Research Progress of Solid Electrolytes in Solid-State Lithium Batteries

Nan Xia[1]*

[1] School of Materials Science and Engineering, Hubei University, Wuhan, 430062 China

Abstract. In today's world where fossil fuels are increasingly depleting, electric energy, this new type of energy, is rapidly developing, the safety of batteries is receiving more and more attention from people as well. The excellent mechanical properties of solid-state batteries significantly enhance their safety features. However, the mainstream solid-state inorganic electrolytes and gel polymer electrolytes still face issues such as low ionic conductivity, poor electrode interface performance, and inadequate environmental stability. This paper is based on years of research by predecessors on the characteristics of Solid inorganic electrolytes and gel polymer electrolytes, summarizing the recent research progress on solid-state composite electrolytes by researchers, discussing the properties of single-phase electrolytes and the improvement of composite-phase electrolytes. It discusses the improvement of solid-state battery performance by solid-state composite electrolytes from three aspects: polymer composite non-polar ceramic materials, the addition of SN catalysts, and three-dimensional skeletal structures. It analyses the problems and challenges of solid-state electrolytes, Pointing out the existing shortcomings of the current solid composite electrolytes. Finally, providing directions for the continued development of solid-state electrolytes.

1 Introduction

As technology and productivity continue to improve, the environmental pollution and energy crisis caused by fossil fuels are becoming increasingly severe, there is an essential to improve the ability of energy retention and conversion technologies. Lithium batteries are widely promoted for their efficient and green energy storage. However, in recent years, incidents of fires and explosions caused by liquid electrolyte leakage, overcharging, and high temperatures in lithium batteries have frequently occurred. In contrast, solid-state electrolyte lithium batteries have garnered widespread attention due to their superior thermal steadiness and safety. Currently, the electrolytes of solid-state batteries mainly include electrolytes made of gel-state polymers, inorganic materials, and composite materials [1]. Whereas because of the solid-solid interaction between the two electrodes and the solid electrolyte, solid-state lithium batteries' conductivity is still beneath that of conventional liquid lithium batteries [2]. Moreover, the issue of Lithium dendritic short circuits in batteries made from solid-state materials still exists, and these factors continue to impact the solid-state lithium

---

* Corresponding author: 202231113021001@stu.hubu.edu.cn

batteries' performance in general [3]. Addressing these issues, researchers have proposed a method of combining inorganic electrolytes and gel-state polymer electrolytes to compensate for each other's shortcomings, thereby enhancing the electrolyte conductivity and interfacial performance while ensuring the safety of the battery.

This paper will respectively explore the characteristics of solid electrolytes that come in two varieties. Indicating the advantages and disadvantages of the two solid electrolytes. Summarizing the recent research progress in improving the safety, conductivity, and electrode interface performance in lithium solid-state batteries. It could supply a reference for the future research directions of composite solid-state electrolytes.

2 Solid inorganic electrolyte

Solid inorganic electrolytes (SIE) have garnered widespread attention in solid-state battery technology because of their excellent physical properties. Its excellent mechanical strength enables it to effectively deal with the battery limited circuitry issues resulting from lithium dendrites generated from the lithium battery anode, this characteristic is of great significance in enhancing battery safety [4]. Currently, there are primarily two types of solid-state inorganic electrolytes.: the electrolytes based on sulfides and oxides [5]. Sulfide-type electrolytes are gaining attention due to their high conductivity, which can reach 10^-2 S/cm [5]. However, its environmental stability and electrochemical stability are relatively poor, which directly affects its safety in high-energy-density batteries [6]. This unstable property may lead to performance degradation and potential safety hazards under prolonged use or high-load conditions. In contrast, although oxide electrolytes do not have as high conductivity as sulfide electrolytes, they possess superior thermal stability and safety [7], making oxide electrolytes more stable under high-temperature environments and extreme operating conditions. Oxide-type electrolytes have good conductivity at room temperature, it can be seen in Table 1. Moreover, the process of getting ready for oxide-type electrolytes is secure and quite mature., making them more reliable and operable in practical applications. Therefore, despite the challenge of high interfacial resistance, oxide-based electrolytes remain an important direction in current research and applications, widely favored by researchers worldwide.

Table 1. Comparison of Three Types of Inorganic Oxide Electrolytes [7-9]

Types of electrolytes	configuration	Maximum electric conductivity electrolyte chemical formula	Operating temperature	Electric conductivity
Perovskite	Tetragonal perovskite type	LLTO ($Li_{0.22}La_{0.60}TiO_3$)	25°C	4.84×10^{-4} S/cm
NASICON	Rhombus structure	$Li_{1.5}Al_{0.4}Cr_{0.1}Ge_{1.5}(PO_4)_3$ (LGP)	25°C	6.65×10^{-3} S/cm
Garnet	Three-dimensional nanostructure	$Li_{6.25}Fe_{0.25}La_3Zr_2O_{12}$	25°C	1.38×10^{-3} S/cm

3 Gel polymer electrolytes

Solid polymer electrolytes (SPE) have garnered widespread attention attributed to their excellent stability, simplicity in preparation and affordability [10]. However, the ionic conductivity of single polymer electrolytes is relatively low, usually around 5×10^-4 S/cm[11], and it is far less than that of inorganic solid-state electrolytes. Common substrate polymers for PSE contain polymethyl methacrylate (PMMA), polyethylene oxide (PEO), polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), poly (vinylidene fluoride-co-hexafluoropropylene) [PVDF-HFP]. and polyvinyl chloride (PVC) [12]. Although these polymers have good stability, their conductivity does not reach the desired level when used alone.

Gel polymer electrolytes (GPE) occupy a unique position in the classification of electrolytes. It is a special form of solid polymer electrolyte (SPE), with a state of matter that lies between liquid and solid, exhibiting characteristics of a gel-like semi-solid material. This type of electrolyte is usually formed by the combination of polymers and liquid electrolytes, resulting in a gel polymer electrolyte (GPE). GPE combines the liquid electrolytes' strong ionic conductivity with solid-state electrolytes' toughness, demonstrating excellent overall performance.

The structure of GPE endows it with excellent hardness and strength, effectively addressing the common issue of lithium dendrites in liquid electrolytes. Lithium dendrites often lead to battery short circuits and performance degradation in liquid electrolytes, whereas GPE significantly reduces this risk through its solid-state structure [3]. Furthermore, the gel-like physical properties of GPE enable it to provide excellent interfacial performance in practical battery applications. Compared to inorganic solid electrolytes, GPE can better adapt to the slight unevenness of the electrode surface when in close proximity to the cathode and anode, enhancing the battery's functionality and interfacial stability. [13].

Further research also supports the advantages of GPE in improving battery performance. For example, Liu's study on solid-state electrolytes of the garnet type points out that Solid-state electrolytes containing GPE interlayers exhibit significantly reduced interfacial resistance compared to non-gel-state solid-state electrolytes without GPE, with a reduction magnitude reaching an exponential level[14]. This improvement not only enhances the cycle life of the battery but also increases its safety and reliability.

Overall, gel-state electrolytes, because of their unique physical state and structural characteristics, offer a promising solution to address key challenges in battery technology, such as lithium dendrite issues and interface performance optimization. Therefore, further research and development of GPE will help promote the advancement of more efficient and safer battery technologies.

4 Solid composite electrolytes

The research on Solid Composite Electrolytes (SCEs) aims to explore composite solid electrolytes that possess high safety, high energy density, high conductivity, and excellent interfacial performance. Although the aforementioned solid ion electrolytes (SIEs) can achieve high conductivity, their solid-solid contact with the electrodes is not tight enough, which leads to increased interfacial resistance in the battery, causing electrons to accumulate in the circuit and directly affecting how well lithium batteries function. Nevertheless, the advantages of SIEs are also very evident, with conductivity far exceeding that of solid polymer electrolytes (SPEs) and stronger mechanical properties, it able to effectively prevent battery short-circuit issues caused by lithium dendrites, as shown in Figure. 1. Relatively speaking, SPEs have lower conductivity and insufficient mechanical strength, but their excellent interfacial properties and low interfacial resistance make their contact with the electrodes better. To solve the issues of interfacial performance and conductivity in solid-state electrolytes, researchers have proposed a strategy of combining GPE with SIE. This approach aims to overcome SIE's elevated interfacial resistance and the low conductivity of GPE, thereby promoting diversified research on solid-state composite electrolyte materials (SCEs) as well as improving solid-state batteries' overall efficiency. Tian and others' research revealed that by introducing polymer additives such as polyisobutylene (PIN) as the electrolyte matrix, conductivity can be significantly improved. The introduction of PIN provides additional weak electrostatic coordination sites to the electrolyte system, encouraging the composite SPE's ionic conductivity to increase to 5.89×10^-3 S/cm [12]. This result not only highlights the limitations of single-base polymers in terms of ionic conductivity but also emphasizes the great potential of composite electrolytes in improving conductivity and optimizing battery performance. It is evident that composite electrolytes are gradually becoming the primary path for enhancing the performance of solid-state batteries.

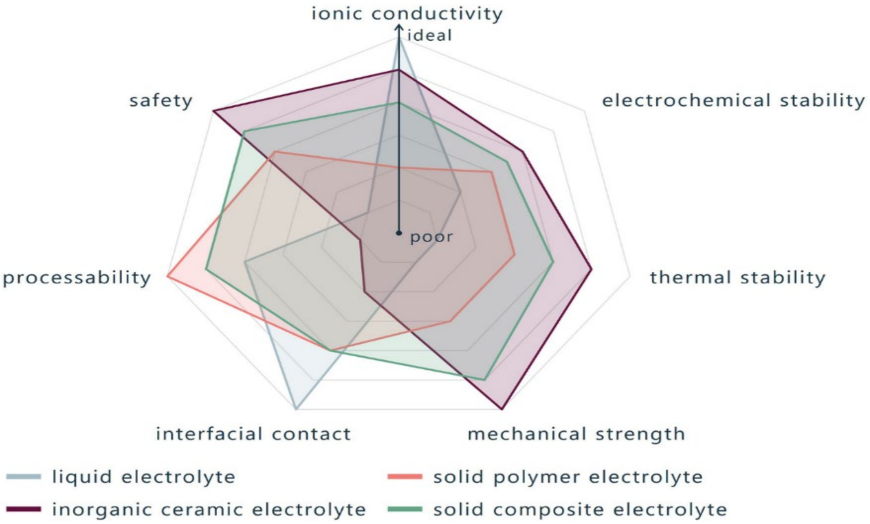

Fig. 1. Comparison of the performance of solid polymer electrolytes, inorganic ceramic electrolytes, solid composite electrolytes, and liquid electrolytes [1].

4.1 Porous inorganic particle composite polymer electrolyte

Combining small particle SIE with GPE-based polymer electrolytes is able to dramatically enhance the mechanical strength and conductivity of the electrolytes [15]. Common inorganic composite particles include LATP, LAGP, LLTO, LLZO, and LLZTaO. However, numerous studies have shown that although the initial addition of these ceramic particles does indeed enhance the conductivity of the electrolyte, the subsequent conductivity decreases. This phenomenon is believed to be related to the porous structure of the ceramic particles [15]. Isaac demonstrated that the initial increase in conductivity is mainly attributed to the dispersion of ceramic particles in the GPE, while the subsequent decrease in conductivity is due to blockage caused by poor particle contact, which is unrelated to the properties of the electrolyte itself or the concentration of the salt [15]. Tao addressed the issue of excessive thickness in SPE electrolytes by introducing nano-SiO2 particles into PVDF-based polymer electrolytes. This PVDF-based solid-state composite electrolyte (PPSE) has a thickness of only 20 μ m but a mechanical strength of up to 64 MPa. At the same time, silica nanoparticles effectively enhance the lithium-ion transference number and ionic conductivity, reaching a conductivity of 4.81 × 10$^{\wedge-4}$ S/cm, and it exhibits good system stability and sustainability [16] (Figure 2).

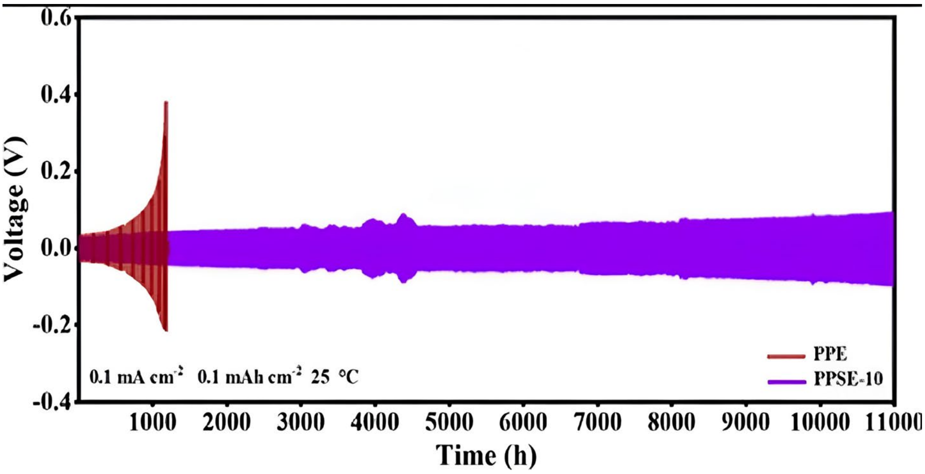

Fig. 2. Relatively stable output voltage over a very long period of PPSE [16]

4.2 Including catalysts to increase SPE's mechanical strength and conductivity

To address the issue of low conductivity in SPE, researchers have proposed doping succinonitrile (SN) as an organic catalyst in gel-state PMMA-based GPE. Experimental results show that doping with SN can greatly increase the electrolyte's conductivity, resulting in a new type of electrolyte (SN-GPE) having 2.02 × 10^-3 S/cm of conductivity, and it also possesses good mechanical properties, compensating for the deficiencies of GPE in terms of conductivity and mechanical performance [17]. However, this new method also exposes its shortcomings: the interfacial performance between SN and the lithium anode is poor due to a large number of side reactions occurring at the interface [18]. To address this, Zhao used metal-organic frameworks (MOFs) to construct the electrolyte and penetrated the MOF's multilayer channels with the LiTFSI-SN (LSN) electrolyte. This method effectively improved the battery's capacity and interfacial performance without negatively impacting ionic conductivity.

4.3 Changing the three-dimensional structure of the spatial volume to improve SCE preparation safety

Lithium batteries in solid state have not yet been put into commercial production, mainly due to issues with their interface and conductivity. Commercial preparation requires a safe and stable manufacturing process as a prerequisite for mass production. Researchers improve the structure of SCEs to enhance their stability. For example, Ruan prepared a nanofiber scaffold with a 3D rebar structure in a PEO-based composite garnet-type inorganic oxide electrolyte, which achieved a conductivity at 30° C, of 0.23 × 10$^{\wedge -3}$ S/cm. This structure significantly improved compared to traditional SCEs structure electrolytes and also enhanced the stability of the battery [19]. Metal-organic frameworks (MOFs) were proposed as early as 2016, but their application regarding solid-state lithium battery technology was officially introduced by Zhou in 2023. They used bimetallic MOFs (NH3+ • SO3-@ZIFs) as fillers for PEO-based solid-state electrolytes. This composite solid-state electrolyte not only enhances conductivity but also prevents lithium dendrites from growing at the anode, which is vital for the stability and cycle efficiency of batteries [20]. On this basis, researchers further proposed a type of SPE with dual-layer asymmetry. This novel material has a mechanical strength of 16.8 MPa and exhibits good ionic conductivity (0.63 × 10^-3 S/cm), establishing a strong basis for the use of MOF in solid-state batteries [21].

5 Conclusion

Overall, in context of increasing demands for new energy storage now, The lithium battery of the future will be solid-state. This paper categorizes the two fundamental forms of solid-state electrolytes of solid-state batteries available so far, elucidating the respective advantages and disadvantages of SIE and SPE. And summarize and categorize the novel SCEs from the past three years, discussing SCEs from three aspects: the composite of inorganic ceramic particles, SN catalysts, and three-dimensional framework structures. However, these three types of SCEs are still not perfect, with the main common issue still being low conductivity, which is the biggest problem affecting the energy cycle efficiency of solid-state batteries. Exceptionally, there are also some individual issues, such as the poor interface performance of the SCEs in the composite SN catalyst and the general mechanical properties of the three-dimensional skeletal structure. This paper focuses on reviewing the two basic electrolytes of solid-state batteries, giving a reference for scholars who have not yet delved into this field but are interested in it. Using the classification models of SCEs from the past three years as a framework, it offers readers the latest developments in this topic, hoping that future readers will make progress.

At present, it seems that the conductivity and interface issues of solid-state electrolytes still require further research, and to guarantee safety, the electrolytes' mechanical strength should also be increased. The method of combining inorganic nanoparticles and MOFs can be attempted by trying to add SN catalysts to the non-polar ceramic composite polymer electrolyte to enhance conductivity, or improve the environmental stability of the sulfide electrolyte during preparation, among other things. All of them have their strengths in terms of performance enhancement.

References

1. K. Daems, et al., Advances in inorganic, polymer and composite electrolytes: Mechanisms of Lithium-ion transport and pathways to enhanced performance. RSER. **191,** 114136 (2024) .
2. H.Yang, N. Wu., Ionic conductivity and ion transport mechanisms of solid‐state lithium‐ion battery electrolytes: A review. ESE, **10**,51643-1671 (2022).
3. Y. Chen, et al., Understanding the lithium dendrites growth in garnet-based solid-state lithium metal batteries. JPS, **521,** 230921 (2022).
4. Q. Lv, et al., Suppressing lithium dendrites within inorganic solid-state electrolytes. CRPS. **3**,1 (2022).
5. Q. Liu, et al. Recent advances in stability issues of inorganic solid electrolytes and composite solid electrolytes for all‐solid‐state batteries. TCR. **22**,10 (2022)
6. L. Lilu, et al. Advances in electrochemical stability of sulfide solid electrolytes. JCC **47**,10 (2019): 1367-1385.
7. K.J. Kim, et al.. Solid‐state Li–metal batteries: challenges and horizons of oxide and sulfide solid electrolytes and their interfaces. AEM. **11**.1 (2021): 2002689.
8. M. Illbeigi, A. Fazlali, M. Kazazi, A.H. Mohammadi. SSI. , **289**, 180.2016
9. R. Wagner, GJ Redhammer, D Rettenwander, et al. Fast Li-ion-conducting garnet-related Li7-3xFexLa3Zr2O12 with uncommon I4-3d structure. CM. **28**, 16, 5943-5951 (2016).
10. G. Yuan, MK Wang, L Long. Research advances on gel electrolytes for lithium-ion batteries. ANRE. **8**, 4 331-338 (2020).

11. H. Yang, et al. PDOL-based solid electrolyte toward Practical application: Opportunities and challenges. NML. **16**,1, 12,7 (2024).
12. X. Tian, Y Yi, P Yang, et al. High-charge density polymerized ionic networks boosting high ionic conductivity as quasi-solid electrolytes for high-voltage batteries. AMI. **11**, 4, 4001-4010 (2019).
13. L.X u, et al. Garnet solid electrolyte for advanced all - solid - state Li batteries. AEM. **11**, 2 (2021)
14. B. Liu, et al. Garnet solid electrolyte protected Li-metal batteries. AMI .**9**,22, 18809-18815 (2017)
15. J.A. Isaac, D Devaux, R Bouchet. Dense inorganic electrolyte particles as a lever to promote composite electrolyte conductivity. NM. **21**, 12, 1412-1418(2022) .
16. Y. Ma, C Wang, K Yang. Ultrathin and Robust Composite Electrolyte for Stable Solid-State Lithium Metal Batteries. AMI. (2023).
17. Z. Zhou, et al. PMMA-Based Composite Gel Polymer Electrolyte with Plastic Crystal Adopted for High-Performance Solid ECDs. POL. **15** (2023).
18. T. Zhao, et al. Laminar composite solid electrolyte with succinonitrile-penetrating metal-organic framework (MOF) for stable anode interface in solid-state lithium metal battery. JPS. (2023).
19. Y. Ruan, et al. A novel reinforced concrete-like composite solid-state electrolyte with enhanced performance for all-solid-state lithium batteries. JSEE. **28**, 8(2024)
20. X. Zhou, et al. Difunctional MOF for dendrite-free all-solid-state lithium metal batteries by the synergistic effect of hydrogen bond and electrostatic interaction. NE. **108** (2023)
21. Q. Cheng, et al. 3D interconnected MOF-derived asymmetric bilayer solid-state electrolyte for enabling homogeneous Li deposition of all-solid-state lithium metal batteries. JSEE. **28**, 8, 2631-2642 (2024)