 1c). During fast discharges, appropriately half of the Li$_2$S$_4$ (i.e., 0.25 M) remained outside the ACFC, assuming 100% sulfur utilization in micropores (Fig. 1a) at the delivered specific capacity of 836 mAh g$^{-1}$. Further, a new cell with E$_{G2}$: 1.5 M Li$_2$S$_4$ (E$_G2$: 1 M LiTFSI:0.9 M LiNO$_3$ in G2) was deliberately discharged at 0.075C, as shown in Fig. 1d. This cell delivered a relatively high specific capacity of ca.1200 mAh g$^{-1}$ and an average CE as high as 99.8%, compared to 96.9% for the cell using 0.5 M Li$_2$S$_4$. The Li$_2$S$_4$ remaining at the outside of ACFC is estimated to be 0.42 M in this cell during cycling. These results clearly suggest that Li$_2$S$_4$ remaining on the outside of the ACFC plays a special role in enabling a high sulfur utilization in the lower discharge plateau with limited solvent permeation (i.e. lean electrolyte conditions).
Fig. 1. A new Li$_2$S$_4$-dictated pathway under lean electrolyte conditions. (a) A typical discharge/charge curve of Li || E$_{G2_0.5}$ M LiS$_4$ || ACFC cell after initial cycles at 0.075 C and 30 °C; (b) PCGA trace of Li||E$_{G2_0.5}$ M LiS$_4$||ACFC at 30 °C. Retention degree of Li$_2$S$_4$ is tuned in the bulk electrolytes using various discharge rates for E$_{G2_0.5}$ M LiS$_4$ (c) and the same low discharge rate of 0.075 C in different concentrations of Li$_2$S$_4$ (d). Fig. 1a is the 9th cycle curve of the Li-S cell in Fig. 1c at 0.075 C. Microporous activated carbon fiber cloth (ACFC) was used as a model material to study electrolyte dependence of the sulfur reduction pathway under lean electrolyte conditions. Different concentrations of Li$_2$S$_4$ were prepared in E$_{G2}$ (1 M LiTFSI_0.3 M LiNO$_3$ in G2) and E$_{G2_0.5}$ (1 M LiTFSI_0.9 M LiNO$_3$ in G2).

We also compared the effect of different sulfur species loaded by different approaches on the performance of Li-S cells, with the same total sulfur loading (including those in electrode and electrolyte) and electrolytes volume. Three Li-S cells using ACFC were prepared as shown in Supplementary Fig. 4. In the Supplementary Figs. 4a–b, sulfur was introduced into ACFC prior to cell assembly (see Method section for details). In the Supplementary Fig. 4c, no sulfur presents in ACFC prior to cell assembly and all the sulfur in the cell originate from electrolyte. The electrolytes used in these three cells are base electrolyte-E$_{DOL/}$DME: 1 M LiTFSI_0.3 M LiNO$_3$ in DOL/DME (Supplementary Fig. 4b), E$_{G2}$ (Supplementary Fig. 4a), and E$_{G2_0.5}$ M LiS$_4$ (Supplementary Fig. 4c). All cells were tested at 0.3 C rate and 30 °C. After 500 cycles, the lower discharge plateau corresponding to reaction [3] totally disappeared and the capacity decay was almost continuous in the cells using E$_{G2}$ and E$_{DOL/DME}$, suggesting the surface pathway of reaction [3] should prevail in these two cells to result in a parasitic loss of surface area by the passivation of Li$_2$S during cycling. However, the length of the lower discharge plateau has a minimal change for the cell using E$_{G2_0.5}$ M LiS$_4$. This indicates that the presence of excess Li$_2$S$_4$ in the electrolyte is helpful to stabilize the lower discharge plateau during cycling.

2.2. Dependence of sulfur utilization efficiency on the content of Li$_2$S$_4$ in electrolyte

To further correlate the interplay between Li$_2$S$_4$ content in the bulk electrolyte and the reduction efficiency of solid Li$_2$S$_4$ under lean electrolyte conditions, ACFC_LiS$_8$ was prepared by preloading 30 µL of 1 M Li$_2$S$_8$ (sulfur mass loading: 6.06 mg cm$^{-2}$) into ACFC. Fig. 2a shows typical discharge curves of Li || E$_{G2_0.5}$ M LiS$_4$ || ACFC cell using 0.5 M Li$_2$S$_4$ with an E/S ratio of 3.0 mL g$^{-1}$ cathode at 0.12 mA cm$^{-2}$ and 30 °C, where g$_{cathode}$ represents the weight of sulfur in cathode (not including those in electrolyte). The achievable discharge capacity shows a strong correlation with the concentration of Li$_2$S$_4$ in the electrolyte. The cell using E$_{G2_0.5}$ M LiS$_4$ shows a significantly high capacity of 1520 mAh g$^{-1}$ cathode based on preloaded Li$_2$S$_8$ and 1268 mA g$^{-1}$ based on the total sulfur loading (including those pre-loaded in ACFC and those in the electrolyte) at an elevated discharge potential. In contrast, limited capacities of <400 mAh g$^{-1}$ cathode were observed for lower (<0.5 M) and higher concentrations (0.75 M) of Li$_2$S$_4$, indicating that an optimal concentration of Li$_2$S$_4$ in the bulk electrolytes is required to reduce preloaded Li$_2$S$_8$ to solid Li$_2$S$_4$ and the following Li$_2$S effectively. This is the first time that nearly 100% solid Li$_2$S reduction has been reported for Li-S coin cells with high sulfur loadings and lean electrolytes.

Cells were both halted near the nucleation stage using the couple of E$_{G2}/$ACFC_LiS$_8$ or E$_{G2_0.5}$ M LiS$_4$/ACFC_S in Fig. 2b and Supplementary Fig. 5 indicate that both the starting sulfur material and the 0.5 M Li$_2$S$_4$ content in electrolyte have a remarkable impact on the sulfur utilization. The cell using E$_{DOL/DME}$ presents a lower discharge potential at 1.85 V, and a limited discharge capacity of 897 mAh g$^{-1}$ cathode far below that of the cell using E$_{G2_0.5}$ M LiS$_4$. Moreover, bulk electrolytes with 2 M [S] were made from 0.25 M Li$_2$S$_8$ and 0.33 M Li$_2$S$_4$ and examined, as shown in Fig. 2c. Interestingly, the cell using 0.33 M Li$_2$S$_4$ shows the absence of a lower discharge plateau. However, the cell using 0.25 M Li$_2$S$_8$ presents a specific capacity of 1884 mAh g$^{-1}$ cathode, indicating that sulfur from the bulk electrolyte of 0.25 M Li$_2$S$_8$...
migrated into the ACFC and contributed to the total capacity due to the concurrent reduction of Li$_2$S$_6$ from the bulk electrolyte and the ACFC, where the intermediate reduced species of Li$_2$S$_6$ are not supposed to generate from E$_{G2}$ 0.25 M Li$_2$S$_6$; otherwise, it would exhibit no lower discharge plateau, as did the cell using E$_{G2}$ 0.33 M Li$_2$S$_6$.

Fig. 2d shows the discharge PGCA traces obtained from cells using E$_{DOL/DME}$ and E$_{G2}$ 0.50 M Li$_2$S$_6$. The PGCA trace of the cell using E$_{G2}$ 0.50 M Li$_2$S$_6$ presented another unusual sulfur reduction pathway, where multiple discharge reactions are shown to take place at 2.09, 1.95, 1.90, and 1.85 V, respectively. It shows a continuously increasing incremental charge upon cathodic sweeping, with the maximum observed at 2.13 V and 1.83 V, with a decreasing incremental charge upon cathodic sweeping, which further corroborates that Li$_2$S$_6$ retention can significantly affect the reduction pathway of sulfur species from high sulfur loadings under lean electrolyte conditions.

### 2.3. A solution-mediated chemical/electrochemical route

To explain the strong correlation between Li$_2$S$_6$ content in electrolyte and the ultrahigh sulfur utilization under lean electrolyte conditions, we propose a solution pathway enabled by Li$_2$S$_6$-mediated reaction (Fig. 3a) to divide reaction [3] into the following steps:

At the potential dip (i.e., the onset of Li$_2$S nucleation):

$$3S_2^2^- (l) \rightarrow 2S_1^- + 2S_2^2^- (l)$$  \hspace{2cm} (4)

$$2S_1^- + 2e^- \rightarrow 2S_1^- (l)$$  \hspace{2cm} (5)

After the potential dip in the elevated discharge plateau:

$$S_1^- (l) + Li_2S_6 (s) \rightarrow Li_2S (s) + S_2^- (l)$$  \hspace{2cm} (6)

$$S_2^- (l) + 2e^- \rightarrow 2S_1^- (l)$$  \hspace{2cm} (7)

$$E^0 = 2.3 \text{ V}$$

The presence of optimal-concentration Li$_2$S$_6$ in the bulk electrolyte drives the chemical disproportionation reaction [4] toward S$_2^-$, which is further reduced to soluble S$_2^2$ by reaction [5] \cite{24, 28}. Reactions [4, 5] have been investigated by in-situ ultraviolet-visible absorption spectroscopy and electron paramagnetic resonance (EPR) spectroscopy in a tetraglyme-based electrolyte \cite{20, 28}. The soluble S$_2^2$ from reaction [4] chemically reacts with quasi-solid Li$_2$S$_6$ (reaction [6]) and generate Li$_2$S precipitate and soluble S$_2^2$; the soluble and replenishable S$_2^2$ is further reduced into soluble S$_2^-$ (reaction [7]) at a higher redox potential (i.e. $E^{th} = 2.3\text{ V}$) \cite{23} than reaction [3] (i.e. $E^{th} = 2.1\text{ V}$) \cite{5, 35}, which prevents further reduction of bulk Li$_2$S$_6$ on cathodes and leads to the voltage dip before the onset of the lower discharge plateau. The reduction efficiency of solid Li$_2$S$_6$ is thus not affected by the decreasing available surface area during single discharge, and could potentially reach 100% by reactions \cite{6, 7}. Fig. 2a shows that the optimal concentration of Li$_2$S$_6$, that can allow reactions [4-7] (i.e., the synergetic chemical/electrochemical reactions) to take place with a low energy barrier and an elevated discharge plateau, is 0.50 M (i.e., optimal concentration ratio of S$_2^2$/S$_2^-$). The solubility of Li$_2$S$_6$ was reported to be as low as 0.0625 M in DOL/DME \cite{30}. The low solubility of Li$_2$S$_6$ and the poor stability of S$_2^-$ in DME and DOL (i.e., low concentration ratio of S$_2^2$/S$_2^-$) \cite{26, 29} means the synergetic chemical/electrochemical reactions are not likely to take place in the DOL/DME-based electrolytes. This is evidenced by the lack of elevation of the lower discharge plateau and a much lower discharge specific capacity, as shown in Fig. 2b. Reaction [6] will not take place in a low concentration ratio of S$_2^2$/S$_2^-$ (CS$_2^2$/CS$_2^-$) if the bulk electrolytes still contain S$_2^-$ when the cell discharges beyond reaction [2], as depicted in Fig. 3b and demonstrated in Fig. 2c, and if the bulk electrolytes contains low concentration of CS$_2^-$ originating from low concentration of CS$_2^-$. Further, a higher concentration of Li$_2$S$_6$ is found to result in a substantial decrease of lithium cation diffusion coefficient by $^{7}$Li PFG-NMR measurements (Supplementary Table 1) to maintain the charge neutrality and then decrease the local supply of S$_2^2$. 

![Image of Fig. 2](https://via.placeholder.com/150)

*Fig. 2. Li$_2$S$_6$ retention dependence on sulfur utilization. Electrolyte dependence of the typical discharge capacity for Li-S cells using ACFC-Li$_2$S$_6$ as the cathode with a sulfur loading of 6 mg cm$^{-2}$ at an E/S cathode ratio of 3.0 mL/g, 0.12 mA cm$^{-2}$, and 30°C. The $g_{S\text{ cathode}}$ represents the weight of sulfur in cathode. (a) Using different concentrations of Li$_2$S$_6$ in E$_{G2}$; (b) using E$_{DOL/DME}$ (1 M LiTFSI, 0.3 M LiNO$_3$ in DOL/ DME), E$_{G2}$, and E$_{G2}$ 0.50 M Li$_2$S$_6$; (c) using different concentrations of LiPS with 2 M [S] in E$_{G2}$; (d) PCGA curves for the discharge of two Li-S cells with different electrolytes.*
To investigate the solvent-dependent of $S_3^-$ in electrolytes, non-invasive EPR measurements were performed for electrolytes of $E_{G2}$, $E_{G2_0.5M Li_2S_4}$ and $E_{DOL/DME_{saturated Li_2S_4}}$ (images shown in Supplementary Fig. 6) in Fig. 3c. EPR spectrum at 125 K of $E_{G2_0.5M Li_2S_4}$ clearly reveals the pattern of $S_3^-$ radical at $g = 2.034$ [17, 20], and the EPR spectrum also shows the persistent presence of the radical at room temperature ($T = 298$ K). Similar pattern was not observed for $E_{G2}$ and greatly weakened for $E_{DOL/DME_{saturated Li_2S_4}}$. The concentration of $S_3^-$ radical is calculated to be 0, 0.6 mM, and 11.2 mM for $E_{G2}$, $E_{DOL/DME_{saturated Li_2S_4}}$ and $E_{G2_0.5 M Li_2S_4}$ respectively; the large difference in the concentration of $S_3^-$ clearly highlights the dramatic impact of solvents on the presence of $S_3^-$ and the resultant $CS_3^2$ that steers distinctive sulfur reduction pathway. Raman results further confirm the presence of $S_3^-$ in $E_{G2_0.5 M Li_2S_4}$ as shown in Supplementary Fig. 7, where a dominant and sharp peak of 534.6 cm$^{-1}$ stemming from $S_3^-$ was observed [36].

2.4. Experimental verification of the $Li_2S_4$-enabled solution pathway

Since $Li_2S_4$ retention in the bulk electrolyte can drastically enhance the sulfur utilization under lean electrolyte conditions, it is very important to directly demonstrate whether or not $Li_2S_4$ plays a role in the proposed solution pathway. To demonstrate the occurrence of synergistic chemical/electrochemical reactions, operando sulfur K-edge X-ray absorption spectroscopy (XAS) was employed to probe sulfur speciation in a Li–S cells. Because the transmission of photon signal in XAS experiment is significantly attenuated by the thickness of the specimen, it is very difficult to obtain high quality signal when a thick ACFC (which comes from a commercial source with a fixed thickness) is used as the cathode host in Li–S cells. Therefore, an electrospun carbon fiber (ECF) with 1/5 of the thickness of ACFC is prepared and used as the cathode host in Li–S cells for operando study of the sulfur reduction pathway, where $E_{G2_0.5 M Li_2S_4}$ was used as the bulk electrolyte. It is worth to note that the electrolytes, not the carbon host, plays a
predominant role in the sulfur reduction pathway [34,37].

Fig. 4a and b shows XAS contours collected from Li-S cells using E_G2 and E_G2_0.5 M Li_2S_4 at ambient temperature, respectively. Pilling-up XAS spectra of each cell are shown in Fig. 4c and d. The intermediate states of polysulfides are supposed to be identified by the ratio between the pre-peak at 2470.2 eV (characteristic pre-peak for polysulfides) and the main peak at 2472 eV (typical peak for elemental sulfur), since the relative intensity of the pre-peak is proportional to the relative amount of Li in Li_2S_x (Supplementary Table 2). The starting material of Li_2S_x (x = 0.25 in Li,S) in both operando XAS measurements (See Fig. 4a and b) was discharged from 0.25 to 0.50. Li-S cells have been reported to be prematurely terminated during this stage due to the rapid drop in the cell potential resulting from the sluggish solid-solid charge-transfer reaction [3] under lean electrolyte reactions. Wucik et al. [38] reported the XAS evolution of a solid Li-S battery with a limited x range in Li,S from 0 to 0.15 in a thick sulfur cathode, where the ratio of main peak to pre-peak area is continuously decreasing (i.e. the evolution from long Li_2S_x to short Li_2S_x) upon discharging, along with a prematurely cell potential failure. In the ether-based electrolytes for the x range from 0.25 to 0.50, the trend of decreasing concentration [S^4_-] and increasing concentration [S^2_-] has been demonstrated by previous Li-S XAS studies [39,40], along with a continuously decrease in the cell potential. Here, the operando XAS cell of LiIE_G2/ECF_Li_2S_4 shows resembling phenomena in terms of the continuously decreases in the ratio of the main peak to pre-peak area (i.e. from long Li_2S_x to short Li_2S_x) and in the discharge cell potential in Fig. 4e. The ratio of the main peak to pre-peak area decreases from 7.0 to 3.0 in the x range from 0.25 to 0.43. In contrast, a distinct increase in the ratio of the main peak to pre-peak area, i.e., an evolution from short Li_2S_x to long Li_2S_x, is observed from 2.8 to 5.1 in the x range from 0.32 to 0.46 for the operando XAS cell using E_G2_0.50 Li_2S_4 in Fig. 4f. In this discharge stage, the elevation of the discharge potential is observed as well. Increases in the peak area ratio and discharge cell potential can be regarded as a strong evidence of the Li_2S_x evolution from Li_2S_4 to Li_2S_x in the bulk electrolyte for this operando cell, which thus strongly corroborate the proposed reactions of [4-7].

In a parallel experiment using the XAS cell of LiIE_G2_0.5 M Li_2S_4 ECF_Li_2S_8 (sulfur loading: >6 mg cm^-2 E/S_cathode ratio: 3.0), the final solid discharge product was harvested when the cell was terminated discharging at 1431 mAh g^-1 cathode (x=1.99) to characterize its composition by ex-situ X-ray photoelectron spectroscopy (XPS) measurement as shown in Supplementary Fig. 8a. The dominant final solid product can be determined as Li_2S by corresponding fitted peaks of S_2 [41,42] as shown in Supplementary Fig. 8b and quantitative calculation with an accuracy of 96.5% in Supplementary Table 3.

2.5. Application of the Li_2S_x-enabled solution pathway

In this work, advantages of Li_2S_x content in bulk electrolytes have been demonstrated (Fig. 1d and Supplementary Fig. 4), in terms of steering the synergistic chemical/electrochemical reactions (Fig. 4) and high compatibility with Li metal (discussed in the Supplementary Notes and shown in Supplementary Figs. 9-13). Li-S cells with high sulfur loadings under lean electrolyte conditions are expected to deliver a high specific capacity and long cycle life if the cell were just cycled between Li_2S_4 and Li_2S_x with a theoretical capacity of 1254 mAh g^-1, by the Li_2S_4-retaining solution pathway.

ACFC was initially used as a model material to study the electrolyte-dependent sulfur reduction pathway under lean electrolyte conditions. Surprisingly, even Li-S cells using ACFC are fully charged at 2.8 V, where the retained Li_2S_4 might be oxidized into Li_2S_6 or migrate toward the Li metal anode with Li^- owing to the stronger interaction between Li^- and short-order LiPS [43], high sulfur utilization and CE are still maintained as observed in Fig. 1. This indicates that Li_2S_4, not the intermediate Li_2S_n, is always generated from the reduction of Li_2S_6 in ACFC; the resultant Li_2S_4 steers the solution pathway in ACFC. Supplementary Fig. 14 shows the cycling performance of LiIE_G2_1.5 M Li_2S_4/ACFC with a high sulfur loading of 7.6 mg cm^-2 at 1/30C (i.e., 0.42 mA cm^-2).

Fig. 4. Experimental corroboration of the Li_2S_x-retaining solution pathway. Normalized operando X-ray absorption spectroscopy (XAS) contours at the sulfur K-edge for (a) LiIE_G2/ECF_Li_2S_8 (sulfur loading: 6 mg cm^-2); applied current density: 0.08 mA cm^-2 and (b) LiIE_G2, Li_2S_4/ECF_Li_2S_4 (sulfur loading: 4.3 mg cm^-2; applied current density: 0.04 mA cm^-2) upon initial discharge using electrospun carbon fiber (ECF) as the carbon matrix at an E/S_cathode ratio of 3.0 mAh g^-1 cathode and ambient temperature; (c-d) the pilling-up XAS spectra for the operando XAS cells of LiIE_G2/ECF_Li_2S_4 and LiIE_G2, Li_2S_4/ECF_Li_2S_4 every 40 mAh g^-1 cathode until x = 0.50; (e-f) operando discharge curves of XAS Li-S cells and corresponding analysis between x in Li,S and the ratio of main peak to pre-peak area.
areal capacity of excellent cycling retention and high CE can be achieved with a stable discharge curve. Fig. 5. Two different charge cut-off potentials of 2.63 V (i.e. oxidation to Li$_2$S$_2$O) and 2.48 V (i.e. roughly oxidation to Li$_2$S$_2$) were selected based on CV measurement of this cell (Supplementary Fig. 16a).

The cell terminated at 2.48 V showed a stable middle discharge potential, but the cell terminated at 2.63 V showed a rapid decrease in the middle discharge potential, indicating the solution pathway is highly sustained when the charge cut-off potential is carefully tuned to terminate the cell charge to the stage of Li$_2$S$_2$.

To demonstrate the general application of the Li$_2$S$_4$-enabled solution pathway, Electrospun carbon fiber (ECF) has been used to replace ACFC as sulfur-loading substrate because ECF is a typical macroporous carbon matrix which cannot prevent diffusion of high-order LiPS (i.e., soluble S$_2^{2-}$ and S$_4^{8-}$) in electrolytes, and thus can be used to verify the Li$_2$S$_4$-enabled solution pathway. The Li$_1$E$_2$G$_2$0.5 M Li$_2$S$_4$/ECF-Li$_2$S$_2$ cell was cycled with a high sulfur loading of 6.2 mg cm$^{-2}$ at an E/S$_{cathode}$ ratio of 3.0, 0.20 mA cm$^{-2}$ and 30 $^\circ$C in the range 1.80–2.45 V, as shown in Fig. 5. The low charge cutoff potential of 2.45 V was deliberately chosen to prevent the oxidation of high-order LiPS into S$_2$ on the ECF and the migration of high-order LiPS toward Li (Supplementary Fig. 16) [44]. The Li–S cell shows potential vs. capacity curves resembling those of the LiIE G2,0.5 M Li$_2$S$_4$/ACFC-Li$_2$S$_2$ cell (Fig. 2). The presence of Li$_2$S$_4$ can be signified by the continuous potential dip at approximatively 50 mAh g$_{cathode}^{-1}$ and by the high average CE of 99.0% upon cycling. It is thus reasonable to postulate that the Li$_2$S$_4$-enabled solution pathway prevails in this Li–S cell. The initial discharge capacity is lower than that observed using ACFC, probably due to the capacity loss from uncontrollable diffusion of S$_2^{2-}$. After 100 cycles, the cell can sustain the lower discharge plateau and deliver a specific capacity as high as 518 mAh g$^{-1}$ based on Li$_2$S$_4$ preloaded in ECF cathode and 328 mAh g$^{-1}$ based on the total sulfur from cathode and 0.5 M Li$_2$S$_2$ in electrolyte. The over-voltage in the initial stage of the discharge curve is related to the activation energy required to trigger reactions of [6,7]. These reactions are associated with the local diffusion of the species [S$^{2-}$] and [S$_4^{8-}$]. In other words, variation in local pore structure of the carbon matrix may affect the diffusion rate of [S$^{2-}$] and [S$_4^{8-}$] and associated over-voltage in the discharge curve.

Very few Li–S coin cells have been reported so far to survive for more than 40 cycles, with the continuous presence of the discharge plateau under similar conditions. The kinetics of the Li–S cell can be further improved by incorporation of a smart material (i.e., possessing high electronic conductivity and high Li$^+$ transport) into the carbon matrix under lean electrolyte conditions [45].

In summary, a solution-mediated pathway for sulfur reduction embracing synergistic chemical and electrochemical processes is described in Li–S cells with high sulfur loadings under lean electrolyte conditions. Excellent cycling performance of prototype Li–S cells validates the feasibility of developing practical Li–S cells using the Li$_2$S$_4$-retaining strategy.

3. Methods

3.1. Electrolyte preparation

The typical electrolyte formulation of 1 M LiTFSI, 0.30 M Li nitrate (LiNO$_3$), 0.5 M Li$_2$S$_4$ in G2 was prepared as follows: in an argon-filled glove box: LiNO$_3$ (99.99%, Sigma-Aldrich) was first added to G2 (99.5%, Sigma-Aldrich) under stirring for 4 h at room temperature. Stoichiometric amounts of Li$_2$S (99.98%, Sigma-Aldrich) and S (99.5%, Alfa Aesar) were then added into this transparent solution and heated with vigorous stirring for 48 h at 80 $^\circ$C. A homogeneous, dark-red solution was then obtained. LiTFSI was finally added to the as-obtained red solution with stirring for 4 h at 80 $^\circ$C. The same method was applied to prepare E$_2$G$_2$0.5 M Li$_2$S$_4$ and E_DOL/DME_saturated Li$_2$S$_4$ except added solvents. When the concentration of Li$_2$S$_4$ increased to 1.50 M, the concentration of LiNO$_3$ was correspondingly increased to 0.90 M. LiTFSI and LiNO$_3$ were dried for four days under vacuum at 120 $^\circ$C, and the G2 was dried over activated 3 Å molecular sieves in a glovebox prior to usage. Battery-grade DME (Gotion) and DOL (Gotion) were directly used as received to prepare the base electrolyte (E_DOL/DME) of 1 M LiTFSI, 0.3 M LiNO$_3$ in DOL:DME (1:1 vol%).

3.2. Materials preparation

The ACFC$_{S_4}$ cathode was prepared by the adsorptive impregnation method described in our recent study [11]. CH700-20-type ACFC (pore...
volume: 0.878 cm\(^3\) g\(^{-1}\); pore size: ≤ 2 nm; Brunauer-Emmet-Teller (BET) surface area: 1635 m\(^2\) g\(^{-1}\); pore-clogged surface area: < 10 m\(^2\) g\(^{-1}\); thickness: ca. 500 μm) from Kuraray Co., Ltd., Japan, was employed as a model material, with a practical sulfur loading range of 6–8.5 mg cm\(^{-2}\), to study electrolyte dependence of sulfur redox chemistry under lean electrolyte conditions. The ACFC-Li\(_2\)S\(_8\) cathode was prepared by drop-casting a solution of 1 M Li\(_2\)S\(_8\) in DME. The solution was prepared by dissolving 0.01 mol of Li\(_2\) (200 μm thick, MTI Corporation) and 0.04 mol of sulfur (99.5%, Alfa Aesar) in 5 mL of DME (battery grade, BASF) solution in a hermetically sealed glass vial at 80 °C. The prepared solution was stirred for about 18 h until a dark-red, homogeneous solution was obtained. Different volumes (20–30 mL) of this mixture were dropped directly onto ACFC with a digital micropipette (NichiPet EX II 100, 10–100 μL, Nichiryo Co., Ltd.), and the DME solvent was allowed to evaporate at 120 °C under vacuum. The final amount of sulfur loading was controlled within the ACFC in the range of 4–6.5 mg cm\(^{-2}\).

ECF was fabricated by electrospinning. Polyacrylonitrile (average MW 150,000, Sigma-Aldrich) and polyvinylcarbazole (MW = 120,000, Sigma-Aldrich) were dispersed at a 5:1 wt% ratio in anhydrous N, N-dimethylformamide (Sigma-Aldrich) and magmacarbonized for 20 h at 80 °C. Vacuum-dried silica nanoparticles (12 nm, LUDOX HS-30 colloidal silica, 30 wt% dispersion in water, Sigma-Aldrich) were then added to this solution 2 wt% at a time. The as-prepared solution was fed to assemble the ECF onto ECF-Li\(_2\)S\(_8\) electrodeposition onto Cu was performed by drop-casting a solution of 1 M Li\(_2\)S\(_8\) in DME. The solution was prepared by dissolving 0.01 mol of Li\(_2\) (200 μm thick, MTI Corporation) and 0.04 mol of sulfur (99.5%, Alfa Aesar) in 5 mL of DME (battery grade, BASF) solution in a hermetically sealed glass vial at 80 °C. The prepared solution was stirred for about 18 h until a dark-red, homogeneous solution was obtained. Different volumes (20–30 mL) of this mixture were dropped directly onto ACFC with a digital micropipette (NichiPet EX II 100, 10–100 μL, Nichiryo Co., Ltd.), and the DME solvent was allowed to evaporate at 120 °C under vacuum. The final amount of sulfur loading was controlled within the ACFC in the range of 4–6.5 mg cm\(^{-2}\)).

The polymer composite membranes were stabilized in air at 250 °C for 1 h and the mass loading was between 1.4 and 3.0 mg cm\(^{-2}\). ECF-Li\(_2\)S\(_8\) cathodes were prepared in the same way as ACFC-Li\(_2\)S\(_8\) to assemble the Li-S cell. In the operando XAS measurement, SiO\(_2\) was not added for the thin specimen of ECF-Li\(_2\)S\(_8\).

### 3.3. Materials characterisation

XPS measurements were performed with a Physical Electronics Quantera scanning X-ray microprobe. This system uses a focused, monochromatic, Al Kα X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 32-element multi-channel detection system. The X-ray beam is incident normal to the sample, and the photoelectron detector is at 45° off normal. High energy resolution spectra were collected using a pass energy of 69.0 eV with a step size of 0.125 eV. For the Ag 3d5/2 line, these conditions produced a resolution spectra were collected using a pass energy of 69.0 eV with a step size of 0.125 eV. For the Ag 3d5/2 line, these conditions produced a full width at half maximum of 0.92 eV ± 0.05 eV. The binding energy scale was calibrated using the Cu 2p3/2 feature at 932.6 ± 0.05 eV and that of Au 4f7/2 at 83.96 ± 0.05 eV. All samples were rinsed with DME several times to remove residual electrolyte and then dried under vacuum for 20 min. To avoid side reactions or electrode contamination with ambient oxygen and moisture, electrodeposited Li was transported from the glovebox to the XPS and scanning electron microscope (SEM) instruments in a hermetically sealed container filled with Ar. The morphology of Li electrodeposited onto Cu was investigated using a Quanta focused-ion-beam SEM (FEI, Quanta 650 ESEM).

All EPR measurements were performed on a Bruker ELEXSYS E580 spectrometer at both 298 K and 125 K. All samples were prepared inside a glove box filled with nitrogen immediately before EPR experiments to minimize the influence of air and moisture. For liquid samples, a capillary with ID 0.8 mm and OD 1 mm was used to hold the solution in the EPR cavity with both ends sealed by CritoSeal™ Leica Microsystems capillary tube sealant; the capillary was further placed inside a 4 mm EPR tube with the open end sealed inside a glove box. The typical settings for the spectra were microwave frequency = 9.32 GHz, sweep width = 1000 G, sweep time = 42 s, time constant = 40.96 ms, power = 20 mW, field modulation amplitude = 15 G. Absolute spin concentrations of the samples were determined by calibration curves of the spin standard TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) with concentrations varying from 0.01 mM to 100 mM.

Lithium cation diffusion coefficient (D\(_{Li}^+\)) of the range of samples was determined by \(^7\)Li pulsed field gradient (PFG) NMR measurement at Larmor frequency of 2x \(\times 232.98\) rad MHz at 20 °C using a 14.1 T (600 MHz \(^1\)H) NMR spectrometer (Agilent, USA) equipped with a 5 mm z-gradient probe (Doty Scientific, USA), which can generate a maximum gradient strength of ~31 T/m. The echo height, S(\(\delta\)), recorded as a function of gradient strength, \(\gamma\), was fitted with the Stejskal-Tanner equation [46].

\[
S(\gamma) = S(0) e^{-\frac{\gamma^2 D g (\Delta - \delta)^2}{2}} \tag{8}
\]

where S(\(\gamma\)) and S(0) are the echo heights at the gradient strengths of \(\gamma\) and 0, respectively, \(D\) is the diffusion coefficient, \(\gamma\) is \(^7\)Li gyromagnetic ratio, \(\Delta\) is the time interval between the two gradient pulses, i.e. diffusion delay, and \(\delta\) is the gradient length. The PFG-echo profiles were obtained using the stimulated echo sequence employing the bipolar gradient pulses (Dbppste, a vendor supplied sequence, Agilent, USA) as a function of gradient strength varied with 16 equal steps. The maximum gradient strength was chosen according to the echo height at the maximum gradient strength. The 90° pulse length, \(\Delta\) and \(\delta\) were 8 μs, 30 and 2 ms, respectively.

Micro-Raman measurements were performed using a 633 nm laser source, which was attenuated using a variable neutral density filter wheel (to 25 μW/μm\(^2\)), reflected off a dichroic beam splitter, and focused onto the sample using a 10X air objective. Our commercial Raman microscope is based on an inverted optical microscope (Nikon Ti-E) coupled to a Raman spectrometer (Horiba LabRAM HR). The back-scattered light is collected through the same objective, transmitted through the beam splitter cube, and dispersed through a 600 l/mm grating. The effective resolution of the instrument in 3 cm\(^{-1}\) using this configuration.

### 3.4. Operando X-ray absorption spectroscopy measurements

Li-S battery cells of Li/Li\(_2\)S\(_8\)/ECF-Li\(_2\)S\(_8\) were assembled in specially prepared CR2032 coin-cell cases. The cathode case was punched with a rectangular hole of 2 mm (horizontal) \(\times\) 1 mm (vertical) at the center and tightly patched using 7 μm-thick Kapton tape, which has X-ray transmission of ~91% at 2470 eV). After assembly, no electrolyte leakage was observed. Li-S cells were tightly sealed in an aluminum foil envelope and then shipped to the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory for the XAS measurements.

The operando XAS experiments were performed at Beamline 10.3.2 and 5.3.1 at the ALS. The X-ray beam size was 8 μm (horizontal) \(\times\) 5 μm (vertical). The XAS spectra were collected in partial fluorescence-yield mode and calibrated using elemental sulfur spectra. All the S K-edge XAS spectra were collected under constant helium gas flow in a small chamber in front of the cell, and were acquired continuously during the discharging process. The peak position of the spectrum was calibrated relative to the sharp main peak of Na\(_2\)SO\(_4\) reference sample. After subtracting the background, all the spectra intensities were normalized by taking the post-edge of S K-edge (the average of 2515–2520 eV).

### 3.5. Electrochemical measurements

The electrochemical characteristics of Li-S cells were investigated by PGCA, which is a common technique for characterization of electrochemical processes. In our case, PGCA was carried out by setting stepwise potential scans of 5 mV with a minimum current limit of 50 μA at 30 °C, using a Bio-Logic Instruments VPX potentiostat. The charge increment (\(\delta\)) was calculated by time integration of the current. Cyclic
voltammetry measurements of Li–S cells were conducted at a scan rate of 0.2 mV s⁻¹ in the range of 1.8–2.8 V at 30 °C.

Cathodes were punched into 1.267 cm² diameter disks and weighed to acquire the accurate sulfur loading for each piece. Added volume of electrolytes was determined by the sulfur loading, based on the E/S ratios, with a digital micropipette (Nichipet EX II 100, 10–100 μL, Nichiro Co., Ltd.). Half-cells with 200 μm thick Li metal foil (MTI Corporation) as the anode and polyethylene (Asahi Kasai, Japan) as the separator were assembled using CR2032 coin cells in an MBraan LAB-master glove box with an Ar atmosphere (<1 ppm O₂ and <1 ppm H₂O). In the Li/LiCu cell without the polyethylene separator, a thin polypropylene spacer r with a central hole was used to eliminate effects of a separator and crumbling pressure on the morphology of Li electrodeposits. The galvanostatic discharge/charge cycles were tested using a LANHE battery tester in an incubator at 30 °C.

Data availability

Data supporting the findings of this study are available within the paper and its Supplementary Information file, and are available from the corresponding author upon reasonable request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement


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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2020.105041.
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