

Toward Dynamic Solvation Networks for Practical Lithium Metal Battery Electrolytes

Published as part of Chemistry of Materials *special issue* "Honoring the Outstanding Scientific Contributions of Clare Grey".

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Cite This: <https://doi.org/10.1021/acs.chemmater.6c02093>



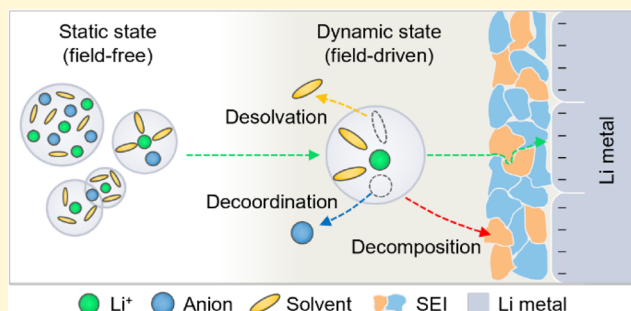
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ABSTRACT: Electrolyte solvation chemistry is central to the advancement of next-generation lithium metal batteries. The Li^+ solvation structure is closely related to ion transport, interphase chemistry, and cell performance. However, most efforts still examine solvation structures at microscopic length scales without accounting for the interfacial electric field that develops during cell operation. Here, we reorganize the reported solvation strategies into a framework integrating two perspectives: the length scale of the solvation structure and the presence of the interfacial electric field, spanning from static (field-free) microscopic solvation to dynamic (field-driven) solvation networks. Within this framework, we benchmark the electrochemical performance of representative strategies, connect the characterization methods and governing physics that operate at each length scale, and identify the failure modes that limit each electrolyte component. We discuss design directions for dynamic solvation networks and provide insights into aligning laboratory advances with industrial requirements.



1. INTRODUCTION

Decarbonization and transport electrification have raised the demand for batteries beyond conventional lithium-ion batteries (LIBs).¹ The Li metal anode, with a specific capacity of 3,860 mAh g⁻¹ and a reduction potential of -3.04 V versus the standard hydrogen electrode, affords theoretical cell-level energy densities of ~750 Wh kg⁻¹ and ~2,000 Wh L⁻¹.^{2,3} Nevertheless, the cycling stability of metallic Li in liquid electrolytes remains limited by its high reactivity and unstable interfacial chemistry. The Li metal anode continuously reduces electrolyte components, while repeated plating and stripping fracture and regenerate the SEI, amplify volume fluctuations, and promote porous Li deposits and electrically isolated dead Li.⁴ These coupled chemical and morphological losses consume active Li and electrolyte, lower CE, and shorten cycle life. For practical cells with limited Li inventory, sustaining CE above 99.95% over 1,000 cycles remains a key requirement for practical operation.⁵

To address these challenges, recent studies have focused on liquid electrolytes, which serve both as ion-conducting media and as key determinants of interfacial stability and electrochemical reversibility.^{6,7} The electrolyte solvation structure governs salt dissociation, ion coordination, charge-carrier transport, and electrochemical stability (Figure 1a). In the bulk electrolyte, the coordination of Li^+ by solvent molecules

and anions regulates charge-carrier transport and field-driven migration.⁸ As solvated Li^+ approaches the electrode, changes in solvent coordination and anion participation control desolvation and decoordination, setting energy barriers for interfacial Li^+ transfer.^{9,10} Owing to its low reduction potential, Li metal drives the preferential reduction of solvation sheath species, leading to solid-electrolyte interphase (SEI) formation at the interface.^{11,12} These interfacial and interphasial properties influence nucleation overpotential, Li^+ flux distribution, and Li morphology during plating and stripping, thereby affecting Li metal anode reversibility.^{13,14} Therefore, the solvation structure provides a molecular-level bridge between bulk ion transport and interfacial evolution, influencing multiple stages of Li metal battery operation.

Practical liquid electrolytes for Li-metal batteries (LMBs) must provide both sufficient ionic conductivity and electrochemical stability against the Li metal anode and high-voltage

Received: July 23, 2026

Revised: September 9, 2026

Accepted: September 10, 2026

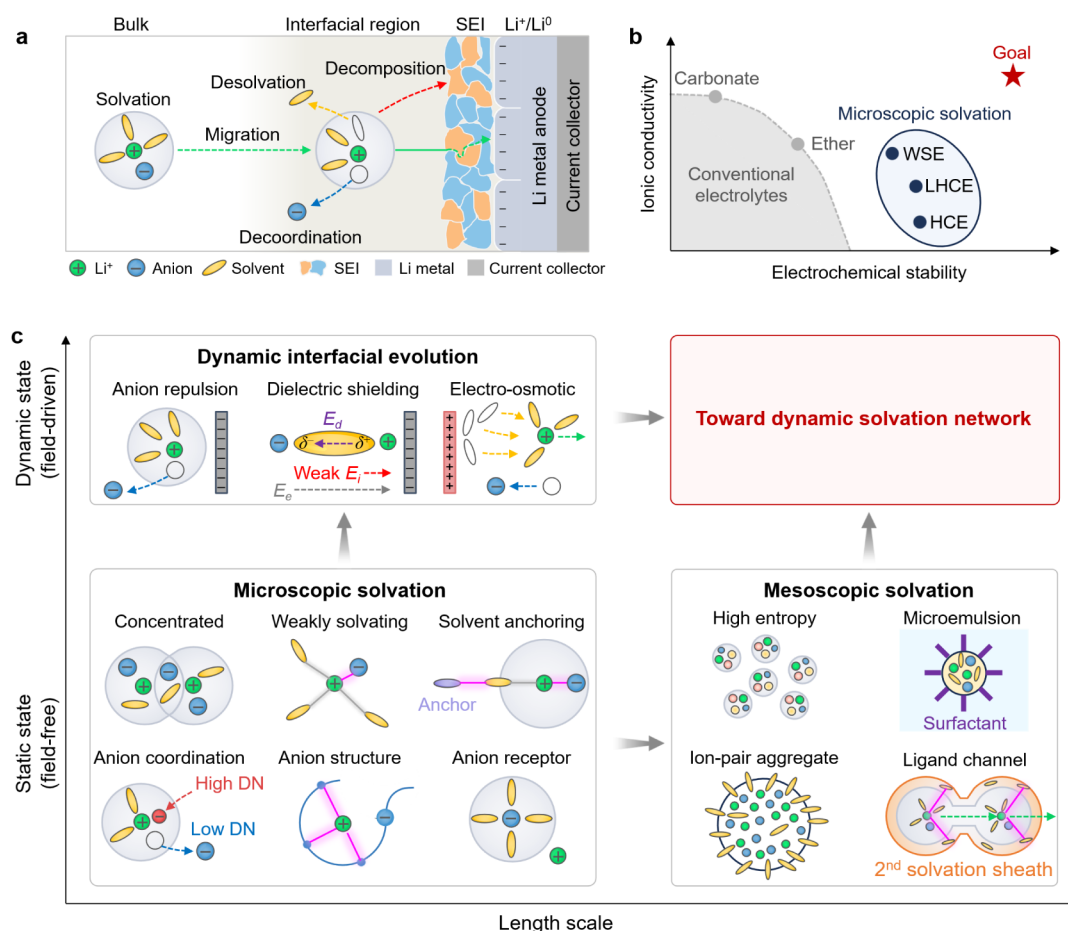


Figure 1. Solvation chemistry of Li metal battery electrolytes. (a) Schematic of Li^+ transport from the bulk electrolyte to the Li metal surface, where the solvation shell undergoes desolvation, decoordination, and decomposition, forming the solid–electrolyte interphase (SEI) that Li^+ migrates through before Li plating. (b) Trade-off between ionic conductivity and electrochemical stability across electrolyte classes. Gray, navy, and red denote conventional carbonate and ether electrolytes, strategies regulating the Li^+ first solvation sheath of Li, and the target of simultaneously high conductivity and stability, respectively. (c) Electrolyte solvation-design strategies mapped by length scale (x -axis) and the presence of an interfacial electric field (y -axis) from the static (field-free) to the dynamic (field-driven) state, with dynamic solvation networks as the frontier. The frontier region denotes dynamic solvation networks as an emerging design space where mesoscale electrolyte organization evolves under interfacial electric fields and couples with species redistribution and reactions that form interphases under operating conditions.

cathodes (Figure 1b). Ethers were widely adopted in early LMB research,^{15,16} given the incompatibility of carbonates with Li metal.¹⁷ As high-voltage cathodes such as lithium nickel manganese cobalt oxide (NMC) were adopted, the limited oxidative stability of ethers emerged as a challenge.^{18–20} Over the past two decades, high-concentration electrolytes (HCEs),^{21–28} localized high-concentration electrolytes (LHCEs),^{29–36} and weakly solvating electrolytes (WSEs)^{37–42} have been extensively investigated to increase anion participation in the first solvation sheath around Li^+ and thereby enhance the contribution of anion-derived species to electrode–electrolyte interphase formation.⁴³ The resulting interphase has improved Li plating/stripping reversibility, but increasing ionic conductivity toward practical targets remains challenging.

To overcome this trade-off, recent studies have begun to explore solvation structures from two emerging perspectives. One direction extends solvation design toward mesoscopic solvation organization beyond the primary Li^+ coordination shell, including high-entropy electrolytes,^{44–51} micelle-like electrolytes,^{52–57} and the regulation of aggregate structure.^{58–62} The other direction examines field-responsive

solvation near electrified interfaces, where the local ionic environment deviates from the bulk electrolyte.⁶³ Research in both directions remains at an early stage and has progressed in separate efforts, leaving a broad design space for connecting solvation across different length scales to interfacial responses under electric fields.

Here, we construct a solvation-centered framework that connects representative electrolyte formulations with evolving solvation networks, practical performance, remaining limitations, and future directions. We first organize solvation strategies using two descriptors: solvation length scale and the influence of interfacial electric fields on solvation structures. This framework places diverse solvation strategies within a continuum extending from microscopic solvation structures in bulk electrolytes to dynamic solvation networks near the electrified interfaces. We benchmark representative electrolyte systems against practical performance criteria for LMBs. For each solvation regime, we summarize the relevant material chemistry, governing physics, characterization methods, and failure modes. We then discuss the frontiers for translating laboratory advances to meet industrial requirements. This work provides a broader basis for electrolyte

design by connecting solvation chemistry to interfacial evolution and the development of practical LMBs.

2. SOLVATION CHEMISTRY ACROSS STATIC AND DYNAMIC REGIMES

The electrolyte design for LMBs has largely been organized by electrolyte class and material composition. Salt concentration, solvent coordinating ability, and diluent chemistry have served as primary variables for improving Li^+ transport, interphase formation, and performance. This materials-centered organization has enabled substantial progress, but a complementary solvation-architecture perspective is needed to connect formulation variables with electrolyte organization. Conventional analyses often describe solvation as a field-free bulk property centered on the Li^+ first solvation sheath. Yet first-sheath coordination alone does not fully describe mesoscale ion organization or field-driven reorganization of solvation architectures near electrified interfaces, leaving their connection to electrochemical behavior less systematically resolved. From this perspective, we reorganize reported solvation design strategies along two descriptors: solvation length scale and interfacial electric field conditions (Figure 1c). This framework places electrolyte formulations within a solvation-centered continuum spanning field-free microscopic coordination, mesoscale solvation organization, and field-driven interfacial solvation. It highlights the need to consider solvation length scale and interfacial electric field conditions as coupled descriptors, rather than as separate design categories.

2.1. Microscopic Solvation Regulation

Microscopic solvation design represents the starting point for Li-metal electrolyte engineering. In this regime, electrolyte behavior is primarily interpreted through the Li^+ first solvation sheath, where the relative participation of solvents and anions governs ion transfer kinetics, interfacial reactivity, and interphase chemistry.⁵ The transition from solvent-rich to anion-rich Li^+ coordination redirects interfacial chemistry toward salt-derived, inorganic-rich interphases and improves Li plating/stripping reversibility.¹¹

HCEs establish salt concentration as a variable for regulating first sheath composition.⁶⁴ HCEs reduce uncoordinated solvent populations and increase anion participation through contact ion pairs (CIPs) and aggregates (AGGs), promoting anion-derived SEI chemistry. However, high salt concentrations increase viscosity, reduce wettability, and raise salt usage.²⁷ LHCEs were developed to retain these local solvation features while reducing bulk formulation constraints.³³ Non-coordinating diluents lower nominal salt concentration and viscosity while remaining largely excluded from the Li^+ first sheath. This design preserves HCE-like coordination and anion-derived interphases, but its effectiveness depends on balancing dilution, phase stability, transport, and preservation of the intended solvation structure.⁵⁷

In WSEs, weakly solvating solvents reduce Li^+ –solvent binding, increase anion participation, and facilitate Li^+ desolvation at electrode interfaces with moderate salt concentrations.^{39,65} However, maintaining salt dissociation and redox stability under weak Li^+ –solvent coordination has motivated diverse solvent molecular designs.⁶⁶ Donor number, steric accessibility, and dielectric response have become key molecular descriptors for weakly solvating electrolyte design.⁶⁷ Solvent-anchoring strategies further expand WSE design by regulating solvent activity beyond intrinsic donor strength.

Molecular docking electrolytes activate recessive siloxane solvents using fluorinated or halogenated inducers, enabling weak Li^+ coordination while preserving ion transport.⁶⁸ Molecular anchoring of free solvents uses hydrogen bonding between diluents and ether solvents to weaken Li^+ –solvent coordination and suppress free-solvent reactivity.⁶⁹

Although anions are often described as free or solvent-separated species with respect to Li^+ in solution, recent studies show that anions are not only precursors for inorganic-rich electrode–electrolyte interphase (EEI) but can also affect the Li^+ coordination environment.⁷⁰ For anion participation in the first solvation sheath, the donor number and anion donicity quantify anion electron-donating ability and relate anion coordination to Li^+ binding and ion transport.^{71–73} Strongly coordinating anions can alter interfacial reaction pathways and promote preferential anion reduction to SEI layers, improving Li metal reversibility.⁷⁴ The molecular structure of anions also regulates Li^+ –anion association.⁷⁵ Ether-like asymmetric anions can promote intramolecular Li^+ coordination, increase apparent donor ability, and enhance Li^+ transference.⁷⁶ Asymmetric sulfonimide anions can suppress Al corrosion while forming favorable interphases on Li metal.⁷⁷ To compensate for formulation constraints associated with designed anion salts, multisalt formulations can improve salt dissociation and ionic conductivity without compromising the advantages of designed anion chemistry.^{78,79}

Anion receptors provide another strategy for regulating the local coordination environment of anions.⁸⁰ Electron-deficient receptors bind anions through electrophilic sites, weakening Li^+ –anion association and assisting salt dissociation.⁸¹ Boron-based and supramolecular receptors have been used to enhance ionic conductivity and Li^+ transference by regulating ion pairing and anion mobility.⁸² Key variables are binding strength and anion selectivity, which determine anion mobility, ion-pair dissociation, and interfacial anion availability.

Overall, microscopic solvation design remains an effective foundation for Li metal electrolyte chemistry, linking Li^+ first-sheath coordination to ion transfer kinetics, interphase chemistry, and Li plating/stripping reversibility.

2.2. Mesoscopic Electrolyte Organization

Although microscopic Li^+ solvation provides a molecular-level basis for electrolyte design, it does not fully capture how neighboring solvation units interact and organize beyond local coordination. In concentrated and multicomponent electrolytes, ion pairs, aggregates, solvent-rich regions, and diluent-rich domains can form mesoscale structures. Mesoscopic solvation organization therefore describes how local coordination units are spatially arranged, packed, and connected over nanometer length scales, influencing ion transport, interfacial species availability, and interphase formation.

High-entropy electrolyte (HEE) design uses component diversity as a thermodynamic variable to increase configurational, mixing, or solvation entropy in liquid electrolytes.^{46,49} Increased molecular diversity raises solvation entropy, reduces ion clustering, and improves ionic conductivity while preserving anion-rich Li^+ solvation structures.⁵⁰ Multianion HEEs diversify anionic groups around Li^+ , weaken average Li^+ –solvent/anion interactions, improve Li^+ diffusivity, and promote inorganic-rich interphases.^{45,48,51} Recent salt-selection studies further show that amphiphilic or multidentate anions can generate anion-dominated solvation configurations and high solvation configurational entropy.⁴⁷

Micelle-like solvation structures in LHCEs connect first-sheath preservation with nanoscale domain formation. Locally concentrated Li^+ -anion-solvent clusters are separated by diluent-rich regions, producing nanoscale heterogeneity that affects Li^+ transport and interfacial species availability.^{53,54,57} Microemulsion electrolytes extend this concept to phase-organized solvation structures. Fluorinated immiscible-phase/amphiphilic-component droplets accumulate at both electrodes through liquid-liquid interfacial tension, decoupling interphase formation from Li^+ solvation migration.⁵⁶ Organic microemulsion electrolytes similarly disperse high-molar-ratio domains in nonpolar diluents, lowering viscosity while preserving ion-solvate-coordinated structures.⁵²

Mesoscopic solvation can also be regulated by aggregate size, compactness, and connectivity beyond the Li^+ first solvation sheath.^{59,60} Compact ion-pair aggregate electrolytes feature densely packed ion pairs that form 3–4 nm aggregates with short Li^+ - Li^+ distances, enabling collective anion reduction and thin inorganic-rich SEI formation.⁶² In contrast, small-cluster strategies reduce excessive aggregation to promote Li^+ transport and desolvation. Diluent electrostatic-potential design can shift large aggregates toward smaller CIP/AGG populations, improving Li^+ transport through the SEI during fast charging.⁵⁸ Symmetric organic salts similarly generate miniature anion- Li^+ solvation by suppressing excessive anion clustering, improving ionic conductivity, desolvation kinetics, and interfacial uniformity.⁶¹ Together, these studies define aggregate dimensions and packing as mesoscopic descriptors that couple ion transport with interfacial reactivity.

From a mesoscopic perspective, electrolyte design should consider not only the identity of Li^+ coordination motifs but also their spatial organization. Nanoscale domain structure, aggregate size, packing density, solvation state distribution, and pathway connectivity provide complementary descriptors that connect local coordination chemistry with collective electrolyte organization.

2.3. Field-Driven Evolution of Interfacial Solvation Structures

Battery electrolytes operate under electric fields, potential gradients, and continuous charge transfer. Solvation analyses often use field-free measurements or simulations to characterize equilibrium electrolyte configurations and transport-related properties. These descriptions are useful for identifying bulk solvation motifs, but they provide limited access to the interfacial solvation structures emerging near electrified electrode surfaces. Interfacial electric fields, preferential adsorption, ion migration, desolvation, and charge-transfer reactions can generate solvation environments that differ from field-free bulk structures.⁶³ These effects are especially important near the inner Helmholtz plane, where the local availability of solvated Li^+ , anions, solvents, and additives shapes EEI-forming reaction pathways.

During charging, the Li metal anode becomes negatively polarized, making field-induced anion repulsion important at the Li metal surface.⁸³ Interfacial anion repulsion then leaves Li^+ associated with fewer and weaker solvent ligands, lowering the desolvation barrier. This field-assisted desolvation supports homogeneous Li deposition under ultralow-temperature conditions, where Li^+ desolvation dominates charge-transfer impedance. Cathode interfaces show a different field response. In situ attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) revealed an anti-synergy effect

between Li^+ solvation and the interfacial electric field.⁸⁴ During early charging, Li^+ release and solvation build a concentrated Li^+ -solvent/anion-rich interface, favoring anion-derived CEI formation. At higher voltages, the strengthened interfacial field drives solvated Li^+ clusters away from the cathode surface, producing a diluted solvent-rich interface and shifting CEI chemistry toward solvent-derived components.

Dielectric-mediated transfer dynamics describe how solvent permittivity regulates interfacial Li^+ solvation at electrified interfaces.⁸⁵ Near charged interfaces, Li^+ and anions form a periodic spatial distribution. This periodic arrangement is described as oscillatory solvation chemistry. Solvents with higher permittivity generate stronger intramolecular counterfields that attenuate the effective interfacial electric field. This attenuated field preserves Li^+ -anion coordination near the electrode, leading to a larger oscillation amplitude and stronger coordinated anion retention. The retained anions then participate in interfacial reduction, promoting the compact fluoride-rich SEI formation.

Electro-osmotic drag links Li^+ migration with solvent motion during fast charging, particularly within porous cathodes.⁸⁶ During cathode delithiation, Li^+ leaving the porous cathode drags solvating solvent molecules, causing solvent withdrawal from thick cathode pores and electro-osmotic-drag polarization. Electrolytes with weak cation solvation and strong anion solvation reduce coupled Li^+ -solvent motion. This solvation design suppresses solvent withdrawal, lowers drag-induced polarization, and improves fast-charge transport.

Together, these studies indicate that interfacial solvation reflects a dynamic configuration continuously reshaped by field-driven species redistribution, dielectric-mediated solvate transfer, partial desolvation, and coupled ion-solvent transport. Such redistribution can alter EEI chemistry by changing the local availability, residence, and reaction probability of solvents, anions, and additives within the reactive interfacial region, thereby linking dynamic solvation environments to interphase formation.

2.4. Toward Dynamic Solvation Networks

Solvation research in battery electrolytes continues to expand from local coordination chemistry toward multiscale descriptions of electrolyte behavior under operating conditions. This expansion requires descriptors that connect Li^+ coordination, the electrolyte microstructure, and interfacial solvation during cell operation. In Figure 1c, the frontier region specifically corresponds to the upper-right design space, where mesoscopic electrolyte organization evolves under interfacial electric fields. Dynamic solvation networks are proposed here as an organizing concept for this frontier region, linking nanoscale domains, ion-pair aggregates, and network connectivity with field-driven species redistribution, dielectric response, ion-solvent transport, and interphase-forming chemistry under operating conditions.

In this framework, solvation design shifts the target from optimizing static solvation structures to controlling how multiscale solvation networks evolve under operating fields. Mesoscopic domains, ionic aggregates, and network connectivity are therefore treated as field-responsive components of electrolyte organization that regulate local species availability and interphase-forming reactions at the electrode/electrolyte interfaces. Future descriptors should quantify how the aggregate size, domain morphology, pathway connectivity, and dynamic exchange among solvation states evolve under

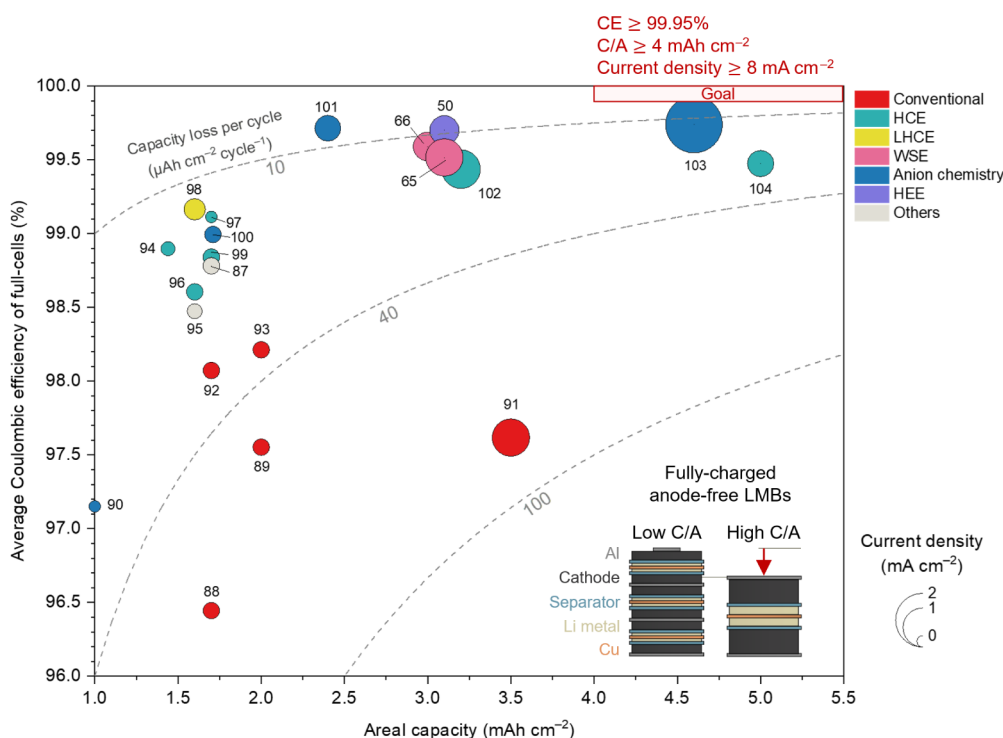


Figure 2. Electrolyte performance in anode-free Li metal full cells. Average full-cell CE (y-axis) versus areal capacity (x-axis), with electrolytes grouped by chemistry (color) and current density (marker size). Dashed contours denote constant capacity loss per cycle, defined as areal capacity $\times (1 - \text{CE})$, at 10, 40, and 100 $\mu\text{Ah cm}^{-2} \text{ cycle}^{-1}$. The shaded red box marks the target ($\text{CE} > 99.95\%$, $\text{C/A} \geq 4 \text{ mAh cm}^{-2}$, and current density $\geq 8 \text{ mA cm}^{-2}$). Inset, anode-free cell stacks in the charged state at low and high C/A.

interfacial electric fields and concentration gradients. Quantifying these relationships connects solvation chemistry to interphase-forming reactions and electrochemical reversibility, guiding electrolyte architectures that sustain favorable solvation environments during practical cycling.

3. PRACTICAL PERFORMANCE GAPS AND MATERIAL CHEMISTRY

To place current solvation-design strategies^{50,65,66,87–104} in a practical full-cell context, Figure 2 summarizes reported anode-free Li-metal full-cell performance using three coupled metrics: average full-cell CE, plated-Li areal capacity (corresponding to the cathode areal capacity (C/A)), and Li plating current density. Individual systems are categorized by the electrolyte-design strategy. There were three key observations.

First, the CE remains the most direct metric of electrolyte reversibility. Per-cycle capacity retention scales as CE^N , such that an improvement from 99% to 99.9% extends the projected cycle life to 80% retention by approximately 10-fold.⁵ The threshold for sustained anode-free operation exceeds 99.95%, with values approaching 99.99% required to reach the 1000-cycle target.⁵ However, the reported CE values of anode-free full cells fall predominantly below 99.2%, leaving a substantial gap from this threshold. Bridging this gap remains the principal objective of ongoing solvation design efforts.

Second, the evaluation of CE depends on the Li plating capacity. Recent battery architectures adopt thick-electrode systems requiring areal capacities of $\geq 4 \text{ mAh cm}^{-2}$ and correspondingly thick-plated Li to reduce the contribution of passive components, such as current collectors and separators, and increase cell-level energy density.^{64,105} Under these configurations, Li deposition transitions from nucleation on

Cu to subsequent Li growth on the preformed Li nuclei, which proceeds through fundamentally different interfacial dynamics.¹⁰⁶ Therefore, achieving high CE under thick-plating/stripping has become a central challenge for practical LMBs. However, most of the reported CE values correspond to a low areal capacity of plated Li, typically below 2 mAh cm^{-2} . The constant per-cycle Li-loss contours show that a given CE deficit translates into a larger absolute Li loss per cycle as plated Li areal capacity increases. Evaluation of CE, therefore, requires explicit consideration of the Li plating capacity.

Third, practical operation imposes constraints on the Li plating/stripping current density. At a fixed C-rate, the Li plating current density scales linearly with plated Li areal capacity, indicating that higher-loading electrodes impose proportionally higher plating current densities. Fast-charging capability has emerged as a key requirement for high-energy LMBs, with current densities exceeding 8 mA cm^{-2} are needed to meet the automotive target of 80% state of charge within 15 min.^{79,107} However, most reported CE values have been evaluated below 2 mA cm^{-2} , conditions incompatible with both high-areal-capacity configurations and fast-charging operation.

Taken together, these three metrics establish a practical evaluation window for next-generation electrolytes: $\text{CE} \geq 99.95\%$ at a plated Li areal capacity of $\geq 4 \text{ mAh cm}^{-2}$ and a Li plating current density of $\geq 8 \text{ mA cm}^{-2}$. The gap between reported performance and this window indicates that solvation strategies should be evaluated beyond CE alone, with explicit consideration of plated Li areal capacity and current density under realistic cell operation. Most electrolyte studies have focused on molecular-level solvation and its correlation with electrochemical performance. Recent studies on mesoscopic

Table 1. Material Chemistry for Li-Metal Battery Electrolytes

Materials	Issues	Underlying causes	Material properties	Proposed solutions
Anion	Poor salt dissociation (transport)	Strong Li^+ –anion pairing	Charge localization; molecular geometry; anion basicity	(1) Charge-delocalized, low-basicity anions (2) Sterically constrained anions
	Al corrosion (interfacial)	Anion-mediated Al dissolution	Anion oxidation potential; free-ion fraction; Al–anion complex solubility	(1) Anion design for intrinsic Al passivation (2) Current collector surface coating
	Hydrolytic instability (chemical)	Moisture-induced hydrolysis	Hydrolytic stability of bonds	(1) Hydrolytically stable anion design (2) Moisture or HF scavenger additives
Solvent	Low ionic conductivity (transport)	Low dissociation and mobility	Dielectric constant; viscosity	(1) Balanced-polarity solvent systems (2) Low-viscosity solvent matrix
	Sluggish Li^+ desolvation (interfacial)	Excessive Li^+ –solvent binding	Donor number; chelating sites	(1) Low-DN solvents (2) Sterically shielded donor sites
	Oxidation instability and poor CEI (interfacial)	HOMO–cathode mismatch	HOMO level; fluorine content	(1) Oxidation-resistant solvents (2) Robust inorganic CEI-forming chemistry
	Reductive instability and poor SEI (interfacial)	LUMO–Li mismatch	LUMO level; bond dissociation energy	(1) Solvent-lean electric double layer (2) Inorganic-rich SEI-forming chemistry
	Flammability (practical)	Volatile organic backbone	Vapor pressure; flash point	(1) Flame-retardant functionalization (2) Nonflammable backbone
Diluent	Insufficient dilution and wetting (formulation)	Cluster aggregation	Viscosity; surface tension	(1) Low-viscosity noncoordinating diluents (2) Solvent-to-diluent ratio tuning
	Phase separation (formulation)	Solvent–diluent immiscibility	Polarity; E_T^N ; ESP_{max}	(1) Miscibility-guided diluent selection (2) Co-diluent or hybrid-diluent design
	Solvation-structure disruption (solvation)	Coordination/overantisolvation	Donor number; Kamlet–Taft β ; ESP_{max}	(1) Low DN, low β , and ESP_{max} guided diluents (2) Fluorination, size, and polarity control
	Interfacial and practical constraints (practical)	Fluorinated diluent dependence	Redox potential; bond dissociation energy; F-content	(1) Thermally stable, low F backbones (2) Hybrid diluent design

electrolyte organization, concentration polarization, and field-driven interfacial solvation suggest that structures beyond the first solvation sheath can provide additional pathways for performance improvement. Resolving these dynamic solvation networks and correlating their evolution with electrochemical performance will be critical for clarifying their practical relevance and the realistic scope of solvation engineering in LMBs.

The practical performance limitations identified above arise from coupled material constraints in electrolyte formulations. Although evaluated at the cell level, electrolyte failure often reflects molecular interactions and formulation properties of anions, solvents, and diluents. Table 1 links these components to practical challenges, origins, material properties, and design strategies.

Anion chemistry influences both bulk ion association and interfacial stability.¹⁰⁸ Poor salt dissociation often arises from localized charge, high anion basicity, and molecular geometry, leading to reduced ionic conductivity.^{109,110} These relationships guide anion design toward charge delocalization, lower basicity, and steric constraints to improve salt dissociation and ion transport.⁶ At electrode interfaces, anions influence Al corrosion and interphase chemistry through oxidative stability, complexation behavior, and decomposition pathways.¹¹¹

Therefore, anion selection requires balancing salt dissociation, Al–anion complex solubility, and passivating decomposition pathways. Moisture-sensitive anions introduce an additional degradation route, as hydrolysis can generate acidic species that accelerate interfacial degradation.¹¹² Hydrolytically stable anions and moisture/HF scavenging strategies support electrolyte stability during storage and cycling.

Solvents couple bulk ion transport with interfacial Li^+ transfer and interphase chemistry. In the bulk electrolyte, insufficient salt dissociation and high solvent viscosity limit ionic conductivity. Dielectric constant and viscosity provide paired descriptors for designing balanced polarity and low viscosity solvent systems.¹¹³ Strong Li^+ –solvent coordination increases the desolvation barrier at the Li metal interface. DN and steric accessibility around donor atoms describe Li^+ –solvent coordination strength, guiding solvent designs that moderate Li^+ coordination while retaining sufficient salt solvation capability.¹¹⁴ Solvents also determine which reactive species participate in interphase chemistry. At high-voltage cathodes, solvent oxidation and insufficient CEI passivation are linked to solvent HOMO levels relative to cathode potentials. Oxidation-resistant solvents and robust inorganic CEI chemistry can suppress continuous electrolyte oxidation.¹¹⁵ At Li metal, solvent reduction and unstable SEI formation are

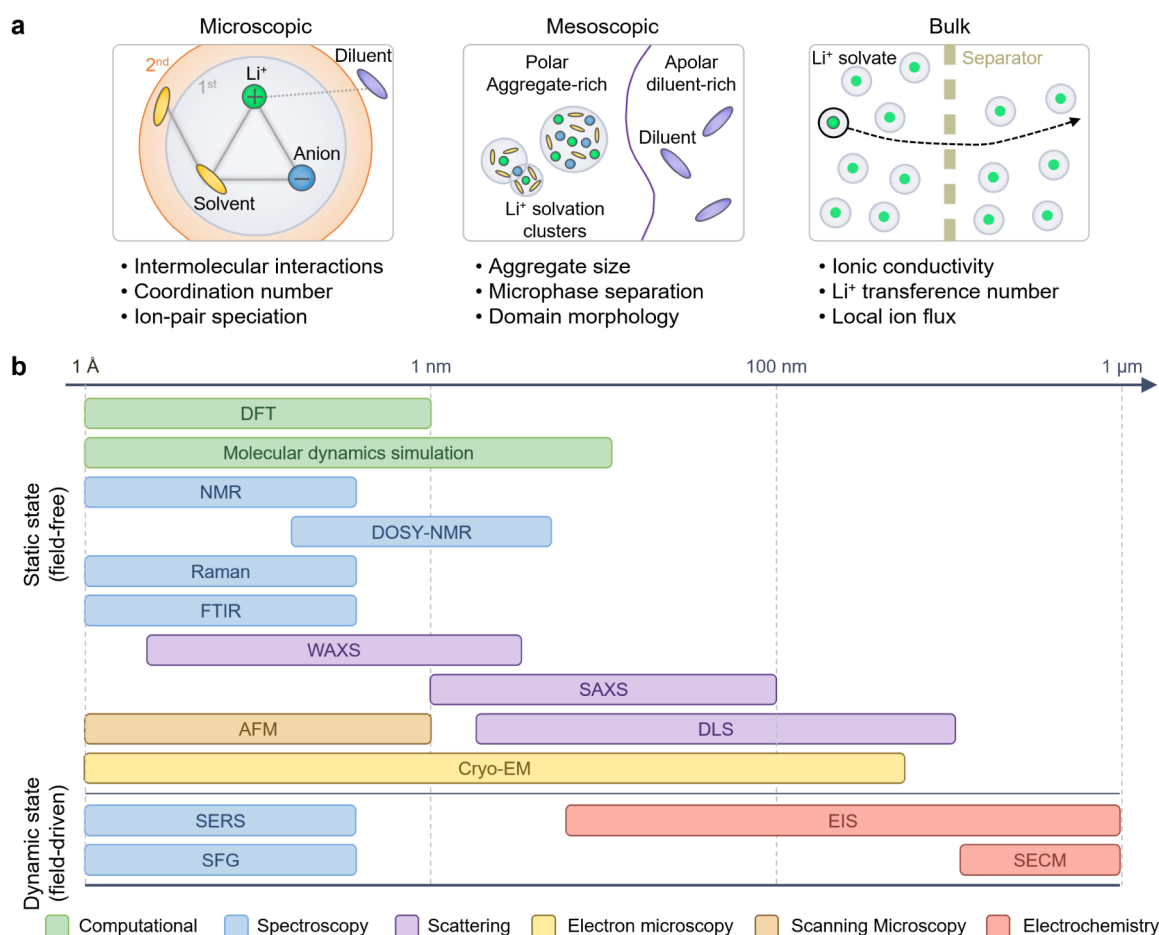


Figure 3. Electrolyte solvation across length scales and the corresponding characterization techniques. (a) Schematic of the electrolyte at three length scales: microscopic (first and second solvation shells around Li^+), mesoscopic (aggregate clusters with polar and apolar microphases), and bulk (long-range ion transport). Green, blue, yellow, and purple symbols represent Li^+ , anion, solvent, and diluent, respectively. The descriptors to be characterized at each scale are listed below. (b) Characterization techniques positioned by the length scale resolved (*x*-axis) and by equilibrium versus operating-bias conditions (*y*-axis), color-grouped by technique category. The length ranges indicate approximate solvation-feature regimes commonly accessed by each method in electrolyte studies, rather than strict instrumental resolution limits.

associated with solvent LUMO levels and bond dissociation pathways during decomposition.¹¹⁶ A solvent-lean electric double layer and inorganic-rich SEI chemistry can limit solvent-driven parasitic reactions.¹¹⁷ Beyond electrochemical stability, solvent flammability remains a practical constraint. Flame-retardant functional groups and nonflammable solvent backbones can improve electrolyte safety.¹¹⁸

Diluents regulate formulation properties while preserving favorable local solvation structures in localized electrolyte formulations.¹¹⁹ Their primary role is to reduce viscosity and improve wetting by diluting aggregated salt–solvent clusters. However, inappropriate diluents can introduce formulation and solvation instabilities. Phase separation arises from solvent–diluent immiscibility.⁵⁷ The normalized Reichardt polarity parameter (E_T^N) describes empirical solvent polarity,¹²⁰ while maximum electrostatic potential (ESP_{max}) reflects electrostatic interaction tendency.¹²¹ These descriptors help evaluate solvent–diluent miscibility. Solvation disruption occurs when diluents coordinate Li^+ or show excessive antisolvating behavior. DN describes Lewis basicity toward Li^+ ,¹²² the Kamlet–Taft basicity parameter (β) describes hydrogen-bond-accepting basicity,^{35,120} and ESP_{max} provides an electrostatic descriptor for diluent interactions.¹²¹ These descriptors help evaluate whether a diluent remains non-

coordinating while maintaining electrolyte homogeneity. Dependence on fluorinated diluents can also introduce interfacial and practical constraints associated with redox stability, bond dissociation, fluorine content, density, and cost.⁶⁴ Low-viscosity noncoordinating diluents and miscibility-guided selection are important directions for practical localized-electrolyte design.¹¹⁹ Low-F diluent backbones further address solvation compatibility and practical fluorine-related constraints.¹²³

Component-level material chemistry provides a basis for screening electrolyte formulations against practical constraints beyond solvation-structure control. Electrolyte behavior depends on how these components are combined in a formulation. The same anion, solvent, or diluent can form distinct solvation structures depending on the salt concentration, solvent-to-diluent ratio, additive content, and electrolyte loading. Practical electrolyte formulation, therefore, requires material selection and solvation-structure control to be considered together.

4. MULTISCALE CHARACTERIZATION AND SOLVATION PHYSICS

Multiscale solvation under an applied electric field provides a framework for electrolyte design, underpinning interphase

formation and ion transport that govern cell performance. The solvation structure spans multiple length scales, from the coordination shell of a single Li^+ to the bulk transport medium, and the relevant descriptors vary across scales (Figure 3a). The microscopic regime focuses on the Li^+ environment, including intermolecular interactions, first-shell coordination, and ion-pair speciation. Beyond the local coordination shell, solvated units organize into mesoscale structures, where aggregate size, polar–apolar microphase separation, and domain morphology become relevant. Macroscopic descriptions shift toward transport properties, including ionic conductivity, Li^+ transference number, and local ion flux.

We summarize multiscale solvation characterization by linking solvation descriptors across length scales, with complementary computational, spectroscopic, scattering, microscopic, and electrochemical methods (Figure 3b). Density functional theory (DFT) computes electronic structure from electron density, providing molecular-level information on bonding, charge distribution, and orbital energetics. In electrolyte design, DFT evaluates Li^+ –solvent and Li^+ –anion interaction energies, coordination preferences, solvation energies, and redox-related descriptors.¹²⁴ Molecular dynamics (MD) samples atomic trajectories over time and converts liquid electrolyte configurations into statistical structural descriptors. MD provides radial distribution functions, coordination environments, ion-pair populations, aggregate formation, and diffusion-related solvation statistics.¹²⁵

Raman spectroscopy monitors vibrational modes whose peak positions and band shapes change with ion–solvent coordination and ion–ion association. Anion-sensitive bands can be deconvoluted into solvent-separated ion pairs (SSIPs), CIPs, and AGGs, providing ion-pair speciation and relative interaction strengths.^{126,127} Fourier transform infrared (FTIR) spectroscopy detects vibrational shifts and intensity changes arising from local coordination and hydrogen bonding. FTIR identifies solvent or anion modes associated with Li^+ coordination, ligand–anion interactions, and operando changes in local ion concentration.^{128,129} Nuclear magnetic resonance (NMR) spectroscopy probes local electronic environments through chemical shifts, relaxation, and intermolecular spin interactions. It identifies Li^+ coordination, solvent–solute association, and short-range interaction patterns.^{130,131} Diffusion-ordered spectroscopy (DOSY) extends NMR by measuring species-resolved diffusion of ions, solvents, and additives. It provides self-diffusion coefficients, coordination ratios, and transport-related information linked to electrolyte structure.^{132,133}

Small-angle X-ray scattering (SAXS) measures the nanoscale electron-density contrast produced by compositionally heterogeneous electrolyte domains. SAXS analysis provides aggregate size, characteristic spacing, and microphase-separation length scales.^{134,135} Wide-angle X-ray scattering (WAXS) complements SAXS by probing short-range ordering and ion-pair or aggregate correlations in liquid electrolytes.^{50,62} Dynamic light scattering (DLS) tracks time-dependent fluctuations in scattered light from diffusing electrolyte heterogeneities. DLS yields apparent hydrodynamic size distributions for solvated clusters, aggregates, and mesoscale electrolyte domains.^{136–138}

Atomic force microscopy (AFM) force–distance measurements probe electrode–electrolyte interfacial structure through distance-dependent tip–surface responses. These measurements reveal near-surface electrolyte layering and spatial organization of electrolyte species.¹³⁹ Charge-profiling three-

dimensional AFM (CP-3D-AFM) combines electrochemical 3D force maps, peak deconvolution, and electrostatic analysis to obtain real-space charge-density profiles of electric double layers with angstrom depth resolution.¹⁴⁰

Transmission electron microscopy (TEM)-based methods provide spatially resolved images and maps of mesoscale electrolyte heterogeneity and domain morphology. Cryogenic TEM (cryo-TEM) resolves liquid–liquid droplet domains in microemulsion electrolytes.⁵⁶ Liquid-phase four-dimensional scanning TEM (4D-STEM) maps short-range structural order in high-salt-concentration domains.¹⁴¹ TEM further reveals self-assembled mesoscopic structures formed by amphiphilic molecules.¹⁴² Future cryo-TEM and liquid-phase TEM/STEM methods could further extend electrolyte characterization toward subnanometer ordering and field-driven interfacial structures.

Surface-enhanced Raman spectroscopy (SERS) uses plasmon-enhanced Raman scattering from metallic nanostructures to probe electrolyte species near solid–liquid interfaces. Nanogap SERS probes Li^+ solvation environments near the solid electrode–liquid interface and estimates Li^+ solvation numbers in the confined nanogap region.¹⁴³ Sum-frequency generation (SFG) spectroscopy provides interface-specific vibrational information on solvent adsorption, static electric-double-layer structure, SEI formation and evolution, and interfacial Li^+ desolvation dynamics.¹⁴⁴

At the bulk scale, electrochemical impedance spectroscopy (EIS) measures frequency-dependent impedance responses from the bulk electrolyte and interfacial processes. High-frequency bulk resistance gives ionic conductivity, while transport-model fitting of diffusion impedance provides the Li^+ transference number and thermodynamic factor information.¹⁴⁵ Scanning electrochemical microscopy (SECM) positions a scanning microelectrode probe near an electrode or separator to measure localized redox mediator responses. Redox mediator SECM maps spatial heterogeneity in ion transport, concentration gradients, ion transfer kinetics, and interphase activity.^{146–148}

Together, these characterization methods relate electrolyte solvation to transport across molecular, interfacial, mesoscale, and bulk regimes. A key opportunity is to translate this relationship to operating cells, where the applied bias, concentration gradients, and interfacial reactions alter local solvation environments. Characterizing a dynamic solvation network requires interfacial chemical speciation and mesoscale structural order to be tracked together under an applied bias. In situ ATR-FTIR resolves bias-dependent changes in interfacial solvent and anion speciation. SAXS, WAXS, and liquid-phase 4D-STEM resolve aggregate size and short-range structural order on the mesoscale. To date, mesoscale characterization has mainly probed equilibrium or near-equilibrium states. Extending mesoscale characterization to operando conditions is needed to determine whether mesoscale solvation structures reorganize under applied bias, as the dynamic solvation network framework proposes. Spatially resolved, nondestructive operando measurements will be needed to quantify mesoscale organization and bulk transport under realistic conditions and relate local solvation to cell-level electrochemical responses for practical electrolyte design.

Physics-based descriptors provide a quantitative basis for relating electrolyte solvation structures to transport and interfacial behavior. In LMB electrolytes, solvation cannot be

Table 2. Representative Descriptors and Relations for Electrolyte Solvation and Transport^a

Regime	Descriptor	Equations	Interpretation and applicability
Local solvation and ion pairing	Born solvation energy	$\Delta G_{\text{Born}} = -\frac{N_A z_i^2 e^2}{8\pi\epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right)$	Describes ion stabilization within a solvent dielectric environment
	Bjerrum length	$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$	Defines the distance scale for Coulomb-driven ion pairing
	Ion association equilibrium	$K_{\text{assoc}} = \frac{a_{\text{ion pair}}}{(a_{\text{Li}^+} \times a_{\text{A}^-})}$	Describes the balance among free ions, ion pairs, and associated species
	Desolvation kinetics	$k_{\text{des}} = \frac{(k_B T)}{h} \exp\left(-\frac{\Delta G_{\text{des}}^\ddagger}{RT}\right)$	Relates solvation strength to Li ⁺ transfer across the electrode interface [†]
Mesoscale screening and organization	Ionic strength	$I = \frac{1}{2} \sum_i c_i z_i^2$	Represents the concentration of charged species governing electrostatic interactions
	Debye length	$\lambda_D = \left(\frac{\epsilon_r \epsilon_0 RT}{2F^2 I}\right)^{1/2}$	Describes the characteristic distance for electrostatic screening [†]
	Activity coefficient	$\log_{10} \gamma_i = -A z_i^2 I^{1/2}$	Quantifies deviations from ideal solution behavior due to electrostatic ion interactions [†]
	Domain spacing	$d = \frac{2\pi}{q^*}$	Characteristic spacing of mesoscale electrolyte domains or ion-aggregate correlations
Macroscopic transport	Nernst–Einstein conductivity	$\sigma_{\text{NE}} = \frac{F^2}{RT} \sum_i z_i^2 c_i D_i$	Provides an ideal diffusion-based reference for ionic conductivity [†]
	Nernst–Planck flux	$J_i = -D_i \nabla c_i - \frac{z_i F D_i}{RT} c_i \nabla \phi$	Describes ion transport under concentration gradients and electric fields
	Li ⁺ transference number	$t_+ = \frac{D_+}{D_+ + D_-}$	Estimates the Li ⁺ current fraction under ideal diffusion-based transport [†]
	Walden relation	$\Lambda_m \eta = \text{constant}$	Relates molar conductivity and viscosity to compare transport efficiency across formulations [†]

^aSymbols are defined as follows: z_i , c_i , D_i , and a_i are the charge number, concentration, diffusion coefficient, and activity of species i , respectively; I is the ionic strength; ϵ_r and ϵ_0 are the relative and vacuum permittivities; r_i is the ionic radius; γ_i is the activity coefficient; A is the Debye–Hückel constant; q^* is the peak scattering vector; σ_{NE} are the Nernst–Einstein conductivities; α is ionicity; Λ_m is the molar conductivity; η is the dynamic viscosity; ϕ is the electric potential; N_A is Avogadro's constant; e is the elementary charge; k_B is the Boltzmann constant; h is Planck's constant; R is the gas constant; F is the Faraday constant; and T is the temperature. Rows marked with [†] indicate descriptors whose links to dynamic solvation under operation rely on indirect evidence, with limited operando observations.

described by a single molecular interaction or a single bulk property. Instead, ion stabilization, ion association, collective screening, structural organization, and macroscopic ion transport are coupled across multiple descriptor regimes. Table 2 summarizes representative equations that are commonly used to interpret these regimes. These equations provide reference descriptors for comparing electrolyte formulations and for identifying how deviations from ideal behavior emerge across different length scales.

At the local level, solvation and ion pairing are governed by electrostatic stabilization, dielectric response, and thermal energy. The Born solvation energy describes the stabilization of an ion within a dielectric medium and provides a reference for evaluating how ion size and solvent permittivity influence salt dissociation.¹⁴⁹ The Bjerrum length defines the distance at which the Coulombic interaction becomes comparable to thermal energy, thereby providing a length scale for ion-pair formation.^{150,151} These descriptors are useful because they connect solvent polarity and ion charge to the tendency for ion dissociation or association. However, they are based on continuum electrostatics and do not explicitly account for specific coordination geometry, steric effects, or local dielectric heterogeneity. Ion association equilibrium extends this local description by representing the balance among free ions, ion pairs, and associated species.¹⁵² This equilibrium is sensitive to

salt concentration, solvent dielectric response, and specific ion–solvent or ion–ion interactions. Desolvation kinetics further links local solvation strength to interfacial Li⁺ transfer.^{153–155} A strongly solvated Li⁺ may improve salt dissociation in the bulk electrolyte, but it can also increase the energetic penalty for Li⁺ transfer across the electrode interface. Therefore, local descriptors should be considered together, because favorable bulk dissociation and facile interfacial desolvation are not always achieved by the same molecular design.

At the mesoscale, electrolyte behavior is influenced by collective screening, thermodynamic nonideality, and structural organization. Ionic strength represents the concentration of charged species, which governs electrostatic interactions, and provides the basis for estimating the Debye length.¹⁵⁶ The Debye length describes the characteristic distance over which the electrostatic potential is screened.¹⁵⁷ These quantities are most rigorous in dilute or moderately concentrated electrolytes. At higher salt concentrations, ion correlations, aggregate formation, and spatially heterogeneous dielectric environments can cause screening behavior to deviate from dilute-solution expectations. The activity coefficient provides a thermodynamic measure of deviation from ideal solution behavior.^{156–158} In classical treatments, Debye–Hückel relations connect activity coefficients to ionic strength through electro-

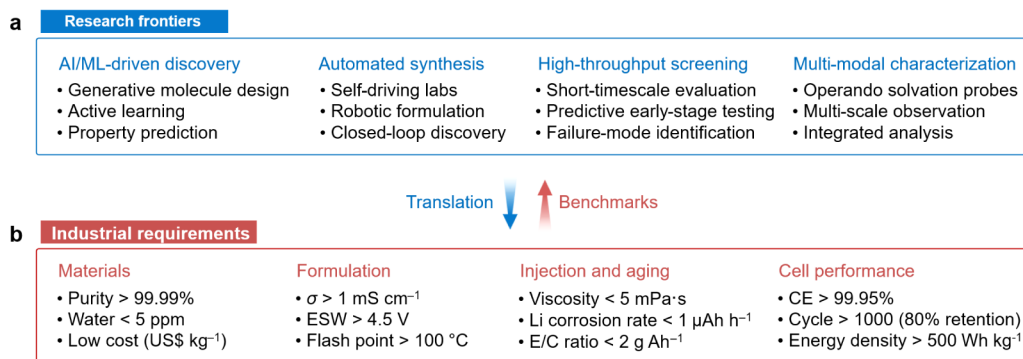


Figure 4. Research frontiers and industrial requirements for Li metal battery electrolytes. (a) Four research frontiers driving next-generation electrolyte development. Forward arrows indicate the research workflow from molecular design to mechanistic analysis. (b) Industrial requirements organized along the four electrolyte development stages spanning materials, formulation, injection and aging, and cell performance.

static interactions. Mesoscale organization can also be represented by domain spacing, which estimates the characteristic spacing of aggregate-rich or heterogeneous domains from a scattering vector.¹³⁴ This descriptor is especially useful when local solvation environments are embedded within larger-scale compositional or structural heterogeneity.

Macroscopic transport descriptors connect ion motion to measurable electrolyte performance. The Nernst–Einstein conductivity estimates an ideal diffusion-based conductivity under the assumption of independent ion motion.¹⁵⁹ Comparing this reference with measured conductivity can reveal the influence of ion association or correlated transport. The Nernst–Planck flux describes ion transport under concentration gradients and electric fields, providing a continuum framework for polarization during battery operation.¹⁶⁰ The Li⁺ transference number estimates the Li⁺ current fraction under ideal diffusion-based transport, which is relevant to concentration polarization near Li metal.^{161,162} The Walden relation further relates molar conductivity and viscosity, allowing transport efficiency to be compared across formulations with different fluidity.¹⁶³

Taken together, these equations provide a quantitative framework for interpreting electrolyte solvation and transport across different descriptor regimes. They clarify how local ion stabilization, mesoscale electrostatic organization, and macroscopic ion motion can be connected using common physical parameters. However, many classical descriptors were derived under dilute-solution, continuum, independent-ion, or near-equilibrium assumptions. These assumptions are not fully satisfied in LMB electrolytes, where salt concentrations often exceed 1 mol L⁻¹ and ion pairing, correlated transport, and interfacial polarization become significant. Therefore, future electrolyte analysis should integrate correlation-aware transport models, activity-based thermodynamic descriptions, and multi-scale characterization that links local solvation, mesoscale organization, and macroscopic transport under operating conditions.

5. RESEARCH FRONTIERS AND INDUSTRIAL REQUIREMENTS

Translating liquid-electrolyte design for LMBs from laboratory concepts to practical cells requires alignment between academic discovery and industrial validation.¹⁶⁴ Academic research establishes the scientific principles and design strategies for emerging electrolyte chemistries, while industrial

development defines the performance, manufacturability, and safety requirements for practical LMBs.¹⁶⁵

Artificial intelligence (AI), particularly machine learning (ML), is emerging as a route to address the high dimensionality, data scarcity, and multiobjective optimization of electrolyte design spaces.^{166–168} Predictive workflows based on molecular descriptors, formulation representations, and interpretable structure–performance models can connect electrolyte composition with transport, interphase chemistry, CE, and cycling stability.^{169–171} Inverse design workflows, including generative models, active learning, knowledge transfer, and closed-loop optimization, enable property-targeted discovery of solvents and formulations for practical battery conditions.^{172–175}

Battery electrolyte development is a high-dimensional formulation problem that remains time-consuming and labor-intensive under manual trial-and-error experimentation.¹⁷⁶ Automated electrolyte preparation provides the experimental infrastructure needed to connect AI-guided discovery with machine-executable workflows,^{177,178} including liquid formulation,¹⁷⁹ coin cell assembly,¹⁸⁰ and electrochemical evaluation.¹⁸¹ Coupling these platforms with Bayesian optimization,^{182,183} autonomous electrochemical measurements,¹⁸⁴ and adaptive mechanistic analysis¹⁸⁵ converts automation into closed-loop discovery, where each measured outcome updates the next experiment and accelerates convergence toward electrolyte performance targets.

High-throughput screening provides an early-stage evaluation layer that links broad electrolyte and electrode design spaces with measurable electrochemical responses on experimentally accessible time scales.^{186–188} These workflows establish short-time scale filters for formulation compatibility, interfacial reactivity, ion-transport limitations, and electrode process variability.¹⁸⁹ When coupled with early-cycle prediction and rapid electrochemical diagnostics, high-throughput data sets can prioritize candidates and reveal degradation-relevant signatures before extended cycling.^{190,191}

Deeper insights into solvation structure and interphase evolution under realistic operating conditions can be obtained through operando probes¹⁹² and multiscale characterization, including electrochemical liquid-cell TEM for real-time visualization of electrochemical processes¹⁹³ and operando heating/cooling electrochemical 4D-STEM for nanoscale structural analysis under controlled electrochemical and thermal conditions.¹⁹⁴ Together, these characterization outputs can support closed-loop workflows in which measured

interfacial and transport responses guide successive iterations of molecular and formulation design.¹⁹⁵

Practical electrolyte candidates must satisfy a coupled set of requirements, from material selection to cell validation (Figure 4b). At the material level, battery-grade purity exceeding 99.99% provides a raw-material quality criterion for scalable electrolyte production.¹⁷⁴ Water content below 5 ppm reduces moisture-driven salt/solvent decomposition and uncontrolled interphase-forming reactions.¹⁹⁶ Low material cost serves as a key criterion for economically viable scale-up.¹⁹⁷ In the formulated electrolyte, ionic conductivity above 1 mS cm⁻¹ provides a minimum screening threshold for ion transport.¹⁹⁸ Oxidative stability beyond 4.5 V enables operation with high-voltage cathodes and Al current collectors.^{64,199} Flash points above 100 °C serve as a thermal-safety margin for electrolyte handling and abuse tolerance.^{200,201} An electrolyte viscosity below 5 mPa·s supports infiltration and wetting in dense electrode stacks.²⁰² Li corrosion rate below 1 μAh h⁻¹ indicates suppressed corrosion-induced active-Li loss during electrolyte soaking, resting, and aging.²⁰³ Electrolyte-to-capacity (E/C) ratios below 2 g Ah⁻¹ limit excess electrolyte while preserving cell-level energy density.^{197,204} CE exceeding 99.95%, more than 1000 cycles to 80% capacity retention, and cell-level energy densities above 500 Wh kg⁻¹ define the final cell-level validation targets for practical LMBs.^{5,204}

Research frontiers and industrial requirements should therefore be considered jointly in the electrolyte design for practical LMBs. Requirement-based metrics can guide discovery and validation workflows, while multiscale descriptors quantify the electrolyte behavior during operation.

6. CONCLUSION

Electrolyte design remains central to the development of future LMBs, as the electrolyte governs Li⁺ transport, interphase formation, and electrochemical reversibility while being in contact with reductive and oxidative electrodes. Solvation control has established the Li⁺ solvation environment as a molecular handle for modulating interphase chemistry. However, the gap between reported performance and practical anode-free cell requirements shows that equilibrium first-sheath regulation provides an incomplete basis for durable operation under practical anode-free conditions. This limitation motivates the evaluation of solvation structures across length scales and under operating fields, as local coordination, mesoscopic organization, and interfacial solvation evolve during operation and modulate interphase chemistry.

Dynamic solvation networks provide an organizing concept for this expanded design space by connecting coordination motifs, aggregate structures, solvent/anion distributions, dielectric response, and coupled ion–solvent transport to the local availability of reactive species at electrode/electrolyte interfaces. This framework emphasizes controlled evolution of solvation environments under operating electric fields and concentration gradients, extending electrolyte design beyond equilibrium bulk configurations.

Looking forward, electrolyte research should move from formulation-level optimization toward predictive, automated, and requirement-aware designs of solvation architectures. AI/ML-guided screening, closed-loop experimentation, multimodal characterization, and multiscale modeling can quantify how solvation networks evolve during cycling and how this evolution affects interphase chemistry, transport, and degrada-

tion. Curated quantitative data sets and practical, requirement-based protocols should connect molecular descriptors, electrolyte structures, interfacial reactions, and cell-level outcomes. Research frontiers and industrial requirements should, therefore, be considered jointly in electrolyte design. Designing dynamic solvation networks that maintain favorable electrolyte environments under realistic cell operation constraints is central to translating liquid electrolyte concepts into practical LMBs.

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Author Contributions

W.-Y.K. conceived the framework, curated the literature, prepared the figures and tables, and wrote the original draft of the manuscript. K.H. contributed to literature curation and analysis. W.B. contributed to literature analysis. Y.S.M. supervised the work and revised the manuscript. All authors reviewed and approved the final manuscript.

Notes

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■ ACKNOWLEDGMENTS

This work at UChicago was supported by the Energy Transition Network (ETN) at the Institute for Climate and Sustainable Growth (ICSG).

■ REFERENCES

- (1) Chu, S.; Cui, Y.; Liu, N. The Path towards Sustainable Energy. *Nat. Mater.* **2017**, *16*, 16–22.
- (2) U.S. Department of Energy *Electrochemical Energy Storage Technical Team Roadmap*; 2017. <https://www.energy.gov/sites/default/files/2017/11/f39/EESTT-roadmap-2017-10-16-Final.pdf>.
- (3) Nitta, N.; Wu, F.; Lee, J. T.; Yushin, G. Li-Ion Battery Materials: Present and Future. *Mater. Today* **2015**, *18*, 252–264.
- (4) Zhang, J. G.; Xu, W.; Xiao, J.; Cao, X.; Liu, J. Lithium Metal Anodes with Nonaqueous Electrolytes. *Chem. Rev.* **2020**, *120*, 13312–13348.
- (5) Hobold, G. M.; Lopez, J.; Guo, R.; Minafra, N.; Banerjee, A.; Shirley Meng, Y.; Shao-Horn, Y.; Gallant, B. M. Moving beyond 99.9% Coulombic Efficiency for Lithium Anodes in Liquid Electrolytes. *Nat. Energy* **2021**, *6*, 951–960.
- (6) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104*, 4303–4417.
- (7) Xu, K. Interfaces and Interphases in Batteries. *J. Power Sources* **2023**, *559*, 232652.
- (8) Meng, Y. S.; Srinivasan, V.; Xu, K. Designing Better Electrolytes. *Science* **2022**, *378*, 1065.
- (9) Zhang, X. Q.; Chen, X.; Hou, L. P.; Li, B. Q.; Cheng, X. B.; Huang, J. Q.; Zhang, Q. Regulating Anions in the Solvation Sheath of Lithium Ions for Stable Lithium Metal Batteries. *ACS Energy Lett.* **2019**, *4*, 411–416.
- (10) Chen, X.; Zhang, Q. Atomic Insights into the Fundamental Interactions in Lithium Battery Electrolytes. *Acc. Chem. Res.* **2020**, *53*, 1992–2002.
- (11) Qian, J.; Henderson, W. A.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Borodin, O.; Zhang, J. G. High Rate and Stable Cycling of Lithium Metal Anode. *Nat. Commun.* **2015**, *6*, 6362.
- (12) Jiang, C.; Jia, Q.; Tang, M.; Fan, K.; Chen, Y.; Sun, M.; Xu, S.; Wu, Y.; Zhang, C.; Ma, J.; Wang, C.; Hu, W. Regulating the Solvation Sheath of Li Ions by Using Hydrogen Bonds for Highly Stable Lithium–Metal Anodes. *Angew. Chem., Int. Ed.* **2021**, *60*, 10871–10879.
- (13) Yan, K.; Lu, Z.; Lee, H. W.; Xiong, F.; Hsu, P. C.; Li, Y.; Zhao, J.; Chu, S.; Cui, Y. Selective Deposition and Stable Encapsulation of Lithium through Heterogeneous Seeded Growth. *Nat. Energy* **2016**, *1*, 16010.
- (14) Yu, Y.; Liu, Y.; Xie, J. Building Better Li Metal Anodes in Liquid Electrolyte: Challenges and Progress. *ACS Appl. Mater. Interfaces* **2021**, *13*, 18–33.
- (15) Koch, V. R.; Young, J. H. The Stability of the Secondary Lithium Electrode in Tetrahydrofuran-Based Electrolytes. *J. Electrochem. Soc.* **1978**, *125*, 1371.
- (16) Paled, E. The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems-The Solid Electrolyte Interphase Model. *J. Electrochem. Soc.* **1979**, *126*, 2047.
- (17) Selim, R.; Bro, P. Some Observations on Rechargeable Lithium Electrodes in a Propylene Carbonate Electrolyte. *J. Electrochem. Soc.* **1974**, *121*, 1457.
- (18) Liu, X.; Dong, X.; Wang, T.; Liu, L.; Cheng, X. B.; He, J.; Zhu, Z.; Eliseeva, S.; Wu, Y. Molecular Design of Ether-Based Electrolyte Solvents for High-Performance Lithium Batteries. *ACS Energy Lett.* **2026**, *11*, 1292–1322.
- (19) Xu, K. A Long Journey of Lithium: From the Big Bang to Our Smartphones. *Energy Environ. Mater.* **2019**, *2*, 229–233.
- (20) Amanchukwu, C. V.; Yu, Z.; Kong, X.; Qin, J.; Cui, Y.; Bao, Z. A New Class of Ionically Conducting Fluorinated Ether Electrolytes with High Electrochemical Stability. *J. Am. Chem. Soc.* **2020**, *142*, 7393–7403.
- (21) Ko, S.; Obukata, T.; Shimada, T.; Takenaka, N.; Nakayama, M.; Yamada, A.; Yamada, Y. Electrode Potential Influences the Reversibility of Lithium-Metal Anodes. *Nat. Energy* **2022**, *7*, 1217–1224.
- (22) Jiang, G.; Li, F.; Wang, H.; Wu, M.; Qi, S.; Liu, X.; Yang, S.; Ma, J. Perspective on High-Concentration Electrolytes for Lithium Metal Batteries. *Small Struct.* **2021**, *2*, 2000122.
- (23) Yamada, Y.; Wang, J.; Ko, S.; Watanabe, E.; Yamada, A. Advances and Issues in Developing Salt-Concentrated Battery Electrolytes. *Nat. Energy* **2019**, *4*, 269–280.
- (24) Cho, S. J.; Yu, D. E.; Pollard, T. P.; Moon, H.; Jang, M.; Borodin, O.; Lee, S. Y. Nonflammable Lithium Metal Full Cells with Ultra-High Energy Density Based on Coordinated Carbonate Electrolytes. *iScience* **2020**, *23*, 100844.
- (25) Fan, X.; Chen, L.; Ji, X.; Deng, T.; Hou, S.; Chen, J.; Zheng, J.; Wang, F.; Jiang, J.; Xu, K.; Wang, C. Highly Fluorinated Interphases Enable High-Voltage Li-Metal Batteries. *Chem* **2018**, *4*, 174–185.
- (26) Ko, S.; Han, X.; Shimada, T.; Takenaka, N.; Yamada, Y.; Yamada, A. Electrolyte Design for Lithium-Ion Batteries with a Cobalt-Free Cathode and Silicon Oxide Anode. *Nat. Sustainable* **2023**, *6*, 1705–1714.
- (27) Yamada, Y.; Yamada, A. Review—Superconcentrated Electrolytes for Lithium Batteries. *J. Electrochem. Soc.* **2015**, *162*, A2406–A2423.
- (28) Suo, L.; Hu, Y. S.; Li, H.; Armand, M.; Chen, L. A New Class of Solvent-in-Salt Electrolyte for High-Energy Rechargeable Metallic Lithium Batteries. *Nat. Commun.* **2013**, *4*, 1481.
- (29) Feng, N.; Chen, L.; Huang, T.; Gao, J.; Zeng, W.; Wei, H.; Liu, J.; Zhang, Q.; Xiao, B.; Hu, J. Low-Concentration Highly Aggregated Solvation Structure Design for Stabilizing Ni-Rich Single-Crystal Cathodes. *Adv. Funct. Mater.* **2026**, *36*, No. e75991.
- (30) Cao, X.; Gao, P.; Ren, X.; Zou, L.; Engelhard, M. H.; Matthews, B. E.; Hu, J.; Niu, C.; Liu, D.; Arey, B. W.; Wang, C.; Xiao, J.; Liu, J.; Xu, W.; Zhang, J.-G. Effects of Fluorinated Solvents on Electrolyte Solvation Structures and Electrode/Electrolyte Interphases for Lithium Metal Batteries. *Proc. Natl. Acad. Sci. U. S. A.* **2021**, *118* (9), No. e2020357118.
- (31) Ren, X.; Gao, P.; Zou, L.; Jiao, S.; Cao, X.; Zhang, X.; Jia, H.; Engelhard, M. H.; Matthews, B. E.; Wu, H.; Lee, H.; Niu, C.; Wang, C.; Arey, B. W.; Xiao, J.; Liu, J.; Zhang, J.-G.; Xu, W. Role of Inner Solvation Sheath within Salt–Solvent Complexes in Tailoring Electrode/Electrolyte Interphases for Lithium Metal Batteries. *Proc. Natl. Acad. Sci. U. S. A.* **2020**, *117* (46), 28603–28613.
- (32) Wu, Z.; Li, R.; Zhang, S.; Lv, L.; Deng, T.; Zhang, H.; Zhang, R.; Liu, J.; Ding, S.; Fan, L.; Chen, L.; Fan, X. Deciphering and Modulating Energetics of Solvation Structure Enables Aggressive High-Voltage Chemistry of Li Metal Batteries. *Chem* **2023**, *9*, 650–664.
- (33) Chen, S.; Zheng, J.; Mei, D.; Han, K. S.; Engelhard, M. H.; Zhao, W.; Xu, W.; Liu, J.; Zhang, J. G. High-Voltage Lithium-Metal Batteries Enabled by Localized High-Concentration Electrolytes. *Adv. Mater.* **2018**, *30*, 1706102.

- (34) Ren, X.; Zou, L.; Cao, X.; Engelhard, M. H.; Liu, W.; Burton, S. D.; Lee, H.; Niu, C.; Matthews, B. E.; Zhu, Z.; Wang, C.; Arey, B. W.; Xiao, J.; Liu, J.; Zhang, J. G.; Xu, W. Enabling High-Voltage Lithium-Metal Batteries under Practical Conditions. *Joule* **2019**, *3*, 1662–1676.
- (35) Moon, J.; Kim, D. O.; Bekaert, L.; Song, M.; Chung, J.; Lee, D.; Hubin, A.; Lim, J. Non-Fluorinated Non-Solvating Cosolvent Enabling Superior Performance of Lithium Metal Negative Electrode Battery. *Nat. Commun.* **2022**, *13*, 4538.
- (36) Zhang, C.; Gu, S.; Zhang, D.; Ma, J.; Zheng, H.; Zheng, M.; Lv, R.; Yu, K.; Wu, J.; Wang, X.; Yang, Q. H.; Kang, F.; Lv, W. N. Localized High-Concentration Electrolyte towards a High-Safety Lithium Metal Battery. *Energy Storage Mater.* **2022**, *S2*, 355–364.
- (37) Boyle, D. T.; Kim, S. C.; Oyakhire, S. T.; Vilá, R. A.; Huang, Z.; Sayavong, P.; Qin, J.; Bao, Z.; Cui, Y. Correlating Kinetics to Cyclability Reveals Thermodynamic Origin of Lithium Anode Morphology in Liquid Electrolytes. *J. Am. Chem. Soc.* **2022**, *144*, 20717–20725.
- (38) Kautz, D. J.; Cao, X.; Gao, P.; Matthews, B. E.; Xu, Y.; Han, K. S.; Omenya, F.; Engelhard, M. H.; Jia, H.; Wang, C.; Zhang, J. G.; Xu, W. Designing Electrolytes With Controlled Solvation Structure for Fast-Charging Lithium-Ion Batteries. *Adv. Energy Mater.* **2023**, *13*, 2301199.
- (39) Chen, Y.; Yu, Z.; Rudnicki, P.; Gong, H.; Huang, Z.; Kim, S. C.; Lai, J. C.; Kong, X.; Qin, J.; Cui, Y.; Bao, Z. Steric Effect Tuned Ion Solvation Enabling Stable Cycling of High-Voltage Lithium Metal Battery. *J. Am. Chem. Soc.* **2021**, *143*, 18703–18713.
- (40) Zhang, J.; Li, Q.; Zeng, Y.; Tang, Z.; Sun, D.; Huang, D.; Tang, Y.; Wang, H. Weakly Solvating Cyclic Ether Electrolyte for High-Voltage Lithium Metal Batteries. *ACS Energy Lett.* **2023**, *8*, 1752–1761.
- (41) Li, X.; Luo, F.; Zhou, N.; Adenusi, H.; Fang, S.; Wu, F.; Passerini, S. Weakly Solvating Electrolytes for Lithium and Post-Lithium Rechargeable Batteries: Progress and Outlook. *Adv. Energy Mater.* **2025**, *15*, 2501272.
- (42) Yao, Y. X.; Chen, X.; Yan, C.; Zhang, X. Q.; Cai, W. L.; Huang, J. Q.; Zhang, Q. Regulating Interfacial Chemistry in Lithium-Ion Batteries by a Weakly Solvating Electrolyte*. *Angew. Chem., Int. Ed.* **2021**, *60*, 4090–4097.
- (43) Wu, H.; Jia, H.; Wang, C.; Zhang, J.-G.; Xu, W. Recent Progress in Understanding Solid Electrolyte Interphase on Lithium Metal Anodes. *Adv. Energy Mater.* **2021**, *11*, 2003092.
- (44) Yang, W.; Chen, A.; He, P.; Zhou, H. Advancing Lithium Metal Electrode beyond 99.9% Coulombic Efficiency via Super-Saturated Electrolyte with Compressed Solvation Structure. *Nat. Commun.* **2025**, *16*, 4229.
- (45) Li, S.; Guo, Z.; Zhu, A.; Wang, Z.; He, Z.; Wang, Z.; Wu, Z.; Mei, L.; Chen, L. Entropy Driven Solvation Structure Stabilization for High-Voltage and Wide-Temperature Lithium Metal Batteries. *Energy Storage Mater.* **2026**, *88*, 105064.
- (46) Ni, Z.; Li, Y.; Wang, Z.; Liu, S.; Liu, J.; Yang, C.; Zhang, H.; Geng, J.; Zhang, C.; Xiong, S.; Xi, B.; Feng, J. Nonflammable F-Rich High-Entropy Electrolytes with Manipulated Solvent Coordination for Intrinsically Safe and High-Energy Lithium Metal Batteries. *Energy Storage Mater.* **2026**, *84*, 104885.
- (47) Xia, Y.; Zhu, D.; Hou, W.; Zhou, P.; Ou, Y.; Zhou, H.; Song, X.; Zhang, W.; Yan, S.; Lu, Y.; Ma, X.; Zeng, Y.; Xu, H.; Liu, K. Rational Lithium Salt Selection Principle for Designing High-Entropy Electrolytes toward High-Performance Lithium Metal Batteries. *J. Am. Chem. Soc.* **2026**, *148*, 3538–3550.
- (48) Wang, Q.; Zhao, C.; Wang, J.; Yao, Z.; Wang, S.; Kumar, S. G. H.; Ganapathy, S.; Eustace, S.; Bai, X.; Li, B.; Wagemaker, M. High Entropy Liquid Electrolytes for Lithium Batteries. *Nat. Commun.* **2023**, *14*, 440.
- (49) Zhao, X.; Fu, Z.; Zhang, X.; Wang, X.; Li, B.; Zhou, D.; Kang, F. More Is Better: High-Entropy Electrolyte Design in Rechargeable Batteries. *Energy Environ. Sci.* **2024**, *17*, 2406–2430.
- (50) Kim, S. C.; Wang, J.; Xu, R.; Zhang, P.; Chen, Y.; Huang, Z.; Yang, Y.; Yu, Z.; Oyakhire, S. T.; Zhang, W.; Greenburg, L. C.; Kim, M. S.; Boyle, D. T.; Sayavong, P.; Ye, Y.; Qin, J.; Bao, Z.; Cui, Y. High-Entropy Electrolytes for Practical Lithium Metal Batteries. *Nat. Energy* **2023**, *8* (8), 814–826.
- (51) Wang, Q.; Zhao, C.; Yao, Z.; Wang, J.; Wu, F.; Kumar, S. G. H.; Ganapathy, S.; Eustace, S.; Bai, X.; Li, B.; Lu, J.; Wagemaker, M. Entropy-Driven Liquid Electrolytes for Lithium Batteries. *Adv. Mater.* **2023**, *35*, 2210677.
- (52) Yang, J.; Liu, X.; Chen, H.; Wang, Z.; Cao, R.; Xie, Z.; Chen, W.; Liang, X.; Feng, J.; Ai, X.; Fang, Y.; Cao, Y. Organic Microemulsion Electrolytes for Advanced Metal Secondary Batteries. *Angew. Chem., Int. Ed.* **2025**, *64*, No. e202516637.
- (53) Zhu, Z.; Cui, H.; Li, Y.; Lu, G.; Li, B.; Sun, Y.; Pan, J.; Qie, L. Micelle-Like Electrolyte Design for 4.6 V LillNCM811 Cells Workable at 70 °C. *Adv. Mater.* **2026**, *38*, No. e13334.
- (54) Qiao, R.; Zhao, Y.; Zhou, S.; Zhang, H.; Liu, F.; Zhou, T.; Sun, B.; Fan, H.; Li, C.; Zhang, Y.; Liu, F.; Ding, X.; Wook Choi, J.; Coskun, A.; Song, J. Non-Fluorinated Electrolytes with Micelle-like Solvation for Ultra-High-Energy-Density Lithium Metal Batteries. *Chem* **2025**, *11*, 102306.
- (55) Wu, Q.; Qi, Y. Revealing Heterogeneous Electric Double Layer (EDL) Structures of Localized High-Concentration Electrolytes (LHCEs) and Their Impact on Solid-Electrolyte Interphase (SEI) Formation in Lithium Batteries. *Energy Environ. Sci.* **2025**, *18*, 3036–3046.
- (56) Ji, H.; Xiang, J.; Li, Y.; Zheng, M.; Yuan, L.; Liao, Y.; Du, L.; Li, Z.; Xie, Z.; Huang, K.; Lin, X.; Xie, Z.; Shen, Y.; Chen, M.; Li, T.; Feng, G.; Sun, Y.; Qie, L.; Li, H.; Zhang, F.; Guo, R.; Feng, X.; Chen, W.; Ai, X.; Lu, J.; Huang, Y. Liquid–Liquid Interfacial Tension Stabilized Li-Metal Batteries. *Nature* **2025**, *643* (8074), 1255–1262.
- (57) Efav, C. M.; Wu, Q.; Gao, N.; Zhang, Y.; Zhu, H.; Gering, K.; Hurley, M. F.; Xiong, H.; Hu, E.; Cao, X.; Xu, W.; Zhang, J. G.; Dufek, E. J.; Xiao, J.; Yang, X. Q.; Liu, J.; Qi, Y.; Li, B. Localized High-Concentration Electrolytes Get More Localized through Micelle-like Structures. *Nat. Mater.* **2023**, *22*, 1531–1539.
- (58) Kim, M.; Kim, J.; Baek, M.; Oh, J.; Lee, J.; Coskun, A.; Choi, J. W. Electrolyte Diluent with Large Electrostatic Potential Difference for Fast Charging and Slow Discharging Lithium Metal Batteries. *Nat. Commun.* **2026**, *17*, 3183.
- (59) Ruan, Q.; Wu, Y.; Wang, Y.; Cheng, H.; Lu, Y. Electrolyte-Centric Strategies for High-Energy-Density Lithium Metal Batteries. *EES Batteries* **2026**, *2*, 721–754.
- (60) Yu, Z.; Balsara, N. P.; Borodin, O.; Gewirth, A. A.; Hahn, N. T.; Maginn, E. J.; Persson, K. A.; Srinivasan, V.; Toney, M. F.; Xu, K.; Zavadil, K. R.; Curtiss, L. A.; Cheng, L. Beyond Local Solvation Structure: Nanometric Aggregates in Battery Electrolytes and Their Effect on Electrolyte Properties. *ACS Energy Lett.* **2022**, *7*, 461–470.
- (61) Jang, J.; Wang, C.; Kang, G.; Han, C.; Han, J.; Shin, J. S.; Ko, S.; Kim, G.; Baek, J.; Kim, H. T.; Lee, H.; Park, C. B.; Seo, D. H.; Li, Y.; Kang, J. Miniature Li⁺ Solvation by Symmetric Molecular Design for Practical and Safe Li-Metal Batteries. *Nat. Energy* **2025**, *10*, 502–512.
- (62) Jie, Y.; Wang, S.; Weng, S.; Liu, Y.; Yang, M.; Tang, C.; Li, X.; Zhang, Z.; Zhang, Y.; Chen, Y.; Huang, F.; Xu, Y.; Li, W.; Guo, Y.; He, Z.; Ren, X.; Lu, Y.; Yang, K.; Cao, S.; Lin, H.; Cao, R.; Yan, P.; Cheng, T.; Wang, X.; Jiao, S.; Xu, D. Towards Long-Life 500 Wh kg^{−1} Lithium Metal Pouch Cells via Compact Ion-Pair Aggregate Electrolytes. *Nat. Energy* **2024**, *9*, 987–998.
- (63) Ye, C.; Tu, S.; Zhang, S.-J.; Wang, C.; Qiao, S.-Z. Harnessing Interfacial Solvation Structure for Next-Generation Secondary Batteries. *Nat. Energy* **2026**, *11*, 167.
- (64) Wang, H.; Yu, Z.; Kong, X.; Kim, S. C.; Boyle, D. T.; Qin, J.; Bao, Z.; Cui, Y. Liquid Electrolyte: The Nexus of Practical Lithium Metal Batteries. *Joule* **2022**, *6*, 588–616.
- (65) Yu, Z.; Rudnicki, P. E.; Zhang, Z.; Huang, Z.; Celik, H.; Oyakhire, S. T.; Chen, Y.; Kong, X.; Kim, S. C.; Xiao, X.; Wang, H.; Zheng, Y.; Kamat, G. A.; Kim, M. S.; Bent, S. F.; Qin, J.; Cui, Y.; Bao, Z. Rational Solvent Molecule Tuning for High-Performance Lithium Metal Battery Electrolytes. *Nat. Energy* **2022**, *7*, 94–106.
- (66) Yu, Z.; Wang, H.; Kong, X.; Huang, W.; Tsao, Y.; Mackanic, D. G.; Wang, K.; Wang, X.; Huang, W.; Choudhury, S.; Zheng, Y.;

- Amanchukwu, C. V.; Hung, S. T.; Ma, Y.; Lomeli, E. G.; Qin, J.; Cui, Y.; Bao, Z. Molecular Design for Electrolyte Solvents Enabling Energy-Dense and Long-Cycling Lithium Metal Batteries. *Nat. Energy* **2020**, *5*, 526–533.
- (67) Zhao, Y.; Zhou, T.; Ashirov, T.; Kazzi, M. E.; Cancellieri, C.; Jeurgens, L. P. H.; Choi, J. W.; Coskun, A. Fluorinated Ether Electrolyte with Controlled Solvation Structure for High Voltage Lithium Metal Batteries. *Nat. Commun.* **2022**, *13*, 2575.
- (68) Ma, B.; Zhang, H.; Li, R.; Zhang, S.; Chen, L.; Zhou, T.; Wang, J.; Zhang, R.; Ding, S.; Xiao, X.; Deng, T.; Chen, L.; Fan, X. Molecular-Docking Electrolytes Enable High-Voltage Lithium Battery Chemistries. *Nat. Chem.* **2024**, *16*, 1427–1435.
- (69) Cui, Z.; Jia, Z.; Ruan, D.; Nian, Q.; Fan, J.; Chen, S.; He, Z.; Wang, D.; Jiang, J.; Ma, J.; Ou, X.; Jiao, S.; Wang, Q.; Ren, X. Molecular Anchoring of Free Solvents for High-Voltage and High-Safety Lithium Metal Batteries. *Nat. Commun.* **2024**, *15*, 2033.
- (70) Von Wald Cresce, A.; Gobet, M.; Borodin, O.; Peng, J.; Russell, S. M.; Wikner, E.; Fu, A.; Hu, L.; Lee, H. S.; Zhang, Z.; Yang, X. Q.; Greenbaum, S.; Amine, K.; Xu, K. Anion Solvation in Carbonate-Based Electrolytes. *J. Phys. Chem. C* **2015**, *119*, 27255–27264.
- (71) Younesi, R.; Veith, G. M.; Johansson, P.; Edström, K.; Vegge, T. Lithium Salts for Advanced Lithium Batteries: Li-Metal, Li-O₂, and Li-S. *Energy Environ. Sci.* **2015**, *8*, 1905–1922.
- (72) Zhou, P.; Xiang, Y.; Liu, K. Understanding and Applying the Donor Number of Electrolytes in Lithium Metal Batteries. *Energy Environ. Sci.* **2024**, *17*, 8057–8077.
- (73) Wang, X.; Song, Z.; Wu, H.; Yu, H.; Feng, W.; Armand, M.; Huang, X.; Zhou, Z.; Zhang, H. Anion Donicity of Liquid Electrolytes for Lithium Carbon Fluoride Batteries. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202211623.
- (74) Wang, Z.; Qi, F.; Yin, L.; Shi, Y.; Sun, C.; An, B.; Cheng, H.-M.; Li, F. An Anion-Tuned Solid Electrolyte Interphase with Fast Ion Transfer Kinetics for Stable Lithium Anodes. *Adv. Energy Mater.* **2020**, *10*, 1903843.
- (75) Liu, Z.; Yan, S.; Lu, Y.; Feng, Q.; Ma, X.; Zhou, P.; Hou, W.; Ou, Y.; Wu, Y.; Li, C.; Feng, J.; Cao, Q.; Peng, X.; Xia, Y.; Song, X.; Zhou, H.; Liu, H.; Liu, K. Non-Corrosive Asymmetric Fluorinated Aryl Sulfonimide Lithium Salt for High-Temperature and High-Voltage Lithium Metal Batteries. *Nat. Commun.* **2025**, *16*, 9721.
- (76) Xia, Y.; Zhou, P.; Kong, X.; Tian, J.; Zhang, W.; Yan, S.; Hou, W. H.; Zhou, H. Y.; Dong, H.; Chen, X.; Wang, P.; Xu, Z.; Wan, L.; Wang, B.; Liu, K. Designing an Asymmetric Ether-like Lithium Salt to Enable Fast-Cycling High-Energy Lithium Metal Batteries. *Nat. Energy* **2023**, *8*, 934–945.
- (77) Qiao, L.; Oteo, U.; Martinez-Ibañez, M.; Santiago, A.; Cid, R.; Sanchez-Diez, E.; Lobato, E.; Meabe, L.; Armand, M.; Zhang, H. Stable Non-Corrosive Sulfonimide Salt for 4-V-Class Lithium Metal Batteries. *Nat. Mater.* **2022**, *21*, 455–462.
- (78) Kwon, H.; Kim, H.; Hwang, J.; Oh, W.; Roh, Y.; Shin, D.; Kim, H. T. Borate–Pyran Lean Electrolyte-Based Li-Metal Batteries with Minimal Li Corrosion. *Nat. Energy* **2024**, *9*, 57–69.
- (79) Kwon, H.; Kim, S.; Hyun, J.; Lee, H. E.; Kim, S. S.; Kim, Y.; Kim, I. J.; Shin, K.; Kim, S.; Park, C.; Kim, H.; Shin, D.; Kim, H. T. Covariance of Interphasic Properties and Fast Chargeability of Energy-Dense Lithium Metal Batteries. *Nat. Energy* **2025**, *10*, 1132–1145.
- (80) Gale, P. A.; Howe, E. N. W.; Wu, X. Anion Receptor Chemistry. *Chem* **2016**, *1*, 351–422.
- (81) Prakash Reddy, V.; Blanco, M.; Bugga, R. Boron-Based Anion Receptors in Lithium-Ion and Metal-Air Batteries. *J. Power Sources* **2014**, *247*, 813–820.
- (82) Qiao, B.; Leverick, G. M.; Zhao, W.; Flood, A. H.; Johnson, J. A.; Shao-Horn, Y. Supramolecular Regulation of Anions Enhances Conductivity and Transference Number of Lithium in Liquid Electrolytes. *J. Am. Chem. Soc.* **2018**, *140*, 10932–10936.
- (83) Holoubek, J.; Liu, H.; Wu, Z.; Yin, Y.; Xing, X.; Cai, G.; Yu, S.; Zhou, H.; Pascal, T. A.; Chen, Z.; Liu, P. Tailoring Electrolyte Solvation for Li Metal Batteries Cycled at Ultra-Low Temperature. *Nat. Energy* **2021**, *6*, 303–313.
- (84) Luo, H.; Ji, X.; Zhang, B.; Chen, M.; Wu, X.; Zhu, Y.; Yu, X.; Wang, J.; Zhang, H.; Hong, Y.; Zou, Y.; Feng, G.; Qiao, Y.; Zhou, H.; Sun, S. G. Revealing the Dynamic Evolution of Electrolyte Configuration on the Cathode-Electrolyte Interface by Visualizing (De) Solvation Processes. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202412214.
- (85) Zhang, S.; Li, R.; Deng, T.; Ma, Q.; Hong, X.; Zhang, H.; Zhang, R.; Ding, S.; Wu, Y.; Zhu, H.; Li, M.; Zhang, H.; Lu, D.; Ma, B.; Lv, L.; Li, Y.; Chen, L.; Shen, Y.; Guo, R.; Fan, X. Oscillatory Solvation Chemistry for a 500 Wh kg^{−1} Li-Metal Pouch Cell. *Nat. Energy* **2024**, *9*, 1285–1296.
- (86) Zhao, C.-X.; Wang, Z.; Jacobson, D.; Li, Y.; Khaykovich, B.; Fayfar, S.; Zheng, L.; LaManna, J.; Chen, X.; Hussey, D. S.; Chen, F.; Veith, G. M.; Wang, C. Electrolytes That Reduce Electro-Osmotic Drag Improve Fast Charging of Lithium-Ion Batteries. *Science* **2025**, *390*, 745–750.
- (87) Rodriguez, R.; Loeffler, K. E.; Edison, R. A.; Stephens, R. M.; Dolocan, A.; Heller, A.; Mullins, C. B. Effect of the Electrolyte on the Cycling Efficiency of Lithium-Limited Cells and Their Morphology Studied Through in Situ Optical Imaging. *ACS Appl. Energy Mater.* **2018**, *1*, 5830–5835.
- (88) Hagos, T. M.; Berhe, G. B.; Hagos, T. T.; Bezabh, H. K.; Abbrha, L. H.; Beyene, T. T.; Huang, C. J.; Yang, Y. W.; Su, W. N.; Dai, H.; Hwang, B. J. Dual Electrolyte Additives of Potassium Hexafluorophosphate and Tris (Trimethylsilyl) Phosphite for Anode-Free Lithium Metal Batteries. *Electrochim. Acta* **2019**, *316*, 52–59.
- (89) Huang, C. J.; Thirumalraj, B.; Tao, H. C.; Shitaw, K. N.; Sutiono, H.; Hagos, T. T.; Beyene, T. T.; Kuo, L. M.; Wang, C. C.; Wu, S. H.; Su, W. N.; Hwang, B. J. Decoupling the Origins of Irreversible Coulombic Efficiency in Anode-Free Lithium Metal Batteries. *Nat. Commun.* **2021**, *12*, 1452.
- (90) Brown, Z. L.; Heiskanen, S.; Lucht, B. L. Using Triethyl Phosphate to Increase the Solubility of LiNO₃ in Carbonate Electrolytes for Improving the Performance of the Lithium Metal Anode. *J. Electrochem. Soc.* **2019**, *166* (12), A2523–A2527.
- (91) Nilsson, V.; Kotronia, A.; Lacey, M.; Edström, K.; Johansson, P. Highly Concentrated LiTFSI-EC Electrolytes for Lithium Metal Batteries. *ACS Appl. Energy Mater.* **2020**, *3*, 200–207.
- (92) Sahalie, N. A.; Assegie, A. A.; Su, W. N.; Wondimkun, Z. T.; Jote, B. A.; Thirumalraj, B.; Huang, C. J.; Yang, Y. W.; Hwang, B. J. Effect of Bifunctional Additive Potassium Nitrate on Performance of Anode Free Lithium Metal Battery in Carbonate Electrolyte. *J. Power Sources* **2019**, *437*, 226912.
- (93) Hagos, T. T.; Thirumalraj, B.; Huang, C. J.; Abbrha, L. H.; Hagos, T. M.; Berhe, G. B.; Bezabh, H. K.; Cherng, J.; Chiu, S. F.; Su, W. N.; Hwang, B. J. Locally Concentrated LiPF₆ in a Carbonate-Based Electrolyte with Fluoroethylene Carbonate as a Diluent for Anode-Free Lithium Metal Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 9955–9963.
- (94) Alvarado, J.; Schroeder, M. A.; Pollard, T. P.; Wang, X.; Lee, J. Z.; Zhang, M.; Wynn, T.; Ding, M.; Borodin, O.; Meng, Y. S.; Xu, K. Bisalt Ether Electrolytes: A Pathway towards Lithium Metal Batteries with Ni-Rich Cathodes. *Energy Environ. Sci.* **2019**, *12* (2), 780–794.
- (95) Xue, W.; Shi, Z.; Huang, M.; Feng, S.; Wang, C.; Wang, F.; Lopez, J.; Qiao, B.; Xu, G.; Zhang, W.; Dong, Y.; Gao, R.; Shao-Horn, Y.; Johnson, J. A.; Li, J. FSI-Inspired Solvent and “Full Fluorosulfonyl” Electrolyte for 4 v Class Lithium-Metal Batteries. *Energy Environ. Sci.* **2020**, *13* (1), 212–220.
- (96) Beyene, T. T.; Bezabh, H. K.; Weret, M. A.; Hagos, T. M.; Huang, C.-J.; Wang, C.-H.; Su, W.-N.; Dai, H.; Hwang, B.-J. Concentrated Dual-Salt Electrolyte to Stabilize Li Metal and Increase Cycle Life of Anode Free Li-Metal Batteries. *J. Electrochem. Soc.* **2019**, *166* (8), A1501–A1509.
- (97) Beyene, T. T.; Jote, B. A.; Wondimkun, Z. T.; Olbassa, B. W.; Huang, C. J.; Thirumalraj, B.; Wang, C. H.; Su, W. N.; Dai, H.; Hwang, B. J. Effects of Concentrated Salt and Resting Protocol on Solid Electrolyte Interface Formation for Improved Cycle Stability of Anode-Free Lithium Metal Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 31962–31971.

- (98) Su, L.; Charalambous, H.; Cui, Z.; Manthiram, A. H.-E. Anode-Free Lithium-Metal Batteries with a Close-Packed Homogeneous Lithium Morphology. *Energy Environ. Sci.* **2022**, *15* (2), 843–854.
- (99) Qian, J.; Adams, B. D.; Zheng, J.; Xu, W.; Henderson, W. A.; Wang, J.; Bowden, M. E.; Xu, S.; Hu, J.; Zhang, J.-G. Anode-Free Rechargeable Lithium Metal Batteries. *Adv. Funct. Mater.* **2016**, *26* (39), 7094–7102.
- (100) Rodriguez, R.; Edison, R. A.; Stephens, R. M.; Sun, H. H.; Heller, A.; Mullins, C. B. Separator-Free and Concentrated LiNO₃ Electrolyte Cells Enable Uniform Lithium Electrodeposition. *J. Mater. Chem. A* **2020**, *8* (7), 3999–4006.
- (101) Weber, R.; Genovese, M.; Louli, A. J.; Hames, S.; Martin, C.; Hill, I. G.; Dahn, J. R. Long Cycle Life and Dendrite-Free Lithium Morphology in Anode-Free Lithium Pouch Cells Enabled by a Dual-Salt Liquid Electrolyte. *Nat. Energy* **2019**, *4*, 683–689.
- (102) Lee, J. A.; Kang, H.; Kim, S.; Lee, K.; Byun, J. H.; Kwon, E.; Seo, S.; Kwak, K.; Ryu, K. H.; Choi, N. S. Unveiling Degradation Mechanisms of Anode-Free Li-Metal Batteries. *Energy Storage Mater.* **2024**, *73*, 103826.
- (103) Mao, M.; Ji, X.; Wang, Q.; Lin, Z.; Li, M.; Liu, T.; Wang, C.; Hu, Y. S.; Li, H.; Huang, X.; Chen, L.; Suo, L. Anion-Enrichment Interface Enables High-Voltage Anode-Free Lithium Metal Batteries. *Nat. Commun.* **2023**, *14*, 1082.
- (104) Lin, L.; Qin, K.; Hu, Y. S.; Li, H.; Huang, X.; Suo, L.; Chen, L. A Better Choice to Achieve High Volumetric Energy Density: Anode-Free Lithium-Metal Batteries. *Adv. Mater.* **2022**, *34*, 2110323.
- (105) Kim, J. H.; Kim, N. Y.; Ju, Z.; Hong, Y. K.; Kang, K. D.; Pang, J. H.; Lee, S. J.; Chae, S. S.; Park, M. S.; Kim, J. Y.; Yu, G.; Lee, S. Y. Upscaling High-Areal-Capacity Battery Electrodes. *Nat. Energy* **2025**, *10*, 295–307.
- (106) Feng, G.; Shi, Y.; Jia, H.; Risal, S.; Yang, X.; Ruchhoeft, P.; Shih, W.-C.; Fan, Z.; Xu, W.; Shan, X. Progressive and Instantaneous Nature of Lithium Nucleation Discovered by Dynamic and Operando Imaging. *Sci. Adv.* **2023**, *9* (21), No. eadg6813.
- (107) Liu, Y.; Zhu, Y.; Cui, Y. Challenges and Opportunities towards Fast-Charging Battery Materials. *Nat. Energy* **2019**, *4*, 540–550.
- (108) Xiao, H.; Li, X.; Fu, Y. Advances in Anion Chemistry in the Electrolyte Design for Better Lithium Batteries. *Nanomicro Lett.* **2025**, *17*, 149.
- (109) Krossing, I.; Raabe, I. Noncoordinating Anions - Fact or Fiction? A Survey of Likely Candidates. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066–2090.
- (110) Li, M.; Wang, C.; Chen, Z.; Xu, K.; Lu, J. New Concepts in Electrolytes. *Chem. Rev.* **2020**, *120*, 6783–6819.
- (111) Chen, H.; Wu, T.; Zhang, J.; Fan, X.; Ju, W.; Chen, J.; Zhu, L.; Nan, H.; Ni, S.; Li, P.; Kong, L. Anion Coordination Strength Mediated Aluminum Corrosion for High-Voltage Lithium-Metal Batteries. *Particuology* **2026**, *111*, 50–57.
- (112) Shen, Y.; Rui, H.; Fang, W.; Liu, L.; Yuan, X.; Gao, X.; Ozoemena, K. I.; Wu, Y. Interfacial Chemistry in High-Voltage Ni–Mn-Based Cathodes: Understanding and Controlling Degradation Pathways. *Chem. – Eur. J.* **2026**, *32* (31), No. e71086.
- (113) Lee, U. H.; Kang, J. Dielectric Constant Guided Solvation Structure Design for Stable Solid Electrolyte Interphase in Lithium Metal Batteries. *Small Struct.* **2026**, *7*, No. e202500760.
- (114) Karbak, M.; Yim, K.; Meng, Y. S.; Shao, Y.; Xu, W. Weakly Solvating Electrolytes: A Solvation-Centric Paradigm for Rechargeable Metal Batteries. *Chem. Sci.* **2025**, *16*, 20694–20717.
- (115) Zhou, J.; Wang, H.; Yang, Y.; Li, X.; Guo, C.; Li, Z.; Wen, S.; Cai, J.; Wang, Z.; Zhang, Y.; Huang, Q.; Zheng, Z. Advanced Liquid Electrolyte Design for High-Voltage and High-Safety Lithium Metal Batteries. *Adv. Energy Mater.* **2025**, *15*, 2502654.
- (116) Gao, Y. C.; Yao, N.; Chen, X.; Yu, L.; Zhang, R.; Zhang, Q. Data-Driven Insight into the Reductive Stability of Ion-Solvent Complexes in Lithium Battery Electrolytes. *J. Am. Chem. Soc.* **2023**, *145*, 23764–23770.
- (117) Zheng, X.; Huang, L.; Luo, W.; Wang, H.; Dai, Y.; Liu, X.; Wang, Z.; Zheng, H.; Huang, Y. Tailoring Electrolyte Solvation Chemistry toward an Inorganic-Rich Solid-Electrolyte Interphase at a Li Metal Anode. *ACS Energy Lett.* **2021**, *6*, 2054–2063.
- (118) Dong, Y.; Zhang, N.; Li, C.; Zhang, Y.; Jia, M.; Wang, Y.; Zhao, Y.; Jiao, L.; Cheng, F.; Xu, J. Fire-Retardant Phosphate-Based Electrolytes for High-Performance Lithium Metal Batteries. *ACS Appl. Energy Mater.* **2019**, *2*, 2708–2716.
- (119) Cao, X.; Jia, H.; Xu, W.; Zhang, J.-G. Review—Localized High-Concentration Electrolytes for Lithium Batteries. *J. Electrochem. Soc.* **2021**, *168*, 010522.
- (120) Reichardt, C. Solvatochromic Dyes as Solvent Polarity Indicators. *Chem. Rev.* **1994**, *94*, 2319–2358.
- (121) Li, R.; Zhang, H.; Zhang, S.; Li, Y.; Guo, R.; Pei, H.; Yang, M.; Zhang, J.; Chen, L.; Xiao, X.; Chen, L.; Shen, Y.; Deng, T.; Fan, X. Unified Affinity Paradigm for the Rational Design of High-Efficiency Lithium Metal Electrolytes. *Nat. Energy* **2025**, *10*, 1155–1165.
- (122) Su, C. C.; He, M.; Amine, R.; Rojas, T.; Cheng, L.; Ngo, A. T.; Amine, K. Solvating Power Series of Electrolyte Solvents for Lithium Batteries. *Energy Environ. Sci.* **2019**, *12*, 1249–1254.
- (123) Burton, T. F.; Gómez Urbano, J. L.; Zhu, Y.; Balducci, A.; Fontaine, O. The Urgent Electrolyte Sustainability Challenges for Electric Vehicle Batteries. *Nat. Commun.* **2025**, *16*, 5957.
- (124) Li, Y.; Zhao, Q.; Xing, Y.; Wang, H.; Yan, Y.; Li, B.; Gu, Q.; Hu, H.; Zhou, L.; Chen, M. Multiscale Simulation for Electrolyte Design: From Microstructure-Property Decoding to Macroscopic Performance Prediction. *Energy Storage Mater.* **2026**, *86*, 104927.
- (125) Yao, N.; Chen, X.; Fu, Z. H.; Zhang, Q. Applying Classical, Ab Initio, and Machine-Learning Molecular Dynamics Simulations to the Liquid Electrolyte for Rechargeable Batteries. *Chem. Rev.* **2022**, *122*, 10970–11021.
- (126) Morita, M.; Asai, Y.; Yoshimoto, N.; Ishikawa, M. A Raman Spectroscopic Study of Organic Electrolyte Solutions Based on Binary Solvent Systems of Ethylene Carbonate with Low Viscosity Solvents Which Dissolve Different Lithium Salts. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3451–3456.
- (127) Fan, Z.; Zhang, J.; Wu, L.; Yu, H.; Li, J.; Li, K.; Zhao, Q. Solvation Structure Dependent Ion Transport and Desolvation Mechanism for Fast-Charging Li-Ion Batteries. *Chem. Sci.* **2024**, *15*, 17161–17172.
- (128) Yu, H.; Xin, X.; Ge, J.; Luo, Y.; Cui, Y.; Zang, X. F.; Xu, T.; Zheng, T.; Mandic, Z.; Xia, Y.; Zhou, M. Bifunctional Ligand-Bridged Electrolyte Enables High-Capacity and High-Energy 600 Wh kg^{−1} Lithium-Metal Battery Pouch Cells. *Nat. Commun.* **2026**, *17*, 5046.
- (129) Meyer, L.; Brow, R.; Weddle, P. J.; Gering, K.; Dufek, E. J.; Colclasure, A. M.; Porter, J. Operando FTIR Investigation of Salt Dynamics in Li-Ion Batteries during Fast Charging. *J. Power Sources* **2025**, *656*, 238058.
- (130) Svirinovsky-Arbeli, A.; Juelscholt, M.; May, R.; Kwon, Y.; Marbella, L. E. Using NMR Spectroscopy to Link Structure to Function at the Li Solid Electrolyte Interphase. *Joule* **2024**, *8*, 1919–1935.
- (131) Gerig, J. T. *Chapter 2 NOE Studies of Solvent-Solute Interactions*; Academic Press Inc., 2008; Vol. 64. DOI:
- (132) Zhu, Y.; Alshareef, H. N. NMR for Liquid Battery Electrolytes: Structure, Motion, and Heterogeneity. *eSci. Energy* **2026**, *2*, 100077.
- (133) Su, C. C.; He, M.; Amine, R.; Chen, Z.; Amine, K. Internally Referenced DOSY-NMR: A Novel Analytical Method in Revealing the Solution Structure of Lithium-Ion Battery Electrolytes. *J. Phys. Chem. Lett.* **2018**, *9*, 3714–3719.
- (134) Liu, X.; Fang, L.; Lyu, X.; Winans, R. E.; Li, T. Unveiling the Liquid Electrolyte Solvation Structure by Small Angle X-Ray Scattering. *Chem. Mater.* **2023**, *35*, 9821–9832.
- (135) Qian, K.; Winans, R. E.; Li, T. Insights into the Nanostructure, Solvation, and Dynamics of Liquid Electrolytes through Small-Angle X-Ray Scattering. *Adv. Energy Mater.* **2021**, *11*, 2002821.
- (136) Wang, Y.; Wang, T.; Bu, S.; Zhu, J.; Wang, Y.; Zhang, R.; Hong, H.; Zhang, W.; Fan, J.; Zhi, C. Sulfonate-Containing Aqueous Electrolyte Solutions for Producing Efficient Ampere-Hour-Level Zinc Metal Battery Pouch Cells. *Nat. Commun.* **2023**, *14*, 1828.

- (137) Zhang, C.; Xu, X.; Chen, Z.; Li, Q.; Zhong, Y.; Wang, X.; Tu, J.; Gu, C. Localized Water Confinement via Micellar Electrolyte for Aqueous Zinc-Vanadium Batteries. *Adv. Mater.* **2026**, *38*, No. e10792.
- (138) Zhang, L.; Liu, H.; Wang, T.; Wang, H.; Yan, D.; Li, M.; Ren, X.; Li, H.; Wang, L. Solvation Structure Modulation via Dipole-Dipole Interactions for High-Rate Lithium Metal Batteries Exceeding 400 Wh kg⁻¹. *Chem. Sci.* **2025**, *16*, 13774–13783.
- (139) Rakov, D. A.; Chen, F.; Ferdousi, S. A.; Li, H.; Pathirana, T.; Simonov, A. N.; Howlett, P. C.; Atkin, R.; Forsyth, M. Engineering High-Energy-Density Sodium Battery Anodes for Improved Cycling with Superconcentrated Ionic-Liquid Electrolytes. *Nat. Mater.* **2020**, *19*, 1096–1101.
- (140) Bonagiri, L. K. S.; Panse, K. S.; Zhou, S.; Wu, H.; Aluru, N. R.; Zhang, Y. Real-Space Charge Density Profiling of Electrode-Electrolyte Interfaces with Angstrom Depth Resolution. *ACS Nano* **2022**, *16*, 19594–19604.
- (141) Xie, Y.; Wang, J.; Savitzky, B. H.; Chen, Z.; Wang, Y.; Betzler, S.; Bustillo, K.; Persson, K.; Cui, Y.; Wang, L.-W.; Ophus, C.; Ercius, P.; Zheng, H. Spatially Resolved Structural Order in Low-Temperature Liquid Electrolyte. *Sci. Adv.* **2023**, *9* (2), No. eadc9721.
- (142) Shi, Z.; Chen, S.; Zan, M.; Zhang, L.; Gong, J.; Zhou, Y.; Müllen, K.; Lai, F.; Liu, T. Surfactant-Mediated Mesoscopic Confinement and Selective Interfacial Shielding for Highly Stable Zinc Anode. *Energy Environ. Sci.* **2026**, *19*, 1385.
- (143) Yang, G.; Ivanov, I. N.; Ruther, R. E.; Sacchi, R. L.; Subjakova, V.; Hallinan, D. T.; Nanda, J. Electrolyte Solvation Structure at Solid-Liquid Interface Probed by Nanogap Surface-Enhanced Raman Spectroscopy. *ACS Nano* **2018**, *12*, 10159–10170.
- (144) Wang, J.; Zhang, J.; Cheng, X.; Zhang, Y.; Li, H.; Guan, Q.; Wu, F.; Li, H.; Wang, D.; Liu, M.; Zhang, Y.; Xiao, Q.; Passerini, S.; Lin, H. Electrode/Electrolyte Interface Studies of Rechargeable Li Batteries with Interface-Specific Sum Frequency Generation Spectroscopy. *J. Am. Chem. Soc.* **2025**, *147*, 44633–44651.
- (145) Single, F.; Horstmann, B.; Latz, A. Theory of Impedance Spectroscopy for Lithium Batteries. *J. Phys. Chem. C* **2019**, *123*, 27327–27343.
- (146) Shibuya, K.; Gossage, Z. T.; Komaba, S. Fast Sodium Ion Tracking at the Battery Electrode Interface During Cycling in Concentrated Aqueous Electrolytes. *ChemElectroChem* **2026**, *13*, No. e70209.
- (147) Zhang, Y.; Li, S.; Wu, M.; Wang, L.; He, N.; Quan, Y.; Wang, P.; Zhao, D.; Cui, X. Construct Favorable Solid Electrolyte Interphase by Applying Alternating Current Discharge during Battery Formation. *Chem. Eng. J.* **2025**, *510*, 161738.
- (148) Seo, J. Y.; Kim, S.; Kim, J. H.; Lee, Y. H.; Shin, J. Y.; Jeong, S.; Sung, D. W.; Lee, Y. M.; Lee, S. Y. Mechanical Shutdown of Battery Separators: Silicon Anode Failure. *Nat. Commun.* **2024**, *15*, 10134.
- (149) Born, M. Volumen Und Hydratationswärme Der Ionen. *Z. Phys.* **1920**, *1* (1), 45–48.
- (150) Adar, R. M.; Markovich, T.; Andelman, D. Bjerrum Pairs in Ionic Solutions: A Poisson-Boltzmann Approach. *J. Chem. Phys.* **2017**, *146*, 194904.
- (151) Lee, A. A.; Perez-Martinez, C. S.; Smith, A. M.; Perkin, S. Scaling Analysis of the Screening Length in Concentrated Electrolytes. *Phys. Rev. Lett.* **2017**, *119*, 026002.
- (152) Fuoss, R. M. Ionic Association. III. The Equilibrium between Ion Pairs and Free Ions. *J. Chem. Phys.* **1958**, *80*, 5059–5061.
- (153) Che, L.; Hu, Z.; Zhang, T.; Dai, P.; Chen, C.; Shen, C.; Huang, H.; Jiao, L.; Jin, T.; Xie, K. Regulating the Interfacial Chemistry of Graphite in Ethyl Acetate-Based Electrolyte for Low-Temperature Li-Ion Batteries. *Battery Energy* **2024**, *3*, 20230064.
- (154) Holoubek, J.; Baskin, A.; Lawson, J. W.; Khemchandani, H.; Pascal, T. A.; Liu, P.; Chen, Z. Predicting the Ion Desolvation Pathway of Lithium Electrolytes and Their Dependence on Chemistry and Temperature. *J. Phys. Chem. Lett.* **2022**, *13*, 4426–4433.
- (155) Eyring, H. The Activated Complex in Chemical Reactions. *J. Chem. Phys.* **1935**, *3*, 107–115.
- (156) Lewis, G. N.; Randall, M. The Activity Coefficient of Strong Electrolytes. I. *J. Am. Chem. Soc.* **1921**, *43*, 1112–1154.
- (157) Debye, P.; Hückel, E. Zur Theorie Der Elektrolyte. I. Gefrierpunktserniedrigung Und Verwandte Erscheinungen. *Phys. Z.* **1923**, *24*, 185–206.
- (158) Ellingsen, L.; Haug-Warberg, T. The Statistics of the Debye-Hückel Limiting Law. *AIP Adv.* **2022**, *12*, 115001.
- (159) Seshadri, A.; Hess, L. T. M.; Yue, S. Exploring the Deviation from Nernst–Einstein Conductivity in Ionic Liquids Using Machine Learning. *Digital Discovery* **2026**, *5*, 1709–1717.
- (160) Kilic, M. S.; Bazant, M. Z.; Ajdari, A. Steric Effects in the Dynamics of Electrolytes at Large Applied Voltages. I. Double-Layer Charging. *Phys. Rev. E: Stat., Nonlin Soft Matter Phys.* **2007**, *75*, 021502.
- (161) Zugmann, S.; Fleischmann, M.; Amereller, M.; Gschwind, R. M.; Wiemhöfer, H. D.; Gores, H. J. Measurement of Transference Numbers for Lithium Ion Electrolytes via Four Different Methods, a Comparative Study. *Electrochim. Acta* **2011**, *56*, 3926–3933.
- (162) Fang, C.; Mistry, A.; Srinivasan, V.; Balsara, N. P.; Wang, R. Elucidating the Molecular Origins of the Transference Number in Battery Electrolytes Using Computer Simulations. *JACS Au* **2023**, *3*, 306–315.
- (163) Schreiner, C.; Zugmann, S.; Hartl, R.; Gores, H. J. Fractional Walden Rule for Ionic Liquids: Examples from Recent Measurements and a Critique of the so-Called Ideal KCl Line for the Walden Plot. *J. Chem. Eng. Data* **2010**, *55*, 1784–1788.
- (164) Zhang, X.; Yang, Y.; Zhou, Z. Towards Practical Lithium-Metal Anodes. *Chem. Soc. Rev.* **2020**, *49*, 3040–3071.
- (165) Frith, J. T.; Lacey, M. J.; Ulissi, U. A Non-Academic Perspective on the Future of Lithium-Based Batteries. *Nat. Commun.* **2023**, *14*, 420.
- (166) Liu, S.; Dong, D.; Xiao, Z.; Bedrov, D.; Xu, K.; Xing, L.; Li, W. Machine Learning in Electrolyte Design: Accelerating Discovery and Multidimensional Optimization for next-Generation Batteries. *Chem* **2026**, *12* (7), 103024.
- (167) Kim, S. C.; Oyakhire, S. T.; Athanitis, C.; Wang, J.; Zhang, Z.; Zhang, W.; Boyle, D. T.; Kim, M. S.; Yu, Z.; Gao, X.; Sogade, T.; Wu, E.; Qin, J.; Bao, Z.; Bent, S. F.; Cui, Y. Data-Driven Electrolyte Design for Lithium Metal Anodes. *Proc. Natl. Acad. Sci. U. S. A.* **2023**, *120*, No. e2214357120.
- (168) Sharma, V.; Giammona, M.; Zubarev, D.; Tek, A.; Nuguyen, K.; Sundberg, L.; Congiu, D.; La, Y. H. Formulation Graphs for Mapping Structure-Composition of Battery Electrolytes to Device Performance. *J. Chem. Inf. Model.* **2023**, *63*, 6998–7010.
- (169) Ma, P.; Kumar, R.; Wang, K. H.; Amanchukwu, C. V. Active Learning Accelerates Electrolyte Solvent Screening for Anode-Free Lithium Metal Batteries. *Nat. Commun.* **2025**, *16*, 8396.
- (170) Ono, M.; Takahashi, M.; Tamura, R.; Matsuda, S. Unveiling Electrolyte Design Principles for Sodium-Ion Batteries Using Combinatorial Electrochemistry and Machine Learning-Assisted Analysis. *ACS Appl. Energy Mater.* **2026**, *9*, 1405–1411.
- (171) Yan, Y.; Hai, F.; Wang, B.; Cao, W.; Li, M.; Wang, C.; Li, N.; Zhao, D. Machine Learning Accelerates High-Voltage Electrolyte Discovery for Lithium Metal Batteries. *Energy Storage Mater.* **2025**, *79*, 104312.
- (172) Kim, J.; Wang, K. H.; Kumar, R.; Ma, P.; Amanchukwu, C. V. Generative Electrolyte Solvent and Formulation Discovery. *JACS Au* **2026**, *6*, 2288–2302.
- (173) Yang, Z.; Wu, Y.; Han, X.; Zhang, Z.; Lai, H.; Mu, Z.; Zheng, T.; Liu, S.; Pu, Z.; Wang, Z.; Yu, Z.; Gong, S.; Yan, W. A Unified Predictive and Generative Solution for Liquid Electrolyte Formulation. *Nat. Mach. Intell.* **2026**, *8*, 186–196.
- (174) Hong, X.; Wang, X.; Harris, S. J.; Zhao, H.; Meng, J.; Jia, Q.; Zhao, Q.; Xu, K.; Pang, Q.; Jiang, B. Deep Active Learning and Knowledge Transfer for Rapid Discovery of Lithium Metal Battery Electrolytes. *Nat. Commun.* **2026**, *17*, 5146.
- (175) Hao, Y.; Su, Y.; Zhu, Z.; Sun, W.; Zhou, L.; Qiu, J.; Wang, X.; Deng, B.; Hua, H.; Ming, J.; He, X.; Zhang, H. The Rise of an Intelligent Partner: How Machine Learning Is Reshaping Electrolyte Research and Development. *Energy Storage Mater.* **2026**, *88*, 105134.

- (176) Robertson, L. A.; Shkrob, I. A.; Vescovi, R.; Ward, L.; Lewis, R.; Paulson, N. H.; Ginsburg, T.; Stone, C.; Diroll, B. T.; Ferrandon, M. S.; Zhang, Z. Navigating the Path to Autonomy: Real-World Lessons from an Air-Free Self-Driving Laboratory. *Digital Discovery* **2026**, *5*, 2787.
- (177) Szymanski, N. J.; Zeng, Y.; Huo, H.; Bartel, C. J.; Kim, H.; Ceder, G. Toward Autonomous Design and Synthesis of Novel Inorganic Materials. *Mater. Horiz.* **2021**, *8*, 2169–2198.
- (178) Szymanski, N. J.; Rendy, B.; Fei, Y.; Kumar, R. E.; He, T.; Milted, D.; McDermott, M. J.; Gallant, M.; Cubuk, E. D.; Merchant, A.; Kim, H.; Jain, A.; Bartel, C. J.; Persson, K.; Zeng, Y.; Ceder, G. An Autonomous Laboratory for the Accelerated Synthesis of Novel Materials. *Nature* **2023**, *624*, 86–91.
- (179) Yik, J. T.; Zhang, L.; Sjölund, J.; Hou, X.; Svensson, P. H.; Edström, K.; Berg, E. J. Automated Electrolyte Formulation and Coin Cell Assembly for High-Throughput Lithium-Ion Battery Research. *Digital Discovery* **2023**, *2*, 799–808.
- (180) Zhang, B.; Merker, L.; Sanin, A.; Stein, H. S. Robotic Cell Assembly to Accelerate Battery Research. *Digital Discovery* **2022**, *1*, 755–762.
- (181) Lee, H.-G.; Han, J.; Kwon, M.; Kwon, H.; Park, J.; Hah, H. J.; Seo, D.-H. ALBATROSS: A Robotised System for High-Throughput Electrolyte Screening via Automated Electrolyte Formulation, Coin-Cell Fabrication, and Electrochemical Evaluation. *Digital Discovery* **2026**, *5*, 1522–1530.
- (182) Dave, A.; Mitchell, J.; Burke, S.; Lin, H.; Whitacre, J.; Viswanathan, V. Autonomous Optimization of Non-Aqueous Li-Ion Battery Electrolytes via Robotic Experimentation and Machine Learning Coupling. *Nat. Commun.* **2022**, *13*, 5454.
- (183) Yik, J. T.; Hvarfner, C.; Sjölund, J.; Berg, E. J.; Zhang, L. Accelerating Aqueous Electrolyte Design with Automated Full-Cell Battery Experimentation and Bayesian Optimization. *Cell Rep. Phys. Sci.* **2025**, *6*, 102548.
- (184) Ramezani, M.; Nandi, P.; De La Fuente-Moreno, P. A.; Beidaghi, M. BRINE: A Cost-Effective Electrochemical Self-Driving Laboratory for Accelerated Discovery of High-Performance Electrolytes. *Digital Discovery* **2026**, *5*, 397–406.
- (185) Sheng, H.; Sun, J.; Rodríguez, O.; Hoar, B. B.; Zhang, W.; Xiang, D.; Tang, T.; Hazra, A.; Min, D. S.; Doyle, A. G.; Sigman, M. S.; Costentin, C.; Gu, Q.; Rodríguez-López, J.; Liu, C. Autonomous Closed-Loop Mechanistic Investigation of Molecular Electrochemistry via Automation. *Nat. Commun.* **2024**, *15*, 2781.
- (186) Lin, D.-Z.; Pan, K.-J.; Li, Y.; Musgrave, C. B., III; Zhang, L.; Jayarapu, K. N.; Li, T.; Tran, J. V.; Goddard, W. A. G., III; Luo, Z.; Liu, Y. A High-Throughput Experimentation Platform for Data-Driven Discovery in Electrochemistry. *Sci. Adv.* **2025**, *11* (14), 4391.
- (187) Martin, W.; Job, H. M.; Liang, Y.; Feng, R.; Gao, P.; Liu, D.; Zhong, L.; Xiao, J.; Wang, W.; Wu, B. High Throughput Electrochemical Screening of Phosphate-Rich Nonflammable Electrolytes in Lithium-Ion Batteries. *J. Electrochem. Soc.* **2024**, *171*, 090526.
- (188) Ismail, M.; Cabañero, M. A.; Orive, J.; Babulal, L. M.; Garcia, J.; Morant-Miñana, M. C.; Dauvergne, J. L.; Bonilla, F.; Monterrubio, I.; Carrasco, J.; Saracibar, A.; Reynaud, M. A. An Automated Drop-Cast Electrode Setup for High-Throughput Screening of Battery Materials. *Digital Discovery* **2025**, *4*, 943–953.
- (189) Peng, Z.; Ding, K.; Lai, M.; Qiu, R.; Xiao, Y.; Shi, J.; Guan, X.; Cai, Y. P.; Xu, C.; Wang, F.; Zheng, Q. Rational Electrolyte Solvent Screening for High-Energy Lithium Metal Batteries at Low Temperatures. *Nat. Commun.* **2026**, *17*, 590.
- (190) Severson, K. A.; Attia, P. M.; Jin, N.; Perkins, N.; Jiang, B.; Yang, Z.; Chen, M. H.; Aykol, M.; Herring, P. K.; Fraggedakis, D.; Bazant, M. Z.; Harris, S. J.; Chueh, W. C.; Braatz, R. D. Data-Driven Prediction of Battery Cycle Life before Capacity Degradation. *Nat. Energy* **2019**, *4*, 383–391.
- (191) Xiao, Y.; Yang, L.; Wu, X.; Zhong, X.; Wang, P.; Liu, Y.; Li, S.; Qin, W.; Fang, S. Rapid Detection of Dynamic Electrochemical Impedance Spectroscopy of Batteries Based on Sampling Function Excitation. *J. Power Sources* **2025**, *641*, 236823.
- (192) Mozhzhukhina, N.; Flores, E.; Lundström, R.; Nyström, V.; Kitz, P. G.; Edström, K.; Berg, E. J. Direct Operando Observation of Double Layer Charging and Early Solid Electrolyte Interphase Formation in Li-Ion Battery Electrolytes. *J. Phys. Chem. Lett.* **2020**, *11*, 4119–4123.
- (193) Yang, R.; Mei, L.; Fan, Y.; Zhang, Q.; Liao, H. G.; Yang, J.; Li, J.; Zeng, Z. Fabrication of Liquid Cell for in Situ Transmission Electron Microscopy of Electrochemical Processes. *Nat. Protoc.* **2023**, *18*, 555–578.
- (194) Kim, S.; Briega-Martos, V.; Liu, S.; Je, K.; Shi, C.; Stephens, K. M.; Zeltmann, S. E.; Zhang, Z.; Guzman-Soriano, R.; Li, W.; Jiang, J.; Choi, J.; Negash, Y. J.; Walden, F. S.; Marthe, N. L.; Wellborn, P. S.; Guo, Y.; Damiano, J.; Han, Y.; Thiede, E. H.; Yang, Y. Operando Heating and Cooling Electrochemical 4D-STEM Probing Nanoscale Dynamics at Solid-Liquid Interfaces. *J. Am. Chem. Soc.* **2025**, *147*, 23654–23671.
- (195) Li, Y.; Wu, C.; Wang, Y.; Li, N.; Liu, T.; Lu, J. Accelerating the Battery Revolution: AI-Driven Multiscale Innovation From Material Discovery to Smart Manufacturing. *Adv. Funct. Mater.* **2026**, *36*, No. e14830.
- (196) Xu, J.; Zhang, J.; Pollard, T. P.; Li, Q.; Tan, S.; Hou, S.; Wan, H.; Chen, F.; He, H.; Hu, E.; Xu, K.; Yang, X. Q.; Borodin, O.; Wang, C. Electrolyte Design for Li-Ion Batteries under Extreme Operating Conditions. *Nature* **2023**, *614*, 694–700.
- (197) He, M.; Hector, L. G.; Dai, F.; Xu, F.; Kolluri, S.; Hardin, N.; Cai, M. Industry Needs for Practical Lithium-Metal Battery Designs in Electric Vehicles. *Nat. Energy* **2024**, *9*, 1199–1205.
- (198) Kumar, R.; Vu, M. C.; Ma, P.; Amanchukwu, C. V. Electrolytics: A Unified Big Data Approach for Electrolyte Design and Discovery. *Chem. Mater.* **2025**, *37*, 2720–2734.
- (199) Suo, L.; Xue, W.; Gobet, M.; Greenbaum, S. G.; Wang, C.; Chen, Y.; Yang, W.; Li, Y.; Li, J. Fluorine-Donating Electrolytes Enable Highly Reversible 5-V-Class Li Metal Batteries. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 1156–1161.
- (200) Hess, S.; Wohlfahrt-Mehrens, M.; Wachtler, M. Flammability of Li-Ion Battery Electrolytes: Flash Point and Self-Extinguishing Time Measurements. *J. Electrochem. Soc.* **2015**, *162*, A3084–A3097.
- (201) Kausthubharam; Vishnugopi, B. S.; Alujjage, A. S. J.; Premnath, V.; Tang, W. S.; Jeevarajan, J. A.; Mukherjee, P. P. Mechanistic Understanding of Thermal Stability and Safety in Lithium Metal Batteries. *Chem. Rev.* **2026**, *126* (1), 404–447.
- (202) Chen, S.; Wu, G.; Jiang, H.; Wang, J.; Chen, T.; Han, C.; Wang, W.; Yang, R.; Zhao, J.; Tang, Z.; Gong, X.; Li, C.; Zhu, M.; Zhang, K.; Xu, Y.; Wang, Y.; Hu, Z.; Chen, P.; Wang, B.; Zhang, K.; Xia, Y.; Peng, H.; Gao, Y. External Li Supply Reshapes Li Deficiency and Lifetime Limit of Batteries. *Nature* **2025**, *638* (8051), 676–683.
- (203) Jin, C.; Huang, Y.; Li, L.; Wei, G.; Li, H.; Shang, Q.; Ju, Z.; Lu, G.; Zheng, J.; Sheng, O.; Tao, X. A Corrosion Inhibiting Layer to Tackle the Irreversible Lithium Loss in Lithium Metal Batteries. *Nat. Commun.* **2023**, *14*, 8269.
- (204) Liu, J.; Bao, Z.; Cui, Y.; Dufek, E. J.; Goodenough, J. B.; Khalifah, P.; Li, Q.; Liaw, B. Y.; Liu, P.; Manthiram, A.; Meng, Y. S.; Subramanian, V. R.; Toney, M. F.; Viswanathan, V. V.; Whittingham, M. S.; Xiao, J.; Xu, W.; Yang, J.; Yang, X. Q.; Zhang, J. G. Pathways for Practical High-Energy Long-Cycling Lithium Metal Batteries. *Nat. Energy* **2019**, *4*, 180–186.