Dean&Francis
ISSN 2959-6157

Developments and Challenges in Lithium-ion Solid-State Batteries

Keming Yang[1, *]

[1]Baotou No.93 Middle School, Nei Mongol, China
*Corresponding author: cowin0518@gmail.com

Abstract:

Under the huge consumption of global fossil energy and the high environmental protection requirements faced by our country, the energy system is gradually developing in the direction of electrification, and the more mature Lithium-ion Batteries (LIBs) have been favored by the majority of users, and have been used in wearable devices, electric vehicles, and even various types of energy storage devices. However, the liquid electrolyte used in Li ion batteries is prone to combustion and risk of leakage. Therefore, solid-state electrolytes (SSEs) have been attempted as an alternative to solve the above challenges. At present, the mainstream solid-state electrolyte materials mainly include: oxides, polymers, halides, sulfides, etc. This paper organizes and categorizes the solid electrolytes, compares the ionic conductivity, interfacial compatibility, mechanical strength, preparation process and other factors; summarizes the latest advances in the optimization of the design of SSE materials, the interfacial regulation strategy, and the large-scale preparation process of SSE, and analyzes the problems faced by the current technology development and looks forward to the future development of SSE. It also analyzes the problems faced by the current technology development and looks forward to the future development trend.

Keywords: lithium-ion battery, solid-state electrolyte, challenges and prospects.

1. Introduction

Accompanied by the gradual transformation of the global energy structure, traditional fossil energy sources are facing increasingly serious depletion and environmental pollution, which forces people to accelerate the pace of research and development of new energy development and energy storage technology [1]. In these researches, electrification is generally regarded as one of the important solutions to deal with the double crisis of energy and environment. As the most mature and widely used energy storage technology, lithium-ion batteries have been widely used in consumer electronics, electric vehicles, and large-scale energy storage systems because of their high energy density, long cycle life, low self-dis-

charge rate, and no memory effect. However, most of the mainstream lithium-ion batteries currently on the market use liquid organic electrolytes, such as carbonate (e.g., ethylene carbonate EC, dimethyl carbonate DMC, etc.) electrolytes [2]. Although these electrolytes have advantages in ionic conductivity and interfacial wettability, they also pose significant safety hazards: flammability, susceptibility to thermal runaway, liquid leakage, and high corrosiveness, which make them a great challenge for use in scenarios with high safety requirements (e.g., electric vehicles, large-scale energy storage power stations).

In response to these problems, solid-state electrolytes have become a hot research topic because of their excellent safety and potential high energy density. Solid-state electrolytes can be broadly classified into three categories according to the material system: (1) polymer-based solid-state electrolytes; (2) inorganic oxide/sulfide solid-state electrolytes; and (3) composite solid-state electrolytes (polymer and inorganic filler composite).

Compared with the traditional liquid electrolyte, solid-state electrolyte has the following advantages: (1) it is not easy to burn, with higher thermal and electrochemical stability, which fundamentally improves the safety of the battery; (2) it can effectively inhibit the growth and penetration of lithium dendrites, significantly improving the cycle life of the battery; (3) it is easier to work with the lithium metal negative electrode, which is expected to achieve a higher energy density. Therefore, all-solid-state lithium batteries are considered to be one of the most promising core technologies for the next generation of high-energy density and high-security energy storage devices.

In this paper, through the study of solid-state electrolytes, the systematic elucidation of its performance, its mechanism of action and its optimization method, which is conducive to people to promote the development of the key technology of solid-state electrolytes, and provide theoretical support and technical reference for the realization of a safer and more efficient energy storage system.

2. Classification and analysis of advantages and disadvantages of solid-state electrolytes

As the core material of the new generation of high safety and high energy density batteries, the structure and performance of solid state electrolyte has become a hot spot in the field of electrochemical energy storage. People have classified solid-state electrolytes into four major categories, namely, oxide-type, polymer-type, halide-type and sulfide-type, according to the different material systems [3]. Each type of solid state electrolyte has its own advantages in ionic conduction, electrochemical stability, process suitability and interfacial properties, and also has certain shortcomings and challenges. Therefore, the study and rational use of solid state electrolytes has become a major focus nowadays. The following part of the article will be its main performance characteristics and development bottlenecks are briefly described and analyzed.

2.1 .Oxide electrolytes

Oxide electrolytes mainly include chalcogenides (e.g., $Li_3xLa_{2/3}$-$xTiO_3$, LLTO), NASICON-type (e.g., Li_{1+x}-$AlxTi_{2-x}(PO_4)_3$, LATP), and garnet (e.g., Li_7La_2-$xTiO_3$, LLTO). $_7La_3Zr_2O_{12}$, LLZO) structures [4]. Such electrolytes are inorganic solid-state electrolytes that are based on oxide ceramics and rely on the migration of lithium ions in the vacancies or interstices in the lattice to achieve electrical conductivity. Compared with the other three electrolytes, oxide electrolytes have a denser crystal structure and stable chemical bonding, which gives them a wider electrochemical stability window, the ability to adapt to high-voltage cathodes, and good thermal stability. Moreover, oxide ceramics are non-flammable, a characteristic that can fundamentally improve the overall safety of the battery system.

However, the ionic conductivity of the oxide type at room temperature is relatively low (usually 10^{-4}~10^{-3} S/cm), which limits its fast charge/discharge performance [5]. Meanwhile, the brittleness of the ceramic material itself leads to the difficulty of machining and assembly, and the high-temperature sintering process not only increases the energy consumption, but also enhances the preparation cost. More critically, a high impedance interface is prone to be formed between the oxide electrolyte and the lithium metal anode, which is usually due to poor contact due to chemical instability or microcracks at the interface. This major drawback has become an important bottleneck limiting its practical application [6]. In addition, the interfacial evolution and volume change of the material during cycling may further deteriorate the interfacial contact and reduce the battery performance. Overall, oxide electrolytes show great potential with excellent thermal stability and safety, but still need to make breakthroughs in improving ionic conductivity and optimizing interfacial stability in order to better meet the practical needs of all-solid-state lithium batteries.

2.2 Polymer electrolyte

Polymer-based electrolytes are usually based on polyether (PEO), polyacrylonitrile (PAN) and other polymers, and lithium salts are added to form a conductive network. This

ISSN 2959-6157

type of electrolyte refers to the polymer chain segment and lithium salt coordination, so that the lithium ion migration in the polymer matrix to realize the ion conduction of the flexible solid-state electrolyte. Polymer-based electrolytes have good flexibility and processability, which can form a close contact with the electrode and reduce the interfacial impedance [7]; moreover, the preparation cost is low, which is suitable for coating and other scale-up processes, and has a good potential for industrialization. Compared with rigid ceramic electrolytes, polymer electrolytes can also effectively buffer the volume change and improve the battery cycle stability.

However, the ionic conductivity of this type of electrolyte is generally low (usually less than 10^{-5} S/cm) at room temperature [8], which is mainly due to the high glass transition temperature of the polymer matrix, which leads to the restricted movement of the chain segments, thus limiting the migration rate of lithium ions, which makes the polymer need to be in an environment of more than 60°C in order to This allows the polymer to be exposed to temperatures above 60°C in order to ensure good conductivity. However, high temperatures tend to cause the polymer chains to move, which reduces the electrochemical stability of the material and affects cycle life. For example, under high voltage cathode or long cycle conditions, the polymer electrolyte is prone to decomposition or side reactions, shortening battery life. Therefore, in order to make up for the lack of conductivity, academics have developed gel polymer electrolytes, using this substance to introduce organic solvents or ionic liquids into the polymer matrix to enhance ionic conductivity, but this also sacrifices some of the originally due to safety, such as flammability, thermal stability and other issues.

The mechanical strength and puncture resistance of polymer-based electrolytes are also low, making it difficult to inhibit lithium dendrite growth alone, and needing to be compounded with inorganic fillers or reinforced with multilayer structures. Therefore, how to achieve higher room temperature conductivity and better thermal stability while maintaining flexibility and processability is still a key issue in the research of polymer-based electrolytes.

2.3 Halide electrolytes

Halide electrolytes, represented by Li_3YCl_6, Li_3InCl_6, etc., have gained extensive attention from researchers in recent years. These electrolytes are inorganic solid-state electrolytes with the halogen anions (e.g., Cl-, Br-, I-, etc.) in lithium salts constituting the crystal skeleton, and lithium ion migration is realized through the vacancies or gaps in the crystal lattice. Its typical structure is mostly a layered or three-dimensional framework, and the diffusion behavior of lithium ions in the crystal channels plays a key role in achieving high electrical conductivity. Halide electrolytes have a room temperature ionic conductivity of about 10^{-3} S/cm, which can be adapted to high voltage cathode systems to a certain extent, and have good interfacial stability. Moreover, compared with sulfides, some halide electrolytes show higher chemical stability in air, and can be exposed to air for a short time without serious decomposition or performance degradation, which facilitates the processing and assembly of batteries.

However, the shortcomings of halide are also more obvious: the mechanical strength is insufficient, not easy to withstand the shortcomings of large external forces, so that the material in the battery assembly or cycling process is more prone to cracking or pulverization; the preparation process usually requires a strict anhydrous and anaerobic environment, in order to avoid the formation of soluble lithium salts after absorbing moisture or the occurrence of side reactions, which largely increases the complexity of the production and cost. In addition to this, some halide materials have electrochemical stability boundaries that are not yet fully defined during cycling, especially in higher voltage regimes or wide temperature ranges where structural or chemical degradation may occur. However, despite this, the development potential of halide electrolytes in power and energy storage batteries should not be ignored, and they are regarded as an important research direction in the future. With the advancement of material design theory and synthesis process, it is expected that the comprehensive performance of halide electrolytes can be further improved through the strategies of crystal structure modulation, doping adjustment or composite with polymer/oxide, so as to better balance the high conductivity, interfacial stability and preparation feasibility, and to bring new breakthroughs for all-solid-state battery technology.

2.4 Sulfide electrolytes

Sulfide-based electrolytes (e.g., $Li_{10}GeP_2S_{12}$, LGPS; Li_6PS_5Cl, LPSC) are one of the solid-state electrolytes with the highest ionic conductivity, which is recognized to be above 10^{-2} S/cm at room temperature. These electrolytes are mainly composed of elemental sulfur and metal elements such as lithium, phosphorus, and germanium, forming a three-dimensional crystal structure with open channels, which is conducive to the rapid migration of lithium ions. Due to its excellent ionic conductivity and low interfacial impedance, sulfide is widely used in all-solid-state lithium batteries. In addition, its outstanding advantages include good compaction, which is easy to achieve a densified structure, and low interfacial imped-

ance can be formed between it and the electrode, which is favorable to the high rate charging and discharging performance [9]. At the same time, sulfide materials usually have good flexibility, which can buffer the volume change of the electrode during the charging and discharging process and improve the cycle stability.

However, sulfide is extremely sensitive to moisture, and it decomposes and releases toxic H_2S gas when exposed to air, thus posing a safety hazard to people and a considerable problem to the environment. In addition, the chemical instability between the sulfide electrolyte and the lithium metal negative electrode and the high voltage positive electrode needs to be resolved, and this interfacial reaction may lead to the decomposition of the electrolyte and an increase in the interfacial impedance, which affects the life and performance of the battery [10]. The high environmental requirements during the preparation and use of sulfide electrolytes also increase the difficulty of their industrial application.

Currently, the industry mainly uses coating modification, compositing, and interfacial engineering to enhance the environmental stability and cycling performance of sulfide electrolytes. However, lithium-sulfur batteries are still facing many problems in the process of commercialization, among which the shorter cycle life and safety issues are more prominent, and the main reasons for the poor cycling performance of lithium-sulfur batteries are as follows:

(1) the sulfur anode and its discharge products have poor electronic and ionic conductivity, limiting the charge and discharge rate of the battery. In order to improve the conductivity, people usually need to add a large number of conductive agents in the preparation process, and these substances lead to a decrease in the overall energy density of the battery.

(2) Discharge intermediates such as lithium polysulfide are easily dissolved in the liquid electrolyte, resulting in the "shuttle effect", which triggers corrosion of the lithium anode and the loss of active material, leading to a reduction in the Coulombic efficiency and cycling performance degradation [11].

(3) The volume of cathode active material changes drastically during the charging and discharging process, from S_8 to Li_2S, the volume shrinkage is up to 79%, and this drastic volume change will destroy the structure of the cathode, which affects the performance of the battery [12].

(4) Lithium anode has dendrite growth and pulverization problems, which seriously affect the stability and life of the battery. Dendrites are needle-like or dendritic structures formed by uneven deposition of lithium ions during the charging and discharging process, which may puncture the diaphragm and cause short circuits or even safety accidents. Powdering is the surface fragmentation of lithium metal during the expansion and contraction process of multiple charging and discharging, which damages the electrode structure, increases the internal resistance of the battery, and reduces the capacity and cycle life.

3. Prospect of solid-state electrolyte

Despite the obvious advantages of solid-state electrolytes in terms of safety and energy density, their commercial application still faces many challenges. Therefore, future development should focus on technological innovation, cost control and industrial optimization, structural design of all-solid-state batteries and exploration of productization paths.

In terms of technology, the current solid-state electrolyte still exists problems such as insufficient ionic conductivity and high interfacial impedance. It is necessary to improve the conductivity and reduce the interfacial impedance through the development of new crystal structures, the introduction of composite strategies (such as oxide/polymer composite, interface modification technology), and accelerate the material research and development with the help of artificial intelligence and high-throughput screening. In terms of cost and process, the main problem is that the existing solid-state electrolytes, especially sulfide and oxide-based materials, are complicated and costly to prepare, which restricts their scale-up applications. Therefore, people are required to develop processes such as low-temperature synthesis, in-situ curing, and adaptive interfaces in the future to improve the yield and reduce the preparation cost. In terms of battery structure design, a good overall battery structure design is crucial in fully utilizing the performance of the electrolyte body. This requires people to achieve high energy density and long life of solid-state batteries need to synchronize the electrode matching, pressure control, interface engineering and other aspects of the breakthrough. Finally, in terms of industrialization path, some companies (e.g., Toyota, Quantum cape, Nande Times) have carried out prototype research and development of solid-state batteries, but they are still a long way from full commercialization. The establishment of a standardized test system, unified evaluation indexes, and the construction of industry chain ecology will be a major goal in the future, and an important path to promote industrialization.

4. Conclusion

With the development of electric vehicles, portable devices and energy storage systems, higher requirements for battery safety and energy density have been put forward. Traditional lithium-ion batteries have gradually exposed

ISSN 2959-6157

their performance bottlenecks and safety hazards, while solid-state electrolytes have shown great potential and received widespread attention due to their non-flammability, high electrochemical stability and compatibility with lithium metal. This paper reviews the current mainstream four types of solid-state electrolyte materials: oxide-type, polymer-type, halide-type and sulfide-type, and analyzes in detail the advantages and disadvantages of each type, the direction of breakthroughs and application prospects.

Although solid-state electrolyte technology is still in the development stage, its performance is being continuously improved through the continuous optimization of material design, interface regulation and manufacturing process. Combined with the industry's promotion and policy support, solid-state batteries are expected to gradually realize large-scale applications in the future, and promote energy storage technology to a safer and more efficient direction. Continuous attention to the innovative development of solid-state electrolytes is of great significance for the construction of a clean and efficient future energy system.

References

[1] Xu Bo, Qian Deyun, Wang Zejia, et al.Recent progress in cathode materials research for advanced lithium ion batteries. Cheminform, 2012, 23(43) : 34-45.

[2] Zhao Wenjia, Yi Jin, He Pingang, et al. Correction to: Solid-State Electrolytes for Lithium-Ion Batteries: Fundamentals, Challenges and Perspectives. Electrochemical Energy Reviews, 2022, 5(3): 1-1.

[3] Hu Lv, Wang Jun, Wang Ke, et al. A cost-effective, ionically conductive and compressible oxychloride solid-state electrolyte for stable all-solid-state lithium-based batteries. Nature Communications, 2023, 14(11): 14332.

[4] Kunimitsu Kataoka, Hiroshi Nakajima, Junji Asada. Lithium-ion conducting oxide single crystal as solid electrolyte for advanced lithium battery application. Scientific Reports, 2018, 8(1): 9965-9987.

[5] Asano Tetsuya, Sakai Akihiro, Ouchi Shohei, et al. Solid Halide Electrolytes with High Lithium-Ion Conductivity for Application in 4 V Class Bulk-Type All-Solid-State Batteries. Advanced Materials, 2018, 30(44): 1803075.

[6] Li Minhui, Xu Xiaofeng, Wang Honglei. Efficient immobilization and bidirectional catalysis of polysulfide conversion by FeCoP quantum dots for lithium-sulfur batteries. Journal of Materials Chemistry, A. Materials for energy and sustainability, 2023, 11(21): 11141.

[7] Yuejin Zhu, Yuanjia Zhu, Fan Yu, et al. Dual-Regulation Strategy to Enhance Electrochemical Catalysis Ability of NiCo2O4-x for Polysulfides Conversion in Li-S Batteries. Chemical Engineering Journal, 2021, 33(23): 89-93.

[8] Luo Dong, Zhu He, Xia Yi. et al. A Li-rich layered oxide cathode with negligible voltage decay. Nat Energy 2023, 23(34): 1078–1087.

[9] Zhu Yizhou, He Xiaobing, Mo Yuanying. Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations. ACS Applied Materials & Interfaces, 2015, 7(42): 23685.

[10] Laiqoiang Xu, Jiayang Li, Wen Tao, et al. Garnet Solid Electrolyte for Advanced All-Solid-State Li Batteries. Adv. Energy Mater. 2021, 11(33): 2000648.

[11] Li Zhuangnan, Sami Iman, Yang Jaesoo, et al. Litigated metallic molybdenum disulfide nanosheets for high-performance lithium–sulfur batteries. Nature Energy, 2023, 8(1): 10.

[12] Gong Yi, Li Jun, Yang Kai, et al. Towards Practical Application of Li-S Battery with High Sulfur Loading and Lean Electrolyte: Will Carbon-Based Hosts Win This Race. Nano, 2023, 15(9): 384-422.