The prospect and challenges of sodium-ion batteries for low-temperature conditions

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Abstract
In recent years, considerable attention has been focused on the development of sodium-ion batteries (SIBs) because of the natural abundance of raw materials and the possibility of low cost, which can alleviate the concerns of the limited lithium resources and the increasing cost of lithium-ion batteries. With the growing demand for reliable electric energy storage devices, requirements have been proposed to further increase the comprehensive performance of SIBs. Especially, the low-temperature tolerance has become an urgent technical obstacle in the practical application of SIBs, because the low operating temperature will lead to sluggish electrochemical reaction kinetics and unstable interfacial reactions, which will deteriorate the performance and even cause safety issues. On the basis of the charge-storage mechanism of SIBs, optimization of the composition and structure of electrolyte and electrode materials is crucial to building SIBs with high performance at low temperatures. In this review, the recent research progress and challenges were systematically summarized in terms of electrolytes and cathode and anode materials for SIBs operating at low temperatures. The typical full-cell configurations of SIBs at low temperatures were introduced to shed light on the fundamental research and the exploitation of SIBs with high performance for practical applications.

KEYWORDS
anode materials, cathode materials, electrolyte, low temperatures, sodium-ion batteries

1 | INTRODUCTION
To meet the requirements of reliable electric energy storage systems, it is imperative to develop secondary batteries with high energy density and stable cycling performance. Lithium-ion batteries, as power sources for electric vehicles, have penetrated into new-energy transportations due to their high energy density, high efficiency, and flexibility. However, the resource of lithium is very limited and the cost is increasing dramatically in recent years, which cannot meet the demand for stationary energy storage. Therefore, sodium-ion batteries (SIBs) have attracted extensive attention as potential substitutes for lithium-ion batteries due to the...
abundant resources of raw materials and low cost.\textsuperscript{[6,7]} In the past decades, great achievements have been made in the development of SIBs with excellent cycling stability and high rate performance through continuous research on the sodium storage mechanism and the design of novel electrode and electrolyte materials.\textsuperscript{[8–10]} With the increasing demand in the applications of grid-scale energy storage, space exploration, and national defense, inferior electrochemical performance is becoming the main issue for SIBs at low temperatures.\textsuperscript{[11–13]} In view of the successful application of lithium-ion batteries at low temperatures, the Mars rover used in the Mars exploration mission in 2003, equipped with lithium-ion batteries with mesocarbon microbeads anode and LiNi\textsubscript{x}Co\textsubscript{1−x}O\textsubscript{2} cathode could operate successfully at −20°C. With the increasing applications for a variety of fields of energy storage, the development of SIBs that can be used in extreme environments was encouraged, and the obstacles need to be clarified.\textsuperscript{[14]} The factors that contribute to the inferior performance of SIBs at low temperatures include the low conductivity of the electrolyte, the reduced rate of ion diffusion in the active materials, and the reduced rate of charge transfer at the electrode/electrolyte interface. Since the relationship between the rate and temperature of these processes is usually described by the Arrhenius equation, these reactions are greatly influenced by decreasing temperature. In addition, the severe polarization during cycling at low temperatures will decrease the efficiency of batteries, and the formation of dendrites on the anode would further deteriorate the electrochemical performance and cause safety issues.\textsuperscript{[15,16]} The recent research progress toward improving the performance of SIBs at low temperatures mainly focuses on the optimization of electrolyte formulations and the modification of electrode materials to enhance the ion diffusion rate, electronic conductivity, and cycling stability. In this review, the strategies to improve the low-temperature performance of SIBs are systematically analyzed, including the design of novel electrolytes with low freezing point and high conductivity, the development of electrode materials through the surface coating, the fabrication of nanostructures to shorten the diffusion distance while maintaining a sufficient diffusion coefficient, and the construction of new interfaces to reduce the charge-transfer resistance at low temperatures. In addition, the electrochemical performance of certain full-cell configurations is introduced, which will contribute to the development of SIBs with high performance at low temperatures and provide further direction for functionalization of electrode materials and optimization of electrolyte formulations for practical applications.

\section*{2 | ELECTROLYTES FOR LOW-TEMPERATURE SIBs}

The electrolytes, as the major components of SIBs, transfer sodium ions between the cathode and anode, and have a significant impact on the specific energy density and cycling stability at low temperatures.\textsuperscript{[17,18]} Recent investigations have shown that the strategies such as adjusting the electrolyte composition can improve the electrochemical performance of SIBs at low temperatures. The following sections will describe the optimization of liquid electrolytes and the functionalization of solid electrolytes for low-temperature SIBs.\textsuperscript{[19,20]}

\subsection*{2.1 | Liquid electrolytes}

\subsubsection*{2.1.1 | Organic liquid electrolytes}

Organic carbonates are the common solvents of electrolytes in SIBs because of their strong ability to dissolve sodium salts. The organic carbonate solvents usually include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC), and their physicochemical properties are summarized in Table 1. The ideal organic solvent should possess a high dielectric constant to achieve high ionic conductivity, low viscosity in a wide temperature range, and high electrochemical stability in a wide voltage range.\textsuperscript{[21]} In general, multiple solvents in a mixed system can meet requirements that are difficult for a single solvent.\textsuperscript{[22]} In addition, as another important component in the electrolyte, sodium salt has an impact on the transfer of sodium ions and the formation of solid electrolyte interphase (SEI). SEI plays a key role in the stability of SIBs, which can effectively prevent the continuous degradation of the electrolyte and avoid damage to the electrode material. At the same time, high energy density and high rate performance through continuous research on the sodium storage mechanism and the design of novel electrode and electrolyte materials.\textsuperscript{[8–10]} With the increasing demand in the applications of grid-scale energy storage, space exploration, and national defense, inferior electrochemical performance is becoming the main issue for SIBs at low temperatures.\textsuperscript{[11–13]} In view of the successful application of lithium-ion batteries at low temperatures, the Mars rover used in the Mars exploration mission in 2003, equipped with lithium-ion batteries with mesocarbon microbeads anode and LiNi\textsubscript{x}Co\textsubscript{1−x}O\textsubscript{2} cathode could operate successfully at −20°C. With the increasing applications for a variety of fields of energy storage, the development of SIBs that can be used in extreme environments was encouraged, and the obstacles need to be clarified.\textsuperscript{[14]} The factors that contribute to the inferior performance of SIBs at low temperatures include the low conductivity of the electrolyte, the reduced rate of ion diffusion in the active materials, and the reduced rate of charge transfer at the electrode/electrolyte interface. Since the relationship between the rate and temperature of these processes is usually described by the Arrhenius equation, these reactions are greatly influenced by decreasing temperature. In addition, the severe polarization during cycling at low temperatures will decrease the efficiency of batteries, and the formation of dendrites on the anode would further deteriorate the electrochemical performance and cause safety issues.\textsuperscript{[15,16]} The recent research progress toward improving the performance of SIBs at low temperatures mainly focuses on the optimization of electrolyte formulations and the modification of electrode materials to enhance the ion diffusion rate, electronic conductivity, and cycling stability. In this review, the strategies to improve the low-temperature performance of SIBs are systematically analyzed, including the design of novel electrolytes with low freezing point and high conductivity, the development of electrode materials through the surface coating, the fabrication of nanostructures to shorten the diffusion distance while maintaining a sufficient diffusion coefficient, and the construction of new interfaces to reduce the charge-transfer resistance at low temperatures. In addition, the electrochemical performance of certain full-cell configurations is introduced, which will contribute to the development of SIBs with high performance at low temperatures and provide further direction for functionalization of electrode materials and optimization of electrolyte formulations for practical applications.

\begin{table}[h]
\centering
\caption{Physicochemical properties of several common carbonate solvents used in electrolytes for sodium-ion batteries}
\label{table:1}
\begin{tabular}{|c|c|c|c|c|}
\hline
Carboxylate solvent & Melting point (°C) & Boiling point (°C) & Viscosity (cP) at 25°C & Dielectric constant at 25°C \\
\hline
EC & 36.4 & 248 & 2.1 & 89.78 \\
PC & −48.8 & 242 & 2.53 & 64.92 \\
DMC & 4.6 & 91 & 0.59 & 3.107 \\
DEC & −74.3 & 126 & 0.75 & 2.805 \\
EMC & −53 & 110 & 0.65 & 2.958 \\
\hline
\end{tabular}
\end{table}

Abbreviations: DEC, diethyl carbonate; DMC, dimethyl carbonate; EC, ethylene carbonate; EMC, ethyl methyl carbonate; PC, propylene carbonate.
time, as an insulating layer for electron transfer, SEI still allows sodium ions to transport through the layer smoothly, which ensures the continuation of charge–discharge cycles.\textsuperscript{[23,24]} At present, the sodium salts used frequently include NaPF$_6$, NaClO$_4$, NaTFSI, NaFTFSI, and NaFSI, which should be readily soluble in the organic solvents.\textsuperscript{[25]}

According to the solvation behavior of seven carbonate solvents (Figure 1A) and four carbonate binary mixtures (EC:PC, EC:DMC, EC:EMC, and EC:DEC) based on molecular dynamics simulations, the EC:PC mixture with sodium salt has the highest binding energy, enthalpy of solvation, and Gibbs free energy of solvation values, indicating the suitability for SIBs\textsuperscript{[26]} Moreover, the matching of electrolyte and electrode is also the focus of research, such as the optimization of carbonate-based electrolytes for the battery system of NaNi$_{1/3}$Fe$_{1/3}$Mn$_{1/3}$O$_2$/hard carbon (HC).\textsuperscript{[27]} The PC:EMC electrolyte with high ionic conductivity can remain liquid at $-40^\circ$C. The cell with the PC:EMC electrolyte showed high-capacity retention at $-20^\circ$C, reaching 82.95% of the specific capacity at room temperature. In addition, a series of electrolyte combinations with different solvent mixtures and sodium salts were investigated to optimize the formulations of liquid electrolytes for SIBs.\textsuperscript{[28]} Notably, there is no endothermic peak in the DSC heating curve of all PC-based electrolytes, showing an extremely low vitreous transition temperature (ca. $-95^\circ$C), further indicating that the PC-based electrolyte was superior to other electrolytes in terms of low-temperature adaptability (Figure 1B). Electrolyte additives have a significant influence on the formation, structure, and composition of the SEI film. In the Na/HC half-cell system,\textsuperscript{[29]} 5 vol% of fluorinated ethylene carbonate (FEC) was used as an additive to promote the formation of a dense SEI layer on the surface of sodium metal (Figure 1C), which enhanced the electrochemical compatibility between PC-based electrolyte and sodium metal. When 3 vol% of adiponitrile (ADN) was added on the basis of 5 vol% FEC, highly conductive and stable cathode electrolyte interphase films were obtained on

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**FIGURE 1** (A) Chemical structure of the organic carbonate solvents. Reproduced with permission.\textsuperscript{[26]} Copyright 2015, American Chemical Society. (B) DSC curves of Na-based electrolytes at a temperature range from room temperature to $-120^\circ$C. Reproduced with permission.\textsuperscript{[28]} Copyright 2012, Royal Society of Chemistry. (C) Schematic illustration of PC decomposition on the surface of the sodium metal used FEC as additive. Reproduced with permission.\textsuperscript{[29]} Copyright 2018, American Chemical Society. (D) The pictures of the Na$_3$V$_2$(PO$_4$)$_3$/$\text{NaClO}_4$/$\text{Na}_3$V$_2$(PO$_4$)$_3$ microbattery taken at different bending angles. (E) The cyclability was measured at different temperatures ranging from 10 to $-40^\circ$C at 0.3 mA cm$^{-2}$. Reproduced with permission.\textsuperscript{[31]} Copyright 2020, Elsevier Ltd. (F) Photograph of the electrolyte with 25 M NaFSI and 10 M NaFTFSI being stored at room temperature for 6 months, and DSC curve at the temperature range from 60°C to $-40^\circ$C. Reproduced with permission.\textsuperscript{[32]} Copyright 2019, American Chemical Society. (G) FT-IR spectra of the aqueous Na$_2$SO$_4$ electrolyte and Na$_2$SO$_4$–SiO$_2$ hydrogel electrolyte. Reproduced with permission.\textsuperscript{[33]} Copyright 2021, Elsevier Ltd. DSC, differential scanning calorimetry; FEC, fluorinated ethylene carbonate; FT-IR, Fourier-transform infrared; PC, propylene carbonate.
the surface of Na_{0.76}Ni_{0.3}Fe_{0.4}Mn_{0.3}O_{2} cathode material, with a 13% increase of specific discharge capacity at −20°C.\[30] In addition, ether-based electrolytes have good electrochemical compatibility with anode materials, such as diglyme as a solvent with a low freezing point (−64°C) and high ionic conductivity commonly used in SIBs at low temperatures. However, due to the low oxidation window (<4 V), the ether-based electrolytes should be carefully designed to match with high-voltage cathode materials for SIBs. The applications of ether-based electrolytes at low temperatures will be discussed in Section 3. Therefore, in addition to continuously searching for organic solvents for low-temperature applications, future research directions could focus on the combination of solvents to achieve the optimized composition of electrolytes, and the selection of suitable additives to improve the safety.

2.1.2     | Aqueous liquid electrolytes

Compared with organic solvents, aqueous electrolytes have broader application prospects due to the advantages of low viscosity and cost, high ionic conductivity, and safety.\[34] However, the aqueous electrolytes also face some challenges at low temperatures. Because the freezing point of pure water as a solvent was 0°C, the frozen electrolyte at low temperature will undoubtedly deteriorate the wettability of the interface between the electrodes and the electrolyte, resulting in a decrease in the discharge-specific capacity of the batteries.

In general, increasing the salt concentration in the electrolyte was an effective approach to broaden the electrochemical stability window and significantly reduce the freezing point to minus tens of degrees Celsius. Recently, water-in-salt (WIS) electrolyte has been used in SIBs at low temperature, which is defined as an aqueous solution in which the proportion of salt surpasses water in both mass and volume. The number of free water molecules was significantly reduced because all water molecules participated in the ion solvation process. A symmetric microbattery of Na_{3}V_{2}(PO_{4})_{3}[NaClO_{4}]Na_{3}V_{2}(PO_{4})_{3} operating in WIS electrolyte (17 M NaClO_{4}) showed impressive flexibility in different bending states (Figure 1D).\[31] Notably, the high-concentration WIS electrolyte exhibited exceptional antifreezing capability with a freezing point of −50°C. A specific capacity of 16 mAh cm\(^{-3}\) was obtained at −40°C, implying that the microbattery based on the low-cost WIS electrolytes held great potential for safe and wearable microelectronics even in harsh environments (Figure 1E). However, high-concentration aqueous electrolytes had a tendency for partial crystallization, which eventually led to the failure of the battery upon a long-term cycling test. This problem could be effectively solved by introducing asymmetric anions.\[32] The electrolyte with mixed salts of NaFSI and NaFTFSI remained liquid after 6 months at room temperature and showed no crystallization peak in the DSC curve in the temperature range from −40°C to 60°C (Figure 1F).

A promising strategy to reduce the freezing point of the electrolyte was to break the hydrogen bond network between water molecules through the introduction of a highly hydrophilic gel matrix, with the formation of a hydrogel electrolyte with a cross-linked network in aqueous SIBs. For example, using fumed SiO\(_2\) as the gel matrix, an Na\(_{2}\)SO\(_4\)–SiO\(_2\) hydrogel-type electrolyte with low cost was investigated.\[33] Fourier-transform infrared spectra revealed that the introduction of SiO\(_2\) can reduce the transmittance of peak intensity at 1081.4 cm\(^{-1}\) and s the peak is shifted to higher wavenumbers (Figure 1G), indicating the formation of a chemical bond between the SiO\(_2\) gel matrix and the SO\(_4^{2-}\). As a result, the battery with the hydrogel electrolyte could reach a high reversible capacity of 61.8 mAh g\(^{-1}\) at 1 C under −30°C.

2.1.3     | Ionic liquids (ILs) electrolytes

ILs, composed entirely of cations and anions, have attracted great interest due to their advantages of high thermal stability, low vapor pressure, wide electrochemical window, and formulation designability.\[35,36\] A wide variety of cations and anions in ILs provide opportunities to adjust the properties of ILs, such as melting point, viscosity, and electrochemical window. The current research on ILs electrolytes for SIBs mainly focuses on imidazolium and pyrrolidinium (Pyr\(^{+}\)) cations, and bis(trifluoromethanesulfonyl)imide (TFSI\(^{−}\)) and bis(fluorosulfonyl)imide (FSI\(^{−}\)) anions. Imidazole-based ILs have received early attention due to their lower viscosity and higher ionic conductivity than other types of ILs. By mixing with NaTFSI, the ILs electrolytes of imidazolium-TFSI (EMIm-TFSI and BMIm-TFSI) could be obtained with a thermal window down to −86°C.\[37\] With regard to low-temperature operation, the half-cell with carbon-coated Na\(_{3}\)V\(_{2}\)(PO\(_{4}\))\(_{3}\) as cathode and Na[FSI]-[1-ethyl-3-methylimidazolium(C2C1im)][FSI] as electrolyte could deliver a reversible capacity of 57.6 mAh g\(^{-1}\) at −20°C.\[38\]

In addition, Pyr\(^{+}\)-based ILs also have broad application prospects in SIBs. According to the recent results of the influence of sodium-ion concentration and operating temperature on the electrochemical performance of Na[Na[FSI]-[N-methyl-N-propylpyrrolidinium (C3C1pyrr)] [FSI]]NaCrO\(_{2}\) half-cells, the optimal ranges of sodium-ion concentration and operating temperature depend on the operating temperature.\[39\] At
temperatures below 0°C, the discharge capacity increased gradually with the increase of sodium-ion concentration, achieving the maximum at 25 mol% Na[FSA]. Subsequently, the discharge capacity decreases with increasing ion concentration because the opposite effect on ion conduction is caused by the increase of electrolyte viscosity. In addition, there are some reports on the anode electrodes in ILs. The electrochemical performance of HC anode in Na[FSA]-[C3C1pyrr][FSA] over a wide temperature range down to −10°C was investigated. Compared with the performance at high temperatures, the reversible discharge capacity of the batteries dropped rapidly when the temperature was lower than 0°C, implying that the HC anode in ILs was more suitable for operating at high temperatures.

In summary, the broad electrochemical window of ILs can satisfy the demand of most of the cathode materials of SIBs due to their unique properties. Unfortunately, the application of ILs for SIBs under low temperatures still faces many challenges because of the high price and viscosity. Therefore, the development of new ILs electrolytes, such as combining ILs with other types of electrolytes, is expected to solve the problems mentioned above.

2.2 | Solid Electrolytes

Although the liquid electrolytes have high conductivity and good wettability on the electrode surface, the major safety issues should be addressed in practical applications, including electrolyte leakage, flammability, uncontrollable side reactions, and the formation of unstable SEI films will induce the formation and growth of sodium dendrites during repeated charge/discharge cycles, which could puncture the traditional porous separator to induce an internal short circuit in the cell. Thus, solid electrolytes have received increasing attention due to their high thermal stability, wide electrochemical window, long-cycling life, and excellent mechanical properties. Solid electrolytes do not have phase transition problems at low temperatures. At present, the investigation of solid electrolytes at low temperatures mainly focuses on two aspects of solid polymer electrolytes and inorganic solid electrolytes.

2.2.1 | Solid Polymer Electrolytes

A sufficient physical contact with the electrode could be achieved due to the excellent flexibility of the solid polymer electrolyte, which could accommodate the volume deformation of the electrode material during charging and discharging, thereby improving the electrochemical performance of batteries. Figure 2A depicted a facile ion-exchange strategy suitable for industrial fabrication to prepare a perfluorosulfonate-based polymer electrolyte (PFSA-Na) membrane. The PFSA-Na membrane showed excellent flexibility before and after the freezing test (Figure 2B), which was beneficial to inhibit the formation of sodium dendrites, and the outstanding
mechanical properties ensured the stable performance of the SIBs under harsh conditions. The electrochemical window was as high as 4.7 V, implying the compatibility of the PFSA-Na membrane with most cathode materials. Furthermore, the half-cell based on the PFSA-Na membrane and Prussian-blue cathode could operate stably at $-35^\circ$C with satisfactory capacity retention. When the temperature increases back, the reversible capacity could restore to its original value, indicating a remarkable temperature tolerance (Figure 2C). The solid-state SIBs exhibited relatively slight polarization at a temperature range from 25 to $-15^\circ$C, which provided additional evidence of the excellent low-temperature electrochemical performance of the PFSA-Na membrane (Figure 2D). In addition, based on PFSA-Na, the assembled Na∥PFSA-Na[Na$_3$V$_2$O$_2$(PO$_4$)$_2$F] half-cells delivered high discharge capacities of 74.0 mAh g$^{-1}$ at 1 C under $-20^\circ$C, suggesting that the solid-state SIBs with PFSA-Na membrane and high-voltage cathode are promising as an energy storage device at low temperatures.$^{[45]}$

### 2.2.2 Inorganic solid electrolytes

Inorganic solid electrolytes have higher ionic conductivity at a relatively low-temperature range, than is an important parameter for developing low-temperature solid-state SIBs (Figure 3).$^{[46]}$ The sodium superionic conductor (NASICON) structured with high ionic conductivity is one of the most promising ionic conductors for solid-state SIBs. The general formula of NASICON-structured electrolyte was Na$_{1+x}$Zr$_3$P$_{3-x}$Si$_{12}$O$_{36}$ (0 ≤ x ≤ 3), which was first reported in 1976.$^{[47]}$ Na$_2$Zr$_2$Si$_2$PO$_{12}$ is the representative one with high ionic conductivity ($6.7 \times 10^{-4}$ S cm$^{-1}$) at room temperature. Doping was used to further improve the ionic conductivity of Na$_2$Zr$_2$Si$_2$PO$_{12}$, and for example, Na$_{1+3x}$Sc$_{2n}$Zr$_{1-6n}$Si$_2$PO$_{12}$ was synthesized through a solution-assisted solid-state reaction method.$^{[48]}$ Benefiting from the extremely close ion radius between Sc$^{3+}$ and Zr$^{4+}$, the substitution would not induce distortion of the crystal structure, and the introduction of additional sodium ions to compensate for the insufficient positive charge result in a high sodium-ion conductivity with $4.0 \times 10^{-3}$ S cm$^{-1}$ at 25°C. However, the high price of the element of Sc makes it unsuitable for large-scale practical applications.

Na$_{3.3}$Zr$_{1.7}$La$_{0.3}$Si$_2$PO$_{12}$ with high ionic conductivity of $3.4 \times 10^{-3}$ S cm$^{-1}$ at room temperature has been obtained with La$^{3+}$-doping.$^{[49]}$ The self-formed Na$_3$La(PO$_4$)$_2$ phase not only modified the concentration of sodium ions but also adjusted the chemical composition at grain boundaries, improving the density of ceramics and resulting in an increase in bulk and grain boundary conductivity. For Na$_2$Zr$_2$Si$_2$PO$_{12}$, the ionic conductivities of the bulk and grain boundary were as low as $8.3 \times 10^{-5}$ and $8.8 \times 10^{-6}$ S cm$^{-1}$ at $-50^\circ$C, respectively. By comparison, the total conductivity of Na$_{3.3}$Zr$_{1.7}$La$_{0.3}$Si$_2$PO$_{12}$ was one order of magnitude higher than that of Na$_2$Zr$_2$Si$_2$PO$_{12}$ at $-50^\circ$C.

Although inorganic solid electrolyte has outstanding advantages of safety, high interfacial impedance limited the reversible capacity and cycling stability of SIBs. Therefore, hybrid solid electrolytes combining the polymer electrolyte and inorganic electrolyte were an effective way to ensure high ionic conductivity and reduce the interface resistance. In addition, it is also a feasible strategy to wet the interface between the solid electrolyte and electrodes through the introduction of a small amount of liquid electrolytes, such as IL, which can effectively reduce the interface resistance and improve the cycling stability of batteries at low temperatures. In general, the investigations on low-temperature solid electrolytes of SIBs are still at the early stage, and it is urgent to develop new solid electrolytes to meet the needs of low-temperature applications.

In summary, an in-depth understanding of the intrinsic mechanism of ion transport in electrolytes and the optimization of electrolyte formulation is essential for low-temperature applications. The possible directions toward the development of electrolytes at low temperatures are customizing special electrolytes for different electrode materials and the construction of multi-component mixed electrolytes.

**Figure 3** A comparison of ionic conductivity of representative solid-state electrolytes. Reproduced with permission.$^{[46]}$ Copyright 2018, Wiley-VCH. EMTIFS, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonylimide); FSI, bis(fluorosulfonyl)imide; NASICON, sodium superionic conductor; PEO, poly(ethylene oxide); TFSI, bis(trifluoromethanesulfonylimide).
3 | ANODE MATERIALS FOR LOW-TEMPERATURE SIBs

Anode materials are also a vital component of SIBs, providing a redox reaction at a low potential with a high specific capacity and safety.\textsuperscript{[50]} According to the sodium storage mechanism and physicochemical properties of anode materials, they can be divided into carbon-based materials, alloy-metal materials, transition-metal compounds, and sodium metal.

3.1 | Carbon-based anode materials

Carbon-based materials, with excellent electrical conductivity, low cost, and environmental friendliness, can be divided into graphitic carbons and nongraphitic carbons according to their microstructures.\textsuperscript{[51]} Unlike lithium-ion batteries, the relatively narrow spacing (~3.3 Å) of the graphite carbon layer was not suitable for the insertion of sodium ions with a large ion radius. On the contrary, nongraphite HC is the preferred carbon-based form of anode for SIBs due to its larger interlayer spacing, with more sodium storage sites and low operating voltage (close to 0 V vs. Na\textsuperscript{+}; Figure 4A).\textsuperscript{[52]} The slow kinetics result in large polarization and would lower the sodiation potential of HC at low temperatures. Related reports indicate that the capacity of HC may be fully utilized by lowering the cut-off potential to 0 V or even below it, although the possibility of Na plating requires prudent investigation. For example, HC with suitable pore size distribution could be synthesized with longan peel as raw material.\textsuperscript{[53]} Under a small current density of 10 mA g\textsuperscript{−1}, only a capacity of less than 100 mAh g\textsuperscript{−1} was obtained with a cut-off voltage of 0 V at −20°C. The thickness of the SEI layer on the HC surface was about 8 and 21 nm after five cycles at 25°C and −20°C, respectively (Figure 4B), and the thick SEI layer formed at low temperature resulted in high impedance according to the results of the electrochemical impedance spectroscopy. In addition, the poor-rate performance and low initial Coulombic efficiency (ICE) of HC at low temperatures.

**FIGURE 4** (A) Schematic illustration of the ion storage mechanism of graphite and HC. Reproduced with permission.\textsuperscript{[52]} Copyright 2019, Wiley-VCH. (B) Nyquist plots of the half-cell based on HC at 25°C and −20°C, and corresponding TEM images of HC after cycling. Reproduced with permission.\textsuperscript{[53]} Copyright 2019, Elsevier Ltd. Schematic illustration of (C) the preparation process and SEM images, and (D) sodium storage mechanism of HCP. (E) Long-term cycle stability of HCP in ether electrolyte at 500 mA g\textsuperscript{−1} under −15°C. Reproduced with permission.\textsuperscript{[55]} Copyright 2019, Wiley-VCH. HC, hard carbon; HCP, hard carbon paper; SEM, scanning electron microscope; TEM, transmission electron microscopy.
need to be solved in the future. HC powders with a uniform carbon coating obtained by physical vapor deposition were reported to exhibit a high reversible capacity of 265 mAh g<sup>−1</sup> at 0.1 C under −15°C.[54] The carbon coating reduced effectively the surface reactivity between HC and the electrolyte, improved significantly the ICE, and diminished the loss of irreversible capacity at the first cycle. Moreover, designing rational morphological structures with excellent electronic conductivity and fast sodium-ion transport rates was also an effective strategy to improve significantly the low-temperature performance of HC. A flexible and self-supporting hard carbon paper (HCP) derived from commercially available tissue (Figure 4C) exhibited excellent electrochemical performance in the NaCF<sub>3</sub>SO<sub>3</sub>/diglyme electrolyte (ICE of 91.2%, rate capability of 170.0 mAh g<sup>−1</sup> at 2000 mA g<sup>−1</sup>).[55] Meanwhile, the sodium storage mechanism of “intercalation-adsorption” was revealed in the ether electrolyte (Figure 4D). More importantly, the HCP anode exhibited outstanding long-cycling performance, providing a capacity of 217.1 mAh g<sup>−1</sup> with high-capacity retention of about 81% after 1000 cycles at 500 mA g<sup>−1</sup> under −15°C (Figure 4E).

In addition to the abovementioned strategies, the surface-induced capacitive process is also an effective approach to improve the electrochemical performance of carbon-based materials, such as introducing defects on the surface of carbon-based materials to create abundant active sites to improve the adsorption capacity of Na<sup>+</sup>-ions. Compared with a diffusion-controlled intercalation process, the surface-induced capacitance process may reduce the adverse effects of low temperature according to the energy storage mechanism.

3.2 | Alloy-metal anode materials

In recent years, alloy-based anodes have become a research hotspot because of their high theoretical specific capacity and appropriate potential.[56] They are mainly composed of elements from the IVA and VA groups and the related compounds (such as oxides and selenides), which can form Na-rich intermetallic compounds through the alloying reaction mechanism with a much higher specific capacity than carbon based. However, during the charge/discharge process, the alloy-based anodes are accompanied by a large volume change, leading to the electrode pulverization with inferior cycling performance of SIBs. Especially at low temperatures, the specific capacity and rate performance of alloy-based anodes are limited by the low electrical conductivity.

Combining carbonaceous matrices with alloy-based anode material is an effective strategy to alleviate the volume change. For example, amorphous selenium with the surface uniformly coated by reduced graphene oxide (rGO) nanosheets to form nanocomposite with a three-dimensional (3D) conductive network exhibited a considerable discharge capacity of 240–250 mAh g<sup>−1</sup> at 0.1 A g<sup>−1</sup> over above 500 cycles without significant capacity fading at −25°C.[57] Moreover, the nanocomposite of Sb@graphene also exhibited excellent low-temperature performance, with a reversible capacity as high as 506.6 mAh g<sup>−1</sup> at 25 mA g<sup>−1</sup> under −20°C.[58]

In addition, some metal-containing compounds, such as oxides, can store sodium ions through reversible conversion reactions. These metal compounds also face the problems of poor electrical conductivity and large volume changes during cycling and the introduction of carbonaceous matrices can still effectively accommodate these problems. For example, the nanocomposites of SnO<sub>2</sub>@graphene prepared via one-pot hydrothermal method delivered a specific capacity of 97 mAh g<sup>−1</sup> after 100 cycles at −20°C.[59] According to the results of transmission electron microscopy and X-ray photoelectron spectroscopy measurement, the conversion reaction dominated in the cycling of the SnO<sub>2</sub>@graphene electrode, which is different from the previous reports that the alloying-dealloying reaction between Sn and sodium metal, providing new insights into metal oxide anode materials for sodium storage.

3.3 | Convention-type anode materials

In this section, we will focus on transition-metal oxides (TMOs) or chalcogenides that store sodium ions based on conversion reactions. Some TMOs, such as nickel oxide and iron oxide, can be used as anode materials for SIBs at low temperatures due to their high theoretical specific capacity and low price.[60] Different from the intercalation reaction of carbon-based materials and the alloying reaction of alloy-metal materials, TMOs mainly undergo reversible redox reactions.[61–63] However, the material also has a large volume expansion, resulting in unsatisfactory rate performance and rapid capacity decay during cycling.[64] Modification strategies, such as nanostructures, hybridization with conductive carbon materials, and morphological engineering have been developed to solve the above problems. The composite of 2D nickel oxide nanosheets coated with nitrogen-doped carbon (NiO@NC) was synthesized, delivering a reversible specific capacity of 178 mAh g<sup>−1</sup> at 0.05 A g<sup>−1</sup> under −15°C.[65] In addition, a low-cost and environmentally friendly all-iron-based SIB was designed.
with excellent performance at low temperature, with Fe₃O₄ nanospheres as anode and Na₄Fe₃(PO₄)₂(P₂O₇)/C as a cathode. [66]

Compared with TMOs, transition-metal sulfides with higher electronic conductivity are also promising anode materials for SIBs. The transition-metal–sulfur bond was weaker than that of the transition-metal–oxygen bond, leading to increased kinetics of the conversion reaction and high ICE. Figure 5A presents a synthetic route for an FeS hierarchical microsphere in which each individual small FeS sphere was encapsulated by graphitic carbon (FeS@C). [67] The in situ formed highly conductive graphite carbon provided an effective buffer to alleviate the large volume changes during cycling, and the 3D porous pomegranate-like structure provide short ion and electron diffusion paths. Benefiting from the above advantages, the FeS@C composite exhibited a high reversible capacity of 311 mAh g⁻¹ at 0.05 A g⁻¹ under −25°C after 80 cycles. Moreover, with iron-based metal-organic frameworks as templates, Fe₁₋ₓS nanosheets wrapped by nitrogen-doped carbon (Fe₁₋ₓS@NC) were synthesized through a postsulfidation strategy, exhibiting excellent low-temperature reaction kinetics with a high reversible capacity of 223.4 mAh g⁻¹ at 2000 mA g⁻¹ under −25°C. [68] Besides, binary metal sulfide composites were also successfully synthesized as anode materials for SIBs, and for instance, CoGa₂S₄/graphene provided a reversible capacity of about 100 mAh g⁻¹ after 1000 cycles at an ultra-low temperature of −60°C at 1 A g⁻¹. [69] The excellent sodium storage performance at low temperatures can be attributed to the presence of Ga-based sulfides as high ionic conductivity media, which promoted the conversion reaction of cobalt sulfides and enabled cobalt sulfides to withstand temperature changes (Figure 5B). Benefited from the synergistic effect of binary metals, including the high conductivity of copper and the self-healing property of the liquid metal of gallium, CuGaS₂/graphene hexagonal nanoplates exhibited excellent Li/Na-storage performance over a wide temperature range, which provided an approach for exploring liquid metal-based electrode for low-temperature applications. [70]

With the development of nanotechnology, transition-metal selenides with larger interlayer spacing and higher electrical conductivity than their oxide and sulfide

![Figure 5](image)

**Figure 5**  (A) Schematic illustration of the synthesis route of FeS@C. Reproduced with permission. [67] Copyright 2018, Royal Society of Chemistry. (B) Schematic illustration for the reaction mechanism of the CoGa₂S₄/graphene electrode at subzero temperature. Reproduced with permission. [69] Copyright 2019, Royal Society of Chemistry. (C) Schematic illustration of the synthesis process and microstructure images of ZnSe@NCNFs. Reproduced with permission. [71] Copyright 2021, American Chemical Society. (D) Cycling performance of the KTiOPO₄ electrode at 3 C under −35°C. (E) Charge/discharge curve and the corresponding in situ XRD pattern of the KTiOPO₄ electrode. Reproduced with permission. [72] Copyright 2020, Elsevier Ltd. DMF, N,N-Dimethylformamide; NCNF, nitrogen-doped carbon nanofiber; PAN, polycrylonitrile; XRD, X-ray powder diffraction; ZIF, zeolitic imidazolate framework.
counterparts were gradually introduced into the field of SIBs.\textsuperscript{[73]} ZnSe nanoparticles uniformly embedded in 1D nitrogen-doped carbon nanofibers (ZnSe@NCNF) were prepared by electrospinning (Figure 5C).\textsuperscript{[71]} The unique nanostructure provided a penetrating network for fast ion and electron transfer, which could alleviate the pulverization of ZnSe in the insertion and extraction reaction of sodium ions to ensure the structural stability of the ZnSe@NCNF electrode during cycling, delivering a reversible capacity of 119.7 mAh g\(^{-1}\) after 200 cycles. Iron-based selenides with high theoretical capacity, such as FeSe\(_2\) and Fe\(_7\)Se\(_8\), have also attracted extensive attention, and the 3D hierarchical hybrids of FeSe\(_2\)/rGO were developed by a hydrothermal method, which exhibited stable performance with a remaining capacity of 216.7 mAh g\(^{-1}\) after 200 cycles at 1 A g\(^{-1}\) under \(-40^\circ\)C.\textsuperscript{[74]} A coral-like Fe\(_7\)Se\(_8@C\) with an efficient charge-transfer system was reported, which could simultaneously meet the requirements of Li/Na-ion batteries to achieve fast ionic and electric conductivities in a wide temperature range. In addition to the single metal selenides mentioned above, double transition-metal selenides coated with nitrogen-doped carbon have been reported, such as Ni\(_{1.8}\)Co\(_{1.2}\)Se\(_4\)/NC and Ni\(_{1.5}\)CoSe\(_5\)/NC, which are assembled with high-voltage Na\(_2\)V\(_2\)(PO\(_4\))\(_2\)O\(_2\)F cathode and exhibit excellent energy storage performance at low temperatures.\textsuperscript{[75,76]}

### 3.4 Insertion-type anode materials

Recently, various titanium-based compounds that store sodium ions through insertion reactions were explored as anode for SIBs due to their low cost, low operating voltage, and structural stability, which can be divided into titanate-based phosphates and oxides. However, the poor electronic conductivity and low discharge-specific capacity limited their applications.\textsuperscript{[77]}

The NASICON-structured NaTi\(_2\)(PO\(_4\))\(_3\) with a 3D open framework structure is expected as a promising candidate material for low-temperature SIBs due to its excellent ionic conductivity and stable crystal structure. A nanocomposite of carbon nanotube (CNT) decorated NaTi\(_2\)(PO\(_4\))\(_3@C\) was explored with a specific capacity of 62.2 mAh g\(^{-1}\) at 10 C under \(-20^\circ\)C, combining the multiple advantages of CNT interconnected network and the NASICON structure.\textsuperscript{[78]} Moreover, KTiOPO\(_4\) with high ionic conductivity was used for Na/K ion batteries at low temperatures. Benefiting from the stable framework structure and highly reversible reactions during insertion and extraction of sodium ions, the electrode showed no capacity fading after 550 cycles at 3 C under \(-35^\circ\)C (Figure 5D).\textsuperscript{[72]} The in situ X-ray powder diffraction (XRD) was performed to elucidate the electrochemical reaction mechanism of the KTiOPO\(_4\) electrode during cycling (Figure 5E), and the diffraction peaks exhibited a highly reversible evolution during cycling, demonstrating the excellent cycling performance.

Titanium-based metal oxides with low lattice strain exhibit excellent long-term cycling performance, represented by layered Na\(_2\)Ti\(_3\)O\(_7\) with a theoretical capacity of 200 mAh g\(^{-1}\) at a low sodium intercalation potential around 0.3 V. With Na\(_2\)Ti\(_3\)O\(_7\) nanotube by the hydrothermal method as an anode, and VOPO\(_4\) as a cathode to construct a sodium-ion full cell, a specific capacity retention of 60% was obtained at \(-20^\circ\)C compared with the performance at 20°C.\textsuperscript{[79]} In addition, NaV\(_{1.25}\)Ti\(_{0.75}\)O\(_4\) with a postspinel structure has excellent electrochemical performance over a wide range of temperatures.\textsuperscript{[80]} Specifically, the NaV\(_{1.25}\)Ti\(_{0.75}\)O\(_4\) electrode could deliver a discharge capacity of 94 mAh g\(^{-1}\) at \(-25^\circ\)C. Compared with the performance at 25°C, the discharge capacity decreased slightly by 8.7%, which was much less than the commercial HC (80.3%) anode under the same condition. When coupled with Na\(_{0.8}\)Ni\(_{0.4}\)Ti\(_{0.6}\)O\(_2\) cathode, the capacity retention of assembled full cell could reach 84% after 200 cycles at \(-20^\circ\)C.

### 3.5 Sodium-metal anodes

Sodium metal is an attractive candidate for anode material for SIBs with a high specific capacity of 1166 mAh g\(^{-1}\), a low redox potential of \(-2.71\) V versus SHE, and crustal abundance. However, the large volume change during cycling, the safety issues caused by dendrite growth, and the unstable SEI hinder the development of large-scale application of sodium-metal anodes.\textsuperscript{[81]}

Although the low-temperature performance of sodium-metal anodes remains largely unexplored, some protection strategies, including the construction of artificial SEI and electrolyte modification, have been developed to achieve highly reversible and stable plating/stripping processes of sodium. The uniform and densely packed sodium deposits at \(-20^\circ\)C were achieved in a weakly solvated electrolyte and with the construction of a Na\(_{0.8}\)Sn\(_4\)/NaF biphasic artificial SEI.\textsuperscript{[82]} Sodium symmetric cell with the electrode surface treated by SnF\(_2\) (Na-SF) exhibited a long-cycling lifespan of 250 h with a low and stable overpotential of 0.42 V at 0.5 mA cm\(^{-2}\) under \(-20^\circ\)C. Furthermore, the cell configuration of Na-SF/Na\(_2\)V\(_2\)(PO\(_4\))\(_2\)O\(_2\)F was fabricated to verify the practicability of the strategies for sodium-metal protection, which provided a capacity of 92.1 mAh g\(^{-1}\) at 0.2 C under \(-30^\circ\)C. After 600 cycles at 0.5 C under \(-20^\circ\)C, high-capacity retention of 88.7% was obtained. From the perspective of electrolyte optimization, a hybrid electrolyte of ether and ILs
with high ionic conductivity and extraordinary desolvation ability was reported to suppress the growth of dendrites of the sodium-metal anode at low temperature, and the Na/Na symmetric cell could be cycled stably with a capacity of 50 mAh cm$^{-2}$ at 2 mA cm$^{-2}$ under $-20^\circ$C.\textsuperscript{[83]} Besides, the assembled NaNa$_3$V$_2$(PO$_4$)$_3$ cell with the hybrid electrolyte of NaPF$_6$/diglyme and [C4C1im][BF$_4$] maintained high-capacity retention of 98 mAh g$^{-1}$ after 1000 cycles at 2 C with an average Coulombic efficiency of 99.6% under $-20^\circ$C.

Thus, the low-temperature performance of anode materials can be improved by designing nanostructures to shorten diffusion distance, introducing carbon matrix to alleviate volume expansion, and promoting ionic and electronic conductivity through surface coating and structural modification. Further theoretical and experimental investigations should be carried out to grasp the mechanism of the sodium nucleation model, dendrite growth behavior, and interface properties between SEI and sodium-metal anode to provide approaches to design fast-charging sodium-metal-based rechargeable batteries for low-temperature applications. The electrochemical performance of several typical types of anode materials for low-temperature SIBs is summarized in Table 2. The transition-metal chalcogenide materials with high theoretical specific capacity and titanium-based materials with excellent cycling stability seem to be promising candidates for practical applications in the future.

4 | CATHODE MATERIALS FOR LOW-TEMPERATURE SIBs

The potential difference between the cathode and anode materials determines the operating voltage of SIBs. The cathode material plays a crucial role in the energy density and cycle life of SIBs. At present, the cathode materials actively investigated for SIBs include TMOs, polyanionic compounds, and Prussian-blue analogs (PBAs). At low temperatures, the ideal cathode materials should possess electrochemical features of high specific energy, sufficient ion diffusivity, and excellent structural stability. This section introduces the research progress of cathode materials under low-temperature conditions.

4.1 | TMO cathode materials

TMO cathode materials have the advantages of a facile synthesis process, adjustable composition, and high power density, represented by the general formula of Na$_{1+x}$MO$_2$ ($0 < x \leq 1$; $M = $ Mn, Cr, Co, Ni, Fe, V, Cu, etc., and their mixtures), which can be divided into layered and tunnel-structured oxides according to the crystal characteristics of TMOs.\textsuperscript{[85,86]} Only a small portion of sodium ions can be extracted and inserted from and into the tunnel-structured TMOs with Na$_{0.44}$MnO$_2$ as a representative, resulting in a low theoretical capacity. The layer-structured TMOs can be classified into O$_2$-, P$_2$-, P$_3$-, and O$_3$ types according to the coordination environment of Na$^+$ and the stacking behavior of oxygen atoms.\textsuperscript{[87,88]} “O” or “P” represents the coordination of Na$^+$ in an octahedral or trigonal columnar coordination environment, and the numbers indicate the repeated stacking units of different oxide layers. The layered oxides investigated currently for SIBs are mainly O$_3$ and P$_2$ phases.

The NaCrO$_2$ cathode is a typical O$_3$-type cathode material with smooth charge/discharge voltage plateaus.\textsuperscript{[89]} However, the bulk NaCrO$_2$ generally exhibits poor-rate performance due to the long diffusion distance. The electrochemical reaction kinetics can be effectively enhanced by designing electrode materials down to the nanoscale to minimize the transfer distance. An electrospinning method was designed to fabricate ultralong NaCrO$_2$ nanowires that could be used at low-temperature conditions.\textsuperscript{[90]} The unique nanowire structure could withstand the stress variation during the insertion and extraction of sodium ions, demonstrating extraordinarily sodium storage behavior with an average capacity of $-108.3$ (0.2 C) and $-60.1$ mAh g$^{-1}$ (10 C) at $-15^\circ$C. As a representative of P$_2$-type cathode material, Na$_{0.65}$MnO$_2$ has a limited reversible capacity (108.3 mAh g$^{-1}$ at 0.2 C under $-20^\circ$C) due to the slow diffusion rate caused by the ordered arrangement of Na$^+$ and vacancies in the crystal framework at low temperatures.\textsuperscript{[91]} The synergistic effect of multiple transition metals is an effective approach to improving electrochemical performance. As a result, a P$_2$-type-layered Na$_{0.67}$Ni$_{0.1}$Co$_{0.1}$Mn$_{0.8}$O$_2$ with an optimized structure was designed, and the doped ions had an obvious inhibitory effect on the Jahn–Teller distortion of Mn ions according to the results of density functional theory calculation, which could effectively shield the electrostatic interaction of Na$^+$/vacancy ordering and enlarge the interstitial space. At temperatures as low as $-20^\circ$C, the Na$_{0.67}$Ni$_{0.1}$Co$_{0.1}$Mn$_{0.8}$O$_2$ cathode delivered a discharge capacity of 147.4 mAh g$^{-1}$ at 0.2 C, with a capacity retention of 80% after 300 cycles at 1.0 C.\textsuperscript{[92]} Recently, lithium-containing or lithium-substituted TMOs with a relatively stable structure have been reported. A comparative study on the full cells composed of Li$_{0.1}$Na$_{0.9}$Co$_{0.2}$Mn$_{0.8}$O$_2$ (or Li$_{0.8}$Co$_{0.2}$Mn$_{0.8}$O$_2$) as cathode material and HC as anode material was carried out, and the cell with Li$_{0.1}$Na$_{0.9}$Co$_{0.2}$Mn$_{0.8}$O$_2$ exhibited higher capacity retention at 0°C.\textsuperscript{[93]} TMOs with compositional and structural diversity were promising candidates for cathode materials
| Anode materials     | Electrolyte                  | Storage mechanism          | Practical capacity at LT                  | Capacity retention                      | Refs. |
|---------------------|------------------------------|----------------------------|-------------------------------------------|------------------------------------------|-------|
| **Carbon-based anode materials** |                              |                            |                                           |                                          |       |
| HC                  | 1 M NaClO₄/[EC/PC]           | Adsorption intercalation   | ≤100 mAh g⁻¹ with a cut-off voltage of 0 V (10 mA g⁻¹, -15°C) | –                                        | [53]  |
| HC                  | 1 M NaPF₆/[EC/PC/DMC]        | Adsorption intercalation   | 265 mAh g⁻¹ with a cut-off voltage of -80 mV, ≤130 mAh g⁻¹ with a cut-off voltage of 3 mV (0.1 C, -15°C) | –                                        | [54]  |
| HC paper            | 1 M NaCF₂SO₃ in diglyme      | Adsorption intercalation   | 300.64 mAh g⁻¹ (50 mA g⁻¹, -25°C)          | 217.1 mAh g⁻¹ after 1000 cycles (500 mA g⁻¹, -15°C) | [55]  |
| **Alloy-metal anode materials** |                              |                            |                                           |                                          |       |
| Se/graphene         | 1 M NaClO₄/[EC/PC + 5% FEC] | Alloying reaction          | 207 mAh g⁻¹ (0.2 A g⁻¹, -25°C)            | 240-250 mAh g⁻¹ after 500 cycles (0.1 A g⁻¹, -25°C) | [57]  |
| Sb@graphene         | 1 M NaClO₄/[EC/PC]           | Alloying reaction          | 472.5 mAh g⁻¹ (50 mA g⁻¹, -20°C), 142.8 mAh g⁻¹ (125 mA g⁻¹, -20°C) | 86.4 mAh g⁻¹ after 50 cycles (125 mA g⁻¹, -20°C) | [58]  |
| SnO₂@graphene       | 1 M NaClO₄/[EC/PC + 5% FEC] | Conversion reaction, allying reaction | –                                      | 97 mAh g⁻¹ after 100 cycles (100 mA g⁻¹, -20°C) | [59]  |
| **Transition-metal oxides and chalcogenides** |                              |                            |                                           |                                          |       |
| NiO@NC              | 1 M LiPF₆/[DEC/EC]           | Conversion reaction        | 178 mAh g⁻¹ (0.05 A g⁻¹, -15°C)           | –                                        | [65]  |
| FeS@C               | 1 M NaClO₄/[EC/PC]           | Conversion reaction        | 562 mAh g⁻¹ (0.2 A g⁻¹, -20°C)            | 311 mAh g⁻¹ after 80 cycles (0.05 A g⁻¹, -25°C) | [67]  |
| Fe₁₋ₓS@NC           | 1 M NaClO₄/[EC/PC + 5% FEC] | Conversion reaction        | 223.4 mAh g⁻¹ (2000 mA g⁻¹, -25°C)        | –                                        | [68]  |
| CoGa₃S₄              | 0.5 M Na₂SO₃CF₃ in C₄H₁₀O₂ | Conversion reaction        | 204 mAh g⁻¹ (2 A g⁻¹, -20°C)              | 100 mAh g⁻¹ after 1000 cycles (1 A g⁻¹, -60°C) | [70]  |
| ZnSe@NCNF           | 1 M NaClO₄ in diethylene glycol dimethyl ether | Conversion reaction, allying reaction | 305.3 mAh g⁻¹ (0.2 A g⁻¹, -20°C) | 119.7 mAh g⁻¹ after 200 cycles (0.2 A g⁻¹, -40°C) | [71]  |
| FeSe₂/rGO            | 1 M NaClO₄ in diethylene glycol dimethyl ether | Conversion reaction, allying reaction | 271.7 mAh g⁻¹ (1 A g⁻¹, -40°C) | 216.7 mAh g⁻¹ after 200 cycles (1 A g⁻¹, -40°C) | [74]  |
| Fe₇Se₈@C            | 1 M NaClO₄/[EC/PC + 5% FEC] | Conversion reaction, allying reaction | ~316 mAh g⁻¹ (0.2 A g⁻¹, -25°C) | –                                        | [84]  |
| **Titanium-based compound anodes** |                              |                            |                                           |                                          |       |
| NaTi₂(PO₄)₃/C       | 1 M NaClO₄/[EC/PC]           | Insertion reaction         | 62.2 mAh g⁻¹ (10 C, -20°C)                | –                                        | [78]  |
| NaV₁.₂₅Ti₀.₇₅O₄     | 1 M NaClO₄/[PC + 2% FEC]     | Insertion reaction         | 94 mAh g⁻¹ (0.2 C, -20°C)                 | –                                        | [80]  |
of SIBs. However, the complex phase transitions of TMOs during cycling hindered the large-scale applications. It is believed that TMOs with high capacity and long cycle life at low temperatures can be designed by employing the synergistic effect of the materials with hybrid P and O phases.

### 4.2 Polyanionic cathode materials

Polyanionic compounds are of great interest as cathode materials for SIBs with stable 3D framework structures composed of strong covalent bonds and fast ion diffusion channels, which ensure excellent cycling stability and remarkable safety. However, the practical applications at low temperatures are greatly limited because of the poor electronic conductivity caused by the bulky anionic groups in the polyanionic compounds. The modifications methods, such as carbon coating, designing micronano structures, and doping with different elements, have been proposed to solve the problems.

NaFePO$_4$ is the first target to be investigated as polyanionic cathode material for SIBs with two different structures of olivine and maricite phases. In view of the successful application of olivine LiFePO$_4$, olivine NaFePO$_4$ with a high theoretical capacity of 155 mAh g$^{-1}$ has attracted great attention. However, the complexity of the synthetic method and the thermodynamic instability limit its application. In addition, although the maricite NaFePO$_4$ is thermodynamically stable, it is generally regarded as an electrochemically inactive structure due to a lack of ion transport channels. Strategies were proposed to break this condition through a variety of modification methods to activate the electrochemical performance of the maricite NaFePO$_4$, and NaFePO$_4$ nanoclusters composed of multiple ultrafine NaFePO$_4$@C subunits were prepared. The unique nanostructure transformed the electrochemically inert maricite NaFePO$_4$ into a highly active amorphous phase because of the increased active sites, showing a capacity of 87.3 mAh g$^{-1}$ after 1000 cycles at 2 C under $-20^\circ$C.

In the past decades, many other types of sodium phosphates have been reported, especially the NASICON-type polyanionic compounds, such as Na$_3$V$_2$(PO$_4$)$_3$. As shown in Figure 6A, the corner-sharing of PO$_4$ tetrahedra and VO$_6$ octahedra in the Na$_3$V$_2$(PO$_4$)$_3$ structure builds a stable 3D open framework, providing sufficient interstitial space to facilitate the transportation of Na$^+$ ions. Due to the disadvantage of the low electronic conductivity of Na$_3$V$_2$(PO$_4$)$_3$, the strategies including carbon coating, nanostructuring, and designing unique structures were carried out to improve the electrochemical performance. For instance, Na$_3$V$_2$(PO$_4$)$_3$ nanoparticles decorated with

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**Table 2 (Continued)**

| Anode materials | Electrolyte | Storage mechanism | Practical capacity at LT | Capacity retention | Refs. |
|-----------------|-------------|-------------------|--------------------------|------------------|-------|
| Sodium metal anodes | Na | 1 M NaPF$_6$ in diglyme/[C$_4$C$_1$im][BF$_4$] | Plating/stripping | 59 mA cm$^{-2}$ with 500 h (2 mA cm$^{-2}$, $-20^\circ$C) | [83] |
| **Note:** Abbreviations: DMC, dimethyl carbonate; EC, ethylene carbonate; FEC, fluorinated ethylene carbonate; HC, hard carbon; LT, low temperature; PC, propylene carbonate; rGO, reduced graphene oxide; SIBs, sodium-ion batteries. |
carbon coatings were prepared by ball milling method with low-cost sucrose as the carbon source.\[99\] The modified Na$_3$V$_2$(PO$_4$)$_3$ showed excellent cycling stability with retention of 75.8% after 500 cycles at 10°C under −20°C. The operating voltage of Na$_3$V$_2$(PO$_4$)$_3$ can be increased through doping with heteroatoms.\[100–102\] For example, a high-voltage cathode material composed of Na$_3$V$_2$(PO$_4$)$_2$O$_2$F was proposed by replacing one-third of PO$_4^{3−}$ in Na$_3$V$_2$(PO$_4$)$_3$ with highly electronegative F$^{−}$ and O$_2^{−}$ in different proportions, which exhibited two voltage plateaus at about 4.01 and 3.60 V (vs. Na$^{+}$/Na) with a specific capacity of 96.1 mAh g$^{−1}$ at 0.2 C under −25°C.\[103\] Besides, the O in Na$_3$V$_2$(PO$_4$)$_2$O$_2$F can be further substituted by F to obtain Na$_3$V$_2$(PO$_4$)$_2$F$_3$ with highly electronegative F$^{−}$ and O$^{2−}$ in different proportions, which exhibited two voltage plateaus at about 4.01 and 3.60 V (vs. Na$^{+}$/Na) with a specific capacity of 96.1 mAh g$^{−1}$ at 0.2 C under −25°C.\[103\] The operating voltage of Na$_3$V$_2$(PO$_4$)$_3$ can be increased through doping with heteroatoms.\[100–102\] For example, a high-voltage cathode material composed of Na$_3$V$_2$(PO$_4$)$_2$O$_2$F was proposed by replacing one-third of PO$_4^{3−}$ in Na$_3$V$_2$(PO$_4$)$_3$ with highly electronegative F$^{−}$ and O$_2^{−}$ in different proportions, which exhibited two voltage plateaus at about 4.01 and 3.60 V (vs. Na$^{+}$/Na) with a specific capacity of 96.1 mAh g$^{−1}$ at 0.2 C under −25°C.\[103\] Besides, the O in Na$_3$V$_2$(PO$_4$)$_2$O$_2$F can be further substituted by F to obtain Na$_3$V$_2$(PO$_4$)$_2$F$_3$ with a theoretical energy density of about 507 Wh kg$^{−1}$ in lithium-ion batteries. However, a lower voltage plateau appeared at about 3.3 V due to the loss of fluorine during synthesis (Figure 6B).\[104\] Changing the pH of the precursor solution is a feasible strategy to stabilize fluorine, which can effectively ensure the presence of fluorine and modulate the local electronic structure of V to eliminate the undesirable plateau at low voltage (Figure 6C). The structure change of the optimized Na$_3$V$_2$(PO$_4$)$_2$F$_3$ was reversible in two consecutive cycles at 0.5 C according to the results of in situ XRD patterns (Figure 6D), indicating the good structural stability; and an excellent cycling performance was obtained with the capacity retention of 95.7% after 200 cycles at −25°C. Building composites with carbon-based materials is a cost-effective approach to overcome the low electronic conductivity of Na$_3$V$_2$(PO$_4$)$_2$F$_3$. Microcubes of Na$_3$V$_2$(PO$_4$)$_2$F$_3$@rGO with Na$_3$V$_2$(PO$_4$)$_2$F$_3$ encapsulated in a 3D graphene network (Figure 6E) maintained a discharge capacity of 75 mAh g$^{−1}$ at 1 C after 180 cycles at 0°C, exhibiting excellent ion diffusion kinetics and electronic conductivity.\[105\]

Cationic substitution is another effective method to optimize the electrochemical performance of NASICON-type polyaniionic compounds.\[106–108\] For example, Na$_3$V$_2$(PO$_4$)$_3$ (NVCP) cathode was prepared by replacing V$^{3+}$ with Cr$^{3+}$, and a 1.5-electron transfer reaction was achieved during cycling.\[109\] Furthermore, because the irreversibility of the phase transition was largely suppressed at low temperature, NVCP exhibited excellent cycling stability with capacity retention of 92% after 200 cycles at 0.5 C under −15°C. In addition to the isovalent substitutions, the aliovalent doping strategy with Mn$^{2+}$ was developed to prepare Na$_3$V$_{1.98}$Mn$_{0.02}$(PO$_4$)$_2$F$_3$, which delivered a discharge-specific capacity of about 79.9 mAh g$^{−1}$ at 0.5 C under −25°C.\[110\]

A series of high-voltage cathode materials with novel structures and high electrochemical activity can be obtained by combining different types of polyaniions. As a typical representative, Na$_4$Fe$_3$(PO$_4$)$_2$P$_2$O$_7$
cathode with mixed phosphate and pyrophosphate is considered a competitive candidate for SIBs due to its low cost, environmental friendliness, and excellent structural stability. The nanocomposite of Na$_4$Fe$_3$(PO$_4$)$_2$P$_2$O$_7$/C exhibited excellent air stability and remarkable electrochemical performance at a low temperature (95.0 mAh g$^{-1}$ at 0.1 C under $-20^\circ$C), showing great potential for practical large-scale applications.\[116\]

### 4.3 PBA cathode materials

PBAs, as a large family of transition-metal cyanides, are an important class of cathode materials for SIBs. The general molecular formula of PBAs can be described as $A_xM_y[M_\alpha(CN)\beta]_{(1-y)}\boxtimes_y\cdot nH_2O$ ($0 \leq x < 2; 0 \leq y < 1$), where A is the alkali metal elements, M$_\alpha$ and M$_\beta$ are transition-metal elements, and $\boxtimes$ indicates the vacancies occupied by coordinating water molecules.\[111-113\] The cyanide ligand connects the coordinated transition-metal ions together and arranges them into a 3D framework structure. The open framework provides large channels for ion diffusion, allowing rapid and reversible insertion and extraction reactions of Na$^+$ ions. The transition metals, including Fe, Mn, Co, and Zn, can occupy the M sites in PBAs, and Fe is currently the most common element. For instance, the PBAs’ composite modified with CNTs displayed a capacity of 52 mAh g$^{-1}$ at 6 C under $-25^\circ$C, with a capacity retention of 86% over 1000 cycles at 2.4 C under $-25^\circ$C.\[114\] PBAs with different kinds of transition metals, such as Na$_{1.86}$Ni[Fe(CN)$_6$]$_{0.88}$·1.88H$_2$O nanoparticles, exhibited impressive cycling performance at low temperatures with a capacity of 87% after 440 cycles at 0°C, reflecting the excellent structural stability of the PBAs cathode.\[115\]

In the future, it is necessary to prepare high-quality PBAs with low content of coordinating water, low amount of vacancy, and high content of sodium. The modification methods, such as metal substitution, dehydron treatment, and the introduction of conductive materials should be further explored to improve the low-temperature electrochemical properties of PBAs’ cathode for SIBs.

The electrochemical performances of various cathode materials at low temperatures have been summarized in Table 3. The polyanionic compounds are currently the most popular choice for low-temperature SIBs, and undoubtedly the Fe-based PBAs have great potential for all-climate and large-scale energy storage applications due to their low-cost and facile synthesis process.

### 5 FULL-CELL PERFORMANCE OF SIBS AT LOW TEMPERATURES

The half-cell configurations were widely used as evaluation systems for basic research of electrolyte and electrode materials due to the high operability. With the combination of scientific research and industrialization gradually closing to each other, the evaluation of the performance of sodium-ion full batteries (SIFBs) is of great significance.\[116\] Recently, various types of SIFBs with excellent electrochemical performance have been reported and show potential for low-temperature applications. The representative SIFB systems will be emphatically introduced to provide inspiration for the basic research and practical applications of SIBs at low temperatures.

#### 5.1 Full cells with nonaqueous liquid electrolyte

Currently, SIFBs based on organic electrolytes are the most reported systems for low-temperature applications. Polyanionic materials and TMOs are generally used as cathode materials, and the choice of the anode materials is more flexible. The types of full-cell configurations will be discussed according to the differences in anode materials. Most full-cell configurations with HC as anode material exhibited unsatisfactory electrochemical performance at low temperatures, such as Na$_{3.5}$V$_2$(PO$_4$)$_2$F$_3$/HC,\[66\] Na$_{0.76}$Ni$_{0.3}$Fe$_{0.4}$Mn$_{0.3}$O$_2$/HC,\[30\] and Li$_{0.1}$Na$_{0.7}$Co$_{0.5}$Mn$_{0.5}$O$_2$/HC.\[93\] The reversible capacity decays rapidly with decreasing temperature, and the cycling stability is inferior due to the increase of resistance on the anode side.

Combining anode materials with high theoretical capacities, such as alloy metals and transition-metal chalcogenides, and cathode materials of high-voltage polyanionic compounds, SIFBs will exhibit excellent low-temperature performance. SIFBs assembled with the anode of Se/graphene composite and a high-voltage cathode of Na$_{3}$V$_2$(PO$_4$)$_2$O$_2$F exhibited superior long-term cycle life at low temperatures. As the operating temperature gradually decreased from 25°C to $-25^\circ$C, the capacity retention of the full cell exceeded 75% after 1000 cycles at 0.4 A g$^{-1}$, indicating the weak performance dependence on temperature and outstanding energy storage ability.\[75\] In terms of using transition-metal chalcogenide as anode materials, the full cell of FeS@C/Na$_{3}$V$_2$(PO$_4$)$_2$O$_2$F with NaClO$_4$ (1.0 M) in PC and EC (v/v, 1:1) as the electrolyte exhibited a capacity of 221.9 mAh g$^{-1}$ at 50 mA g$^{-1}$ under $-25^\circ$C.\[105\] When the coral-like Fe$_2$Se$_5$@C as anode and Na$_3$V$_2$(PO$_4$)$_2$O$_2$F as a
The electrochemical performances of cathode materials for SIBs at low temperature

| Cathode materials                                                                 | Electrolyte                  | Voltage window | Practical capacity at LT | Capacity retention | Refs. |
|----------------------------------------------------------------------------------|------------------------------|----------------|--------------------------|--------------------|-------|
| **Transition-metal oxides**                                                      |                              |                |                          |                    |       |
| NaCrO₂ nanowires                                                                | 1 M NaPF₆/[EC/DEC]           | 2.0–3.6V       | ~108.3 mAh g⁻¹ (20 mA g⁻¹, −15°C) | 80.6% after 300 cycles (200 mA g⁻¹, −15°C) | [90]  |
| Na₀.₆₇Ni₀.₁Co₀.₃Mn₀.₆O₂                                                          | 1 M NaPF₆/[EC/PC + 5% FEC]   | 1.5–4.2V       | 123.2 mAh g⁻¹ (170 mA g⁻¹, −20°C) | 80% after 300 cycles (170 mA g⁻¹, −20°C) | [91]  |
| Na₀.₆₇Ni₀.₁Co₀.₃Mn₀.₆O₂                                                          | 1 M NaPF₆ in diglyme         | 1.5–4.2V       | 132.2 mAh g⁻¹ (34 mA g⁻¹, −40°C) | 83% after 300 cycles (170 mA g⁻¹, −40°C) | [92]  |
| **Polyanionic compounds**                                                        |                              |                |                          |                    |       |
| NaFePO₄/C                                                                       | 1 M NaClO₄/[PC + 5% FEC]     | 1.5–4.5V       | 111.5 mAh g⁻¹ (31 mA g⁻¹, −10°C); 98.6 mAh g⁻¹ (31 mA g⁻¹, −20°C) | 100.1 mAh g⁻¹ after 1000 cycles (310 mA g⁻¹, −10°C); 87.3 mAh g⁻¹ after 1000 cycles (310 mA g⁻¹, −20°C) | [96]  |
| Na₀.₇₅V₂(PO₄)₃@C                                                                | 1 M NaClO₄ in [EC/PC]        | 2.5–4.3V       | 91.3 mAh g⁻¹ (10 C, −20°C) | 75.8% after 500 cycles (10 C, −20°C) | [99]  |
| Na₀.₇₅V₂(PO₄)₂O₂F                                                               | 1 M NaClO₄/[EC/PC + 5% FEC]  | 2.0–4.3V       | 96.1 mAh g⁻¹ (0.2 C, −25°C) | 80.9% after 2000 cycles (20 C, 25°C) | [103] |
| Na₀.₇₅V₂(PO₄)₂F₃                                                                | 1 M NaClO₄/[EC/PC + 5% FEC]  | 2.5–4.5V       | ~96.5 mAh g⁻¹ (44 mA g⁻¹, −25°C) | 95.7% after 200 cycles (44 mA g⁻¹, −25°C) | [104] |
| Na₀.₇₅V₂(PO₄)₂F₅@rGO                                                             | 1 M NaClO₄/[EC/DMC + 5% FEC] | 2.0–4.3V       | 68 mAh g⁻¹ (1 C, 0°C) | 75 mAh g⁻¹ after 180 cycles (1 C, 0°C) | [105] |
| Na₀.₇₅V₂(PO₄)₃@C                                                                | 1 M NaClO₄/[EC/DMC + 5% FEC] | 2.5–4.3V       | ~90 mAh g⁻¹ (0.1 C, −15°C) | 92% after 200 cycles (0.5 C, −15°C) | [109] |
| Na₀.₇₅V₁.₉₈Mn₀.₀₂(PO₄)₃F₃                                                        | 1 M NaClO₄/[PC + 5% FEC]     | 2.0–4.3V       | 79.9 mAh g⁻¹ (64 mA g⁻¹, −25°C) | 93.3% after 400 cycles (64 mA g⁻¹, −25°C) | [110] |
| Na₀.₇₅Fe₂(PO₄)₄(P₂O₇)/C                                                         | 1 M NaClO₄/[EC/PC + 5% FEC]  | 1.9–4.1V       | 95 mAh g⁻¹ (12 mA g⁻¹, −20°C) | 92.1% after 250 cycles (160 mA g⁻¹, −20°C) | [66]  |
| **Prussian-blue analogs**                                                        |                              |                |                          |                    |       |
| Na₄Fe(CN)₆/CNT                                                                  | 1 M NaClO₄/[EC/PC]           | 2.0–4.2V       | 142 mAh g⁻¹ (0.1 C, −25°C) | 86% after 1000 cycles (2.4 C, −25°C) | [114] |
| Na₄.₈₆Ni₄[Fe(CN)₆]₃·1.₈H₂O                                                      | 1 M NaClO₄/[EC/DMC]          | 2.0–4.1V       | 65.1 mAh g⁻¹ (8.5 mA g⁻¹, −25°C) | 84% after 440 cycles (85 mA g⁻¹, −25°C) | [115] |

Table 3: The electrochemical performances of cathode materials for SIBs at low temperature.

Abbreviations: CNT, carbon nanotube; DEC, diethyl carbonate; DMC, dimethyl carbonate; EC, ethylene carbonate; FEC, fluorinated ethylene carbonate; LT, low temperature; PC, propylene carbonate; rGO, reduced graphene oxide; SIBs, sodium-ion batteries.

cathode assembled a full cell, the specific capacity was 165.6 mAh g⁻¹ at 0.05 A g⁻¹ after 440 cycles under −25°C with an average Coulombic efficiency higher than 99%. Notably, the fabricated full cell could light 27 LED bulbs at −25°C (Figure 7A). In addition, full cells with modified double transition-metal chalcogenides as anodes also showed great potential for low-temperature applications. Specifically, the capacity retentions of full cells of Na₁.₈Co₂Se₉@NC/Na₀.₇₅V₂(PO₄)₂O₅ and Na₁.₈CoSe₉@NC/Na₀.₇₅V₂(PO₄)₂O₅ could reach capacity retention of 83% and 77% at 0.1 A g⁻¹ under −25°C, respectively, indicating the workability of the SIFBs at low temperatures. [75,76]

Except for the anode materials mentioned above, titanium-based compounds with excellent structural stability have also manifested their application prospect in SIFBs. An SIFB composed of 3D porous Na₀.₆₇Ni₀.₁Co₀.₁Mn₀.₈O₂ 1 M NaPF₆ in diglyme 1.5 and Na₀.₆₇Ni₀.₁Co₀.₁Mn₀.₈O₂ 1 M NaPF₆ in diglyme 1.5 foams was fabricated (Figure 7B). Benefiting from the increased Na⁺ transport performance due to the 3D interconnected porous structure and the excellent absorption ability of electrolyte, the full cell delivered a capacity close to the theoretical value. Besides, the full-cell configurations with titanium-based compounds as the anode materials, such as Na₂Ti₃O₇/VOPO₄, [15] or...
NaV_{1.25}Ti_{0.75}O_4/Na_{0.8}Ni_{0.4}Ti_{0.6}O_2 system, \[105\] displayed remarkable electrochemical performance at low temperatures.

5.2 | Full cells with aqueous and solid electrolytes

The aqueous sodium-ion full batteries (ASIFBs) are promising to meet the requirements of large-scale energy storage because of their high safety and low cost. Polyanionic compounds and TMOs/hydroxides are the cathode materials currently investigated in full cells with aqueous electrolytes. The sodium insertion potential of NaTi_2(PO_4)_3 was slightly higher than the hydrogen evolution potential of water (Figure 7C).\[118\] NaTi_2(PO_4)_3 with NASICON-structure was particularly suitable for ASIFB systems to achieve fast ion transport. An aqueous full cell of NaTi_2(PO_4)_3/NaV_2(PO_4)_2O_2F with the mixed electrolytes containing 25 M NaFSI and 10 M NaFTFSI, displayed a capacity retention of 74% after 500 cycles at 0.2 C under \(-10^\circ C\).\[32\] In addition, the aqueous full cell of NaTi_2(PO_4)_3@C/Ni(OH)_2 showed strong adaptability to varying temperature conditions, and the specific capacity was 94.8 mAh g\(^{-1}\) when the temperature was returned from \(-20^\circ C\) to 25°C (Figure 7D).\[119\] Meanwhile, after 10000 cycles at \(-20^\circ C\), the capacity retention was 85% at 10 C (Figure 7E). The long-cycling stability endowed the full-cell configuration with promising potential as energy storage devices under harsh conditions. In addition to the above examples, the full-cell configurations with the low-cost active carbon (AC) as the cathode also showed application potential in ASIFBs. The constructed ASIFB of NaTi_2(PO_4)_3@C/AC with an antifreezing hydrogel electrolyte of Na_2SO_4–SiO_2 delivered a reversible capacity of 61.8 mAh g\(^{-1}\) at 0.13 A g\(^{-1}\) under \(-30^\circ C\).\[33\]

Although solid-state sodium-ion full batteries (SSSIFBs) with high safety, high power density, and excellent mechanical strength provide a promising option for next-generation energy storage devices, the low ionic conductivity and the high interfacial resistance are the main challenges to the development of SSSIFBs. Most of the solid-state sodium batteries were tested at high
| Cathode | Anode | Electrolyte | Operating potential | Electrochemical performance at LT | Ref. |
|---------|-------|-------------|---------------------|----------------------------------|------|
| **SIFBs based on organic liquid electrolytes** | | | | | |
| Na$_{3.5}$V$_2$(PO$_4$)$_2$F$_3$ | HC | 1 M NaClO$_4$/[EC/PC] | 3.62 V at 25°C | ~75 mAh g$^{-1}$ after 10 cycles at −20°C (based on anode) | [53] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | Se/graphene | 1 M NaClO$_4$/[EC/PC + 5% FEC] | − | 76 mAh g$^{-1}$ at 0.04 A g$^{-1}$ at −25°C (based on cathode), 75% after 1000 cycles at 0.4 A g$^{-1}$ at −25°C | [57] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | FeS@C | 1 M NaClO$_4$/[EC/PC] | −2.5 V at −25°C | 221.9 mAh g$^{-1}$ at 50 mA g$^{-1}$ at −25°C (based on anode) | [67] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | Fe$_7$Se$_8$@C | 1 M NaClO$_4$/[EC/PC + 5% FEC] | −2.5 V at 25°C | 165.6 mAh g$^{-1}$ after 440 cycles at 0.05 A g$^{-1}$ at −25°C (based on anode) | [84] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | Ni$_{1.8}$Co$_{1.2}$Se$_4$@NC | 1 M NaClO$_4$/[EC/PC + 5% FEC] | ~2.5 V at −25°C | 221.9 mAh g$^{-1}$ at 50 mA g$^{-1}$ at −25°C (based on anode) | [75] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | Ni$_{1.5}$CoSe$_5$@NC | 1 M NaClO$_4$/[EC/PC + 5% FEC] | ~2.5 V at −25°C | 165.6 mAh g$^{-1}$ after 440 cycles at 0.05 A g$^{-1}$ at −25°C (based on anode) | [76] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$FNi | NaTi$_2$(PO$_4$)$_3$/C | 1 M NaClO$_4$/[EC/PC + 5% FEC] | ~2.5 V at −25°C | 165.6 mAh g$^{-1}$ after 440 cycles at 0.05 A g$^{-1}$ at −25°C (based on anode) | [117] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$FNi | NaTi$_2$(PO$_4$)$_3$/C | 1 M NaClO$_4$/[EC/PC + 5% FEC] | ~2.5 V at −25°C | 165.6 mAh g$^{-1}$ after 440 cycles at 0.05 A g$^{-1}$ at −25°C (based on anode) | [117] |
| VOPO$_4$ | Na$_3$Ti$_3$O$_7$ | 1 M NaClO$_4$/[PC + 2% FEC] | − | 55 mAh g$^{-1}$ at 1 C at −20°C (based on cathode) | [79] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$FNi | Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | 1 M NaClO$_4$/[EC/PC + 5% FEC] | ~2.5 V at −25°C | 165.6 mAh g$^{-1}$ after 440 cycles at 0.05 A g$^{-1}$ at −25°C (based on anode) | [84] |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$FNi | Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | 1 M NaClO$_4$/[EC/PC + 5% FEC] | ~2.5 V at −25°C | 165.6 mAh g$^{-1}$ after 440 cycles at 0.05 A g$^{-1}$ at −25°C (based on anode) | [84] |
| SIFBs based on ionic liquid electrolytes | | | | | |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$FNi | Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | 1 M NaClO$_4$/[EC/PC + 5% FEC] | ~2.5 V at −25°C | 165.6 mAh g$^{-1}$ after 440 cycles at 0.05 A g$^{-1}$ at −25°C (based on anode) | [84] |
| SIFBs based on aqueous electrolytes | | | | | |
| Na$_3$V$_2$(PO$_4$)$_2$F | NaTi$_2$(PO$_4$)$_3$/C | 25 M NaFSI/10 M NaFTFSI | ~1.44 V at 30°C | 74% after 500 cycles at 0.2 C at −10°C | [32] |
| Ni(OH)$_2$ | NaTi$_2$(PO$_4$)$_3$/C | 2 M NaClO$_4$ | 1.25 V at −20°C | ~75 mAh g$^{-1}$ at 10 C at −20°C (based on anode), 85% after 10,000 cycles at 10 C at −20°C | [119] |
| Active carbon | NaTi$_2$(PO$_4$)$_3$/C | Na$_2$SO$_4$-SiO$_2$ hydrogel | − | 61.8 mAh g$^{-1}$ at 0.13 A g$^{-1}$ at −30°C (based on anode) | [33] |
| SIFBs based on solid polymer electrolytes | | | | | |
| Na$_3$V$_2$(PO$_4$)$_2$O$_2$F | HC | Perfluorosulfonate-based polymer | − | 40.6 mAh g$^{-1}$ after 30 cycles at 1 C at −25°C | [45] |

Abbreviations: EC, ethylene carbonate; FEC, fluorinated ethylene carbonate; HC, hard carbon; LT, low temperature; PC, propylene carbonate; SIFB, sodium-ion full battery.
temperatures to improve the ionic conductivity of the electrolyte and reduce the polarization of the cell. Nevertheless, there are few reports on the low-temperature performance of SSSIFBs, and most of the reports are based on solid polymer electrolytes. For example, the full cell of HC-[(PFSA-Na)][Na3V2O2(PO4)2F@rGO was successfully operated at −25°C but could maintain limited capacity retention of 40.6 mAh g⁻¹ after 30 cycles. Therefore, the large-scale application of low-temperature SSSIFBs still faces many challenges. The electrochemical performance of low-temperature SIFBs is summarized in Table 4.

6 | CONCLUSIONS AND PERSPECTIVES

Significant progress has recently been made for SIBs with high energy density, long cycle life, and excellent rate capability under normal conditions. Besides, the emerging applications of SIBs have been expanded to the fields of deep-sea exploration, aerospace technology, and military equipment. The low-temperature tolerance becomes increasingly important for SIBs in practical applications. The performance of SIBs at low temperatures can be improved by optimizing the major components, including electrolyte and anode and cathode materials. New challenges are raised not only for the conductivity and structural stability of electrode materials but also for the formulation of electrolytes and functional additives. Combining titanium-based insertion-type anodes and polyanionic cathodes that have excellent structural stability and compatibility with organic carbonate electrolytes containing functional components is expected to construct promising SIFBs for low-temperature conditions. The possible directions for the future development of low-temperature SIBs are proposed. First, the effects of composition on the properties of electrolytes, including electrochemical window, freezing temperature, and ionic conductivity, should be clarified. By revealing the formation mechanism of SEIs in different electrolytes, new formulations of electrolytes suitable for low-temperature conditions could be designed to improve the compatibility between electrolytes and electrodes. The electrochemical reactions of SIBs can be accurately analyzed through in situ technologies to explore the reason for the formation of an abnormally thickened SEI layer on HC anode in organic electrolytes at low temperatures. Second, in addition to the conventional modification strategies of electrode materials, such as the preparation of carbon composites and heteroatom doping, the development of nanostructured electrode materials with a capacitive charge-storage mechanism should be a promising approach to accelerate the electrode reactions at low temperatures. Third, the overall performance of SIFBs should be further improved at low temperatures. The specific energy density is a key parameter in practical applications, which is determined by the voltage and capacity of the electrodes. Nevertheless, most reports only mentioned the energy density of SIBs at room temperature. It is necessary to balance the mass ratio of the cathode to anode and the compatibility between electrodes and electrolytes and improve the Coulombic efficiency of SIFBs at low temperatures. In summary, the challenges should be addressed before realizing the commercial application of SIBs with remarkable low-temperature adaptability.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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