Sodium-Ion Batteries: Exploration of Electrolyte Materials

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Abstract. In recent years, as fossil energy sources such as oil and coal continue to be consumed, the issue of resources and the environment has become one of the main challenges to the sustainable development of human society. People's electricity consumption has increased dramatically, and the demand for energy storage batteries has also increased. Sodium-ion batteries (SIBs) are a very worthwhile development because of high Na reserves in the world, which can bring many advantages. The electrolyte can control the battery's inherent electrochemical window and performance, influence the nature of the electrode/electrolyte interface, and is one of the most important material choices for SIBs. The electrolyte simultaneously influences the electrochemical performance and safety of SIBs. This paper focuses on electrolyte materials in SIBs, explaining the fundamental needs and categorization of sodium ion electrolytes and highlighting the most recent advances in liquid and solid electrolytes. It is found that SIBs still have problems such as lower energy density, narrower electrochemical stability windows, poorer solid electrolyte interphase (SEI) stability, etc. Solving the related technical problems is of great significance for commercializing SIBs.

Keywords: Sodium-Ion batteries, liquid electrolytes, solid electrolytes, electric vehicle.

1. Introduction

Lithium-ion batteries (LIBs) have effectively altered our way of life. However, the safety and environmental issues associated with the flammable and poisonous non-aqueous electrolytes are a significant barrier to their widespread use in larger-scale applications like transportation electrification and grid storage [1].

Back in the 1970s, SIBs and LIBs were researched almost simultaneously, and then the research on SIBs stalled due to the successful commercialization of LIBs. It was not until after 2010 that sodium-ion batteries again ushered in their golden development period with the massive demand for renewable energy utilization and the urgent need for large-scale energy storage technology.

Sodium-ion batteries (SIBs), which work on a similar principle to LIBs, have been considered a replacement for LIBs because of their widespread occurrence in the natural world, inexpensive cost, and compatibility with devices already using LIBs. It has been found that SIBs also have good power characteristics, extensive temperature range adaptability, exceptional safety, and no over-discharge problems. Therefore, SIBs have the advantages of low cost, prolonged cycle life, a wide range of applications, and high safety, and they can be a useful supplement to LIBs.

The key materials for SIBs include cathode materials, anode materials, and electrolytes. Among them, cathode materials include oxides, polyanion, Prussian blue, and organic ones; anode materials include carbon, titanium, organic, and alloy cathode materials; electrolytes include liquid and solid electrolyte systems [2]. Numerous effective materials, both cathode and anode, have been developed by scientists for SIBs. As a medium for the redox reaction of the electrode materials, the redox window, the Na-ion migration and diffusion, and the coupling association between Na+ and anions or solvents are the key factors determining the interfacial traits. Thus, the SIB electrolyte has an important influence on the thermodynamic and kinetic properties of the SIB system, such as the structural stability of the electrode material, the composition and structure of solid electrolyte interphase (SEI), the multiplicative performance, cycling stability, and thermal stability of the battery [3].

In recent years, "Water-in-salt (WiS)" high salt concentration electrolyte and Inert cation assisted WiS (IC-WiS) electrolyte have made significant progress in energy density and kinetic performance, and a $NaPF_6$/EC+PC ultra-low concentration electrolyte with a wide operating temperature window has been proposed. Concentration electrolyte has also been proposed, and the research on SIBs electrolyte materials has entered a rapid development path.

This paper will focus on the electrolyte materials for SIBs, and the objective is to find electrolyte materials suitable for sodium-ion batteries applied in different scenarios. Through the investigation and study of the currently available electrolyte materials, analyze the currently available sodium ion electrolyte (SIE) materials, and summarize the relevant research progress, including liquid and solid electrolytes. It is found that the current SIB electrolytes still suffer from a narrow electrochemical stability window, poor SEI membrane stability, and low conductivity. Therefore, developing electrolyte materials with high conductivity, good durability in electrochemistry across a large potential spectrum, good thermal stability, low cost, simple process, low toxicity, and environmental friendliness is important for commercializing SIBs.

2. Types of electrolytes for SIBs

SIB electrolytes are primarily categorized into liquid, solid-liquid composite, and solid electrolytes. The main factors influencing sodium ion migration are solvation effects and electric field driving. In contrast, polymers' chain segment movement and vacancy migration are considered factors influencing movement in solid SIEs and gel SIEs [4].

3. Liquid electrolyte materials

Liquid electrolyte, also known as electrolyte, is mainly composed of solvents, solutes, and additives, which determine the nature of the electrolyte. SIB electrolyte needs to meet the following characteristics: high ion conductivity, wide liquid path (liquid temperature range), good chemical/electrochemical stability, thermal stability, low cost, and environmentally friendly characteristics [2].

In general, liquid electrolytes have a higher ionic conductivity than solid electrolytes because they have better flow properties and facilitate the rapid migration of sodium ions. Organic systems are divided into ester and ether electrolytes among liquid electrolytes depending on the solvent. The difference between the two mainly lies in the characteristics of the interface formation to solid electrolytes and the different energy storage mechanisms in different anode materials [5]. Aqueous electrolytes are generally considered low-cost and environmentally friendly systems, but their limited electrochemical window restricts their use in situations with a lot of energy and power. The electrochemical stability window (ESW) of aqueous electrolytes is limited by the H_2 precipitation and O_2 absorption reactions, while the ESW of organic electrolytes is mainly limited by the choice of solvent, which can withstand different electrochemical windows. The usual methods of improving ESW are using ionic liquids, polymers, and inorganic solid-state electrolytes. Researchers have also targeted highly concentrated salt electrolytes to improve electrochemical stability [6].

3.1. Aqueous electrolytes

Without the widespread deployment of energy storage systems, intermittent renewables like wind and solar electricity cannot be included in the grid. Aqueous electrolytes contribute greatly to large-scale energy storage systems. Aqueous electrolytes have a wide possibility in the use of sodium-ion batteries as a result of their many benefits, including their strong ionic conductivity, superior safety, cheap cost, and ease of availability.

3.1.1. "Water-in-salt (WiS)" electrolyte

The electrochemical stability window is an important indicator of electrolyte performance, and a larger electrochemical stability window is more favorable for redox reactions at high potentials. The ESW of aqueous electrolytes has been relatively low, which has prevented major progress in the study of cycle life and energy density of water-based SIBs. In recent years, sodium-ion water-in-salt electrolyte (NaWiSE) has made great progress in providing an ESW of 2.5 V. This electrolyte reduces the activity of water on the cathode and thus reduces the production of hydrogen gas.

In a sodium-concentrated WiS electrolyte, Suo et al. demonstrated the feasibility of creating a Na^+-conducting SEI. By including $NaTi_2(PO_4)_3$ and $Na_{0.66}[Mn_{0.66}Ti_{0.34}]\ O_2$, this SEI raises the Na-ion battery's electrochemical range to 2.5 V. Several analysis methods showed that the cation-anion interaction is considerably stronger in sodium-ion electrolytes, enables better clustering of ions and, more importantly, close Na-F interactions. As a result, a stable and repairable SEI may be created with far less salt than its Li analogues, which is crucial for preventing water breakdown and enhancing the anion reduction capacity. This SEI provided kinetic protection that minimized parasitic processes in the full Na-ion battery, leading to significant capacity retention benefits when the battery was kept at 100% SOC. Na^+-conducting aqueous SEI may play an important role in highly efficient next-generation SIBs [1].

3.1.2. Inert cation-assisted WiS (IC-WiS) electrolyte

WiS electrolytes offer a novel method of expanding the ESW of aqueous electrolytes. Nevertheless, their composition greatly relies on the selected salts' solubility, severely limiting the number of viable WiS systems. Using tetraethylammonium triflate (TEAOTF) salt, Jiang et al. propose an inert-cation-aided WiS (IC-WiS) electrolyte. By raising the total concentration of the Sodium IC-WiS electrolyte (NaOTF-TEAOTF) to 31 $mol \cdot kg^{-1}$, the ESW can be extended to more than 3 V. Since the TEA^+ cation has a very large radius, it cannot intercalate into most electrodes, including the Prussian blue analog (PBA): a colorant with a free-form structure; hence the mixed-cation co-intercalation event is avoided during cycling. In this case, $NaTiOPO_4$, with a low redox potential of 1.5 V and connected with PBA at the cathode, is used effectively. As a bonus, the Na IC-WiS electrolyte effectively prevents Fe and Mn from dissolving at the cathode, greatly improving the battery's cycle performance. In addition, the electrolyte properties contribute to the high cycling stability of the battery [2].

3.1.3. NaPF6/EC+PC ultra-low concentration electrolyte

Altering the concentration of the electrolyte is a key method for enabling functioning. Recently, it has been demonstrated that raising the salt concentration is efficient for LIBs. (Figure 1a) [7]. In contrast, methods to reduce salt concentration have not been investigated, which could produce ultra-dilute electrolytes. For this reason, 1 M is still often used as the reference concentration. However, low electrolyte concentrations may allow the SIBs to achieve satisfactory kinetics because of the smaller radius and easier movement of sodium ions between electrode interfaces.

In addition, reducing the salt concentration may effectively minimize the price of SIBs, which is useful for large-scale electricity storage [8]. Surprisingly, Li et al. suggest employing a special electrolyte which is the ultra-low concentration for the practical SIBs, which provides high performance across a wide operating temperature range thanks to the chemistry of diluted electrolytes. This appealing electrolyte composition resulted from an inverted design and offered new perspectives on preventing secondary battery failure under extreme situations.

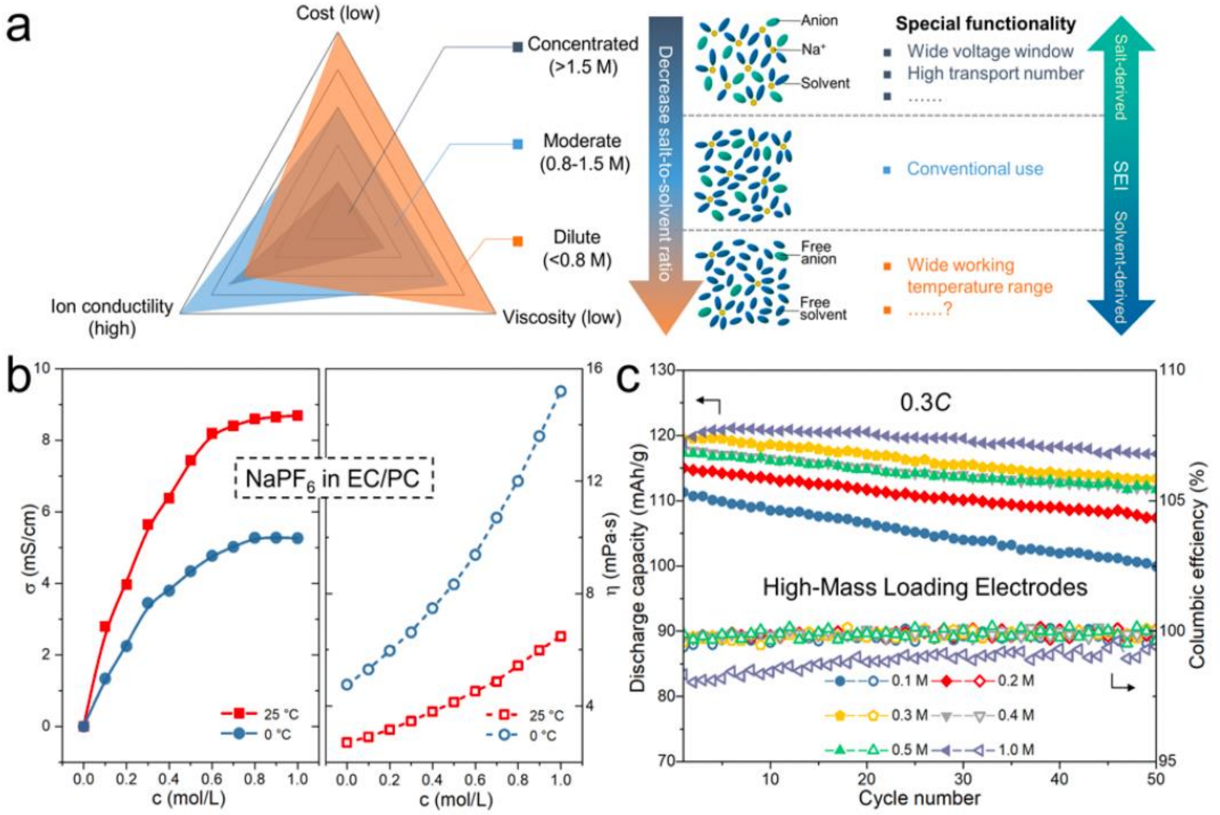

Figure. 1. (a) Summary of the physicochemical characteristics of electrolytes. (b) Concentration dependence of ionic conductivity and viscosity. (c) The capacity of NIBs to cycle with varying electrolyte concentrations [7].

3.2. Organic electrolytes

3.2.1. Carbonate electrolytes for SIBs

Carbonate esters are commonly used as a class of organic electrolyte solvents for SIBs and usually have a strong salt solubility. The main carbonate solvents commonly used in SIBs are ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), etc. Their physicochemical properties are shown in Table 1. EC solvents can provide a more stable passivation layer by reducing the carbon anode surface, inhibiting the continued decomposition of the solvent at low potentials. However, EC solvents have a high melting point (36.4 °C) and exist as solids at about 25 °C, and the effectiveness in cold environments of EC-rich organic electrolytes is generally poor [5]. PC solvents have the advantage of low cost and a wide temperature window and are considered organic solvents that can be used as SIE on their own. However, PC solvents have difficulty forming stable SEI films on the hard carbon (HC) cathode surface, leading to continuous side reactions with the cathode and affecting the battery's cycle life. Therefore, researchers in SIB electrolyte applications have received attention from binary or ternary carbonate solvents containing EC or PC. Ponrouch et al. found that when the fixed sodium salt was $NaClO_4$, the conductivity of EC and PC binary mixed solvent electrolytes was much higher than the ionic conductivity of single-component solvent electrolytes. Hard carbon showed the best capacity retention in the NaClO4/EC: PC electrolyte compared to other mixed solvents. Kamath et al. simulated the interaction of Na^+ with four different types of carbonate solvents by molecular dynamics and found that EC: PC with Na^+ with the highest binding energy, solvation enthalpy, and free energy of solvation (Figure 2a), which is a suitable carbonate binary solvent for SIBs [9]. Passerini et al. investigated the reactivity of carbonate electrolytes with different sodium salts on the surface of sodium hard carbon (Na_x-HC) electrodes by differential scanning calorimetry (DSC) (Figure 2b) [9]. The Na_x-HC electrode and the EC: PC-based electrolyte system showed high thermal stability in the different sodium salt electrolytes. The sulphonate-based EC: PC electrolytes (e.g., NaFSI) generate the least heat for side reactions with the hard carbon cathode and easily form stable SEI films. $NaPF_6$-based electrolytes are more thermally stable, less expensive, and can form an AlF_3 passivation layer on the Al foil surface to avoid Al foil corrosion. Therefore, NaPF6 salts may emerge as the optimal sodium salt for use in SEIs.

Table 1. Physicochemical parameters of carbonates solvents [3].

Solvent	Dielectric constant ε (25°C)	Viscosity η (25°C)/mPa·s	Melting point T_m/°C
EC	89.78 (40°C)	1.90 (40°C)	36.4
PC	64.92	2.53	-48.8
DMC	3.107	0.59	4.6
EMC	2.958	0.65	-53
DEC	2.805	0.75	-74.3

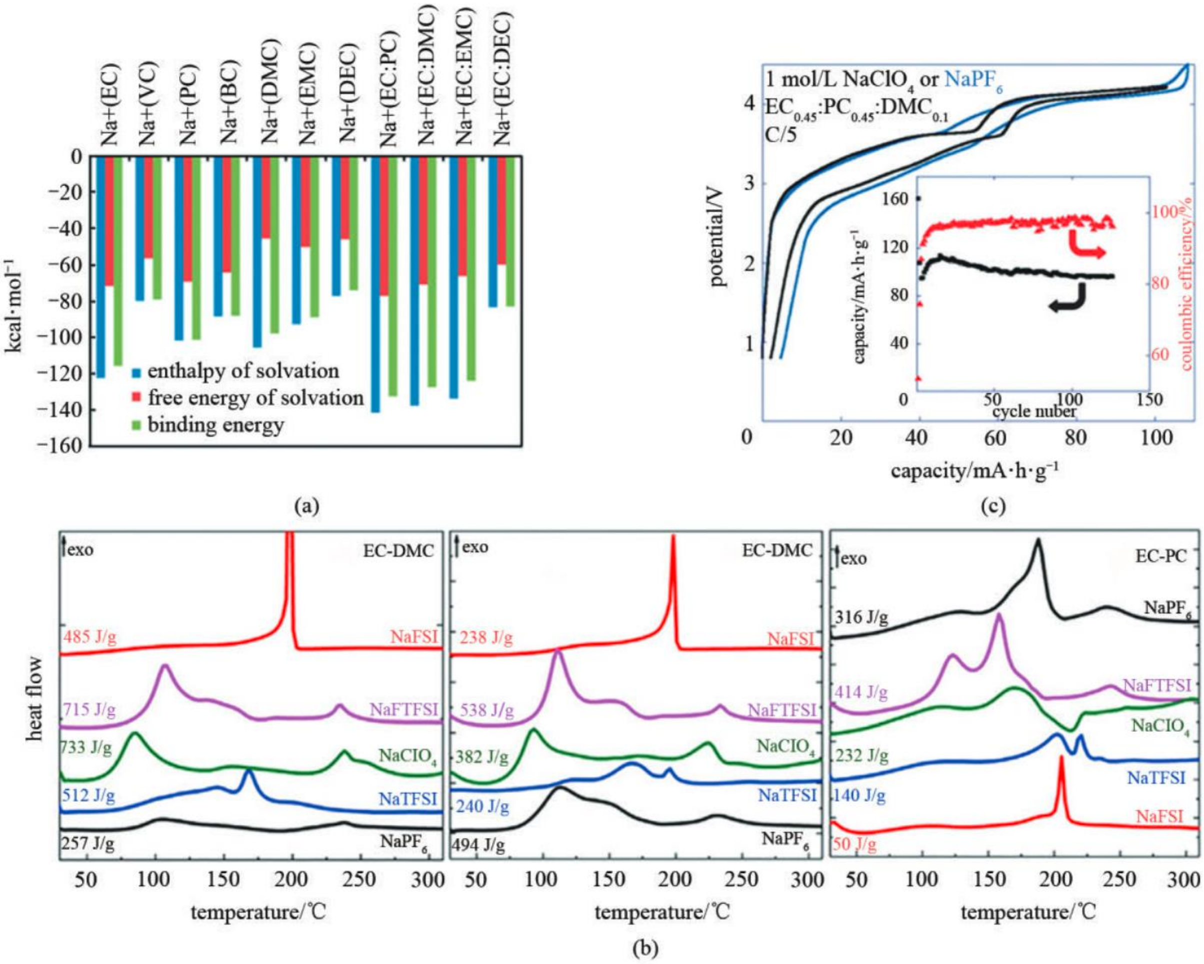

Figure. 2. (a) Three types of free energy of Na^+ ion with various carbonate solvents; (b) DSC measurements of Nax-HC electrode [5]; (c) Charge/discharge profiles for HC||NVPF full cells [9].

3.2.2. Ether electrolytes for SIBs

In carbonate-based electrolytes, Na^+ cannot form stable binary graphite intercalation compounds (b-GIC) structures between graphite layers, making it difficult for Na^+ to insert into graphite electrodes effectively and reversibly. Adelhelm et al. found that diethylene glycol dimethyl ether (DEGDME) molecules can co-embed with Na^+ between graphite layers without causing the graphite lamellar structure to peel off. The negative graphite electrode of this electrolyte has a very considerable capacity, and the storage voltage of sodium ions is relatively high (Figure 3a). This phenomenon has sparked interest in ether-based electrolytes for SIBs, and Kang et al. proposed a mechanism for Na^+ storage between graphite layers in ether electrolytes, suggesting that Na^+ co-exists with ether solvent molecular co-embedding and pseudo-capacitive behavior [10]. The reversible de-embedding of solvent zed Na^+ between graphite layers and the reversible change of graphite structure from ordered-disordered-ordered were verified by FTIR and HRTEM (Figure 3b-e). In addition, Kang et al. found that the storage plateau potential of Na^+ in graphite increased with the growth of the molecular chain length of the ether solvent (Figure 3f), which may be related to the more stable energy of the co-embedded compounds formed between the graphite layers by Na^+ and the long-chain ether solvent. Varzi et al. further found that the long-chain ether solvent was more conducive to the rearrangement of graphite particles in the electrode at the end of the sodium removal process, which could inhibit the co-integration process and result in a more complete and reversible graphite structure.

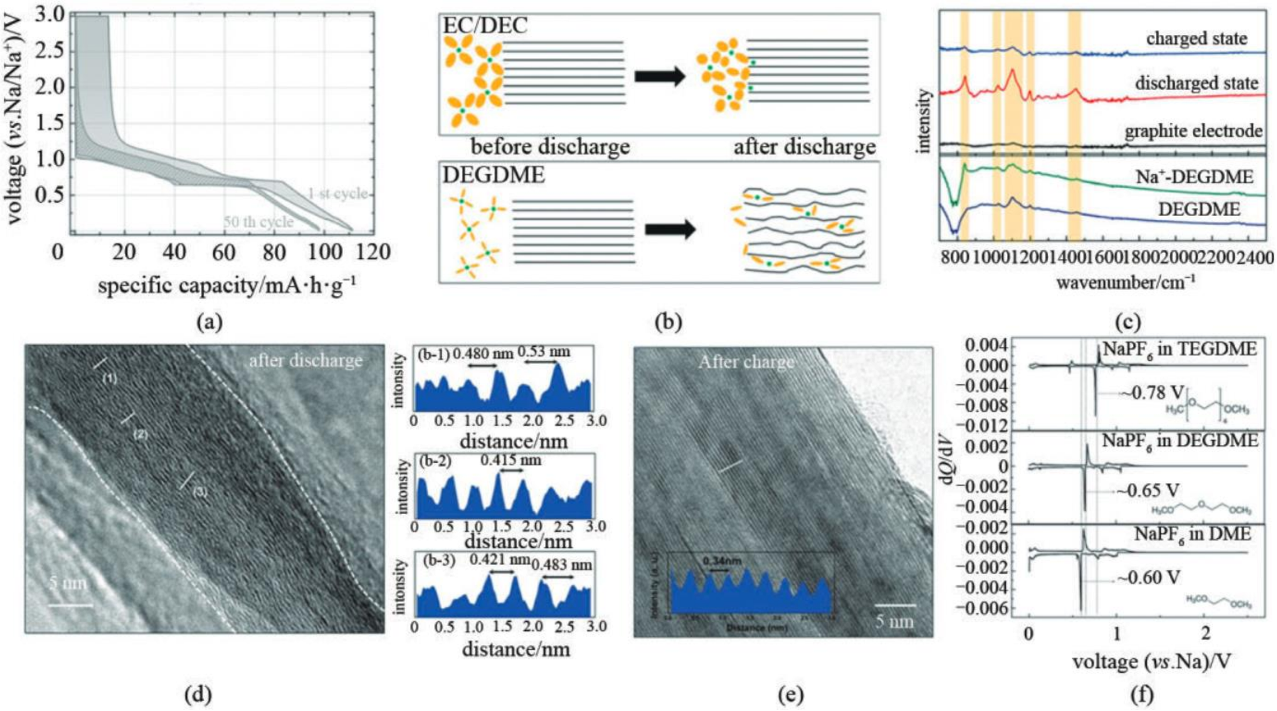

Figure. 3. (a) Charge/discharge characteristics of Na||graphite cells; (b) Schematic of sodium storage using different electrolytes. (c) FTIR analysis for the Na^+ and DEGDME co-intercalation process, HR-TEM images of natural graphite samples (d) after discharge and (e) after chargeback, (f) dQ/dV profiles of Na||graphite half cells in ether-based electrolytes with different length of ether molecules [10].

4. Solid electrolyte materials

The volatile and flammable organic solvents in the organic electrolyte of SIBs are a safety hazard during battery use, while the solid electrolyte has none of these disadvantages [2].

4.1. Solid-state polymer electrolytes

Solid-state polymer electrolyte (SPE) consists of a solid polar polymer matrix and a metal salt dissolved in it, which is a widely studied solid-state electrolyte for SIBs due to its good ductility, cost advantage, lightweight, and safety. In addition, the polymer electrolyte has good flexibility. It can easily form a good solid contact interface with the electrode material when assembling the battery, improving the battery's efficiency and cycle life. Lithium-ion solid polymer electrolytes research has been more in-depth, guiding the development of solid polymer SIEs [3].

Polyethylene oxide (PEO) is one of the earliest reported and most intensively studied solid-state polymer electrolytes due to its good solventization, complexation, and ion dissociation abilities. Qi et al. found that NaFSI-PEO has good compatibility and interfacial stability with sodium metal and

SIB cathode materials. The solid-state polymer battery with P2-type $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$(NNM) and sodium metal as the electrode materials, respectively, and $NaTFSI(PEO)_{20}$ as the electrolyte exhibited almost the same reversible capacity and polarization as the liquid battery. Liu et al. further prepared a PEO/NaFSI-Al_2O_3 solid-state electrolyte [11]. Using the hydrolytic nature of the NaFSI salt to consume the remaining solvent, NaFSI exchanged protons with H_2O in the PEO-based electrolyte to form HF, which reacted with the Al_2O_3 additive to produce a robust AlF_3-$6H_2O$ phase. The aqueous PEO/NaFSI-Al_2O_3 showed good compatibility with the $Na_3V_2(PO_4)_3$ cathode, with the solid-state battery's remarkable capacity retention rate (Figure 4).

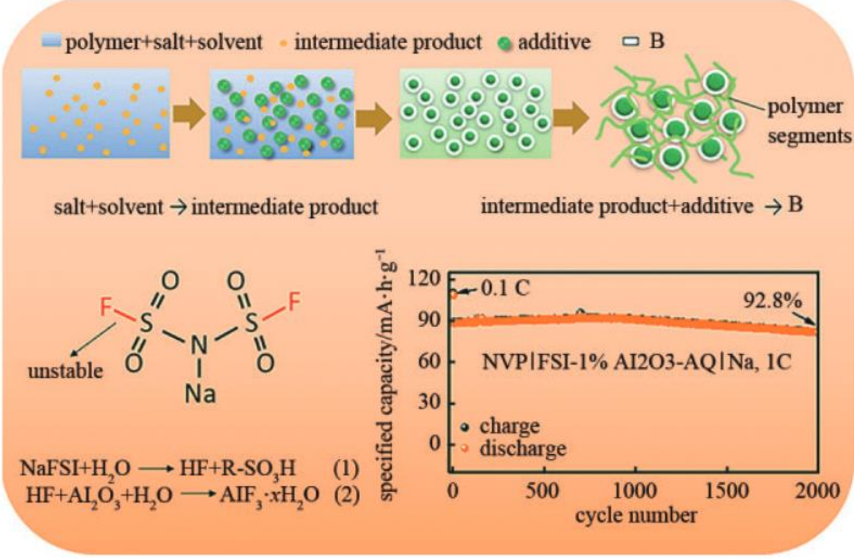

Figure. 4. Design process of NaFSI-PEO-Al_2O_3 solid polymer electrolyte using H_2O as the solvent [11].

5. Conclusion

This paper currently summarizes several electrolyte materials with good performance for sodium ion batteries. The aqueous electrolyte is an economical and reliable because of its good ionic conductivity and flows characteristics. Solid electrolytes effectively avoid the safety hazards of organic electrolytes with flammability and volatility in liquid electrolytes, and the application of solid electrolytes can effectively improve the efficiency and cycle life of batteries. Different types of electrolyte materials are suitable for different application scenarios of sodium-ion batteries, and we should consider the selection of electrolyte materials from various aspects such as performance, cost, and environmental friendliness.

After more than 30 years of rapid development, SIBs have the most potential for industrialization. The vast availability of sodium resources, the wide temperature range, fast charging and discharging, and the high safety characteristics of SIBs give them a natural first-mover advantage for large-capacity power storage devices. However, the current SIBs still need to be improved, and the authors would like to summarize the development of electrolytes for SIBs. For electrolyte materials, accurate SEI or solemnization models should be developed to guide the formation of functional protective layers at the electrodes; the interaction between active materials, conductive additives, and binders on the formation and influence of SEI should be further investigated. In addition, the concentration and formulation of the electrolyte should be rationalized, considering cost, and compatibility with carbon cathodes for high-voltage applications. In addition, considering the fundamental security of aqueous and solid electrolytes, solid and aqueous SIBs have attracted extensive research interest, but issues need to be addressed before they can be used in practice. Overall, SIBs will change the energy storage landscape with their low cost, wide temperature range, long life, ease of manufacture, high safety, and high multiplicity.

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