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Investigation on Failure Mechanisms and Countermeasures of All-Solid-State Lithium-Metal Batteries

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Abstract. Lithium metal batteries are considered the premier option for next-generation high energy density storage device. Utilizing lithium metal as the anode is anticipated to surpass the energy density constraints of existing lithium-ion batteries, due to its exceptionally high theoretical particular capacity (3860 $mAhg^{-1}$) and the lowest electrochemical potential (-3.04 V). Nonetheless, interfacial issues between Solid-State Electrolytes (SSEs) and lithium metal anodes hinder the pragmatic execution and extensive commercialization of All-Solid-State Lithium Metal Batteries (ASSLMBs). This research begins by discussing the current mainstream classifications of Solid-State Electrolyte (SSE), which primarily include inorganic SSE and polymer SSE. Inorganic SSE mainly consist of oxide-based, sulfide-based, and halide-based SSE. The study subsequently explored three major interfacial issues between SSE and lithium metal anodes, from the most fundamental thermodynamic instability-chemical failure, to the kinetically driven process caused by chemical failure under electric fields, namely electrical failure and electrochemical failure, and ultimately to the macroscopic physical manifestations—mechanical failure—resulting from both chemical and electrochemical degradation processes. Among these, the main reason for chemical failure is that lithium metal, as a potent reducing agent, will react with most SSE. Electrical and electrochemical failures are mainly attributed to interfacial side reactions caused by uncontrolled lithium dendrite growth during battery cycling. The mechanical failure stems from the inability of rigid SSE to can cope the significant volume fluctuations of lithium metal during deposition/stripping processes. For each failure, this research gives the latest research progress on mechanistic solutions.

Keywords: All-Solid-State Lithium-Metal Batteries (ASSLMBs), Solid-State Electrolyte (SSE), Interfacial issues

1. Introduction

In practical applications, the energy density of lithium-ion batteries is drawing near to its inherent theoretical maximum. Furthermore, the safety and stability of lithium-ion batteries have also been questioned due to the widespread use of flammable and corrosive organic liquid electrolytes. In this case, replacing conventional liquid electrolytes with SSEs for ASSLMBs is the ultimate solution for achieving battery systems that simultaneously exhibit high energy density and safety stability. Lithium metal as anode has high theoretical specific capacity (3860mAh g^{-1}), low chemical potential

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(-3.04 V vs standard hydrogen electrode) and low density (0.534 g cm^{-3}). The use of SSEs simultaneously addresses safety concerns associated with flammable organic solvents. However, interfacial issues arising between SSEs and lithium metal anodes have seriously hampered the practical realization of ASSLMBs. The problems of poor interfacial contact and low total ionic conductivity require urgent solutions.

Currently, mature ASSLMBs are generally composed of a cathode, lithium metal anode, and SSE. Dudney's research group used LiPON solid electrolyte, $LiNi_{0.5}Mn_{1.5}O_4$ (LNM) cathode, and lithium metal anode to verify the feasibility of ASSLMBs [1]. Due to the intrinsic properties of lithium metal, most solid-state electrolytes will spontaneously reduce when contacting with lithium anode. Consequently, elucidating the interfacial failure mechanisms is critical for advancing high-performance ASSLMBs [2].

This research will analyze and discuss the classification and characteristics of SSE for ASSLMBs, and investigate the interfacial issues between SSE and lithium metal anodes. Through the classification and discussion of these interfacial challenges, it will explore solution strategies for interface failure problems across different SSE materials. Furthermore, it will present feasible solutions based on the latest scientific research advancements.

2. Classification and characteristics of SSEs

ASSLMBs mainly utilize two distinct electrolyte systems: Solid Inorganic Electrolytes (SIEs) and Solid Polymer Electrolytes (SPEs). Solid inorganic electrolytes mainly include oxide-based, sulfide-based, and halide-based solid electrolytes and so forth [3,4].

2.1. SIEs

The advantages of solid inorganic electrolyte include excellent mechanical modulus, wide electrochemical window and favorable ionic conductivity, but its inherent rigidity makes the interfacial impedance high and the interface compatibility poor.

2.1.1. Oxide-based solid electrolytes

Oxide-based solid electrolytes for ASSLMBs can be classified into the following main categories: garnet-type, perovskite-type, and NASICON-type. Among these, garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) has emerged as a representative oxide solid electrolyte due to the following characteristics: Its advantages are as follows: (1) A high ionic conductivity of 2 mS cm^{-1} is achieved at 25 °C which can be further regulated through elemental doping; (2) Straightforward processability in ambient air without requiring inert atmospheres; (3) High shear modulus compared to lithium metal anodes, ensuring excellent mechanical properties for interfacial stability; (4) Excellent thermal stability at elevated temperatures, which is the characteristic of ceramic oxides; (5) It has a wide electrochemical stability window, spanning from the low potential of lithium metal to voltages exceeding those of all commercial cathode materials [5].

2.1.2. Sulfide-based solid electrolytes

Sulfide-based electrolytes typically exhibit the highest ionic conductivity among solid electrolytes, and possess exceptional ionic conductivity comparable to liquid electrolytes along with favorable processability. Compared to rigid oxide electrolytes, sulfide electrolytes usually demonstrate

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superior ductility and flexibility. Under appropriate pressure, they can achieve effective "solid-solid contact" with lithium metal anodes, significantly mitigating mechanical failure at the interface.

Additionally, compared with oxide solid electrolyte, it can be processed at lower temperature, which is more suitable for manufacturing and large-scale production. These advantages position sulfide-based electrolytes as a highly promising category of solid electrolytes [6].

2.2. SPEs

Polymer electrolytes are typically synthesized by incorporating lithium salts into a polymer matrix, forming all-solid or gel-state solid electrolytes. Solid Polymer Electrolytes has exceptional flexibility and interfacial compatibility, which enables intimate contact with electrodes. At the same time, they offer advantages such as superior processability and low-cost manufacturing. However, Solid Polymer Electrolytes possess relatively low mechanical strength, which is difficult to inhibit the growth of lithium dendrites, posing a risk of battery short circuits. At the same time, they have narrower electrochemical window and lower ionic conductivity compared to solid inorganic electrolytes. Additionally, they are prone to side reactions with lithium metal anodes, leading to interfacial degradation.

The thermal stability of SPEs is mainly dictated by the structural units and degree of polymerization of the polymer. Polyethylene oxide, a low-cost representative SPE material, has has garnered considerable attention due to its flexibility, suitable ionic conductivity, and ease of processing [7].

2.3. Characteristics of ideal solid-state electrolytes

Under the ideal conditions, SSEs for practical applications in ASSLMBs should possess the following characteristics:

(1) High Ionic Conductivity – to approach the ionic conductivity of liquid electrolytes at room temperature as closely as possible.

(2) Low Electronic Conductivity- preventing spontaneous charge transfer between the cathode and anode that leads to self-discharge and consequent autonomous decay of battery capacity.

(3) Excellent Chemical and Electrochemical Stability – improving interfacial kinetics and reduce interfacial resistance. Thermodynamic instability between SSEs and electrode materials can trigger chemical reactions, leading to interfacial failure.

(4) High Thermal Stability- solid electrolyte may melt or decompose at high temperature, and its heat release may cause internal short circuit.

(5) Wide Electrochemical Stability Window – an excessively narrow window may cause oxidation and decomposition of the SSE under high voltage conditions. And then the high-impedance layers will form at the interface that result in capacity decay and increased internal resistance.

(6) High Mechanical Strength – enhancing the mechanical modulus of SSEs can effectively prevent lithium dendrite growth, mitigate interfacial gaps caused by volume expansion, and suppress short circuits caused by cyclic stress [8].

To explore how to optimize the performance of the current mainstream SSEs, this research investigates the interfacial issues between these electrolytes and lithium metal anodes, and presents recent research progress on optimization strategies for existing electrolytes.

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3. Interfacial issues and solution strategies for lithium metal solid-state batteries

3.1. Chemical failure

3.1.1. Failure mechanism

The chemical failure is due to the spontaneous reduction reactions driven by thermodynamics. Due to the high reactivity and strong reducibility of lithium metal, when lithium metal anode contacts with the SSE, it will irreversibly reduce the cations in the electrolyte, resulting in interfacial degradation and battery performance damage.

When lithium metal anode contacts with sulfide-electrolytes, Li_2S, Li_3P, are generated by interfacial reduction. When it contacts with oxide-electrolyte, the interface will be reduced to Li_2O, lithium salt or metallic lithium. In the case of halide-electrolytes, reduction yields LiF, LiCl, LiBr, or corresponding metals.

3.1.2. Mitigation strategies for sulfide-based solid electrolyte failure

The interface reaction can be effectively blocked by inserting an interlayer between the lithium metal anode and SSE. For example, ultra-thin coatings of BN, ZnO or lithium phosphorus oxynitride (LiPON) can effectively inhibit interfacial reactions between oxide-electrolyte and sulfide-electrolyte [9].

Su et al. found that the argyrodite-type Li_6PS_5Cl ceramics Exhibit high ionic conductivity (exceeding 1 mS cm^{-1}) under ambient temperature conditions, coupled with relatively favorable ductility, making them an ideal material for solid-state electrolytes. However, Li_6PS_5Cl exhibits poor chemical and electrochemical stability when in contact with lithium metal anodes, leading to decomposition into an insulating interphase layer containing a variety of lithium compounds. To address this, the study employed radio-frequency sputtering to introduce a thin amorphous lithium-ion-conducting LiPON interlayer between the argyrodite-type Li_6PS_5Cl SSE and the lithium metal anode. The LiPON interlayer will promote uniform lithium deposition/stripping, which can reduce the interfacial resistance between the Li_6PS_5Cl SSE and the lithium metal anode to 1.3 Ω cm^2 in symmetric cells. As indicated by the experimental results, this design enables significant improvements in interfacial wettability, ionic conductivity, and interfacial stability between the argyrodite-based solid electrolyte and lithium metal anode [10].

3.2. Electrical and electrochemical failure

3.2.1. Failure mechanism

First, in SSE systems, electrical failure is often caused by the growth of lithium dendrites which easily grow at low current density, especially in soft solid polymer electrolytes.

The electrochemical failure focuses on the chemical instability and charge transfer imbalance at the interface between the solid-state electrolyte and solid lithium metal anode [11]. The general understanding of solid-state electrolytes is that they possess a wide electrochemical window. However, according to research, the intrinsic stability window of various solid electrolytes, including most sulfide and garnet-types, is considerably narrow. For instance, the voltage window of the sulfide solid electrolyte $Li_{10}GeP_2S_{12}$is limited between 1.71 V and 2.41 V. Once the electrochemical stability window of the solid electrolyte is exceeded, undesirable side reactions will

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occur at the electrode-electrolyte interface. These reactions lead to the formation of new interphases, which ultimately result in interfacial degradation [12].

In addition, surface defects including pores, cracks, grains and grain boundaries-as the key characteristics of the microstructure of SSEs, will disrupt the uniformity of lithium-ion transport and lead to localized concentration imbalances. The consequences primarily manifest as: initiating lithium dendrite nucleation, intensifying crack propagation, and ultimately destroying the electrochemical and mechanical stability of the interface.

3.2.2. Recent advances in mitigation strategies

Ning et al. used the continuous in-situ X-ray computed tomography (XCT) technology to monitor the initiation and propagation of cracks in the process of constant-current electroplating. And the study found that the short circuit occurred in multiple cycles could be prevented by inhibiting the propagation of dendritic cracks or limiting the net growth of lithium dendrites in existing cracks [13].

Liu et al. studied how to inhibit dendrite growth by altering the microstructure of sulfide electrolytes. They synthesized $Li_{5.3}PS_{4.3}ClBr_{0.7}$ by three distinct routes: solid-state sintering, mechanical grinding and post-milling annealing, and studied how synthesis pathways affect the electrochemical performance of this solid electrolyte. Although $Li_{5.3}PS_{4.3}ClBr_{0.7}$ synthesized by different routes has the identical crystal structure, the synthesis route significantly influenced its microscopic morphology. Annealing after high-speed mechanical grinding can make the solid electrolyte have exceptional lithium dendrite suppression capability. This approach comprehensively improved electrochemical performance and mitigated the impacts of electrochemical failure [14].

3.3. Mechanical failure

3.3.1. Failure mechanism

The commercialization process of ASSLMBs is restricted by mechanical failure issues. The reason is that the rigid solid electrolyte cannot effectively accommodate the substantial volume changes of lithium metal in the deposition/stripping process, which easily lead to the instability of interface mechanical structure. Specifically, this failure manifests in two forms: repeated volume changes cause delamination at the lithium anode/electrolyte interface, forming a contact gap, resulting in a sharp rise in interfacial impedance; particularly for inherently brittle oxide electrolytes, continuous cyclic stress may lead to structural damage and internal short circuit and related failures.

3.3.2. Recent advances in mitigation strategies

Xiong et al. explored the correlation between the mechanical failure in SSEs and the morphology of interfacial defects, the quantity and distribution of internal defects based on Butler Volmer equation and the electrochemical mechanical coupling model of damage mechanics [15].

Zhou et al. explored the chemical structure for anion migration, and used the solid electrolyte $Li_{3.2}$ PS_4 $I_{0.2}$ doped with lithium iodide (LiI) to form DAI between the anode and the SSE interface for experimental verification.

The experimental results show that in the process of lithium stripping, the controllable migration of iodine ions forms a DAI between the lithium metal anode and electrolyte. This interface effectively adjusts local strain and stress while homogenizing internal pressure distribution, thereby promoting maintained solid-solid contact between the lithium metal anode and SSE throughout

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prolonged stripping cycles and preserving interfacial integrity [16]. Therefore, the construction of DAI through controlled anion migration and pre-implanting of SSE has a practical significance for addressing interfacial mechanical failure issues [17].

4. Conclusion

In this research, the SSEs of solid lithium metal batteries are classified into SIEs and SPEs. The advantages of solid inorganic electrolytes lie in their excellent mechanical modulus, wide electrochemical window, and favorable ionic conductivity. Nevertheless, their inherent rigidity tends to exacerbate mechanical failure at the interface. Concurrently, sulfide-based solid electrolytes within the category of solid inorganic electrolytes are prone to chemical failure due to their inherent characteristics. However, the SPEs exhibit relatively low mechanical strength, which is inadequate to effectively inhibit the growth of lithium dendrites, which is easy to cause electrical failure. Their electrochemical window and ionic conductivity are also lower than that of solid inorganic electrolytes, thereby increasing their susceptibility to electrochemical failure.

This study also systematically investigates interfacial issues between lithium metal anodes and SSEs, analyzing three distinct failure mechanisms—chemical failure, electrical failure, and electrochemical failure, along with mechanical failure—along with their corresponding mitigation strategies.

The three failure mechanisms are categorized as follows: Chemical Failure - caused by reactions between the highly reactive lithium metal and electrolytes; Electrical Failure and Electrochemical Failure - resulting from the inevitable growth of lithium dendrites; Mechanical Failure - comprising interfacial chemical instability coupled with charge imbalance, as well as mechanical stress induced by substantial volume fluctuations of the lithium metal anode during deposition/stripping processes. While investigating these failure mechanisms, this research presents recent scientific advances in addressing these failures using sulfide-based solid electrolytes as an example.

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