Chinese Chemical Letters 36 (2025) 110654

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Editorial

Sulfur reduction reaction mechanism elucidated with *in situ* Raman spectroscopy

Lithium metal batteries (LMBs) have attracted great intention due to the high energy density [1]. Among various battery technologies, lithium-sulfur (Li-S) batteries are also very unique but important due to its high energy density, low cost and available sources [2]. Although Li-S batteries exhibit high energy density, the cycling life is poor, especially for large-capacity pouch cells [3]. The cycling performance of Li-S batteries is crucially determined by 16-electron complex sulfur reduction reaction (SRR) from S_8 molecules to Li_2S solid, which involves the multiple potential interwoven branches among lithium polysulfide intermediates (LiPS, *e.g.*, S_8, Li_2S_8, Li_2S_6, Li_2S_4 and Li_2S) [4]. The obvious shuttle for soluble LiPS across the cathode and anode leads to the battery capacity fading. Thus, it is necessary to decrease the accumulation of soluble LiPS in the electrolyte through catalysts fastening the key conversion step from high-order polysulfides to insoluble Li_2S_2/Li_2S. Although some effort has been devoted to catalyze SRR, the complex mechanism remains unclear. To address this issue, Duan *et al.* tried to solve it based on nitrogen, sulfur, dual-doped holey graphene framework (N, S-HGF) electrocatalyst in *Nature* [5].

In their work, Duan *et al.* profiled the SRR encompassing the sophisticated 16-electron conversion process from S_8 molecules to Li_2S solid was involved with multiple soluble LiPS intermediates (Fig. 1a). In the CV curve for SRR with N, S-HGF (Fig. 1b), there are two main peaks (one centered at 2.2–2.5 V and another centered at 1.9–2.1 V) during discharge process. Through calculating the charge number by the integrated area in CV, Li_2S_4 is believed as the primary intermediate for separating the two reduction peaks, $S_8 + 4Li^+ + 4e^- \rightarrow 2Li_2S_4$ and $2Li_2S_4 + 12Li^+ + 12e^- \rightarrow 8Li_2S$. They further employed *in situ* Raman spectroscopy technique (Fig. 1c) for probing the specific reaction intermediates in following part.

In situ Raman spectroscopy was used to probe the specific reaction intermediates along a discharge CV scan (Figs. 2a and b). The S_8 signal (469 cm^{-1}) decreased to disappear at ~2.36 V, followed by Li_2S_8 signal at 508 cm^{-1} at ~2.44 V and the Li_2S_6 signal at 399 cm^{-1}, which is attributed to the electrochemical transformation of Li_2S_8 to Li_2S_4 peak emerged at 501 cm^{-1}. As the potential decreased, Li_2S_4 and Li_2S_6 became the main polysulfide species, with the decrease of the Li_2S_6 peak at 399 cm^{-1} at ~2.30 V. In the voltage-dependent concentration profile (Fig. 2c), each LiPS derived from the peak area exhibited a similar sequence of concentration evolution for S_8, Li_2S_8, Li_2S_6 and Li_2S_4 with the decrease of the potential. The above analysis validated the SRR molecular pathway: $S_8 \rightarrow Li_2S_8 \rightarrow 2Li_2S_4\ (Li_2S_8 + Li_2S_4 \rightleftarrows 2Li_2S_6) \rightarrow 8Li_2S$.

In summary, Duan *et al.* successfully established the complex 16-electron SRR network for Li-S batteries. The work not only gives the example on the electrocatalytic approach for studying complex SRR mechanism for Li-S batteries, but also provides useful insights into SRR electrocatalyst design for Li-S batteries. In addition, this research methodology is also expected to study other catalytic reactions in future. This work demonstrates to be perfect from foundation understanding to practical application.

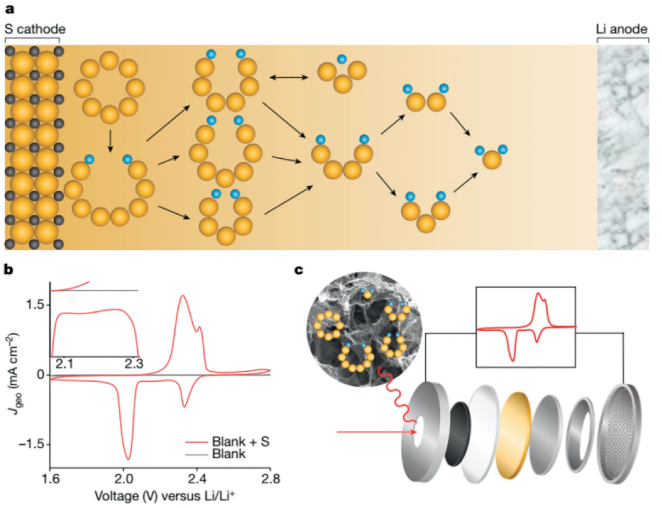

Fig. 1. (a) Illustrative SRR network involved in the Li-S battery. (b) Cyclic voltammetry of the SRR catalyzed by N, S-HGF. (c) Illustrative *in situ* Raman technique used. Reprinted with permission [5]. Copyright 2024, Nature.

https://doi.org/10.1016/j.cclet.2024.110654

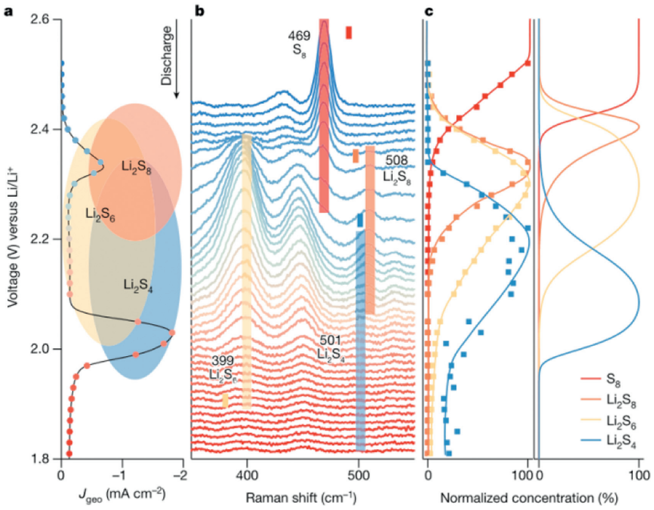

Fig. 2. (a) CV profile and (b) experimental *in situ* Raman spectra of the SRR catalyzed by N, S-HGF. (c) Comparison between voltage-dependent experimental concentrations derived from *in situ* Raman spectra and simulated concentrations from DFT. Reprinted with permission [5]. Copyright 2024, Nature.

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

Haixia Wu: Writing – original draft, Project administration, Formal analysis. **Kailu Guo:** Funding acquisition, Formal analysis.

Haixia Wu*
Kailu Guo
College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China

*Corresponding author.
E-mail address: haixiawu@lynu.edu.cn (H. Wu).

Received 2 September 2024
Revised 8 November 2024
Accepted 19 November 2024
Available online 20 November 2024

References

[1] Z.H. Chu, S.D. Zhuang, J.H. Lu, et al., Chin. Chem. Lett. 34 (2023) 107563.
[2] Q.J. Shao, S.D. Zhu, J. Chen, Nano Res. 16 (2023) 8097–8138.
[3] C. Zhao, G.L. Xu, Z. Yu, et al., Nat. Nanotechnol. 16 (2021) 166–173.
[4] Y.X. Yin, S. Xin, Y.G. Guo, et al., Angew. Chem. Int. Ed. 52 (2013) 13186–13200.
[5] R.L. Liu, Z.Y. Wei, L.L. Peng, et al., Nature 626 (2024) 98–104.