

Study On Electrolyte of Low Temperature Sodium-Ion Battery

Bohao Chang *

School of Chemistry and Materials, Nanning Normal University Guangxi China

* Corresponding Author Email: 2221483930@qq.com

Abstract. With the rapid development of electronic devices, energy storage systems with excellent performance are required. To be used in cold climates and high-altitude areas, it is required that the battery should work stably and operate safely even when the temperature drops below freezing point. Sodium-ion batteries arouse great attention, because of their high safety, good capacity in both high and low-temperature environments, along with their abundant sodium resources in the earth's crust. But for practical applications, the kinetics of sodium-ion batteries become slow when working at low temperatures. The performance deteriorates with the temperature decreases. Therefore, researchers have carried out a lot of research to overcome these problems in the low-temperature environment. For example, the energy storage performance of sodium-ion batteries can be improved by optimizing the positive and negative electrodes, separators, and electrolytes. Among them, optimizing the electrolyte is critical to improving the energy storage performance of sodium-ion batteries. Because the electrolyte is an important part, which is in contact with each part of the battery as a medium, which is mainly composed of solvents, electrolyte salts, and additives. During the charge/discharge processes of the battery, the electrolyte plays a role to act as an ionic conductor to transfer Na^+ between the positive and negative electrodes and link them together. Additionally, the electrolyte will also directly participate in the reaction on the electrode surface and form SEI film. Thus, it is one of the most economical and effective means to enhance the low-temperature performance by modifying the electrolyte. This paper, summarizing the reports on the electrolyte of low-temperature sodium-ion batteries at home and abroad, sorting out and analyzing the solid, liquid, and gel electrolytes, clarifies how to making the electrochemical performance of sodium-ion batteries better by optimizing electrolytes.

Keywords: low temperature; sodium ion battery; solid electrolyte; liquid electrolyte.

1. Introduction

With the rapid development of the electronic market, energy storage systems with excellent performance are required. Sodium-ion batteries need both have higher energy/power density and can further adapt to the extreme working environment brought by different regions and seasons. Low-temperature and high-efficiency energy storage system is an indispensable development to achieve this goal. Low-temperature batteries are widely used in electric vehicles, aerospace, solar cells, and other fields [1]. As a new type of energy storage technology, sodium-ion battery has many upsides. The energy density of a sodium ion battery is $100 \sim 150 \text{ W} \cdot \text{h} / \text{kg}$, higher than that of a lithium-ion battery, which means that a sodium ion battery can restore more battery energy. The diameter of sodium ions is smaller than that of lithium-ion Stokes, the ionic conductivity of sodium salt electrolytes with the same concentration is higher than that of lithium salt electrolytes, and the fast-charging performance is better [2]. The interface ion diffusion ability is stronger, with the bipolar electrode being used to increase the volume energy density. For sodium-ion batteries, aluminum foil can be adopted as the current collector for both positive and negative electrodes. Its working theory is similar to that of lithium-ion batteries, and is compatible with lithium battery production equipment [3]. The most important thing is that the abundant sodium resources distribute evenly and are simple to refine. The elemental abundance of sodium in the nature is 1300 times that of lithium. Under the same capacity and voltage, both metal oxide type and Prussian blue type sodium ion batteries, the cost is lower than the current lithium iron phosphate battery [4]. Thus, in terms of low-temperature application prospects sodium-ion battery is better. In a low-temperature environment, the traditional lithium-ion battery will be seriously affected, resulting in its bad performance. But the sodium ion

battery can work relatively stable at low temperatures and maintain high-efficiency output. Its good performance under low-temperature environments is due to its unique electrolyte. Compared with traditional lithium-ion batteries, the electrolyte of sodium-ion batteries can maintain high ionic conductivity at low temperatures, because the electrolyte of sodium-ion batteries contains a higher concentration of salt [6]. Therefore, sodium-ion batteries have good low-temperature application prospects and are expected to replace lithium-ion batteries in the future.

When sodium-ion battery operates in a low-temperature environment, the problems such as serious capacity attenuation, short cycle life, and difficulty in charging, are still existing. The low-temperature energy storage performance of sodium-ion batteries is related to the cathode material, anode material, and electrolyte [7]. At present, the research reports on low-temperature sodium-ion batteries are limited. To improve the low-temperature performance, various components of the battery have been studied. Among them, researchers have conducted a lot of research on low-temperature electrolytes and found that electrolytes can effectively improve low-temperature performance. The main problems of sodium-ion batteries at low temperatures are caused by the slow diffusion process, including the diffusion process of Na^+ at the interface of electrolyte and electrode solid electrolyte and the charge transfer process of Na^+ and e^- at the interface of electrode/electrolyte, which hinder by the decrease of temperature, resulting in a significant decrease in the kinetic performance of the battery, seriously affecting the electrochemical performance of SIBs [8]. What's more, the electrolyte is in direct contact with all parts of the battery, which means that it can effectively improve low-temperature performance. In addition, the problem of poor contact between the active material and the current collector may also be caused under low-temperature conditions, which in turn affects the battery performance. The electrolyte can alleviate the problems caused by poor contact [9]. Improving the sodium storage performance of sodium-ion batteries under extreme working conditions is of great significance to promote the industrialization process of sodium-ion batteries.

To have a deeper understanding of low-temperature sodium-ion batteries, this paper systematically summarizes the recent development of low-temperature sodium-ion batteries, together with the development status of liquid electrolytes and solid electrolytes, as well as the performance improvement of low-temperature sodium-ion batteries. (Figure 1)

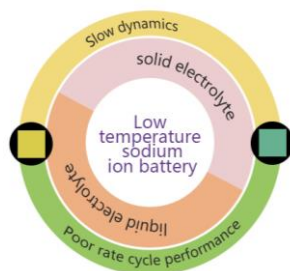


Fig. 1 Thinking diagram

2. Development status of electrolyte

2.1. Liquid electrolyte

In the wide range of research practicing on ionic liquids (ILs), where cations and anions could be integrated in a incomparable method, and being tight-consisted. As for their natures, those are distinguished according to their functional advantageous such as the elevated thermal robustness, the low vaporous pressure, the wider electrochemical window, with the variety in the selection on formulation designing. These qualified merits have stirred a fervent fascination among experts and publics [10,11]. Cations and anions with amount of heterogeneity could be manifested in ionic liquids (ILs), which offers huge possibilities for adjusting their natures that involved with the viscosity, melting point, and electrochemical window in these elements. The latest research refer to the IL

electrolytes for sodium-ion batteries lays a concentration on the imidazolium and pyrrolidinium (Pyr⁺) cations, and also combining with bis(trifluoromethanesulfonyl)imide (TFSI⁻) and bis(fluorosulfonyl)imide (FSI⁻) anions. In regard to its superiority than other ILs can be attribute to its higher ionic conductivity and lower viscosity, Imidazole-derived ILs had beckoned attention in previous studies particularly. Under the concoction with NaTFSI, the ILs electrolytes of imidazolium-TFSI could be extracted at -86°C by the force of a thermal window. [12] In the matter of the testing condition under microtherm standard, a cathode existed in the half-cell combined with carbon-coated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ in tandem with Na [FSI]- [1-ethyl-3-methylimidazolium(C2C1im)][FSI] as the electrolytic partner. When they intergating together, they will release the reversible capacity within the condition of 57.6 mAh g^{-1} and -20°C . [13] Moreover, the Pyr⁺-based ILs also owns great potential on being performed in various technical realms, practically.

In a recent exploration delving into the intricate interaction of sodium-ion concentration and the temperature alteration involved with the electrochemical functioning of Na // Na[FSI]-[N-methyl-N-propylpyrrolidinium (C3C1pyrr)] [FSI] // NaCrO₂ half-cells. In this process, a observation draw the clue that the ideal spectrum of has an indivisible interlinkage with the temperature when implementing relevant experiments. When the temperature below the freezing threshold(0°C), the discharge capacity, which will be busted in a large efforts and augmented with the amplified intensity of sodium-ion concentration, at the threshold of 25 mol% Na [FSA] to the maximum.

In subsequent procedures, as ion concentration amplified, the discharge capacity, once an ascending efforts, finally takes a descent. This is a consequence of the the rise amount of electrolyte viscosity. Furthermore, relevant research had illustration on these phenomenon on ILs, especially on the electrochemical functioning when Na [FSA]-[C3C1pyrr][FSA] took part in HC node at -10°C with more broad thermal extent. [15] Within the contraction of high temperatures, the batteries' reversible discharge capacity could diminished sharply below the 0°C . Therefore, the HC anode in the alliance with ILs could be better adapted in under high-thermal conditions.

In essence, the expansive electrochemical breadth that resides within the ILs emerges, which is catering aptly to the technical requirement of SIBs' cathode materials, bearing with their intrinsic uniqueness. Regrettably, under low temperatures, ILs always encounter sorts of challenges, such as the up-rise of high cost and their functions on viscosity. Thus, involving with the new innovations, which bringing up the emergence of novel ILs electrolytes, as for the integration of ILs with electrolytics of other specialties, which could offer the technical support on tackling the bottlenecks from above researching process.

2.2. Solid electrolytes

While liquid electrolytes boast the elevated conductivity and affinity for electrode's surface, the practical application should mainly focus on the upon technical safety. The perils of electrolyte leakage, the incendiary potential of flammability, the capricious realm of uncontrollable side reactions, and the emergence of unstable SEI (Solid-Electrolyte Interphase) are targets waiting for solves. If keep them unchanged, the rise of sodium dendrites will be resulted in repeated charge/discharge cycles. These could pierce the the old-patterned porous separator, thus initiating an internal short circuit within the cell. An insisting research hot-topic emerges in solid electrolytes, emboldened by their qualities of unwavering thermal stability, a boundless electrochemical window, an enduring cycling life, and a superb of mechanical power. [16] Solid electrolytes, in their steadfast natures, they usually sidestep the quandary of phase transitions in microtherm. In the current research, under low-temperature conditions, it primarily spotting on the exploration of solid polymer electrolytes and the revelation of inorganic solid electrolytes (Fig.2).

In the lower temperature range, compared to solid polymer electrolytes, inorganic solid electrolytes have higher ionic conductivity, which is of great significance for low-temperature solid SIB [17] Currently, in the field of solid-state SIBs research, sodium superionic conductors with high ionic conductivity structures (NASICON) have attracted widespread attention. In the 1970s, NASICON structured electrolytes were developed and their chemical formula $\text{Na}_{1+x}\text{Zr}_2\text{P}_3$ –

$x\text{Si}_2\text{O}_7$ ($0 \leq x \leq 3$) was given. [18] $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ is a high-performance ionic conductivity that reaches a high level at room temperature ($6.7 \times 10^{-4} \text{ S cm}^{-1}$). After doping treatment, its ion conductivity can be significantly improved. Some scholars have prepared $\text{Na}_{3.4}\text{Sc}_{0.4}\text{Zr}_{1.6}\text{Si}_2\text{PO}_{12}$ based on solution assisted solid-state reaction methods, and tested its room temperature conductivity. [19] Thanks to the close radius of Sc^{3+} and Zr^{4+} , substitution does not cause significant lattice distortion, and additional sodium ions are introduced, resulting in a conductivity of $4.0 \times 10^{-3} \text{ S cm}^{-1}$ for this material at room temperature. The high price of Sc element has a significant constraint on its practical application. Some scholars have used La^{3+} doping to prepare a $\text{Na}_{3.3}\text{Zr}_{1.7}\text{La}_{0.3}\text{Si}_2\text{PO}_{12}$ material to solve this problem. Testing has found that the ion conductivity of this material at room temperature is $3.4 \times 10^{-3} \text{ S cm}^{-1}$. [20] The $\text{Na}_3\text{La}(\text{PO}_4)_2$ phase in this material changes the concentration of sodium ions, significantly changes the chemical composition of grain boundaries, and significantly increases the conductivity of grain boundaries. The experimental detection results show that the ionic conductivity of the bulk phase and grain boundary of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ material is 8.3×10^{-5} and $8.8 \times 10^{-6} \text{ S cm}^{-1}$, while the total conductivity of $\text{Na}_{3.3}\text{Zr}_{1.7}\text{La}_{0.3}\text{Si}_2\text{PO}_{12}$ significantly increased.

Inorganic solid electrolytes have high safety, but their interface impedance is high, which limits the cycling performance of SIBs. To solve this problem, it is necessary to combine polymer electrolytes with inorganic electrolytes, or introduce a small amount of liquid electrolytes (such as IL) into the system to wet the interface between the solid electrolyte and the electrode. This can significantly reduce the interface resistance and improve the cycling performance of the battery. Overall, the research on low-temperature solid electrolytes related to SIBs is not yet in-depth, and it is necessary to develop more efficient solid electrolytes to provide support for the application and promotion of such batteries.

In total, an deeply investigate of the ion transport intrinsic mechanism in electrolytes and to design the electrolyte is critical for actual application at low temperatures.

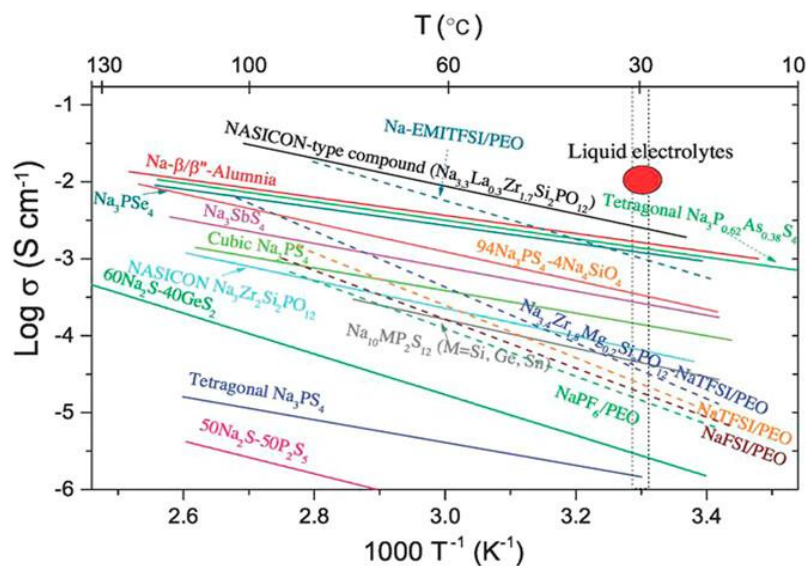


Fig. 2 datagram

3. Conclusion

The development of low-temperature sodium batteries has gradually attracted attention in recent years, but so far it is not systematic and immature, and lacks comprehensive technical indexes and parameters, indicating that it is still far away from practical application. As mentioned above, the most influential factor of electrolyte on low temperature performance is ionic conduction. Therefore, the potential development direction of electrolyte is polymer electrolyte, because polymer electrolyte combines the advantages of both liquid and solid electrolytes, liquid electrolyte has good ionic

conductivity, solid electrolyte can inhibit the growth of dendrites, so the polymer electrolyte can make the sodium-ion battery have good low-temperature performance.

References

- [1] Yuan Ziwei, Lin Chuyuan, Yuan Ziyang, etc.. Research Progress on Low Temperature Performance of Zinc Ion Batteries [J]. Energy Storage Science and Technology, 2023, 12(1): 278-298.
- [2] Mei Xiaoxian, Shi Zhiqiang. Research Progress on Low-Temperature of Sodium Ion Batteries [J]. Shandong Chemical Industry, 2022, 51(20): 93-96.
- [3] Wang Yixiao, Xie Leqiong, Sheng Li, etc. Research progress on Low Temperature of Lithium Ion Batteries [J]. Battery Industry, 2022, 26(5) : 251-262.
- [4] Song Liu Bin, Wang Yixuan, Kuang Yinjie, etc.. Development and Prospect of Key Materials and Technologies in Sodium Ion Batteries [J]. Journal of Chemical Industry, 2022, 73(11) : 4814-4825.
- [5] Dang Rongbin, Lu Yaxiang, Rong Xiaohui, etc.. Progress in Research and Engineering Exploration of Key Materials for Sodium Ion Batteries [J]. Science Bulletin, 2022, 67(30): 19.
- [6] Zhang Ping, Kang Libin, Wang Mingju, etc.. Energy Storage Technology and Economic Analysis of Sodium Ion Batteries[J]. Energy Storage Science and Technology, 2022, 11(6): 1892-1901.
- [7] Zhou Xing, Huang Shengjun, Zhu Wenkai, etc.. Sodium Ion Batteries -- A New Choice to Solve the Dilemma of Electrical Energy Storage in Cold Regions [J]. National Defense Technology, 2023, 44(01): 103-111.
- [8] LI Q, LIU G, CHENG H, et al. Low-Temperature Electrolyte design for Lithium-Ion batteries: Prospect and challenges[J]. Chemistry-A European Journal, 2021, 27(64): 1521-3765.
- [9] ZOU Y G, SHEN Y B, WU Y Q, et al. A Designed Durable Electrolyte for High -Voltage Lithium Ion Batteries and Mechanism Analysis[J]. Chemistry European Journal, 2020, 26(35): 7930-7936 .
- [10] Liu H, Yu H. Ionic Liquids for Electrochemical Energy Storage Devices Applications. J Mater Sci Technol. 2019;35(4): 674-686.
- [11] Zhu N, Zhang K, Wu F, Bai Y, Wu C. Ionic Liquid-Based Electrolytes for Aluminum/Magnesium/Sodium-Ion Batteries. Energy Mater Adv. 2021;2021:1-29.
- [12] Monti D, Jonsson E, Palacín MR, Johansson P. Ionic Liquid Based Electrolytes for Sodium Ion Batteries: Na⁺ Solvation and Ionic Conductivity. J Power Sources. 2014;245:630-636.
- [13] Hwang J, Matsumoto K, Hagiwara R. Na₃V₂(PO₄)₃/C Positive Electrodes with High Energy and Power Densities for Sodium Secondary Batteries with Ionic Liquid Electrolytes That Operate Across Wide Temperature Ranges. Adv Sustain Syst. 2018;2(5):1700171.
- [14] Ding C, Nohira T, Hagiwara R, et al. Na[FSA]-[C3C1pyrr] [FSA] Ionic Liquids As Electrolytes for Sodium Secondary Batteries: Effects of Na Ion Concentration and Operation Temperature. J Power Sources. 2014;269:124-128.
- [15] Ding C, Nohira T, Hagiwara R, Fukunaga A, Sakai S, Nitta K. Electrochemical Performance of Hard Carbon Negative Electrodes for Ionic Liquid-Based Sodium Ion Batteries over a Wide Temperature Range. Electrochim Acta. 2015;176:344-349.
- [16] Gao H, Xin S, Xue L, Goodenough JB. Stabilizing a high- energy-density rechargeable sodium battery with a solid electrolyte. Chem. 2018;4(4):833-844.
- [17] Zhao C, Liu L, Qi X, et al. Solid-State Sodium Batteries. Adv Energy Mater. 2018;8(17):1703012.
- [18] Goodenough JB, Hong YP, Kafalas JA. Fast Na⁺-ion Transport in Skeleton Structures. Mater Res Bull. 1976;11(2): 203-220.