

# Enabling 5V-class lithium metal batteries via an aggregation-enhanced solvation electrolyte

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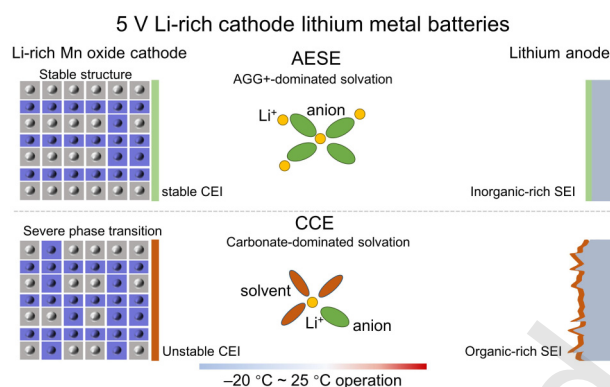
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This study presents an aggregation-enhanced solvation electrolyte (AESE) that stabilizes 5 V-class Li||LRMO batteries by promoting an anion-rich solvation structure, which simultaneously forms a robust CEI on the cathode and a LiF/Li<sub>2</sub>O-rich SEI on the lithium anode, enabling excellent cycling stability at both room temperature and -20 °C.

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**ABSTRACT:** High-voltage lithium metal batteries (LMBs) utilizing lithium-rich manganese oxide (LRMO) cathodes offer a promising way towards high energy densities yet remain impractical when operating at high voltages, primarily due to electrolyte instability at interfaces of LRMO and Li metal electrodes. In this study, we report stable cycling of LRMO-based LMBs under ultra-high voltage conditions of 5 V via employing an aggregation-enhanced solvation electrolyte (AESE). The AESE features a solvation structure dominated by anion-wrapped aggregates, in which Li<sup>+</sup> ions are under a coordination environment surrounded by numerous anions. With such a solvation structure, the AESE concurrently stabilizes the Li metal anode and LRMO cathode. It promotes a protective cathode–electrolyte interphase on LRMO and an inorganic-rich interphase on Li metal, collectively suppressing electrolyte oxidation and transition metal dissolution. Thereby, Li||LRMO cells can deliver exceptional cycling stability at 5 V, retaining >87% capacity after 200 cycles. It also sustains stable operation for 100 cycles at −20 °C. This work demonstrates the electrolyte design for 5 V-class LMBs capable of reliable operation under low-temperature conditions.

**KEYWORDS:** aggregation-enhanced solvation electrolyte, lithium metal battery, lithium-rich layered oxide, 5.0 V operation, low-temperature performance

## 1 Introduction

Lithium metal batteries (LMBs) employing high-voltage cathodes with high capacities are promising for high-energy-density applications, including electric vehicles and electric aircraft [1-3]. Conventional high-voltage cathode materials, such as Ni-rich layered oxides (e.g., LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>1-x-y</sub>O<sub>2</sub>, NMC), are intrinsically limited by their moderate specific capacities (~230 mAh g<sup>-1</sup>), hindering significant improvements in cell energy density [4-10]. In comparison, lithium-rich manganese-based layered oxide (LRMO) can deliver substantially higher capacities (250–300 mAh g<sup>-1</sup>) when the cell voltage is >4.5 V, owing to synergistic participation of both cationic and anionic redox processes [11-14]. When paired with the Li metal anode, the Li||LRMO configuration presents a promising pathway to realizing superior energy densities exceeding 600 Wh kg<sup>-1</sup> [15]. Nevertheless, the practical deployment of LRMO-based LMBs still faces critical challenges, particularly the lack of electrolytes that can stabilize both cathode- and anode-electrolyte interfaces [16, 17]. At the cathode–electrolyte interface, severe electrolyte decomposition generates

corrosive species that trigger cathode phase transition and dissolution of transition metal (TM) ions, leading to catastrophic capacity decay [18, 19]. At the anode–electrolyte interface, dendrites easily evolve and propagate in electrolytes, causing rapid cell failure with large polarization, short-circuiting, etc [20-23]. Besides, dissolved TM ions may deposit onto Li anode surface, thereby accelerating lithium dendrite formation and triggering parasitic reactions [24, 25].

Recently, extensive research efforts have been put on designing electrolytes for LRMO-based LMBs [26]. Carbonate electrolytes have been a prevalent system due to their relatively higher oxidative stability compared to ether electrolytes [27]. So far, efforts to improve the stability of LRMO and Li metal electrodes through electrolyte engineering have largely centered on introducing fluorine atoms into carbonate-based solvents [28, 29] or the use of electrolyte additives [30-34]. Beyond additive and solvent fluorination strategies, localized high-concentration electrolytes (LHCEs) have recently been explored for stabilizing LRMO cathodes (summarized in Table S1) [35-39]. Despite the progress, the LRMO cathode cycled with

LHCEs remains plagued by a low attainable capacity when cycled at high rates and/or low temperature due to its poor rate capability, e.g.,  $\sim 200 \text{ mAh g}^{-1}$  at 1 C with cutoff charging voltage of 4.8 V. Raising LRMO operating voltage offers a viable strategy for enhancing the cathode capacity. However, further elevating the voltage of LRMO-based LMBs (for instance, 5.0 V) remains challenging, since it typically induces exacerbated electrolyte oxidation and irreversible cathode phase transitions [40]. Moreover, detailed investigation of the solvation structure of LHCE, particularly the population and distribution of aggregate species and their role in stabilizing high-voltage interfaces, has largely focused on the ether-based system, which are widely thought to be unstable under high voltage.

Herein, we report the stable cycling of 5 V-class LRMO-based LMBs via an aggregation-enhanced solvation electrolyte (AESE). The AESE employs ethyl methyl carbonate (EMC) as the primary solvent and a hydrofluoroether as the diluent. The choice of EMC as the primary solvent is central to this design. Compared with ethylene carbonate (EC) and dimethyl carbonate (DMC), EMC has a substantially lower dielectric constant ( $\sim 3.0$ ), a moderate donor number ( $\sim 16.8 \text{ kcal mol}^{-1}$ ) and a moderate  $\text{Li}^+$  binding affinity among the solvents [41–45]. Consequently, its participation in the solvation shell is substantially weakened, while the diluent synergistically amplifies the formation of extended anion- $\text{Li}^+$  networks. MD simulations show that 90% of  $\text{Li}^+$  reside in  $\text{Li}^+$ -anion clusters, with a high proportion coordinating to three or more anions. Spectroscopy and microscopy characterizations indicated that such an aggregation-enhanced solvation structure promotes the development of a protective CEI on LRMO, thereby maintaining a well-defined cathode phase structure and suppressing transition metal dissolution. Meanwhile, a  $\text{LiF/Li}_2\text{O}$ -rich solid-electrolyte interphase (SEI) is formed on Li anode, realizing a high Li reversibility with a Coulombic efficiency (CE) of 99.4%. Consequently,  $\text{Li}||\text{LRMO}$  cells with the AESE exhibit exceptional cycling stability at 5.0 V, retaining  $>87\%$  capacity after 200 cycles. It also sustains stable operation for 100 cycles at  $-20^\circ\text{C}$ . This study presents an electrolyte formulation tailored for 5 V lithium metal batteries, enabling stable and robust performance at subzero temperatures.

## 2 Experimental Section

### 2.1 Materials and Electrolyte Preparation

Conventional carbonate-based electrolyte (CCE) comprising 1 M  $\text{LiPF}_6$  dissolved in a ternary solvent mixture of dimethyl carbonate (DMC), ethylene carbonate (EC), and ethyl methyl carbonate (EMC) in a 1:1:1 weight ratio, as well as the pure EMC solvent, were purchased from DodoChem. Ethylene carbonate (EC), lithium bis(fluorosulfonyl)imide (LiFSI), 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE), and DMC were obtained from the Zhangjiagang Guotai Huarong New Chemical Materials Co., Ltd. The Celgard 2325 microporous polypropylene separator, CR2032 coin-cell components, and aluminum-coated current collector foils were supplied by Canrd. AESE was prepared by mixing LiFSI and TTE at 1:3 (molar ratio), followed by the addition of EMC at a volume 5% above the threshold required for complete dissolution (1LiFSI-1.8EMC-3TTE,

molar ratio). The molar concentration of LiFSI is 1.4 M. TTE-free electrolyte (1LiFSI-1.8EMC, molar ratio) was prepared by mixing LiFSI and EMC at 1:1.8 (molar ratio).

The cathode electrodes fabricated using LRMO employed two distinct active material loadings:  $3\text{--}4.2 \text{ mg cm}^{-2}$  and  $8 \text{ mg cm}^{-2}$ . Each electrode comprised 80 wt.% LRMO (supplied by the Tianjin Institute of Power Sources), along with 10 wt.% Super P carbon black (Canrd) as the conductive additive and 10 wt.% polyvinylidene fluoride (PVDF, Canrd) as the binder. Current collectors including carbon-coated aluminum foil, plain aluminum foil, and copper foil were purchased from Shenzhen Kejing. Lithium metal foil (15.4 mm in diameter,  $500 \mu\text{m}$  thick) and lithium-copper composite foil ( $50 \mu\text{m}$  thickness) were provided by China Energy Lithium Co., Ltd.

### 2.2 Electrochemical Measurements

Galvanostatic charge/discharge cycling was carried out on either a WUHAN LAND or NEWARE battery test system. For  $\text{Li}||\text{LRMO}$  coin cells, aluminum-coated stainless-steel cases were employed, supplemented with an extra layer of Al foil. Each cell was filled with  $70 \mu\text{L}$  of electrolyte. Electrochemical evaluation spanned voltage windows of 2.0–4.8 V and 2.0–5.0 V, respectively. The cycling protocol began with two formation cycles at a low rate of 0.1 C (where 1 C corresponds to  $220 \text{ mA g}^{-1}$ ), followed by subsequent cycling at elevated rates as specified. Aurbach-type testing was conducted under following conditions: constant current density of  $0.5 \text{ mA cm}^{-2}$  and areal capacity of  $1 \text{ mAh cm}^{-2}$  for 10 cycles. Formation cycles for this test used a higher areal capacity of  $5 \text{ mAh cm}^{-2}$ . In  $\text{Li}||\text{Cu}$  cells, the charge cutoff voltage limit was set to 1.0 V. Each  $\text{Li}||\text{Cu}$  and  $\text{Li}||\text{Li}$  cell was filled with  $60 \mu\text{L}$  of electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Solartron Analytical EnergyLab XM system. Cyclic voltammetry (CV) test was conducted on a CHI workstation.

### 2.3 Characterization

Raman spectra of the electrolytes were acquired using a Renishaw inVia Raman Microscope.  $^7\text{Li}$  and  $^{19}\text{F}$  nuclear magnetic resonance (NMR) spectra were performed on a JEOL JNM-ECZ600R/S1 spectrometer (600 MHz). After cycling, electrodes were rinsed with pure EMC solvent. Surface morphology was examined by scanning electron microscopy (FEI Apreo). Near-surface cathode particle structure was analyzed by Field-emission high-resolution transmission electron microscopy (HRTEM; JEOL JEM-F200). Elemental and chemical state information from both as-prepared and electrochemically cycled electrode surfaces was obtained through X-ray photoelectron spectroscopy (XPS), conducted on a Thermo Scientific ESCALAB 250Xi spectrometer. Concentrations of TM ions leached into the anode were determined quantitatively by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo Scientific iCAP RQ system. Soft X-ray absorption spectroscopy (sXAS) was tested at the XMCD-b beamline of the Hefei Light Source. Thermal stability of the charged cathode material was evaluated by differential scanning calorimetry (DSC) using a Netzsch DSC 204F1 instrument; specifically, fully charged LRMO powder was

homogeneously blended with liquid electrolyte inside a sealed, high-pressure crucible prior to thermal analysis. The self-extinguishing time (SET) was calculated by normalizing

the combustion time with respect to the electrolyte mass ( $\text{s g}^{-1}$ ).

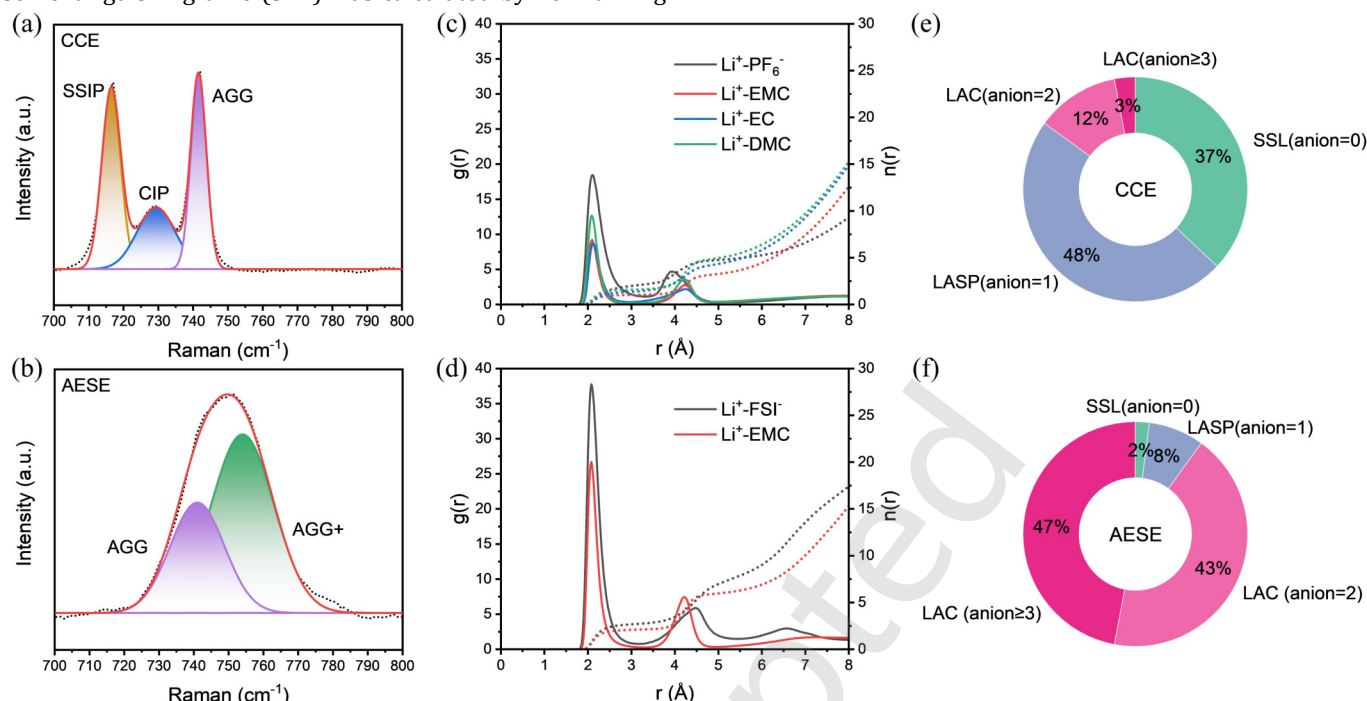


**Figure 1** Solvation structure. (a–b) Raman spectra obtained for the (a) CCE and (b) AESE systems. (c–d) Radial distribution functions ( $g(r)$ ) and corresponding coordination numbers ( $n(r)$ ) in (c) CCE and (d) AESE. (e–f) Distributions of solvated species within the (e) CCE and (f) AESE systems.

## 2.4 Computational methods

Classical molecular dynamics (MD) simulations were carried out using GROMACS (version 2020.3) to investigate mesoscale solvation structures [46]. Prior to MD simulations, force field parameters for the custom diluents were parametrized using Jaguar (version 8.8) at the PBE/6-31+G\* level [47]. Three systems were built: CCE (60  $\text{LiPF}_6$  in 206 EMC, 243 EC, 238 DMC; cubic box 4.66384 nm) and AESE (60  $\text{LiFSI}$  in 108 EMC, 180 TTE; 4.17786 nm). After energy minimization ( $1.0 \times 10^{-4}$ ), each system was equilibrated via NVT at 300 K for 1.0 ns, NPT at 1 bar for 2.0 ns, and final NVT for 1.0 ns, using a velocity-rescaling thermostat ( $\tau=0.1$  ps) and Berendsen barostat ( $\tau=0.5$  ps). Radial distribution functions and solvation cluster statistics were extracted from the equilibrated trajectories.

## 3 Results and Discussion

The bulk solvation structures of CCE and AESE systems were characterized via Raman spectroscopy (Fig. 1(a–b)). For CCE, two peaks of the  $\text{PF}_6^-$  anion could be seen, which are centered at  $\sim 716 \text{ cm}^{-1}$  (SSIP, solvent-separated ion pairs) and  $\sim 740 \text{ cm}^{-1}$  (AGG, ion aggregate) with comparable intensities [48]. This indicates a mixed solvation environment for the  $\text{Li}^+$  ion first solvation sheath, in which nearly half portion of  $\text{Li}^+$  are solvated by solvent molecules with fully dissociated anions, while others are coordinated with  $\text{PF}_6^-$  anions. Such a structure suggests the presence of considerable free or weakly bound anions in the CCE. Conversely, the Raman spectrum of the AESE showed a distinct profile. The SSIP and CIP signals were nearly absent, and the spectrum was dominated by AGG and AGG+ (more coordinated ion aggregates) species [49–52], with the AGG+ peak ( $\sim 755 \text{ cm}^{-1}$ ) showing a notably higher intensity, indicating the prevalence of aggregated coordination

structures in the AESE.

MD simulations were performed to quantify the solvation environment (Fig. S1 in the Electronic Supplementary Material (ESM)). In CCE, each  $\text{Li}^+$  ion is coordinated on average by 2.15  $\text{PF}_6^-$  ions together with  $\sim 2$ -fold solvents (1.59 DMC, 1.02 EMC, and 1.36 EC molecule, Fig. 1(c)), indicating a solvent-dominated solvation sheath. By contrast, the first solvation sheath in AESE becomes strongly anion-rich, comprising on average 2.74  $\text{FSI}^-$  ions and only 2.11 EMC molecules per  $\text{Li}^+$  (Fig. 1(d)). The coordination environments were further categorized into three cluster states: (i) lithium ions fully coordinated by solvent molecules (solvent-surrounded  $\text{Li}^+$ , SSL, with zero anion), (ii)  $\text{Li}^+$ -anion single pair (LASP, with one anion), and (iii)  $\text{Li}^+$ -anion cluster (LAC, with two or more anions) [53, 54]. In CCE, the population distribution is 37% SSL, 48% LASP, and 15% LAC (Fig. 1(e)), confirming that solvent-coordinated species dominate the solvation environment. Even within the small LAC fraction, the aggregates are mostly low-order: 12% of  $\text{Li}^+$  are coordinated by two anions, and only 3% by three or more. Because aggregate formation relies on anion-mediated bridging between neighboring  $\text{Li}^+$  ions, the low fraction of high-order LAC species suggests that CCE provides limited driving force for the formation of extended aggregate networks. In sharp contrast, the coordination environment changes dramatically in AESE. The population distribution shifts overwhelmingly toward LAC species, reaching 90%, while SSL and LASP decrease to only 2% and 8%, respectively (Fig. 1(f)). More importantly, the internal composition of the LAC species also changes substantially. Among the  $\text{Li}^+$  ions participating in LAC species, 43% are coordinated by two  $\text{FSI}^-$  ions, whereas 47% are coordinated by three or more anions. This cluster distribution, together with the near disappearance of SSL and LASP species, demonstrates that AESE is not merely an anion-rich electrolyte; rather, it forms an extensive and highly

interconnected anion- $\text{Li}^+$  aggregate network.

To gain deeper insights into the role of TTE in this solvation environment, we compared AESE with its TTE-free

counterpart (1LiFSI-1.8EMC, molar ratio) using Raman and NMR spectroscopy. The TTE-free electrolyte exhibits a

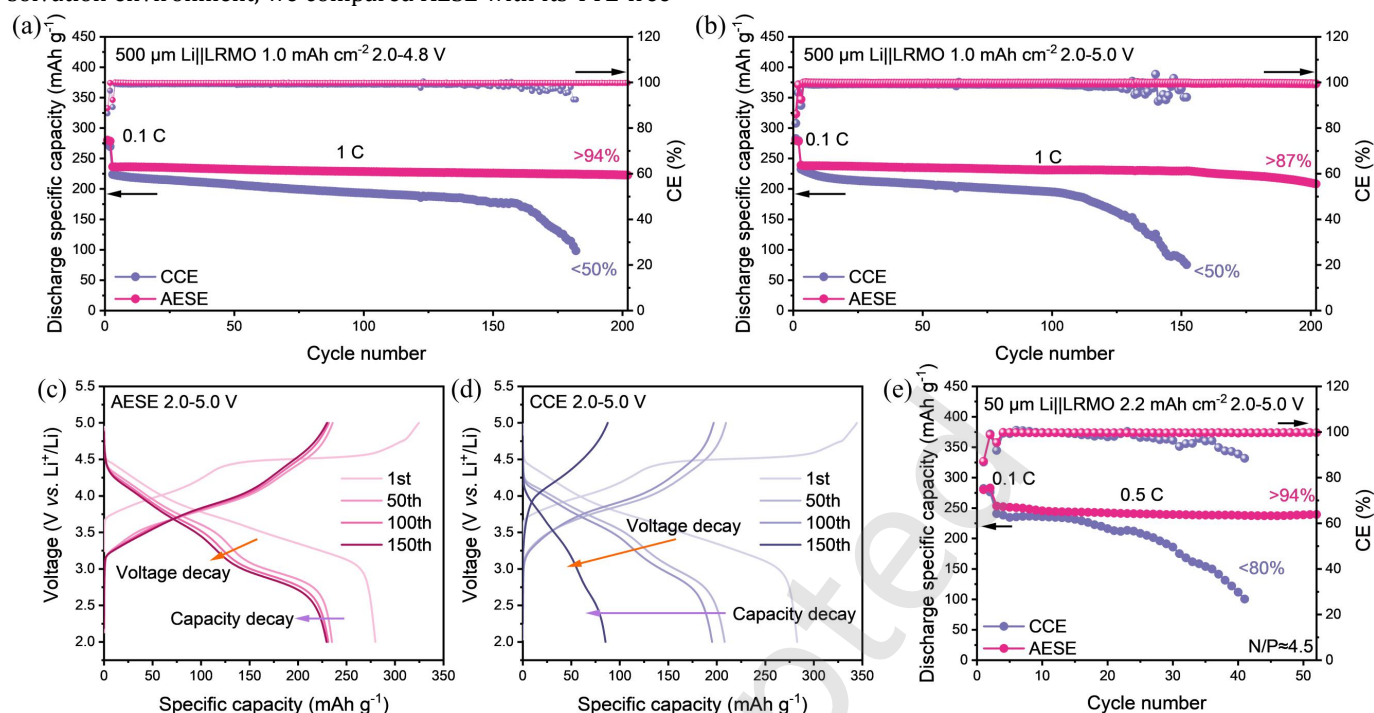


**Figure 2** Electrochemical performance. (a–b) Long-term cycling stability of Li||LRMO full cells operated within voltage windows of (a) 2.0–4.8 V and (b) 2.0–5.0 V, respectively, at a current rate of 1 C, employing lithium metal anodes with a thickness of 500  $\mu\text{m}$ . (c–d) Galvanostatic charge/discharge profiles for the (c) CCE and (d) AESE configurations tested under a cutoff voltage of 5.0 V. (e) Cycling performance of cells incorporating ultrathin (50  $\mu\text{m}$ ) lithium anodes cycled between 2.0 and 5.0 V. The N/P ratio is approximately 4.5.

dominant AGG peak but weak AGG+, whereas AESE shows an increased AGG+ intensity, indicating that TTE promotes the formation of higher-order aggregates (Fig. S2 in the ESM).  $^7\text{Li}$  NMR further reveals a downfield shift from  $-0.73$  ppm in the TTE-free electrolyte to  $-0.66$  ppm in AESE, reflecting stronger anion coordination and reduced solvent contribution in the primary solvation sheath [55].  $^{19}\text{F}$  NMR shows a slight upfield shift of the FSI $^-$  resonance from 51.4 ppm to 51.0 ppm in AESE, indicating enhanced  $\text{Li}^+$ -FSI $^-$  interactions in the presence of TTE [56]. These findings are consistent with previous reports that hydrofluoroether diluents, although nominally non-coordinating, can promote anion- $\text{Li}^+$  association through interactions with solvates [42, 49]. Collectively, the MD simulations and spectroscopic analyses indicate that TTE acts synergistically to reinforce the aggregation-enriched solvation network in AESE.

To demonstrate the compatibility between 5.0 V LRMO-based LMBs and the two electrolytes, systematic electrochemical measurements were performed. First, we tested cycling performance using Li||LRMO cells at cutoff voltages of 4.8 V and 5.0 V, respectively. When operated under 4.8 V, the AESE cell demonstrated exceptional cycling stability, maintaining 94% of its initial capacity and achieving an average CE of 99.75% across 200 cycles (Fig. 2(a)). Conversely, the CCE system underwent a progressive capacity decay for each cycle and sudden capacity drop, retaining only 44% capacity after cycling. Under 5.0 V, the AESE system maintained cell stability during 200 cycles, with an 87% capacity retention. By comparison, the CCE system exhibited much faster capacity fading after 100 cycles (Fig. 2(b)). We next evaluated the rate capability of Li||LRMO cells under both 4.8 V and 5.0 V cutoff conditions (Fig. S3 in the ESM). Under 4.8 V, the AESE cell outperforms the CCE cell across all tested rates from 0.2 C to 3 C,

delivering 199  $\text{mAh g}^{-1}$  at 3 C compared to 182  $\text{mAh g}^{-1}$  for CCE. Upon increasing the cut-off voltage to 5.0 V, the AESE cell maintained nearly identical high-rate capability, still achieving 199  $\text{mAh g}^{-1}$  at 3 C. Meanwhile, the CCE cell exhibited significantly greater sensitivity to high-current operation, with its 3 C capacity dropping to 172  $\text{mAh g}^{-1}$ . This divergence underscores the superior high-voltage tolerance of AESE.

The charge-discharge profiles of cells operating at 5.0 V are presented in Fig. 2(c–d). At the first cycle, a typical oxygen oxidation plateau near 4.55 V could be observed, which disappeared in the following cycles. From the 3rd cycle, both the curves displayed an apparent stepwise feature, with the CCE suffering from more pronounced voltage decay than AESE during operation. Figure S4 in the ESM shows the evolution of the differential capacity ( $dQ/dV$ ) curves during cycling. Two primary redox regions are identified: the lower-voltage region near 3.25 V corresponds predominantly to Mn redox coupled with oxygen redox, whereas the higher-voltage region around 3.75 V arises from the redox processes of nickel and cobalt, coupled with further oxygen redox participation [57, 58]. In the AESE system, the redox peaks in both regions remain stable, with peak positions shifting by only  $\sim 0.1$  V and minimal attenuation of peak area after extended cycling. In stark contrast, the CCE system displays a pronounced peak shift of approximately 0.33 V accompanied by significant peak area reduction. Such progressive peak shift and intensity loss are well-documented electrochemical signatures of irreversible phase transition in LRMO cathodes [59]. The suppressed evolution observed in AESE therefore suggests effective mitigation of this detrimental structural degradation.

To assess the cell's performance under more realistic operating conditions, a 50- $\mu\text{m}$ -thick lithium metal anode was coupled with the LRMO cathode (Fig. 2(e) and S5 in the ESM). When operated at a cathode areal capacity of approximately

1.0  $\text{mAh cm}^{-2}$ , corresponding to an N/P ratio of  $\sim 10$ , the AESE achieved high capacity retentions of 95% and 94% within 120

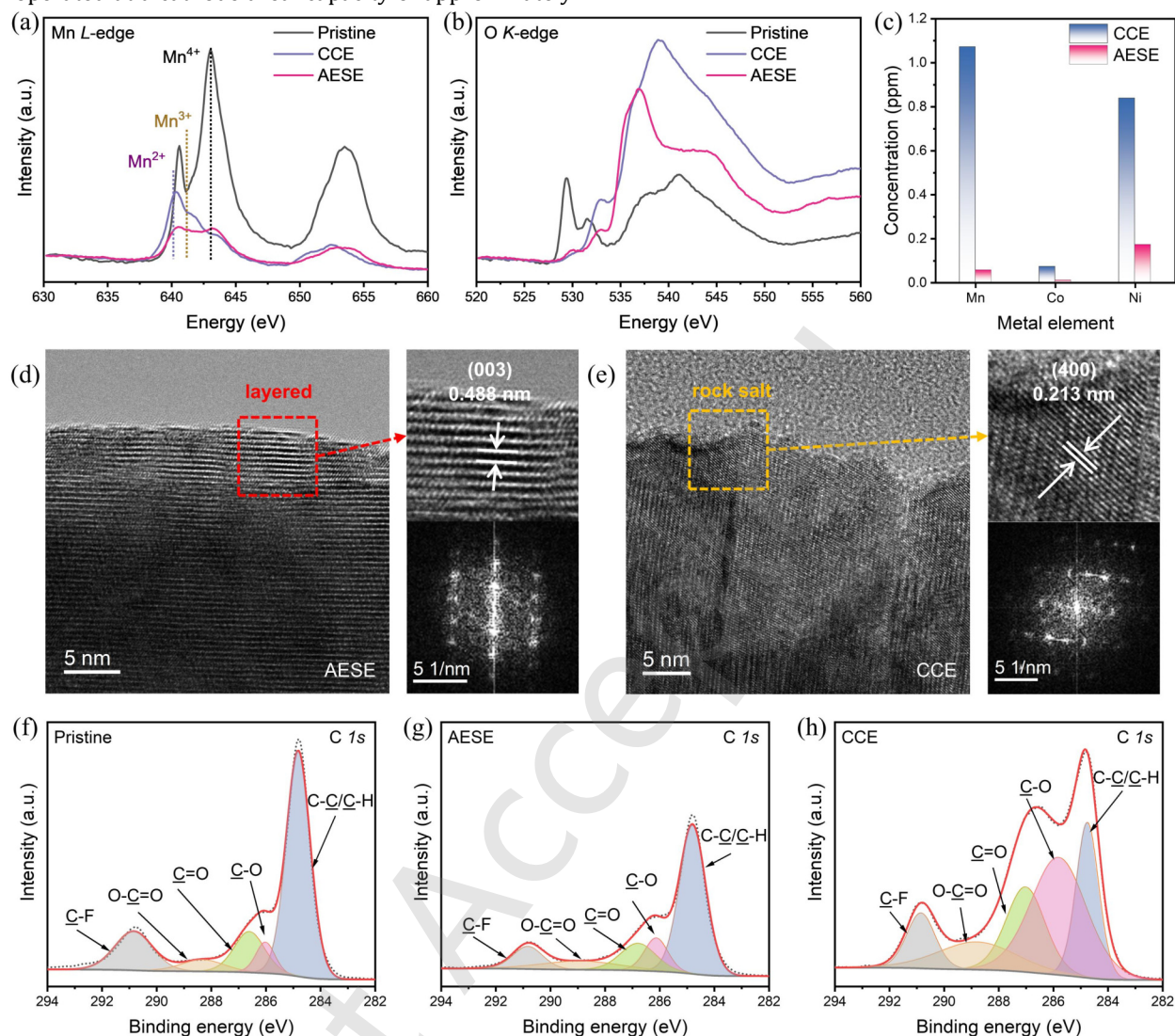


**Figure 3** Surface and structural analysis of the cathode material. (a–b) sXAS results acquired from the cathode surface pre- and post-cycling: (a) Mn L-edge and (b) O K-edge spectra. (c) Quantification of transition metal dissolution following electrochemical cycling. (d–e) HRTEM images of cycled cathode particles obtained from cells employing the (d) AESE and (e) CCE, respectively. (f–h) C 1s XPS profiles recorded from the cathode surface of the (f) as-prepared electrode, and after 100 cycles in (g) AESE and (h) CCE systems, respectively.

cycles under 4.8 V and 5.0 V, respectively. In contrast, the CCE could only sustain stable operation for about 60 cycles, followed by a sudden capacity drop. To further probe the lean-Li tolerance, the areal capacity was raised to 2.2  $\text{mAh cm}^{-2}$ , thereby lowering the N/P ratio to approximately 4.5. Under a 5.0 V cutoff at 0.5 C, the AESE cell maintained more than 94% of its initial capacity after 50 cycles, highlighting exceptional cycling durability despite a significantly reduced lithium inventory. This clearly manifests that the performance gap becomes more pronounced under the thin Li condition, and the AESE can substantially extend the Li||LRMO cycle life. Overall, the AESE exhibits outstanding compatibility with both the LRMO and Li electrodes.

To gain deeper insights into how electrolyte composition influences LRMO cathode, sXAS was employed to analyze the oxidation states of key elements on both as-prepared and electrochemically cycled cathode. As shown in Fig. 3(a), the Mn L-edge spectra reveal that the initial cathode mainly

exhibits spectral features consistent with  $\text{Mn}^{4+}$  state [60–62]. After 100 cycles in the CCE system, the Mn L-edge signals were significantly broadened, and a new feature corresponding to  $\text{Mn}^{2+}$  emerged [63], indicating extensive irreversible reduction of Mn at the cathode surface. In contrast, the  $\text{Mn}^{2+}$  feature was substantially weaker in the AESE system, suggesting effective suppression of Mn reduction. The O K-edge spectra (Fig. 3(b)) are consistent with this trend, showing a higher oxidation state of oxygen in the CCE system [64]. Additionally, ICP-MS results (Fig. 3(c)) confirm that metal-ion dissolution is lower in the AESE system.

HRTEM was utilized to examine the surface microstructure of the LRMO cathode material in both its pristine state and after electrochemical cycling (Fig. S6 in the ESM and 3(d–e)). A well-defined layered structure was observed on the pristine cathode with approximately 0.484 nm lattice spacing, corresponding to the (003) plane of the

LRMO material, which was visualized by the fast Fourier transform analysis. After 100 cycles, the cathode with the AESE robustly retained the layered structure, indicating good capability of the AESE to maintain the crystal structure of the LRMO cathode. In comparison, a drastic structural

change of the LRMO cathode had been evolved in the CCE. Severe phase transition from layered to rock-salt type was evident [28, 38], propagating from the surface inward to a depth of >20 nm.

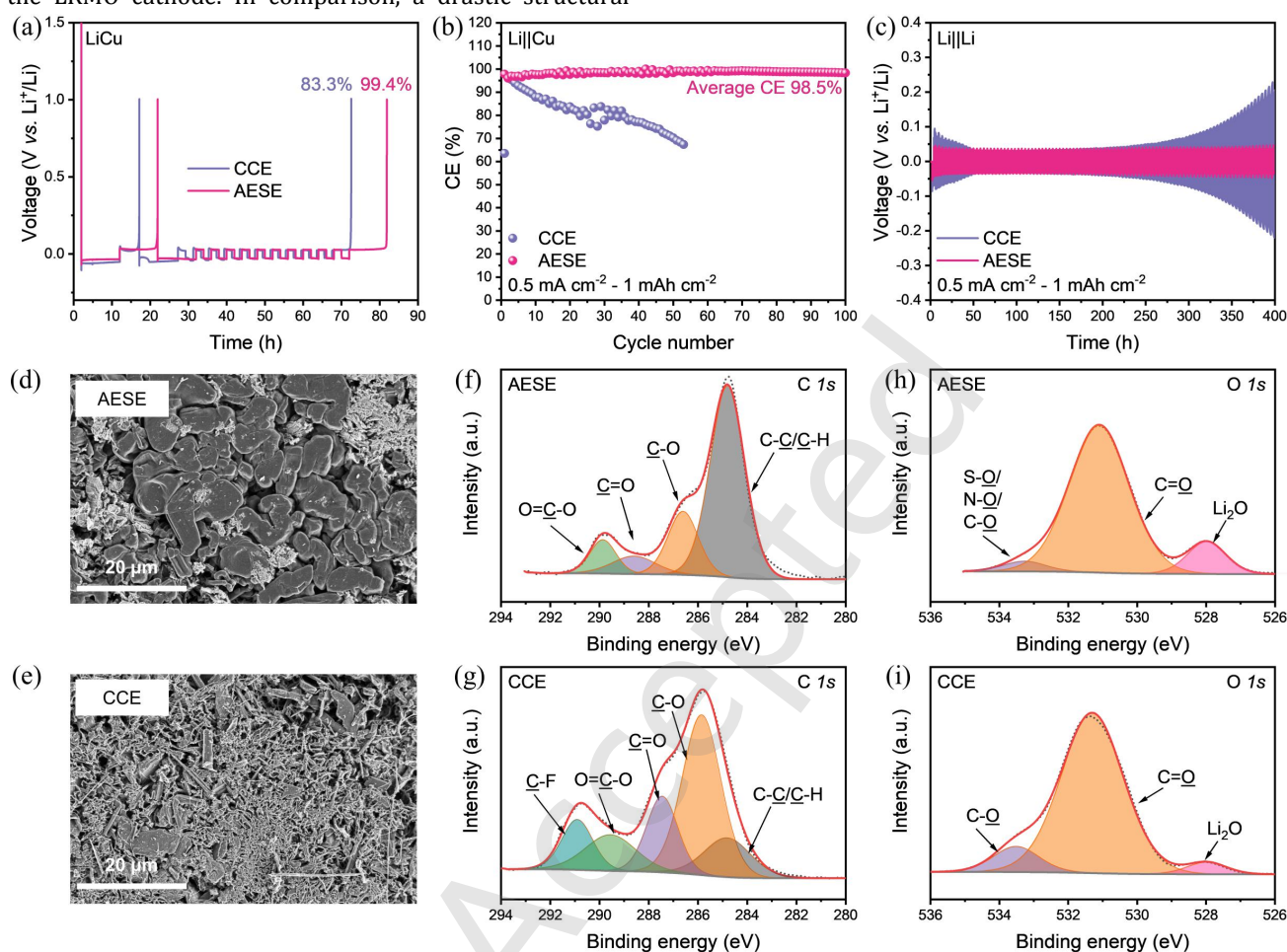


**Figure 4** Electrochemical performance and anode characterization. (a) Average CE determined by the Aurbach's method. (b) Extended cycling stability of Li||Cu half-cells operated with AESE and CCE. (c) Cycling performance of Li||Li symmetric cells using AESE and CCE. (d-e) Morphologies of lithium deposits after 10 cycles in the (d) AESE and (e) CCE systems, respectively. (f-g) Corresponding C 1s and (h-i) O 1s XPS spectra of the anode surface.

Moreover, the cathode surface exhibited a rough morphology, indicative of transition metal ion leaching caused by aggressive corrosion from electrolyte decomposition byproducts, such as hydrogen fluoride (HF) [65]. In brief, AESE effectively maintains the interfacial structural integrity of the LRMO cathode, suppressing adverse phase transformations. This observation provides direct microscopic evidence for the outstanding cycling performance of Li||LRMO cells.

XPS was employed to analyze the chemical compositions of the CEI formed on the LRMO cathode. Figure 3(f-h) and S7 in the ESM show the C 1s and O 1s spectra in the pristine and cycled electrodes from AESE and CCE systems. For the pristine electrode, peaks corresponding to the binder and conductive carbon agent (C-F, C-C/C-H) were present. Besides, minor O-C=O, C=O, and C-O signals could be detected, which likely originate from residual species introduced during electrode fabrication [66]. After the cycling, the noticeable changes in the C-O, C=O, and O-C=O peak intensities are indicative of electrolyte decomposition [35]. These decomposition-related signals were significantly stronger in the CCE electrode than in the AESE counterpart,

implying more severe interfacial decomposition in the CCE system. In the O 1s spectra, clear metal-oxygen peaks were observed in the pristine sample. After the cycling, both systems show stronger signals from decomposition products. In the AESE, the peak corresponding to C=O is weaker compared to the control electrolyte, suggesting suppressed solvent decomposition. Meanwhile, the overall O 1s intensity in the AESE is higher, which can be attributed to the contributions from S-O and N-O species originating from the decomposition of the FSI<sup>-</sup> anion. XPS analysis reveals substantial solvent decomposition in CCE, likely initiating cathode surface degradation. This finding highlights the direct link between the solvation environment and the interfacial stability of LRMO cathodes. In AESE, the primary solvation shell is dominated by FSI<sup>-</sup> ions, while EMC molecules are largely excluded from direct Li<sup>+</sup> coordination. As a result, fewer solvent molecules are present near the cathode surface during cycling, suppressing oxidative decomposition of carbonate solvents. This is reflected in the weaker C-O and C=O signals observed in AESE. Suppression of solvent decomposition effectively interrupts the cascade of cathode degradation, including transition metal

dissolution, surface phase transformation, and associated Mn valence changes. sXAS, ICP, and HRTEM results confirm this observation: while CCE undergoes significant degradation, AESE largely preserves the cathode surface structure. Taken together, these XPS observations establish a clear mechanistic link between the electrolyte solvation

environment and cathode stability: the anion-rich solvation sheath in AESE limits solvent decomposition, thereby preserving the structural integrity of the LRMO cathode.

To elucidate the mechanism of the remarkable compatibility between the AESE and Li||LRMO full cells, we

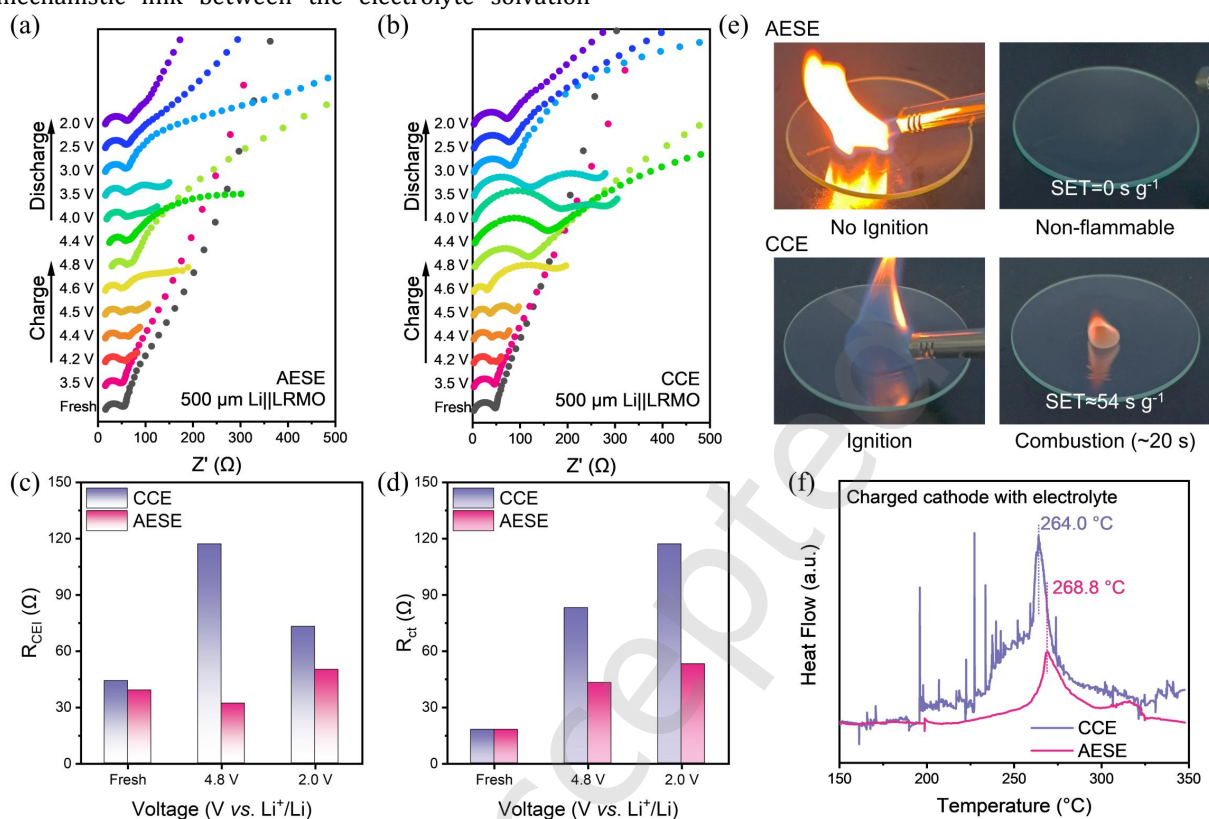


**Figure 5** Electrochemical impedance, safety characterization and thermal stability. (a–b) In-situ EIS measurements of the (a) AESE and (b) CCE systems, respectively, during the first cycle. (c–d) Corresponding (c)  $R_{\text{CEL}}$  and (d)  $R_{\text{ct}}$  at different states of charge. (e) Combustion behavior of the AESE and CCE. (f) DSC curves of the fully delithiated LRMO cathode from cells using different electrolytes (heating rate: 5 °C min<sup>-1</sup>).

further performed a comprehensive study on the cycled Li anode. First, the difference in Li metal anode reversibility and kinetics between the CCE and AESE was evaluated. Notably, when evaluated via Aurbach's protocol, the AESE achieved an impressive average CE of 99.4%, markedly surpassing that of the CCE (83.3%) (Fig. 4(a)). Furthermore, long-term cycling assessments demonstrated that the Li||Cu cell employing AESE maintained an average CE of 98.5% across 100 cycles, while the CCE cell underwent rapid and irreversible failure (Fig. 4(b)). Throughout the cycling, the polarization voltage of the AESE cell increased gradually, while that of the CCE cell rose sharply (Fig. S8 in the ESM). Those CE tests indicate that the AESE enables a highly reversible Li anode. CV test showed that the AESE exhibited higher anodic and cathodic currents than CCE (Fig. S9 in the ESM), indicating better kinetics for the former [67]. Li||Li symmetric cell tests further revealed that with the AESE, the cell overpotential was stable and nearly unchanged after 400 hours of cycling. Conversely, the CCE system enlarged abruptly by over 100 mV, indicating much deteriorated electrode kinetics (Fig. 4(c)). Rate capability was also examined across a current density range of 0.25 to 2 mA cm<sup>-2</sup>. The AESE cell exhibited lower overpotentials than the CCE cell across the tested range (Fig. S10 in the ESM). Collectively, the CE tests, CV analysis, and symmetric cell cycling and rate measurements demonstrate that AESE supports highly

reversible lithium plating/stripping and maintains robust, stable electrode/electrolyte interfacial kinetics.

The morphology of lithium deposits on Cu substrates after cycling was examined using SEM. Li chunks predominated after cycling in the AESE (Fig. 4(d)), which contributes to the high CE due to its small surface area and low tendency to form dead Li. Conversely, needle-like Li dendrites were the characteristic morphology in the CCE (Fig. 4(e)), which have a strong correlation with the low CE of the Li anode. XPS analysis was carried out to characterize the chemical species present on the lithium metal surface after cycling. As revealed by the C 1s spectra, the CCE system displays prominent C–O and C=O signals, indicative of extensive electrolyte degradation. In sharp contrast, the weak intensities of these same peaks in the AESE system suggest a marked reduction in solvent decomposition (Fig. 4(f–g)). The O 1s spectra further showed enhanced intensities for both C–O and C=O bonds in the CCE, consistent with observations from the C 1s analysis. In contrast, the AESE displayed stronger Li<sub>2</sub>O signal and LiF signal (Fig. 4(h–i) and S11 in the ESM), indicating preferential formation of an inorganic-rich SEI. Prior studies have associated a high inorganic content in the SEI with improved structural compactness and effective suppression of lithium dendrite growth [68]. Additionally, morphology analysis of cycled Li metal anode in Li||LRMO full cells was performed to

characterize the Li plating compactness. The AESE system showed relatively dense degradation layer on the anode, with 50  $\mu\text{m}$ , whereas the layer formed in CCE was loose and porous, with a thickness up to 250  $\mu\text{m}$  (Fig. S12 in the ESM). These results consistently demonstrate that the AESE electrolyte possesses superior lithium metal compatibility, effectively suppressing dendritic growth, minimizing side reactions, and thus better protecting the anode interface.

The kinetics of Li||LRMO batteries at different voltages were systematically investigated via in situ EIS measurements. Figure 5(a-b) shows the Nyquist plots of cells within a charge/discharge process at selected voltage states.

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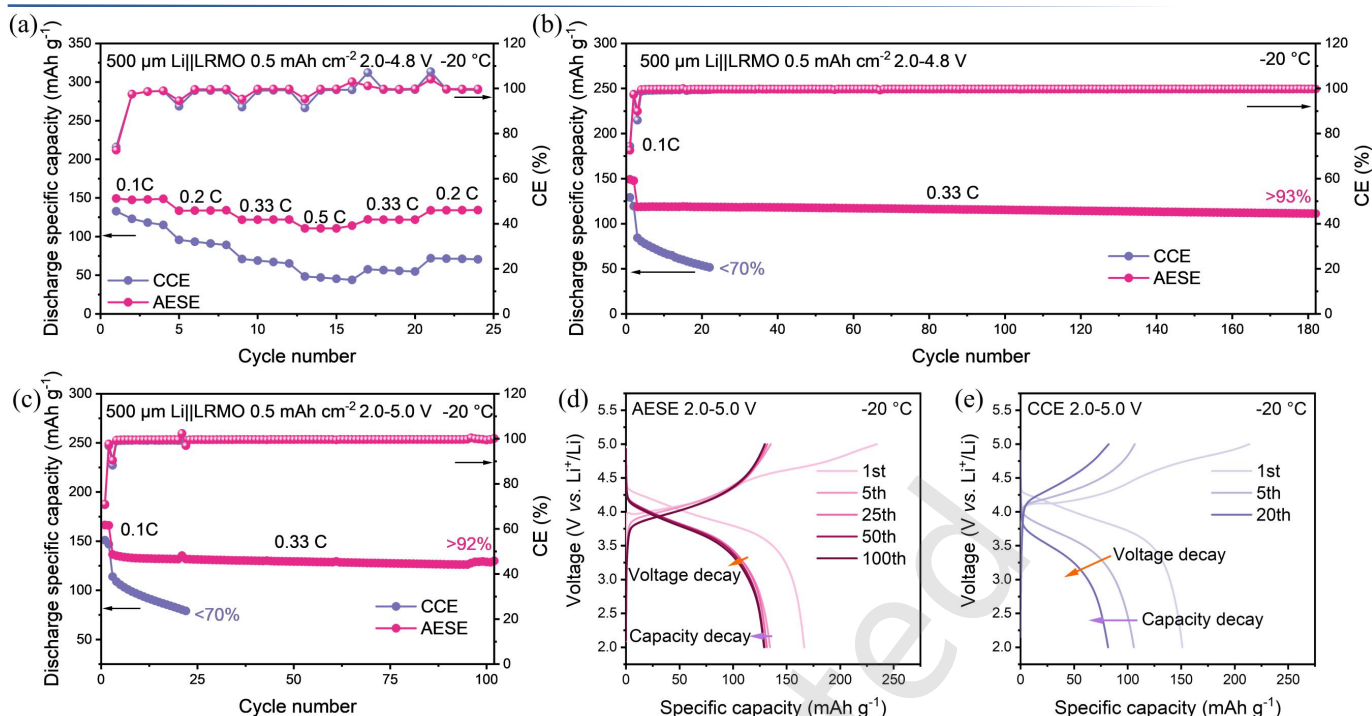


**Figure 6** Electrochemical performance at  $-20\text{ }^{\circ}\text{C}$ . (a) Comparative rate capability of cells employing the CCE and AESE with a cutoff voltage of 4.8 V. (b) Long-term cycling performance with cutoff voltages of 4.8 V. (c) Long-term cycling performance with cutoff voltages of 5.0 V. (d–e) Corresponding charge-discharge profiles of the (d) AESE and (e) CCE systems under 5.0 V.

Throughout the charge–discharge process, the AESE exhibited relatively minor variations in impedance, whereas the CCE displayed pronounced changes in the shape of the Nyquist plots. The overall cell impedance can be separated into two distinct components: the CEI resistance ( $R_{\text{CEI}}$ ), associated with relaxation times in the range of  $\sim 10^{-6}$  to  $\sim 10^{-2}$ , and the charge-transfer resistance ( $R_{\text{ct}}$ ), corresponding to relaxation times between  $\sim 10^{-2}$  and  $\sim 10^1$  based on the distribution of relaxation times (DRT) analysis (Fig. S13 in the ESM) [69–71]. After cell assembly, both electrolytes exhibited relatively low interfacial resistances, with initial  $R_{\text{CEI}}$  values of 44  $\Omega$  (CCE) and 39  $\Omega$  (AESE) and identical  $R_{\text{ct}}$  of 18  $\Omega$ . Upon charging to 4.8 V, the AESE maintained a low  $R_{\text{CEI}}$  (32  $\Omega$ ), while the CCE displayed a sharp increase to 117  $\Omega$ , likely caused by severe electrolyte decomposition at high voltage. The  $R_{\text{ct}}$  at 4.8 V also showed a clear contrast: 83  $\Omega$  for the CCE versus 43  $\Omega$  for the AESE, indicating more sluggish oxygen-redox kinetics in the CCE system. After discharging to 2.0 V, the AESE retained modest  $R_{\text{CEI}}$  (50  $\Omega$ ) and  $R_{\text{ct}}$  (53  $\Omega$ ), whereas the CCE remained at considerably higher values (73  $\Omega$  for  $R_{\text{CEI}}$  and 117  $\Omega$  for  $R_{\text{ct}}$ ) (Fig. 5(c–d)). These results demonstrate that the superior cycling performance can be attributed to the robust and conductive interface enabled by the AESE.

To evaluate safety performance, tests at the electrolyte and cell levels were conducted. First, the combustibility of the electrolytes was evaluated quantitatively through determination of the SET. As shown in Fig. 5(e), CCE ignited immediately and burned vigorously, with a SET of  $\sim 54\text{ s g}^{-1}$ . In striking contrast, AESE could not be ignited under the same conditions (SET = 0  $\text{s g}^{-1}$ ), demonstrating the excellent nonflammability of AESE. To further investigate the difference of the CCE and AESE on the LRMO cathode thermal stability, DSC experiment was performed on the

charged cathodes after cycling. Figure 5(f) displays the heat flow of CCE and AESE systems mixed with fully delithiated cathode powder. The exothermic peak for the CCE system was observed at 264.0  $^{\circ}\text{C}$ , which was accompanied by a substantial heat release of 1208  $\text{J g}^{-1}$ . In comparison, the AESE system not only exhibited a higher exothermic peak temperature (268.8  $^{\circ}\text{C}$ ) but also a significantly lower heat release of 633  $\text{J g}^{-1}$ . These results demonstrate that AESE possesses good capability against ignition and flaming, and effectively improves the cathode thermal stability, which can substantially reduce the heat generated during potential thermal runaway events.

The applicability of the two electrolytes under harsher conditions was further assessed via their low-temperature performance. When evaluating the Li reversibility via Aurbach's method at  $-20\text{ }^{\circ}\text{C}$ , the AESE achieved a high CE of 98.8%, whereas the CCE retained only 75.3% (Fig. S14 in the ESM). AESE also exhibited significantly enhanced cycling stability during extended cycling evaluations. In Li||Cu half-cells, it sustained stable operation for over 50 cycles. In Li||Li symmetric cells, it maintained consistent voltage profiles for more than 300 hours. The rate capability of Li||Li symmetric cells at  $-20\text{ }^{\circ}\text{C}$  was systematically evaluated across a current density range from 0.1 to 0.5  $\text{mA cm}^{-2}$  (Fig. S15 in the ESM). The AESE cell exhibited lower and more stable overpotentials across the tested range, consistent with the superior Li metal reversibility observed at room temperature. In addition, AESE demonstrated exceptional rate performance in Li||LRMO cells operated at 4.8 V (Fig. 6(a)), delivering discharge specific capacities of 149, 133, 122, and 110  $\text{mAh g}^{-1}$  under rates ranging from 0.1 C to 0.5 C, considerably higher than those of the CCE. When the cut-off voltage was further raised to 5.0 V, the AESE system exhibited an increase in specific capacity of approximately

20 mAh g<sup>-1</sup> across all tested rates, maintaining a clear advantage over CCE (Fig. S16 in the ESM). Extended cycling tests at 4.8 V and 0.33 C revealed the superior stability of the AESE, which sustained >93% capacity retention after 180 cycles, far exceeding the CCE that retained only 61% after 20 cycles (Fig. 6(b)). Even at 5.0 V, the AESE system retained its superior electrochemical performance, with an initial discharge capacity of 166 mAh g<sup>-1</sup> at 0.1 C and retaining over 92% of that capacity at 0.33 C across 100 cycles. Conversely, the CCE showed pronounced capacity degradation under identical conditions (Fig. 6(c-e)). Altogether, the AESE system displays much better electrochemical performance and cycling stability under extreme conditions, including low temperature and high voltage.

## 4 Conclusions

In summary, we have demonstrated an aggregation-enhanced solvation electrolyte (AESE) that enables highly stable 5.0 V-class LMBs employing LRMO cathodes. By pairing EMC, a carbonate solvent with low dielectric constant and moderate donor number, with a hydrofluoroether diluent, AESE builds an anion-rich solvation structure in which 90% of Li<sup>+</sup> reside in Li<sup>+</sup>-anion clusters, with nearly half of these clusters involving three or more FSI<sup>-</sup> anions. In this configuration, the primary solvation sheath is predominantly occupied by FSI<sup>-</sup> anions, which limits the presence of carbonate solvent at the electrode surface and thereby suppresses oxidative solvent decomposition at high voltages. Such solvation chemistry facilitates the construction of robust interphases on both electrodes, i.e., a protective CEI on LRMO that mitigates surface reconstruction and TM dissolution, and an inorganic-rich LiF/Li<sub>2</sub>O-based SEI on Li metal that stabilizes deposition. Accordingly, Li||LRMO cells with AESE achieve exceptional high-voltage and low-temperature performance: 87% capacity retention across 200 cycles at 25 °C and 100 stable cycles at -20 °C under 5.0 V. Meanwhile, high Li CE of 99.4% was achieved, underscoring the superior reversibility enabled by the AESE. This study introduces a carbonate-based electrolyte design centered on aggregation-enhanced solvation, which paves the way for developing robust 5.0 V Li metal batteries even under demanding operational conditions.

**Electronic Supplementary Material:** Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908856>.

## Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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## Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

## Author contribution statement

Y. Z. G.: Experimental design, data curation, project administration, validation, writing – original draft, writing – review & editing. Y. L. J.: Experimental design, data curation, writing – original draft, writing – review & editing. Z. Z.: Experimental design, data curation, writing – original draft, writing – review & editing. Y. H. Y.: Experimental design, data curation. Y. W.: Experimental design, data curation. Y. Q. D.: Experimental design, data curation. K. W.: Experimental design, data curation. Y. L.: Experimental design, data curation. Z. W. L.: Experimental design, data curation. T. C.: Project administration, funding acquisition, writing – review & editing. R. G. C.: Project administration, funding acquisition, writing – review & editing. Y. Y.: Project administration, funding acquisition, writing – review & editing. S. H. J.: Project administration, funding acquisition, writing – review & editing. All the authors have approved the final manuscript.

## Use of AI statement

None.

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## Electronic Supplementary Material

# Enabling 5V-class lithium metal batteries via an aggregation-enhanced solvation electrolyte

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## Supporting Information

Table S1. Comparison of representative LHCE-based electrolyte systems for LRMO cathodes.

| Electrolyte                                                                               | Cycling performance                                                                                             | Reference                                                         |
|-------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------|
| 1.4 M LiFSI in DMC, EC and TTE (2 : 0.2: 3 by mol.)                                       | Gr  LRMO cells<br>Voltage range: 2.7–4.7 V<br>C/3 cycling<br>Cycle life: 91.7% after 100 cycles (25 °C)         | <i>J. Power Sources Adv.</i> <b>2020</b> , 5, 100024.             |
| 1 M LiPF <sub>6</sub> /TMP + TTE (5:5, v/v)                                               | Li  LRMO cells<br>Voltage range: 2.0–4.8 V<br>10 mA g <sup>-1</sup> cycling<br>Cycle life: 100 cycles (6~38 °C) | <i>J. Phys. Chem. Lett.</i> <b>2022</b> , 13, 11307-11316.        |
| 1LiFSI-1.1DME-5BTfE by mol.                                                               | Li  LRMO cells<br>Voltage range: 2.0–4.6 V<br>C/4 cycling<br>Cycle life: 97% after 100 cycles (25 °C)           | <i>ACS Appl. Mater. Interfaces</i> <b>2023</b> , 15, 45764-45773. |
| 2 m LiPF <sub>6</sub> and 1 m LiTFSI in FEC/DMC (3/7 wt. ratio) diluted by 66.7 vol.% TTE | Li  LRMO cells<br>Voltage range: 2.0–4.6 V<br>C/3 cycling<br>Cycle life: 90.2% after 100 cycles (25 °C)         | <i>Small</i> <b>2024</b> , 20, 2401364.                           |
| 1.2 M LiFSI EMS-HFE (1:1 in mol)                                                          | Li  LRMO cells<br>Voltage range: 2.5–4.8 V<br>C/2 cycling<br>Cycle life: 90% after 200 cycles (25 °C)           | <i>ACS Nano</i> <b>2025</b> , 19, 35141-35153.                    |

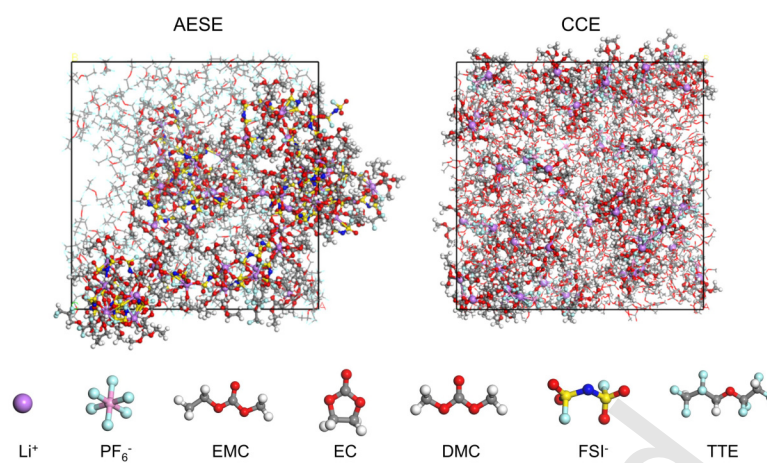


**Figure S1** Snapshots of the MD simulation boxes of the AESE and CCE systems.

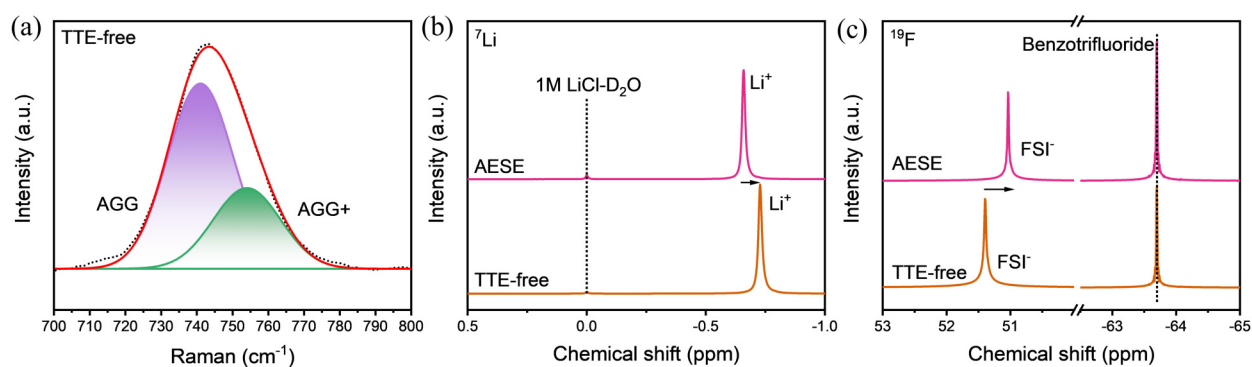


**Figure S2** (a) Raman spectra of the TTE-free electrolyte system. (b) <sup>7</sup>Li NMR spectra of the AESE and the TTE-free electrolyte systems. (c) <sup>19</sup>F NMR spectra of the AESE and the TTE-free electrolyte systems.

<sup>7</sup>Li NMR chemical shifts were externally referenced to 1 M LiCl in D<sub>2</sub>O ( $\delta = 0$  ppm). <sup>19</sup>F NMR chemical shifts were externally referenced to benzotrifluoride ( $\delta = -63.7$  ppm).

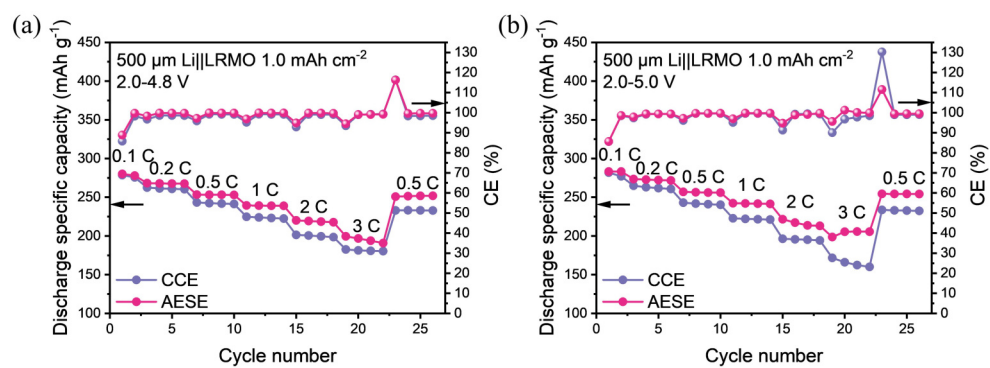


**Figure S3** Rate performance of the AESE and CCE systems with cutoff voltages of (a) 4.8 V and (b) 5.0 V, respectively.

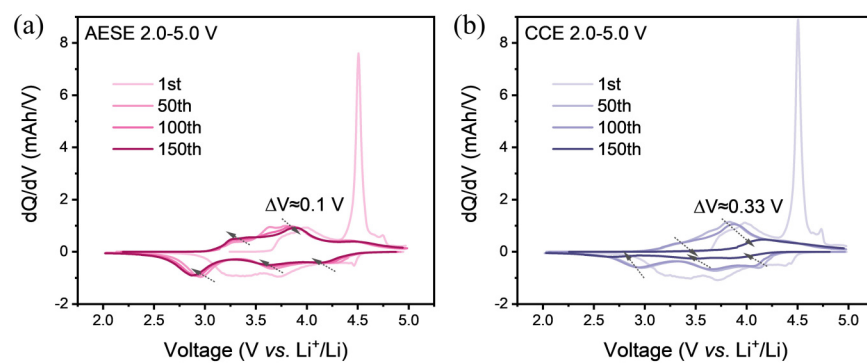


**Figure S4** (a-b)  $dQ/dV$  curves of the (a) AESE and (b) CCE systems, respectively, at a cutoff voltage of 5.0 V.

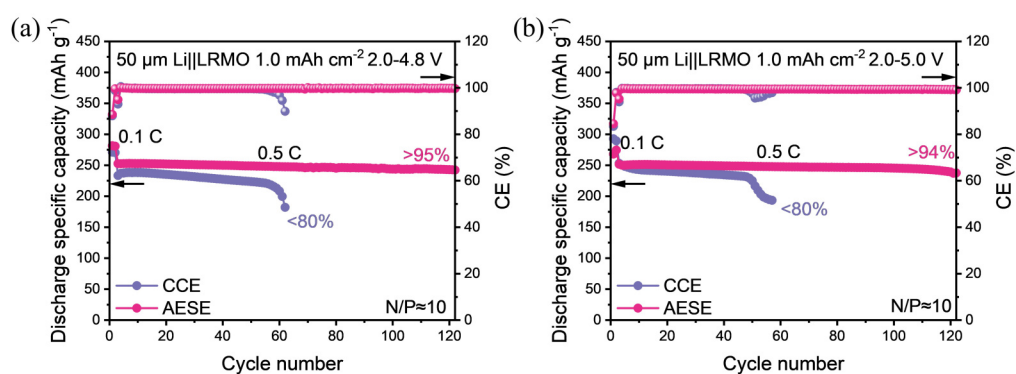


**Figure S5** Cycling performance of the AESE and CCE cells using 50-μm-thick Li at the cutoff voltage of (a) 4.8 V and (b) 5.0 V. The N/P ratio is approximately 10.

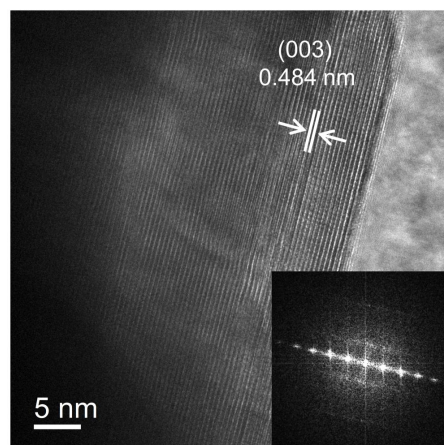


**Figure S6** HRTEM image of the pristine cathode particles.

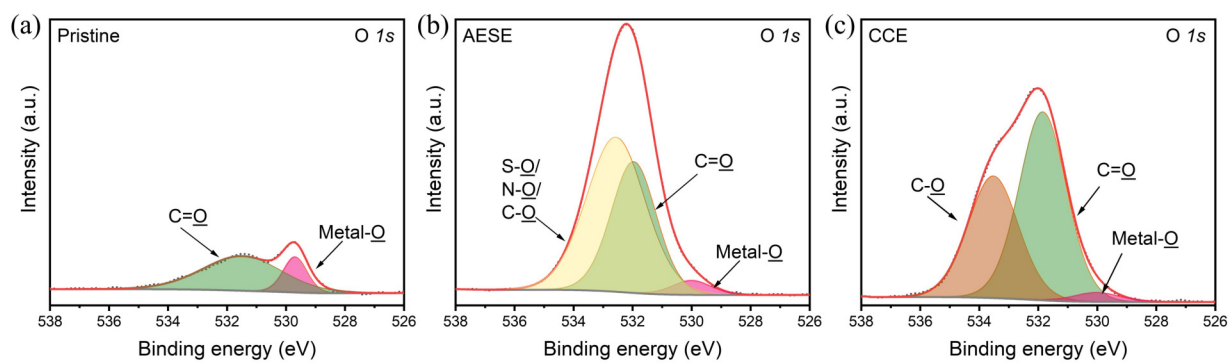


**Figure S7** (a-c) O 1s XPS spectra of the cathode surface for (a) the pristine electrode, and after cycling in the (b) AESE and (c) CCE systems, respectively.

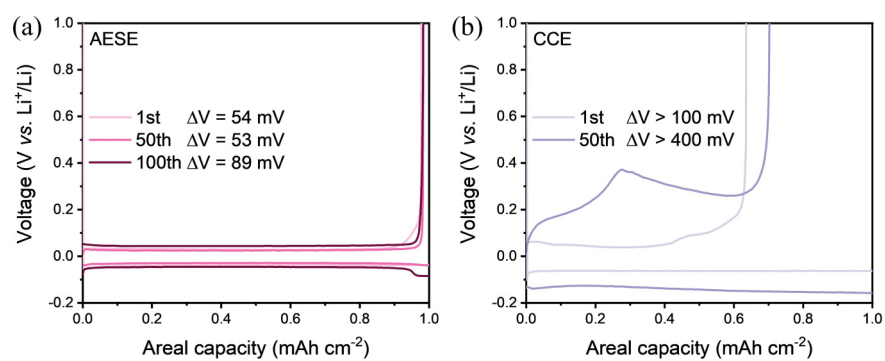


**Figure S8** (a–b) Galvanostatic charge-discharge curves of Li||Cu cells for the (a) AESE and (b) CCE systems, respectively.

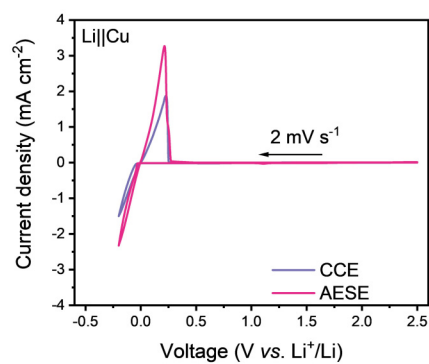


**Figure S9** CV curves of Li||Cu cells for the AESE and CCE systems.

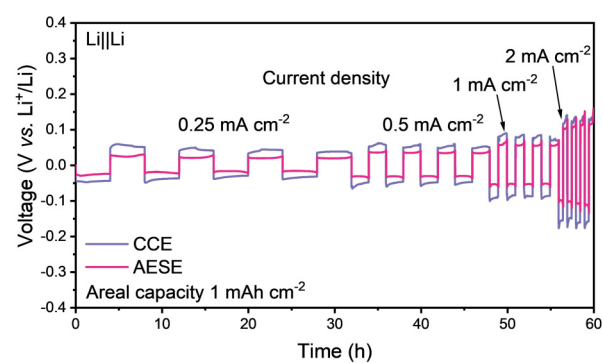


**Figure S10** The rate performance of Li||Li symmetric cells under current densities from 0.25 to 2  $\text{mA cm}^{-2}$ .

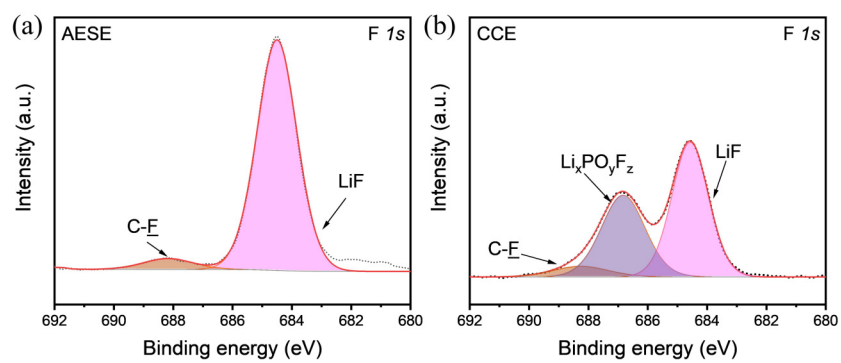


**Figure S11** F 1s XPS spectra of the (a) AESE and (b) CCE anode surface.

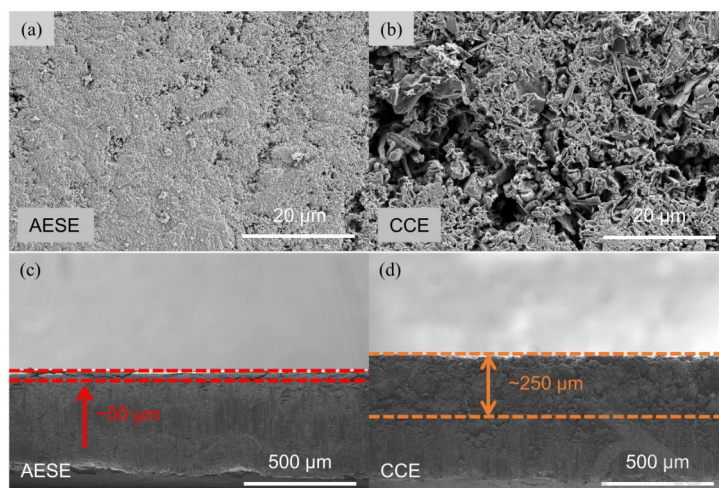


**Figure S12** (a–b) Top-view and (c–d) corresponding cross-sectional SEM images of the lithium anodes from Li||LRMO cells after 100 cycles in the AESE and CCE systems, respectively.

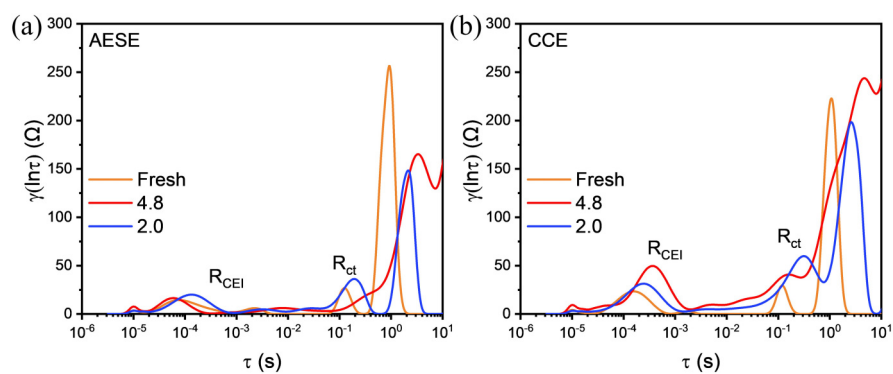


**Figure S13** (a–b) Results of the distribution of relaxation times (DRT) analysis for the impedance of cells with the (a) AESE and (b) CCE systems, respectively, at different states of charge.

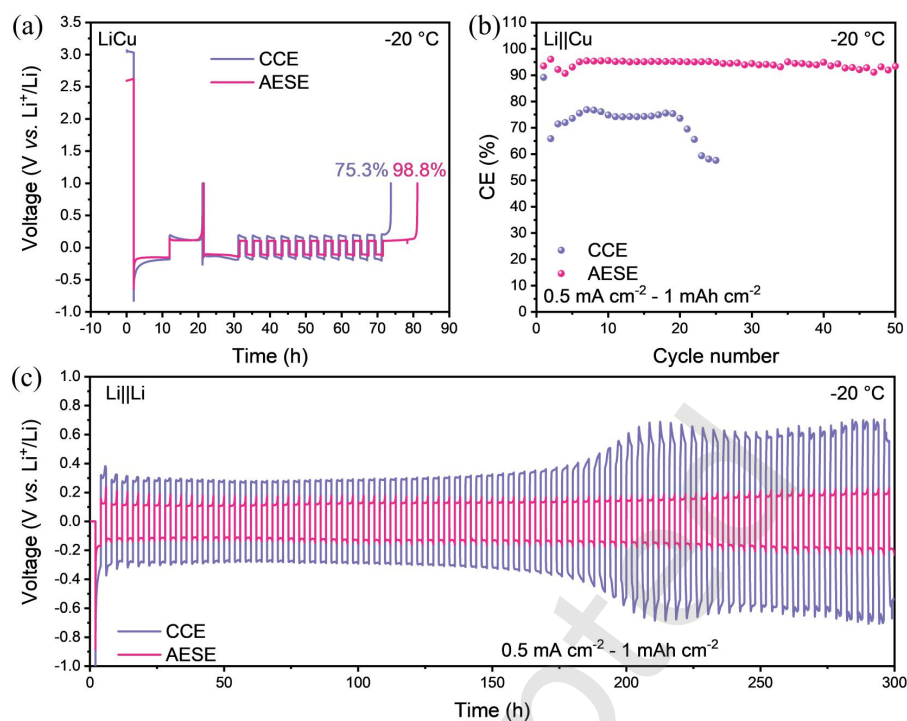


**Figure S14** Lithium metal compatibility tests at  $-20\text{ }^{\circ}\text{C}$ . (a) Average Coulombic efficiency determined by the Aurbach's method for the AESE and CCE systems. (b-c) Long-term cycling performance of (b)  $\text{Li}||\text{Cu}$  and (c)  $\text{Li}||\text{Li}$  cells, respectively, employing the two electrolytes.

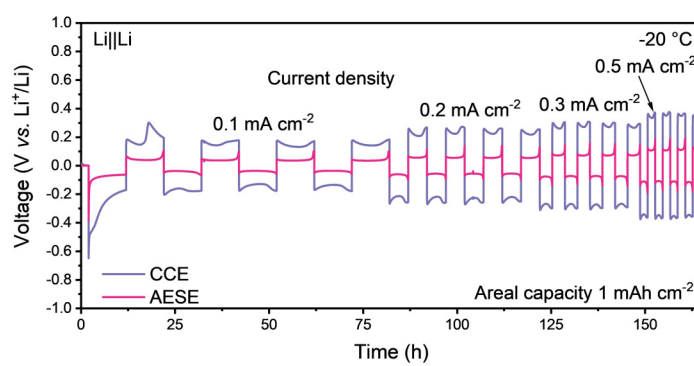


**Figure S15** The rate performance of Li||Li symmetric cells under current densities from 0.1 to 0.5 mA cm<sup>-2</sup> at -20 °C.

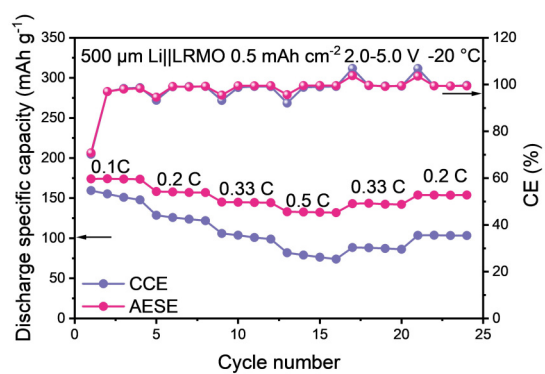


**Figure S16** Rate performance of the AESE and CCE systems with cutoff voltages of 5.0 V at  $-20\text{ }^{\circ}\text{C}$ .