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Progress of all-solid-state lithium battery profile and ionic conductivity of oxide fillers

Ziqi Wang*, Chunyang Cui

School of Energy and Power Engineering, Northeast Electric Power University, Jilin, China
**Corresponding author: 3130592012@qq.com*

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Abstract: With the rapid development of energy storage technology, all-solid-state lithium batteries have received widespread attention for their high safety and high energy density.In this paper, we systematically sort out the development history of all-solid-state lithium batteries and the current technical challenges and research hotspots, introduce the classification and characteristics of oxide fillers, and focus on the role and conductivity mechanism of oxide fillers in composite electrolytes.By exploring the structural properties and functions of different kinds of oxide fillers, this paper clarifies the mechanism of the fillers to enhance the ionic conductivity in composite electrolytes and proposes an optimisation strategy of oxide fillers in electrolytes with a view to improving the overall performance of all-solid-state lithium batteries.The proper selection and structural design of oxide fillers are crucial to enhance the performance of all-solid-state lithium batteries.The purpose of this paper is to systematically introduce the research progress of various types of oxide fillers in ionic conductivity, and then lay the foundation for the practical application of energy storage batteries.

1. Introduction

The rapid development of energy storage technology is leading the innovation of global energy structure. Lithium-ion batteries have been widely used in mobile communications, portable electronic devices, and electric vehicles by virtue of their excellent energy density and long cycle performance. However, it is often difficult to strike a balance between high energy density and safety in traditional liquid lithium batteries, especially under extreme conditions, where the risk of leakage and combustion of the liquid electrolyte limits their application scope. All-solid-state lithium batteries, with their solid-state electrolyte replacing the flammable liquid electrolyte, show great safety and higher energy density potential, and are regarded as an important development direction for the next-generation energy storage system.

Nevertheless, the widespread commercial application of all-solid-state lithium batteries still faces great technical challenges. Electrolyte materials are one of the core factors limiting the performance development of all-solid-state lithium batteries, especially the bottleneck in improving ionic conductivity and interfacial stability. In recent years, organic-inorganic solid composite electrolyte, as a new type of electrolyte material, provides a new idea to solve this problem by virtue of its plasticity and high conductivity. In particular, the application of oxide fillers in composite electrolytes is not only conducive to improving the mechanical strength of solid-state electrolytes, but also may significantly enhance the ion migration rate through specific conductive mechanisms.

Meanwhile, the type of oxide filler and microstructure design have a great influence on the ionic conductivity, which requires researchers to have a deeper understanding and exploration of the related mechanisms. The effects of different oxide fillers such as TiO2 and Al2O3 on the performance of composite electrolytes have been reported in the literature, but a great deal of systematic research work is still needed on the optimal design and application strategies of oxide fillers in high-performance all-solid-state lithium batteries.

This thesis looks at the composition of organic and inorganic electrolytes, the classification of currently available oxide fillers, and the role of fillers in them. The research progress of oxide fillers is comprehensively introduced in terms of the conductive mechanism of various fillers, etc., and the role played by different oxide fillers in composite electrolytes to improve the overall performance of all-solid-state lithium batteries is further explored in depth. In addition, a scientifically sound experimental design is proposed in this paper with a view to providing new ideas for electrolyte design and performance optimisation of all-solid-state lithium batteries. In summary, this paper aims to find a breakthrough development direction for the practical application of new high safety and high energy density energy storage batteries at an early date.

2. Overview of Solid State Lithium Battery

2.1 The development of all-solid-state lithium batteries

Since first proposed in the late 1970s, all-solid-state lithium batteries have experienced a long journey from proof of concept to practicality. Initially, researchers focused on exploring polycrystalline ionic conductors as electrolyte materials, and although their ionic conductivity was able to reach high levels at higher temperatures, they performed poorly at room temperature.Since then, research has gradually shifted to improving the ionic conductivity of the electrolyte at room temperature and the interfacial matching problem with the electrode materials.[11]

Into the 21st century, the research focus of all-solid-state lithium batteries began to shift to inorganic solid electrolytes, inorganic solid electrolytes (ISEs), including there are oxide, sulfide, halide solid electrolytes.The oxide class is well known for the garnet type (LLMO), sodium superionic conductor type (LAMP) and calomel type (LLTO).

Sulphide-based electrolytes[7]are considered the most promising class of electrolytes for the future, attracting attention for their excellent ionic conductivity and flexible mechanical properties, but although they are theoretically the best, they suffer from poor compatibility with lithium metal, and are expensive to produce and extremely difficult to process.Oxide solid electrolytes, on the other hand, have been the focus of research due to their excellent chemical stability and high voltage window.It is worth noting that, although oxide solid electrolytes have better chemical stability, their brittleness, poor interfacial contact with electrode materials, and tendency to form lithium dendrites limit their practical applications.

In order to overcome these limitations, researchers have explored organic-inorganic composite solid state electrolytes in an attempt to improve the mechanical properties of the electrolyte and the interfacial quality with the electrode material by introducing soft organic components, with a view to balancing the high conductivity of inorganic electrolytes and the flexibility of polymer electrolytes.In this context, the application of oxide fillers in organic-inorganic solid composite electrolytes has gradually become a hot spot.Its ability to not only improve the mechanical strength of the electrolyte, but also enhance ionic conductivity by providing more lithium ion conduction paths, is important for improving the overall performance of all-solid-state lithium batteries.

Despite the remarkable achievements in this field, factors such as the type, size, and distribution of oxide fillers have a great influence on their performance, and systematic studies on these factors are still insufficient.For this reason, this paper systematically combs the structural properties of oxide fillers in organic-inorganic solid composite electrolytes and their functional mechanisms, and thoroughly explores the conductive action mechanisms of different types of fillers, aiming to further understand and guide the design and optimisation of organic-inorganic solid composite electrolytes.

The research on all-solid-state lithium batteries is in rapid evolution from pure solid oxide electrolytes to multifunctional composite electrolyte systems.With the continuous emergence of new high-performance fillers and the gradual clarification of their mechanism of action, it can be expected that the all-solid-state lithium battery will make greater breakthroughs in the near future, and open up a new path for the development of high safety and high energy density energy storage technology.

2.2 Current technical challenges and research hotspots

As a new generation of energy storage devices, all-solid-state lithium batteries have significant advantages in terms of safety and energy density, but still face multiple technical challenges that need to be solved to meet the needs of large-scale commercialisation.Currently, the main challenges of all-solid-state lithium battery technology focus on improving the ionic conductivity of the solid-state electrolyte,[1][3]ensuring the stability of the electrode-electrolyte interface, and quality control in the battery assembly process.Among the many research hotspots, the development of organic and inorganic solid composite electrolytes has received special attention, especially for the study of the role of oxide fillers in composite electrolytes and the impact of conductivity.[5]

Current research has found that oxide fillers play a crucial role in improving ionic conductivity.Specifically, oxide fillers can form ion transport channels in organic and inorganic composite electrolytes, reduce the interfacial resistance, and optimise the movement path of charge carriers.

In addition, by changing the particle size, morphology, and dispersion of fillers, the microstructure of composites can be effectively regulated, thus affecting their macroscopic electrical conductivity. Experimental data show that under specific conditions, suitable oxide fillers can significantly enhance the ionic conductivity of solid-state electrolytes, which has a positive impact on the energy output of all-solid-state lithium batteries.

At the same time, it has been found that the structural properties of different kinds of oxide fillers have significant effects on the conductivity. For example, oxides with high ionisation and good spatial compatibility can be more efficiently inserted into the electrolyte matrix to form a more stable ion transport network. Further, through atomic layer deposition (ALD) and sol-gel methods, the nanoscale precision control of oxide fillers not only improves the conductivity of the electrolyte, but also enhances the cycling stability of the battery.

However, the improvement of electrolyte performance by oxide fillers is not unlimited. It was pointed out that the incorporation of excessive fillers may lead to interfacial mismatch and introduce excessive interfacial defects in the composite electrolyte, which is counterproductive and affects the battery performance. Therefore, while optimising the filler, the addition ratio and dispersion uniformity of the filler should be strictly controlled. In summary, the structural design and physical property modulation of oxide fillers are crucial to the performance enhancement of all-solid-state lithium batteries, which not only requires a deep understanding of the underlying physicochemical theories, but also requires continuous exploration of the optimal composite solutions through experimental studies and data analysis. The current research progress marks another step towards the practicality and industrialisation of all-solid-state lithium battery technology, which is of great practical significance and far-reaching impact on the transformation of global energy structure and energy conservation and emission reduction.

3. Organic inorganic solid composite electrolytes

3.1 Organic inorganic electrolyte structure characteristics

Organic inorganic electrolytes assume a key role in all-solid-state lithium batteries, and their structural characteristics directly affect the performance and stability of the battery. This paragraph focuses on the structural characteristics of organic-inorganic solid composite electrolyte (SCE), involving the material's microscopic morphology, molecular arrangement and intrinsic connection with ionic conductivity. On this basis, the interface state formed by the interaction between the organic polymer matrix and the inorganic solid filler and its effect on electron and ion migration are explored in depth. Considering the crystal structure, ionic radius, and electron cloud distribution and other factors, we analyse the macroscopic and microscopic characteristics of SCE, especially in terms of electrochemical performance.

Studies have shown that organic substrates such as polyethylene oxide (PEO)[14][4] can provide good mechanical support and a large space of flexible chain segments, which is conducive to the dispersion of applied fillers and ionic conduction.As for inorganic components, oxides such as silicon oxide (SiO2), alumina (Al2O3), and lithium oxide (Li2O) effectively improve the ion transport ability of the electrolyte by interacting with the organic matrix.[2]The rationale lies in the fact that the surface hydroxyl groups of the inorganic oxides can form hydrogen bonds with the oxygen atoms of the polymer matrix, thus acting synergistically in the construction of the migration pathway for lithium ions.In addition, the inorganic solid fillers form a continuous conduction network in the electrolyte, which plays a crucial role in the improvement of the lithium ion transport mechanism.

In terms of structure optimisation, size effect and surface modification are the two main strategies to improve the conductivity of electrolytes.Using nanoscale fillers, the ion transport distance can be effectively shortened and the lithium ion migration channel can be optimised at the microscopic level.In addition, surface modification techniques such as surface coating and doping can improve the dispersion of fillers and compatibility with the substrate, further enhancing the electrochemical stability and ionic conduction efficiency of SCE.

Overall, the structural properties of organic and inorganic electrolytes are the key to modulate the performance of all-solid-state lithium batteries.[9]Through in-depth analysis of the coupling between the internal structure and performance parameters of the materials, screening of suitable inorganic fillers and their processing methods, and optimisation of their synergistic effects with organic substrates are of great significance in achieving high ionic conductivity and long-term stability of all-solid-state lithium batteries.Current research is moving towards finding new efficient conductive fillers, improving the surface chemistry of fillers and their dispersion in organic matrices, aiming to continuously break through the performance boundaries of electrolyte materials and provide solid material technology support for the commercial application of all-solid-state lithium batteries.

3.2 Classification and function of oxide fillers

As a key component of organic-inorganic solid composite electrolyte, the type and function of oxide filler directly affect the electrochemical performance and long-term stability of all-solid-state lithium battery.In the composite electrolyte, the main role of oxide filler is to improve the conduction efficiency of lithium ion and the mechanical properties of electrolyte through its unique structure and chemical properties.Research on the function of oxide fillers usually involves the selection of materials, surface modification, particle size control and interfacial compatibility with organic matrix.In terms of material selection, common oxide fillers include silica, titanium dioxide, zinc oxide and alumina, etc., which have good chemical stability and high lithium ion conductivity.In particular, anion-doped oxides, such as fluorine-doped lithium lanthanum zirconium oxide (LLZO), can effectively inhibit the growth of lithium dendrites while improving lithium ion conductivity, thus enhancing the safety performance of the battery.

In addition, the preparation technology of the filler is also very critical.Dr Tao Shengdong of Central South University had prepared LLZO materials by high temperature calcination using PTA lanthanum-zirconium metal framework compounds as a template in 2022. After optimising the process parameters, LLZO has a cubic phase structure and a large specific surface area of 158.44 m^2/g compared to the previous one, which allows for strong adsorption of lithium salts.

Surface modification is an important means to further enhance the performance of oxide fillers by introducing different functional groups to improve the compatibility of the fillers with the polymer matrix, thus achieving the effective construction of conductive channels and the enhancement of ion mobility.

Particle size also has an impact on the conductive function of the filler. Studies have shown that nanoscale oxide fillers can provide more diffusion channels for lithium ions and reduce their migration resistance. Meanwhile, the smaller particle size helps to build a denser electrolyte network and improve the contact area between the electrolyte and electrode interface. The reduction of particle size also enhances the mechanical properties of the composite, thus playing a significant role in suppressing the volume expansion of the electrode and maintaining the stability of the electrolyte.

Interfacial compatibility is one of the key factors determining the overall performance of composite electrolytes. Good bonding between the oxide filler and the polymer matrix can build lithium ion transport channels in an orderly manner and reduce the interfacial resistance.Therefore, the capacitation of oxide fillers through surface chemical modification and functionalization strategies to optimize the interfacial properties has received much attention in research.

Through the above analyses, this study deeply recognises the important role and optimisation strategy of oxide fillers in composite electrolytes for solid-state lithium batteries, especially their great potential in providing efficient lithium ion transport channels and improving interfacial compatibility.Further combined with particle size control, surface modification and other technical means, the comprehensive performance of the electrolyte can be effectively improved to achieve the systematic improvement of the overall performance of all-solid-state lithium battery.The study of oxide fillers provides new ideas and methodology to enhance the performance of all-solid-state lithium batteries, which is of great theoretical and practical significance for advancing the development of battery technology and its application in the field of energy storage.

4. The conductivity factors affecting the analysis

4.1 Conductivity mechanism of oxide filler

In the research and development of all-solid-state lithium battery, oxide filler as one of the key factors to enhance the conductivity of the solid electrolyte, and its mechanism has attracted much attention. Oxide filler by forming a stable interface between organic and inorganic electrolytes, can effectively reduce the internal grain boundary impedance, thus enhancing the overall ionic conductivity of the material.[16]For the conductive mechanism of oxide filler, this study focuses on the relationship between microstructure and macro performance to carry out in-depth analysis.

First of all, the microstructure of the oxide filler directly affects the strength of its interaction with the electrolyte matrix.[12]Oxide nanoparticles with high specific surface area can provide more contact points, strengthen the interfacial interaction between materials, and promote ion transport at the phase interface. Secondly, different types of oxide fillers significantly affect the ion mobility by constructing different conduction paths in the composite electrolyte. For example, depending on the charge size and uniformity of distribution, the selection of appropriate oxide fillers can form ion channels and improve the transport efficiency of lithium ions in the composite electrolyte.

Specifically, the crystal structure and electron cloud distribution characteristics of oxide fillers are directly related to their electron and ion conductivity. Some oxides, such as lithium titanate, form natural lithium ion channels inside their unique layered structure, which not only promotes the rapid transport of lithium ions, but also lowers the energy barrier. By introducing such oxides into inorganic electrolytes, the mobility number of lithium ions can be effectively increased and the overall conductivity of the materials can be improved.

In the empirical study, by comparing the effects of different ratios and types of oxide fillers on the performance of the electrolyte, the components and structures of the composite materials are precisely regulated to find the balance point to achieve the optimal ionic conductivity. For example, controlling the size, morphology, and dispersion of oxide fillers can substantially improve the ion transport kinetics in solid-state electrolytes.

In summary, the conductive effect of oxide filler in electrolyte not only comes from its own physical and chemical properties, but also closely related to its microstructure formed inside the material. The scientific design and fine tuning of oxide fillers can achieve their optimal performance in solid-state batteries and improve the overall performance of all-solid-state lithium batteries.[8]These research results have important theoretical value and practical significance for the design and optimisation of electrolyte materials for all-solid-state lithium batteries.

4.2 Analysis and outlook of optimisation strategies for oxide fillers

In a large number of studies on all-solid-state lithium batteries, the rational selection of oxide fillers and their structural design have been proved to be the key to improve the performance of electrolytes. Oxide fillers effectively improve the ionic conductivity of solid-state electrolytes by providing fast channels for lithium ion transport, and also help to inhibit interfacial reactions and enhance the overall stability of the battery. In this paper, a systematic optimisation strategy analysis of oxide fillers is carried out.

Firstly, for different types of oxide fillers, their crystal structures and ionic conduction paths can be analysed. In terms of particle size and morphology selection, the literature points out that nanoscale fillers are able to provide more lithium ion adsorption sites and transport channels compared to micron level due to their higher specific surface area, which can significantly improve the ionic conductivity. However, nanoparticles may also lead to agglomeration and affect the formation of conductive networks. Therefore, the nanoparticles were functionalized by means of surface modification and doping to enhance their dispersion with a view to forming a uniform and stable composite electrolyte.

Secondly, the effect of heat treatment process on the performance of fillers is explored. Appropriate heat treatment can remove the impurities on the filler surface and perhaps improve its crystal quality and interfacial contactability, thus enhancing the lithium ion mobility in the electrolyte. In addition, the precise control of heat treatment temperature and time is crucial to maintain the structural stability of the composite electrolyte, and too high or too long heat treatment will lead to the destruction of the filler structure, which in turn reduces its conductivity.

Meanwhile, regulating the microstructure of composite electrolytes by adding additives is also an important direction to improve the performance. For example, the addition of materials with high dielectric constants can effectively promote the dissociation of lithium ions in the electrolyte and enhance their migration rate.

Taken together, the components, structure, and addition method of oxide fillers have a significant impact on the performance of all-solid-state lithium batteries.This paper presents a series of optimisation strategies and expects them to be effective in enhancing electrolyte conductivity and battery performance.This not only deepens the public's understanding of the ion transport mechanism within all-solid-state lithium batteries, but also provides a new direction to further improve the battery performance, especially the long-term stability at high current densities.Future research should pay more attention to the synergistic effect of oxide fillers and the complex interfacial interaction[10]with organic and inorganic electrolytes to further promote the commercialisation of all-solid-state lithium batteries

5. Conclusions

From the current study, the effects of oxide fillers in organic-inorganic composite electrolytes on ionic conductivity in all-solid-state lithium batteries are complex and multifaceted.[15]These fillers can significantly improve the performance of all-solid-state lithium batteries by improving the stability of the electrolyte, enhancing the ion transport rate, and inhibiting the growth of lithium dendrites. However, different types of oxide fillers may produce different effects, and therefore a combination of their chemical and structural characteristics needs to be considered when designing and optimising the fillers.

Although some positive research results have been achieved,[6]the application of oxide fillers in all-solid-state lithium batteries still faces some challenges, such as the interfacial stability of fillers and electrolytes, the uniform distribution of fillers, and the complexity of the preparation process.[13]Therefore, future research needs to further explore in depth the interaction mechanism between oxide fillers and electrolytes and seek more effective methods to improve the performance of all-solid-state lithium batteries.

In summary, the effect of oxide fillers in organic-inorganic composite electrolytes on ionic conductivity in all-solid-state lithium batteries is a challenging but promising research field. Through continuous exploration and innovation, it is believed that greater breakthroughs will be made in this field in the near future, providing new ideas and methods for the development of all-solid-state lithium batteries.

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