

Materials Science

Electrolyte engineering for a thermally and electrochemically stable interphase on 4.6 V LiCoO₂ at 45 °C

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The pursuit of high-energy-density lithium-ion batteries has driven the development of high-voltage cathodes such as LiCoO₂ (LCO) [1]. However, cycling beyond 4.5 V (vs. Li/Li⁺), especially at elevated temperatures, introduces severe challenges of accelerated interfacial side reactions, e.g., dissolution of the cathode electrolyte interphase (CEI) and transition metal ions [2,3]. Conventional carbonate-based electrolytes form CEI layers rich in organic components with poor thermal and electrochemical stability, which leads to rapid capacity fade, gas evolution, and safety hazards, thereby putting rigorous requirements on deliberate electrolyte design [4,5].

In a recent study, Chen *et al.* [6] reported an engineered electrolyte (FEDTP) using triethyl phosphate (TEP) and 1,3-propane sultone (PS) as functional additives to construct a robust tri-layer CEI on LCO, dramatically improving performance under high voltage (4.6 V) and high temperature (45 °C). The resulting CEI is composed of an inner layer of Li₃PO₄ (ionic conductivity $\sim 10^{-6}$ S cm⁻¹), a middle layer of LiF, and an outer adhesive layer of Li₂SO₃-each playing a distinct role: facilitating Li⁺ transport, blocking electrons, and providing strong adhesion, respectively (Figure 1a). Density functional theory and *ab initio* molecular dynamics (AIMD) simulations confirm the high thermal stability and binding energy of these components (Figure 1b, c). The FEDTP electrolyte also alters the Li⁺ solvation structure, promoting contact ion pairs and reducing the desolvation energy barrier, as evidenced by nuclear magnetic resonance and Raman spectroscopy.

Electrochemically, the cells with FEDTP electrolyte deliver a high specific capacity of 190 mAh g⁻¹ and retain 81.9% capacity after 500 cycles at 1 C and 45 °C, significantly outperforming conventional electrolytes (Figure 1d, e). It also exhibits excellent rate capability (110 mAh g⁻¹ at 8 C) and low interfacial impedance. Through advanced characterization, the authors demonstrate effective suppression of oxygen loss, cobalt dissolution, and CEI breakdown. Practical 1 Ah pouch cells (LCO||graphite) show markedly improved cyclability and voltage retention, with a floating current below 0.05 mA and a CEI decomposition temperature delayed to 483 °C.

In summary, Chen *et al.* provided a holistic and practicable strategy for designing highly stable interphases for high-voltage cathodes under thermal stress. By integrating multiple inorganic components with

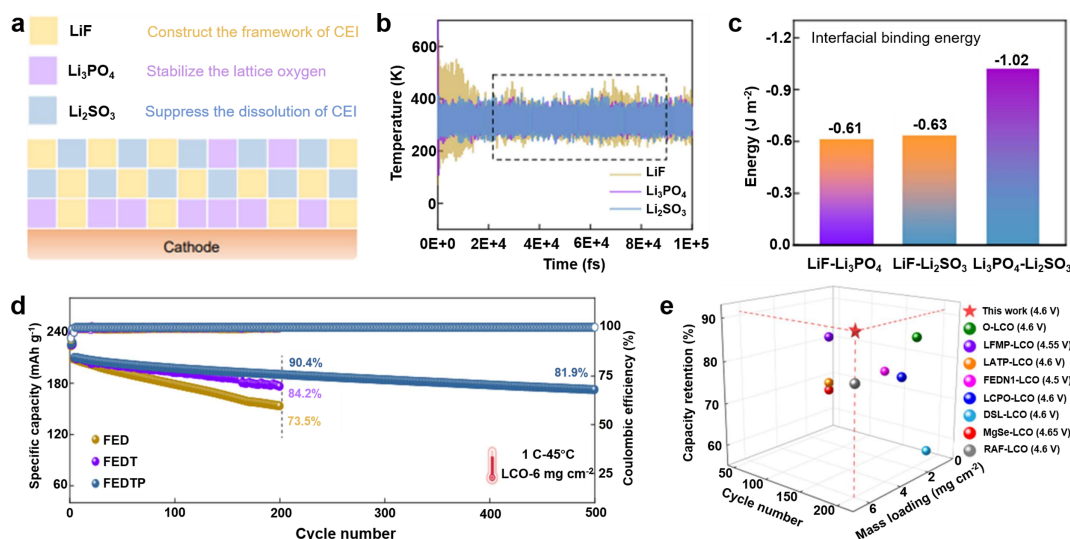


Figure 1 (a) Schematic illustration of CEI design. (b) Temperature curves of LiF, Li_3PO_4 and Li_2SO_3 in AIMD calculation at 45 °C (the more curve fluctuation corresponding the more unstable component). (c) Interfacial binding energies between LiF (100), Li_3PO_4 (101) and Li_2SO_3 (010). (d) Galvanostatic cycling performance and coulombic efficiency of LCO cathodes with various electrolytes at a rate of 0.2 C for the first 3 cycles and 1 C for the subsequent cycles. (e) Comparison of the LCO electrochemical performance under elevated temperature condition. Reprinted with permission from Ref. [6]. Copyright 2025, The Author(s).

complementary properties through electrolyte additives, ultra-stable cycling durability and interfacial robustness are achieved in LCO at 4.6 V and 45 °C. This work not only offers immediate implications for improving high-energy-density lithium-ion batteries but also establishes a CEI design paradigm that could be extended to other cathode materials operating under extreme conditions.

Conflict of interest

The authors declare no conflict of interest.

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