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Research progress on improving ionic conductivity of NZSP solid electrolyte

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Abstract. Due to the limited resources of lithium batteries, and the safety of liquid electrolytes, and the working principle of sodium batteries and lithium batteries are similar, and the cost is relatively low, so the development of sodium ion solid state batteries has its feasibility and necessity. Among them, NASICON solid electrolyte with its unique three-dimensional structure, and good thermoelectric performance has been widely concerned, in order to better understand the development of such materials and the latest developments, this paper reviews the crystal structure of NZSP solid electrolyte, conductive mechanism, preparation methods of research progress. NZSP solid electrolyte with its room temperature asymmetric monoclinic phase and large grain boundary resistance, resulting in ionic conductivity is not enough to meet the application needs, on the basis of the above content, for the existence of NZSP ionic conductivity low problem, related discussions were carried out. The research progress of improving the ionic conductivity of NZSP based on preparation technology, grain control and grain boundary control is discussed. And in the end, the possible future development trend of NZSP material is summarized and prospected, which will play a certain reference and promotion role for the future research on NASICON solid electrolyte.

Keywords: NASICON, Ionic conductivity, NZSP, Solid electrolyte, Ion doping, sintering.

1. Introduction

Energy is the core element of modern social operation and human civilization progress. Fossil energy has a long history, but its non-renewability and pollution limit its application. In the new energy industry, lithium battery with its high energy density, high power and other advantages occupy a very important position.

However, some elements in lithium batteries are low in abundance in the Earth's crust and unevenly distributed around the world [1, 2]. Sodium and lithium are in the same family, the properties of the two are very similar, and sodium resources are distributed around the world, which can avoid development constraints caused by resource shortages [3]. The structure and working principle of the two batteries are similar (as shown in Figure 1), so sodium-ion batteries can be a perfect substitute for lithium-ion batteries.

Sodium-ion liquid batteries have the disadvantages of low safety, flammability and volatility. In contrast, solid-state batteries have good safety, good thermal stability and high energy density [4]. The oxide solid electrolyte in the inorganic solid electrolyte has good comprehensive performance, among

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which the NASICON solid electrolyte has a stable three-dimensional frame structure and shows excellent electric heating performance. However, its ionic conductivity is still not enough to meet the requirements of practical applications. Tsai et al. [5] prepared a solid electrolyte with $5\times10^{-3}S\cdot cm^{-1}$ ionic conductivity, which verified the potential of improving NASICON ionic conductivity. Zahra [6] found through research that doped ions and process conditions would affect the ionic conductivity of NASICO, thus confirming the feasibility of ion doping to improve the ionic conductivity. In this paper, the current research on improving the ionic conductivity of NASICON solid electrolyte is reviewed, with the purpose of understanding the development direction and advantages of different relevant research, and the existing problems in the research, the preliminary solution and prospect are put forward.

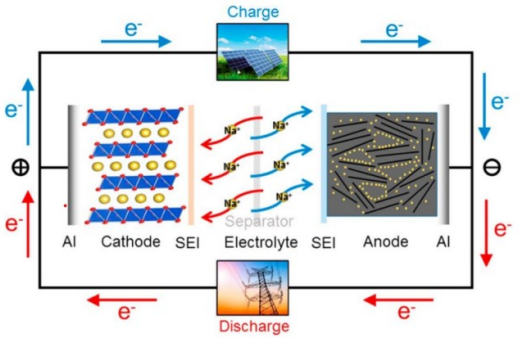

Figure 1. Schematic diagram of the operation of a NASICON ion battery [7]

2. NASICON's conductive mechanism

2.1. NASICON's crystal structure

The general formula of the NASICON type electrolyte is $Na_{3+x}Zr_{2-x}Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 3$), which can be seen as a solid solution of $NaZr_2P3O_{12}$ and $Na_4ZrSi_3O_{12}$. As can be seen from the figure, the crystal configuration of $Na_{3+x}Zr_{2-x}Si_xP_{3-x}O_{12}$ includes the SiO_4/PO_4 tetrahedron, the ZrO_6 octahedron and the three structural units of Na+ ions. By sharing oxygen atoms with the apex angles of the SiO_4/PO_4 tetrahedron and the ZrO_6 octahedron, a three-dimensional rigid skeleton is constructed, that is, each SiO_4/PO_4 tetrahedron and four ZrO_6 octahedra coordination, and a single ZrO_6 octahedron is connected to the surrounding six SiO_4/PO_4 tetrahedra.

Because of the difference in Si content, $Na_{3+x}Zr_{2-x}Si_xP_{3-x}O_{12}$ can be divided into monoclinic crystal and rhombohedral crystal in general. When $x < 2.8$ and $x > 3.2$, $Na_{3+x}Zr_{2-x}Si_xP_{3-x}O_{12}$ is rhombic phase. In the Rhombohedral phase, each ZrO_6 octahedron is connected with six $(P/Si)O_4$ via the form of common vertices to form a three-dimensional skeleton, Na+ is located in the skeleton gap, and the rhombohedral structure has two Na^+ sites, Na1 and Na2, i.e. only one ion transport path, Na1-Na2. When $1.8 \leq x \leq 2.2$, these compounds belong to the monoclinic phase and are stable at room temperature. Monoclinic phase is the rotation deformation of rhomboid phase, in which the original Na2 site splits into new Na2 and Na3 sites [8]. There are three sites in NZSP: Na1, Na2 and Na3. The increase of sites makes Na1-Na2 and Na1-Na3 have transport paths at the same time. The monoclinic phase and rhombic phase can be transformed into each other at a certain temperature. Compared with the rhombohedral phase, the monoclinic phase has a relatively wide Na^+ conduction path, resulting in higher ionic conductivity. While monoclinic phase is asymmetric phase, rhombic phase is symmetric phase, and its activation energy is lower than monoclinic phase, while rhombic phase is stable at high temperature and difficult to stabilize at lower temperature, which hinders the development of rhombic phase to improve ionic conductivity [9].

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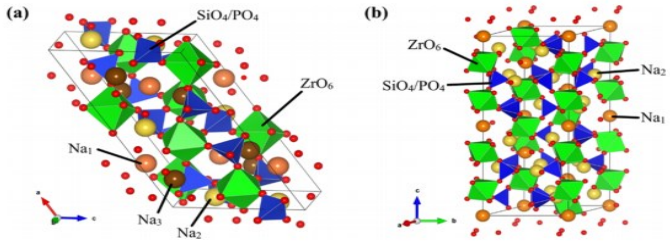

Figure 2. Crystal structure of NASICON electrolyte. (a) monoclinic crystal (b) rhombic crystal [10]

2.2. Ion transport mechanism of NASICON

The conduction mechanism of ions in solid electrolyte depends on the type of electrolyte. NASICON solid electrolyte is a kind of ionic electrolyte, while the ion transport in inorganic electrolyte is related to its vacancy and defect, as shown in FIG. 3. It mainly includes (1) the transport mechanism in the vacancy, (2) the transport mechanism in the gap, and (3) the co-transport mechanism between the vacancy and gap. This classical model of ion transport believes that a single ion jumps from one lattice site to another adjacent lattice site through the ion transport channel inside the crystal, so as to achieve ion transport. The ionic conductivity of inorganic solid electrolyte conforms to Arrhenius formula:

$$\sigma = \sigma_0 e^{-\frac{E_A}{K_B T}} \quad (1)$$

Where σ_0 refers to the pre-factor, E_A is the diffusion activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. It can be seen that the ionic conductivity is related to the pre-factor, the diffusion activation energy and the temperature. In the actual reference research, the ionic conductivity can be optimized by adjusting the above several parameters. In addition, there are other mechanisms related to ion transport mechanisms. For example, He et al [11]., through AIMD simulation study, found that rapid diffusion in superionic conductors is not simply through the typical isolated ion jump in solid, but through the cooperative migration of multiple ions with low energy barrier. This provides theoretical support for ion doping to improve the conductivity; Wang et al [12]. revealed how non-Arrhenius transport in ion transport is caused by classical MD model simulation. This transport mechanism further modified the ion diffusion activation transport model and can be widely applied to superionic conductors.

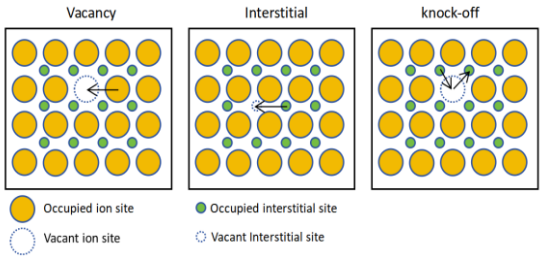

Figure 3. Schematic diagram of ion transport mechanism in inorganic solid electrolyte [13]

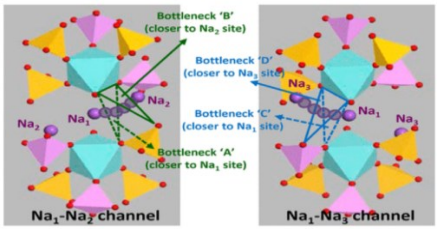

Figure 4. Four different types of bottlenecks in the monoclinic Nasicon structure [14]

For the NASICON solid electrolyte, in the monoclinic structure of the NZSP electrolyte, sodium ions are transported through a triangular bottleneck area. This bottleneck region is formed by oxygen atoms that share angles in the octahedral (ZrO_6) and tetrahedral structures (SiO_4/ PO_4). The diffusion of Na ions is closely related to the bottleneck area. Anurag Tiwari et al [15]. used VESTA software to measure the crystal structure of NZSP sintered at 1250°C and found that the shortest distances between Na1-Na2, Na1-Na3 and Na2-Na3 sites were 3.5 Å, 3.0 Å and 4.4 Å, respectively. The shortest distance between Na1 and Na3 sites indicates that the most efficient transport route of Na ions is through the Na1-Na3-

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Na1 pathway [16], which means that the transport between Na1-na2 is the limiting factor of ionic conductivity.

Furthermore, in the two transport paths of the monoclinic phase structure mentioned above, there will be four different bottleneck regions A- bottleneck region D. As can be seen from the figure, regions A and B are located at the NA1-NA2 transport channel, regions C and D are located at the NA1-NA3 transport channel, the centers of regions A and C are located near the Na1 site, and the centers of regions B and D are located near the Na2 and Na3 sites respectively. The area of bottleneck region A to bottleneck region D is 6.2719, 5.0648, 5.9995, and 5.6488Å^2, respectively. Since Ea is mainly determined by the smallest bottleneck, bottleneck region B in the NA1-NA2 transport path may be a limiting factor for Na^+ conduction.

3. Preparation process of NASICON

3.1. Solid State reaction method

Solid phase reaction method is a traditional and simple method to synthesize Nasicon type solid electrolyte, its general process is: batching → ball milling → pre-firing → molding → sintering. In the sintering process, the choice of sintering temperature and sintering time is an important factor affecting the density of the material, and the density is an important factor [17] affecting the conductivity of NASICON ion. For the sintering of NZSP generally choose 1100℃, because it can be melted [18] at such a temperature, in addition to its pre-sintering and ball milling, the purpose of pre-burning is to obtain a relatively high purity of the sintering phase, the purpose of ball milling is to mix raw materials evenly and the pre-sintered particles fine.

In addition to the classical solid-phase sintering method, other solid-phase sintering methods in recent years have also been applied to the preparation of NZSP, Basitti Hitesh [19] use SPS method to prepare NZSP solid electrolyte, and annealing treatment. The traditional sintering of materials requires a temperature of up to 1225℃; However, SPS requires temperatures as low as 1050C. In addition, the relative density of the sample prepared by conventional sintering can reach 91%, while the maximum density of the sample prepared by SPS and annealed is about 98%, allowing the ionic conductivity to reach $3.5\times10^{-4}S\cdot cm^{-1}$. Ren et al. [20]. use instantaneous sintering method to further reduce the sintering temperature and time relative to SPS, so as to avoid Na, P evaporation and secondary phase precipitation due to high temperature and sintering time is too long, and the conductivity can reach 10^{-4}-10^{-3} $S\cdot cm^{-1}$. In addition, Sahir Naqash et al. [21]. adopted liquid-phase assisted solid phase sintering, and finally obtained a total conductivity of up to $1\times10^{-3}S\cdot cm^{-1}$, which shows that the development prospect of this method is very broad.

3.2. Sol-gel method

Compared with the traditional solid phase method, the sol-gel method can achieve the atomic-level mixing of raw materials, shorten the mass transfer process, and produce more uniform products. At the same time, the temperature required for densification can be effectively reduced to avoid the generation of impurity phase. The sol-gel method is first to form a colloidal solution, and then heated to form a gel network, after drying for heat treatment crystallization, and then sintering. The process flow is shown in Figure 5. Among them, the crystallization of $Na_3Zr_2Si_2PO_{12}$-based material usually starts at 600℃and is completedbetween 750 ℃ and 900℃ [22].

Jin Xiaojian et al. [23] prepared NASICON powder with different proportions by sol-gel method, and characterized it by XRD, SEM and Agilent test equipment. It was found that when the P source is excessive by 10%, the formation of ZrO_2 can be inhibited, and new impurity phosphates will not be generated due to the excess of P source. At this time, the ionic conductivity can reach 3.87×10^{-3} $S\cdot cm.^{-1}$

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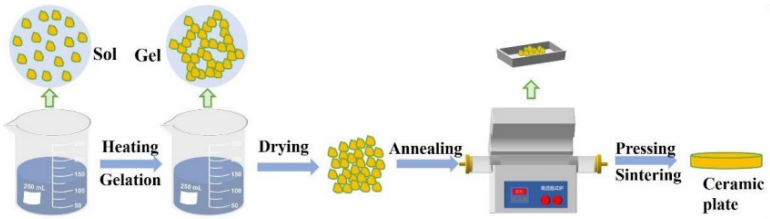

Figure 5. Process flow chart of sol-gel method [24]

3.3. Other preparation methods

In addition to the above, there are many other methods for the preparation of NZSP solid electrolytes, each of which presents its own unique advantages. For example, Liu et al. [25] used the LF-FSP method to produce NASICON nano powder, thus eliminating many steps necessary in the traditional solid-state process. Nanoscale final grains and higher sintering properties are achieved, and better performance is obtained at lower sintering temperatures. D. N. Grishchenko et al. synthesized NASICON with composition $Na_3Zr_2Si_2PO_{12}$ by pyrolysis of organic solution mixture [26]. The composition and morphology of the compound were confirmed by X-ray diffraction analysis and scanning electron microscopy. The synthesis of NASICON took an average of nine hours, the shortest time of all known methods for preparing the material.

Different preparation methods and process parameters will have a great impact on the ionic conductivity of NZSP materials, and the ionic conductivity of NZSP solid electrolytes can be controlled by controlling the preparation method and process.

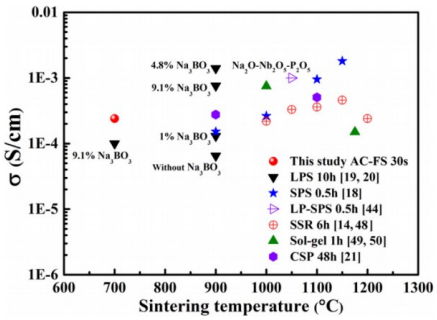

Figure 6. Relation between room temperature conductivity of NASICON ceramics and sintering temperature under different conditions [20]

4. Methods for increasing the ionic conductivity of NASICON solid electrolyte

4.1. Improving ion conductivity based on the preparation process

According to the second part above, it can be seen that for NZSP materials, different process parameters of the same process and different synthesis processes will affect the density, grain growth, impurities and other factors in the preparation, and then make the final ionic conductivity of NZSP materials change, so the first aspect is to regulate the process parameters and change the process. To achieve the improvement of ionic conductivity.

4.1.1. Process parameters

Therefore, the optimization effect of the change of process parameters on the ionic conductivity in sintering is discussed. The two important parameters in sintering are heating temperature and holding time. And often high heating temperature and long holding time there is a synergistic effect.

Through the comprehensive comparative analysis of electrochemical impedance spectroscopy at normal temperature, Chen Dan [27] explored the influence of different sintering temperature and holding time on density and conductivity. The analysis showed that the conductivity first increased with the

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increase of sintering temperature, and then decreased. With the extension of holding time, the conductance rises first and then becomes stable. Mihaela Iordache et al. [28] measured the particle size of NASICON powder sintered at different temperatures by dynamic light scattering (DLS) particle size: About 1000 nm at 1100°C, between 618.6 and 1315.4 nm at 1150°C and between 500.6 and 1008 nm at 1175°C. And found that sintering at 1175 ° C, the highest ionic conductivity.

In addition to the parameters in sintering, the optimization of process parameters in forming can also optimize the ionic conductivity of NASICON solid electrolyte. Man Kit Chong et [29] al. found that different grinding times lead to the formation of different types of ZrO_2, which is the reason for the different ionic conductivity. The NZSP milling for 24 h obtained the highest total ionic conductivity (9.66×10^{-4} S·cm^{-1}) at room temperature.

4.1.2. Preparation method

It can be seen from the second part of the preparation method that there are many different preparation methods for the preparation of NZSP, and different preparation methods have different effects on the ionic conductivity of NZSP materials due to their different characteristics.

The cold sintering, LF-FSP method and pyrolysis method mentioned above can respectively shorten the preparation time, save work steps, and reduce the sintering temperature and other needs. This section will introduce some of them and other related preparation methods on the basis of improving the ionic conductivity.

By fitting the composite impedance data with equivalent circuits, Diksha N. Karmalkar et [30] al. found that the grain and grain boundary total resistance of materials prepared by HT-SSR method were smaller than those prepared directly by SSR, except the parent phase. The basic principle of hydrothermal solid phase combination (HT-SSR) is that HT method can produce nanoparticles from a uniform water-based cationic mixture. This is expected to increase the density and thus reduce the grain boundary resistance of the sintered pellets. Li Zhi [31] made a comparative analysis of NZSP prepared by conventional sintering method and spray drying method, and found that the room temperature ionic conductivity of the material obtained by spray drying method was significantly higher than that obtained by conventional sintering method through the analysis of the EIS fitting data.

Table 1. Room temperature ionic conductivity of CS-NZSP and SD-CS-NZSP [31]

Sample	σ_b	σ_{gb}	σ_t	E_a/eV
CS-NZSP	1.28×10^{-3}	8.03×10^{-4}	4.94×10^{-4}	0.34
SD-CS-NZSP	1.664×10^{-3}	1.21×10^{-3}	6.96×10^{-4}	0.32

4.2. Improvement of ionic conductivity based on grain regulation

For Nasicon type ion conductors, the conduction mechanism of Na+ within the grain and at the grain boundary is different. Therefore, the improvement of its ion conductivity can be considered [32, 33] from the two aspects of grain and grain boundary respectively. For grains, according to the first part of the preceding description, in addition to the concentration of Na+ in sodium superionic conductors, the bottleneck area of the Na site transport path is also a factor limiting the improvement of ionic conductivity, so the next will be discussed from this aspect and the synergistic co-doping of the two.

4.2.1. Improving Na^+ concentration

The concentration of sodium ions is directly related to the number of sodium ions to participate in the transport, obviously the more sodium ions to participate in the transport of its higher conductivity, low ion doping is commonly used to increase the concentration of Na+ a way, its principle only according to the charge balance principle that can be seen, doping is equivalent to low ion instead of Zr^{4+} site, in order to balance the positive charge, The concentration of sodium ions in the crystal cell will be increased, so the ionic conductivity will be increased accordingly. Adam G. Jolley et [34] al. doped a variety of trivalent (Al^{3+}, Fe^{3+}, Y^{3+}) and divalent cations (Co^{2+}, Ni^{2+}, Zn^{2+}) respectively, and found that

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the ionic conductivity was higher than that of undoped at room temperature. Luo et al. [35] found that the ionic conductivity of NZSP doped transition metal elements (Fe, Co, Ni) was also improved.

4.2.2. Enlarge the size of Na+ transport bottleneck area

As discussed in the previous part, the size of the bottleneck region will affect the size of the activation energy, and the increase of the diffusion bottleneck will lead to the increase of the ionic conductivity. According to Arrhenius formula, it can be found that it will further affect the ionic conductivity. To enlarge the bottleneck size, ions with larger radius are usually doped at the Zr site [24].

Liu et [25] al. substituted Zr4+ by Ce4+ and found that the Na+ diffusion "bottleneck" expanded sharply from 5.4 to 5.6 A2, resulting in a very high ionic conductivity of $2.4 \times 10^{-2} S \cdot cm^{-1}$ at 140°C. In addition, by doping Ca^{2+} in the system, the size of the sodium ion migration channel is effectively regulated, and the ionic conductivity of the solid electrolyte at room temperature is greater than $10^{-3} S \cdot cm^{-1}$ [36]. As for Ga doping, the triangular bottleneck area of the original sample is $5.234 Å^2$, but the triangular bottleneck area is increased by gallium substitution. When replaced by Ga0.1, the area can reach $6.165 Å^2$. The material has a superior total conductivity [37] of 1.06×10^{-3} S cm^{-1} at 25°C.

4.2.3. Co-doping

In addition to the above two methods carried out independently, there are also relevant studies on co-doping methods to improve ionic conductivity. Co-doping technology refers to adding another ion while adding a low-priced state ion, which can increase the Na+ concentration, and other ions can choose ions with larger radius, expand the size of the bottleneck area or assist sintering. Reduce the resistance of the grain boundary and improve the ionic conductivity. Luo et al. [35] co-doped transition metals to obtain NZSP with $5.03 \times 10^{-6} S \cdot cm^{-1}$ electronic conductivity. Omar et al. [38] synthesized NZSP co-doped with Sc/Yb. Sc^{3+} doping increased the carrier content in the system, while Yb with larger ionic radius expanded the size of Na+ transport channel. The synergistic effect of the two made the optimal ionic conductivity of the synthesized material $1.62 \times 10^{-3} S \cdot cm^{-1}$.

4.3. Improvement of ionic conductivity based on grain boundary regulation

The last aspect of this paper to improve the ionic conductivity is based on grain boundary regulation. Compared with the ion transport within the grain, the ion transport at the grain boundary is more difficult [24], so the ionic conductivity at the grain boundary is often lower than the ion conductivity in the grain. In this paper, the improvement of phase purity and the modification of grain boundaries are discussed.

4.3.1. Improving phase purity

In the preparation process, sometimes due to high temperature, element volatilization will cause the formation of impurity phase, and the formation of impurity phase will sometimes increase the grain boundary resistance, causing a very adverse effect on the grain boundary conductivity. The impurity phase can be avoided by the change of the aforementioned process parameters to adjust, in sintering usually occurs when the expected NASICON phase rises to a certain sintering temperature, and the impurity phase gradually decreases with the increase of sintering temperature, but sometimes if the sintering temperature is too high, it may reappear such as $Na_2ZrSi_2O_7$ and ZrO_2 impurity phase [39]. Increase the grain boundary resistance, resulting in a decrease in ionic conductivity. And often for the sintering of NZSP need a certain high temperature, so try to reduce the sintering temperature and time, reduce volatilization to avoid the formation of impurity phase is an important idea here. Jin An Sam Oh et al. [10] used the method of adding sintering agent Na_2SiO_3 to reduce the sintering temperature and sintering time of NZSP electrolyte, and provide the liquid phase for the sintering process. The highest ionic conductivity at room temperature is 1.45 $mS \cdot cm^{-1}$. In addition, the above improvements [29, 40] in process parameters and different processes such as SPS, instantaneous sintering, pyrolysis of organic solution mixture, etc. [19, 20, 26], have respectively reduced the sintering temperature or sintering time and avoided the formation of impurity phase.

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4.3.2. Grain boundary modification

Grain boundary modification is the method of introducing certain elements or phases into the grain boundary to regulate the electrical conductivity at the grain boundary. By changing the structure and chemical composition of the grain boundary, the properties of the material can be changed. When synthesizing NZSP, Zhang et al. [41] introduced a certain amount of La into the system. It was found by XRD pattern that the presence of La would cause $Na_3La(PO_4)_2$ phase to form at the grain boundary and fill the grain boundary, increasing the relative density of the ceramic sheet from 87.6% to 99.6%. The room temperature ionic conductivity of the obtained $Na_{3.3}Zr_{1.7}La_{0.3}Si_2PO_{12}$ electrolyte reached $3.4\times10_{-3}S\cdot cm_{-1}$. Shao et al. [42] added NaF to the precursor when synthesizing NZSP. Through SEM observation, it is found that the amorphous phase containing fluorine is formed around the grain, this amorphous phase modifies the grain boundary, making the density increase, the obtained solid electrolyte room temperature ionic conductivity up to $3.6\times10^{-3}S\cdot cm^{-1}$. In addition, a new preparation method can be used, such as the Si/P ratio in NASICON structure can be adjusted by the phosphate grain boundary phase formed by rare earth oxide assisted sintering method, so as to improve the ionic conductivity of the electrolyte [43].

5. Summary and Prospect

solid electrolyte was first proposed in 1976 and has made great progress in recent years. However, the current practical application of NZSP is still facing many problems and challenges, among which the ionic conductivity is low and does not meet the application needs of the problem remains to be solved. To this end, this paper first reviewed the crystal structure of the material, ion transport mechanism, preparation process, intended to fundamentally understand the NZSP in different factors on the ionic conductivity of the influence of the situation, on this basis, from the preparation process, grain control and grain boundary control of three aspects of the promotion of ionic conductivity methods. Through the ion transport mechanism found, based on Arrhenius equation, found that sodium ion concentration and bottleneck area size affect the grain conductivity, mainly through the optimization of process parameters, the development of new preparation process, ion doping, avoid impurity phase generation and grain boundary modification several aspects to improve the ionic conductivity. At present, good progress has been made in all aspects of research. However, for NASICON solid electrolyte, there are still some other problems, such as dendrite growth, electrode volume change, etc. For solid electrolyte, this is also an aspect that must be improved, so it also needs to be further studied. Based on these, In the future, the research focus of NASICON solid electrolyte should be focused on improving the ionic conductivity at the same time, ensuring the flexibility of its solid state interface, so as to reduce the interface problem, which can be improved by introducing a film or adding sintering additives.

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