COMMENTARY

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Beyond non-flammability: A polymerizable electrolyte strategy for thermal runaway-free Na-ion batteries

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Rechargeable sodium-ion batteries (SIBs) are regarded as one of the most promising technologies for grid energy storage due to low cost, abundant sodium resources, and compatibility with the existing lithium battery industry [1]. However, safety becomes the defining challenge limiting commercialization, as the series of exothermic reactions that occur during operation would potentially trigger fires or explosions [2]. In this regard, common strategies have primarily focused on developing non-flammable electrolytes, driven by the widespread assumption that eliminating electrolyte flammability alone is sufficient to suppress thermal runaway [3,4]. Nevertheless, recent studies have revealed that SIBs based on non-flammable electrolytes still undergo severe thermal runaway, thus calling for a more comprehensive consideration of the thermal stability of the electrolyte, the stability of electrode-electrolyte interfaces, and the high-temperature interactions between the cathode and anode.

Recently, a breakthrough by Hu's team, published in *Nature Energy*, established a new safety paradigm by designing a polymerizable non-flammable electrolyte (PNE) that not only resists ignition but also suppresses thermal runaway through thermally triggered *in-situ* polymerization mechanisms (Figure 1) [5]. This design demonstrated the successful realization of thermal runaway-free Ah-level SIBs even at 300 °C, substantially expanding the safety envelope of SIBs.

The core innovation relies on the *in-situ* polymerization of phosphoric acid at elevated temperatures, decomposition products from triethyl phosphate in a nonflammable electrolyte, which would form an insulating polymer network, thereby suppressing mechanical and chemical crosstalk between the cathode and anode at high temperature. More importantly, the polymerization process itself is endothermic, enabling the electrolyte to absorb heat rather than amplify exothermic reactions. This represents a major conceptual advance beyond traditional nonflammable electrolyte design.

Another critical contribution of this work is the ingenious engineering of the solvation structure and electrode-electrolyte interphase chemistry through a synergistic anion-cation solvation effect, employing a mixed salt of $NaBF_4$ and $NaPF_6$. The incorporation of BF_4^- weakens Na^+-solvent interactions, facilitating the desolvation and improving compatibility with hard carbon anodes. Meanwhile, the different energy level of the two salts contributes to the formation of P-rich solid-electrolyte interphase and B-rich cathode-electrolyte

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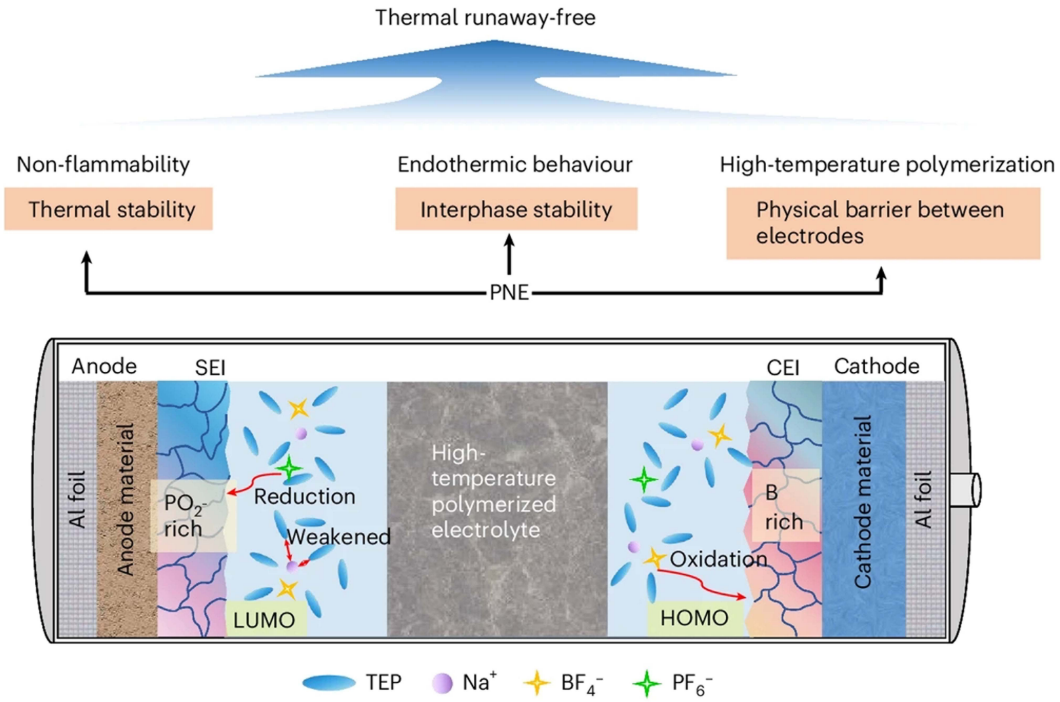


Figure 1 Schematic illustration of PNE exhibiting thermal runaway-free performance. Reproduced with permission from Ref. [5]. Copyright 2026, Springer Nature.

interphase, which effectively suppress transition-metal dissolution, reduce electrolyte decomposition, and enhance both electrochemical and thermal stability.

As a result, the synergetic design leads to exceptional safety and electrochemical performance. The PNE-based SIBs successfully passed the nail penetration test without smoke, fire, or explosion, in both 1.45-Ah and 3.5-Ah cylindrical cells. In accelerating rate calorimetry experiments, no thermal runaway occurred even when the cell was heated to 300 °C. In contrast, cells with conventional carbonate or trimethyl phosphate electrolytes experienced severe thermal runaway at much lower temperatures. Moreover, the 3.5 Ah cell demonstrated long-term cyclability with 85.7% capacity retention after 700 cycles at room temperature and a wide operating temperature range (–40 to 60 °C). When paired with a high-voltage (4.3 V) cathode, the pouch cylindrical cell achieved an ultrahigh energy density of 211 Wh kg^{-1} while also passing the stringent nail penetration test. These results demonstrate that distinguished safety does not need to come at the expense of energy density or practical performance.

In summary, this work establishes guiding principles for achieving intrinsic battery safety that is free from thermal runaway, going beyond simply making the electrolyte non-flammable. The concept of thermally responsive *in-situ* polymerization electrolytes may also be extendable beyond SIBs to lithium-ion and other battery systems. For instance, applying a similar PNE strategy to a high-energy lithium-rich layered oxide cathode and a silicon anode could simultaneously mitigate thermal runaway and extend cycle life, thereby addressing two critical challenges in next-generation lithium-based batteries. As grid energy storage continuously expands, this study provides an important scientific and technological foundation for developing truly safe and high-performance rechargeable battery systems suitable for future deployment.

Conflict of interest

The authors declare no conflict of interest.

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