Potential Applications of NASICON-Structured Solid Electrolytes in Low-Temperature Lithium-Ion Batteries

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Abstract. NASICON type solid electrolytes are widely regarded by researchers as ideal materials for next generation all solid state batteries due to their high ionic conductivity, wide electrochemical window, and low interfacial side reactions. However, several practical challenges hinder their real world applications, such as unstable interfaces between electrodes and electrolytes, high grain boundary resistance, and immature large scale manufacturing processes. These issues require systematic investigation to identify their underlying causes and to develop effective solutions. This paper reviews recent research advances in the material design, interface engineering, and scale up fabrication of NASICON electrolytes. It focuses on the degradation mechanisms of ionic transport kinetics, the imbalance in interfacial chemical and mechanical compatibility, and issues in powder compaction and sintering during mass production. Through innovative strategies at multiple scales atomic level doping modifications, mesoscopic interface buffer layer design, and macroscopic sintering parameter control this work establishes a"material structure process" co-optimization framework, revealing key pathways to performance enhancement and practical engineering implementation. The study aims to clarify the logical progression from fundamental research to industrial application for NASICON electrolytes, offering the industry a solid state battery model that balances high energy density with low manufacturing costs. Future research should integrate high throughput computational methods and intelligent process control technologies to develop dynamically stable interface strategies and a comprehensive evaluation system that considers electrochemical performance, mechanical reliability, and cost effectiveness, thereby accelerating commercial adoption.

Keywords: NASICON, superionic conductor, all solid state battery, solid electrolyte, low temperature lithium ion battery

1. Introduction

Amid the ongoing transformation of the global energy landscape and the implementation of carbon neutrality strategies, developing high-safety electrochemical energy storage technologies has become a core issue for the large-scale adoption of renewable energy. For energy storage in extreme environments, the development of low-temperature solid-state lithium-ion batteries holds significant theoretical value and engineering potential. Breakthroughs in this technology play a key role in

advancing both military-civil fusion strategies and the construction of modern technological systems [1].As activities such as high-altitude exploration and polar expeditions expand, and as emerging fields like new energy vehicles and space navigation equipment continue to evolve, the performance stability of energy storage devices under low-temperature conditions has become a major bottleneck for their practical application. This challenge mainly arises because, at low temperatures, the electrolyte tends to solidify, which dramatically increases charge transfer impedance and slows down interfacial kinetics, resulting in degraded battery performance. Research into solid-state electrolyte systems presents an important technological pathway to overcome these problems.

Currently, this field faces three main technological bottlenecks. First, failure at the solid–solid interface disrupts charge transport pathways, requiring interface modification strategies to construct three-dimensional conductive channels. Second, while sulfide-based electrolytes offer high ionic conductivity, they suffer from a trade-off between chemical stability and manufacturing feasibility, which hinders their industrialization. Existing element doping approaches have not fully resolved the inherent material defects. Third, oxide-based electrolytes need to overcome high grain boundary resistance, while polymer-based materials face challenges in achieving a balance between mechanical strength and ionic conductivity. These challenges demonstrate that despite promising research progress, the practical application of solid-state electrolytes still faces significant hurdles.

Solid-state electrolytes are the core component of all-solid-state batteries and are generally categorized into four main types: oxides, sulfides, polymers, and composite electrolytes. Perovskite-type electrolytes, such as LLTO, offer relatively high ionic conductivity ($\sim 10^{-4}$ S/cm), but suffer from severe interfacial side reactions with metallic sodium. Garnet-type electrolytes, like LLZO, have excellent chemical stability but require sintering at temperatures above 1200 °C, which leads to high grain boundary resistance. Sulfide-based electrolytes, such as Na_3PS_4, exhibit ionic conductivities up to 10^{-3} S/cm at room temperature, but are extremely sensitive to moisture and lack thermal stability [2]. In contrast, NASICON-type sodium superionic conductors have attracted significant attention due to their three-dimensional interconnected pore structures, wide electrochemical window, and excellent thermal stability [3].

In this paper, we systematically summarize several key aspects of NASICON-type electrolytes—as shown in Figure 1—including their crystal structures, ion transport mechanisms, practical applications, and doping modification strategies. We aim to provide a comprehensive overview of the current challenges facing NASICON materials and offer forward-looking perspectives and potential solutions.

Figure 1. Key Analytical Aspects of NASICON-Type Electrolytes

2. Crystal Structure and Ion Transport Mechanism of Nasicon-type Lithium-ion Electrolytes

2.1. Crystal Structure Characteristics

NASICON-type solid electrolytes generally adopt the formula $AM'M''P_3O_{12}$, where A is a monovalent alkali metal cation (e.g., Li^+, Na^+, or K^+), and M', M'' are multivalent metal cations such as Ti^{4+}, Zr^{4+}, or Ge^{4+}. When A is lithium, the compound becomes a NASICON-type lithium-ion electrolyte, typically with the formula $Li(A_2P_3O_{12})$. The structure comprises a three-dimensional framework of interconnected $[AO_6]$ octahedra and $[PO_4]$ tetrahedra, creating open ion-conducting channels. Lithium ions mainly occupy the M1 sites, which are octahedrally coordinated and provide low-energy migration pathways, while M2 sites in interstitial spaces assist in ion diffusion. Doping with ions like Ti^{4+} at M2 sites can distort the lattice and widen migration channels, improving ionic conductivity. Despite these favorable structural features, performance is still limited by factors such as material densification and the concentration of mobile lithium ions [4].
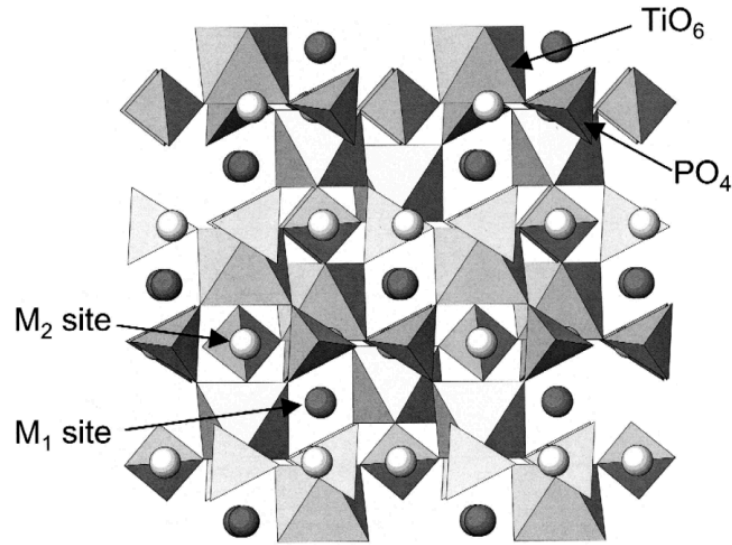
Figure 2. Crystal Structure of NASICON-Type Electrolyte

2.2. Ion Transport Mechanism

Li^+ ions in NASICON-type structures migrate through a three-dimensional network via two main pathways: straight channels along the c-axis and zigzag routes involving hopping between M1 and M2 sites. This migration is influenced by local energy barriers caused by distortions in the $[MO_6]$ octahedra. Enhancing ionic conductivity depends on minimizing these distortions and improving channel connectivity [5].For instance, doping with Sc^{3+} reduces activation energy to around 0.2 eV, enabling conductivities up to 10^{-3} S/cm at room temperature. However, excessive Li^+ concentration (>50%) can lead to electrostatic repulsion and hinder diffusion. Thus, optimizing the M-site environment through doping (e.g., with Sc^{3+} or Al^{3+}) is critical for improving ion transport performance in NASICON electrolytes.
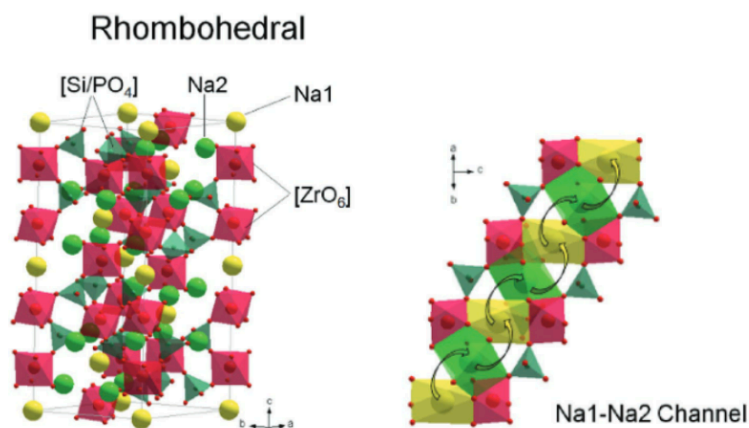

Figure 3. Ion Transport Pathways in NASICON Structures

3. Applications of Nasicon-type Solid Electrolytes

3.1. $LiTi_2(PO_4)_3$ (LTP)

$LiTi_2(PO_4)_3$ (LTP) is a representative NASICON-type solid electrolyte, demonstrating excellent battery performance with a discharge capacity of $80\,mAh\cdot g^{-1}$ when used with a $LiMn_2O_4$ thin-film cathode, as shown by Dokko et al [6]. using a sol–gel coating method. The synthesis approach significantly affects LTP's properties; for example, Sharma et al. enhanced grain boundary conductivity by forming a glass–ceramic composite through ball-milling LTP with ion-conducting glass (($Li_2SO_4)_3$–$(LiPO_3)_2$), achieving an ionic conductivity of $\sim10^{-4}$ S/cm at room temperature.

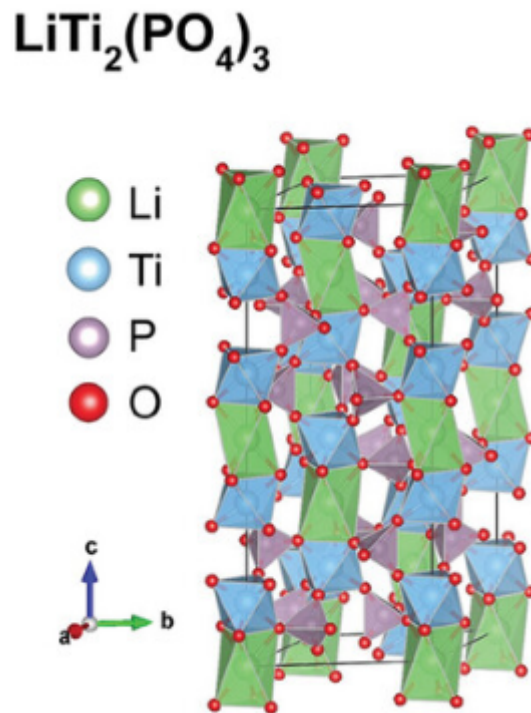Figure 4. Crystal Structure of $LiTi_2(PO_4)_3$ (LTP)

3.2. $LiGe_2(PO_4)_3$ (LGP)

$LiGe_2(PO_4)_3$ (LGP) is a NASICON-type solid electrolyte with mobile Li^+ ions and exhibits high ionic conductivity ($\sim10^{-4}$ S/cm) when doped with Al^{3+}. Unlike $LiTi_2(PO_4)_3$ (LTP), which suffers from Ti^{4+} undergoing redox reactions with lithium metal, compromising stability, LGP's Ge^{4+} is more chemically stable. Additionally, LGP offers a wide electrochemical stability window (1.8–7 V), making it a promising candidate for high-voltage lithium-ion batteries [7].
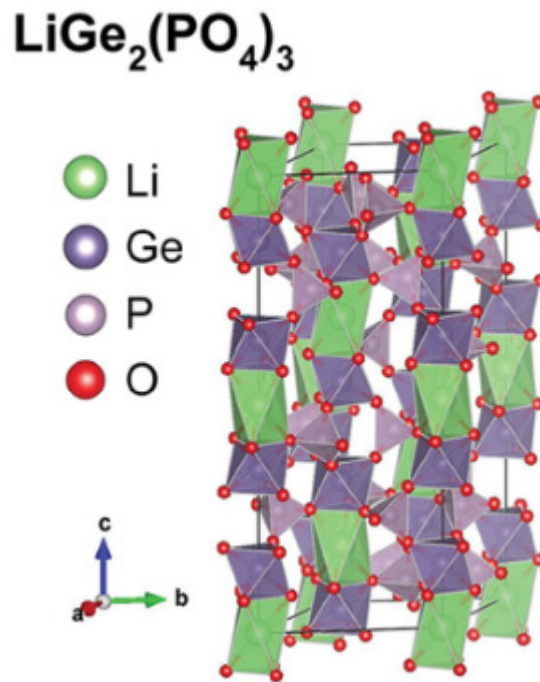
Figure 5. Crystal Structure of $LiGe_2(PO_4)_3$ (LGP)

3.3. LiZr2(PO4)3(LZP)

$LiZr_2(PO_4)_3$ (LZP) is a NASICON-type solid electrolyte with good compatibility with lithium metal and moderate ionic conductivity ($\sim 5 \times 10^{-6}$ to 2×10^{-4} S/cm), attributed to Frenkel-type defect migration. Unlike LTP and LGP, LZP forms a stable solid electrolyte interphase (SEI) through redox reactions with lithium, enhancing interfacial stability [8]. It remains electrochemically stable up to 5.5 V and demonstrates good cycling performance, with discharge capacities of 140 and 120 mAh·g⁻¹ at different current densities. However, its lower conductivity compared to titanium-based materials and higher processing demands limit broader application [9].
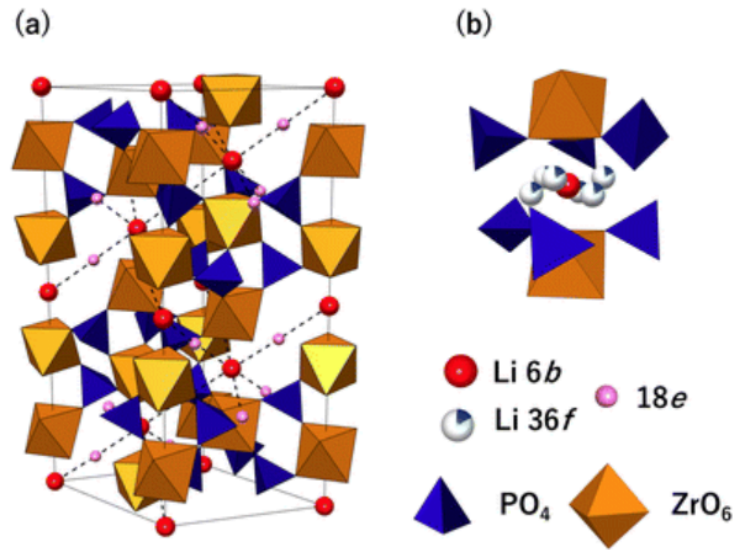
Figure 6. (a) LiZr2(PO4)3 crystal structure. (b) Arrangement of ions and polyhedra around the Li 6b site

4. Preparation Methods of Nasicon-type Lithium-ion Electrolytes

4.1. Conventional Synthesis Techniques

Conventional methods for preparing NASICON-type lithium-ion electrolytes include high-temperature solid-state reactions and the sol–gel method [10].The solid-state method involves mixing oxide precursors and calcining at >1000 °C, offering simplicity and low cost but suffering from issues like uneven particle size and high grain boundary resistance[11].In contrast, the sol–gel method forms nanoscale powders through hydrolysis and low-temperature treatment (600–800 °C), yielding higher surface area and improved ionic conductivity (up to 6.15×10^{-4} S/cm) [12].Though more complex and costly, the sol–gel method is favored for producing high-performance NASICON electrolytes [13].

4.2. Emerging Preparation Techniques

Emerging techniques for synthesizing NASICON electrolytes include co-precipitation, spark plasma sintering (SPS), and melt-quenching. Co-precipitation yields fine, high-purity powders with enhanced conductivity (up to 4.2×10^{-4} S/cm). SPS enables rapid densification at lower temperatures, significantly reducing grain boundary resistance. Melt-quenching forms glass-ceramics with tunable phase composition and high ionic mobility, though it requires precise process control[14]. These advanced methods improve performance and highlight future efforts to simplify processing, ensure uniformity, and enhance material purity.

5. Modification Strategies and Performance Optimization

Modification strategies for NASICON-type electrolytes focus on reducing impedance from grain boundaries and the bulk phase through optimized synthesis and doping. A-site doping—by introducing lower-valence ions like Ca^{2+} or higher-valence ions such as Sc^{3+}, Y^{3+}, or Cr^{3+}—can

adjust lattice parameters, create vacancies, and widen Li^+ migration channels, significantly enhancing ionic conductivity. Co-doping (e.g., Y^{3+}/Er^{3+}) further improves performance. Though less studied, P-site substitution—replacing PO_4 groups with $[SiO_4]$ or $[VO_4]$—modifies the crystal framework, lowers migration barriers, and boosts conductivity.

6. Challenges and Future Perspectives

Despite their advantages in ionic conductivity and stability, NASICON-type solid electrolytes face key challenges: limited ionic conductivity (typically $\sim10^{-3}$ S/cm), poor interfacial compatibility with lithium metal (e.g., Ti^{4+} reduction), and manufacturing difficulties due to high sintering temperatures and material costs. To overcome these issues, future research should explore broader doping strategies—including substitutions at M, P, or Li sites—and develop advanced composite materials to lower grain boundary resistance and enable efficient low-temperature Li^+ transport, supporting the practical application of NASICON electrolytes.

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