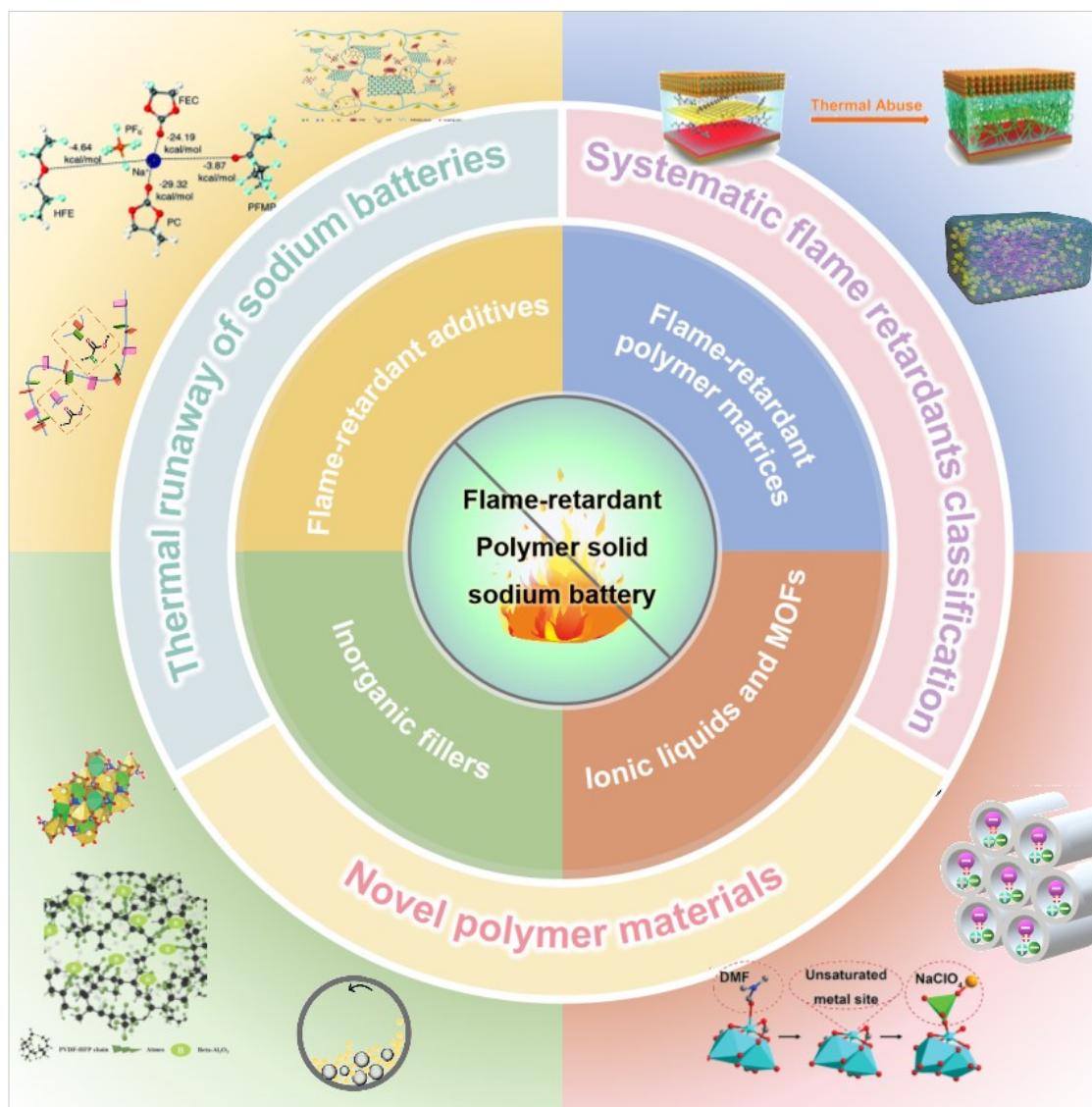


Flame-Retardant Polymer Electrolyte for Sodium-Ion Batteries

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Sodium-ion batteries present an appealing option for large-scale energy storage applications due to their high natural abundance and low production costs. However, the safety issue remains a major obstacle in current development, primarily owing to the use of liquid electrolytes (LEs), which can lead to leakage and combustion. To achieve both high energy density and enhanced safety, researchers are increasingly focusing on solid-state electrolytes (SSEs). Solid-state polymer electrolytes (SPEs) have garnered notable attention due to their superior mechanical flexibility and electrochemical stability. Nonetheless, traditional SPEs can also undergo combustion and decomposition under extreme conditions due to polymer inherent flammability. Therefore, it is imperative to conduct research and

design flame-retardant SPEs in order to enhance their reliability and safety in practical applications. This review provides a comprehensive overview of the mechanisms underlying battery thermal runaway and offers guidance for designing batteries with enhanced safety. In addition to reviewing recent advancements in flame-retardant polymer solid-state sodium battery research, it also presents a systematic classification and introduction of studies on high-safety polymer electrolytes. Furthermore, it delves into diverse perspectives and approaches towards addressing the issue of safety in polymer sodium battery, ultimately outlining future research directions for this particular field.

1. Introduction

Lithium-ion batteries (LIBs) have rapidly developed since their commercialization in the 1990s and have quickly dominated the consumer market due to their excellent performance.^[1–3] In recent years, with the blooming development of new energy vehicles and other industries, the demand for energy storage systems is increasing, stimulating the vigorous development of rechargeable batteries other than lithium-ion batteries. Sodium-based batteries are considered as the promising substitute for lithium-based batteries because of the similar physicochemical properties with lithium metal, the wide distribution and low cost, so they are expected to be used in large-scale energy storage. Furthermore, the increasing demand for higher energy densities has prompted the exploration of alternative anodic materials, sodium metal stands out as a promising candidate due to its high theoretical specific capacity (1165 mAh g^{-1}) and low redox potential (-2.71 V vs. SHE). Nevertheless, the broader adoption of metal batteries remains impeded by their serious safety concerns.^[4–6]

The conventional organic LEs system currently used in sodium-based batteries, such as ethylene carbonate (EC) and propylene carbonate (PC), cause serious safety problems due to its volatility, leakage, and flammability. These characteristics lead to them easy to be ignited and release large amounts of toxic gases during thermal runaway. Simultaneously, the issues of inferior mechanical properties and diminished interface stability can precipitate a significant degradation of the electrode/electrolyte interphase. This deterioration can manifest in the form of severe sodium dendrite proliferation, which poses a substantial risk of internal short circuit in the battery.

Such events can markedly shorten the operational lifespan of the battery. Instead, the SSEs serve as an effective upgrade for organic LEs since they offer high energy density, improved safety, and can match sodium metal and high-voltage cathode.^[7,8] Among them, the SPEs has attracted wide attention due to its low cost, easy processing and soft texture. SPEs are anticipated to find widespread application in flexible electronics and large-scale energy storage due to their superior mechanical flexibility and electrochemical stability.^[9–11] Poly(ethylene oxide) (PEO) with high molecular weight is widely used as the SPEs due to its good mechanical properties and electrode compatibility. The presence of $-\text{CH}_2-\text{CH}_2-\text{O}-$ repeating unit in the polymer chains allows the complexation of sodium ions (Na^+), while the segmental motion of the backbone offers sufficient ion dynamics to exhibit high sub-conductivity and good film-forming capability.^[12,13] Polyacrylonitrile (PAN) contains polar electron-withdrawing nitrile group CN, which has excellent electrochemical stability, a broad electrochemical window, good thermal stability, and considerable mechanical strength. In particular, the high oxidation potential of the PAN-based electrolyte allows it to be adapted to high-voltage cathode materials to achieve high energy density.^[14,15] The strong electron-withdrawing C–F functional group endows polyvinylidene fluoride (PVDF) with relatively high polarization and dielectric constant ($\epsilon=8.4$), which is conducive to the dissolution of salts.^[16,17] Although there is no risk of leakage and volatilization compared to the liquid electrolyte, the polymer itself is generally combustible.^[18,19]

When exposed to sufficient heat, the polymer undergoes thermal decomposition, causing polymer chain breakage, the release of volatile fragments, and the formation of flammable gas mixture.^[4,20,21] The polymer combustion process is a complex physical and chemical process, polymer absorbs external heat at the beginning, resulting in temperature elevation and physical transformations such as softening, melting, and expansion. As temperature rises, the polymer tends to pyrolysis and decompose into smaller molecules, which include combustible molecules such as hydrocarbons, alcohols, ketones. The pyrolysis process involves various chemical reactions including random decomposition, depolymerization, cyclization, and crosslinking. When the concentration of the combustible gas reaches a certain level (combustion limit) and the temperature

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rises to the ignition point of the polymer, it begins to burn. This process may be accompanied by the generation of a flame. More seriously, the heat from combustion propagates to adjacent materials via heat transfer and if the heat is sufficient to sustain the combustion state, the polymer will continue to burn. During the combustion process, the combustion characteristics of the polymer (such as combustion rate, heat release rate, smoke production) are affected by its chemical structure, molecular weight, additives, and environmental conditions like oxygen concentration and temperature.^[20,22] Consequently, the solid-state polymer battery also has the risk of thermal runaway. These dangers could endanger battery performance in addition to seriously undermining users' safety. Therefore, researching and creating flame-retardant SPEs is crucial.

This review initially delves into the mechanism underlying battery thermal runaway and proposes valuable insights for the design of safe batteries. Subsequently, recent advances on flame-retardant polymer solid-state sodium batteries are comprehensively reviewed. Various studies on high-safety SPEs are systematically classified and presented, while diverse perspectives and methodologies are explored to solve the safety concerns associated with polymer sodium batteries. Finally, future research directions for safe polymer sodium batteries are outlined. With the continuous improvement in demand for battery safety and energy density, high-safety solid-state polymer sodium batteries can effectively tackle these challenges.

2. Flame-Retardant Polymer Electrolyte

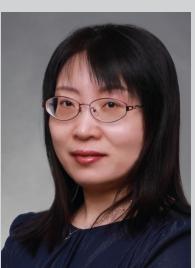
2.1. Thermal Runaway of Sodium Batteries

The initial phase of thermal runaway is usually triggered by abnormal conditions inside the battery, such as mechanical abuse (extrusion or impact), electrical abuse (overcharge or short circuit), or thermal abuse (high temperature exposure), resulting in a sharp rise in the battery temperature, which may eventually lead to fire or explosion.^[23,24] When the battery temperature exceeds the safe operation limit, it experiences a heat-temperature-reaction (HTR) cycle. Within this cycle, the heat triggers an exothermic chemical reaction that generates additional heat, resulting in a faster temperature rise. The thermal runaway process shows in Figure 1 usually involves the

following key steps: (1) Decomposition of solid electrolyte interphase (SEI): Thermal runaway is usually accompanied by the SEI decomposition on the surface of anode. The temperature at this time is the critical temperature for thermal safety (T_1), which is the triggering factor of exothermic chain reactions. The SEI is a passivation film formed when the battery is charged and discharged, protecting the anode material and allowing Na^+ to pass through. In the T_1 stage, the SEI layer breaks down, releasing heat and gas. (2) Decomposition of electrolyte: As the temperature further increases, the organic solvents of LEs begin to decompose, releasing more heat and combustible gases. These gases may include flammable organic solvent vapors, further increasing the risk of the battery catching fire. (3) Battery separator melting: When the temperature is high enough to trigger thermal runaway (T_2), the battery enters a critical state with uncontrollable reactions. At this point, the chemical reaction inside the battery accelerates accompanied by rapidly incremental heat production, resulting in a sharp elevation of the battery temperature. Consequently, the separator material melts, facilitating direct contact between the anode and cathode, forming an internal short circuit. This short circuit can quickly increase the current inside the battery, creating a lot of joule heat. (4) Decomposition of cathode materials: The rise in temperature may lead to a phase transformation and subsequent breakdown of the cathode material. This can result in the release of oxygen, when an organic solvent in the electrolyte combines with the oxygen, a dramatic exothermic reaction could occur. (5) Chain reaction: The elevated temperature and gas produced in the above process can initiate the chain reaction, resulting in a rapid increase in the battery's internal temperature. This establishes a vicious cycle known as the HTR cycle. Ultimately, thermal runaway leads to a rapid escalation of the battery temperature to the maximum level attained during thermal runaway (T_3), exceeding the ignition point of the organic component. The combustible gas inside the battery, when mixed with oxygen and exposed to high temperatures, undergoes a violent chemical reaction that invariably leads to combustion or explosion.^[25–30] Given the complexity and severity of thermal runaway, designing safe SPEs becomes even more important and challenging.



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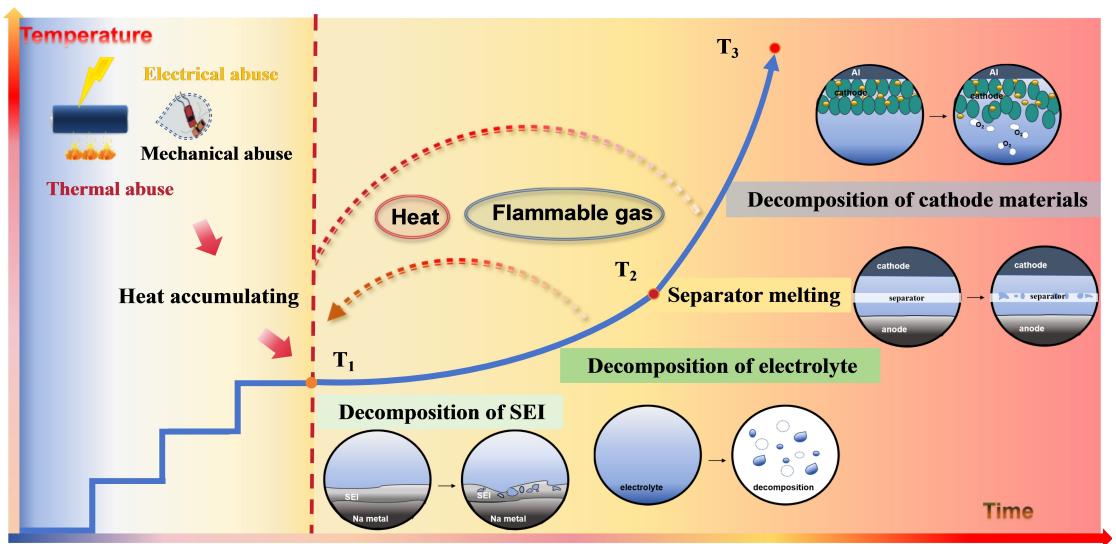


Figure 1. Schematic diagram of battery thermal runaway.

2.2. Flame-Retardant Additives

After exploring the whole process mechanism of battery thermal runaway, a variety of strategies have been proposed to enhance the flame retardancy of polymer electrolytes, the most commonly used method is to add flame-retardant additives to the polymer. Based on the mechanism of polymer pyrolysis and combustion decomposition process, these flame-retardant additives can be categorized as follows:

- (1) Free radical scavengers: This type relies on interrupting combustion chain reactions. During battery thermal runaway, combustible substances in the electrolyte break down, generating free radicals that initiate or accelerate combustion. Additives interrupt the combustion chain reaction by trapping highly reactive free radicals (such as H[•] and OH[•]) produced during combustion.^[31] For instance, phosphate radicals (e.g., PO[•] and PO₂[•]) generated from phosphorus-based flame retardants during decomposition can react with H[•] and OH[•] free radicals, reducing heat accumulation during combustion, thereby decreasing the risk of fire and explosion.
- (2) Formation of protective layer: Additives facilitate the formation of a carbonized or vitrified protective layer on the material surface during combustion.^[11,32] This layer inhibits combustion reactions by isolating oxygen, while also slowing down the diffusion of heat and combustible gases, thereby retarding the thermal runaway process.
- (3) Dilution of flammable gas concentration: This approach reduces the risk of combustion by diluting the concentration of combustible gas in the polymer.^[33,34] For instance, halogen-based flame-retardants decompose to hydrogen halide (HX) when heated, which is a non-combustible gas that can dilute the oxygen content and inhibit combustion.
- (4) Improvement of thermal stability: Certain flame-retardant additives enhance the thermal stability of polymers, making them less prone to decomposition at high temper-

atures or reducing the rate of polymer burning.^[35,36] Alternatively, additives can enable polymer continuous polymerization when heated, absorbing heat as chain length increases. This approach raises the temperature at T₂ and increases the difficulty of thermal runaway. In some instances, the synergistic effect of combining multiple flame-retardant additives will enhance material flame retardancy more effectively than a single additive. For example, the combination of halogen additives and inorganic fillers results in excellent flame retardant properties while maintaining considerable electrochemical properties.^[37] Subsequently, the specific mechanism of action of various flame-retardant additives and their performance in different applications will be discussed in detail, aims to provide theoretical and practical guidance for optimizing flame retardant formulations and achieving higher safety standards in electrolyte design.

2.2.1. Halogen-Based Additives

Halogen-based additives possess the advantages of low viscosity, high solubility, and excellent low-temperature performance, rendering them widely used in SPEs. The flame-retardant effect decreases in the order of bromine (Br), chlorine (Cl) and fluorine (F), among which fluorine additives are widely used because of their excellent flame-retardant effect.^[38,39] As shown in Figure 2a, a chain reaction's competition for propagation and termination leads to the formation of a fire. The dissociation of halogen flame retardants, the production of free radical scavengers (X[•]), and the chain termination process brought about by the interaction of H[•] and OH[•] radicals are all represented by the blue portion. The combustion of organic materials (RH: R stands for the composition of the organic material, H is hydrogen) and the addition of oxygen, which quickens the chain reaction's spread, are represented by the red

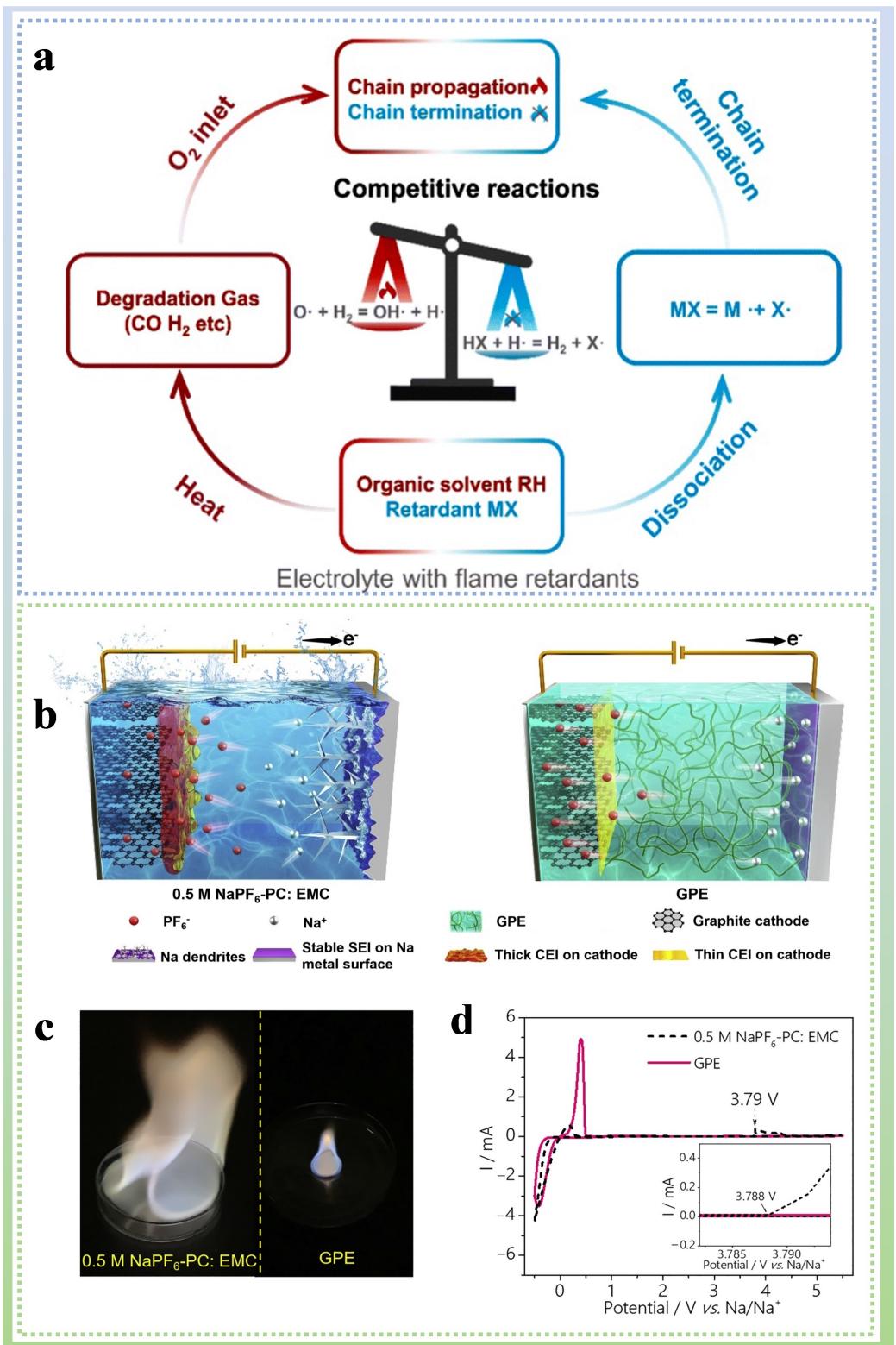


Figure 2. (a) Mechanisms of flame: the extinguishing or occurrence of gas flame depends on the competitive reaction process between radical chain propagation reactions (red) and chain termination reactions (blue).^[33] Copyright 2024, Royal Society of Chemistry. (b) Illustration of the batteries system using 0.5 M $\text{NaPF}_6\text{-PC: EMC}$ liquid electrolyte (left) or GPE (right). (c) Combustion tests of 0.5 M $\text{NaPF}_6\text{-PC: EMC}$ electrolyte (left) and GPE (right). (d) CV curves of the 0.5 M $\text{NaPF}_6\text{-PC: EMC}$ electrolyte and GPE at a scan rate of 1 mV s⁻¹.^[32] Copyright 2020, Elsevier.

portion. Adding halogen flame retardant chemicals is to optimize the chain termination process, increase the percent-

age of the blue phase of the reaction, and achieve the flame-retardant effect. Due to the lower bond energy of C–X in

halogen-based flame-retardant additive, they readily generate halogen free radicals (such as $\text{Cl}\cdot$ or $\text{Br}\cdot$) during the combustion process. These free radicals are capable of reacting with active free radicals ($\text{H}\cdot$ and $\text{HO}\cdot$) in combustion reactions, thereby decelerating or terminating the combustion chain reaction. In addition, the halogen compound residues generated by halogen flame retardants during combustion promoted the dehydration and carbonization of polymer materials, resulting in the formation of a flame-retardant carbonization layer. This layer can reduce the formation of low molecular weight cracking products and hinder the normal progress of the combustion reaction, thereby acting as a flame retardant.^[33,40,41]

Xu et al. reported a high-performance and multifunctional gel polymer electrolyte (GPE). This GPE is in-situ synthesized by thermally polymerizing ethoxylated pentaerythritol tetraacrylate (EPTA) monomer, using fluoroethyl carbonate (FEC) as a cosolvent and 1,3-propanesulfonate (PS) as an additive.^[32] Figure 2a shows the constitution and basic characterization of GPE. For the combustion test, a 5 g electrolyte sample was poured into a dish and an optical photograph was taken after the electrolyte was exposed to a match flame for 5 s. Figure 2b shows that GPEs are significantly lower flammable than highly flammable LEs (left) and are resistant to ignite by a flame source (right). This is mainly due to the immobilization of the liquid solvent by the GPE polymer matrix, which effectively reduces volatility, as well as the addition of non-flammable FEC co-solvent. The flame retardancy of this improved GPE contributes to the safety of high-voltage batteries.

In addition to flame-retardant properties, the synergistic effect of FEC co-solvent and PS additive resulted in excellent electrochemical properties of the GPE. Among them, the role of FEC is obvious. First, FEC has a lower Highest Occupied Molecular Orbital (HOMO) energy than other typical carbonate solvents, it is less prone to oxidative degradation at high voltages and enhances the chemical stability of the electrolyte (Figure 2c). Furthermore, FEC can be decomposed on the surface of sodium metal anode to create a stable SEI layer, which can successfully impede the growth of sodium dendrites to decreases the risk during battery cycling. Simultaneously, the preferential oxidation of FEC during charging process contributes to the formation of a thin and stable cathode electrolyte interphase (CEI) layer, preventing solvent molecules from co-intercalating and mitigating the irreversible breakdown of the electrolyte.^[4] Moreover, the existence of FEC in the creation of an equable flow of Na^+ and hexafluorophosphate ions (PF_6^-) inside the electrolyte, therefore promoting homogeneous sodium plating and uniform graphite cathode embedding. Consequently, adding FEC to GPEs greatly enhances the cycling stability and coulombic efficiency – two critical factors in enhancing the battery's overall performance.

However, in terms of flame retardant alone, the defects of halogen flame retardants are obvious. Halogen flame retardants decompose non-flammable gases, such as hydrogen halide (HX) when heated, which can dilute the flammable gases and diminish the oxygen concentration in the combustion zone, preventing the combustion from proceeding. However, these acid gases can corrode the metal parts of the battery (such as

metal current collector, sodium metal anode and metal elements in the cathode material), resulting in damage to the surface structure of the material and having several ill-effects on the electrochemical performance of the battery. Hydrogen halide may disrupt the SEI and impede sodium-ion transmission, and react with the electrolyte, thereby affecting both the charge-discharge efficiency and cycle life of the battery. Additionally, the generation of HX can cause harm to the human health and the environment. As research on environmentally friendly flame retardants continues to deepen, more alternatives to replace halogen flame retardants are expected to emerge in the future.

2.2.2. Phosphorus-Based Additives

Phosphorus-based flame-retardant additives have been widely studied in batteries due to their diverse types, low toxicity, suitable physical and chemical properties, and low cost. They decompose and produce $\text{PO}\cdot$ free radicals that combined with $\text{H}\cdot$ and $\text{OH}\cdot$ to cut off the propagation route of free radicals. The pyrolysis products of phosphorus compounds can promote the formation of a char layer on the polymer surface. This layer acts as a barrier to isolate oxygen and heat, protecting the interior of the material from further combustion. This process reduces internal heat generation, prevents the combustion of organic solvents, and enhances safety performance (Figure 3).^[31,42]

It has been proved that the flame-retardant performance of phosphorus-based additives is effective, but only when their content is high.^[43–45] As the content increases, the viscosity of the electrolyte increases greatly, and the side reaction with the electrode is obvious. Additionally, researchers have investigated and tried to find solutions.

Triethyl Phosphate (TEP) is widely used as a phosphorus-based flame retardant, due to its low cost and flame retardant effectiveness.^[46,47] Zeng's group used TEP as electrolyte in lithium-based batteries.^[42] Under the high salt-to-solvent molar ratio, TEP plays a multifaceted role in improving the safety of lithium-based batteries, including improving the non-flammability of electrolytes, stabilizing solvent molecules, improving electrochemical performance, enhancing compatibility with electrode materials, and protecting lithium metal anodes. These characteristics make TEP ideal for the development of the next generation of safe batteries.

TEP is also widely used in sodium-based electrolytes. Yang et al. designed a novel flame-retardant gel polymer electrolyte (A-FRGPE) with excellent interfacial stability by in-situ encapsulating non-flammable phosphate into a porous g-C₃N₄-coated asymmetric glass fiber matrix.^[48] Abundant sodiophilic active sites and well-defined nanochannels are formed on the sodium anode side, thereby enhancing the interfacial compatibility with Na metal anode by promoting interfacial dynamics and regulating uniform Na^+ deposition. The Na/A-FRGPE/Na symmetrical cell exhibits significantly improved cycling stability at a 0.1 mA cm⁻² for more than 950 h (Figure 4a). The flame-retardant properties of the A-FRGPE are improved by the non-

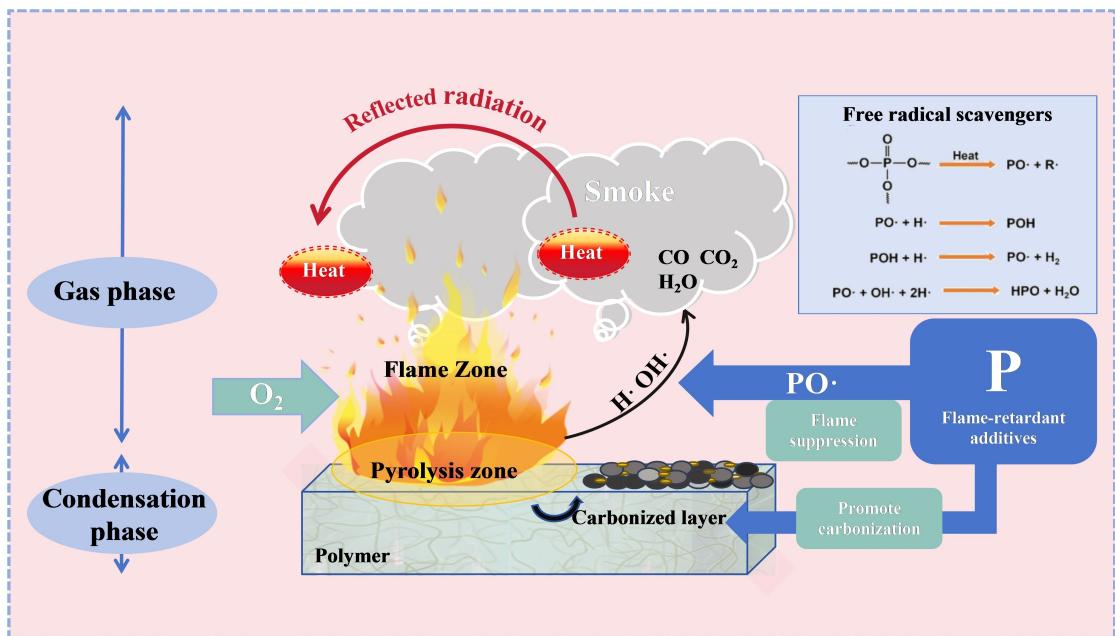


Figure 3. Combustion of polymer materials and the role of phosphorus-based flame retardants.

flammable phosphate in the porous g-C₃N₄ layer. Figure 4b shows flame retardant test, compared to the traditional organic liquid electrolyte, A-FRGPE can automatically extinguish after combustion, which shows that A-FRGPE has excellent flame-retardant properties.

Besides, Yang et al. have demonstrated a multi-performance sodium-metal battery with a quasi-solid polymer electrolyte that is flame-retardant, leak-resistant and has superior battery performance.^[49] The flame-retardant quasi-solid polymer electrolyte consists of a poly(methyl vinyl ether-alt-maleic anhydride) (P(MVE-alt-MA)) frame, a bacterial cellulose (BC) reinforcing agent, and a plasticizer (TEP/VC/NaClO₄). As can be seen from Figure 4c, glass fibers soaked in 1.0 M NaClO₄/PC electrolyte can be easily ignited and the quasi-solid polymer electrolyte (QSPE) are extinguished immediately after removal from fire. The non-flammable character mainly due to the high boiling point (216 °C) and flash point (115.5 °C) of TEP. The leak-free performance and flame resistance of QSPE greatly enhance the safety of sodium batteries, especially for sodium metal batteries.

Additionally, Chen et al. used poly(ethylene glycol) methyl ether methacrylate(PEGMA) to in-situ solidify TEP, FEC and sodium salts (Figure 4d), and investigated the effect of different TEP dosages on the performance of the electrolyte.^[50] The tensile stress-strain curve in Figure 4e shows that despite the increase in ionic conductivity of GPEs with higher TEP contents, the low mechanical strength makes it impossible to generate self-supporting films. Therefore, the entire experiment is based on glass fiber separator. And the flammability of the electrolyte is evaluated by its self-extinguishing time (SET). As shown in Figure 4f, the solid polymer membrane without TEP is completely flammable with a SET of 45 s. As the content of TEP was increased, the SET of GPEs decreased and the quantity of white

smoke increased. Some of the black substance remaining on the surface of the electrolyte membrane is residual unburned carbon. Notably, the glass fiber membrane impregnated solely with TEP cannot be ignited using a butane spray gun and producing amount of white smoke. In summary, the incorporation of TEP substantially enhanced both the ionic conductivity (0.91 mS cm⁻¹ at 27 °C) and the flame retardancy of the electrolyte system, though with a concomitant diminution in mechanical properties.

In addition to TEP, trimethyl phosphate (TMP) is also a commonly used phosphorus-based flame-retardant additive.^[51,52] Tae-Hyun Park et al. reported the synthesis of a non-flammable GPE by thermal curing of a liquid electrolyte containing TMP (Figure 4g) using an ionically conductive polypropyllactone triacrylate (PCL-TA) as a crosslinker.^[53] Figure 4h shows a digital image of a liquid electrolyte that has been tested for flammability. When the TMP content is less than 10 vol%, the electrolyte solution ignites immediately and continues to burn for a longer period of time. In contrast, electrolytes with TMP content above 15 vol% were not ignited upon prolonged exposure (> 5 s). Unfortunately, phosphate-based solvents are known to electrochemically decompose and form an unstable SEI on the anode surface. Therefore, minimizing the amount of TMP is necessary to reduce these side reactions. Based on the above results, 15 vol% TMP is the minimum content to obtain high ionic conductivity and non-flammability. Therefore, subsequent experiments employed a liquid electrolyte containing 15 vol% TMP for the fabrication of GPE and greatly improve the thermal safety of sodium metal batteries.

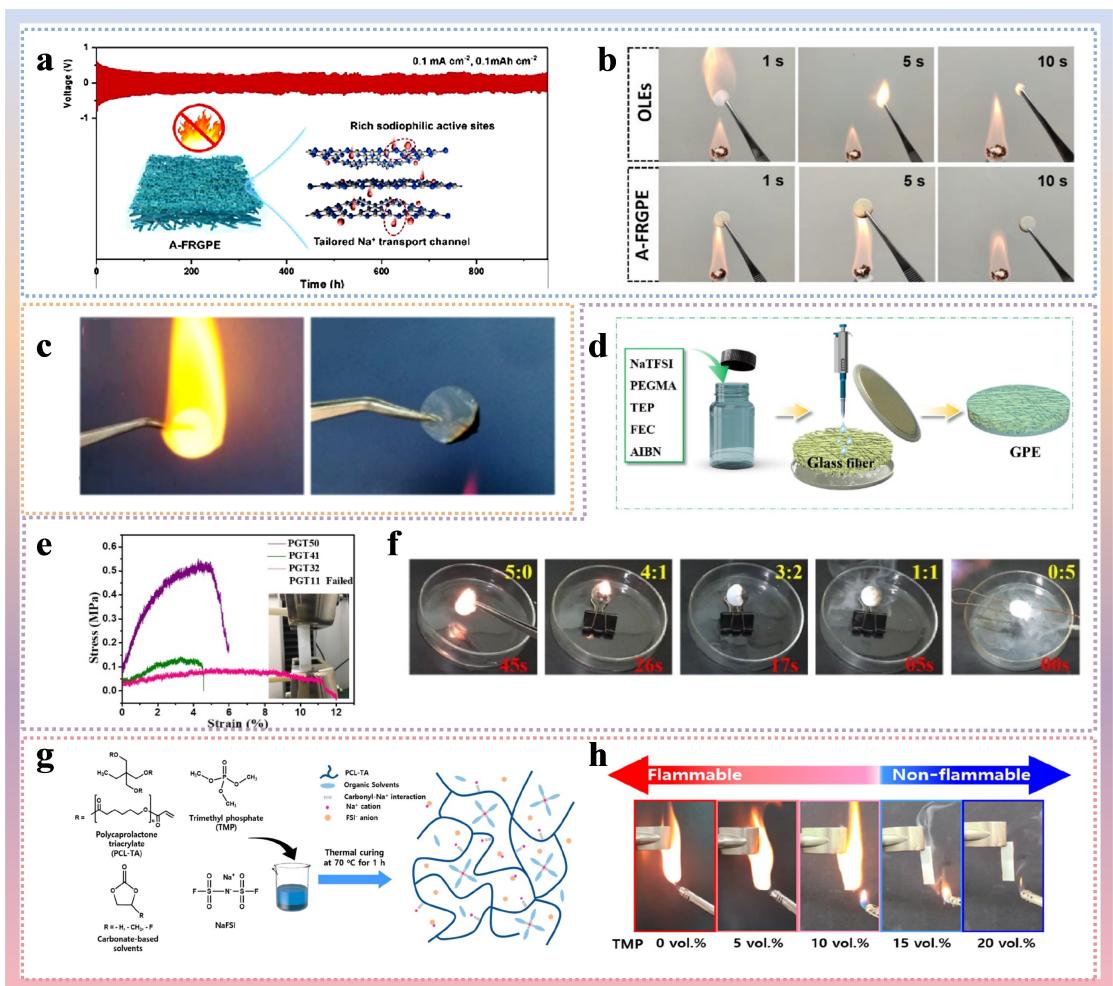


Figure 4. (a) Overview of the basic structure and Symmetrical battery long-cycle performance of the A-FRGPE; (b) Flammability test of conventional organic liquid electrolyte and the A-FRGPE.^[48] Copyright 2023, Elsevier. (c) Flame test of glass fiber saturated with 1.0 M NaClO₄/PC (left) and QSPE (right).^[49] Copyright 2019, Springer Nature. (d) Schematic illustration of preparation route of GPEs; (e) tensile stress-strain curves of GPEs; (f) Flammability tests of GPEs and TEP solution.^[50] Copyright 2020, Elsevier. (g) Schematic illustration of the synthesis of nonflammable GPE with ion-conductive polyester networks; (h) Photographic images of the liquid electrolytes subjected to the flammability test.^[53] Copyright 2021, American Chemical Society.

2.3. Inorganic Fillers

Inorganic fillers are frequently added to SPEs to enhance their flame-retardant qualities. Since inorganic fillers cannot be combined with polymers in the same phase as the polymers, unlike flame-retardant additives, their addition is likely to cause problems with phase interfaces and aggregation. Nonetheless, inorganic fillers are relatively stable that have no ability to burn and can create a solid, heat and oxygen-isolating layer that slows down the combustion process. Still, the inclusion of inorganic fillers typically results in an increase in the polymer's mechanical strength, as well as an increase in its amorphous portion, which improves the polymer's ability to transport ions. For instance, Wang et al. proposed a heterogeneous layered composite polymer electrolyte (CPE),^[54] which significantly improved the mechanical strength (13.84 MPa) and ionic conductivity ($1.62 \times 10^{-4} \text{ Scm}^{-1}$) of the CPE by adding Na₃Zr₂Si₂PO₁₂ (NZSP) nanofiller and nanocellulose frame (Figure 5a) to the polymer matrix. As shown in Figure 5b, this CPE

exhibits good room temperature cycling stability (capacity retention 93.73 % after 200 cycles) and temperature tolerance up to 80°C when integrated with the ferrohexacyanoferrite (FeHCF) cathode and sodium metal anode. Figure 5c shows that this CPE retains good structural stability at temperatures up to 180°C, due to the addition of nanocellulose scaffolds and NZSP nanofillers in the CPE, which improve the mechanical strength and temperature resistance of the polymer matrix. This means that CPE is able to maintain its structure and function under extreme temperature conditions, which is essential for the safe operation of batteries in high-temperature environments.

Wu's group demonstrated a GPE (PSB60, presents the mass percent of beta-Al₂O₃ powder in the PVDF-HFP-beta-Al₂O₃ composites is 60) consisting of a silane-modified beta-Al₂O₃ powder and a Poly(vinylidene fluoride-co-hexafluoropropylene)(PVDF-HFP) matrix with a cross-linked structure(Figure 5d) to eliminate incompatibilities between the inorganic and organic interface, thereby improving the electrochemical performance of the synthesized composite electrolyte.^[55] The

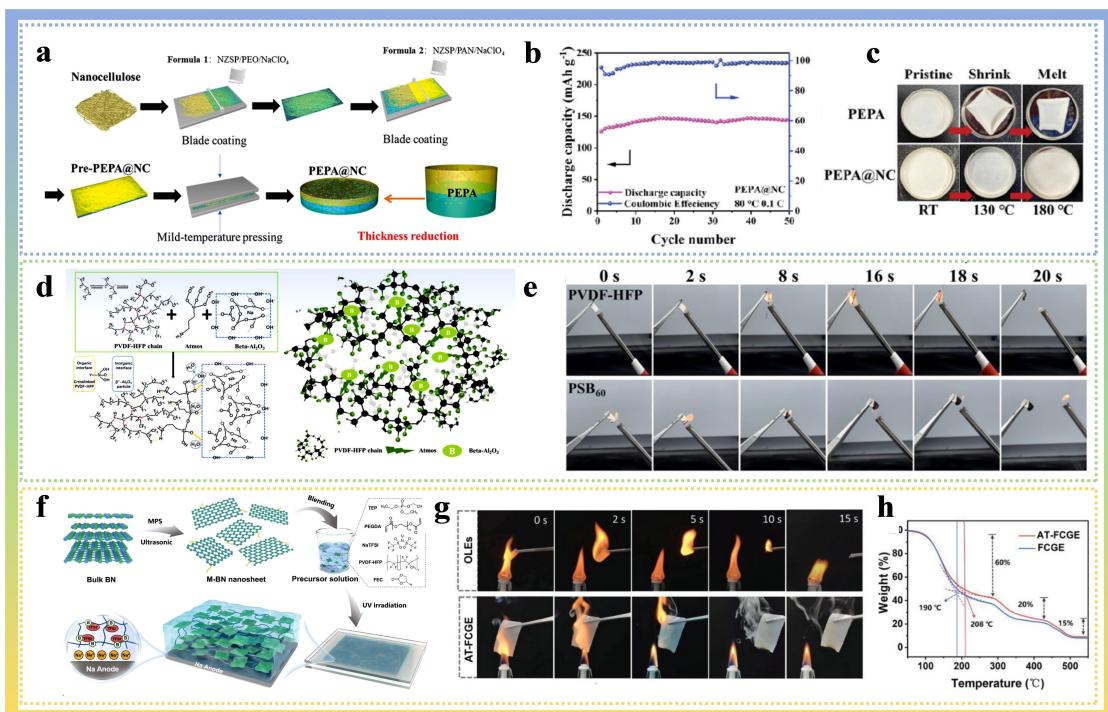


Figure 5. (a) Schematic illustration of the preparation procedures of the hetero-layered CPEs with nanocellulose reinforcement (PEPA@NC); (b) The high-temperature cyclability (80°C) and Coulombic efficiency of FeHCF | PEPA@NC | Na model at 0.1 C ; (c) Photo images of PEPA and PEPA@NC membranes upon the storage at different temperatures for 5 h.^[54] Copyright 2023, Wiley. (d) Schematic of the PSBX and possible crosslinking structure of PSBX. (e) Burning test of PSB₆₀ and PVDF-HFP.^[55] Copyright 2023, Elsevier. Schematic illustration of the (f) *in situ* preparation process of AT-FCGE via graft-coupling strategy; (g) Flammability comparison of conventional organic liquid electrolyte and the AT-FCGE. (h) TGA curves of AT-FCGE and FCGE without M-BNNs.^[37] Copyright 2023, Wiley.

combustion test results in Figure 5e show that PSB₆₀ exhibits significantly better fire-retardant performance compared to pure PVDF-HFP. This means that PSB₆₀ is less prone to combustion, even at high temperatures, thus opening up the possibility of achieving a highly safe sodium-metal battery. The excellent flame-retardant effect of the composite GPE is mainly due to the inorganic-organic crosslinking structure, and the effective combination between the inorganic β -Al₂O₃ powder with high thermal stability and the organic PVDF-HFP matrix through the use of silane coupling agent ((3-aminopropyl) trimethoxysilane, Atmos). This cross-linked structure enhances the overall stability of the material, especially thermal stability at high temperatures. At the same time, due to the interaction between β -Al₂O₃ and the polymer matrix, the amorphous components in PVDF-HFP polymers increased. Finally, in terms of chemical structure stability, the silane molecule reacts with the hydroxyl group on the surface of the β -Al₂O₃ particles to form robust Si-O bonds, which contribute to maintain the structural integrity even at high temperatures.

In addition to their significant flame-retardant properties, inorganic fillers can effectively improve ion conductivity of the polymer matrix. The incorporation of these fillers reduces the crystallinity of the polymer, thus increasing the amorphous regions, so as to provide more migration paths for Na⁺ and facilitate their movement. Inorganic fillers can form interfaces that help inhibit the growth of dendrites, assisting in increasing battery cycle stability and service life. Meanwhile, the addition

of inorganic fillers also broadens the electrochemical window. However, inorganic fillers are prone to agglomeration in polymer electrolytes due to the phase separation, which affects the conduction of Na⁺. By optimizing the dispersion and interfacial compatibility of the filler, agglomeration can be reduced.^[56] Researchers are still overcoming related dilemmas. Yang et al. combined phosphorus-based additives with inorganic fillers to achieve excellent flame-retardant effect. They constructed a fireproof composite gel electrolyte (AT-FCGE) with good interfacial stability by grafting coupling strategy, in which boron nitride nanosheets (BNNs) were chemically coupled with poly(ethylene glycol) diacrylate (PEGDA) by a silane couplant in a PVDF-HFP matrix.^[37] The implementation of graft coupling is introduced to form a highly cross-linked semi-interpenetrating network that encapsulates non-flammable phosphate in situ without sacrificing the ionic conductivity. In addition, BNNs as anion trappers can effectively promote the dissociation of sodium salts and limit the movement of anions in the electrolyte due to the abundant boron-Lewis acid sites, thereby improving Na⁺ migration capacity and smaller concentration gradients. (Figure 5f) Due to these advantages, AT-FCGE has excellent ionic conductivity, high Na⁺ transfer number, enhanced mechanical properties, and interfacial stability.

As shown in Figure 5g, glass fibers with liquid electrolytes burned rapidly after exposure to an open flame and contracted completely after 10 s. Conversely, AT-FCGE with a large area do not undergo severe combustion when exposed to flames. After

removal, the flame of the AT-FCGE was extinguished immediately, emitting a large amount of white smoke without obvious shrinkage. The superior flame-retardant performance of AT-FCGE is attributed to the introduction of phosphate groups and BNNs. Once heated, the phosphate group in the electrolyte generates PO[·] free radicals, which capture the H[·] and OH released by the polymer, further effectively retarding and inhibiting the combustion of the polymer electrolyte. Additionally, as an inorganic filler, the ability of BNN to tolerate high temperatures without altering their structure or morphology contributes to increased flame retardancy of the electrolyte. As illustrated from the thermogravimetric analysis (TGA) results in Figure 5h, there is no weight loss of the electrolyte below 100°C, indicating that the semi-interpenetrating network effectively encapsulated the liquid components and prevent them from volatilizing at high temperatures. The initial weight loss temperature of AT-FCGE is significantly higher than that of FCGE due to the enhanced adsorption capability and improved thermal stability resulting from the cross-linking network between the BNNs and the polymer chain. In addition to thermal stability and flame retardancy, positive mechanical properties can also improve the safety and extended cycling life of the battery during operation.

2.4. Flame-Retardant Polymer Matrices

The use of flame-retardant additives and inorganic fillers are typically less costly and involves a simpler procedure. The quantity of flame retardants can be modified to meet the specific requirements of diverse materials, thereby enhancing the flexibility of their application. In essence, flame-retardant additives are versatile and can be integrated into a wide range of polymers to enhance their fire resistance. Nonetheless, it is crucial to consider that the incorporation of these additives and fillers influence the material's physical properties, battery performance, and overall processability. It is essential to carefully balance the benefits of flame retardancy with potential trade-offs in these areas to ensure optimal material performance. Additionally, the mitigation of flame-retardants may lead to a gradual deterioration of its flame-retardant properties over time. Developing new intrinsic flame-retardant polymers, as opposed to simply adding additives to the polymer system, is indeed a more resource-intensive and time-consuming endeavor. However, these intrinsically flame-retardant polymers offer significant benefits over their additive-enhanced counterparts. Notably, compared to simple additives, these polymers are less likely to release toxic gases when subjected to combustion, thereby minimizing their impact on the environment and health. Moreover, the flame-retardant properties of these polymers are inherent to their molecular structure, ensuring sustained efficacy and stability against degradation over time or alterations in environmental conditions. In addition, while maintaining flame-retardant properties, it can also maintain even improve other properties of the material, such as mechanical strength and thermal stability. This dual functionality of these materials not only enhances their safety but also

improves their durability for everyday use. Therefore, the research on intrinsic flame-retardant polymer electrolytes has also been highly focused on.^[20,57–59] Liu et al. designed a novel zwitterionic GPE with intrinsic flame-retardant properties to weaken ionic-solvent interactions by introducing 3-(1-vinyl-3-imidazolio) propanesulfonate (VIPS) zwitterionic into the polymer matrix (Figure 6a), thereby improving ion transport kinetics.^[60] Figure 6b demonstrates that the GPE-VIPS-5 did not sustain combustion once the flame source was removed, indicating its superior flame-retardant properties. In contrast, the LE continued to burn, highlighting a significant difference in the flammability behavior between the two materials. This enhanced flame resistance can be largely attributed to the polymer matrix's efficient immobilization of liquid solvents and generation of N- and S-containing radicals. This immobilization reduces the mobility of the solvent molecules, thereby limiting their ability to evaporate and fuel the combustion process. The radicals resulting from the decomposition of the VIPS additives can further absorb a portion of the thermal energy and interfere the transport of oxygen to the combustion zone. It is worth noting that VIPS zwitterion is involved in the solvation structure of electrolyte ions, thereby weakening the solvent-ion interaction and improving the desolvation kinetics of ions. In addition, the decomposition of VIPS contributes to the formation of an S and N-based SEI on the surface of the hard carbon anode, which promotes the transport of Na⁺ and improves electrochemical compatibility. At the same time quasi-solid-state battery using GPE-VIPS-5 (5% PEGDA) demonstrate superior rate performance and cycle stability (capacity retention of 95.3% after 9000 cycles), with an energy density of up to 140.2 Wh kg⁻¹ and a high power density of 5230 W kg⁻¹ (Figure 6c and d).

Chen's team prepared a polymer backbone by in-situ thermal copolymerization containing a phosphate crosslinker (METEPP), methyl methacrylate (MMA), and trifluoroethyl methacrylate (TFMA), with a liquid electrolyte accounting for 90% by weight, which was physically mixed with the chemical crosslinking components to form a gelatinous polymer electrolyte through in-situ thermal polymerization.^[61] Researchers utilized TGA and differential scanning calorimetry (DSC) to measure the thermal ability of polymer matrix. The TGA curves showed that the polymer had good thermal stability at an initial thermal decomposition temperature of 320°C. Exothermic peaks are also found in the DSC curve. Further assessments of the polymer's flammability were conducted through measuring the SET and performing a flame propagation test. The results of these tests are presented in Figure 6e. It is observed that as the concentration of METEPP (a flame-retardant additive) varies, the rate of flame propagation correlates with the SET, showing a similar trend of change. Notably, the blank electrolyte (without METEPP) is highly flammable, with a SET of 28 s. Upon the introduction of METEPP, there is a significant decrease in both the SET and the rate of flame propagation through the electrolyte. The SET decreases progressively with an increasing concentration of METEPP. Figure 6e illustrates that the most pronounced retardation effect occurs when the METEPP concentration is at 7.5 wt%. This optimal concentration aligns

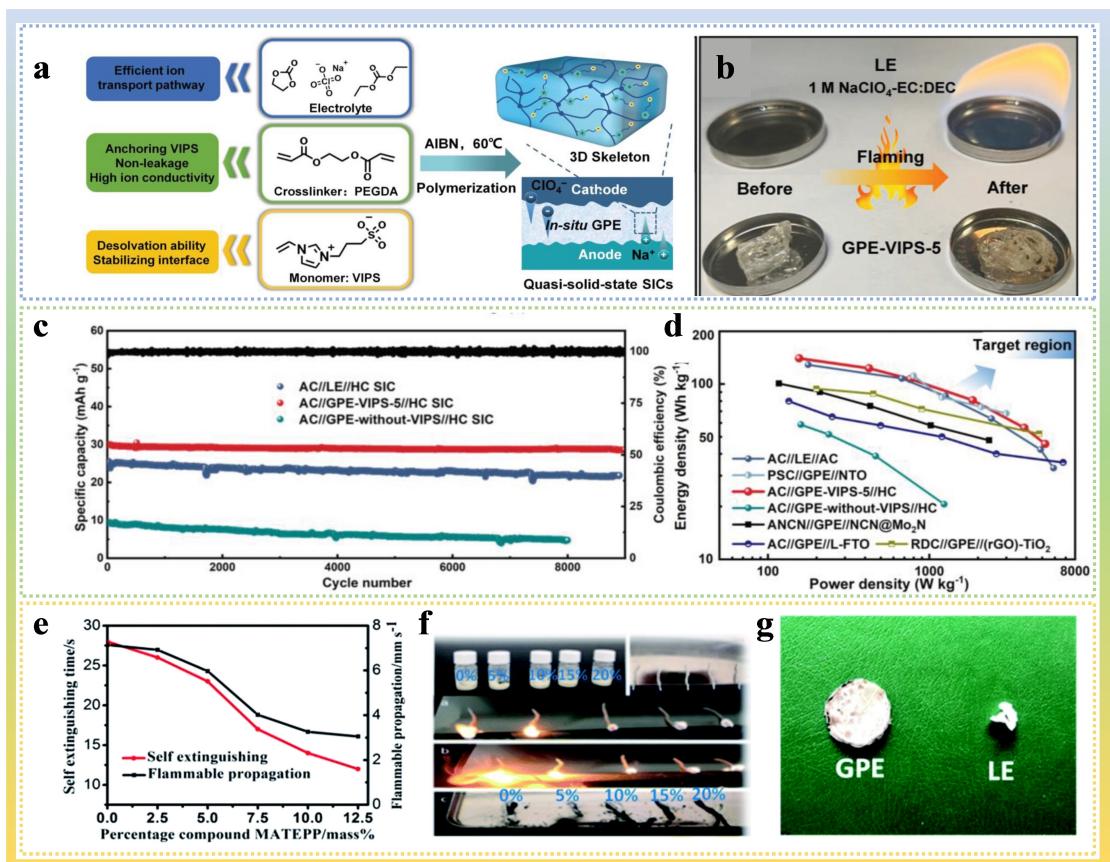


Figure 6. (a) The design strategy of GPE-VIPS electrolyte and the construction of quasi-solid-state SICs; (b) Flame tests of the 1 M NaClO₄-EC:DEC and GPE-VIPS-5 electrolytes; (c) Cycling performance and Coulombic efficiency at 0.5 A g⁻¹; (d) Ragone plot of AC//GPE-VIPS-5//HC SIC compared with current advanced quasi-solid-state SICs.^[60] Copyright 2024, Wiley. (e) Self-extinguishing time and linear flame propagation of the electrolyte containing different contents of MATEPP.^[61] Copyright 2018, Royal Society of Chemistry. (f) The burning and residue of cotton fiber wicks soaked with LE with different flame-retardant content; (g) The residue of glass fiber with GPE and LE after burning, respectively.^[62] Copyright 2020, Royal Society of Chemistry.

with the amount of METEPP used in the GPE, suggesting that this content provides the best balance between flame retardancy and other material properties. The findings underscore the importance of optimizing the additive concentration to achieve the desired flame retardancy without compromising the electrolyte's performance.

Chen's group designed and prepared another novel multi-functional monomer that combined a non-flammable radial helical cyclic spirocyclic pentaerythritol diphosphate hydroxethyl acrylate (SPDPA) with an easily polymerized acrylate. They then synthesized the corresponding cross-linked gel copolymer electrolyte by in-situ polymerization using ethyl acrylate and trifluoroethyl methacrylate. Na₃V₂(PO₄)₃||Na cells using GPE outperformed the corresponding liquid electrolytes in terms of long-term cycling stability, respectively retaining 81.4% and 69.5% of their capacity after 1600 cycles.^[62] SET tests performed by the cotton fiber wick method showed that the flame size of the LE decreases as the SPDPA content increases, and the cotton fiber wick retains better integrity after combustion.(Figure 6f) When 5 wt% SPDPA was added, an effective flame-retardant effect had been shown, which was almost consistent with the amount of SPDPA in the GPE. In addition, the process of burning glass fibers with GPE and LE

was evaluated, and the residue after combustion is shown in Figure 6g. The glass fiber with LE burns quickly and shrinks into smaller fragments, while GPE's diaphragm retains better integrity after combustion. Both of these electrolyte systems have flame retardancy due to the phosphate ester groups contained in the polymer matrixes of METEPP and SPDPA inherently. They can mitigate the corrosion of phosphate esters on the anode, ensuring excellent electrochemical performance and simultaneously providing stable flame retardancy. While the advantages of intrinsic flame-retardant polymers in terms of environmental sustainability and long-term durability are clear, the challenges associated with their higher costs and potentially more complex processing requirements cannot be overlooked. It is crucial for material scientists and engineers to continue innovating and exploring to enhance the accessible and practicality of these advanced polymers for a wide range of applications.

2.5. Others

In addition to flame-retardant additives, inorganic fillers and the construction of intrinsically flame-retardant polymers, many

new materials have emerged to be applied as electrolytes, and they have both obvious flame-retardant effects and excellent electrochemical properties, such as ionic liquids (ILs) and metal-organic frameworks (MOFs) materials.

ILs are a class of salts composed consisting of cations and anions that exhibit liquid state at or near room temperature. Compared with traditional organic solvents, ILs possess a series of unique physical and chemical properties. The chemical structure of ILs electrolytes lacks carbon-hydrogen bonds that can burn rapidly, contributing to low flammability, low vapor pressure, and low volatility, which greatly reduces the risk of combustion or explosion under overheating and abuse.^[63] Moreover, the ILs electrolyte remains stable at high temperatures and its incorporation into the polymer improves the thermal stability of the composite, which benefits for the expansion of the operating temperature range of the battery and extending its service life-span. Meanwhile, the high ionic conductivity of ILs electrolytes and the good chemical stability of counter electrode materials help to improve the charge-discharge efficiency and power density, reduce the side reactions in the process of charging and discharging, and improve the cycle life and performance of the battery.^[64] In summary, the flame-retardant advantages of ILs electrolytes are

mainly reflected in their non-flammability, high thermal stability, low volatility and excellent intrinsic electrochemical properties. These properties give ILs electrolytes great potential to improve battery safety.

Gao et al. proposed an ionic gel electrolyte containing an SBA-15 body, an ionic liquid N-propyl-N-methylpyrrolidinium bis-(fluorosulfonyl)imide (PY₁₃FSI), sodium salt, and PVDF-HFP by mechanical ball milling and rolling.^[65] After the optimized ratio of gel electrolyte matched to the Na₃V₂(PO₄)₃ cathode and sodium metal anode, SIBs had an initial discharge specific capacity of up to 110.7 mAhg⁻¹ at room temperature and maintained a capacity retention of 92% after 300 cycles. Due to the presence of SBA-15 and ILs, ionic gel electrolytes show better thermal stability than conventional LEs. The thermal stability of ionic gel electrolytes was tested by TGA and DSC (Figure 7a and b). The result shows that the ionic gel electrolyte remained stable at high temperatures without significant decomposition, indicating its good thermal stability and flame-retardant properties. The ionic gel electrolyte was directly exposed to a butane flame for the combustion test. Figure 7c and d shows that the ionic gel electrolyte does not burn under flame and remains stable even under continuous flame contact

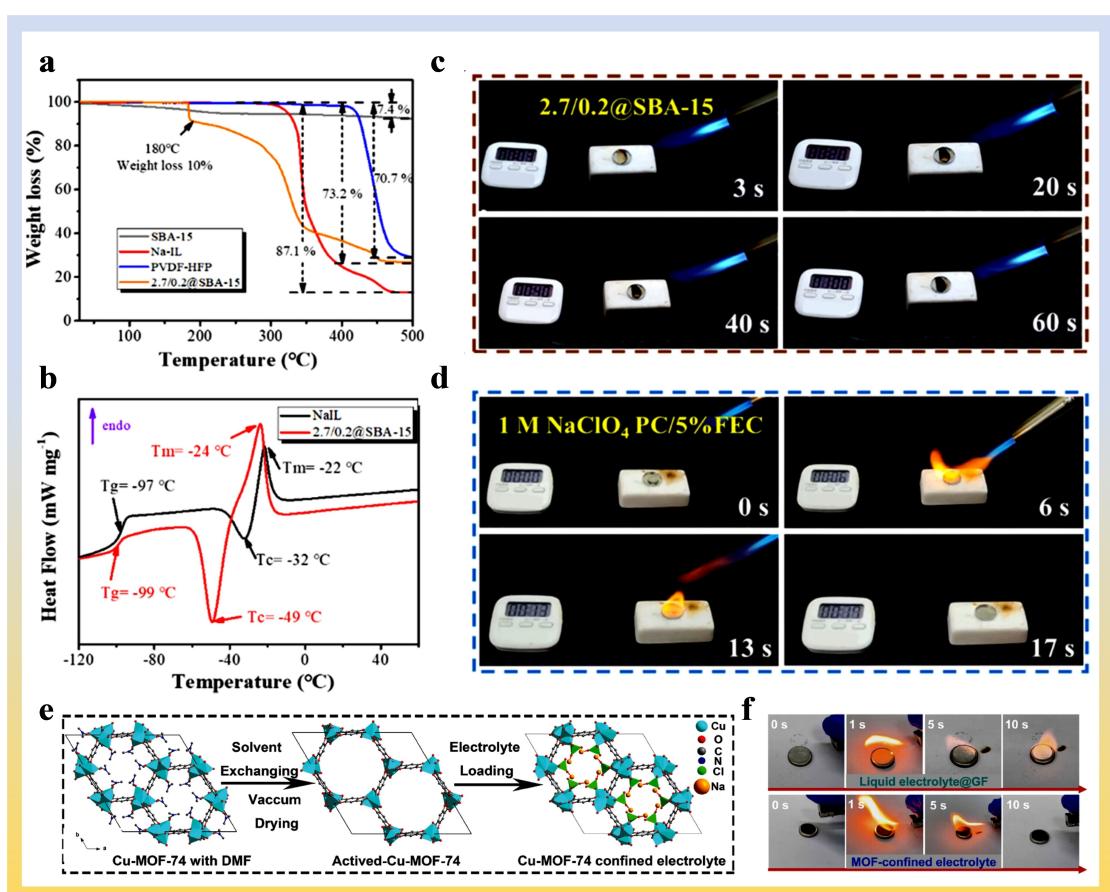


Figure 7. (a) TGA plots of SBA-15, Na-IL, PVDF-HFP, and 2.7/0.2@SBA-15; (b) DSC curves of Na-IL and 2.7/0.2@SBA-15; (c) prepared 2.7/0.2@SBA-15 electrolyte membrane; and (d) conventional LE flammability test using a flame gun.^[65] Copyright 2020, American Chemical Society. (e) Evolution coordination environment of Cu²⁺ open metal sites during liquid electrolyte loading; (f) Photographs of flammability tests of the as-prepared MCE and LE infiltrated in the glass fibers.^[66] Copyright 2024, Wiley.

compared to conventional organic LEs, which is a direct proof of its non-flammability.

MOFs are a class of crystalline materials composed of metal ions or clusters coordinated by organic ligands to form a repeating network structure. The structural and compositional properties of MOFs provide unique benefits that greatly enhance their ability to suppress smoke and resist flames. Since MOFs are inherently porous, there is an absorption effect and a potential area for the reaction of active pyrolysis products, which causes an emission delay. In addition, the breakdown products of MOFs increase the production of char. Moreover, the release paths for harmful gases and products of pyrolysis are complicated by the presence of porous substances within the char layer. The MOFs' organic ligands provide elements or groups that are flame-resistant and guarantee outstanding compatibility with the polymer matrix. These consist of groups containing phosphorus, groups containing nitrogen, and aromatic derivatives. Degradation products are widely exposed to metal compounds located within the porous structure of MOFs or their decomposition byproducts. As a result, their catalytic effect on the oxidation of harmful gases and the reduction of smoke emissions is maximized.^[4,67–69]

Fan et al. used a copper-based MOF (Cu-MOF-74) with uniform nanopores of ~1.1 nm to confine the electrolyte.^[66] This MOF-confined electrolyte exhibits superior electrochemical and thermal stability due to its highly aggregated solvation configuration, thus guaranteeing interfacial compatibility and flame retardancy. Evolution coordination environment of Cu²⁺ open metal sites during liquid electrolyte loading process shows in Figure 7e. In this work, the researchers applied a typical LEs to glass fibers and a MOF-confined electrolyte, respectively, to test their flammability (Figure 7f). After ignition, the typical LEs burn completely within one second. On the contrary, even after five seconds of continuous exposure to flame, the MOF contained electrolyte remains non-combustible. This result demonstrates the notable improvements in thermal stability and flame-retardant qualities of the MOF confined electrolyte. The electrolyte's unique confinement effect in the MOF nanopores, which reduces the concentration of free solvent molecules and hence lowers the electrolyte's flammability, is mostly to blame for this performance increase.

MOFs are a potential material for enhancing the safety of batteries because of their distinctive combination of metal clusters, organic ligands, and porous architectures, which offer a multifaceted approach to flame retardancy and smoke suppression capabilities. The thoughtful incorporation of MOFs into polymer matrices may, as research develops, result in substantial strides toward the creation of safer and more effective energy storage devices.

3. Conclusions and Perspectives

The safety aspect has always been a fundamental concern in the research and development of sodium-ion batteries. As battery energy density continues to improve and application fields expand, there is an increasing demand for enhanced

battery safety. The thermal and chemical stability of SPEs remains a concern under extreme conditions such as high temperatures, overcharge, or external shocks, despite their ability to reduce the risk of leakage and enhance the mechanical stability of batteries. The electrochemical stability and interface compatibility of SPE also require further optimization to avoid unnecessary side reactions during battery operation. In an effort to address these concerns, researchers have explored the incorporation of flame-retardant additives into SPEs. The utilization of this approach always entails certain trade-offs. For instance, the presence of hydrogen halides and the corrosive nature exhibited by specific phosphate esters, can exert a detrimental influence on the ionic conductivity and other electrochemical properties of the electrolyte, thereby significantly affecting the overall performance of battery. Additionally, the flame-retardant effect is not significantly evident at low concentration of additives. As the concentration of these additives increases, the improvement in flame retardancy becomes more pronounced, however, this also leads to the detrimental effects on the battery performance. The design of SPEs poses a challenge in striking the delicate balance between enhancing safety and maintaining battery efficiency. Inorganic fillers do not form a homogeneous phase with polymers, and some inorganic fillers may inherently possess high ionic conductivity, such as NZSP, which is different from common additives. When added in small amounts, the inorganic fillers do not create a continuous pathway, and the increase in ionic conductivity is not significant. However, as the content increases, the flexibility of the electrolyte decreases, leading to poorer contact with the electrodes, and the tendency for inorganic particles to aggregate can also affect the battery's performance. Materials MOFs and ILs have attracted much attention due to their unique physicochemical properties. The high cost of these materials hinders their widespread application in mass production, despite their demonstrated potential for enhancing the fire resistance of batteries. The performance and testing methods of the different flame-retardant polymer electrolytes mentioned earlier are all categorized and displayed in Table 1. To address these challenges, it is imperative to continue research and development endeavors. The primary focus should be on identifying or developing cost-effective flame-retardant strategies that not only maintain but also enhance the electrochemical performance of SPEs.

To ensure a significant advancement in the safety of sodium-ion batteries with SPEs, the key issues mainly contain five aspects: (1) Improvements in the electrolyte are of paramount importance, it is imperative to adopt a strategic approach encompassing the development of multifunctional additives and advanced materials. (i) The development of multifunctional additives that should simultaneously improve the flame-retardant properties and conductivity of SPEs and inhibit the growth of sodium dendrites. The challenge lies in how to enhance the safety of the battery without sacrificing its electrochemical performance. For instance, phosphate ester additives can incorporate additives or sodium salts with low Lowest Unoccupied Molecular Orbital (LUMO) energy to preferentially react with sodium metal anodes to form a stable

Table 1. Summary of the matrices, flame-retardant methods, test methods and electrochemical performance of diverse electrolytes for Na-based SPEs.

Matrices	Flame-retardant methods	Test methods	Electrochemical performance.	
			Symmetric cells (current density, areal capacity, cycling time, and overpotential)	Full cells (cathode, rate/current densities, and capacity retention)
EPTA ^[32]	Halogen-based additives (FEC)	Combustion tests	1 mA cm ⁻² , 2 mAh cm ⁻² , 800 h, 20 mV	Graphite, 100 mA g ⁻¹ , 86.7% (1000 cycles)
PEGDA ^[48]	Phosphorus-based additives (TEP)	Combustion tests, TGA	0.1 mA cm ⁻² , 0.1 mAh cm ⁻² , 950 h, ~250 mV	Na ₃ V ₂ (PO ₄) ₃ , 1 C, 96.1% (1100 cycles)
P(MVE-alt-MA) ^[49]	Phosphorus-based additives (TEP)	Combustion tests	–	Na ₃ V ₂ (PO ₄) ₃ , 1 C, 84.4% (1000 cycles)
PEGMA ^[50]	Phosphorus-based additives (TEP)	Combustion tests, TGA	–	Na ₃ V ₂ (PO ₄) ₃ , 0.2 C, 91% (400 cycles)
PCL-TA ^[53]	Phosphorus-based additives (TMP)	Combustion tests	0.5 mA cm ⁻² , 1 mAh cm ⁻² , 400 h, ~100 mV	Na ₃ V ₂ (PO ₄) ₃ , 1 C, 99.4% (100 cycles)
PEO/PAN ^[54]	Inorganic fillers (NZSP)	Thermal shrinkage test, High-temperature cyclability test. (80 °C)	0.3 mA cm ⁻² , –, 380 h, 40 mV (60 °C)	Iron hexacyanoferrate, 0.1 C, 93.73% (200 cycles 25 °C); 97.65% (150 cycles 60 °C)
PVDF-HFP ^[55]	Inorganic fillers (β -Al ₂ O ₃)	Combustion tests, TGA, DSC	0.5 mA cm ⁻² , –, 800 h, 250 mV	Na ₃ V ₂ (PO ₄) ₃ , 3 C, 92.2% (1000 cycles)
PVDF-HFP ^[37]	Phosphorus-based additives (TEP) and Inorganic fillers (BNNs)	Combustion tests, TGA	0.1 mA cm ⁻² , 0.1 mAh cm ⁻² , 1000 h, 500 mV	Na ₃ V ₂ (PO ₄) ₃ , 1 C, 91.7% (500 cycles)
PEGDA-VIPS ^[60]	Flame-Retardant Polymer Matrices	Combustion tests	–	Activated carbon, 0.5 A g ⁻¹ , 95.3% (9000 cycles)
MATEPP-MMA-TFMA ^[61]	Flame-Retardant Polymer Matrices	TGA, DSC, Combustion tests	–	Na ₃ V ₂ (PO ₄) ₃ , 5 C, 69.17% (10000 cycles)
SPDPA ^[62]	Flame-Retardant Polymer Matrices	TGA, Thermal shrinkage test, Combustion tests	–	Na ₃ V ₂ (PO ₄) ₃ , 270 mA g ⁻¹ , 81.4% (1600 cycles)
PVDF-HFP ^[65]	ILs (PY ₁₃ FSI)	Combustion tests, TGA, DSC	–	Na ₃ V ₂ (PO ₄) ₃ , 0.1 C, 92% (300 cycles)
MOFs ^[66]	MOFs (Cu-MOF-74)	Combustion tests	0.25 mA cm ⁻² , 0.25 mAh cm ⁻² , 350 h, 220 mV	Na ₃ V ₂ (PO ₄) ₃ , 2 C, 93% (3000 cycles)

SEI that prevents corrosion by the phosphate esters.^[70] Additionally, functional groups capable of ion transport can be grafted onto the phosphate ester molecules to enhance the ionic conductivity of the phosphate ester additives, ensuring a balance between safety and electrochemical performance. (ii) The other is to construct novel intrinsic flame-retardant polymers. This could involve the creation of materials that are inherently more stable and less prone to failure under extreme conditions. For example, grafting phosphate ester or halogen groups onto a polymer substrate can prevent the uneven loss of flame retardants over time.^[71] (iii) For inorganic fillers, the key is to increase the formation of continuous ionic transport channels and prevent particle agglomeration. Currently, electro-spinning technology can be used to orderly compound inorganic particles with polymers, which greatly reduces agglomeration and effectively enhances ionic conductivity.^[56] Additionally, different template methods can form an inorganic material skeleton, and then fill it with polymers, which is also an effective approach.^[72] (2) In addition to improvements in the electrolyte, reducing safety risks of the battery under extreme conditions can also be achieved by improving electrode materials, designing more stable SEI, applying advanced surface treatment technologies for electrodes, or assembling safer

battery packaging structures. (3) Even more, the test methods for battery safety should be systematically developed. Table 1 presents recent research progress and representative studies on enhancing the safety performance of Na-ion SPEs. While the current test methods are relatively simplistic and urgently requires systematic refinement. Current tests typically include direct ignition experiments, which are necessary but not fully replicate the complexities that batteries encounter during actual usage. Batteries may be exposed to abusive conditions such as mechanical stress, high temperatures, or electrical abnormalities. Therefore, researchers should focus their efforts on evaluating assembled batteries under abusive conditions, such as pouch cells, in order to more accurately simulate the challenges that batteries may encounter over their lifespan. (4) The development of more comprehensive battery safety test standards is concurrently pursued to ensure the safety of batteries under various extreme conditions. Only with the standards of specific quantitative testing can researchers more efficiently and effectively enhance the flame-retardant performance of batteries. For example, the commonly method in flame-retardant electrolytes, the SET test, currently lacks a defined experimental procedure and standard. There is a significant variation in the SET tests conducted in various works, such as

the duration of continuous ignition, whether the electrolyte uses a separator or carrier, which is no unified standard.^[73] For instance, Wang's team, in order to assess the fire safety of liquid electrolytes for lithium-ion batteries, proposed a unified testing method by systematically summarizing and researching key test parameters.^[74] This method involves using a 16 mm glass fiber separator to absorb 0.1 g liquid electrolyte for horizontal combustion. Additionally, the concept of Self-Extinguishing Efficiency (SEE) was introduced, and new assessment criteria were established, categorizing electrolytes into three levels: flammable, flame-retardant, and non-combustible. The study validated the feasibility of the new method and unveiled the underlying flame-retardant mechanisms by evaluating the impact of 15 representative flame retardants on the combustion behavior of liquid electrolytes. By integrating machine learning technology, this research provides a benchmark for the safety assessment of LE, meanwhile, offers significant guidance for the development of fire safety battery technology. For SPEs, testing requires more rational experimental design to enhance universality. Further exploration in this area is needed. Essentially, the goal is to establish a synergistic system where advancements in material science, additive technology, and testing protocols harmoniously collaborate to produce batteries that not only exhibit safety but also maintain elevated levels of performance and reliability. This comprehensive strategy will be key to the future success and widespread adoption of solid-state batteries in various applications. These investigations provide valuable insights into the construction of solid-state polymer batteries, aiming to achieve both enhanced safety and high electrochemical performance.

In conclusion, improving the safety of polymer solid-state batteries is a multifaceted challenge that necessitates comprehensive considerations and optimizations across various aspects, including material selection, battery design, test methods, and performance evaluation. The safety concerns associated with current battery technologies need to be addressed in order to facilitate wider adoption and integration into various applications, ranging from portable electronics to large-scale grid storage, without compromising on the safety of users or the environment. Through a systematic approach to battery safety research, it is anticipated that sodium-ion battery systems with enhanced safety and reliability will be introduced in the near future. These advancements will be crucial in satisfying the escalating global demand for energy storage solutions.

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Conflict of Interests

The authors declare no conflict of interest.

Keywords: Flame-retardant • Polymer electrolyte • Sodium batteries • Solid-state electrolyte

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