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COMMENTARY

The Innovation Materials

The "Black Box" of Li-S batteries unveiled by liquid cell transmission electron microscopy

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Received: April 1, 2024; Accepted: July 2, 2024; Published Online: December 17, 2024; https://doi.org/10.59717/j.xinn-mater.2024.100114

Citation: Zhou S., Xu G., Amine K., et al. (2025). The "Black Box" of Li-S batteries unveiled by liquid cell transmission electron microscopy. *The Innovation Materials* **3**:100114.

Ever since the first attempt to use sulfur as the cathode, lithium-sulfur (Li-S) batteries have undergone over sixty years development, and emerge as promising next-generation energy storage due to their high energy densities and cost-effectiveness. The remarkable milestones of Li-S batteries mainly include three stages: achieving rechargeable sulfur cathodes, enhancing sulfur utilization, and optimizing electrochemical reactions under practical conditions. Central to these advancements is the understanding of sulfur's role within the electrode/electrolyte interface dynamics. Fundamentally, Li-S battery operation involves the reversible redox conversion between sulfur and lithium sulfide (Li_2S), predominantly occurring through a series of soluble lithium polysulfide intermediates with variable chain length (LiPSs, Li_2S_n, $2<n<8$). The mechanisms governing the distribution and conversion of highly concentrated LiPSs, involving intricate interactions between the active sites and LiPSs, as well as LiPSs intermolecular, remain decisive for the electrochemical performance and efficiency of Li-S batteries. A widely acknowledged mechanism in Li-S electrochemical deposition involves the nucleation of Li_2S from soluble LiPSs, followed by the further growth along the conductive electrode surface. However, due to the insulating property, the reaction should be prevented once the active sites have been taken up, which is in contradictory to thick deposition of Li_2S. Unravelling these complex interactions is imperative for not only enhancing the fundamental understanding of Li-S battery chemistry but also for guiding the design and optimization strategies.

Over the past few decades, there has been an intensified focus on elucidating the fundamental electrochemical reaction mechanisms in Li-S batteries (Figure 1A). The pivotal role of *in-situ* characterization techniques in providing a mechanistic understanding of these batteries has promoted a multitude of studies employing different methods.[1] These mainly include X-ray-based diffraction and absorption spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, ultraviolet-visible spectroscopy, scanning and transmission electron microscopy (TEM), etc. A comprehensive understanding of the interfacial reactions in Li-S batteries necessitates that these characterization techniques possess capabilities such as maintaining the liquid electrolyte environment, distinguishing between solid and liquid LiPSs species, and probing the distribution of LiPSs at specific micro- or nano-scale areas. However, due to the extreme sensitivity of LiPSs species, cutting-edge *in-situ* characterization techniques must be meticulously designed to mitigate the influence of environmental factors, atmospheric conditions, and high-energy detection sources such as electron beams and synchrotron X-rays. For X-ray-based techniques, limitations arise in detecting crystalline materials and an inability to identify amorphous or ultrafine particles. In molecular spectroscopy, the identification of individual

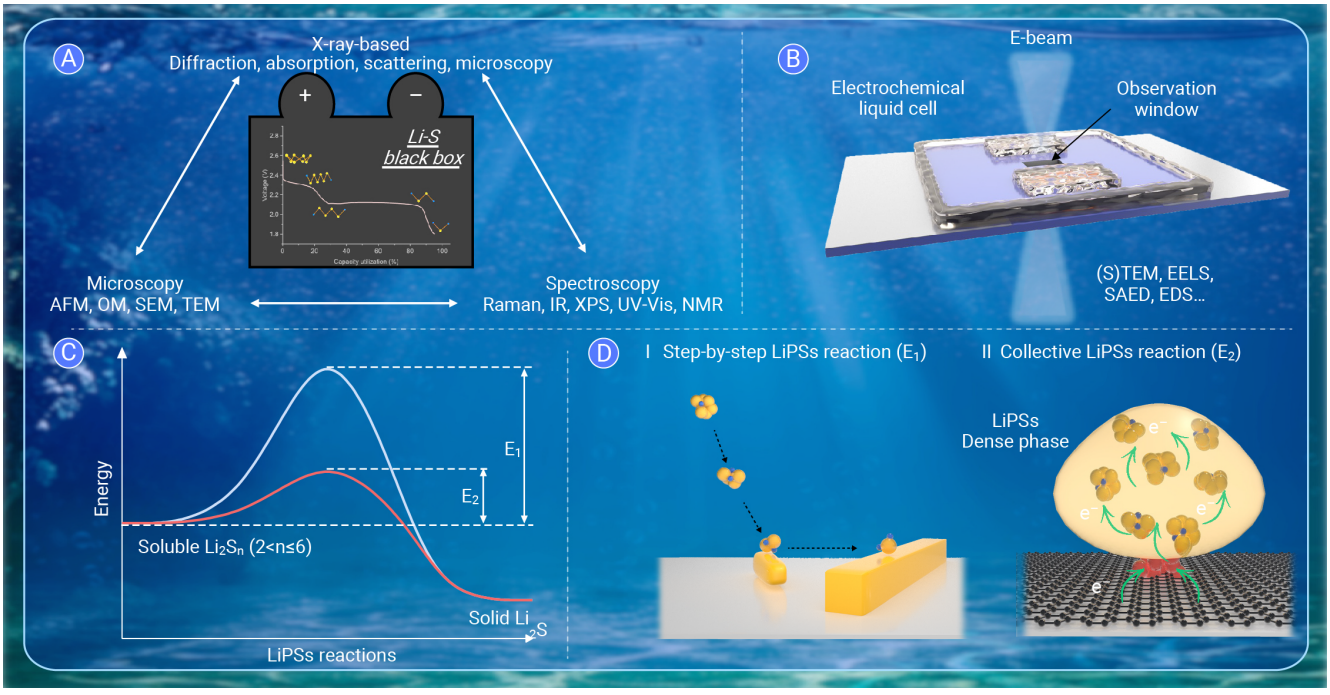

Figure 1. Unveiling the "black box" of Li-S batteries (A) Schematic summary of the recent characterization techniques in investigating the black box of Li-S batteries. (B) Schematic illustration of liquid-cell EC-TEM. (C, D) Investigation of different LiPSs interfacial reaction pathways in Li-S batteries.

LiPSs relies on S–S vibration analysis. However, the detection is complicated as all LiPSs exhibit vibration peaks within a narrow range around 500 cm^{-1}, leading to difficulties in discerning mixed LiPSs from overlapping spectra. *In-situ* electron microscopy employs mainly two types of devices: open-cell and liquid-cell configurations. The open-cell configuration, using a Li_2O layer as a solid electrolyte, is hindered by its limited ability to investigate electrode/electrolyte interface information accurately, not to mention the evaporation of sulfur in high-vacuum chambers. Conversely, the liquid-cell configuration faces limitations due to the resolution constraints imposed by the thickness of the liquid layer and the SiN_x membrane, as well as the complexity of the experimental setups. Therefore, despite the significant strides made in the analysis of mechanisms through *in-situ* electrochemical characterizations, numerous questions and challenges persist in this rapidly evolving field, underscoring the need for further innovative research and development.

A recent publication in the Nature journal reported a significant advancement in the field of Li-S batteries with the development and utilization of an *in-situ* liquid-cell electrochemical transmission electron microscopy (EC-TEM) technique (Figure 1B).[2] This method, which integrates a liquid environment with an electric field, has illuminated the previously obscure electrochemical reactions occurring within Li-S batteries, effectively unveiling the 'black box' of their internal processes. The genesis of EC-TEM can be traced back to 2003 when Ross et al. introduced nanofabrication techniques to create a liquid-cell featuring two electrodes, utilizing an electron transparent silicon nitride (SiN_x) membrane as the observation window.[3] Progressing further, in 2009, Zheng et al. refined this approach by employing thinner SiN_x membranes (25 nm) to serve as the electron transparent window, coupled with a reduced liquid thickness (200 nm).[4] This innovation facilitated an impressive imaging resolution of 1 nm. To enhance the imaging resolution further and ensure the structural integrity of the window film under high vacuum, a smaller rectangular window (50 μm) was adopted instead of the previously used square window (100 μm). Comparatively, the SiN_x membrane-based liquid cell has superior mechanical strength over the small liquid droplet encapsulated in graphene sheets of the graphene liquid cell reported by Yuk et al. in 2012.[5] This has propelled the SiN_x membrane liquid cell with different integrated external fields, such as electric, light, fluid, gas, etc., to become the mainstream technology in this domain. In the Nature article, it involved concerted efforts to optimize the achievable resolution by meticulously thinning the liquid layer and observation membranes, as well as refining the window area configuration. A comprehensive analysis was conducted to assess the stability and environmental sensitivity of the system, addressing challenges posed by unstable LiPSs, volatile electrolytes, and the susceptibility of Li_2S to beam damage. Through a synergetic enhancement of both the instrumental and experimental design, the *in-situ* EC-TEM has enabled real-time, atomic-scale visualization of the interfacial reactions within Li-S batteries, while minimizing beam-induced damage to the observation. We could highlight three specific aspects to demonstrate the immense potential of this technique in advancing our understanding and optimization of Li-S batteries.

(1) The observations have uncovered a previously unidentified interfacial-reaction pathway in Li-S batteries, characterized by the rapid deposition of nanometer-scale Li_2S crystals from a dense liquid phase of LiPSs (Figures 1C-D). It was discovered that this collective pathway, which is energy-favourable for the conversion from soluble Li_2S_n ($2<n\leq6$) to solid Li_2S, deviates from the conventional step-by-step pathway in classical electrochemical reactions. This collective-reaction phenomenon is driven by long-range interactions between LiPSs and clusters of metal atoms, termed active centers, on the electrode surface. By conceptualizing the aggregated LiPSs as a reaction unit, the reaction mechanism of Li-S batteries is investigated through their collective motion, charge transfer, and crystallization behaviour. The charge transfer extends beyond the surface and can be coordinated through the dense phase of LiPSs at the interface. The focus should shift towards trade-off between the utilization of active centers and the increasing concentration of LiPSs. For instance, if the gathered LiPSs can actively participate in the reaction, modifying their distribution and conversion process could significantly enhance the instantaneous deposition, thereby boosting the fast-charging performance of Li-S batteries under practical conditions.

(2) Due to their inherent instability and transient property, capturing and discriminating between different soluble and insoluble LiPSs species presents a significant challenge. By employing a combination of advanced detectors in TEM (Figure 1B), such as selected area electron diffraction (SAED), electron energy loss spectroscopy (EELS), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS), it is possible to confirm the presence of distinct discharge products in Li-S batteries at specific reaction states. For instance, the structure of Li_2S_2 has been a contentious topic, and its detection has proven to be experimentally elusive. In this study, by precisely controlling the potentiostatic program and discharge state, Li_2S_2 intermediates were formed and maintained without further conversion into Li_2S or dissolution into the electrolyte. This state allowed sufficient time for detailed structural and image analyses via SAED and TEM investigations. Furthermore, the investigation of Z-contrast in HAADF-STEM images elucidated the structure and morphology of the droplet-like dense phase, which was further corroborated by SAED patterns and EDS mappings. Complementing these techniques, EELS spectra further provided solid evidence to distinguish between the composition of LiPSs electrolyte and solid Li_2S particles. Looking forward, it deserves efforts to further unravel how solid Li_2S_2 particles or the droplet-like dense phase influence the subsequent growth of Li_2S as well as their interactions between multiple Li_2S_2 particles or multiple droplets. Additionally, incorporating detection techniques such as mass or optical spectrometry and X-ray will enable a more comprehensive and cross-scale understanding of the electrochemical reactions occurring within batteries at both the atomic and cell levels.

(3) Theoretical calculations, including density functional theory (DFT) and molecular dynamics (MD), have been employed to elucidate the interactions between metallic active centers and LiPSs, as well as the intricate multi-electron reactions within Li-S batteries. These studies have explored how the variation of LiPSs concentration at the interface impacts the dynamic charge redistribution. The findings indicate that long-range electrostatic interactions between active centers and LiPSs induce the formation of the dense phase. Furthermore, the application of electrode potential has substantiated the collective charge transfer within this LiPSs dense phase. Looking ahead, it is recommended that future investigations delve into the changes in electronic structure, geometric structure, Gibbs free energy, etc., under more realistic conditions, particularly when increasing LiPSs concentrations, which corresponds to the high-sulfur loading and lean electrolyte condition. By expanding our understanding of these complex interactions and reactions at a molecular level, we can pave the way for the next generation of high energy-density Li-S batteries.

In conclusion, this research offers a detailed elucidation of the interfacial reactions in Li-S batteries, shedding light on complex electrochemical processes. This enhanced understanding paves the way for innovative designs of Li-S electrocatalysts and refined optimization strategies, which hold the promise of yielding more efficient and robust battery systems. Future endeavours should focus on tailoring electrode materials to leverage the observed collective-reaction phenomena, thereby boosting the performance of Li-S batteries. Moreover, it is crucial to investigate the universality of this collective-reaction behaviour across different battery systems to broaden its applicability.

While achieving clear observations of electrochemical reactions in liquid electrolyte is a significant advance, there are potential divergences from the actual state in coin-type or pouch cells due to several limitations, including sluggish diffusion in the thin liquid layer, limited reactants, cumulative electron beam damage, and restricted internal space. To address this, the advancement of *in-situ* EC-TEM techniques is imperative to deepen our understanding of the dynamics within operating batteries, such as increasing the reservoir space of the liquid or introducing liquid flow without sacrificing spatial resolution. Additionally, experiments should focus on the initial stages of structural and chemical evolution under low e-beam dose rate and include different cross-scale characterizations of X-ray-based techniques, spectroscopy, and microscopy. Future development should strive to enhance these *in-situ* methodologies and extend their application to real-time analysis of batteries under practical operating conditions. It is also essential to consider the integration of physical variables such as temperature fluctuations, phase transitions, and pressure variations within the liquid environment. These comprehensive approaches will significantly contribute to the evolution of battery technology and energy storage systems.

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FUNDING AND ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants no. 223B2905, 22288102, 22021001, U22A20396, 32101217, 21991151, 2191150, 91934303) and the Fundamental Research Funds for the Central Universities (20720220009). The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.