



High heat-tolerance and safety of lithium metal batteries using a high-concentration phase-change electrolyte

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HIGHLIGHTS

- Nonflammable high-concentration phase-change electrolyte (HPCE) was designed.
- Single-layer anode-free battery (AFB) pouch cells were developed using HPCE.
- A cycling stability of 76 cycles with 80 % capacity retention at 60 °C was achieved.
- HPCE cells exhibit superior safety over LHCE cells.

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ABSTRACT

Although lithium metal batteries using localized high concentration electrolytes (LHCEs) exhibit promising life, their safety and survivability in hot summers are of great concern due to highly flammable and volatile solvents and diluents comprising LHCEs. In this work we present a nonflammable high-concentration phase-change electrolyte (HPCE) by addition of sulfolane (SF) and demonstrate it in single-layer Cu/NMC811 anode-free batteries (AFBs). The high dielectric constant of SF raises the LiFSI concentration of HPCE, enabling the AFB cells to possess stable solid electrolyte interphase (SEI) and operate at 60 °C with exceptional cycling stability of 76 cycles at 80 % capacity retention. In addition, the solidified HPCE at room temperature due to the high melting point of SF allows the AFB cells to rest under open circuit with low degradation and high safety. Moreover, the high boiling point and high autoignition temperature of SF as well as the low amount of volatile components in the HPCE thermodynamically suppress the potency of electrolyte combustion; consequently in the single-layer internal short circuit test, the HPCE-cell needs much higher shorting current (104.3 A) (i.e. heating power) than the LHCE-cell (80.1 A) to trigger a battery fire.

1. Introduction

Emergence of localized high concentration electrolytes (LHCEs) dramatically improves the lifetime of lithium metal batteries (LMBs) by facilitating the construction of high-strength inorganic-rich solid electrolyte interphase (SEI) on Li metal anode [1,2]. However, flammable and volatile components in large quantity required in LHCEs, such as 1, 2-dimethoxyethane (DME) and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE), are considered deleterious to thermal stability and safety of LMBs [3–5]. Hence, it is essential to find heat-tolerant electrolytes that are compatible with lithium metal for high safety of LMBs.

Also, conventional LMBs need bulky and sophisticated liquid cooling systems and even refrigeration systems in hot summer environments to maintain cell operation at room temperature (RT). These thermal management systems significantly lower a pack's energy density and add cost, especially for unmanned air vehicles and flying cars [6]. To overcome these drawbacks, LMBs operating at elevated temperatures, such as 60–90 °C, are highly desirable, enabling elimination of bulky and heavy liquid-cooling and refrigeration systems. In a RT ambient, such heat-tolerant batteries without active cooling would warm up by electrochemical processes and then reach a high operating temperature of 60 °C through balance of internal electrochemical heat and external natural convection cooling by a large temperature difference (i.e. from

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cell 60 °C to the ambient RT). Such a passively cooled battery maximizes the pack energy density and greatly enhances energy efficiency without consuming parasitic power for liquid pumps and/or refrigerating compressors, a significant system advantage for electric aircraft. Moreover, these heat-tolerant batteries, when resting under open circuit, will naturally cool down towards the RT ambient and resume sluggish reactivity and hence high safety state during calendar storage. Prior examples of heat-tolerant batteries use PEO-based polymer electrolytes [7] or hybrid polymer-inorganic solid electrolytes [8]; but they are susceptible to oxidation of high-voltage cathodes such as NMC and NCA that are necessary for high energy density applications like electric aircraft.

Here, we develop a nonvolatile high-concentration phase-change electrolyte (HPCE) consisting of lithium bis(fluorosulfonyl)imide (LiFSI), sulfolane (SF) and 1,2-dimethoxyethane (DME) with a molar ratio of 2.1:0.8:0.4. The use of SF with high boiling point (285 °C), high flash point (165 °C), high autoignition temperature (528 °C), high oxidized potential and large dielectric constant (44) and consequently high LiFSI concentration, combined with a much smaller amount of DME than that in LHCEs and the absence of TTE, promises this HPCE to exhibit excellent thermal stability [9,10]. We show that the HPCE in a single-layer Cu||NMC811 (3.4 mAh cm⁻²) anode-free battery (AFB) pouch cell achieves a lifespan of 76 cycles with 80 % capacity retention at 60 °C, better than a corresponding LHCE-cell (52 cycles, LiFSI:DME: TTE = 1:1.2:3, by molar). Additionally, as the most severe safety test, a Resistance-controlled Internal Short Circuit (RISC) method recently developed [11] was carried out to quantify the safety of HPCE cells vs. LHCE cells under same conditions of performance tests. Marked improvement in safety of HPCE cells is demonstrated.

2. Experimental

2.1. Materials

Li foils (99.9 %) with the thickness of 20 μm was purchased from Tianjin China Energy Lithium Co., Ltd. LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathode was purchased from Li-Fun Technology. Lithium bis(fluorosulfonyl)imide (LiFSI) (99.9 % min) was purchased from Nippon Shokubai. 1,2-Dimethoxyethane (DME) (99.95 %), sulfolane (SF) (analytical standard) were purchased from Sigma Aldrich. 1,1,2,2-Tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE) (99 % & water content 50 ppm max) was purchased from Synquest Laboratories. All solvents for electrolyte preparation were dried over molecular sieve in the glove box for 24 h before use.

2.2. Electrolyte preparation

To prepare LHCE, LiFSI was added in DME solution with molar ratio 1:1.2 and stirred for 0.5 h to form a homogenous solution. After that, the corresponding amount of TTE solvent with a molar ratio to LiFSI of 3:1 was added in the solution and stirred for 0.5 h to get LHCE. For the HPCE, LiFSI, SF and DME were mixed with molar ratio of 2.1:0.8:0.4 and stirred at 70 °C for 2 h to form a homogenous solution. The obtained electrolytes were stored in glove box with H₂O content <0.1 ppm and O₂ content <0.1 ppm. Before assembling the pouch cells, the HPCE was heated to 60 °C to become liquid and then filled in. Afterwards, the assembled HPCE cells were kept at 60 °C to ensure good wettability with the separator and electrodes.

2.3. Pouch cell fabrication

0.1-Ah single-layer AFB pouch cells were built using LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) cathodes of 16.8 mg/cm² on 12 μm Al current collector and 8 μm Cu foil as the anode current collector. The cell design is detailed in Fig. 1a and Table S1. Each single-layer AFB pouch cell consists of two Cu current collectors and one double-side coated cathode

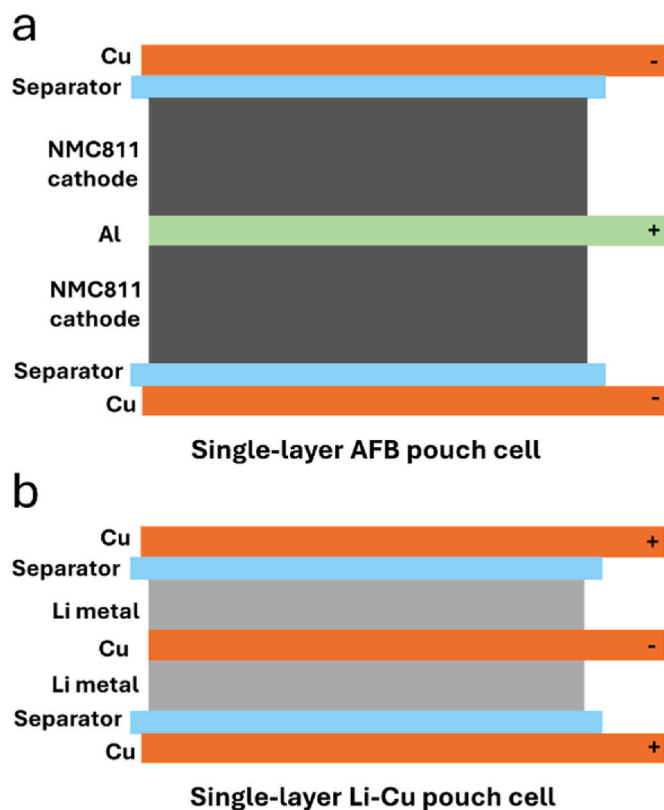


Fig. 1. Cell structure of single-layer (a) AFB pouch cells and (b) Li||Cu pouch cells.

with a 25-μm thick ceramic-coated separator (Lucky) in between. Each cell was filled with 0.3 g of electrolyte. For the assembly of single-layer Li||Cu pouch cells (Fig. 1b), two Cu foils pair with one double-side Li metal foil (20 μm) and 25-μm thick ceramic-coated separators (Lucky) are in between. The Li metal anode is the same size as NMC811 cathode.

2.4. Resistance-controlled internal short circuit (RISC) experimentation

To allow for quantitative comparisons between parametric safety experiments and to ensure high reproducibility, we deploy the RISC method on single-layer cells, which can perform quantitative internal short circuit (ISC) testing through precise control of shorting resistance as previously described in Ref. [11]. A major difference of RISC method from prevalent nail penetration or accelerated rate calorimetry (ARC) is that the latter ones are statistically random and difficult to reproduce [12] without deliberate control of shorting resistance, whereas the former exhibits a high degree of quantitative reproducibility [11] and is performed under identical conditions of performance tests, such as under stacking pressures. Fig. 2 schematically shows the experimental apparatus with details described in Ref. [11]. In brief, thin Al and Ni chips are placed against the cathode and anode current collectors of a single-layer AFB pouch cell to induce internal shorting, respectively. The area of the porous cathode material covered by Al chip was removed for direct contact between Al chip and cathode current collector. A multi-layer lithium-ion battery pouch cell is connected in parallel to the single-layer AFB cell as the external power source, and a thermocouple was planted in the center of the shorting area to detect the internal temperature. Al and Ni chips are connected externally by a shunt and a switch. Physically, this setup simulates the most severe failure scenario, i.e. ISC of a single layer in a multi-layer battery where a huge amount of local heat is generated in the shorted layer due to discharge of energy from all the neighboring intact layers into the shorted single layer.

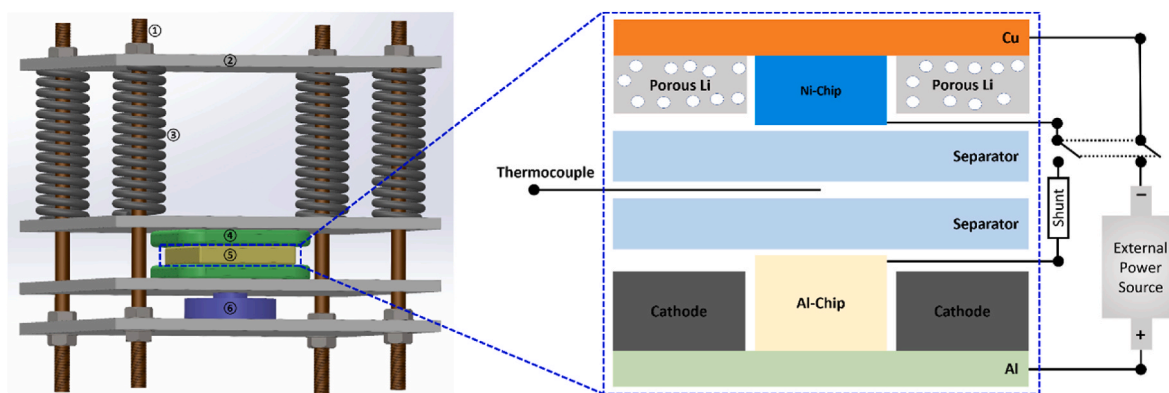


Fig. 2. Illustration of resistance-controlled internal short circuiting (RISC) experimentation, adapted from Ref. [11]. ① Screw; ② Steel plate; ③ Spring; ④ Ceramic layer; ⑤ Cell under study; ⑥ Load cell.

2.5. Characterization

The ionic conductivity of electrolytes was measured by VWR Traceable Bench/Portable Conductivity Meter (Catalog Number: 23226-505). The morphologies of Li metal anodes were observed by SEM (Thermo Fisher Scientific, Verios 5 XHR SEM). XPS measurements were carried out at a PHI 5000 VersaProbe II system (Physical Electronics) spectrometer, which is equipped with a hemispherical analyzer. The spectrometer was attached to the Ar glovebox and sample transfer was directly through it to avoid any contact with air and moisture. Monochromatic Al-K α excitation ($h\nu = 1486.6$ eV) was used at power of 25 W, additionally applying a low-energy electron charge neutralizer. The high-resolution spectrum of each element was collected with a pass energy of 23.25 eV in an analysis area of $100 \times 100 \mu\text{m}$. The binding energy scale was corrected based on the C1s peak from contaminations (C-C at 284.7 eV) as internal binding energy standard. EIS test was carried out on Solartron analytical ModuLab 2100 A with a 10-mV perturbation in the frequency range of 1 MHz to 100 mHz.

3. Results and discussion

The obtained HPCE is shown to be solid at room temperature and changes to liquid at $\sim 60^\circ\text{C}$ due to the high content and melting point (27.5°C) of SF (Fig. 3a and b). The high boiling point of SF (285°C) and the high LiFSI content lend the HPCE excellent nonflammability. As shown in Fig. 3c and Video S1, the HPCE gradually changes from solid to liquid during the ignition process. There is no noticeable change in flame strength even after igniting for 10s, and the flame extinguishes immediately when the ignition source is removed, demonstrating the nonflammability of HPCE. In contrast, a fierce flame and dense smoke are obviously observed when the LHCE (LiFSI:DME:TTE = 1:1.2:3, by molar) is ignited, due to the low flash points of DME (-2°C) and TTE (29°C) (Fig. 3d and Video S2). The high Li salt concentration and high freezing point of HPCE result in low ionic conductivity. As shown in Fig. 3e, HPCE exhibits inferior ionic conductivity in its solid state ($<0.1 \text{ mS cm}^{-1}$). However, as the temperature increases, the liquid-state HPCE shows a markedly increased ionic conductivity (1.31 mS cm^{-1} at 60°C)

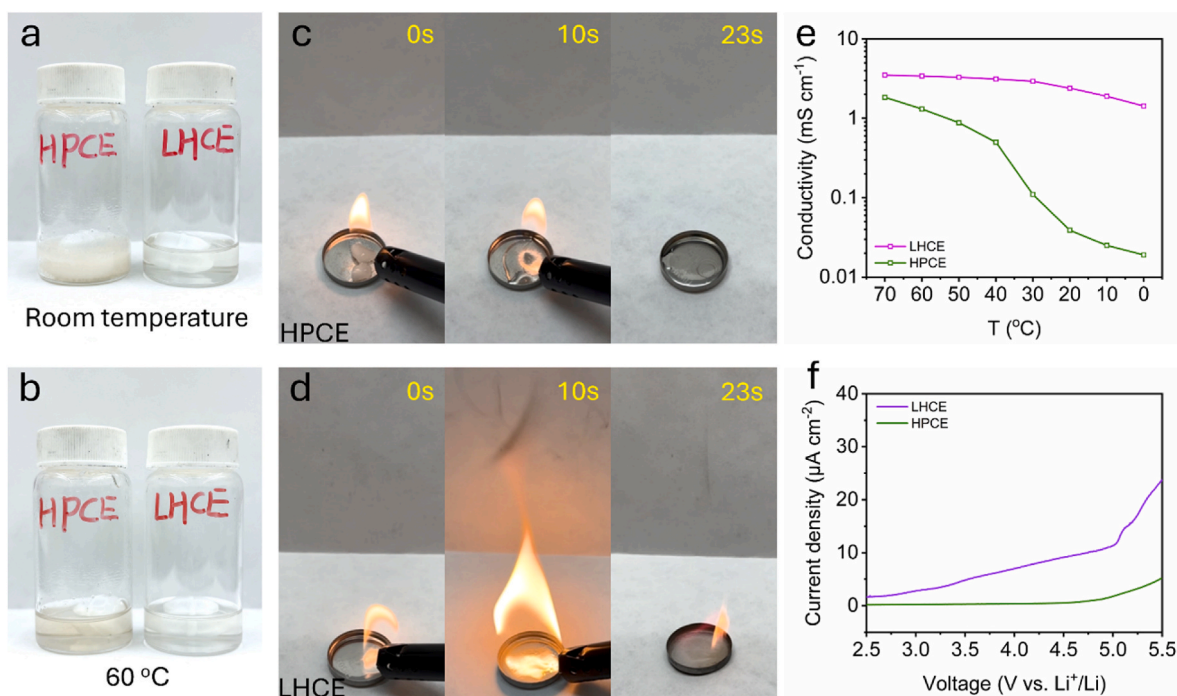


Fig. 3. Physical properties of HPCE and LHCE. Digital photos of electrolytes at (a) room temperature and (b) 60°C . Ignition tests of (c) HPCE and (d) LHCE. (e) Ionic conductivity of the electrolytes at different temperatures. (f) Linear scanning voltammetry (LSV) of Li||Al cells in the electrolytes with a scan rate of 1 mV s^{-1} at 60°C .

though it is still lower than that of LHCE (3.42 mS cm^{-1} at 60°C), demonstrating a higher Li salt-to-solvent concentration of HPCE than that of LHCE [13]. On the other hand, the high LiFSI content and the strong oxidation resistance of SF endow HPCE with a much better oxidative stability than that of LHCE at 60°C (Fig. 3f).

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Subsequently, single-layer AFB pouch cells with a capacity of 0.1 Ah were assembled to investigate Li deposition behavior and SEI

compositions in HPCE and LHCE, respectively (Fig. 1a and Table S1-Table S3). Fig. S1 shows the charge/discharge curves of the AFB pouch cells during formation process at 60°C . A shallow voltage range of 3.6–4.5 V was employed during formation with a charge/discharge current density of $C/10$, to achieve dense Li metal anodes. The similar shapes of the charge/discharge curves demonstrate the comparable electrochemical behavior of AFB cells in HPCE and LHCE. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) tests were conducted after the second charge to 4.5 V. Fig. 4a–d shows

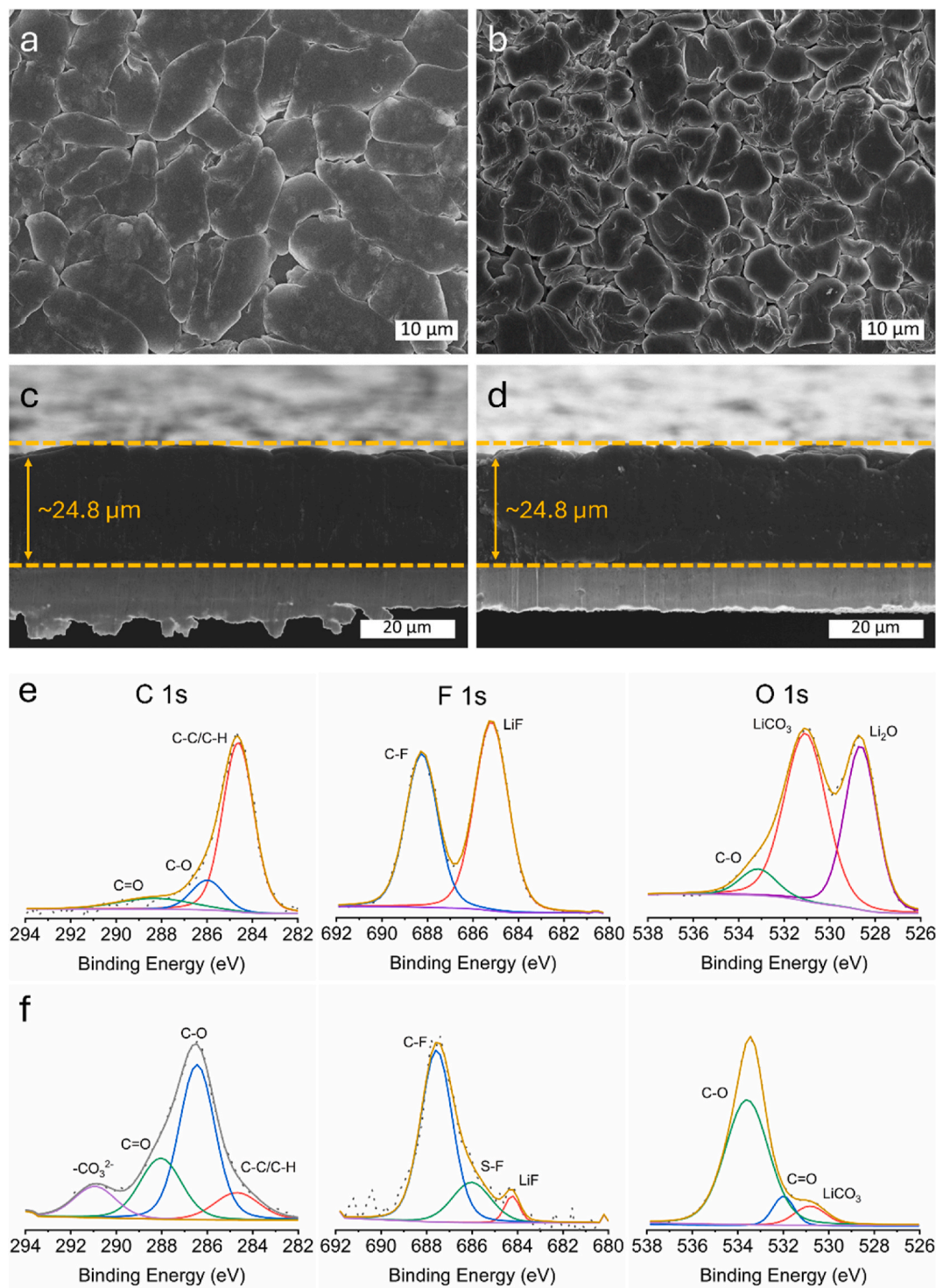


Fig. 4. Li deposition in HPCE and LHCE. (a) Top-view and (c) cross-sectional morphologies of deposited Li on Cu foil in HPCE. (b) Top-view and (d) cross-sectional morphologies of deposited Li on Cu foil in LHCE. C 1s, F 1s and O 1s XPS characterizations of the SEI formed in (e) HPCE and (f) LHCE.

top-view and cross-sectional SEM images of Li deposited on Cu foil in HPCE and LHCE. The physical properties of Li metal, such as low melting point, low hardness, and significantly reduced creep stress with the temperature increasing, enable the deposited Li to exhibit dense and large chunk structure in both HPCE and LHCE at 60 °C [14–16].

The components of SEI layers formed on Li metal anodes in HPCE and LHCE were analyzed by XPS. The higher Li^+ concentration in HPCE promotes formation of stable SEI on Li metal anode, even at high temperatures [13]. As shown in Fig. 4e, the intense F 1s XPS peak at 684.6 eV indicates the presence of LiF on the surface of Li metal in HPCE, and the observed F 1s XPS peak at 688 eV assigned to C-F bond demonstrates the existence of organic fluoride in the SEI layer. In addition, the SEI layer formed on Li metal anode in HPCE contains Li_2O and Li_2CO_3 according to the observation of O 1s XPS peaks at 528 eV and 531 eV, respectively [17–19]. The presence of inorganic species strengthens the stability of SEI layer on Li metal anode [20]. In contrast, the high intensity of C-F and C-O peaks observed from F 1s and O 1s XPS spectra indicates the formation of an organic-dominated SEI on Li metal anode in LHCE at 60 °C (Fig. 4f) [21,22]. Besides, observation of the S-F bond in LHCE indicates the decomposition of FSI^- , demonstrating the instability of LHCE at high temperatures. On the contrary, the absence of the S-F bond confirms the high stability of HPCE, attributed to its higher LiFSI content.

A more stable Li metal anode is expected in HPCE due to better compositions of the SEI layer constructed in HPCE than in LHCE. To assess the stability of Li metal in both HPCE and LHCE, the Coulombic efficiency (CE) of Li metal anode was measured using single-layer Li||Cu pouch cells operating at 60 °C (Fig. 1b). As shown in Fig. 5a, the Li metal anode exhibits an exceptional CE of 99.6 % in HPCE, which is much

higher than that in LHCE (99.1 %), demonstrating a more stable SEI on Li metal anode and dramatically restricted side reaction between solvent molecules and Li metal in HPCE [23]. The cycling of AFB pouch cells was proceeded with charge/discharge current densities of C/6 and C/3, respectively, over a deep voltage range of 2.8–4.2 V at 60 °C after secondly charging to 4.5 V (Fig. S2). The HPCE-cell shows a lower capacity than that of LHCE-cell due to the high viscosity and low ionic conductivity of HPCE (Table S2). Notably, the high freezing point of HPCE can effectively suppress all the chemical/electrochemical reactions and force the batteries into “dormant state” at room temperature, thereby increasing battery safety when at rest. As shown in Fig. 5b, the self-discharge of HPCE-cell and LHCE-cell was measured at room temperature with 100 % state of charge (SOC). Apparently, the voltage of LHCE-cell continuously decreases, whereas the voltage of HPCE-cell has barely dropped for over 40 days, demonstrating the superior stability of HPCE batteries during open circuit.

Fig. 5c and d shows the cyclic stability and CE of HPCE-cell and LHCE-cell at 60 °C with an electrolyte amount of 3 g Ah^{-1} . The HPCE-cell exhibits a higher CE and better cycling stability up to 76 cycles with 80 % capacity retention due to less free solvent molecules. Although the LHCE shows a high salt-to-solvent concentration, the more DME molecules escape from Li^+ cation solvation shell into the TTE matrix at high temperatures increases the side reaction between free DME molecules and Li metal, resulting in a medium CE and a cycle life of 51 cycles with 80 % capacity retention [13,24]. After cycling, the aged Li metal anodes were disassembled for SEM analysis. As shown in Fig. 5e, the aged Li metal anode in HPCE displays a flat surface with some observable active Li chunks. In contrast, the surface of the aged Li metal anode in LHCE shows obvious porous structure with no visible

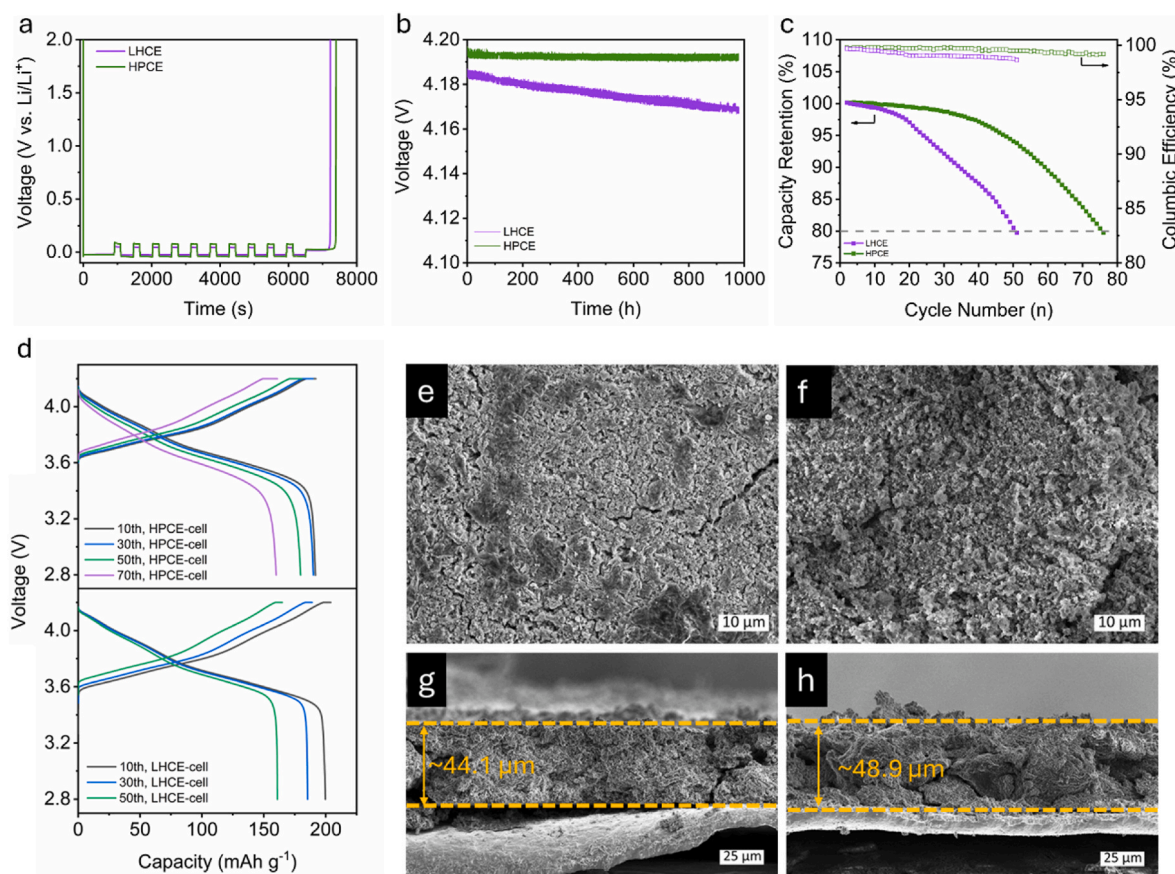


Fig. 5. AFB pouch cells in HPCE and LHCE electrolytes. (a) Aurbach protocol [25] using single-layer Li||Cu pouch cells to calculate the average Li metal CE. (b) Self-discharge at room temperature after full charge to 100 % SOC. (c) Cycling performance and CE of AFB cells at 60 °C. (d) The voltage profiles of AFB pouch cells for ageing evaluation. (e) Top-view and (g) cross-section SEM images of aged Li metal anode in HPCE. (f) Top-view and (h) cross-section SEM images of aged Li metal anode in LHCE.

active Li (Fig. 5f). In addition, although the HPCE-cell has a longer cycle life than LHCE-cell, the thickness of the aged Li metal anode is thinner (Fig. 5g and h), indicating the higher stability of the SEI formed on Li metal anode in HPCE.

The safety of HPCE-cells was evaluated using the RISC test (Fig. 2) simulating single-layer internal shorting in a multi-layer battery. Fig. 6 presents the ISC results on various AFB cells. Our previous research [11] elucidated that heat, oxidizer (O_2 released from the NMC811 cathode) and fuel (Li metal) constitute the three key factors for battery thermal runaway. Changing electrolytes doesn't alter the cell structure, hence upon internal shorting, the initial voltage drop, shorting current, shorting resistance and heating power of the HPCE-cell remain similar to those of the LHCE-cell when a 2.6-Ah external power source is employed. However, the high boiling point of SF (285°C) suppresses the access of O_2 generated from the cathode to the Li metal in the anode. Therefore, it is seen that the ISC consequence of the HPCE-cell is milder, as reflected by a lower internal temperature, a slower heating rate, a more sluggish shorting resistance change, and a slower heating power drop. Correspondingly, the LHCE-cell catches fire around 2.6 s but the HPCE-cell only mildly smokes after 7.5 s without catching fire (Video S3).

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According to our previous research [11], shorting current controlling heat input is a critical factor that triggers battery combustion, and it can vary by changing the external power source's cell capacity. A higher cell capacity of the power source corresponds to a greater number of intact layers surrounding the shorted single layer in a larger-capacity cell. As shown in Fig. 6, when the single-layer HPCE-cell is connected to a 5.0-Ah external power source for ISC testing, a higher initial shorting voltage (2.99 V) and larger initial shorting current (85.9 A) are observed, leading to higher internal temperature, faster heating rate, quicker shorting resistance increasing, and higher heating power. Note also that the LHCE-cell catches fire when the internal temperature

reaches $\sim 332^\circ\text{C}$ at 2.6 s, whereas the internal temperature in the HPCE-cell can rise to $\sim 485^\circ\text{C}$ at the onset of smoke and spark due to the high autoignition temperature (528°C) of SF (Video S4). After further increasing the external power source to 9.5 Ah, a very high shorting current through the HPCE-cell is achieved (104.3 A), which leads to battery fire after 1.5 s and the internal temperature rises as high as 583°C (Video S5).

Supplementary data related to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2024.236094>.

4. Conclusion

We have developed a high-concentration phase change electrolyte (HPCE) by incorporating a large amount of non-volatile SF to achieve a high LiFSI concentration, a low ratio of flammable solvent (DME), and the absence of volatile and flammable diluent (TTE). The high melting point of SF makes HPCE solid at room temperature, effectively eliminating all the chemical/electrochemical reactions to force the batteries into "dormant state" for maximal battery safety during rest. The very high LiFSI content reduces the ratio of free solvent molecules and increases the concentration of FSI^- , which favors stable SEI and high CE at elevated temperatures. Consequently, a single-layer Cu|NMC811 AFB cell using HPCE as the electrolyte shows cycling stability of up to 76 cycles with 80 % capacity retention at 60°C , outperforming the control LHCE-cell (51 cycles). In addition, the safety of single-layer internal shorting was investigated using RISC experimentation for internal short circuiting. The small amount of DME in HPCE reduces the fuel quantity in the cell. The high boiling point and high autoignition temperature of SF effectively block the access of O_2 generated from the cathode to lithium metal in the anode, thus dramatically enhancing the safety of such HPCE-cells. Indeed, ultrahigh shorting current (104.3 A) and internal temperature (583°C) are needed to trigger a battery fire in HPCE-cells versus much more fire-prone LHCE-cells (80.1 A and 332°C). HPCEs thus show great promise for achieving heat-tolerant and safe

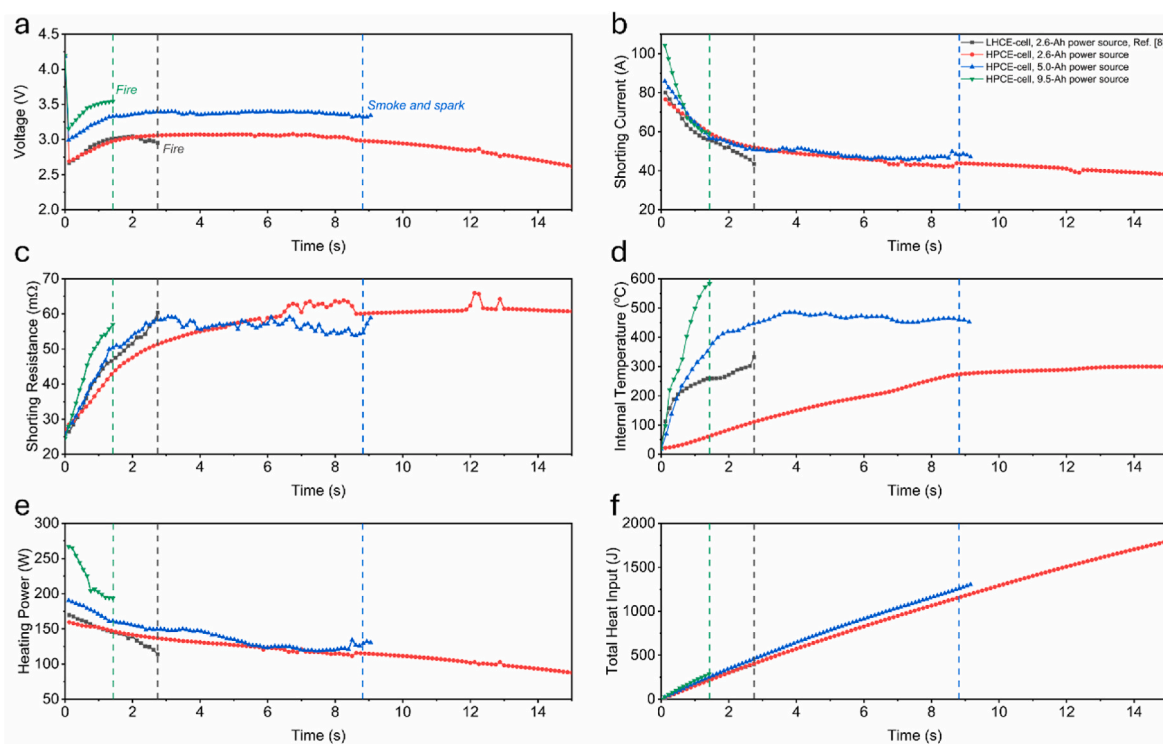


Fig. 6. Single-layer internal shorting of HPCE- and LHCE-cells. (a) Cell voltage, (b) Shorting current, (c) Shorting resistance, (d) Internal temperature, (e) Heating power and (f) Heating input after single-layer ISC. All the data after the battery fire/explosion was not shown due to cell disintegration and sensing probe dislocation from violent fires.

lithium metal batteries with high energy density.

CRedit authorship contribution statement

Kaiqiang Qin: Writing – original draft, Methodology, Investigation, Conceptualization. **Shanhai Ge:** Methodology, Investigation, Conceptualization. **Nitesh Gupta:** Methodology, Investigation. **Tatsuro Sasaki:** Writing – review & editing, Methodology. **Chao-Yang Wang:** Writing – review & editing, Supervision, Conceptualization.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2024.236094>.

Data availability

Data will be made available on request.

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