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The Progress of Cathode and Electrolyte for Low Temperature Sodium-Ion Battery

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Abstract. The expanding demand for efficient energy storage systems that operate effectively in low-temperature environments has led to increased research interest in sodium-ion batteries (SIBs) due to their affordability, safety, and the abundance of sodium resources. With the development of industry, SIBs need to face the challenge of extreme temperatures, especially at low temperatures where the decrease in ion conductivity leads to a significant decrease in SIB capacity. This review article presents a comprehensive analysis of the recent advancements, persisting challenges, and future perspectives of low-temperature SIBs. We begin by highlighting the fundamental challenges that impede the performance of SIBs at low temperatures, such as decreased ionic conductivity, increased charge transfer resistance, and the risk of sodium plating. The review then delves into innovative strategies that have been developed to enhance the low-temperature performance of SIBs. These strategies include the design of novel cathode materials with improved electronic and ionic conductivity, the synthesis of advanced electrolytes with lower freezing points and higher ionic conductivities, and the optimization of battery architecture to minimize adverse effects caused by low temperatures. This review aims to provide a solid foundation for researchers in the field of energy storage and to inspire further advancements in the development of high-performance low-temperature SIBs.

Keywords: Sodium-ion battery; low temperature; cathode; electrolyte.

1. Introduction

In the rapidly evolving domain of energy storage technologies, the shift towards renewable and sustainable sources has become imperative to meet the increasing energy demands of the 21st century. Lithium-ion batteries (LIBs) have been at the forefront of this transition, powering everything from portable electronics to electric vehicles. However, the growing penetration of LIBs in various societal applications has led to a surge in demand for upstream resources, significantly inflating costs and revealing limitations in meeting the scalability required for stationary energy storage systems. Against this backdrop, sodium-ion batteries (SIBs) emerge as a compelling alternative, drawing upon the similar energy storage mechanisms to LIBs, coupled with the abundant reserves of sodium metal. The promise of SIBs extends across a spectrum of applications, from large-scale grid storage to low-speed electric vehicles, heralding a broad horizon of application prospects.

Over the past decades, SIBs have witnessed significant advancements, particularly in developing batteries that boast remarkable cycle stability and rapid charge capabilities. Nonetheless, the quest for optimizing SIBs for low-temperature (LT) environments presents a complex challenge, spurred by the critical demand in sectors such as grid storage, aerospace, maritime exploration, and defense applications. The inherent advantage of SIBs over LIBs in LT scenarios is fast charging performance, attributed to the smaller Stokes diameter of Na^+ leading to higher ionic conductivity in electrolytes, positioning SIBs as an indispensable supplement to LIBs in LT applications. Notably, the first generation of SIBs introduced by Contemporary Amperex Technology Co., Limited (CATL) has set new benchmarks in energy density, nearing the performance of $LiFePO_4$ and $Li(NiCoMn)O_2$[1] batteries, while demonstrating exceptional fast charging and LT performance.

The pursuit of enhancing LT performance in SIBs has predominantly centered around electrolyte formulation optimization and electrode material modification. These efforts aim to address the viscosity-related decreases in ionic conductivity at lower temperatures, the high desolvation energy challenges, and the solid electrolyte interface (SEI) layer's impact on ion diffusion. Innovations in electrode material design, such as the construction of 3D ion channels, have been pivotal in optimizing ion/electron conductivity and enhancing electrodynamics, thereby facilitating Na^+ diffusion kinetics at LT.

This review delves into the comprehensive analysis of current research progress in LT SIBs, examining electrolytes (liquid, solid, polymer), and cathode materials. By evaluating the limitations of organic electrolytes at LT and proposing performance requirements and design guidelines, this paper provides a thorough examination of the advancements in ester-based, ether-based, and ionic liquid LT electrolytes. Additionally, it offers insights into the LT sodium storage characteristics of various electrolytes and cathode materials and highlights the potential of solid-state electrolyte technologies in overcoming existing LT challenges in low temperature.

Through this exploration, we aim to present a detailed review and forward-looking perspective on improving the LT performance of SIBs, emphasizing the importance of advancements in electrolyte and electrode materials. This endeavor seeks not only to contribute to the scholarly discourse on energy storage solutions but also to guide future research directions that could unlock the full potential of SIBs in low-temperature applications.

2. Progress

2.1. Cathode materials for SIBs

The development of efficient and durable cathode materials for low-temperature SIBs is crucial for their broader application in areas such as electric vehicles and aerospace. While significant strides have been made, continuous efforts in research and development are necessary to overcome the current limitations and achieve high-performance LT SIBs.

The practical application of SIBs in LT environments presents significant challenges due to their diminished ion conductivity and increased charge transfer resistance at reduced temperatures. This chapter delves into cathode materials that are pivotal in optimizing the LT performance of SIBs, with a focus on transition metal oxides (TMOs), polyanionic compounds (PACs), and Prussian blue analogues (PBAs).

2.1.1. Transition Metal Oxides (TMOs)

TMOs, represented by the general formula Na_xMO_2 where M can be Mn, Fe, Cr, Co, Ni, Cu[2], or combinations thereof, play a critical role as cathode materials in SIBs. These materials are prized for their simple synthesis, high operating potential, and suitability for commercial production. TMOs are structurally classified into four main types based on the Na^+ sites and oxygen stacking sequence: P2, P3, O2, and O3.

TMOs exhibit diverse structural frameworks that impact their electrochemical behavior:

P2 and O2 Phases: Feature Na^+ in edge-sharing trigonal prismatic sites with specific oxygen sequences that influence ionic diffusion.

O3 and P3 Phases: Contain Na^+ in octahedral sites, offering different stacking and potentially more stable structures during cycling.

These materials offer high energy density and capacity due to their ability to undergo multiple redox reactions. However, they are subject to phase transitions and metal dissolution, particularly at low temperatures, which can severely limit their performance and lifespan.

At low temperatures, TMOs encounter increased risks of irreversible phase changes and metal dissolution, leading to decreased capacity and rate capability. To address these issues, researchers have employed several innovative strategies:

Doping TMOs with elements like Niobium (Nb) has proven effective in stabilizing the electrode structure and enhancing low-temperature performance. For instance, Nb doping in P2-type $Na_{0.78}Ni_{0.31}Mn_{0.67}Nb_{0.02}O_2$ enhances electron and ion transport, reduces the electronic bandgap, and lowers the energy barrier for ion diffusion.

Applying protective coatings and modifying the microstructure of TMOs can help maintain their integrity under stress. Techniques such as nanostructuring with $NaCrO_2$ nanowires improve the interface between the electrolyte and active material, facilitating faster charge transport and accommodating volume changes during cycling.

The introduction of high-entropy biphasic cathode materials like $Na_{0.7}Mn_{0.4}Ni_{0.3}Cu_{0.1}Fe_{0.1}Ti_{0.1}O_{1.95}F_{0.1}$ shows promising results in mitigating phase transitions and enhancing the structural stability of TMOs at low temperatures.

The development of TMO cathodes for low-temperature applications continues to be a vibrant area of research. Further improvements in doping strategies and surface coating techniques are needed to increase the robustness of TMOs against structural degradation. Optimizing. Innovations in interface engineering could provide breakthroughs in reducing charge transfer resistances and enhancing ionic conductivity at low temperatures. Exploring new synthesis methods that yield better-aligned crystal structures and purer phase materials may lead to cathodes with superior performance and longer life cycles.

Transition metal oxides remain at the forefront of cathode material research for SIBs, particularly for applications requiring operation under harsh thermal conditions. Continued advancements in material engineering and chemical modification are crucial to unlocking the full potential of TMOs in energy storage technologies.

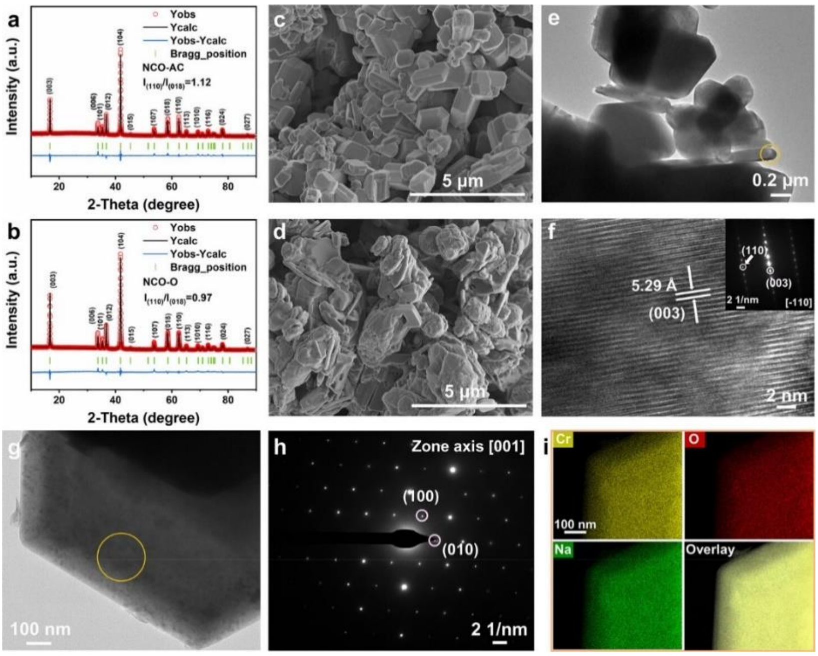

Figure 1. XRD patterns of both (a) NCO-AC and (b) NCO-O, along with their corresponding Rietveld refinement analyses. The SEM images of (c) NCO-AC and (d) NCO-O. (e) TEM image of NCO-AC and (f) corresponding HRTEM image along with the inset of the SAED pattern. (g) TEM image of NCO-AC and (h) corresponding SAED pattern. (i) The elemental mappings of the NCO-AC particle.[3]

2.1.2. PBAs Cathode Materials

PBAs are a large family of transition metal cyanides known for their open framework structures, which are highly beneficial for SIBs due to their large ionic channels. These channels facilitate the reversible de/intercalation of Na^+, making PBAs promising cathode materials for SIBs, especially under LT conditions.

PBAs typically have a general formula of $Na_xM_1[M_2(CN)_6]_{(1-y)}\cdot\square y\cdot nH_2O$, where M1 is an N-coordinated transition metal, M_2 is a C-coordinated transition metal, and □ represents vacancies often occupied by coordinating water. These materials are usually synthesized via liquid chemistry techniques, which unfortunately can result in a significant number of vacancies filled by zeolitic water due to rapid precipitation processes. Such structural vacancies and the presence of coordinated water can induce lattice distortion or even structural collapse during cycling at low temperatures, leading to reduced specific capacity and degraded electrochemical performance.[3]

To improve the performance of PBAs at low temperatures, several strategies have been adopted. By decreasing the number of zeolitic water vacancies and increasing the sodium content in the framework, the structural integrity of PBAs during cycling can be maintained, thus improving their electrochemical performance at LT. Introducing a high-entropy effect into the PBA framework can enhance structural stability. For example, the synthesis of high-entropy hexacyanoferrate (HE-HCF) has shown substantial improvements in cycling performance at low temperatures. The increased entropy within the HCF structure enhances its stability and provides a reversible zero-strain two-phase system for effective sodium storage. Incorporating carbon materials, such as carbon nanotubes (CNTs), into the PBA framework can further enhance structural stability and facilitate Na^+ transport. For instance, Prussian blue (PB) nanocubes nucleated on a CNT conductive network form a robust and flexible composite cathode material. This composite delivers excellent cycling performance at low temperatures due to its larger lattice parameter and a high ratio of 24d sites for sodium, which reduces the activation energy required for 3D sodium diffusion.

The PB/CNT composite, in particular, has demonstrated remarkable performance at −25 °C, delivering a capacity of 142 mAh g^{-1} after 1000 cycles at a current density of 2.4 C with a capacity retention of 86%. Such performance is attributed to the enhanced electronic and ionic conductivity provided by the CNT network, which maintains excellent electrical contact between the active cathode particles and the current collector, particularly under LT conditions.

The structural stability provided by the modified synthesis methods and composite formulations is critical for the low-temperature performance of PBAs cathodes. These advancements underscore the potential of PBAs as effective cathode materials for SIBs operating in extreme conditions, offering a promising direction for future research and development in energy storage technologies.

2.1.3. PACs Cathode Materials

This section discusses the utilization of PACs in SIBs, specifically designed for enhanced performance in LT conditions.

PACs typically consist of tetrahedral polyanionic units $(XO_4)^{n-1}$ where X can be elements like P, S, Si, B, etc., linked by transition metal polyhedral MO_6. These materials are recognized for their high oxidation stability and adjustable operating potentials. Nonetheless, PACs suffer from poor electronic conductivity at LT due to their large anionic structures, making them less effective in these conditions.

Several innovative strategies have been adopted to overcome the limitations of PACs at low temperatures:

Enhancing the electronic and ionic conductivity of PACs is crucial. For instance, carbon-coated nanostructured $Na_4Fe_3(PO_4)_2(P_2O_7)$ has shown stable electrochemical properties at LT, owing to its fast electron and ion transport capabilities. Similarly, $Na_3V_2(PO_4)_3$@reduced graphene oxide (NVP@rGO) exhibits a high capacity at 0 °C due to its improved ion diffusion and electron transport rates.

Introducing dopants such as Cl in $Na_3V_2(PO_4)O_2F_{0.99}Cl_{0.01}$ (NVPFCl) has been found to enhance ionic conductivity by widening Na^+ migration channels, thus significantly improving LT performance.

The development of high-voltage cathodes like $Na_3V_2(PO_4)_2O_2F$ nano-tetraprisms (NVPF-NTP) has also proved beneficial. These materials support high Na^+ transport kinetics, crucial for maintaining capacity at sub-zero temperatures.

The structural configuration of PACs greatly influences their performance. The NASICON structure, which features robust 3D frameworks that facilitate rapid Na^+ ion transport, is particularly effective. For example, the NASICON-type $Na_3V_2(PO_4)_3$ (NVP) coated with carbon shows nearly 100% Coulombic efficiency even at -30°C, demonstrating excellent LT stability and cycling reversibility.

While PACs present a promising solution for SIBs operating in low-temperature conditions, their efficacy largely depends on strategic modifications such as carbon coating, nanostructuring, and element doping. These modifications are essential for enhancing the electronic and ionic conductivity of PACs, thereby optimizing their performance and enabling their practical application in extreme environments. Future research should focus on these strategies to further enhance the low-temperature capabilities of PAC cathode materials.

2.2. Electrolytes

2.2.1. The Gel-Polymer Electrolyte

Gel-polymer electrolytes (GPEs) have emerged as a critical component in the development of SIBs, particularly due to their enhanced safety features and superior mechanical properties compared to liquid electrolytes. In this review, we delve into the synthesis, characteristics, and electrochemical performance of GPEs based on cross-linked poly(methyl methacrylate) (PMMA). The gel-polymer electrolyte under consideration was synthesized using a radical polymerization technique involving methyl methacrylate (MMA) and tetraethylene glycol dimethacrylate (TEGDMA) with azobisisobutyronitrile (AIBN) as the initiator. The resulting cross-linked PMMA forms a gel when combined with a liquid electrolyte solution, typically consisting of sodium perchlorate ($NaClO_4$) in a mixture of propylene carbonate (PC) and fluoroethylene carbonate (FEC). This gelation process occurs upon heating and subsequent cooling of the precursor solution, which is cast onto a porous cellulose membrane.[4]

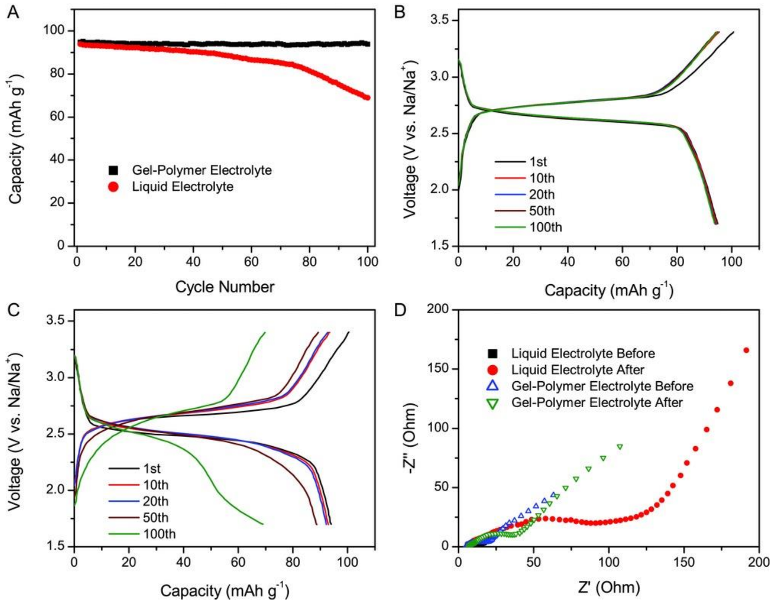

Figure 2. Electrochemical properties of the sodium-ion full-cell Sb/$Na_3V_2(PO_4)_3$ with liquid electrolyte or gel-polymer electrolyte at 60 °C. A) Cycling performance of the sodium-ion full-cells at a constant current density of 1 C. B) Galvanostatic charge/discharge profiles of the sodium-ion full-cell with the gel-polymer electrolyte at a constant current density of 1 C. C) Galvanostatic charge/discharge profiles of the sodium-ion full-cell with the liquid electrolyte at a constant current density of 1 C. D) Electrochemical impedance spectroscopy of the sodium-ion full-cells with the gel-polymer electrolyte or liquid electrolyte before and after 100 cycle tests.

The gel-polymer electrolyte exhibits excellent transparency, indicating strong compatibility with the cellulose membrane substrate. This compatibility is crucial as it ensures uniform coverage and effective separation of polysaccharide chains within the membrane, which is confirmed by scanning electron microscopy. The FT-IR spectroscopy analysis of the electrolyte highlights the presence of characteristic CO and OCH3 stretching vibrations, alongside the successful incorporation of the CC double bonds from the monomers, which underpins the cross-linked structure of the polymer.

The thermal stability of the cross-linked PMMA is demonstrated by its ability to withstand temperatures up to 200 °C without significant degradation. Mechanically, the electrolyte supports the structural integrity of the battery by preventing internal short circuits and mitigating self-discharge, a critical feature for maintaining battery reliability and lifespan.

Electrochemically, the gel-polymer electrolyte is characterized by its stability up to 4.8 V versus Na/Na, which is sufficient for most anode and cathode materials used in SIBs. The ionic conductivity of the electrolyte increases significantly with temperature, indicating enhanced Na^+ mobility at elevated temperatures. This is further supported by a low activation energy for ion transport, suggesting that ion migration is predominantly facilitated by Na^+ hopping rather than through the segmental motion of the polymer chains.

Lastly, the interfacial stability of the electrolyte with sodium metal electrodes is assessed using impedance spectroscopy. The findings reveal an initial low resistance that gradually increases over time, suggesting the formation of a more resistive SEI on the sodium metal compared to lithium-based systems.

The development of PMMA-based GPEs represents a significant advance in the quest for safer and more reliable SIBs. Future research should focus on optimizing the electrolyte composition and synthesis parameters to further enhance the electrochemical stability and reduce interfacial resistances, thereby extending the practical applications of SIBs in energy storage technologies.

2.2.2. High-Voltage Cyclic Ether-Based Electrolytes

In the pursuit of advancing SIBs suitable for low-temperature applications, the development of electrolytes that can operate effectively under such conditions has become paramount. One innovative approach is the utilization of high-voltage cyclic ether-based electrolytes, which have shown promising results in enhancing the performance and stability of SIBs at low temperatures.

A notable composition in this domain is the TPP electrolyte, which combines tetrahydrofuran (THF) with co-solvents like PC and ethoxy(pentafluoro)cyclotriphosphazene (PFPN). This mixture leverages the low-temperature characteristics of ether solvents while enhancing the antioxidant capabilities of the electrolyte due to the co-solvents. The unique composition helps in forming a stable cathode electrolyte interface layer, which is crucial for maintaining battery integrity and performance during operation.

The TPP electrolyte exhibits significantly improved electrochemical stability compared to traditional THF-only electrolytes. Through experimental measurements, such as linear scan voltammetry, the TPP electrolyte has shown a higher resistance to oxidation up to 5.1 V at low temperatures (−40 °C), compared to 4.7 V for the THF electrolyte. This stability is indicative of the TPP electrolyte's capacity to support high-voltage operations without significant degradation.[5]

In practical applications, the TPP electrolyte demonstrates superior performance metrics. For instance, $Na_{2/3}Mn_{2/3}Ni_{1/3}O_2 \parallel Na$ cells utilizing the TPP electrolyte retained 97.2% of their capacity after 140 cycles at room temperature (25 °C) and 94.1% after 100 cycles at −40 °C. The enhanced performance at low temperatures is particularly noteworthy, with the first discharge capacity maintaining 89.3% of the room temperature value.

The TPP electrolyte also shows advantageous physical properties, such as a suitable viscosity range that prevents crystallization and maintains ionic conductivity across a broad temperature spectrum. Specifically, it maintains a viscosity conducive to ionic movement even at −40 °C, unlike the THF electrolyte which faces challenges like crystallization and reduced salt solubility at lower temperatures.

The development of the TPP electrolyte marks a significant advancement in the design of high-voltage, low-temperature electrolytes for SIBs. This work provides a strong foundation for future research, focusing on optimizing these electrolytes for even broader applications in extreme environmental conditions. The integration of such electrolytes into SIBs holds the potential to enhance their usability in critical applications such as electric vehicles and aerospace technologies, where performance in a wide range of temperatures is crucial. This innovative approach not only addresses the immediate need for better low-temperature operation but also opens new avenues for the further development of SIB technology.

3. Conclusion

This review has examined the advancements in the field of low-temperature SIBs, highlighting the significant strides made in electrolyte and cathode material development to enhance their performance under extreme conditions. The exploration of high-voltage cyclic ether-based electrolytes, the gel-polymer electrolyte, and innovative cathode materials such as transition metal oxides, Prussian Blue Analogues, and polyanionic compounds has opened new avenues for the application of SIBs in environments where traditional batteries falter.

The development of the TPP electrolyte, which intelligently combines THF with co-solvents like PC and PFPN, is particularly noteworthy. This composition not only retains the low-temperature capabilities of the ether solvent but also significantly enhances the overall stability and antioxidant capacity of the electrolyte. This innovation has proven to be a game-changer, allowing for high-voltage operations and remarkable capacity retention even at temperatures as low as −40 °C, which is critical for applications in electric vehicles and aerospace technologies.

Furthermore, the review has underscored the role of advanced characterization techniques and the need for continuous research to refine these materials and their interactions. The potential of solid-state electrolytes and the enhancements in cathode materials through doping and structural modifications have shown that even with existing challenges, there are viable pathways to significant improvements in SIB performance at low temperatures.

As we look to the future, it is evident that interdisciplinary approaches combining materials science, electrochemistry, and engineering are essential to overcoming the remaining hurdles in low-temperature applications of SIBs. Continued innovation in electrode and electrolyte design will not only extend the operational limits of these batteries but also expand their practical applications, contributing to the broader adoption of renewable energy systems and aiding in the transition towards more sustainable energy storage solutions. The promising results obtained thus far serve as a robust foundation for further research, poised to unlock the full potential of SIBs in low-temperature environments.

References

[1] H. Bai, X. Zhu, H. Ao, G. He, H. Xiao and Y. Chen Journal of Energy Chemistry 2024 Vol. 90 Pages 518-539 DOI: 10.1016/j.jechem.2023.11.004

[2] Li, Y., et al., Recent advances in research on cathodes for low-temperature sodium-ion batteries. Progress in Natural Science: Materials International, 2023. 33(6): p. 767-779.

[3] Bo Peng, Zihao Zhou, Jie Xu, Nazir Ahmad, Shunqin Zeng, Mingyu Cheng, Lianbo Ma, Yongtao Li, and Genqiang Zhang. ACS Materials Letters 2023 5 (8), 2233-2242. DOI: 10.1021/acsmaterialslett.3c00625

[4] Gao H., Zhou W., Park K., Goodenough J. B. (2016). A Sodium-Ion Battery with a Low-Cost Cross-Linked Gel-Polymer Electrolyte. Adv. Energy Mater., 6: 1600467. DOI: 10.1002/aenm.201600467

[5] Luming Yin, Meilong Wang, Can Xie, Chao Yang, Jin Han, and Ya You. ACS Applied Materials & Interfaces 2023 15 (7), 9517-9523. DOI: 10.1021/acsami.2c23008