

Applying lewis acid-base chemistry towards a 4.8 V PEO-based solid-state lithium metal battery

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Solid-state batteries (SSBs) are gaining considerable attention as the next-generation energy storage technology due to their potential for high energy density, enhanced safety, and long cycle life compared to conventional liquid electrolyte-based batteries^[1,2]. Among the various types of SSBs, solid polymer-based electrolytes (SPEs) stand out due to their flexibility and processability, which facilitate better electrode-electrolyte contact and enable safer, compact designs^[3]. Notably, polyethylene oxide (PEO)-based electrolytes have emerged as promising candidates due to their ease of fabrication, low cost, and environmental friendliness^[4].

However, the poor high-voltage compatibility of PEO-based SPEs leads to the compromise of the energy density of SSBs^[5]. The primary challenge lies in their intrinsically poor oxidative stability, especially at voltages exceeding 4.2 V^[6,7]. Additionally, the strong interactions between the ether oxygen (EO) chains in PEO and the high-voltage cathode active materials (e.g. $\text{LiNi}_x\text{Mn}_y\text{Co}_{(1-x-y)}\text{O}_2$) lead to electrochemical side reactions at the cathode/electrolyte interface, which hampers the capacity of the battery and shortens its cycle life^[8–11]. Overcoming these challenges is crucial to unlocking the potential of PEO-based electrolytes in high-voltage batteries, and consequently, high-energy applications.

As summarized in our recent review^[12], manipulating Lewis acid-base coordination interactions, including the hydrogen bond, the dipole-dipole interaction and the positive vacancy-salt interaction, have proven fruitful in regulating the chemical structure of PEO-based SPEs to extend the electrochemical stability window (Figure 1). This concept is further validated in a recent study published in *Nature Communications*, Prof. Jiajun Wang and colleagues from Harbin Institute of Technology propose a novel Lewis-acid coordination strategy to enhance the high-voltage performance of PEO-based SPEs^[13]. By introducing Mg^{2+} and Al^{3+} ions as Lewis-acidic electron-

withdrawing ligands into the EO chains (Figure 2a), the electron density of the EO chains is decreased, leading to reduced coordination between Li^+ and EO chains and decreased highest occupied molecular orbital (HOMO) of the salt-polymer complex (Figure 2b). The presence of $\text{Mg}^{2+}/\text{Al}^{3+}$ ions also decreases the adsorption energy of the SPE on the high-Ni cathode (Figure 2c), indicative of increased energy barrier for the parasitic reactions. Meanwhile, the modified electrolyte enables the formation of a more stable inorganic-rich cathode-electrolyte interphase (CEI) as a result of more TFSI^- anions participating in the solvation sheath of the electrolyte (Figure 2d). Consequently, this innovative design effectively mitigates cathode/electrolyte interfacial degradation and improves the oxidative stability of the PEO-based electrolyte up to 4.8 V.

Electrochemical testing demonstrates the remarkable performance of the PEO-based SSBs using the Lewis-acid coordinated electrolyte. The batteries demonstrate good cycling stability of over 300 cycles at 4.8 V. Notably, Ah-level pouch cells with an impressively high energy density of 586 Wh kg^{-1} were achieved (Figure 2e), retaining 80.6% of their capacity after 50 cycles and 63.5% after 100 cycles. These results underscore the great potential of the modified electrolyte to support high-energy-density applications while maintaining robust cycle stability.

Moreover, the scalability of the Lewis-acid coordinated electrolyte is showcased through the successful production of industrial-scale flexible membranes (Figure 2f). These membranes, manufactured via a cost-effective, continuous slurry-casting processes, exhibit uniform thickness and good surface quality, making them suitable for large-scale battery production. This demonstration bridges the gap of solid-state batteries between laboratory-scale research and practical implementation, highlighting both the feasibility and economic potential of the proposed strategy.

In summary, this work represents a significant advance in the development of high-voltage PEO-based solid-state batteries. By addressing the oxidative stability and interfacial challenges of PEO-based electrolytes through Lewis-acid coordination, Prof. Jiajun Wang and colleagues provide a pathway to enhance the performance and scalability of polymer-based solid-state batteries. This study not only introduces a novel electrolyte design but also lays the groundwork for future innovations in next-generation energy storage technologies.

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Received 10 January 2025; Accepted 17 January 2025; Published online 14 February 2025

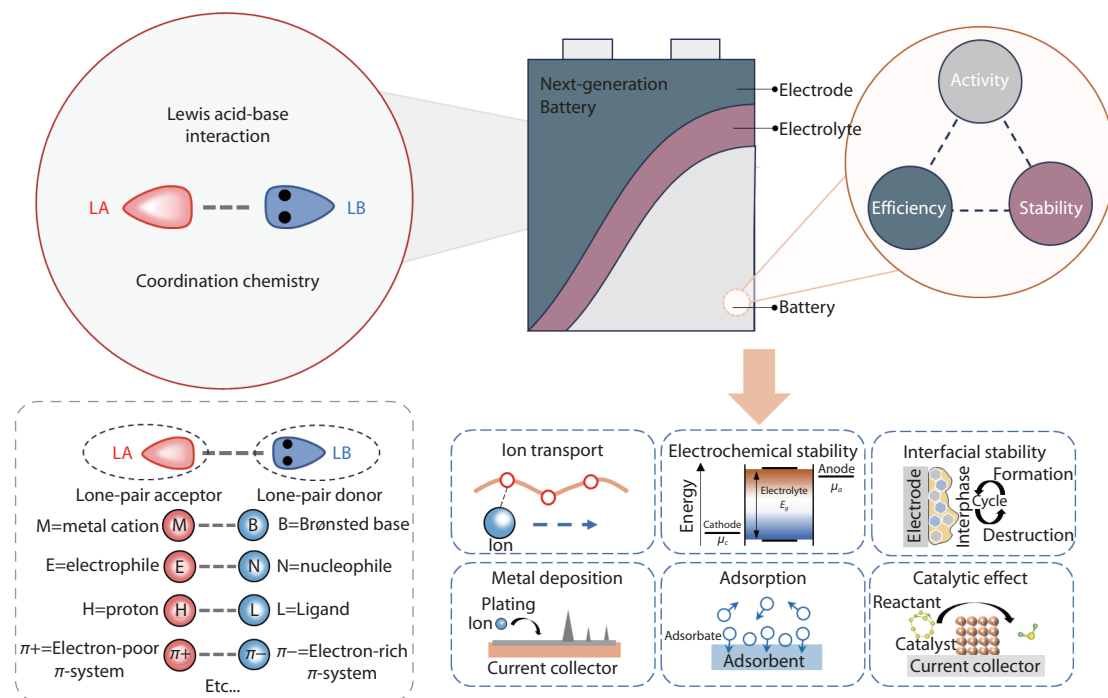


Fig. 1 Lewis acid (LA)-base (LB) interaction in next-generation battery chemistry^[12].

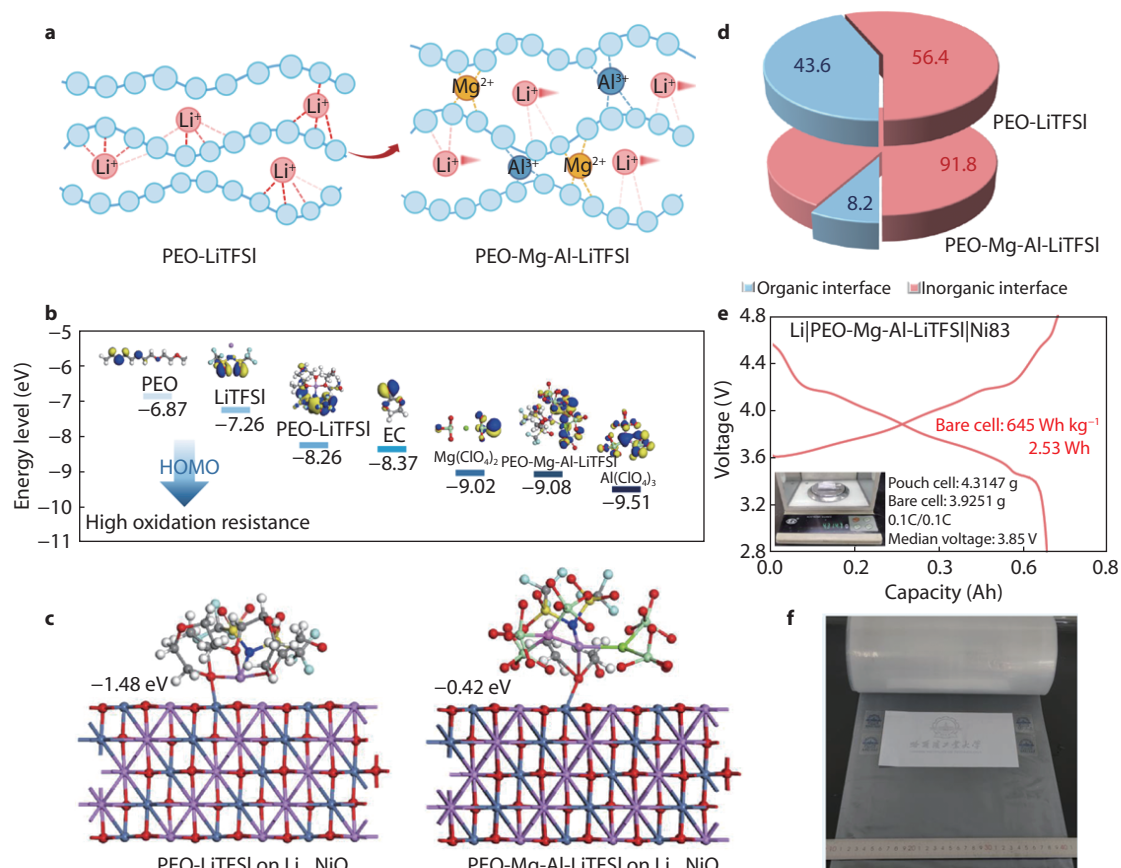


Fig. 2 **a** Schematic of Lewis-acid coordinated PEO-based SPEs. **b** The HOMO energy of different electrolyte components. **c** Adsorption energies of PEO-based electrolytes with and without Lewis-acid additives on the high-Ni cathode. **d** Quantitative analysis of the CEI organics and inorganics. **e** Galvanostatic charge/discharge voltage profiles of a high-voltage pouch cell. **f** A roll of industrial-scale flexible electrolyte membranes^[13].

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