

**Link Foundation Energy Fellowship  
Final Report**

**Developing High-Capacity Rechargeable Batteries Based on  
Lithium-Sulfur Chemistry**

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## Introduction

The development of portable and transportation applications, such as the booming electrical vehicles, heavily relies on high-energy battery technologies. As the current Li-ion batteries approach the energy storage limit, the new battery chemistry that promises higher theoretical energy density should be pursued.<sup>1</sup> Lithium-sulfur (Li-S) batteries use light-weight lithium as the anode and low-cost sulfur as the cathode and ether-based solution as the electrolyte. With the chemical conversion reaction of  $16 \text{ Li} + \text{S}_8 \leftrightarrow 8 \text{ Li}_2\text{S}$ , Li-S batteries can provide a theoretical specific energy (2600 Wh/kg), 5 times over that of current Li-ion batteries.<sup>2, 3</sup> Practical Li-S batteries require a low electrolyte amount and a limited amount of Li metal, otherwise, they cannot outperform the state-of-the-art Li-ion batteries in energy density.<sup>4, 5</sup> But in most cases, both of these important parameters are compromised in order to achieve long cycle life. The project aims at understanding the electrochemical behavior of the batteries at the application-relevant conditions (low amount of electrolyte and Li metal) and then designing practical electrodes (S and Li) based on the acquired knowledge, and eventually building high capacity rechargeable batteries based on Li-S chemistry.

## Results

Our work started out by studying the relationship between the electrochemical behavior and the electrolyte amount in a Li-S battery. Using a carbon nanotube/sulfur composite (CNT-S) as S cathode, we compared the electrochemical behavior of Li-S cells under flooded electrolyte and lean electrolyte (limited amount of electrolyte).<sup>6</sup> The former shows the typical charging-discharging performance of Li-S batteries whereas the latter exhibits abnormal electrochemical behavior, showing the large overpotential in both charging and discharging steps. We thus uncovered the dependence of electrochemical sulfur conversion on the electrolyte amount: the kinetics of sulfur redox reactions becomes sluggish as electrolyte amount decreases, resulting in deactivation of Li-S batteries. A molybdenum phosphide (MoP) catalyst was then developed to address the sluggish kinetics problem. The presence of only 5% of MoP in the CNT-S electrode could effectively catalyze the sulfur conversion under lean electrolyte condition and maintain a normal charging-discharging behavior. The conductive surface of MoP with good adsorption of lithium polysulfide ( $\text{Li}_2\text{S}_x$ ,  $x=3-8$ ) intermediate plays a key role in the electrocatalysis of S

conversion. We have demonstrated an electrocatalytic way to achieve high-performance Li-S batteries under the practical lean electrolyte condition.

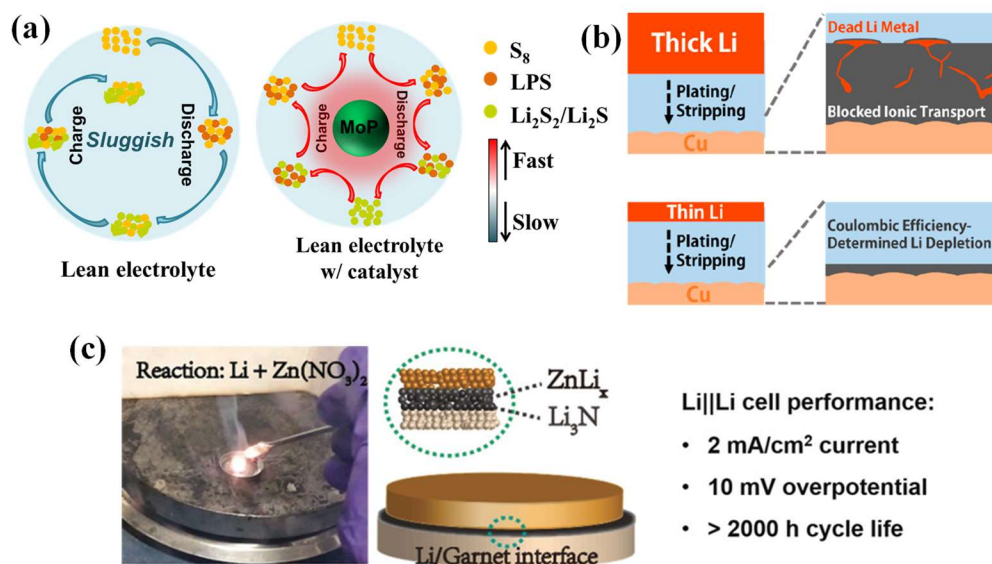


Figure 1. (a) Schematic illustration of electrochemical behaviors of the Li-S batteries under lean electrolyte condition with and without MoP catalyst. (b) Schematic illustration of failure mechanisms of thick and thin Li electrodes. (c) Structure of the Li/garnet interface induced by energetic reactions between Li and  $Zn(NO_3)_2$  and performance summary of the interface-enabled Li||Li cell.

Thick Li foil with excessive amount of Li is generally used in Li-S and other Li metal batteries to compensate the Li loss during cycling. Given that only thin Li metal (limited Li amount) is of practical interest, we studied the failure mechanism of both thick and thin Li electrodes to understand the difference.<sup>7</sup> We repeated the deposition and removal of Li metal (also called Li plating/stripping) on a Cu electrode in the commercial carbonate electrolyte to evaluate the reversibility and cyclicity of a Li metal electrode. Although both thick and thin Li metal electrodes have side reactions with the organic solvent in the electrolyte, their failure reasons are different. The failure of the thick Li electrode is because the side reaction produces a dense and resistive solid electrolyte interphase (SEI) layer on the surface, which blocks the Li ion transport. By contrast, the failure of the thin Li electrode is owing to the fast Li metal depletion caused by side reactions, and their cycle life is determined by Coulombic efficiency (CE), namely the

reversibility of the Li plating/stripping process. We, therefore, put emphasis on the necessity of limiting side reactions and improving CE to realize practically useful thin Li metal electrodes.

In fact, the CE of Li metal electrode should be at least 99.7% to rival the stability of Li-ion batteries.<sup>8</sup> With this purpose, the electrolyte composition was systematically tuned by various additive-solvent combinations to reduce the side reactions.<sup>9</sup> However, we found that CE of Li metal electrode can hardly exceed 99% since at least one of the components, salt, organic solvent, or additive, constantly decomposes with Li metal plating/stripping. By comparison, garnet-structure solid-state electrolytes, a class of ceramic oxides, are intrinsically stable against Li metal and promise not only high CE value but also better battery safety. The only downside is the poor contact between the Li metal and garnet at their solid-solid interface. We have developed a solid-state interface (ZNR interface) from an energetic reaction between Li and  $\text{Zn}(\text{NO}_3)_2$  that can successfully glue Li metal and the garnet electrolyte.<sup>10</sup> This interlayer, composed of Zn, Zn-Li alloy,  $\text{Li}_3\text{N}$ ,  $\text{Li}_2\text{O}$ , and other species, affords highly efficient conductive pathways for Li-ion transport through the interface. The solid-state Li metal battery with such interface achieves high capacity, fast charging-discharging rate, and low overpotential comparable to those of the liquid-electrolyte Li metal cells, but with longer cycle life, and better safety. Using a thin Li metal electrode, we confirm that the CE of the Li/garnet solid-state interface is over 99.5%, which is indeed higher than that of a Li metal electrode operated in the liquid electrolyte.

## **Significance, impact, and perspective**

Realization of the practical Li-S batteries requires combinatorial research efforts in the sulfur cathode, the lithium anode, and the electrolyte. This project provides fundamental understanding on the limitation of Li-S batteries under practical conditions and further offers innovative strategies to overcome these problems at cathode/electrolyte and anode/electrolyte interfaces. The as-designed rechargeable batteries represent an important step towards commercially relevant Li metal and Li-S batteries.

The catalysis-enabled sulfur cathode and high-efficiency solid-state Li/electrolyte interface are readily integrated into a future all-solid-state Li-S battery concept with high capacity and better safety.

## Reference

1. Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M., Li-O<sub>2</sub> and Li-S Batteries with High Energy Storage. *Nat. Mater.* **2011**, *11*, 19-29.
2. Wild, M.; O'Neill, L.; Zhang, T.; Purkayastha, R.; Minton, G.; Marinescu, M.; Offer, G. J., Lithium Sulfur Batteries, a Mechanistic Review. *Energy Environ. Sci.* **2015**, *8*, 3477-3494.
3. Lim, W. G.; Kim, S.; Jo, C.; Lee, J., A Comprehensive Review of Materials with Catalytic Effects in Li-S Batteries: Enhanced Redox Kinetics. *Angew. Chem. Int. Ed.* **2019**, *58*, 18746-18757.
4. Zhao, M.; Li, B. Q.; Peng, H. J.; Yuan, H.; Wei, J. Y.; Huang, J. Q., Lithium-Sulfur Batteries under Lean Electrolyte Conditions: Challenges and Opportunities. *Angew. Chem. Int. Ed.* **2020**, *59*, 12636-12652.
5. Zhu, K.; Wang, C.; Chi, Z.; Ke, F.; Yang, Y.; Wang, A.; Wang, W.; Miao, L., How Far Away Are Lithium-Sulfur Batteries From Commercialization? *Front. Energy Res.* **2019**, *7*.
6. Yang, Y.; Zhong, Y.; Shi, Q.; Wang, Z.; Sun, K.; Wang, H., Electrocatalysis in Lithium Sulfur Batteries under Lean Electrolyte Conditions. *Angew. Chem. Int. Ed.* **2018**, *130*, 15775-15778.
7. Zhang, Y.; Zhong, Y.; Shi, Q.; Liang, S.; Wang, H., Cycling and Failing of Lithium Metal Anodes in Carbonate Electrolyte. *J. Phys. Chem. C* **2018**, *122*, 21462-21467.
8. Zheng, J.; Kim, M. S.; Tu, Z.; Choudhury, S.; Tang, T.; Archer, L. A., Regulating Electrodeposition Morphology of Lithium: towards Commercially Relevant Secondary Li Metal Batteries. *Chem. Soc. Rev.* **2020**, *49*, 2701-2750.
9. Zhang, Y.; Zhong, Y.; Liang, S.; Wang, B.; Chen, X.; Wang, H., Formation and Evolution of Lithium Metal Anode–Carbonate Electrolyte Interphases. *ACS Mater. Lett.* **2019**, *1*, 254-259.
10. Zhong, Y.; Xie, Y.; Hwang, S.; Wang, Q.; Cha, J.; Su, D.; Wang, H., A Highly Efficient All-Solid-State Lithium/Electrolyte Interface Induced by an Energetic Reaction. *Angew. Chem. Int. Ed.* **2020**, *59*, 14003-14008.

## List of publications and conferences that have acknowledged Link Foundation support

### Publication

<sup>||</sup>denotes equal contribution

1. **Y. Zhong**; Y. Xie; S. Hwang; Q. Wang; J. Cha; D. Su; H. Wang, A Highly Efficient All-Solid-State Lithium/Electrolyte Interface Induced by an Energetic Reaction. *Angew. Chem. Int. Ed.* **2020**, *59*, 14003-14008.
2. **Y. Zhong**; F. Lin; M. Wang; Y. Zhang; Q. Ma; J. Lin; Z. Feng; H. Wang, Metal Organic Framework Derivative Improving Lithium Metal Anode Cycling. *Adv. Funct. Mater.* **2020**, *30*, 1907579.

3. Y. Yang<sup>||</sup>; **Y. Zhong<sup>||</sup>**; Q. Shi; Z. Wang; K. Sun; H. Wang, Electrocatalysis in Lithium Sulfur Batteries under Lean Electrolyte Conditions. *Angew. Chem. Int. Ed.* 2018, *130*, 15775-15778.
4. Y. Zhang<sup>||</sup>; **Y. Zhong<sup>||</sup>**; Q. Shi; S. Liang; H. Wang, Cycling and Failing of Lithium Metal Anodes in Carbonate Electrolyte. *J. Phys. Chem. C* 2018, *122*, 21462-21467.
5. Y. Zhang; **Y. Zhong**; Z. Wu; B. Wang; S. Liang; H. Wang, Solvent Molecule Cooperation Enhancing Lithium Metal Battery Performance at Both Electrodes. *Angew. Chem. Int. Ed.* 2020, *59*, 7797-7802.
6. Y. Hu; **Y. Zhong**; L. Qi; H. Wang, Inorganic/Polymer Hybrid Layer Stabilizing Anode/Electrolyte Interfaces in Solid-State Li Metal Batteries. *Nano Res.* 2020, Accepted.
7. Y. Zhang; **Y. Zhong**; S. Liang; B. Wang; X. Chen; H. Wang, Formation and Evolution of Lithium Metal Anode–Carbonate Electrolyte Interphases. *ACS Mater. Lett.* 2019, *1*, 254-259.
8. Y. Zhang; Q. Shi; **Y. Zhong**; H. Wang, Intrinsically High Efficiency Sodium Metal Anode. *Sci. China Chem.* 2020, Accepted.

### Conference

1. **Y. Zhong**. Surface Chemistry and Electrocatalysis in Phosphide-Stabilized Lithium-Sulfur Batteries, Oral, MRS Fall Meeting, 2019, USA. (**MRS Graduate Student Silver Award**)

### **How did the Fellowship make a difference?**

The Link Foundation Energy Fellowship is a great honor and encouragement for me during my PhD study. The Fellowship allows me to pursue the research area I am interested in and motivates me to work on some risky but rewarding projects. For example, I have spent almost one year exploring the materials synthesis and processing of the solid-state electrolyte, where I learned many valuable knowledge and techniques used in the battery research frontier. The funding support also gives me the opportunity to attend the 2019 MRS fall meeting and win the MRS Graduate Student Award. With the freedom offered by the Fellowship, I was also able to mentor some younger lab members, from which I have gained a deeper understanding of my research work and tasted the flavor of leading and advising projects. All of these experiences are important and valuable assets for my PhD study as well as for my future research career.