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Editorial

New electrolyte concept: Compact ion-pair aggregate electrolyte

Lithium metal batteries (LMBs) show great potential in delivering high energy density (>500 Wh/kg) with cycling [1]. The cycling life of LMBs is mainly improved by regulating the composition and structure of solid/cathode electrolyte interphase (SEI/CEI) with electrolytes [2]. However, both Li anode and transition metal oxide cathode have high interfacial reactivity at extreme voltages, which highly needs compatible electrolytes. Recently, localized high-concentration electrolytes (LHCEs) have promisingly stabilized the dual electrodes of high-voltage LMBs [3]. However, it remains challenging to explore their solvation structures and interfacial reaction mechanisms associated with LHCEs, which hinders further development [4]. Fortunately, Jie *et al.* recently addressed this question, which published in *Nature Energy* [5].

In Jie *et al.*'s work, they explored the compact ion-pair aggregate (CIPA) electrolyte, in which 2 mol/L lithium difluorosulfonimide (LiFSI) was dissolved in a 1:1 mixture (v/v) of ethylene glycol di-*n*–butyl ether (EGBE) and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE). The CIPA electrolyte is different from the conventional LHCEs. Here, the labelled LHCE-G3 was consisted of LiFSI, TTE and triethylene glycol dimethyl ether (G3) with 1:1 (v/v). The mesoscopic solvation structure on the nanoscale in Figs. 1a and b indicates the CIPA electrolyte consists of large (3–4 nm) and compact aggregates (AGGs) formed by densely arranged ion pairs, and define these large compact AGGs as CIPA. In contrast, small, segregated AGGs (~1.2 nm) were dominated in the LHCE-G3 electrolyte. In the Li^+-Li^+ radial distribution functions (RDFs, g(r)) of CIPA and LHCE-G3 electrolytes (Fig. 1c), the RDF curve of the CIPA electrolyte has a peak at 5.0–6.7 Å due to the coordination of the ion pairs, which is well accorded with the distance of two Li-ions (5–6 Å). This indicates that significant proportion of the CIPA electrolyte's ion pairs were coordinated to promote the formation of compact large CIPA while the LHCE-G3 electrolyte has no significant peak in this range. In addition, the reaction mechanism of CIPA electrolyte on Li surface was analyzed by MD (AIMD) simulations (Fig. 1d). The preferential reduction of CIPA was captured in the CIPA electrolyte, while TTE did not react throughout the simulation. The rapid decrease of FSI^- anions in the CIPA electrolyte suggests that the CIPA electrolyte promoted the rapid reduction kinetics of anions through a collective electron transfer mechanism to form inorganic-rich SEI for terminating the parasitic reaction and suppressing solvent reduction.

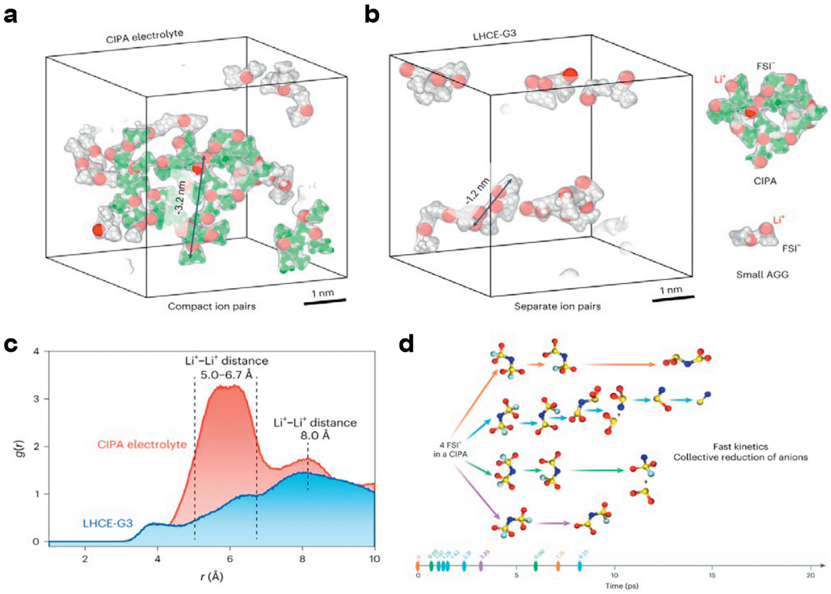

Fig. 1. (a, b) MD snapshots of the AGG structures in the CIPA and LHCE-G3 electrolytes. (c) Li^+-Li^+ RDFs (g(r)) in the two electrolytes. (d) Kinetics and reaction pathways of the CIPA electrolyte on Li surface. Reproduced with permission [5]. Copyright 2024, Springer Nature.

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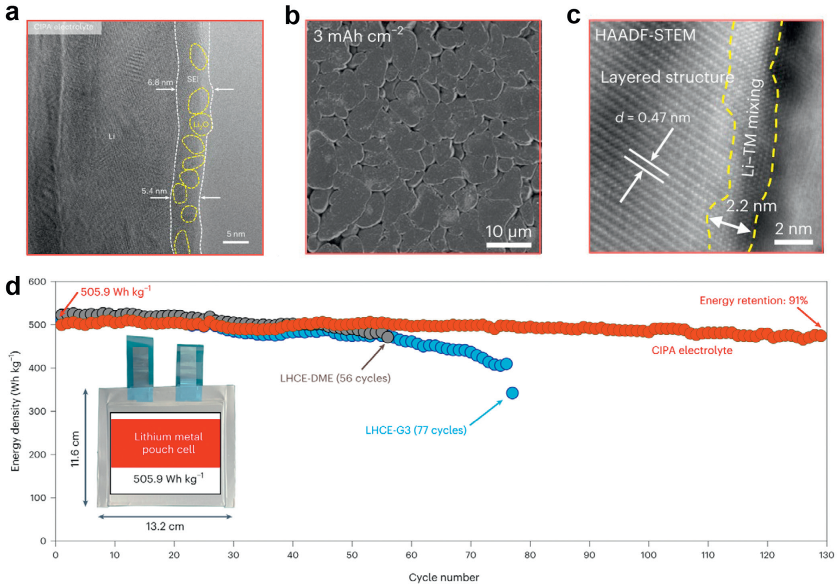

Fig. 2. (a) Cryo-TEM image of the SEI formed in the CIPA electrolyte at 0.5 mA/cm^2 after 30 min. (b) Top-view SEM image of the Li plating morphologies on Cu substrates in CIPA electrolyte at a current density of 0.5 mA/cm^2 and areal capacity of 3 mAh/cm^2. (c) HAADF-STEM image of the NCM811 particle cycled in CIPA electrolyte. (d) Cycling performance of Li||NCM90 pouch cells at a voltage of 3.0–4.3 V and a charge/discharge rate of 0.1 C/0.1 C. Reproduced with permission [5]. Copyright 2024, Springer Nature.

The Li|Cu cell with CIPA electrolyte achieved approximately twice the cycling life (400 cycles) than LHCE-G3 electrolyte. As shown in cryogenic transmission electron microscopy in Fig. 2a, the SEI on Li surface formed in CIPA electrolyte was thin (~6.2 nm) and conformal, which was composed of uniform Li_2O nanocrystalline domains for suppressing the dendrite growth and improving the Li reversibility. As resulted, the dendrite-free planar Li is demonstrated even though the area deposited capacity was as high as 3 mAh/cm^2 (Fig. 2b). In addition, the NCM811 electrode cycled after 200 cycles could maintain its structural integrity in CIPA electrolyte, which remarkably suppressed the interfacial structural phase transition, presenting only a thin (~2.2 nm) phase transition layer on the surface (Fig. 2c). The excellent interfacial stability of the anode and cathode effectively mitigates the electrolyte depletion caused by parasitic reactions. Thus, the Li||NCM90 pouch cells with CIPA electrolyte achieved 505.9 Wh/kg and a high energy retention of 91% after 130 cycles, with an average Coulombic efficiency of 99.94%, which is superior to the pouch cells with conventional LHCEs (Fig. 2d).

In summary, Jie *et al.* demonstrates the effectiveness of CIPA electrolytes to enable >500 Wh/kg Li||NCM90 pouch cells cycle well due to their unique solvation structure and interfacial reaction mechanism. The characteristics of CIPA electrolytes is capable to stabilize the anode and cathode interfaces in solvation structure manner. The proposed concept is expected to be used for exploring high-voltage electrolytes for desirable high energy-density battery systems. It will help us to obtain >600 Wh/kg pouch cells with long cycling life or even higher. Their work gives us an insight on how to design effective electrolytes for desirable battery system.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jing Guo: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Conceptualization.

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