

Research Highlight

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# Full-performance coordinated design for polymer-in-salt solid electrolyte

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Solid-state lithium batteries (SSLBs) using solid electrolytes have been identified as one of the most promising next-generation energy storage devices due to their improved safety and high energy density. In particular, solid polymer electrolytes (SPEs; excluding gel polymer electrolytes and polymer electrolytes with free solvents) have been widely chosen in SSLBs due to their high lithium metal compatibility, good contact with electrodes, and more favorable manufacturing process<sup>[1-3]</sup>. Nonetheless, there are still key challenges that SSLBs with SPEs must overcome. These include low ionic conductivity ( $10^{-7}$ - $10^{-5}$  S cm<sup>-1</sup>) at room temperature and the difficult balance among mechanical strength, ionic conductivity, and high-voltage applications for long-term cycling<sup>[4]</sup>. Polymer-in-salt solid electrolytes (PISSEs), defined as a small amount of a high-molar-mass polymer mixed with high fraction of lithium salts (generally exceeding 50 wt%), have been proposed to address the ionic conductivity issue<sup>[5]</sup>. By using PISSEs, the ionic conductivity of typical SPEs can be increased by an order of magnitude (promoted to  $10^{-4}$  S cm<sup>-1</sup>), since PISSEs can construct a unique Li<sup>+</sup> transport channel through the ion clusters in the system, compared with the Li<sup>+</sup> migration in ordinary SPEs that only depends on the segmental movement of the polymer matrix.



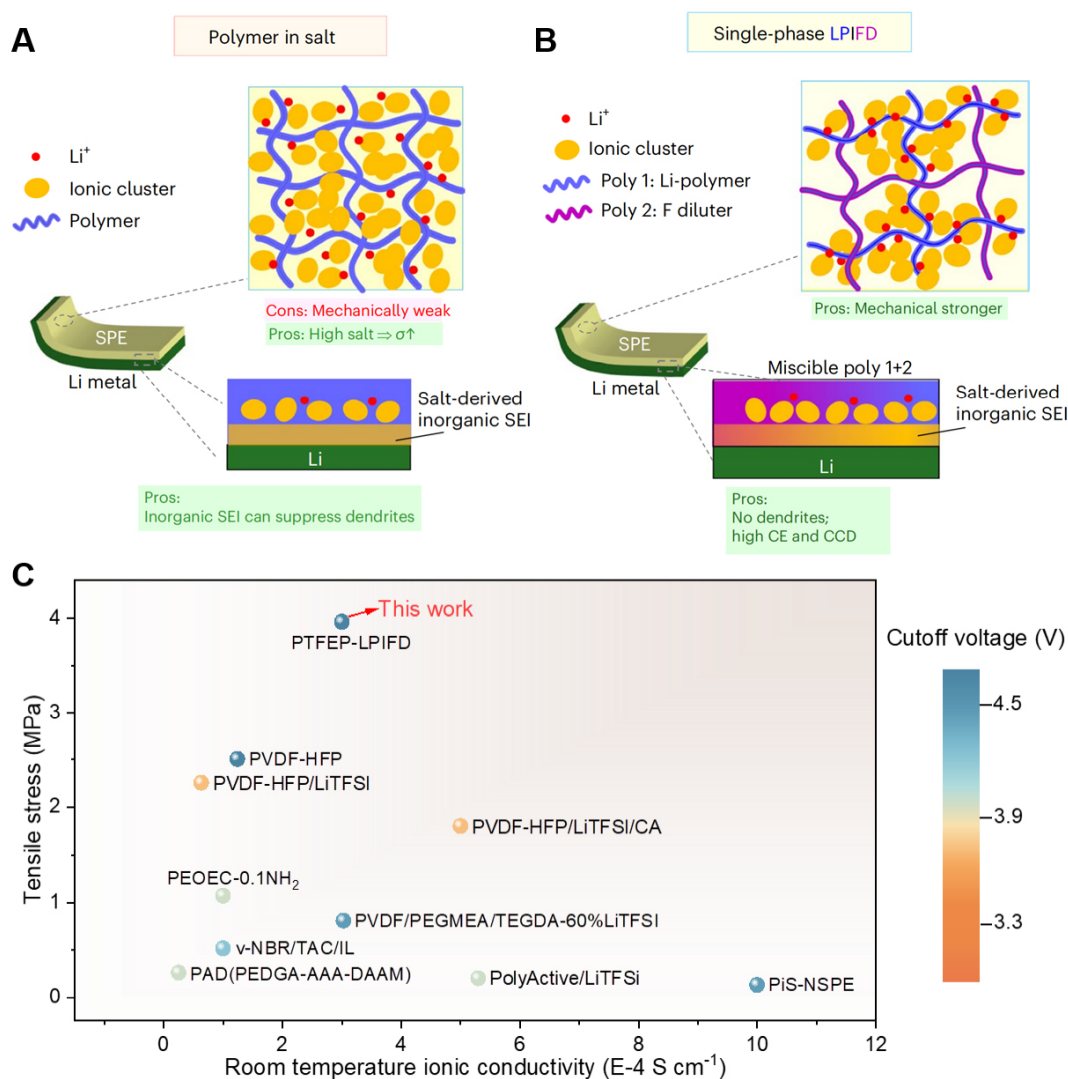
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However, two key issues of performance regulation continue to hinder the further development of PISSEs. On the one hand, the mechanical property is typically deteriorated with ultrahigh concentration of lithium salt. For example, when the weight ratio of lithium salt is as high as 1.3, the tensile stress of PISSE is only 1-3 MPa, while that of the conventional SPE is 8-10 MPa<sup>[6]</sup>. Inferior mechanical properties could not effectively suppress the dendrite growth and thus still pose a risk of battery short circuits. In general, the mechanical strength is directly related to the nature of the polymer matrix<sup>[7]</sup>; therefore, choosing an ideal polymer framework is highly desired. On the other hand, the instability of high-voltage cathodes in PISSEs remains an unresolved challenge, limiting the commercialization of related SSLBs. It is well known that the pristine poly(ethylene oxide) (PEO)-based electrolytes are generally able to match low lithium storage potential cathodes of less than 3.8 V (vs. Li<sup>+</sup>/Li)<sup>[8]</sup>; some PEO electrolytes with tuned chemistry can be matched with high-voltage cathodes above 4.0 V<sup>[9]</sup>, but they were not designed as PISSEs. Further research has found that poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) electrolytes could be compatible with over 4 V cathode materials (LiCoO<sub>2</sub>, LCO; LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>2</sub>O<sub>2</sub>, NCM; *etc.*)<sup>[10,11]</sup>, but stable long-cycling with these high-voltage cathodes has yet to be demonstrated. Notably, an unstable interphase is easy to generate at most high-voltage electrode/electrolyte interfaces, so the control of the solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) are considered to be crucial to achieve long-cycling of high-voltage cathodes with PISSEs<sup>[12]</sup>.

To address the above two issues, Zhang *et al.* recently proposed the concept of “local high concentration” in PISSEs<sup>[13]</sup>, which is analogous to that in traditional organic electrolytes and different from the “high concentration” design in traditional PISSEs<sup>[14-22]</sup> [Figure 1]. The traditional local high concentration liquid electrolyte (LHCE) consists of an inert diluent and original high concentration electrolyte (HCE). The diluent must be easily miscible with the solvating solvent in HCEs, but does not participate in dissociating salts. Therefore, the salt content and electrolyte viscosity per unit volume can be lowered while maintaining the coordination of HCE's original salt and solvent. The new PISSE is based on a polymer blend that is called Li-polymer in F diluter (LPIFD). In LPIFD, PVDF-HFP, an inert fluorinated polymer (called the F diluter; FD), is utilized because of its outstanding mechanical properties and high stability with lithium metal and high-voltage cathodes, while Li-polymer (LP) is PISSE, equivalent to HCE, providing continuous Li<sup>+</sup> conduction channels. For the selection of LP, the authors discussed five polymers: Poly(propylene carbonate) (PPC), Poly(ethylene oxide) (PEO), Poly(methyl methacrylate) (PMMA), Poly(vinyl sulfone) (PVSF), and Poly(bis(trifluoroethoxy)phosphazene) (PTFEP). It was revealed that the two fluorinated polymers, PVSF and PTFEP, can exhibit superior miscibility with PVDF-HFP, forming a stable, single-phase structure. Furthermore, PTFEP and PVDF-HFP were selected to construct the PTFEP-LPIFD electrolyte for in-depth investigations.

The results showed that this electrolyte not only inherited excellent lithium-ion conductivity of PISSE, but also showcased significant advancements in two critical indicators: mechanical properties and stability for high-voltage cathodes, demonstrating a high comprehensive performance as compared to traditional PISSEs<sup>[14-22]</sup>. In detail, PTFEP-LPIFD possessed a high room-temperature ionic conductivity of  $3.0 \times 10^{-4} \text{ S cm}^{-1}$  with a Li-ion transference number ( $t_{\text{Li}^+}$ ) of 0.64. The high mechanical strength of PVDF-HFP (stress of about 3.7 MPa) and the highly miscible single-phase structure formed in PTFEP-LPIFD resulted in a superior tensile stress of 3.96 MPa and an elastic modulus of 23.3 MPa. In addition, stability of high-voltage cathodes in PISSE has been significantly improved. The Li|PTFEP-LPIFD|NCM811 full cells demonstrated an average coulombic efficiency (CE) of 99.95% and a long cycle life of over 450 cycles at a high cutoff voltage of 4.5 V. Moreover, under more stringent test conditions (at 45 °C), the cells can be charged to 4.6 V and exhibited reversible capacities of 202.2, 146.7, and 105 mAh g<sup>-1</sup> when cycled at 2C, 3C, and 4C rates, respectively. The high-voltage stability is attributed to the high LiF content in the PTFEP-LPIFD-derived inorganic CEI layer.



**Figure 1.** Schematic for designing (A) PISSEs and (B) single-phase LPIFD PISSEs. Reprinted with permission from ref.<sup>[13]</sup>. Copyright © 2024 Springer Nature Limited. (C) Comparison of the room temperature ionic conductivity, tensile stress and cutoff voltage of various PISSEs<sup>[14-22]</sup>.

The built-in PTFEP-LPIFD in Li||Cu half cells further demonstrated exceptional compatibility with Li anodes. At 0.5 mA cm<sup>-2</sup>, the Li||Cu cell exhibited a CE of 99.1% after 300 cycles. Additionally, the Li anode showed a dense and uniform surface structure after plating at 2.0 mAh cm<sup>-2</sup>, which arises from the homogeneous, organic-less and LiF-rich SEI in PTFEP-LPIFD suppressing dendritic Li growth<sup>[23]</sup>.

The full-performance coordinated design for PISSE by Zhang *et al.* was based on the straightforward blade-coating technique, which is easy to scale and developed as a low-cost, scalable, and controllable manufacturing technique<sup>[13]</sup>. Nevertheless, there are still certain limitations in this work, which also exist in most other PISSE systems. Firstly, the selection of solvent in this electrolyte still leaves considerable room for improvement. It was demonstrated that there were small residual amounts of 1,2-Dimethoxyethane (DME) solvent that can enhance the ionic conductivity of PISSEs. However, the challenges related to

interface contact degradation induced by such highly polar solvents require further refinement<sup>[24]</sup>. Secondly, the selection of the two polymers for the construction of the LPIFD system is still empirical. In this regard, utilizing computational methods in materials science such as density functional theory (DFT) and molecular dynamics (MD) can help evaluate the microstructure and some key physical/chemical properties of PISSEs, facilitating optimal selection of polymers, salts, and salt concentrations<sup>[25]</sup>. In addition, high-throughput computing (HTC), which has recently received significant attention, can rapidly screen a large number of material combinations, efficiently providing theoretical guidance and potential solutions<sup>[26]</sup>. These avant-garde computational tools are poised to shorten cycles of scientific understanding and technological innovation, aiding in the realization of more efficient, stable and durable PISSEs. Thirdly, high-energy-density SSLBs have not been demonstrated at the device level. To enable the practical application of PISSE in SSLBs in the future, key techniques to reduce the thickness of PISSE while maintaining the electrochemical attributes are highly desired. With further pairing with high mass-loading cathodes and addressing the interfacial issues of solid-solid contact, PISSE-based high energy SSLBs can be anticipated.

## DECLARATIONS

### Authors' contributions

Proposed the topic: Ma, Q.

Performed literature survey: Shen, S.; Lu, J.

Prepared the manuscript: Ma, Q.; Shen, S.; Ai, L.

Collectively discussed and revised the manuscript: Ma, Q.; Shen, S.; Lu, J.; Ai, L.; Hou, Y.

Review, conceptualization, and supervision: Liu, J.; Li, Y.

### Availability of data and materials

Not applicable.

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### Conflicts of interest

Liu, J. is the Guest Editor of the Special Issue "Solid-State Lithium Batteries: Material Innovations and Future Perspectives", while the other authors have declared that they have no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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