ENHANCING THE AIR AND INTERFACIAL STABILITY OF SULFIDE-BASED SOLID ELECTROLYTE

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ABSTRACT

Sulfide electrolyte is one of most promising candidates for solid-state batteries, but the poor air and interfacial stability hinder its practical applications. In our work, Sn-O dual-substituted chlorine-rich argyrodite electrolyte exhibits a high reversible ionic conductivity over 8 mS cm^{-1} after exposure in humid air. At the anode side, in-situ polymerized poly-dioxolane interlayer enables dendrite-free lithium deposition/stripping at 0.5 mA cm^{-2} over 1200 hours. Furthermore, Cu^{2+}-substituted chloride electrolyte in composite cathode enables all-solid-state batteries stably cycling over 200 cycles with a high reversible capacity of 139.2 mAh g^{-1}.

KEY WORDS

Solid-state batteries, sulfide electrolyte, air stability, lithium-anode compatibility, electrochemical stability.

1. INTRODUCTION

Sulfide solid electrolytes (SEs) are well-known for their high ionic conductivity over 10 mS cm^{-1}, but suffers from extreme sensitivity to H_2O and will generate toxic H_2S. Most current studies for enhancing air stability of sulfide SEs sacrifice their conductivity to some extent. [1] Besides, sulfide SEs exhibit a narrow electrochemical window (1.7-2.0 V vs Li/Li^+), which are intrinsically unstable to lithium anode and high-voltage cathode ($\geq$ 4.3 V).[2] Comparatively, ether-based polymer electrolytes have higher lowest unoccupied molecular orbital (LUMO) energy than chemical potential of lithium, indicating their stability with lithium anode; meanwhile, chloride electrolytes possess higher oxidation potential than that of sulfide SEs, suggesting their compatibility with high-voltage cathode.

2. STRATEGIES FOR ENHANCING THE AIR AND INTERFACIAL STABILITY

2.1 Enhancing air stability

Our first study focuses on enhancing the air stability of chlorine-rich sulfide-based SEs, guided by the Hard-Soft-Acid-Base theory.[3] Employing dual-substitution, the electrolyte $Li_{5.5}P_{0.9}Sn_{0.1}S_{4.2}O_{0.2}Cl_{1.6}$ (with Sn and O substituted for P and S, respectively) demonstrates improved moisture tolerance while maintaining a high conductivity of 8.7 mS cm^{-1}. This advancement reduces the environmental requirements for sulfide electrolyte production.

2.2 Enhancing lithium-anode compatibility

The second study targets the interfacial issues between the lithium anode and chlorine-rich sulfides.[4] A poly-dioxolane-based (PDOL) interlayer through in-situ polymerization was introduced at lithium|sulfide interface, enabling dendrite-free lithium stripping and deposition for over 1200 hours at 0.5 mA cm^{-2}. The PDOL interlayer contributes to the formation of a robust solid electrolyte interphase consisting of ether-based polymer and F- and N-rich inorganic compounds, facilitating uniform lithium stripping/deposition and mitigating the risk of short circuits.

2.3 Enhancing electrochemical stability

Lastly, the third study focuses on enhancing the electrochemical stability of the SEs in the composite cathode.[5] A novel Cu^{2+}-substituted chloride-based SE ($Li_{2.1}Zr_{0.95}Cu_{0.05}Cl_6$) was developed, characterized by reduced anodic current over 4 V, minimal electrochemical polarization, and rapid lithium-ion diffusion kinetics. SSLBs assembled with the Cu^{2+}-substituted electrolyte demonstrate a high residual capacity of 139.2 mAh g^{-1} with a retention rate of 96.9% after 200 cycles at a 0.5 C rate.

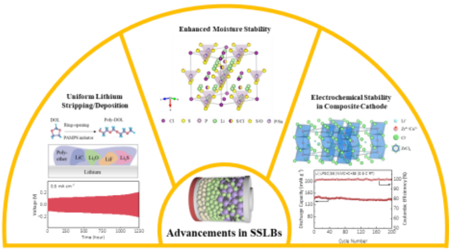

Fig.l: The schematic of advancements in solid-state lithium batteries: enhancing the air and interface stability of sulfide-based electrolyte.

REFERENCES

1. Q. Zhao, S. Stalin, C. Zhao, L.A. Archer, *Nat. Rev. Mater.* 5 (2020) 229.
2. Y. Liang, H. Liu, G. Wang, C. Wang, Y. Ni, C. Nan, L. Fan, *InfoMat*. 4 (2022) e12292.
3. G. Li, S. Wu, H. Zheng, Y. Yang, J. Cai, H. Zhu, X.

Huang, H. Liu, H. Duan, *Adv. Funct. Mater*. 33 (2023) 2211805.

4. G. Li, S. Wu, C. Gao, Y. Shen, H. Zheng, M. Yang, H. Liu, H. Duan, *Nano Energy*. 127 (2024) 109786.
5. G. Li, Y. Shen, C. Gao, A. T. Med, M. Yang, H. Liu, H. Duan, *Energy Storage Mater*. 71 (2024) 103673.