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Advantages and Sustainability of Sodium-Ion Batteries Integrated with Fire Suppressants: A Pathway to Safer and Greener Energy Storage

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Abstract: Sodium-ion batteries (SIBs) are gaining attention as safer and cost-effective alternatives to lithium-ion batteries, but challenges remain in improving their safety, performance, and sustainability. This study explores advancements in electrolyte additives, polymer electrolytes, separators, and poly-ionic membranes to enhance SIB efficiency and safety. Sodium bis(oxalato)borate (NaBOB) was identified as a non-flammable and fluoride-free alternative to toxic $NaPF_6$ in trimethyl phosphate (TMP), achieving thermal stability up to 300°C, high ionic conductivity (5×10^{-3} S cm^{-1}), and 97% coulombic efficiency. Incorporating vinylene carbonate (VC) mitigates discharge capacity degradation over cycling.

Flexible polymer electrolytes, such as PPEGMA-gel systems, demonstrate resilience to mechanical shocks with a capacity retention of 91% after 400 cycles and a wide voltage range of 4.8 V, though high-temperature performance requires further investigation. Organic electrolyte blends with 10 vol% fluoroethylene

carbonates (FEC) improve electrode stability, enabling energy densities of up to 1246 Wh kg^{-1} after 300 cycles. Advanced separators, such as ZrO_2/PVDF-HFP-coated polyolefins, exhibit enhanced Na^+ conductivity (7×10^{-4} S cm^{-1}) but require ceramic modifications for higher thermal resilience, achieving stability up to 500°C with barium titanate integration.

Hierarchical poly-ionic liquid-based solid electrolytes (HPILSE) outperform conventional membranes in flexibility, thermal stability (up to 300°C), and resistance to mechanical stress. Future studies are essential to optimize ionic conductivity through additive research. This comprehensive exploration of materials and configurations offers promising directions for the development of safe, efficient, and durable sodium-ion batteries.

Keywords: Sodium-ion batteries, NaBOB, non-flammable electrolytes, ionic conductivity, thermal stability, polymer electrolytes, energy density, cycle stability

Introduction: The increasing adoption of sodium-ion batteries (SIBs) as a sustainable and cost-effective alternative to lithium-ion batteries (LIBs) has drawn considerable attention in recent years [7], [8]. This shift toward SIB technology is driven by several key factors, including the abundant availability of sodium resources, the lower production costs associated with sodium-based materials, and the potential for reduced environmental impact when compared to LIBs. With these advantages, SIBs have emerged as a promising energy storage solution, particularly in applications such as renewable energy grids, large-scale storage systems, and electric vehicles (EVs). However, alongside these opportunities comes a set of unique challenges that must be addressed to ensure their safe and reliable integration into modern energy systems.

Safety is a critical concern for any battery technology, and sodium-ion batteries are no exception. While LIBs have been extensively studied for decades, their well-documented issues with thermal runaway and associated fire hazards have led to the development of various fire suppression and mitigation strategies [9]. However, the application of these strategies to SIBs is not straightforward. The distinct chemical and physical properties of sodium-ion batteries necessitate a reevaluation of their safety profile. Thermal runaway: a self-sustaining, exothermic reaction sequence triggered by factors such as overcharging, mechanical damage, or internal short-circuits poses a significant risk for SIBs. In the event of thermal runaway, the heat generated can ignite the electrolyte or other flammable components within the cell, leading to fire or even explosion [10]. This issue becomes particularly concerning in large-scale applications where a single-cell failure can propagate to neighboring cells, resulting in catastrophic damage.

The chemical behavior of sodium-ion batteries differs from that of lithium-ion systems due to the unique characteristics of sodium. Sodium's larger ionic radius influences ion transport dynamics, electrode interactions, and electrolyte formulations. These differences, while advantageous in certain respects, also introduce complexities in terms of safety. For instance, the flammability and combustion pathways of SIB electrolytes and electrode materials may diverge from those observed in LIBs, necessitating dedicated research to understand these processes [11]. Moreover, the higher reactivity of sodium compared to lithium under certain conditions can exacerbate fire hazards, particularly when exposed to air or moisture [12]. These factors underline the importance of developing tailored fire suppression strategies that address the specific risks associated with sodium-ion technology.

Fires in sodium-ion batteries can originate from various triggers, including overcharging, mechanical abuse, or manufacturing defects that result in internal short-circuits [13]. Overcharging, for example, can lead to the breakdown of electrolyte components and the release of flammable gases, which can ignite under high temperatures. Mechanical damage, such as that caused by impact or puncture, can compromise the battery's structural integrity and expose reactive materials to the external environment [14]. Internal short-circuits, often arising from dendrite formation or separator failure, create localized hot spots that can initiate thermal runaway. Once thermal runaway begins, the exothermic reactions within the cell release significant amounts of heat and gas, creating a feedback loop that accelerates the process [15]. The resulting flames and toxic emissions pose severe risks to both human safety and infrastructure, particularly in enclosed environments such as EV battery packs or energy storage facilities.

Traditional fire suppression systems designed for LIBs may not be fully effective for sodium-ion batteries due to the differences in chemical composition and combustion behavior. For example, LIB fire suppression often relies on halogenated compounds, foam-based extinguishers, or inert gas systems to suppress flames and cool the affected area. While these methods have demonstrated efficacy in lithium-based systems, their applicability to SIBs remains uncertain [16], [17].

Sodium-ion cells may exhibit distinct flammability characteristics or produce different combustion byproducts, which could render conventional suppressants less effective or even counterproductive [18]. As a result, there is an urgent need for research into specialized fire suppression technologies tailored to sodium-ion batteries.

One promising avenue of research involves chemical suppressants designed to interrupt the combustion process at a molecular level. These suppressants may include powdered agents, such as sodium bicarbonate or specialized phosphate-based compounds, that act by smothering flames and absorbing heat [19]. Gas-based systems, such as those employing carbon dioxide or nitrogen, offer another approach by displacing oxygen in the vicinity of the fire and reducing the likelihood of re-ignition [20]. Thermal barriers, including intumescent coatings or phase-change materials, can also play a critical role in preventing the spread of heat and fire between cells within a battery module [21]. These solutions, while conceptually promising, must be rigorously tested under realistic conditions to evaluate their effectiveness and feasibility for large-scale deployment.

This paper aims to provide a comprehensive review of the current state of research on fire suppression technologies for sodium-ion batteries. It examines a range of approaches, including chemical suppressants, gas-based systems, and thermal barriers, to identify their strengths and limitations. By analyzing the effectiveness of these methods in preventing or mitigating fire propagation, the review seeks to highlight key areas where further research is needed. Particular attention is given to the unique chemistries of sodium-ion systems, which demand a tailored approach to safety and fire suppression. In doing so, this paper aims to bridge the gap between theoretical understanding and practical application, offering insights that can guide the development of next-generation safety solutions for sodium-ion batteries.

The transition to sodium-ion technology represents a significant step forward in the quest for sustainable energy storage solutions. However, ensuring the safety and reliability of these systems is paramount to their success. By addressing the challenges associated with fire hazards and thermal runaway, the research community can pave the way for the widespread adoption of sodium-ion batteries in diverse applications. This review contributes to that effort by synthesizing existing knowledge, identifying critical gaps, and proposing pathways for future innovation in fire suppression for sodium-ion systems. Through collaborative efforts spanning academia, industry, and regulatory bodies, it is possible to unlock the full potential of sodium-ion technology while safeguarding against its inherent risks.

METHODOLOGY

This study investigates advancements in materials and configurations for sodium-ion batteries (SIBs), focusing on electrolyte additives, polymer electrolytes, separators, and poly-ionic membranes. The methodology is designed to evaluate material properties, performance metrics, and safety aspects of these components under controlled laboratory conditions.

Materials Synthesis and Preparation

Electrolyte Systems

Non-Flammable Electrolyte: Sodium bis(oxalato)borate (NaBOB) was synthesized and dissolved in trimethyl phosphate (TMP). Vinylene carbonate (VC) was added to mitigate discharge capacity degradation. Ionic conductivity, thermal stability, and coulombic efficiency were tested.

Polymer Electrolytes

Flexible Gel Polymer Electrolyte: Poly(polyethylene glycol methyl ether methacrylate) (PPEGMA) gels were synthesized and evaluated for cycling stability and resilience to mechanical stress.

Separator Development

ZrO_2/PVDF-HFP Coatings: Polyolefin separators were coated with ZrO_2 and PVDF-HFP for enhanced Na^+ conductivity. Ceramic modifications with barium titanate were incorporated to achieve higher thermal resilience.

Characterization Techniques:

Thermal Stability: Thermogravimetric analysis (TGA) was conducted to determine degradation temperatures.

Ionic Conductivity: Electrochemical impedance spectroscopy (EIS) was used to measure Na^+ conductivity.

Hierarchical Poly-Ionic Liquid-Based Solid Electrolytes (HPILSE)

Fabrication: HPILSE membranes were synthesized using hierarchical structuring methods to enhance flexibility and ionic conductivity. Additive research was conducted to optimize ionic pathways.

Performance Metrics: Thermal stability and mechanical stress resistance were evaluated at temperatures up to 300°C.

Electrochemical Testing

Cell Assembly:

SIB prototypes were assembled with the developed electrolytes, polymer systems, and separators.

Standardized half-cell and full-cell configurations were used with sodium metal as the counter electrode.
Testing Protocols:
Cycling Stability: Capacity retention was measured over 300–400 charge-discharge cycles.
Energy Density: Gravimetric energy densities were calculated after cycling.
Voltage Range: Cycling performance was tested across a wide voltage range (up to 4.8 V).

Safety Assessments

Thermal Resilience: Thermal stability was tested for separators and electrolytes at temperatures up to 300°C.
Mechanical Shock Resistance: Polymer electrolytes and HPILSE membranes were assessed under simulated operational conditions to evaluate their durability.

Additives to Electrolytes for Safety against Thermal Runaway Situations

Use of NaBOB as non-flammable additive to Electrolyte-TMP (Tetramethyl phosphate) instead of highly toxic NAPF$_6$.

A study was conducted to find an electrolyte mixture to make the Na-ion batteries non-flammable. So far, in the previous research, the additives added are high concentrations of Fluoride or salt, which would increase the const of production and toxicity like toxic hexafluorophosphate (NaPF$_6$). However, this study has come up with sodium bis(oxalato)borate (NaBOB), that added to nonflammable solvent trimethyl phosphate (TMP), due to its solvability. This study also found that NaBOB salt is stable until 300^{0}C, compared to 140^{0}C with NaPF$_6$. This combination promises an ionic conductivity of 5 X 10^{-3} S cm^{-1} (at 0.5 M NaBOB) at room temperature, with 97% coulomb efficiency and fluoride free alternative to costly and highly toxic NaPF$_6$ [1]. Figure 1 shows the conductivity of NABOB and NAPF$_6$ at various concentrations

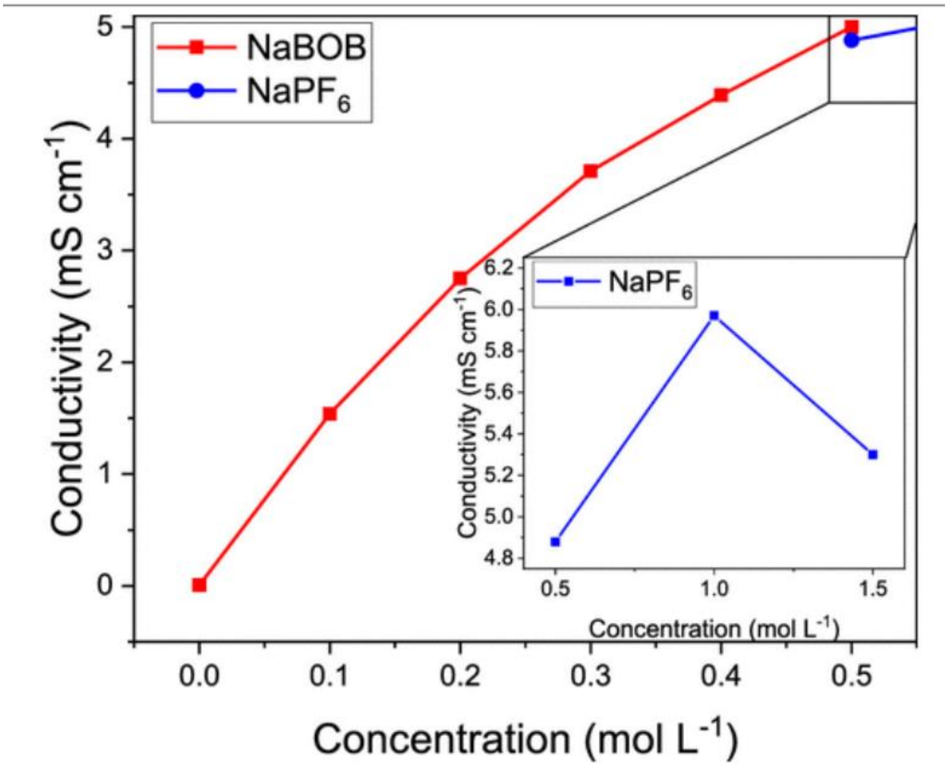

Figure 1: Conductivity vs Concentration for NaBOB and NAPF$_6$ [1]

However, the discharge capacity goes down with the number of cycles. To combat the drop, 5 and 10 vol% of vinylene carbonate (VC) can be added, and this greatly improved the discharge capacity as shown in the following figure 2.

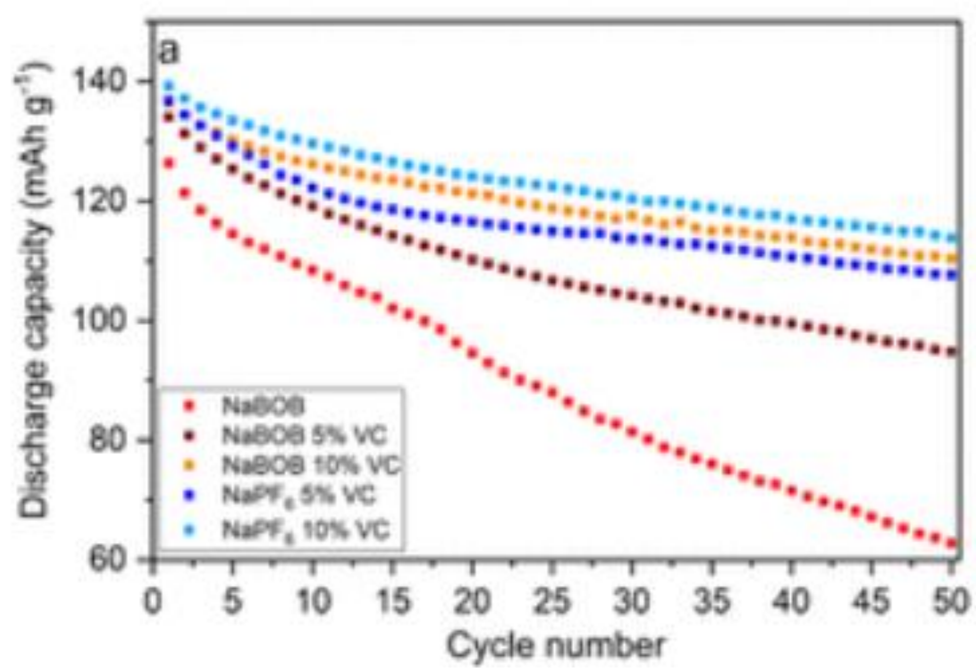

Figure 2: Charge cycles vs discharge capacity for NaBOB and NAPF$_6$ [1]

Organic Polymer Electrolyte with decent ionic conductivity

Numerous studies have shown that batteries experience high amplitude shocks especially while installed on EVs. This may not be a problem unless the amplitudes are high enough to flex the batteries that triggers thermal runaway. To tackle such events, many researches were done to improve the flexibility of the battery. One such study focused on developing the polymer electrolyte gel.

However, these gels are constrained by low ionic conductivity at room temperatures. A study performed by Guanghai Y. [2] and his team and came up with flexible PPEGMA-gel polymer electrolyte (GT32-5%) was prepared via in-situ thermal cured technique, plasticized by nonflammable triethyl phosphate and supported by glass fiber.

This electrolyte exhibited capacity retention of 91% after 400 charge and discharge cycles, 9.1 X 10^{-4} S cm^{-1} at 27 °C and the wide voltage range of 4.8V. This shows that there is a potential area that needs to be explored more to make batteries safer to operate. Even though this electrolyte is good with the mechanical vibrations and shocks, the paper doesn't specify the performance at a higher temperature. This demands some research that needs to be carried out to include fire suppressants, which are discussed in the study below.

10 vol% FEC additives to Organic Electrolytes for safe batteries

A study was performed with Phosphorous electrolyte (Trimethyl phosphate, TMP with and without 10 vol% FEC (Fluoroethylene carbonate)) with $NaNi_{0.35}Mn_{0.35}Fe_{0.3}O_2$ cathode and Sb-based alloy anode has a decent ionic conductivity, cyclic voltammetry, & charge–discharge capacities (490 $mAhg^{-1}$ after 1st cycles, capacity retention of 86% after 50 cycles) and no ignition is seen when tried to trigger. The FEC's main purpose is to enhance the stability of the electrode surface at high temperatures (80°C) and improve battery performance. The electrochemical range is between 0-4.5 volts as shown in figure 3. The major drawback with the 0.8M $NaPF_6$ additive, which has fluoride in its chemistry makes it toxic to produce on a large scale [3].

However, in the recent research it was found that inorganic electrolyte composition of NaTFSI/TMP+FEC electrolyte delivers a remarkable reversible capacity of 788 mAh g^{-1} (Energy density 1246 Wh Kg^{-1}) after 300 cycles at 1C [4]. With the Room Temperature (RT) Sodium as an anode and sulfur/carbon composite as cathode. With this in mind, organic electrolytes need more research and advancement to improve the number of cycles with decent capacity retention.

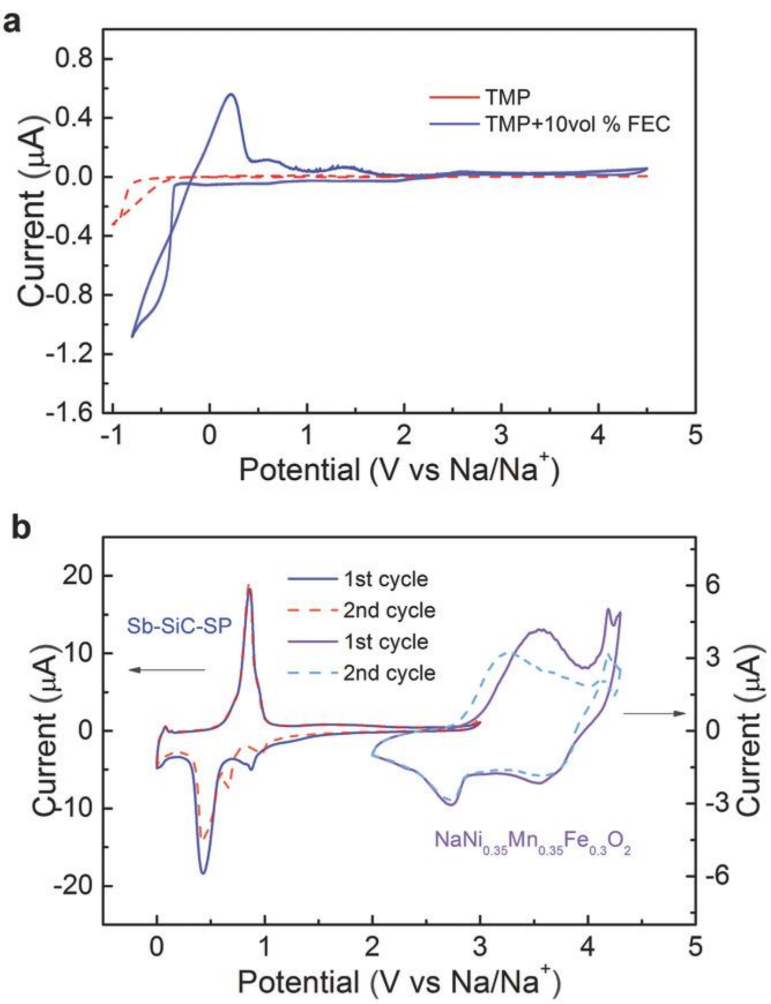

Figure 3: Cyclic voltammograms of a) 0.8 m $NaPF_6$/TMP electrolyte with or without 10 vol% FEC b) the Sb-based anode and $NaNi_{0.35}Mn_{0.35}Fe_{0.3}O_2$ cathode materials in 0.8 m $NaPF_6$/TMP + 10 vol% FEC [3]

High Safety Separators for SIBs

The separators from LIBs can't be directly used in SIBs due to the wettability uses (low ionic conductivity). Research has performed on polyolefin (PE (C_nH_{2n})) separators, however as mentioned above they have poor wettability with Na^+ ionic conductivity. To make it a better performer a layer of ZrO/PVDF-HFP coating can be used making Z-PE as shown in the following figure 4

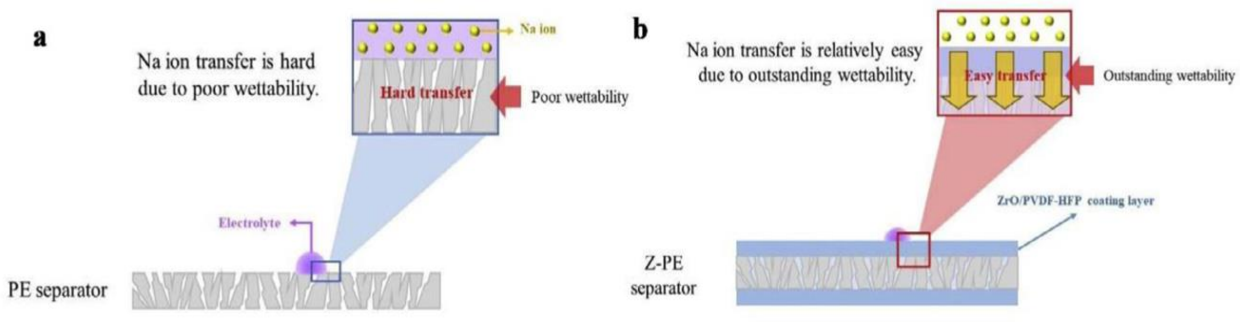

Figure 4: Schematic illustration of Na+ transfer paths in (a) PE separator (b) and Z-PE separator [5].

These Z-PE separators exhibited decent ionic conductivity of 7 X10^{-4} S cm^{-1}. However, the thermal stability of these separators tends to be very low, with a 20% shrinkage at 200^0C. With the addition of porous ceramic membrane (PCM) by incorporating barium titanate ($BaTiO_3$) in PVDF-HFP/poly (butyl methacrylate) (PBMA) polymers, the separator withstood the temperatures of 500^0C [5]. This application can make the batteries very safe even in harsh environments

Poly-Ionic Electrolyte with relevant membrane for More Safety

A study found that poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (PDDATFSI) porous membrane, when integrated with 1,4-bis[3-(2-acryloyloxyethyl)imidazolium-1-yl]butane bis[bis(trifluoromethanesulfonyl)imide] (C1-4TFSI based Ionic gel), a uniform transparent film with high resistance to the mechanical fluctuations is formed that is hierarchical poly (ionic liquid)-based solid electrolyte (HPILSE). The stress and strain curve are plotted for pristine PDDATFSI and Li-HPILSE in figure 5. The plot conveys the HPILSE can flex over 15% compared to 7% by PDDATFSI before failure. Besides, the mechanical properties, the HPILSE even demonstrates higher thermal stability between 10^{0}C through 300^{0}C (with weight loss of just under 6.5%) as shown in figure 6 when compared to commercial carbonate electrolyte with polyolefin separator.

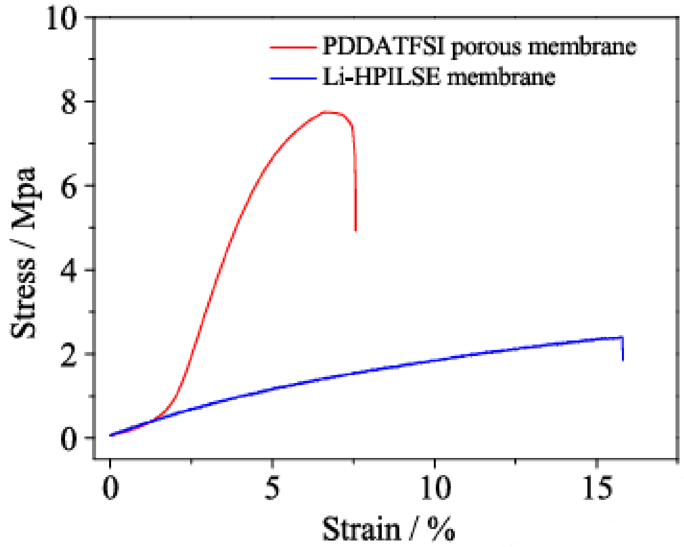

Figure 5: stress–strain curves of PDDATFSI porous membrane and Li-HPILSE membrane [6]

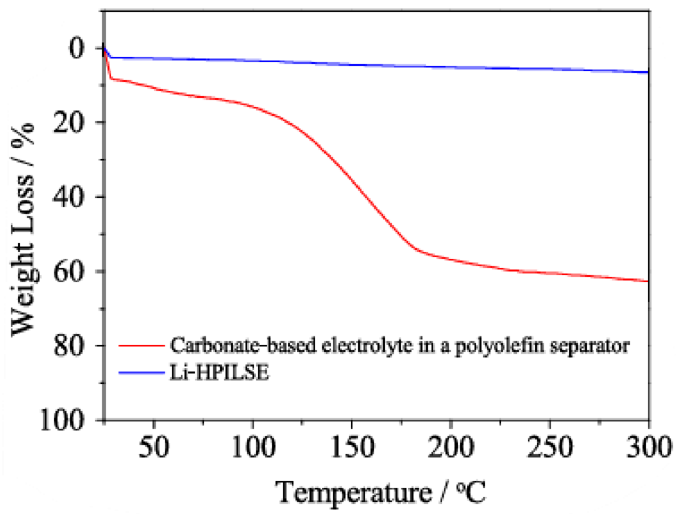

Figure 6: Weight Loss % with increase in temperature of carbonate-based electrolyte in a polyolefin separator and Li-HPILSE [6]

When it comes to electrolyte, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI)-based electrolyte is recommended, with Na-EMITFSI-based electrolyte (0.5M NaTFSI in EMITFSI with 10wt% FEC), even though it has higher thermal stability, the ionic conductivity is relatively at 1.8 X 10^{-4}S cm^{-1}. However, future research on additives is necessary to improve the ionic conductivity [6].

Future Work

This study highlights several advancements in sodium-ion battery (SIB) technology, but there remain opportunities for further exploration to optimize safety, performance, and cost-effectiveness. The following areas are proposed for future research:

Enhancing Discharge Capacity Retention: The use of NaBOB and vinylene carbonate (VC) shows promise, but the decline in discharge capacity with cycling requires additional studies. Future work could explore alternative additives or combinations to enhance long-term performance without compromising safety.

Thermal Stability Improvements: Polymer electrolytes, such as PPEGMA-gel and Z-PE separators, demonstrate improved mechanical resilience, but their thermal stability remains a concern. Research should focus on integrating fire-resistant additives or advanced materials to withstand extreme conditions, particularly in electric vehicle (EV) applications.

Optimization of Organic Electrolytes: While TMP-based electrolytes with FEC additives exhibit favorable properties, their cycle life and capacity retention need improvement. Further studies should explore alternative organic compounds or synergistic additives that could maintain ionic conductivity and stability at elevated temperatures

Advanced Separators: High-performance separators like Z-PE and PCM-incorporated membranes show potential but still require enhanced durability under operational stresses. Future studies could focus on optimizing ceramic-polymer composites for increased mechanical and thermal stability.

Development of Poly-Ionic Electrolytes: The hierarchical poly(ionic liquid)-based solid electrolyte (HPILSE) demonstrates mechanical flexibility and thermal stability but suffers from limited ionic conductivity. Research on novel additives or modifications to the ionic gel matrix could address this limitation.

Cost Reduction Strategies: A focus on finding cost-effective, non-toxic, and scalable alternatives to current materials, such as fluoride-free additives and NaTFSI derivatives, is necessary to accelerate commercial adoption of SIBs

CONCLUSIONS

This study presents significant progress in addressing key challenges in sodium-ion battery technology, including flammability, toxicity, and mechanical resilience. Sodium bis(oxalato)borate (NaBOB) emerges as a promising fluoride-free alternative to $NaPF_6$, offering enhanced thermal stability and non-flammability. Similarly, innovations in polymer electrolytes, organic electrolyte formulations, and separators highlight viable pathways for safer, more efficient batteries.

However, these advancements are accompanied by challenges such as cycle life degradation, limited ionic conductivity, and thermal performance gaps, particularly under high-temperature conditions. Collaborative efforts in material science, electrochemistry, and engineering are essential to overcome these obstacles.

With continued research into safer additives, flexible and thermally stable separators, and cost-effective electrolyte formulations, sodium-ion batteries can play a pivotal role in enabling sustainable and safe energy storage solutions for future applications, particularly in electric vehicles and grid-scale storage.

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CONFLICT OF INTEREST STATEMENT

NA

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