

PERSPECTIVE • OPEN ACCESS

Beyond cations: the rise of anion-shuttle chemistries in the emerging battery landscape

To cite this article: Soutam Panja *et al* 2026 *J. Phys. Energy* **8** 031002

View the [article online](#) for updates and enhancements.

You may also like

- [Lead-free perovskites and derivatives for photogeneration: a roadmap to sustainable approaches for photovoltaics and photo\(electro\)catalysis](#)
Isabella Poli, Teresa Gatti, Yan Li et al.
- [Substrate-induced optimization of the electrocatalytic hydrogen evolution reaction \(HER\) performance of MoS₂ thin films](#)
Hafiz Sami-Ur-Rehman, Arpana Singh, Nunzia Coppola et al.
- [From wedge libraries to record \$V_{oc}\$: MoO_x hole transport layer optimization in ZnO_x/S_x transparent solar cells](#)
Marta Miró-Llorente, Gustavo Álvarez, Victoria Rotaru et al.

 COMSOL

Power Next-Gen Renewables with Multiphysics Simulation

Overcome design challenges and find innovative solutions.

Meeting demand to deliver renewable energy efficiently, safely and reliably calls for data-driven designs.

By using COMSOL Multiphysics® to simulate the real-world behaviour of solar cells, wind farms, hydrogen-powered EVs and more, engineers can accurately predict and fine-tune performance when developing of innovative green energy solutions.



» comsol.com/industry/energy/renewable



PERSPECTIVE

OPEN ACCESS

RECEIVED
30 April 2026

REVISED
6 August 2026

ACCEPTED FOR PUBLICATION
17 August 2026

PUBLISHED
18 September 2026

Original content from
this work may be used
under the terms of the
[Creative Commons
Attribution 4.0 licence](#).

Any further distribution
of this work must
maintain attribution to
the author(s) and the title
of the work, journal
citation and DOI.



Beyond cations: the rise of anion-shuttle chemistries in the emerging battery landscape

Soutam Panja^{1,3} , Jagjit Nanda⁴ , Maximilian Fichtner^{1,2,3,*} and Ahamed Irshad^{4,*}

¹ Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), 89081 Ulm, Germany

² Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany

³ CELEST Green Energy Lab Ulm, Ulm University, Lise-Meitner-Str. 16, 89081 Ulm, Germany

⁴ SLAC-Stanford Battery Center, Applied Energy Division, SLAC National Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, United States of America

* Authors to whom any correspondence should be addressed.

E-mail: m.fichtner@kit.edu, irshad@slac.stanford.edu and soutam.panja@kit.edu

Keywords: anion-shuttle batteries, chloride-ion batteries, fluoride-ion batteries, hydride-ion batteries, dual-ion batteries, bromide-ion batteries, beyond lithium-ion batteries

Abstract

The search for electrochemical energy storage beyond lithium-ion batteries has yielded a broad landscape of alternative chemistries, yet most still adhere to the fundamental paradigm of cationic charge carriers. Anion-shuttle batteries (ASBs), spanning dual-ion, chloride-ion, fluoride-ion, hydride-ion, bromide-ion, and polyiodide systems, represent a mechanistically distinct departure in which anions serve as the primary electroactive charge carriers, functioning as the exclusive shuttling species in fluoride-ion, chloride-ion, hydride-ion, and bromide-ion systems, while in dual-ion batteries anion intercalation at the cathode is coupled to simultaneous cation insertion or deposition at the anode. This Perspective provides a critical and comprehensive account of this emerging field, covering charge-transfer mechanisms, the development of electrode and electrolyte materials, and the failure modes that currently separate laboratory demonstrations from practical relevance. The thermodynamic case is compelling: fluoride-ion conversion chemistries project material-level theoretical energy densities exceeding 1500 Wh kg⁻¹ (and up to 588 Wh kg⁻¹ at the stack level under techno-economic modeling), chloride-ion electrode screening identifies over 1225 anode–cathode combinations with thermodynamic volumetric densities exceeding 2000 Wh L⁻¹, and dual-ion architectures sustain operating voltages of 4.5–5.5 V with near-unity Coulombic efficiency over thousands of cycles. Yet three material challenges persist across all chemistries, regardless of anion identity: the kinetic penalties of anion solvation and interfacial desolvation, the electrochemical instability of the electrode–electrolyte interphase, and mechanical degradation arising from large volumetric strains during conversion cycling. We differentiate between limitations intrinsic to anionic charge-carrier physics and those addressable through rational materials design. ASBs will not broadly displace lithium-ion technology, but their natural domain, grid-scale storage, high-temperature operation, and applications free from critical mineral dependencies, represent a strategically significant and scientifically compelling frontier.

Abbreviations:

SS	solid-state
SSE	SS electrolyte
RT	room temperature
IL	ionic liquid
WISE	water-in-salt electrolyte
HGPE	halide-ion-conducting gel polymer electrolyte

LDH	layered double hydroxide
CE	Coulombic efficiency
TSbCl ₃	triphenylantimony chloride (anion acceptor in CsF–DMSO liquid electrolyte)
NHBrEG	NH ₄ Br–ethylene glycol non-aqueous electrolyte
aq.	aqueous
non-aq.	non-aqueous
org.	organic solvent-based
PEO	polyethylene oxide

1. Introduction

Lithium-ion batteries (LIBs) underpin nearly all portable electronics and are rapidly becoming the dominant power source for electric vehicles and stationary storage, owing to their high energy density, long cycle life, and mature manufacturing ecosystem. State-of-the-art cells employing nickel-rich layered oxides such as LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) paired with graphite anodes already achieve $\approx 250\text{--}300\text{ Wh kg}^{-1}$ at the cell level, approaching the practically attainable range for current conventional intercalation chemistries in EV-type cells [1, 2]. This technological maturity brings several fundamental constraints into sharper focus. Current systems depend heavily on critical transition metals and lithium, creating notable supply-chain vulnerabilities. At the same time, the push for ever-higher specific energy intensifies safety risks, particularly oxygen release from Ni-rich cathodes and parasitic reactions in flammable organic electrolytes. Similarly, in prospective Li-metal batteries, dendritic lithium growth introduces an additional layer of safety and performance concern. Finally, there is a growing mismatch between the cost structure and design priorities of LIBs and the needs of emerging applications such as ultra-low-cost, long-duration grid storage and operation in harsh environments where non-flammable or aqueous systems may offer more practical solutions [1, 2].

These limitations have spurred intensive exploration of alternative battery chemistries, which can be broadly classified into three mechanistically distinct directions. The first, cation-substitution strategies retain the intercalation framework, while replacing Li⁺ with more abundant charge carriers such as Na⁺ (ionic radius 102 pm, -2.71 V vs. SHE (standard hydrogen electrode)), K⁺ (138 pm, -2.93 V), or multivalent carriers (Mg²⁺, Ca²⁺, Zn²⁺, Al³⁺). In particular, multivalent systems offer a compelling benefit through multi-electron redox per ion transferred, potentially enabling higher charge storage densities [3]. However, the larger ionic radii of Na⁺ and K⁺ impose anisotropic lattice strain on host structures, and the high charge density of divalent and trivalent cations generates strong electrostatic interactions with host lattice anions that raise the activation barriers for SS ion hopping, complicating the design of suitable intercalation hosts [4]. The second approach, architecture modification, preserves Li⁺ as the charge carrier while replacing flammable liquid carbonate electrolytes with ceramic, polymer, or composite SS analogs. This substitution eliminates the exothermic solvent–cathode reactions underlying thermal runaway [5] and enables the use of lithium metal anodes (3860 mAh g^{-1}) by suppressing dendrite nucleation and growth. The third direction, conversion chemistries, abandons intercalation entirely in favor of bond-breaking multi-electron redox reactions. For instance, lithium–sulfur cells exploit the S₈/Li₂S couple (1675 mAh g^{-1} , $\sim 2600\text{ Wh kg}^{-1}$ theoretical) [6], and metal–air batteries leverage the O₂/Li₂O₂ couple ($>3500\text{ Wh kg}^{-1}$) [7]. However, both are hindered by irreversible failure mechanisms. In the Li–S system, soluble polysulfide intermediates (Li₂S_{*x*}, $4 \leq x \leq 8$) undergo shuttling across the separator driven by concentration gradients leading to active material loss and insulating Li₂S deposition at the anode, while in metal–air batteries, large oxygen evolution overpotentials ($>1.2\text{ V}$) and the formation of reactive singlet oxygen (¹O₂) drive parasitic decomposition of both the electrolyte and carbon cathode [8].

Anion-shuttle batteries (ASBs) constitute a fourth, conceptually distinct paradigm in electrochemical energy storage, in which anions, rather than cations, serve as the primary charge carriers. In these systems, anions shuttle between electrodes via Faradaic processes governed by anion solvation, desolvation, and SS diffusion kinetics that are fundamentally different from those of Li⁺. This definition encompasses a diverse set of chemistries unified by an anionic charge carrier, yet mechanistically heterogeneous in their underlying reaction pathways. Two mechanistically distinct configurations exist within this paradigm: exclusive-anion systems such as fluoride-ion, chloride-ion, and hydride-ion batteries (HIBs), in which the anion is the sole mobile charge carrier and any cationic redox at the electrode is a structural consequence of the conversion reaction confined to the electrode surface; and coupled dual-carrier

systems such as dual-ion batteries (DIBs), in which anion intercalation at the cathode proceeds simultaneously with cation insertion or deposition at the anode, the electrolyte serving as the shared ionic reservoir for both mobile species.

Prominent examples include dual-ion batteries (DIBs), in which large, weakly solvated molecular anions (e.g. PF_6^- , FSI^- , ClO_4^- , BF_4^-) undergo staged intercalation into graphite cathodes via a gallery expansion mechanism, while the corresponding cations in the electrolyte (Li^+ , Na^+ , K^+ , Zn^{2+} , Ca^{2+}) are simultaneously inserted into the anode. This decoupling of electrode reactions enables operating voltages that exceed those of conventional single-ion intercalation systems [9–11].

Another category of ASBs includes halide-based systems, such as chloride-, fluoride-, and iodide-ion batteries, in which halide ions participate in conversion or intercalation reactions at the electrode, depending on the host material and electrolyte configuration. Chloride-ion batteries (CIBs), in which Cl^- ions drive electrochemical reactions at metal chloride electrodes through diverse reaction pathways, including direct conversion, displacement, and stepwise intermediate phase formation, depending on the structural nature of the electrode material, in aqueous or non-aqueous electrolytes [12]. Fluoride-ion batteries (FIBs) in which F^- ions, bearing the highest charge density and smallest ionic radius among all monovalent halide anions, drive direct conversion, displacement, and stepwise defluorination–refluorination reactions at metal fluoride electrodes such as CuF_2 , BiF_3 , FeF_3 , etc, with theoretical energy densities exceeding 1500 Wh kg^{-1} arising from the high thermodynamic stability of the M–F bond [13]. Polyiodide-shuttle systems, in which the $\text{I}^-/\text{I}_3^-/\text{I}_5^-$ redox cascade underpins a multi-electron charge storage mechanism, are characterized by soluble higher-order polyiodide anions forming through sequential iodine complexation equilibria ($\text{I}^- + \text{I}_2 \rightleftharpoons \text{I}_3^-$; $\text{I}_3^- + \text{I}_2 \rightleftharpoons \text{I}_5^-$) and migrating between electrodes in aqueous zinc–iodine or lithium–iodine configurations, where confinement of the polyiodide species within the cathode host remains the central materials challenge [14].

HIBs are unique in that they rely on the migration of H^- ions through SS superionic conductors, primarily rare-earth oxyhydrides and complex hydride phases, via vacancy-mediated anion diffusion. These systems enable reversible hydrogenation and dehydrogenation reactions at intermetallic and complex-hydride electrodes, driven by coupled hydride transfer and electron exchange [15–19].

The fundamental appeal of ASBs lies in their unique combination of physicochemical attributes that arise directly from the electrochemical properties of anions as charge carriers. In DIBs, the decoupled intercalation of anions at the cathode and cations at the anode across independent redox couples yields operating voltages of 4.5–5.5 V, a consequence of the large electrochemical potential difference between anion intercalation into graphite and cation insertion into the opposing electrode. This thermodynamic configuration is not accessible to single-ion intercalation chemistries operating within a single redox couple. Conversion-type FIBs and CIBs access high theoretical capacities through multi-electron redox per formula unit, governed by the number of transferable anions and the oxidation state change of the metal center: CuF_2 delivers 528 mAh g^{-1} via a two-electron $\text{Cu}^{2+}/\text{Cu}^0$ couple, FeF_3 reaches 713 mAh g^{-1} through a three-electron $\text{Fe}^{3+}/\text{Fe}^0$ reduction [20, 21], and FeCl_3 offers 496 mAh g^{-1} through the analogous $\text{Fe}^{3+}/\text{Fe}^0$ chloride transfer process. From a safety standpoint, aqueous CIB electrolytes are inherently non-flammable by virtue of their water-based composition, eliminating the exothermic oxidation of organic solvents that underlie thermal runaway. All-SS (ASS) FIBs and HIBs suppress both solvent decomposition pathways and the electrochemical nucleation instabilities at the electrode–electrolyte interface that are responsible for lithium dendrite formation in liquid-electrolyte systems. However, these advantages are chemistry-specific and do not extend uniformly across all anion-shuttle systems. Simple metal chloride cathodes remain prone to dissolution in both aqueous and IL electrolytes; CEI layers on graphite cathodes in DIBs are mechanically fragile and ionically resistive under prolonged high-voltage cycling; SS FIBs and HIBs exhibit large interfacial polarization and poor room-temperature anion transport kinetics; and polyiodide systems continue to suffer from active material loss through soluble intermediate migration. These failure modes are addressed in detail in section 2.

This Perspective critically examines ASBs as a mechanistically distinct and scientifically compelling class of electrochemical energy storage, assessing both their fundamental physicochemical advantages and the intrinsic materials challenges that currently separate laboratory demonstrations from practical applications. We systematically evaluate the charge-transfer mechanisms, electrochemical performance metrics, and failure modes of each ASB family, benchmarking their thermodynamic and kinetic attributes against competing post-lithium-ion chemistries. Additionally, we diagnose three universal scientific bottlenecks that constrain all anion-shuttle systems, regardless of chemistry: anion solvation and ionic transport, cathode-electrolyte interphase (CEI) instability, and chemo-mechanical degradation. Critically, we distinguish between limitations that are fundamental and potentially insurmountable and those that are tractable materials engineering challenges. ASBs are particularly well-suited for long-duration grid storage, high-temperature and harsh-environment operation, and cost-sensitive applications. In these

domains, the unique attributes of anionic charge transfer offer advantages that are difficult for existing cation-based chemistries to replicate simultaneously.

2. The anion-shuttle paradigm: mechanisms, materials, and performance

Although unified by the central role of anions in cathode-side Faradaic charge storage, anion shuttle batteries encompass a breadth of electrochemical mechanisms that reflect profound differences in ionic radius, solvation free energy, SS diffusivity, and redox potential among the anion species serving as charge carriers. In conversion-type halide and hydride systems, the anion functions as the sole mobile charge carrier, while in dual-ion systems, anion intercalation at the cathode is coupled to independent Faradaic reactions driven by cation insertion or deposition at the anode. Large, polarizable molecular anions such as PF_6^- , FSI^- , and ClO_4^- , which have weak solvation shells, undergo reversible staged intercalation into graphitic carbon hosts via gallery expansion. In contrast, highly electronegative atomic anions, primarily F^- and Cl^- , participate in bond-forming conversion and displacement reactions that are thermodynamically driven by the stability of M-F and M-Cl bonds. The hydride ion (H^-), whose reactivity precludes liquid-phase transport, migrates exclusively through vacancy-mediated pathways in SS superionic conductors.

In all cases, the electrode–electrolyte interface is the critical performance-limiting factor, with anion desolvation kinetics, interfacial charge-transfer resistance, and the electrolyte’s electrochemical stability window collectively determining the gap between what electrode-level thermodynamics permits and what practical full-cell configurations currently deliver. The following subsections systematically address each ASB family, including dual-ion, chloride-ion, fluoride-ion, hydride-ion, and polyiodide-shuttle systems, examining charge-transfer mechanisms, electrochemical performance metrics, materials design principles, and the fundamental scientific challenges that must be resolved to advance each chemistry beyond its current state.

While the aforementioned frameworks establish the broader operational mechanics, the specific choice of charge carrier dictates the kinetic limitations. Yet, its physicochemical character differs fundamentally with anion identity. In DIBs, incomplete desolvation of PF_6^- and FSI^- at the graphite cathode is the primary kinetic bottleneck: residual solvent co-intercalation triggers irreversible graphite exfoliation, and oxidative electrolyte decomposition above 4.5 V generates a CEI that is mechanistically distinct from the reductive solid-electrolyte interphase (SEI) formed at the anode and considerably less well understood [22, 23]. In CIBs, Cl^- carries a lower charge density than Li^+ or F^- , which reduces its desolvation penalty at the electrode interface, but cathode dissolution and interfacial stability are strongly electrolyte-dependent and must be assessed independently for aqueous, IL, and SS configurations [24]. In FIBs, F^- carries the highest charge density among all monovalent halide anions; its strong solvation shell in liquid electrolytes imposes a large desolvation penalty that limits room-temperature kinetics, while SS electrolytes bypass solvation but introduce grain-boundary resistance and interfacial polarization at elevated current densities [25, 26]. In HIBs, the absence of a liquid phase eliminates solvation, but solid–solid electrode–electrolyte contact generates interfacial space-charge layers and mechanical stress upon cycling that remain unresolved [15, 16]. These contrasts confirm that interfacial engineering strategies, such as CEI stabilization, electrolyte formulation, and electrode surface modification, must each be tailored independently for each chemistry.

2.1. Dual-Ion Batteries (DIBs)

2.1.1. Electrochemical significance and operating mechanism

Among post-lithium battery chemistries, DIBs occupy a uniquely privileged position because they depart from the conventional cation-intercalation paradigm. Unlike the ‘rocking-chair’ model of LIBs, which relies solely on cation intercalation, DIBs simultaneously exploit both anionic and cationic species in the electrolyte as active charge carriers. During charging, cations (Li^+ , Na^+ , K^+ , Al^{3+}) intercalate into the graphite anode, while anions (PF_6^- , TFSI^- , FSI^- , BF_4^-) intercalate into the graphite cathode. Upon discharge, both species return to the electrolyte. Among these anions, BF_4^- forms anion-based graphite intercalation compounds (AGICs) with solvent-dependent intercalation gallery heights (IGHs) that vary discontinuously between 0.80 nm and 1.07 nm, depending on whether ethyl methyl sulfone or sulfolane co-intercalates. This solvation-mediated structural competition directly governs in-plane anion density and cathode discharge capacity [27]. This co-intercalation mechanism imparts a thermodynamically distinct character. The open-circuit voltage (OCV) depends not only on electrode potentials but also on the concentration and chemical nature of the electrolyte salt, a feature absent in conventional LIBs, granting additional tunability through rational electrolyte engineering. Anion intercalation in graphite occurs

at 4.5–5.2 V vs. Li^+/Li [28, 29], substantially exceeding the ~ 3.7 V ceiling of state-of-the-art LIBs, providing a compelling thermodynamic basis for high energy density and a favorable kinetic foundation for high power output. Furthermore, the resource and cost profile of DIBs underscores their significance: the complete elimination of transition-metal oxides (Co, Ni, Mn) reduces estimated material costs to 50–80 kWh^{-1} on a materials-only basis and directly addresses the geopolitical supply-chain vulnerabilities that increasingly constrain the scaling of LIB technology [30].

Zhang *et al* pioneered the aluminum-graphite dual-ion battery (AGDIB), in which aluminum foil serves as both anode and current collector, enabling an EC-free 4 M LiPF_6 /ethyl methyl carbonate (EMC) electrolyte that eliminates PF_6^- solvation suppression. A VC-derived SEI layer stabilizes the AlLi alloying anode against pulverization, delivering 104 mAh g^{-1} at 2 C with 88% capacity retention over 200 cycles and an estimated full-cell packaged energy density of $\sim 220 \text{ Wh kg}^{-1}$ (incorporating both electrodes and electrolyte under specific loading assumptions) [31], comparable to high-performance LIBs under the specific benchmarking conditions used in figures 1(a)–(c) [32]. Kravchyk *et al* showed that maximizing electrolyte concentration directly unlocks cell-level energy density in lithium-free DIBs: a 5 M KFSI/EC/DMC electrolyte delivered 207 Wh kg^{-1} at 4.7 V, with FSI^- intercalation confirmed by *in situ* XRD and ^{19}F NMR to follow a stage-1 mechanism ($I_c = 7.85 \text{ \AA}$). The cell sustains >300 cycles at 93%–99% CE with a peak power density of 1338 W kg^{-1} , as shown in figures 1(d)–(f) [33]. Guo *et al* demonstrated that increasing NaPF_6 concentration to 3 m in an EMC/PC/FEC electrolyte extends oxidative stability beyond 4.7 V and, crucially, forms a significantly thinner CEI on the graphite cathode—confirmed by XPS depth profiling—reducing charge-transfer resistance and enabling 92.7 mAh g^{-1} at 2 A g^{-1} with 92% retention after 1 000 cycles. An all-carbon full cell using a lignin-derived carbon fiber mat Na-host validated practical feasibility with 90% retention over 200 cycles (figures 1(g)–(i)) [34]. Kravchyk and Kovalenko systematically established that in ADIBs, the chloroaluminate IL is not merely a conducting medium but a capacity-limiting active component, simultaneously supports Al electroplating and supplies AlCl_4^- for cathode intercalation. Theoretical capacity scales with molar acidity (r), rising from ~ 19 to $\sim 46 \text{ mAh g}^{-1}$ as $\text{AlCl}_3:\text{EMIMCl}$ increases from $r = 1.3$ to $r = 2.0$, while deep eutectic solvents offer lower-cost alternatives but remain constrained by narrow electrochemical windows (~ 2.2 V) and unresolved current collector corrosion (figures 1(j) and (k)) [35].

2.1.2. Key advantages

The advantages of DIBs extend well beyond high operating voltage. Their Li-graphite-based symmetric electrode configuration sustains a CE of 99.1% over 3500 cycles at 10 C, reflecting notable cycling stability, though one that falls short of the >99.8% CE benchmark of commercial LIBs; a per-cycle irreversibility of 0.9% can accumulate substantially over extended operation unless compensated by excess electrolyte [28]. The anion intercalation mechanism, however, proceeds through well-defined, reversible staging transitions, as confirmed by *in situ* XRD, Raman spectroscopy, and electrochemical dilatometry, providing mechanistic predictability rarely matched in conversion-type chemistries [36–39]. Because both ionic intercalation reactions occur in parallel, and graphite supports fast SS diffusion, charge rates of 10–100 C have been demonstrated, positioning DIBs as compelling candidates for fast-charge buffer applications and grid-level frequency regulation [40]. The DIB framework is also chemically versatile: sodium-, potassium-, aluminum-, zinc-, magnesium-, and calcium-based systems have all been demonstrated, offering viable pathways to fully lithium-free energy storage. Notably, in 2019, Holoubek and colleagues reported that DIBs at low-temperature conditions (-60°C) exhibit capacity retention more than 11 times that of conventional graphite- LiCoO_2 cells, attributable to intrinsically lower desolvation energy barriers for anion intercalation at reduced temperatures [23].

2.1.3. Fundamental limitations and inherent drawbacks

Notwithstanding these merits, DIBs harbor several fundamental limitations that currently preclude commercialization. The theoretical specific capacity of graphite cathodes for anion intercalation is intrinsically low: complete PF_6^- intercalation forms C_{20}PF_6 , corresponding to only $\sim 112 \text{ mAh g}^{-1}$ [40], while TFSI^- yields $\sim 86 \text{ mAh g}^{-1}$ at 20°C [37]. This is far below the $\sim 200 \text{ mAh g}^{-1}$ of NMC811 cathodes in Li-ion batteries. The large ionic radii of relevant anions, relative to graphite's 0.335 nm interlayer spacing, impose severe kinetic penalties and often promote co-intercalation of solvent molecules, triggering irreversible graphite exfoliation and progressive structural degradation [41]. Operating voltages above 4.5 V also drive oxidative decomposition of the electrolyte, generating corrosive byproducts (HF , POF_3) that suppress CE, often below 90% in early cycles [22, 42]. Because the electrolyte is the sole reservoir of active ions, minimum loadings of $\sim 13 \text{ g Ah}^{-1}$ are required for a 4 M system, several times the 2–3 g Ah^{-1} typical of commercial LIBs, directly inflating cell mass, constraining full-cell energy density,

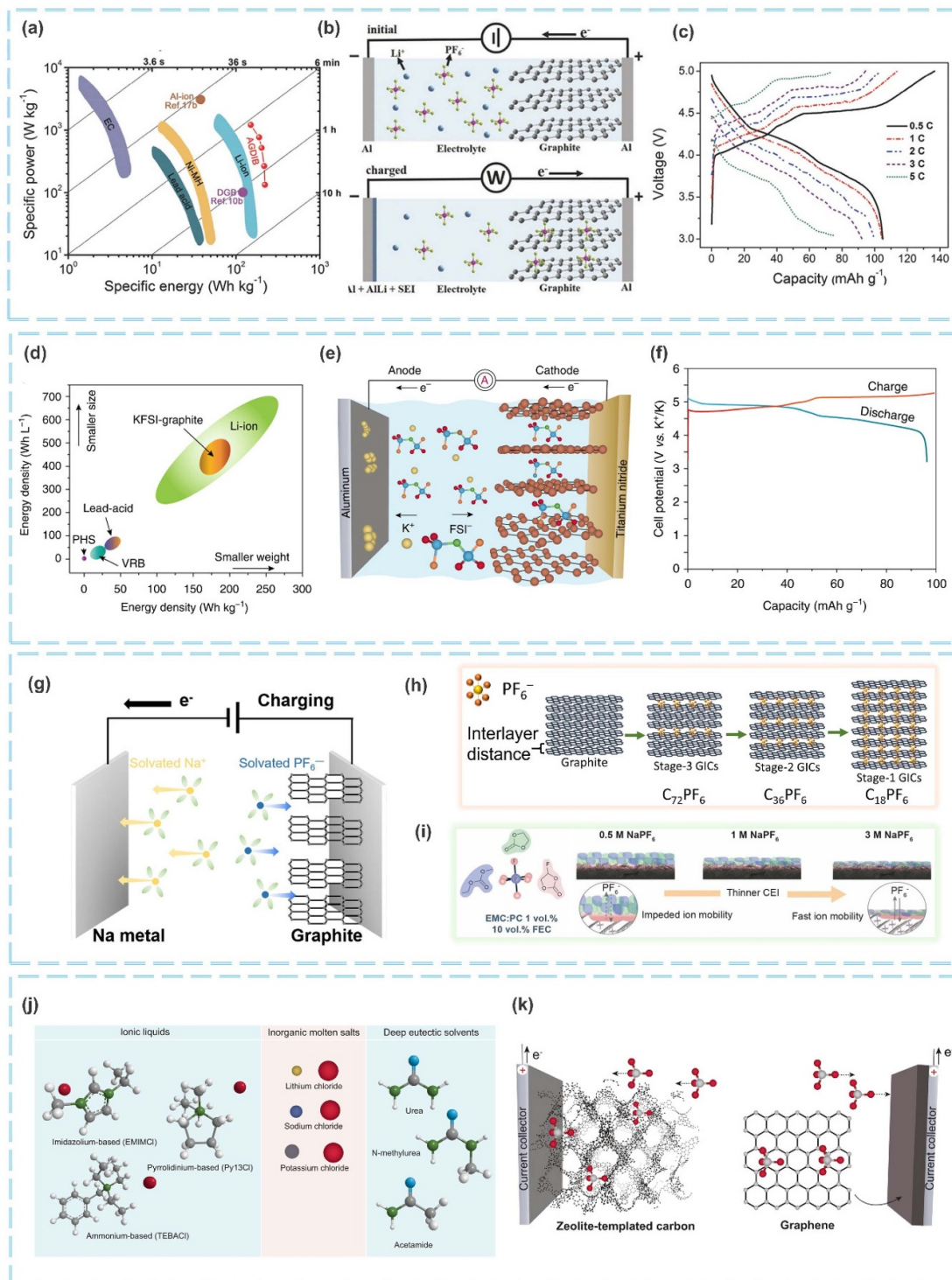


Figure 1. (a)–(c) Electrochemical performance of the aluminum-graphite dual-ion battery (AGDIB): (a) benchmarking of AGDIB energy density against conventional storage technologies; (b) operating principle showing simultaneous Al anode deposition and PF_6^- intercalation into the graphite cathode during charging; (c) rate capability at 0.5–5 C (1 C = 100 mA g^{-1}) [32]. Reproduced from Zhang, X. *et al.* Adv. Energy Mater. 6, 1502 588 (2016), under a Creative Commons CC BY-NC 4.0 license. (d)–(f) Potassium dual-ion battery based on KFSI-graphite: (d) comparison of volumetric and gravimetric energy densities with PHS, vanadium redox battery (VRB), lead-acid, and Li-ion batteries; (e) schematic of FSI^- intercalation into graphite during charging, with fluorine, oxygen, sulfur, and nitrogen atoms colored brown, red, blue, and green, respectively; (f) galvanostatic voltage profiles confirming a stable high-voltage plateau near 4.7 V [33]. Reproduced from Kravchyk, K. V. *et al.* Nat. Commun. 9, 4469 (2018), under a Creative Commons CC BY 4.0 license. (g)–(i) Sodium dual-ion battery with concentrated electrolytes: (g) working principle of a Na metal||graphite cathode configuration upon charging; (h) staging intercalation model from graphite to stage-1 graphite intercalation compound; (i) schematic of CEI layer formation as a function of electrolyte concentration [34]. Reproduced from Guo, Z. *et al.* ChemSusChem 16, e202201583 (2023), under a Creative Commons CC BY-NC 4.0 license. (j) and (k) Aluminum dual-ion battery electrolytes and cathode materials: (j) Lewis-base additives used to tune chloroaluminate ionic-liquid electrolyte acidity, and (k) schematic charging process using zeolite-templated carbon and graphene positive electrodes [35]. Reproduced from Kravchyk, K. V. and Kovalenko, M. V. Commun. Chem. 3, 120 (2020), under a Creative Commons CC BY 4.0 license.

and increasing cost [39]. The CEI that forms spontaneously on graphite cathodes at high voltage is typically non-uniform, mechanically fragile, and ionically resistive. It is a far less understood analog of the SEI, and its instability remains one of the foremost contributors to long-term capacity fade [43].

2.1.4. Recent progress in electrode and electrolyte engineering

Significant advances have been reported across all principal DIB components. On the cathode side, nitrogen-doped artificial graphite with an expanded interlayer spacing of 0.51 nm reduces anion migration barriers through electron cloud redistribution, delivering 240 mAh g⁻¹ at 100 mA g⁻¹ in full-cell configurations, more than doubling the theoretical limit of conventional graphite [44–47]. Boron-doped graphite achieved 178.5 Wh kg⁻¹ with 93.8% retention after 1 500 cycles at 10 C [48], while vertically aligned graphene nanosheets exploited combined intercalation–adsorption storage, reaching 220 mAh g⁻¹ [49]. Beyond graphite, a mixed-valence ferrocene-based MOF (metal–organic framework) cathode, Co₂(II)Co(III)DFc₂(OH) · 3 H₂O, abbreviated as Co(DFc)_x, leveraging cooperative Co²⁺/Co³⁺ and Fe²⁺/Fe³⁺ redox couples, delivered 170 mAh g⁻¹ at 50 mA g⁻¹ with 99% capacity retention after 8 000 cycles, representing arguably the highest cycling stability reported for any DIB cathode [50]. On the anode side, aluminum, which simultaneously serves as the current collector and active material (AlLi alloy, theoretical capacity of 993 mAh g⁻¹), has been stabilized through graphdiyne decoration [51], amorphous carbon nanointerface coatings [52], and ~20 nm thiophdiyne films that mitigate volumetric pulverization, enabling 145 mAh g⁻¹ with stable long-term cycling [53]. Silicon–carbon composites deposited on flexible CuNi-modified nylon substrates reduce peak compressive stress from 724 MPa to 182 MPa, demonstrating a viable route toward flexible high-energy DIBs [54]. In sodium-based dual-ion batteries (SDIBs), Zn²⁺-mediated carbon microdomain engineering simultaneously accelerates Na⁺ desolvation kinetics through tailored nitrogen-doped active sites and enhances plateau-capacity sodium storage through molecular-scale closed-pore architectures, with the optimized carbon anode material MEC₃ (microdomain engineered carbon) delivering 253 mAh g⁻¹ at 1 C and 80.6% capacity retention after 10 000 cycles at 10 C in a full MEC₃ || expanded graphite cell [44]. On the alloying anode side, interfacial phonon scattering has been shown to dissipate mechanical stress accumulated during repeated Na-alloying volume changes, stabilizing the electrode against pulverization and enabling sustained high-rate cycling in full SDIB configurations [55].

Electrolyte engineering has delivered the most transformative advances. High-concentration electrolytes (2–4 M LiPF₆ in EMC, sulfolane/EMC, or DMSO-based formulations) drastically reduce free solvent in the PF₆⁻ solvation shell, suppressing co-intercalation and enabling stable operation up to 5.5 V vs. Li⁺/Li, a window previously inaccessible with conventional 1 M systems. BF₄⁻-based electrolytes show more concentration-sensitive intercalation behavior: In LiBF₄-sulfolane systems, optimal discharge capacity exceeding 100 mAh g⁻¹ is achieved at 2 M, where BF₄⁻ co-intercalates with a complete sulfolane shell, forming AGICs with IGH = 1.07 nm. Above 3 M, strong Li⁺-sulfolane coordination depletes free solvent, producing a compact AGIC phase with IGH = 0.80 nm, lower in-plane anion density, and suppressed capacity. In binary ethyl methyl sulfone and sulfolane electrolytes, the solvent volume ratio controls the phase formed, with BF₄⁻ co-intercalating preferentially with ethyl methyl sulfone at lower potentials and transitioning to sulfolane-solvated species at higher voltages. The graphite electrode further retains structural memory of its prior intercalation history, as confirmed by *ex situ* XRD on pre-cycled electrodes [27]. A dual-graphite cell with 2 M LiPF₆ in EMC: SL (1:4 v/v) achieved 94.7% retention after 1 000 cycles at 5.3 V via *in situ* formation of a sulfonyl-rich CEI. The additive LiDFOB, which undergoes preferential oxidative decomposition at the graphite cathode due to its higher HOMO (highest occupied molecular orbital) level, forms a uniform, low-resistance CEI, enabling 88.8% capacity retention at 40 C and 6 500 cycles at 10 C [56]. Hexafluoroglutaric anhydride (HFGA) copolymerizes with PF₅ at the cathode surface, forming a CF₂-rich CEI that drives CE above 99% at 5.5 V [30], while PVDF-HFP/PEO/graphene oxide gel polymer electrolytes achieve ionic conductivities of ~10⁻³ S cm⁻¹ and exhibit thermal stability up to 90 °C, positioning them as leading candidates for quasi-SS and wearable DIB platforms [57].

2.1.5. Outstanding challenges and areas requiring further investigation

Despite this broad progress, several critical challenges remain unresolved. Full-cell energy density, when rigorously calculated to include the substantial mandatory electrolyte mass, remains significantly lower than the values typically reported on a per-electrode-active-mass basis in the literature [33, 58, 59]. This underscores the need for standardized full-cell evaluation protocols that incorporate realistic electrolyte-to-electrode mass ratios [9]. The CEI layer's spatial composition, nanoscale heterogeneity, and temporal evolution under prolonged high-voltage cycling remain poorly characterized, necessitating advanced *operando* investigations using synchrotron x-ray scattering, cryo-TEM, and time-resolved

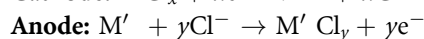
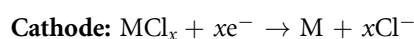
Raman spectroscopy. The dynamic equilibrium among contact ion pairs, solvent-separated ion pairs, and aggregate clusters in high-concentration electrolytes, which governs anion desolvation kinetics and co-intercalation propensity at the cathode interface, lacks established rational design principles and merits dedicated mechanistic study. Non-lithium DIB systems (Na, K, Al, Zn, Mg), while strategically vital from a resource standpoint, continue to suffer from lower operating voltages, inferior kinetics, and limited cycle life. Additionally, the fundamental role of solvation-shell reorganization during anion intercalation in these systems remains largely uncharacterized, representing a critical knowledge gap that warrants focused attention [40, 60, 61].

2.2. Chloride-ion batteries (CIBs)

CIBs are governed by conversion reactions at the metal anode (e.g. $\text{Li} + \text{Cl}^- \rightarrow \text{LiCl} + \text{e}^-$, or $\text{Sn} + 2\text{Cl}^- \rightarrow \text{SnCl}_2 + 2\text{e}^-$), where the anode metal undergoes oxidation. Cl^- itself does not change its valence state during cycling and functions exclusively as the shuttling species. Hence, the term ‘chloride shuttle battery’ is arguably more precise, though CIB remains the established convention in the literature. Beyond serving as a simple shuttle species, Cl^- confers several intrinsic advantages as a charge carrier: its anionic transport mechanism eliminates anode-side metal plating and dendrite formation entirely, while the multi-electron redox capability of metal chloride cathodes enables high volumetric capacities. The global abundance and low cost of chloride sources make CIBs particularly attractive from a resource and supply-chain perspective. With several anode–cathode combinations theoretically exceeding volumetric energy densities of $2\,000\text{ Wh L}^{-1}$, nearly twice that of commercial Li-ion batteries ($\sim 1\,015\text{ Wh L}^{-1}$) and the unrivaled elemental abundance and global availability of chlorine-containing materials, CIBs have attracted growing research interest as a cost-competitive, post-lithium electrochemical energy storage paradigm [62, 63].

2.2.1. Operating mechanism

The fundamental electrochemistry of CIBs is governed by conversion reactions at both electrodes. During discharge, the cathode material is reduced as Cl^- is released into the electrolyte, while the metal anode is oxidized to form its corresponding metal chloride. The general half-reactions can be expressed as:



The OCV of a CIB cell is determined by the difference in chlorine chemical potential between the anode and cathode, which can be approximated from the formation enthalpies of the corresponding metal chloride phases. A theoretical screening of over 1225 anode/cathode combinations from the Materials Project database identifies 18 pairings with thermodynamic volumetric energy densities exceeding 2000 Wh L^{-1} and 26 with gravimetric energy densities above 1000 Wh kg^{-1} , values that substantially outperform conventional Li-ion systems at $\sim 387\text{ Wh kg}^{-1}$ (theoretical electrode-pair basis; $250\text{--}300\text{ Wh kg}^{-1}$ at the practical cell level) [31, 68]. However, it is important to note that these are thermodynamic upper limits, and practical performance is strongly influenced by electrolyte compatibility, electrode kinetics, and interfacial stability [68].

2.2.2. Merits of CIBs

CIBs offer a combination of intrinsic advantages that distinguish them from both cation- and anion-based batteries. The elemental abundance and low cost of chloride-containing materials sourced from seawater, brine deposits, and mineral salts offer a compelling supply-chain advantage over lithium- and cobalt-dependent chemistries, with iron chloride cathode materials costing merely 1%–2% of conventional LIB cathode raw materials on a mass basis [62]. The anionic charge transport mechanism inherently precludes metal electrodeposition on the anode surface, thereby eliminating the risk of dendrite formation and the associated short-circuit failures that remain a persistent safety concern in lithium metal batteries. Furthermore, the high electronegativity and thermodynamic stability of Cl^- confer a wide electrochemical stability window, and the prospect of air-stable, non-flammable cell configurations using aqueous or SS electrolytes offers a substantial safety advantage over conventional organic-electrolyte systems. The multi-electron nature of conversion reactions, in which divalent and trivalent metal chlorides release two or three electrons per metal atom, enables theoretical gravimetric capacities that far exceed those achievable via single-electron intercalation [62, 68]. From a charge-carrier perspective, Cl^- is a large, polarizable anion with low charge density, which reduces its desolvation energy at

the electrode–electrolyte interface and facilitates insertion into host structures compared to hard, small cations such as Li^+ or Mg^{2+} that carry higher charge densities and stronger solvation shells [69–71].

2.2.3. Cathode materials

The rational design of cathode materials has been a central focus of CIB research, as cathode stability and Cl^- storage capacity are the primary determinants of practical cell performance. The earliest CIBs employed simple metal chloride cathodes such as CoCl_2 , VCl_3 , and BiCl_3 in IL electrolytes. Although these systems demonstrated proof-of-concept reversibility, their pronounced solubility in the electrolyte medium caused rapid capacity fade. BiCl_3 , for instance, delivered an initial discharge capacity of 140 mAh g^{-1} but lost more than half its capacity within three cycles [24].

To avoid cathode dissolution, metal oxychlorides such as FeOCl , BiOCl , and VOCl were introduced as structurally stabilized alternatives for cathodes [72]. In these layered compounds, metal cations are coordinated to strongly Lewis-basic O^{2-} anions, significantly reducing solubility while retaining electrochemical activity through a combination of conversion and minor intercalation processes. Among these, FeOCl has emerged as the most extensively studied candidate owing to its low toxicity, high theoretical specific capacity of 250 mAh g^{-1} , and wide availability [73, 74]. Nanoconfinement of FeOCl within mesoporous carbon frameworks (CMK-3) demonstrated a maximum discharge capacity of 202 mAh g^{-1} and a high reversible capacity of 162 mAh g^{-1} after 30 cycles, confirming that structural engineering at the nanoscale can effectively mitigate volume expansion during phase transitions [75]. VOCl has similarly shown promising performance, delivering an initial capacity of 189 mAh g^{-1} at 0.5 C in a $\text{VOCl}|\text{Li}$ cell, with PP_{14}^+ cation co-intercalation proposed to pre-expand the interlayer spacing and facilitate subsequent Cl^- uptake [76].

LDHs are another structurally distinct cathode class offering intercalation-type Cl^- storage in their interlayer galleries. CoFe-Cl LDH delivered a maximum capacity of 239.3 mAh g^{-1} and a high reversible capacity of $\approx 160 \text{ mAh g}^{-1}$ over 100 cycles, with interlayer crystal water proposed to buffer structural collapse during cycling [77]. Further advancement was achieved with NiMn-Cl LDH/CNT composites, which leveraged the conductive CNT backbone to overcome the intrinsically poor conductivity of LDHs, achieving an initial capacity of 284.7 mAh g^{-1} and retaining 130 mAh g^{-1} after 150 cycles with near-unity CE [78]. Integrating electrochemically inert Al into the NiFe-Cl LDH framework induces ‘lattice softening,’ which provides the structure with the elastic flexibility needed to withstand repeated volumetric changes during Cl^- intercalation. This defect-driven structural adaptability results in exceptional durability, maintaining a reversible capacity of 101.4 mAh g^{-1} over 1000 cycles at a high current density, with a near-perfect CE of 99.91% [79]. The XRD pattern, SEM morphology, and extended cycling stability of this NiFe-Cl LDH cathode are presented in figures 2(i)–(k).

Organic conductive polymers, including polypyrrole chloride (PP_yCl) and polyaniline (PANI), have also been shown to be lightweight and structurally flexible cathode materials [80, 81]. Cl^- -doped PP_y/CNT composites achieved a maximum discharge capacity of 118 mAh g^{-1} , and more than 90 mAh g^{-1} reversible capacity was retained after 40 cycles, with coordination of Cl^- to N-sites in the pyrrole backbone proposed as the storage mechanism [82]. Recently, polyxylylviologen chloride (PXVCl_2) composited with graphene delivered an improved discharge capacity of 175 mAh g^{-1} , highlighting the scope for molecular engineering of organic cathodes through increased active site density [83].

Expanding the perovskite electrode space, K_2SnCl_6 (KSC), an antifluorite-structured perovskite halide, was recently synthesized for the first time via a facile one-pot mechanochemical route and evaluated as a conversion-type cathode in a non-aqueous CIB with a lithium metal counter electrode (figures 2(g) and (h)) [63]. KSC delivered a high initial discharge capacity of 350 mAh g^{-1} . However, an irreversible conversion of KSC in the first cycle resulted in a significant capacity loss, which stabilized at a reversible capacity of 51 mAh g^{-1} after 50 cycles, with 85% capacity retention from the 50th to the 200th cycle. *Ex situ* XRD and XPS confirmed that the initial KSC phase does not reform upon charging; instead, the material permanently transforms into amorphous KCl , metallic Sn, and K-Sn alloy decomposition products, which act as the active material for the remainder of cycling. DFT calculations further supported these findings by mapping the full decomposition pathway as a function of electrode potential, revealing that structural irreversibility in this liquid electrolyte environment is the primary factor limiting long-term capacity retention in perovskite-type CIB cathodes [63].

2.2.4. Anode materials

Li metal remains the most prevalent anode in non-aqueous CIBs, valued for its high electrochemical potential and compatibility with ionic-liquid and fluorinated electrolyte systems. In a $\text{Li}|\text{FeOCl}$ cell, the anode reaction proceeds via $\text{Li} + \text{Cl}^- \rightarrow \text{LiCl} + \text{e}^-$. However, dissolution of LiCl into polar

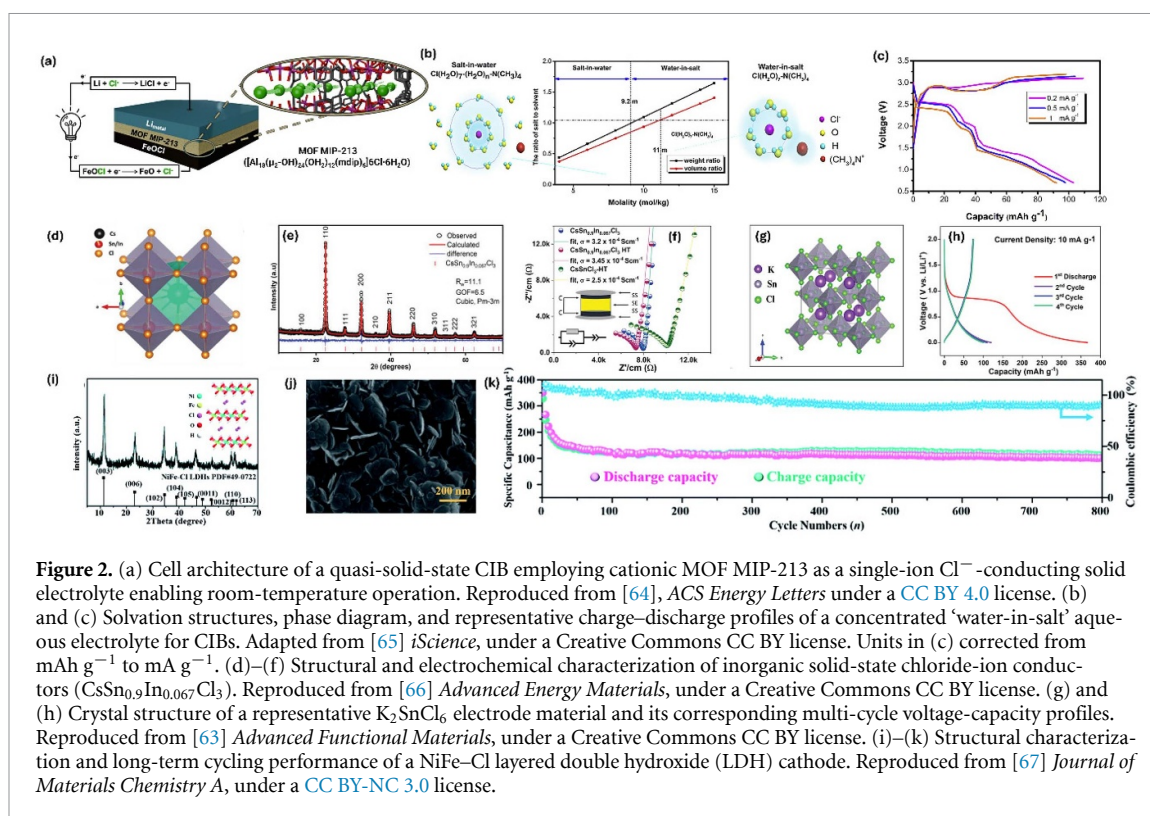


Figure 2. (a) Cell architecture of a quasi-solid-state CIB employing cationic MOF MIP-213 as a single-ion Cl^- -conducting solid electrolyte enabling room-temperature operation. Reproduced from [64], *ACS Energy Letters* under a CC BY 4.0 license. (b) and (c) Solvation structures, phase diagram, and representative charge-discharge profiles of a concentrated ‘water-in-salt’ aqueous electrolyte for CIBs. Adapted from [65] *iScience*, under a Creative Commons CC BY license. Units in (c) corrected from mAh g^{-1} to mA g^{-1} . (d)–(f) Structural and electrochemical characterization of inorganic solid-state chloride-ion conductors ($\text{CsSn}_{0.9}\text{In}_{0.067}\text{Cl}_3$). Reproduced from [66] *Advanced Energy Materials*, under a Creative Commons CC BY license. (g) and (h) Crystal structure of a representative K_2SnCl_6 electrode material and its corresponding multi-cycle voltage-capacity profiles. Reproduced from [63] *Advanced Functional Materials*, under a Creative Commons CC BY license. (i)–(k) Structural characterization and long-term cycling performance of a NiFe-Cl layered double hydroxide (LDH) cathode. Reproduced from [67] *Journal of Materials Chemistry A*, under a CC BY-NC 3.0 license.

solvents triggers parasitic Li^+ shuttling to the cathode, undermining reversibility. Fluorinated low-polarity co-solvents suppress LiCl solubility and promote a LiF -rich SEI that accommodates the $\sim 56.5\%$ volumetric expansion from Li to LiCl , enabling 85.2% capacity retention after 250 cycles and 68.3% after 500 cycles at 125 mA g^{-1} in quasi-SS HGPE configurations [84]. Tin (Sn) has emerged as one of the most actively studied anodes for ASS-CIBs, undergoing the reversible conversion $\text{Sn} + 2\text{Cl}^- \rightarrow \text{SnCl}_2 + 2\text{e}^-$. Its suitability is reinforced by the fact that SnCl_2 is itself a chloride-ion conductor, pairing naturally with inorganic solid electrolytes such as CsSnCl_3 -based perovskites [85]. The primary limitation of bulk Sn is poor material utilization and volumetric expansion upon SnCl_2 formation, which disrupts the critical solid–solid interface. Sn -carbon nanocomposite (Sn@NC) architectures embed nano- Sn in N-doped CMK-3, improving discharge capacity by $\sim 12\%$ over conventional Sn anodes while suppressing mechanical degradation [86]. Silver (Ag) is the most established anode for aqueous CIBs, operating through the highly reversible $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^-$ conversion, where the negligible solubility of AgCl inherently suppresses electrode dissolution. Paired with a BiOCl cathode in 1 M NaCl , Ag delivered 92.1 mAh g^{-1} at 400 mA g^{-1} with $\sim 99\%$ CE after 40 cycles and has been demonstrated in desalination cells, achieving 115 mg g^{-1} desalination capacity at a cell voltage as low as $\sim 200 \text{ mV}$ [87]. Despite its excellent reversibility, the high cost of Ag limits its large-scale applicability. In aqueous configurations, zinc (Zn) offers a lower-cost alternative, notable for its unique mechanism in which Cl^- interacts electrostatically with a transient $\text{Zn}^{\delta+}$ intermediate, rather than through formal bond formation. This enables highly reversible anode reactions, as confirmed by XRD and XPS. The lower electrochemical potential of Zn reduces the cell OCV to $\sim 0.8 \text{ V}$, an acceptable trade-off in cost- and safety-conscious aqueous formats [65]. Finally, Mg has been explored as a two-electron, earth-abundant anode alternative, although reports remain limited. Insulating MgCl_2 passivation layers and large volumetric expansion persistently disrupt electronic continuity. While a pre-discharged Mg/MgCl_2 composite strategy, analogous to the half-charged approach in FIBs, partially reduces the kinetic barrier for Cl^- migration, residual capacity decay limits Mg to a niche role in current CIB research [74].

2.2.5. Electrolyte development

The electrolyte is arguably the most consequential component in CIB design, as it must simultaneously provide sufficient Cl^- conductivity, electrochemical stability, and compatibility with electrode materials that are prone to dissolution. Early-stage CIBs exclusively employed binary IL electrolytes, combining a Cl^- -donor IL salt such as 1-methyl-3-octylimidazolium chloride ($[\text{OMIM}][\text{Cl}]$) or 1-butyl-1-methylpiperidinium chloride ($[\text{PP}_{14}][\text{Cl}]$) which serves as both the source of mobile Cl^- ions and the ionic medium with a non-chloride co-IL salt such as 1-butyl-3-methylimidazolium tetrafluoroborate

([BMIM][BF₄]) or 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide ([PP₁₄][TFSI]), the latter often dissolved in a molecular co-solvent such as propylene carbonate (PC) [24]. A secondary Cl[−]-donor component, such as a tetraalkylammonium chloride or the same Cl[−]-donor IL salt at a defined concentration, must be explicitly included to maintain a sufficient reservoir of free Cl[−] ions available for shuttling between electrodes during charge and discharge. Together, these components provide the necessary Cl[−] activity while maintaining a wide electrochemical window. Although these systems enabled the first demonstrations of reversible CIB operation, their high viscosity limits electrolyte infiltration into electrode pores, and their high cost and residual flammability are barriers to practical application.

Aqueous electrolytes offer an intrinsically safer and more cost-effective alternative, but the thermodynamic stability window of water (~1.23 V) traditionally limits cell voltage. This limitation was overcome with the water-in-salt strategy, in which highly concentrated tetramethylammonium chloride (CH₃)₄NCl solutions (up to 25 mol kg^{−1}) disrupt the hydrogen-bond network of bulk water and suppress the activity of free water molecules, expanding the electrochemical stability window to 3.1 V. Using this electrolyte, a Zn anode/graphene cathode CIB achieved a discharge plateau of ~2.6 V and a cycle life of 2 000 charge–discharge cycles, with 95 mAh g^{−1} of capacity retained, the longest cycle life reported in CIBs at the time. This performance was validated by comprehensive TEM, XPS, FTIR, and Raman spectroscopic characterization of reversible Cl[−] absorption/desorption in the carbon cathode. The solvation structure and phase diagram of this concentrated water-in-salt system are depicted in figure 2(b), and the corresponding galvanostatic charge–discharge profiles confirm stable electrochemical performance, as shown in figure 2(c) [65].

SS and quasi-SS electrolytes (QSSEs) represent the most advanced frontier in CIB research, addressing electrode dissolution and flammability simultaneously. Organic polymer electrolytes, notably ternary PEO–TBMACl–SN (polyethylene oxide–tributylmethylammonium chloride–succinonitrile) systems, enabled ASS Li|FeOCl CIBs delivering an initial capacity of 129.4 mAh g^{−1} at 323 K, with an electrochemical window of 4.24 V vs. Li⁺/Li [88]. A key mechanistic insight underpinning QSSE design came from Yang *et al* who demonstrated that halide-ion battery failure stems from dissolution of transition metals and elemental halogens from the positive electrode into the electrolyte. By combining fluorinated low-polarity solvents, a binary FDMA/HFE (1:1 v/v) mixture with TBMACl salt was gelled into an HGPE, which suppressed interfacial dissolution and yielded 210 mAh g^{−1} in a Li|FeOCl pouch cell. The cell exhibited ~80% capacity retention after 100 cycles at 25 °C. This design principle was further extended to fluoride- and bromide-ion cells [84].

A particularly notable recent advance was the first demonstration of a MOF as a single-ion QSSE for CIBs. The cationic Al-based MOF MIP-213 (Al₁₈(μ₂-OH)₂₄(OH)₂₁₂(mdip)₆·6Cl·6 H₂O) achieved a Cl[−] conductivity of 1.1 × 10^{−6} S cm^{−1} at 25 °C, with a low activation energy of 0.18 eV. It is also demonstrably non-flammable under direct flame exposure, and electrochemically stable up to 4.2 V vs. Li⁺/Li. The assembled Li|MIP-213|FeOCl full cell cycled stably for over 100 cycles, with CE exceeding 90% at RT, while post-mortem PXRD and SEM-EDX analysis confirmed complete structural integrity of the MOF framework and negligible cathode dissolution. These results establish MOF-based QSSEs as a transformative platform for addressing the long-standing dissolution and thermal instability challenges in CIB design. The non-flammable character and single-ion conduction of MIP-213 are schematically illustrated in figure 2(a) [64].

Among inorganic solid conductors, cubic-phase CsSnCl₃ perovskite exhibited a calculated ionic conductivity of 3.6 × 10^{−4} S cm^{−1} and an electrochemical window exceeding 6.1 V. However, achieving comparable performance experimentally and integrating it with electrode interfaces remain active challenges. A key obstacle is the intrinsic tendency of CsSnCl₃ to rapidly transform from the cubic to the monoclinic phase at RT. Stabilization has been pursued through B-site substitution with smaller-radius cations, notably Mn²⁺, Y³⁺ and In³⁺, which extend cubic phase stability [66, 85, 89]. As well as through alkali-ion doping strategies [90]. Complementarily, introducing excess Cl[−] to generate interstitial chloride defects has been shown to further enhance Cl[−] conductivity and improve structural stability in Bi/Cl dual-doped CsSnCl₃ analogs [91]. The structural and electrochemical characterization of these CsSn_{0.9}In_{0.067}Cl₃ (CSIC) SS conductors is captured in (figures 2(d)–(f)) [66]. Recent ASS-CIBs combining a VOCl cathode, CSIC solid electrolyte and an In-based anode show that cathode composite architecture, CSIC microstructure, electrode–electrolyte contact and applied stack pressure together govern the transport and reaction processes that enable high-capacity, long-life cycling [92].

2.2.6. Outstanding challenges and areas requiring further investigation

Despite considerable progress, several fundamental challenges must be addressed before practical CIB deployment can be realized. Cathode dissolution in liquid electrolytes remains the most critical

bottleneck, leading to irreversible loss of active material and rapid capacity fade. Although metal oxy-chlorides partially mitigate the dissolution issue, they exhibit generally lower theoretical capacities than simple metal chlorides (FeOCl at 250 mAh g^{-1} compared to FeCl_3 at 496 mAh g^{-1}) and the large volumetric strains accompanying their conversion and co-intercalation phase transformations nonetheless induce mechanical fracture over extended cycling. Developing cathode hosts with improved structural reversibility, alongside electrode architectures that accommodate repeated volume expansion without failure, remains a primary design priority.

While meaningful advances have been achieved across liquid, IL, and QSSE systems, the interfacial processes governing CIB operation remain poorly understood. The precise nature of Cl^- solvation, ion-pairing behavior, and electrochemical double-layer structure at cathode surfaces all warrant deeper systematic investigation. *Operando* spectroscopic and computational approaches will be essential for rationally guiding next-generation electrolyte designs that concurrently suppress dissolution, widen stability windows, and stabilize electrode interfaces.

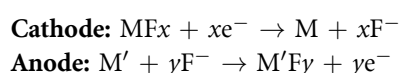
On the anode side, Sn has emerged as a promising low-cost alternative, yet other candidates, such as Ag and In, remain too expensive for large-scale applications. Li metal, while widely used, raises resource and safety concerns that conflict with the low-cost rationale of CIBs. Its chemical incompatibility with perovskite-based solid electrolytes, due to reductive interfacial decomposition, further limits stable high-voltage operation. Ultimately, bridging the significant gap between theoretical energy densities exceeding 2000 Wh L^{-1} and current modest practical performance will require concurrent progress across cathode reversibility, electrolyte design, and anode engineering. However, steady progress in the field suggests that this goal is realistically attainable with coordinated advances in these areas.

2.3. Fluoride-ion batteries (FIBs)

While the conversion mechanism of FIBs is formally analogous to that of CIBs, the significantly smaller ionic radius of F^- ($\approx 1.33 \text{ \AA}$ vs. $\approx 1.81 \text{ \AA}$ for Cl^-) [93], its higher electronegativity, and the greater thermodynamic stability of M–F bonds [26, 94] impose fundamentally different electrolyte requirements and failure modes, warranting dedicated treatment.

2.3.1. Working principle

FIBs are electrochemical cells that rely on the reversible shuttling of fluoride anions (F^-) between a metal fluoride cathode and a metallic anode through a fluoride ion-conducting electrolyte. Unlike LIBs, where electrons and cations travel in the same direction, FIBs drive F^- through the electrolyte and electrons through the external circuit in opposite directions. During discharge, the anodic metal is oxidized, combining with F^- from the electrolyte to form a metal fluoride, releasing electrons through the external circuit, while the cathode metal fluoride is simultaneously reduced to its metallic state, releasing F^- back into the electrolyte. These electrode reactions are:



The process is fully reversible upon charging. Because charge neutrality is maintained solely by F^- transport, no cationic species participate in the electrochemical cycle, a fundamental distinction from all alkali metal battery chemistries.

2.3.2. Why FIBs are promising

The appeal of FIBs stems from a combination of thermodynamic, resource, and safety considerations. Fluorine is the most electronegative element, and its low atomic mass (19 g mol^{-1}) combined with a high redox potential ($+2.87 \text{ V}$ vs. SHE) enables multi-electron conversion cathodes to achieve theoretical material-level volumetric energy densities approaching 5000 Wh L^{-1} , depending on the choice of fluoride cathode and metal anode. Techno-economic modeling of optimized liquid-cell FIBs projects a stack-level energy density of 588 Wh kg^{-1} and 1393 Wh L^{-1} , compared to $250\text{--}300 \text{ Wh kg}^{-1}$ and $700\text{--}1015 \text{ Wh L}^{-1}$ at the practical cell level for state-of-the-art LIBs [31, 95, 96]. Theoretical screening confirms that over 130 binary fluoride electrode combinations outperform LiCoO_2 -based systems in volumetric energy density [25]. From a resource perspective, fluorine is the 13th most abundant element in the Earth's crust, present at concentrations roughly 50 times that of lithium, and global annual production exceeds 3.5 million tonnes, dwarfing lithium output by nearly two orders of magnitude [97]. On safety grounds, molecular F_2 evolution is thermodynamically suppressed under normal operating conditions, eliminating the gas-driven thermal runaway characteristic of lithium metal cells, and the anionic shuttle mechanism significantly mitigates the risk of anode-side dendrite formation.

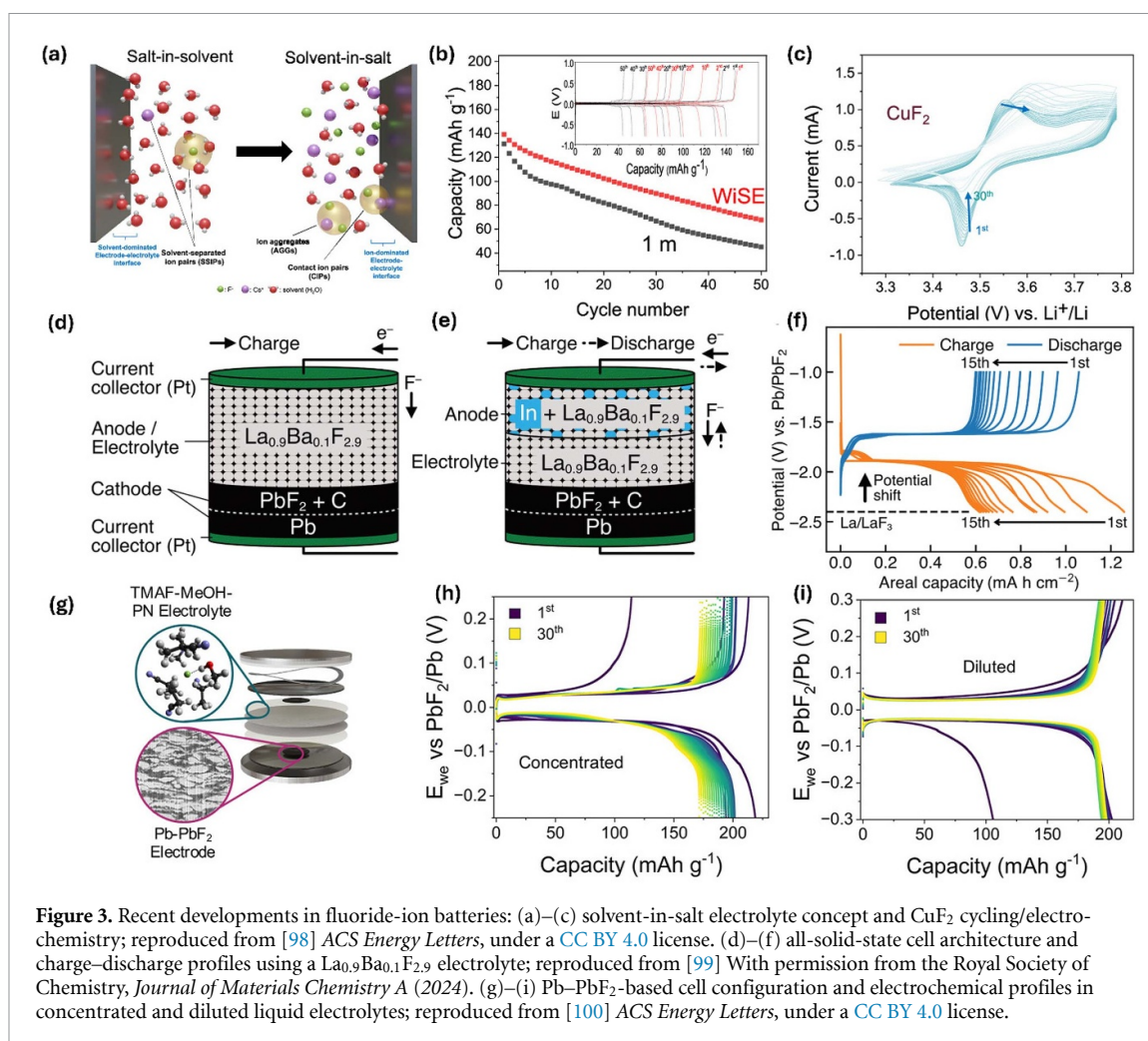
2.3.3. Electrode materials

Conversion-type cathodes have formed the foundation of FIB research since the earliest demonstrations. In our group's 2011 work (Reddy and Fichtner) [101], we demonstrated the first rechargeable ASS FIB at 150 °C, using BiF₃, CuF₂, SnF₂, and KBiF₄ as cathodes against a Ce metal anode, with La_{0.9}Ba_{0.1}F_{2.9} as the solid electrolyte [97, 102]. This study established the conversion reaction framework that subsequent work has built upon. Among these, CuF₂ remains the most energy-dense practical cathode with a redox potential of 3.54 V vs. Li/LiF and a theoretical specific capacity of 528 mAh g⁻¹, and near-theoretical reversible capacity was demonstrated in Cu thin-film cells at 150 °C. FeF₃ offers the highest theoretical capacity (713 mAh g⁻¹), with an experimentally achieved capacity of 579 mAh g⁻¹ during the first discharge cycle at 160 °C [103]. More recently, in 2025, Cu₃N was reported as a structurally distinct intercalation cathode: its anti-ReO₃ framework with linear N–Cu–N chains supports reversible incorporation of up to 6 F⁻ per formula unit, delivering a record capacity of approximately 550 mAh g⁻¹ with only about 5% volume change. *Operando* (x-ray absorption spectroscopy) and (resonant inelastic x-ray scattering) spectroscopy revealed the first nitrogen redox (N³⁻/N²⁻) charge compensation pathway observed in any FIB cathode, opening a new direction for multi-electron intercalation chemistry [104].

Intercalation-type cathodes based on Ruddlesden–Popper (RP) oxides with the general formula A_{n+1}B_nX_{3n+1} represent a structurally distinct and increasingly pursued direction, as F⁻ ions insert into the rock-salt interlayers with minimal disruption to the host lattice [97, 105]. Among these, LaSrMnO₄ stands out for its high fluoride uptake and substantially lower environmental footprint compared to Ni- and Co-based analogs. Its tetragonal structure (*I4/mmm*) accommodates F⁻ in the interlayer gaps of the (La/Sr)O sublattice, with fluorination proceeding stepwise: first forming LaSrMnO₄F₁ (*P4/nmm* symmetry) and then LaSrMnO₄F₂ upon full occupancy, restoring *I4/mmm* symmetry. A recent study by Mezzadra *et al* (2026) provided the first experimental visualization of F⁻ diffusion pathways in this material class using combined maximum entropy method (MEM) and Bond Valence Site Energy analysis of neutron powder diffraction data. Both approaches consistently identified F⁻ migration along the $\langle 100 \rangle / \langle 010 \rangle$ directions within the *ab*-plane via nearest-neighbor vacancy hopping, with no evidence of interlayer transport, confirming strictly two-dimensional F⁻ conduction. Molecular dynamics simulations on LaSrMnO₄F_{0.8} yielded an activation energy of 0.14 eV for this process, comparable to Li⁺ and Na⁺ diffusion in established layered electrode materials [106].

Critically, the same study revealed that oxygen over-stoichiometry in RP oxides, with experimental compositions as high as LaSrMnO₄₋₀₆ under standard synthesis conditions, significantly impairs F⁻ transport. In oxygen-rich compositions, three additional oxygen migration mechanisms emerge above 450 K. The most detrimental case involves F⁻ substituting at apical oxygen sites, while the displaced O²⁻ occupies the F⁻ conduction layer, directly blocking the hopping network. As a result, the F⁻ diffusion coefficient at 450 K falls from 8.12×10^{-8} cm² s⁻¹ in the stoichiometric material to 2.5×10^{-8} cm² s⁻¹ in LaSrMnO_{4.2}F_{0.8}, with the activation energy rising from 0.14 to 0.18 eV. These findings place precise oxygen stoichiometry control at the center of RP cathode design, with direct consequences for capacity utilization and rate capability in practical cells [106].

On the anode side, Mg/MgF₂ has been extensively studied, though the non-fluoride-conducting rutile structure of MgF₂ promotes rapid surface passivation and limits reversibility in most cell configurations. In earlier work from our group (Rongeat, Reddy, and Fichtner), Mg–MgF₂ composite anodes prepared in a semi-discharged state showed improved interfacial contact and partial reversibility with both Bi and Cu cathodes at 150 °C [26, 96]. CaF₂/Ca remains thermodynamically attractive, with a near-zero reduction potential, a theoretical capacity of 686.5 mAh g⁻¹, and only about 7% volume change, but suffers from a resistive passivation layer on the Ca surface [105]. LaF₃/La anodes, whose tysonite crystal structure is intrinsically F⁻ conducting, have shown the best practical results to date: thin-film La/LaF₃ cells delivered 820 mAh g⁻¹ at 150 °C and 350 mAh g⁻¹ at RT with 93.8% CE [105]. To further improve the stability of tysonite-based SS cells, composite anode designs have incorporated indium (In) with the La_{0.9}Ba_{0.1}F_{2.9} electrolyte (figures 3(d) and (e)) [99, 101]. This alloying approach upwardly shifts the anode operating potential by ~0.6 V vs. Pb/PbF₂, effectively preventing the detrimental reduction and decomposition of the solid electrolyte that typically occurs with bare La metal (figure 3(f)). Beyond Mg⁻, Ca, and La-based anodes, Pb/PbF₂ and Cu/CuF₂ couples have also served as important benchmark systems in FIB research. The Pb/PbF₂ redox couple is particularly attractive as a counter/reference electrode because Pb has a low melting point and PbF₂ exhibits comparatively favorable room-temperature fluoride-ion conductivity, enabling reliable conversion behavior and practical two-electrode coin-cell configurations. In parallel, Cu/CuF₂ remains one of the most intensively studied high-energy conversion couples. The practical reversibility of CuF₂ has recently been demonstrated even in bulk-type ASS



cells, underscoring its continuing importance as a model positive electrode for evaluating electrolyte and counter-electrode development [107].

2.3.4. Electrolyte development

Electrolytes are currently the most limiting component in FIBs because they govern usable temperature, power capability, and cycle life through their fluoride ion conductivity, electronic insulation, electrochemical stability window, and chemical compatibility with electrodes. Early solid electrolytes were aliovalently doped rare earth fluorides with tysonite or fluorite structure. Tysonite-type materials such as LaF_3 adopt a hexagonal structure ($P6_3/mcm$) with three distinct F^- sublattices that enable fast vacancy-mediated fluoride hopping, making them the predominantly employed solid electrolyte class in FIBs. Fluorite-type materials such as BaF_2 and CaF_2 share a simpler cubic ($Fm3m$) symmetry and conduct F^- via both vacancies and interstitials, but typically require heavier aliovalent doping or elevated temperatures to achieve comparable conductivities [95, 108]. Ba-doped LaF_3 ($\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$) can reach conductivities on the order of $10^{-4} \text{ S cm}^{-1}$ at 60°C – 160°C . For example, $\text{La}_{0.95}\text{Ba}_{0.05}\text{F}_{2.95}$ prepared by co-precipitation and sintering at 800°C [26, 109, 110]. Related tysonite compositions such as $\text{Ce}_{0.975}\text{Sr}_{0.025}\text{F}_{2.975}$ and $\text{Sm}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$ reach about $3 \times 10^{-4} \text{ S cm}^{-1}$ and $2.8 \times 10^{-5} \text{ S cm}^{-1}$ at RT [111, 112], respectively, showing that vacancy-rich rare-earth fluorides can support reasonably fast fluoride transport, although most cells still need elevated temperatures. Fluorite-type $\text{Ba}_{1-x}\text{La}_x\text{F}_{2+x}$ and $\text{Ba}_{1-x}\text{Sb}_x\text{F}_{2+x}$ give similar conductivities near $10^{-4} \text{ S cm}^{-1}$ at 160°C , with nanocrystalline pellets benefiting from enhanced grain boundary conduction compared with single crystals [113, 114].

A major step toward RT operation came from layered tin(II) fluorides. Tetragonal BaSnF_4 provides about $3.8 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C , and PbSnF_4 can reach roughly $1.8 \times 10^{-3} \text{ S cm}^{-1}$ after suitable processing [115–117]. These structures contain Sn^{2+} lone pairs that distort the fluoride sublattice and open low-energy migration pathways, but the Ba–Ba (or Pb–Pb) layers still act as partial barriers. Substituting Ba^{2+} with small amounts of Nd^{3+} , Ce^{3+} , Eu^{3+} , or Mn^{2+} weakens this blocking effect and introduces additional mobile fluoride, giving RT conductivities of about 2.7 – $5.8 \times 10^{-4} \text{ S cm}^{-1}$ for

compositions such as $\text{Ba}_{0.98}\text{Nd}_{0.02}\text{SnF}_{4.02}$, $\text{Ba}_{0.95}\text{Ce}_{0.05}\text{SnF}_{4.05}$, and $\text{Ba}_{0.96}\text{Mn}_{0.04}\text{SnF}_4$ with activation energies down to 0.15 eV [118–121]. All solid cells using these electrolytes with BiF_3 cathodes and Sn anodes can deliver initial discharge capacities above 120–170 mAh g⁻¹ at RT and maintain more than 70–100 mAh g⁻¹ for 20–30 cycles. Perovskite-type $\text{CsPb}_{0.9}\text{K}_{0.1}\text{F}_{2.9}$ is another important development, combining a RT conductivity near 1.2×10^{-3} S cm⁻¹ with a wide stability window. $\text{Ag}|\text{CsPb}_{0.9}\text{K}_{0.1}\text{F}_{2.9}|\text{Pb}/\text{PbF}_2$ cells show capacities around 140–150 mAh g⁻¹ over more than 70 cycles [122].

Mixed and composite electrolytes complement these single-phase systems. LaF_3 – PbF_2 composites such as $\text{LaF}_{30.4}\text{PbF}_{20.6}$ use both vacancies and interstitial fluoride pathways and reach approximately 2.78×10^{-4} S cm⁻¹ at 120 °C [123]. Composite membranes embedding $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ particles in polyethylene oxide give fluoride conductivities around 5.75×10^{-6} S cm⁻¹ at 90 °C but offer better interfacial contact and electrochemical stability windows close to 4.7 V versus Li^+/Li [124], which is useful for high-voltage operation. Polymer-rich gels such as PVA–borax–glycerol composites, have demonstrated promise as flexible fluoride-conducting matrices with good interfacial wetting [125, 126]. Among these, $\text{NH}_4\text{HF}_2/\text{PEO}$ – PbSnF_4 reaches about 10^{-3} – 10^{-4} S cm⁻¹ at 60 °C and has enabled $\text{CuF}_2||\text{Pb}/\text{PbF}_2$ cells cycling near 140 mAh g⁻¹ for 50 cycles at RT, showing that soft electrolytes can combine reasonable conductivity with good interfacial wetting [127].

Liquid electrolytes can achieve even higher conductivity, but must address fluoride salt solubility and stability against reduction and oxidation. The intrinsically low solubility of simple fluoride salts (e.g. KF, CsF) in aprotic organic solvents arises from their high lattice energies and the poor solvation of the small, hard F^- anion, which lacks the polarizability to form strong interactions with low-dielectric-constant organic media. Moreover, the strongly nucleophilic and basic character of free F^- promotes proton abstraction from protic functional groups and nucleophilic attack on electrophilic solvents, narrowing the choice of compatible organic media. In aprotic solvents, large organic cations reduce lattice energies and improve F^- solubility. Early liquid-electrolyte FIB studies employed tetrabutylammonium fluoride (TBAF) dissolved in tetrahydrofuran (THF) as a straightforward fluoride source. This system was used to demonstrate the first electrochemical fluorination of an oxide perovskite (ReO_3) [128] and to evaluate cathodes such as CsMnFeF_6 [129], owing to TBAF's relative stability and reasonable electrochemical window [130]. However, commercially available TBAF typically contains non-trivial amounts of water and HF, making it difficult to prepare fully anhydrous electrolytes. This limitation motivated the development of purpose-synthesized, fully anhydrous fluoride salts with bulkier organic cations [128, 129].

Neopentyl-substituted tetraalkylammonium fluoride, dissolved in bis (2,2,2-trifluoroethyl) ether, enables fluoride concentrations near 0.75 mol L⁻¹ and supports cycling of metal fluoride electrodes over a voltage range of 0–3.4 V vs Li/LiF [130]. Anion acceptor (AA)-assisted aprotic systems, such as organoborate Lewis acids (FBTmPhB, TPhBX) or the soft Lewis acid 6-thioguanine paired with CsF in glyme or DMSO span conductivities from roughly 0.2–2.4 mS cm⁻¹ at 25 °C, enabling reversible CuF_2 capacities up to ~380 mAh g⁻¹ over several tens of cycles at RT [131, 132]. A further advance was achieved by employing triphenylantimony chloride (TSbCl) as a novel AA in a CsF–DMSO electrolyte, forming so-called acceptor-multi-F states that minimize thermodynamic interfacial resistance and promote fluoride release at the electrode surface. The resulting CuF_2/Sn – SnF_2 full cell delivered a reversible capacity of 580 mAh g⁻¹ after 40 cycles at 100 mA g⁻¹, while the CuF_2/Pb half-cell sustained an average CE of 99.5% over 3700 cycles [133]. Fluorohydrogenate ionic liquids (FHILs) such as $[\text{C}_2\text{C}_1\text{im}][(\text{FH})_{2.3}\text{F}]$ ($\text{C}_2\text{C}_1\text{im}$ = 1-ethyl-3-methylimidazolium) FHIL containing electrolyte push conductivity to ~100 mS cm⁻¹ at 25 °C and yield CuF_2 first-cycle capacities near 517 mAh g⁻¹, but their narrow negative potential window, limited by hydrogen evolution and electrode reactivity still requires optimization before high-voltage FIBs can be fully realized [134].

Highly concentrated aqueous and protic formulations offer an alternative route. Water-in-salt electrolytes based on very high CsF or TMAF concentrations (up to about 37 mol kg⁻¹) provide electrochemical windows around 3 V and conductivities near 30 mS cm⁻¹ at RT, allowing reversible Pb/PbF_2 and CuF_2 cycling [98, 135]. This transition to a concentrated solvent-in-salt regime minimizes free solvent molecules through extensive ion aggregation (figure 3(a)). Consequently, this structural electrolyte shift significantly enhances capacity retention (figure 3(b)) and enables highly reversible CuF_2 conversion electrochemistry (figure 3(c)) [100]. However, their cathodic stability is currently insufficient for deep-reducing anodes, and the high viscosity and salt cost at such concentrations pose practical concerns. To mitigate these limitations, recent efforts have explored optimally diluted electrolytes, for example, a ternary TMAF–MeOH–PN system paired with a dry-cast Pb – PbF_2 counter electrode (figure 3(g)). Compared to the concentrated counterpart, which suffered from severe polarization and rapid capacity fade (figure 3(h)), the diluted system delivered stable cycling and high-capacity retention over 30 cycles

(figure 3(i)), demonstrating a viable pathway toward cost-effective liquid-state FIBs. Overall, the best inorganic solids now reach RT conductivities in the 10^{-4} – 10^{-3} S cm $^{-1}$ range, while liquid and gel systems approach or exceed millisiemens per centimeter. The remaining challenge is to combine this transport with broad stability windows and benign interfacial chemistry within cell configurations compatible with scalable fabrication.

2.3.5. Key challenges

Several interconnected problems must be addressed before FIBs can approach practical use. While suppression of F $_2$ evolution improves operational safety, HF generation via $F^- + H_2O \rightarrow HF + OH^-$ represents an equally critical concern. In non-aqueous liquid electrolytes, ppm-level moisture contamination generates corrosive HF that promotes metal fluoride cathode dissolution and irreversible interfacial decomposition [136]. In SS FIBs, moisture ingress during electrolyte synthesis introduces OH $^-$ substitution defects into the fluoride conductor lattice, reducing ionic conductivity and generating HF upon thermal processing [137]. Stringent anhydrous fabrication conditions are therefore indispensable across all electrolyte formats. Volume expansion during conversion reactions, 237% for Cu/CuF $_2$ and 311% for Fe/FeF $_3$, remains the primary cause of capacity fade in SS cells, leading to electrode pulverization and loss of contact with the electrolyte [102, 103]. For intercalation RP cathodes, oxygen overstoichiometry has now been identified as a subtle but consequential synthesis variable that must be actively controlled to preserve F $^-$ mobility [106]. Room-temperature solid electrolytes with conductivities above 1 mS cm $^{-1}$, the practical threshold for ambient operation, have not yet been demonstrated to have the chemical and mechanical stability needed for full-cell integration. Liquid electrolytes, though promising in optimized half-cell formats, remain constrained by the nucleophilicity of unsolvated F $^-$ in most organic solvents, making it difficult to simultaneously achieve high conductivity, a broad electrochemical stability window, and long-term chemical stability [138]. The electrode-electrolyte interface in both solid- and liquid-cell designs remains poorly characterized with respect to anion desolvation kinetics, interphase composition, and fluoride-ion charge-transfer mechanisms. *Operando* techniques capable of tracking structural changes and fluoride transport under real-world cycling conditions are still required. Techno-economic modeling projects that optimized liquid-cell FIBs could achieve stack-level energy densities of 588 Wh kg $^{-1}$ and 1 393 Wh L $^{-1}$ at materials costs below 20 kWh $^{-1}$, but reaching these targets demands coordinated progress across electrolyte chemistry, electrode architecture, and interfacial engineering [105, 138].

2.4. Bromide-ion batteries (BIBs)

BIBs extend the halide-ion shuttle concept to Br $^-$ as the active charge carrier, leveraging its high redox potential (1.065 V vs. SHE) and substantial theoretical capacity (335 mAh g $^{-1}$), while avoiding the toxicity of elemental bromine by operating exclusively via a Br $^-$ adsorption-desorption mechanism at carbon cathodes rather than conventional Br $_2$ /Br $^-$ redox. The first BIB used carbon black as the cathode and zinc foil as the anode in a non-aqueous NH $_4$ Br-ethylene glycol electrolyte, selected to suppress hydrogen and oxygen evolution reactions that degrade aqueous configurations. It delivered 175 mAh g $^{-1}$ at 2 A g $^{-1}$, with 141 mAh g $^{-1}$ retained after 3000 cycles. XPS and FTIR confirmed reversible C–Br bond formation on charging and complete Br $^-$ release on discharge [139].

In the SS configuration, Inoishi *et al* demonstrated the first all-SS BIB using a K-doped PbBr $_2$ electrolyte, a BiBr $_3$ cathode, and a Pb anode, achieving an initial discharge capacity of 157 mAh g $^{-1}$ (87% of the theoretical BiBr $_3$ capacity) and demonstrating reversible cycling over 10 cycles at 160 °C and 50 μ A cm $^{-2}$, with XPS confirming reversible Bi/BiBr $_3$ interconversion driven by the Br $^-$ shuttle. The theoretical energy density of a Mg/CuBr $_2$ cell reaches 429 Wh kg $^{-1}$ gravimetrically and 1728 Wh L $^{-1}$ volumetrically, roughly twice and three times the values of a standard lithium-ion battery, respectively. The low Young's modulus of bromide salts allows dense solid electrolyte pellets to be obtained by cold pressing alone, without sintering, a fabrication advantage not available in FIB processing. The water-in-salt strategy was introduced more recently to address Br $_2$ volatility in aqueous systems: in a 3 M AlCl $_3$ /1 M NH $_4$ Br electrolyte, Br $^-$ coordinates with AlCl $_3$ during charging to form AlCl $_3$ Br $^-$ complex ions that intercalate into graphite paper at 1.74 V, suppressing free Br $_2$ generation, expanding the electrochemical stability window from 2.11 V to 2.68 V, and enabling In $_2$ O $_3$ anode cells to retain 83.5% capacity over 500 cycles [140].

Despite these early demonstrations, BIBs remain the least mature among the anion-shuttle chemistries examined here. SS configurations are currently restricted to elevated temperatures ($\sim$ 160 °C), as PbBr $_2$ -based electrolytes exhibit insufficient room-temperature ionic conductivity, and interfacial resistance at the Pb electrode increases over extended cycling. Room-temperature Br $^-$ solid conductors beyond PbBr $_2$ have yet to be developed. The atomic-scale structure of the AlCl $_3$ Br $^-$ GIC

phase has not been characterized because *operando* diffraction measurements are entirely absent, thereby preventing rational cathode design. The mechanistic role of NH_4^+ in enabling metal anode reactions and the reasons why metals such as Al, Mg, Fe, and Ti show no electrochemical activity remain unexplained. Several areas require focused investigation. Room-temperature Br^- solid conductors beyond PbBr_2 have yet to be developed, and *operando* XRD and cryo-TEM characterization of AlCl_3Br^- graphite intercalation compound phases is still needed. Systematic anode material screening, alongside a mechanistic study of the NH_4^+ induction effect, represents a further priority. Finally, standardized reporting of full-cell energy density under realistic electrolyte-to-electrode mass ratios is essential for enabling meaningful comparisons across halide-ion battery systems [141].

2.5. Hydride-ion batteries (HIBs)

The hydride ion (H^-) represents a fundamentally distinct charge carrier for electrochemical energy storage, with a standard redox potential of -2.3 V vs. SHE, high polarizability, and a moderate ionic radius of 1.4 Å. H^- offers a greater electrochemical driving force than conventional cation carriers, and its anionic transport mechanism eliminates metallic dendrite formation. When paired with hydrogen-rich electrode materials NaAlH_4 (993 mAh g^{-1} theoretical), MgH_2 ($2\,037$ mAh g^{-1}), or LiH ($>3\,000$ mAh g^{-1}), HIBs offer a theoretical pathway to energy densities that substantially exceed those of state-of-the-art lithium-ion systems, drawing directly on six decades of thermodynamic hydrogen storage knowledge [15].

2.5.1. Solid electrolyte design and early demonstrations

The conceptual foundation of SS HIBs was established by Kobayashi *et al*, who demonstrated pure H^- conduction uncoupled from electron transport in K_2NiF_4 -type oxyhydrides of the $\text{La}_{2-x-y}\text{Sr}_{x+y}\text{LiH}_{1-x+y}\text{O}_{3-y}$ ($0 \leq x \leq 1$, $0 \leq y \leq 2$, $0 \leq x+y \leq 2$) series, achieving conductivities up to 2.1×10^{-4} S cm^{-1} at 590 K [142]. The all-SS $\text{Ti}|\text{o-LiH}_2\text{O}_3|\text{TiH}_2$ cell discharged at 300 °C with ~ 200 mAh g^{-1} , and synchrotron XRD confirmed reversible H^- -driven phase transformations at both electrodes. However, the elevated operating temperature and low room-temperature conductivity of these oxyhydrides, compounded by the intrinsic mixed ionic and electronic conductivity of rare-earth trihydrides that causes parasitic electron leakage, prevented room-temperature rechargeability for nearly a decade. A significant advance came from Zhang *et al*, who mechanically deformed LaH_3 to suppress its electronic conduction while preserving H^- mobility. This produced a superionic conductor with H^- conductivity of 10^{-2} S cm^{-1} at 40 °C, enabling the first primary room-temperature all-SS HIB discharge, though rechargeability remained undemonstrated [143].

2.5.2. Electrolyte strategies enabling room-temperature rechargeability

Full rechargeability at RT was reported in two independent studies advancing complementary electrolyte design philosophies. Cui *et al* developed a core-shell composite electrolyte, $3\text{CeH}_3@ \text{BaH}_2$, by ball milling CeH_3 with a conformal 2 nm BaH_2 coating. The resulting $\text{CeH}_3|\text{BaH}_2$ heterojunction exploits BaH_2 's wide bandgap (3.85 eV) to block electron transfer from the conducting CeH_3 core while preserving its fast H^- mobility. This yields an H^- conductivity exceeding 10^{-4} S cm^{-1} at 25 °C, an ionic transfer number of 0.99 , and electronic conductivity suppressed to 3.2×10^{-6} S cm^{-1} , with thermal stability confirmed over 200 h at 140 °C. The $\text{CeH}_2|3\text{CeH}_3\text{-BaH}_2|\text{NaAlH}_4$ full cell delivered an initial capacity of 984 mAh g^{-1} (99.1% of theoretical) and retained 402 mAh g^{-1} after 20 cycles at 25 °C. ^{27}Al NMR confirmed reversible NaAlH_4 to Na_3AlH_6 conversion at the cathode, and a stacked tandem cell demonstrated 1.9 V output, sufficient to power an LED [144].

Concurrently, Hirose *et al* reported the discovery of a structurally distinct superionic conductor, anti- β -AgI-type $\text{Ba}_{0.5}\text{Ca}_{0.35}\text{Na}_{0.15}\text{H}_{1.85}$, developed through systematic exploration of the pseudoternary $\text{BaH}_2\text{-CaH}_2\text{-NaH}$ compositional space. In this body-centered cubic ($Im3m$) framework, disordered cations occupy the $2a$ positions, and H^- undergoes three-dimensional conduction between face-sharing tetrahedral ($12d$) and octahedral ($6b$) sites, as established by neutron Rietveld refinement and molecular dynamics simulations. The material exhibits a total ionic conductivity of 2.1×10^{-5} S cm^{-1} at 25 °C, with electronic conductivity of only 1.3×10^{-9} S cm^{-1} , and an electrochemical stability window spanning -0.13 to $+0.53$ V vs. $\text{Ti}|\text{TiH}_2$, enabling compatibility with a wide range of metal-hydride electrodes. ASS TiH_2 cells cycled reversibly at 84% of theoretical capacity over 10 cycles at 60 °C, while MgH_2 cells achieved a reversible capacity of $2\,030$ mAh g^{-1} at 90 °C, corresponding to full two-electron Mg/MgH_2 cycling, as confirmed by ex situ XRD, the highest reversible capacity reported for any SS hydride cell to date. The same platform further enabled a $\text{Mg}|\text{H}_2$ hydrogen storage device, achieving 7.7 wt% gravimetric capacity at 90 °C, surpassing conventional thermodynamic and proton-driven liquid-electrolyte storage methods [16].

2.5.3. Persisting challenges and future directions

Despite these advances, HIB technology remains in its early stages of development. Capacity retention in the $3\text{CeH}_3\cdot\text{BaH}_2$ system is limited by the incomplete reversibility of the NaAlH_4 cathode and CeH_2 anode reactions. Electrochemical modeling showed that monotonic growth of interfacial resistance reduces delivered capacity from $\sim 0.43\text{ Ah m}^{-2}$ in the first cycle to $\sim 0.19\text{ Ah m}^{-2}$ by the 50th cycle, identifying electrode-electrolyte interfacial stability as the primary lifetime-limiting factor. In the $\text{Ba}_{0.5}\text{Ca}_{0.35}\text{Na}_{0.15}\text{H}_{1.85}$ system, hydrogen crossover through incompletely densified electrolyte pellets complicates mechanistic separation of electrochemical and thermochemical hydrogenation pathways, necessitating further advances in electrolyte densification and cell engineering. The strict requirement for inert-atmosphere fabrication and the cost of cerium extraction impose additional scalability constraints. Nevertheless, the two complementary electrolyte design strategies now establish nanoscale heterostructure engineering to decouple ionic and electronic transport and intrinsic superionic structure design through compositional disorder in the anti- β -AgI framework, defining a rich and rapidly expanding materials space that positions HIBs as a scientifically compelling and potentially transformative complement to existing battery chemistries for high-energy, dendrite-free energy storage [144, 145].

2.6. Other emerging anion-shuttle systems

Beyond the four principal anion-shuttle families discussed above, several structurally and chemically distinct anion-based electrochemistries have been reported, each occupying a unique position within the broader mechanistic landscape of anionic charge transport in solid and liquid-phase systems.

2.6.1. Polyiodide redox batteries

Aqueous zinc-iodine batteries (ZIBs) belong to the anion-shuttle paradigm because the charge-carrying species are iodine-derived anions I^- , I_3^- , and higher-order polyiodides that shuttle between electrode and electrolyte phases during cycling, rather than metal cations migrating through the cell. This places ZIBs in direct conceptual alignment with the systems discussed in this article, with the distinguishing feature that anion transport occurs through solvation-mediated dissolution rather than SS lattice diffusion [146].

Two redox pathways are accessible in ZIBs. The two-electron I_2/I^- conversion (2e-ZIBs) operates at $\sim 1.28\text{ V}$ vs. Zn^{2+}/Zn , delivering 211 mAh g^{-1} and $\sim 290\text{ Wh kg}^{-1}$. The four-electron $\text{I}^+/\text{I}_2/\text{I}^-$ pathway (4e-ZIBs) additionally exploits the I^+/I_2 couple at $\sim 1.8\text{ V}$, doubling the theoretical capacity to 422 mAh g^{-1} and raising the energy density to 630 Wh kg^{-1} . In 2e-ZIBs, I_3^- formed by comproportionation ($\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$) migrates to the zinc anode and undergoes spontaneous reduction ($\text{I}_3^- + \text{Zn} \rightarrow \text{Zn}^{2+} + 3\text{I}^-$), causing irreversible iodine loss and Zn passivation. In 4e-ZIBs, I^+ interhalogen intermediates (ICl , IBr_2^-) are also susceptible to hydrolysis via nucleophilic attack by water, forming hypoiodous acid (HOI), which disproportionates irreversibly to I_2 and O_2 , fundamentally undermining reversibility [146].

Three mitigation strategies have been developed. In electrolyte engineering, highly concentrated $\text{ZnCl}_2/\text{LiCl}/\text{acetonitrile}$ electrolytes (19 M/19 M/8 M) provide abundant Cl^- to catalyze I^+ stabilization through interhalogen complex formation while suppressing hydrolysis by reducing water activity, yielding 594 mAh g^{-1} and 6 000 cycles at 2 A g^{-1} [147]. Eutectic electrolytes based on ZnSO_4 -choline chloride-glycerol extend this to 15 000 cycles by coupling iodophilic choline interactions with disruption of free-water hydrogen bonding [148]. In spatially confined catalysis, single-atom Fe catalysts with Fe-N_4 coordination sites suppress I^+ hydrolysis through p - p orbital coupling with iodine species while accelerating interhalide electron transfer via d - p hybridization, achieving near-unity CE over 10 000 cycles [149]. Coordination structure cathodes, including metal-halide perovskites ($\text{ABX}_3/\text{A}_2\text{BX}_4$; A = alkylammonium, diammonium cations; B = Pb^{2+} , Bi^{3+} , Sn^{2+} ; X = I^- , Br^-) and quaternary ammonium-iodine complexes, physically confine iodine intermediates through lattice coordination and electrostatic interactions, as demonstrated in ODASnI_4 and BADBiI_4 cathode architectures [150, 151].

Key mechanistic questions remain open: the precise speciation of I^+ complexes (ICl vs. ICl_2^- vs. I_2Br^-) under operating conditions is unresolved, and the cross-parasitic reaction between the two redox pathways wherein incomplete I_3^- conversion quenches I^+ species generated during 4e charging has not been addressed by any single strategy to date [146, 152].

2.6.2. Oxyanion-based anion-shuttle systems: perchlorate, sulfate, and nitrate

The preceding sections focused on anion intercalation in non-aqueous DIBs, where fluorinated anions such as PF_6^- , TFSI^- , and FSI^- dominate. A distinct and growing body of work has since explored oxyanions, including ClO_4^- , HSO_4^- , and NO_3^- , as charge carriers in fully aqueous configurations. These systems warrant separate treatment because they deviate from classical DIB design principles in

two important respects: the electrolyte is water-based, introducing OER as an ever-present parasitic competitor at high cathode potentials, and some oxyanion chemistries operate via insertion into transition metal oxide hosts rather than graphite, thereby expanding the cathode design space beyond carbon. Their practical appeal lies in the natural abundance, low toxicity, and low cost of the parent salts. However, a shared thermodynamic constraint governs their behavior. The intercalation potential of oxyanions into graphite scales inversely with gallery height ($\propto 1/d_i$), placing it in direct conflict with OER in aqueous media [153].

Among these, ClO_4^- has been most extensively studied owing to its chaotropic character and low hydration enthalpy (-229 kJ mol^{-1}). In a standard NaClO_4 electrolyte, OER competition suppresses CE to only 21%, a fundamental barrier that was addressed through a decoupled Zn-graphite battery (DAZIB) architecture in which an acidic ClO_4^- catholyte is separated from a neutral Zn anolyte by an ion-selective membrane, kinetically retarding OER while protecting the zinc anode. DFT calculations confirmed a low in-plane diffusion barrier of 0.093 eV within the graphite galleries, and *in situ* XRD captured reversible GIC formation through a shift of the (002) Bragg reflection from 26.14° to 24.13° upon full intercalation, partially recovering to 25.90° on discharge. Raman spectroscopy provided corroborating evidence through G-band splitting into $\text{E}_{2g}(\text{i})$ and $\text{E}_{2g}(\text{b})$ components, the hallmark signature of staged intercalation. This configuration delivered 231 Wh kg^{-1} with 81% capacity retention after 600 cycles. In an alternative approach, a 15 m $\text{Al}(\text{ClO}_4)_3$ WISE expanded the electrochemical stability window to 4.0 V, enabling greater than 95% CE over 2 000 cycles in HOPG half-cells, with *operando* XRD confirming a mixed stage-4/stage-5 GIC (graphite intercalation compound) with a gallery height of $7.08 \text{ \AA}$ [154, 155].

HSO_4^- intercalation into graphite, despite its discovery in 1938, was only recently shown to be electrochemically competitive for energy storage. In 17 M H_2SO_4 , where four distinct intercalation stages are fully resolved, free-standing natural graphite electrodes delivered 81 mAh g^{-1} corresponding to $\text{C}_{20}\text{HSO}_4^-$ stoichiometry, exceeding the $\text{C}_{24}\text{HSO}_4^-$ reported for HOPG (highly oriented pyrolytic graphite) due to superior edge-plane accessibility in randomly oriented graphite particles. PITT (potentiostatic intermittent titration technique) analysis revealed diffusion coefficients of approximately $10^{-12} \text{ cm}^2 \text{ s}^{-1}$, an order of magnitude faster than PF_6^- intercalation at $10^{-13} \text{ cm}^2 \text{ s}^{-1}$, while ^1H MAS NMR (magic-angle spinning NMR) directly confirmed the presence of intercalated HSO_4^- and co-inserted H_2SO_4 molecules within the charged graphite bulk. The system demonstrated less than 5% capacity fading after more than 1 200 cycles at 10 C with greater than 97% CE at 1 C. The proton released into solution during HSO_4^- intercalation directly inspired pairing the graphite cathode with a Ti_3C_2 MXene anode, exploiting proton pseudocapacitance in the same 17 M H_2SO_4 electrolyte. This full dual-ion cell achieved a 1.5 V potential window and 35 mWh g^{-1} energy density, the highest reported for any aqueous asymmetric MXene-based system [156].

NO_3^- follows a mechanistically distinct pathway, operating through insertion into transition metal oxide hosts rather than graphite. Reversible NO_3^- insertion into spinel Mn_3O_4 in 1 M NH_4NO_3 was confirmed by a comprehensive characterization suite including TGA, FTIR, x-ray absorption near-edge structure (XANES), extended x-ray absorption fine structure (EXAFS), electrochemical quartz crystal microbalance (EQCM), and HRTEM, with the latter revealing local de-crystallization of the Mn_3O_4 lattice and anion storage in defect and amorphous nanoregions rather than ordered intercalation sites. Capacity rose from 114 mAh g^{-1} at the 3rd cycle to a maximum of 183 mAh g^{-1} at the 7th cycle upon structural activation, with 75% of the charge storage non-diffusion-controlled, indicating a predominantly capacitive mechanism. Significant self-discharge, with only 75% capacity retained after 24 h of open-circuit rest, however, remains a practical limitation requiring further investigation [157].

Collectively, these oxyanion systems demonstrate that aqueous DIB chemistries beyond fluorinated anions are electrochemically viable, yet advancing them toward practical devices requires either advanced electrolyte engineering, such as WISE formulations and decoupled cell architectures, or host-material innovation to circumvent the fundamental OER competition inherent in high-potential aqueous operation. Addressing these challenges through rational electrode and electrolyte co-design will be critical to realizing the full potential of this emerging class of aqueous energy storage systems [153].

The preceding sections (2.1–2.6) have individually examined the charge-transfer mechanisms, electrode and electrolyte materials, and outstanding challenges of each anion-shuttle chemistry. Table 1 provides a consolidated cross-chemistry comparison of the six principal systems: DIB, CIB, FIB, HIB, BIB, and polyiodide-shuttle batteries, covering representative electrochemical metrics, dominant materials challenges, and prospective application domains. The additional systems discussed in section 2.6, including oxyanion and mixed-anion configurations, are not included in table 1 given the limited number of primary reports currently available for those chemistries. The range of development stages and cycling

Table 1. Comparative overview of the key properties and performance metrics of the six anion-shuttle battery chemistries discussed in this Perspective.

	DIB	CIB	FIB	HIB	BIB	Polyiodide
Charge Carrier	PF ₆ [−] /FSI [−] /BF ₄ [−] (cathode); Li ⁺ /Na ⁺ /K ⁺ /Al ³⁺ (anode)	Cl [−]	F [−]	H [−] (solid-state only)	Br [−]	I [−] /I ₃ [−] /I ₅ [−]
Mechanism	Staged anion intercalation (AGIC) at graphite cathode; Cation insertion/deposition at anode	Conversion, displacement, and intercalation at metal chloride/oxychloride/LDH cathodes	Conversion, displacement, stepwise defluorination, and F [−] intercalation (host-dependent)	Vacancy-mediated H [−] hopping in superionic SS conductors	Br [−] adsorption/conversion at carbon cathode; Complex anion intercalation into graphite (aq.)	I [−] ↔ I ₃ [−] ↔ I ₅ [−] redox cascade; 2e [−] or 4e [−] pathway (condition-dependent)
Voltage Window ^a	~4.5–5.2 V vs. Li/Li ⁺ (Li/Al-graphite, organic); ~4.7 V (K-graphite, FSI [−]); ~2.0 V (Zn-graphite, aq.)	~2.6 V (Zn-graphene, WISE aq.); ~1.0–2.7 V (Li-VOCl, IL); ~4.24 V vs. Li/Li ⁺ (Li-FeOCl, PEO-based SSE)	~3.54 V vs. Li/LiF (CuF ₂ , SS, >150 °C); 0–3.4 V vs. Li/LiF (CuF ₂ /Sn, RT liquid, TSbCl ₃) [133]; ~1.2–1.5 V vs. Pb/PbF ₂ (La-BiF ₃ , SS, 150 °C) [158]	~1.9 V (CeH ₃ @BaH ₂ -NaAlH ₄ , SS, 25 °C, tandem); ~1.0–2.3 V (all-SS; electrode pair-dependent); ~0.5–1.0 V (TiH ₂ -La, SS, >300 °C)	~1.7 V (C-Zn, non-aq., NHBrEG); ~2.1–2.7 V (graphite-In ₂ O ₃ , WISE aq., AlClBr complex) [141];	~1.28 V (2e [−] , aq. Zn-I ₂ , I [−] /I ₃ [−]); ~1.8 V (4e [−] , aq. Zn-I ₂ , I [−] /IO ₃ [−]) [147, 159]; ~2.9–3.5 V (org. Li-I ₂) [160]
Capacity/Energy ^b	• 220 Wh kg^{−1} [full-cell] [32]; • 240 mAh g^{−1} [electrode, N-doped graphite] [47];	• 285 mAh g^{−1} [electrode, NiMn-Cl LDH] [78]; • 210 mAh g^{−1} [full-cell, pouch] [84];	• 580 mAh g^{−1} [full-cell, RT, CuF₂/Sn] [133]; • 579 mAh g^{−1} [electrode, 160 °C, FeF₃] [103]; • 588 Wh kg^{−1} [stack-level projection] [135]	• 984 mAh g^{−1} [electrode, 25 °C, CeH₃@BaH₂] [144]; • 2,030 mAh g^{−1} [electrode, 90 °C, MgH₂] [16]	• 157 mAh g^{−1} initial (Bi-BiBr₃, SS, 160 °C) [139] • 175 mAh g^{−1} [electrode, non-aq.] [141]	• 211 mAh g^{−1} [electrode, 2e[−], aq.]; • 422 mAh g^{−1} [theoretical, 4e[−]] [159]
Cycle Life ^c	• 10000 cycles/80.6% (SDIB, 10 C) [44]; • 99.1% CE/3,500 cycles (Li-graphite) [28]	• 2000 cycles/95 mAh g^{−1} (WISE aq.) [65]; • 1,000 cycles/99.91% CE (NiFe-Al LDH) [79]; • 100 cycles (pouch cell, RT) [84]	• 3700 cycles/99.5% avg. CE (CuF₂/Pb, RT half-cell) [133]; • 40 cycles/580 mAh g^{−1} (CuF₂/Sn, RT full-cell) [133]	• 20 cycles/~41% retained (CeH₃@BaH₂, 25 °C) [144]	• 3000 cycles/141 mAh g^{−1} (non-aq.)¹; • 500 cycles/83.5% (WISE aq.) [141]	• 10 000 cycles/92% capacity retention (aq. Zn-I₂, 4e[−]) [161]

(Continued.)

Table 1. (Continued.)

	DIB	CIB	FIB	HIB	BIB	Polyiodide
Dominant Bottleneck	• Electrolyte loading $\geq 13 \text{ g Ah}^{-1}$ constrains full-cell energy density; • CEI on graphite cathode poorly understood and mechanically fragile; • Solvent co-intercalation above 4.5 V reported in most systems	• Cathode dissolution in liquid/IL electrolytes is the primary failure mode; • Li anode shows limited compatibility with perovskite SSEs; • Cl^- interfacial dynamics largely uncharacterised	• Large F^- desolvation penalty limits RT liquid-electrolyte operation • RT SS cells demonstrated but interfacial resistance and cycle life remain critical • Moisture sensitivity raises HF generation concerns	• Practically useful RT H^- conductor not yet demonstrated; • Solid–solid interfaces generate space-charge layers; • Cycle life critically limited in all reported formats	• Br_2 evolution during charging requires active suppression; • Br^- crossover reported to reduce CE; • Cross-study comparison limited by absence of standardised full-cell protocol	• Soluble $\text{I}_3^-/\text{I}_5^-$ reported to migrate through separator causing active-material loss; • Low aq. operating voltage (~ 1.0–1.4 V) limits cell-level energy density; • Iodine redistribution under prolonged cycling observed
Development Stage	Most advanced; full-cell and pouch-cell formats demonstrated	Full-cell and pouch-cell demonstrated (RT, HGPE) [84]	RT pouch cell demonstrated (2024) [133]; RT full-cell 580 mAh g^{-1}	First RT all-SS demonstration (2025) [144];	Non-aq. and WISE aq. full-cells demonstrated [141]; SS at 160°C ; no pouch-cell reported	Aq. Zn– I_2 most mature; soft-pack formats explored [162]
Prospective Application	• Fast-charge buffer; • grid frequency regulation; • Li-free stationary storage	• Long-duration stationary storage; • Desalination-coupled systems	• Thermally stable all-SS systems; • Downhole/geothermal energy sources	• Dual-function storage + H_2 release (emerging); • High-T SS niche	• Zn–Br_2 flow battery architecture; • Cost-driven grid storage	• Aqueous grid-scale storage; • Seawater-compatible systems

^aVoltage windows are approximate galvanostatic operating ranges under stated electrolyte and temperature conditions. All FIB SS voltages are vs. Pb/PbF_2 unless stated; RT entries refer to BaSnF_4 or PbSnF_4 -based cells (25°C); entries marked $>150^\circ\text{C}$ employ tysonite-type electrolytes.

^bCapacity/energy values are electrode-level unless explicitly stated as full-cell or stack-level.

^cCycle life refers to galvanostatic cycling unless otherwise indicated.

stabilities reflected in table 1 shows that these six chemistries are not in direct competition but address distinct application requirements and occupy different positions on the maturity scale.

3. Conclusions and outlook

ASBs are not yet mature systems, and this Perspective has not attempted to obscure that reality. Electrolytes remain at the frontier of materials discovery, and electrode interfaces remain poorly characterized with respect to anion desolvation kinetics, interphase composition, and charge-transfer mechanisms. The gap between thermodynamic projections and practical cycling performance remains substantial across all chemistries examined here. The inversion of charge-carrier identity is not an incremental refinement of existing chemistry but a mechanistic reorientation that removes entire classes of failure: dendrite nucleation is structurally suppressed, thermal-runaway pathways are narrowed, and the accessible electrode-material space expands far beyond conventional intercalation frameworks. The resource profiles of chloride, fluoride, and hydride chemistries further decouple energy storage capacity from the supply-chain vulnerabilities that increasingly constrain critical-mineral-dependent technologies. Room-temperature All-SS hydride cells have now been demonstrated using superionic complex-hydride electrolytes. Acceptor-engineered fluoride electrolytes have enabled near-unity CE over thousands of cycles. Dual-ion architectures, by exploiting simultaneous anionic and cationic intercalation across decoupled redox couples, have unlocked operating voltages inaccessible to conventional single-ion chemistries, while purpose-designed SS conductors are now demonstrating meaningful suppression of the electrode dissolution that has historically limited halide-ion battery cycle life. Together, these developments signal that the field is passing through its formative period of growth. The natural domain of these systems encompasses long-duration grid storage, high-temperature and harsh-environment operation, and cost-sensitive applications. In these settings, the unique attributes of anionic charge transfer offer advantages that no existing chemistry can replicate. The fundamentals of anion-shuttle chemistry are sound, and the development trajectory is clear. The central question is no longer whether these chemistries will establish themselves as a significant class of electrochemical energy storage. It is how rapidly coordinated progress in electrolyte design, interfacial characterization, and electrode engineering can close the gap between what thermodynamics permits and what technology currently delivers.

Within this landscape, chloride-ion batteries (including aqueous and solid/quasi-solid implementations), polyiodide-shuttle systems, and lithium-free DIB systems based on earth-abundant elements emerge as particularly attractive candidates for low-cost, long-duration stationary storage and grid services, because they can leverage inexpensive active materials and, in many cases, non-flammable electrolytes. By contrast, solid-state fluoride- and hydride-ion batteries, which intrinsically employ thermally stable solid electrolytes, are more naturally aligned with high-temperature and harsh-environment applications, provided that remaining challenges in interfacial stability and mechanical robustness can be resolved.

Looking forward, several chemistry-specific research priorities emerge from this Perspective. For DIBs, rational electrolyte and additive design that yields thin, ionically conductive and mechanically robust CEI layers, while reducing the mandatory electrolyte excess, is central to translating electrode-level metrics into competitive full-cell performance. For CIBs, suppressing cathode dissolution in aqueous, IL, and SS media without sacrificing chloride-transport kinetics remains the decisive challenge. For FIBs and HIBs, the key bottlenecks are achieving higher room-temperature anion conductivity and lower interfacial resistance in solid electrolytes, together with mitigating chemo-mechanical degradation at solid–solid interfaces under cycling. Across all anion-shuttle chemistries, there is a pressing need for standardized full-cell testing protocols that incorporate realistic electrolyte-to-electrode ratios and cycle-life benchmarks, enabling meaningful comparison with incumbent Li-ion technologies.

Acknowledgment

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy—EXC 2154—Project ID 390874152 (POLiS Cluster of Excellence). This work was part of the US-German joint collaboration on 'Interfaces and Interphases in Rechargeable Li-Metal Based Batteries: Cathode/Solid Electrolyte (CatSE and CatSE2)' supported by the US Department of Energy (DOE) and the German Federal Ministry of Education and Research (BMBF). Financial support from the BMBF under Grant Number 03XP0223 A to E,

3XP0510 A to E, and DOE under the Grant Numbers DE-ACO5-000R22275, DE-EE0008858 and DE-AC02-06CH11357 is acknowledged.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Soutam Panja  0009-0007-6479-1701

Jagjit Nanda  0000-0002-6875-0057

Maximilian Fichtner  0000-0002-7127-1823

Ahamed Irshad  0000-0001-7107-9623

References

- [1] Chen Y *et al* 2021 A review of lithium-ion battery safety concerns: the issues, strategies, and testing standards *J. Energy Chem.* **59** 83–99
- [2] Tarascon J-M and Armand M 2001 Issues and challenges facing rechargeable lithium batteries *Nature* **414** 359–67
- [3] Palacin M R *et al* 2024 Roadmap on multivalent batteries *J. Phys. Energy* **6** 031501
- [4] Jeschull F, Hub C, Kolesnikov T I, Sundermann D, Hernández G, Voll D, Mindemark J and Théato P 2024 Multivalent cation transport in polymer electrolytes—reflections on an old problem *Adv. Energy Mater.* **14** 2302745
- [5] Janek J and Zeier W G 2016 A solid future for battery development *Nat. Energy* **1** 16141
- [6] Shao Y, Pang B, Bird L, Robinson J B and Shearing P R 2026 Contemporary trends in lithium-sulfur battery design: a comparative review of liquid, quasi-solid, and all-solid-state architectures and mechanisms *Adv. Energy Mater.* **16** e03239
- [7] Dong S, Tang L, Cheng C, Li Q, Duan C, Chen Z, Xiang Q, Yu X, Liang X and Liu J 2025 Stability challenges and solutions in aprotic lithium–air batteries: review of electrolyte and electrode instabilities *ACS Appl. Energy Mater.* **8** 14947–70
- [8] Olabi A G *et al* 2021 Metal-air batteries—a review *Energies* **14** 7373
- [9] Qiu X, Liu H, Duan Y, Wu M, Li Y, Wang X, Nan C-W and Fan L-Z 2025 Designing high-performance dual-ion batteries: insights into electrode, electrolyte, and interface engineering *Adv. Energy Mater.* **15** 2501016
- [10] Ghosh S, Bhattacharjee U, Patchaiyappan S, Nanda J, Dudney N J and Martha S K 2021 Multifunctional utilization of pitch-coated carbon fibers in lithium-based rechargeable batteries *Adv. Energy Mater.* **11** 2100135
- [11] Ghosh S, Nihad MP, Muduli S, Bhowmik S and Martha S K 2023 Optimizing anion storage performances of graphite/ non-graphitic carbon composites as cathodes for dual-ion batteries *Electrochim. Acta* **441** 141754
- [12] Chen S, Wu L, Liu Y, Zhou P, An Q and Mai L 2024 Chloride ion battery: a new emerged electrochemical system for next-generation energy storage *J. Energy Chem.* **88** 154–68
- [13] Zou P, Yu K and Lin R 2024 Toward practical fluoride-ion batteries: a review and perspective on liquid electrolyte development *ACS Mater. Lett.* **6** 4526–32
- [14] Chen H, Li X, Fang K, Wang H, Ning J and Hu Y 2023 Aqueous zinc-iodine batteries: from electrochemistry to energy storage mechanism *Adv. Energy Mater.* **13** 2302187
- [15] Cui J, Cao H and Chen P 2025 Hydride-ion batteries: an emerging frontier in energy storage *Innov. Mater.* **3** 100175
- [16] Hirose T, Matsui N, Itoh T, Hinuma Y, Ikeda K, Gotoh K, Jiang G, Suzuki K, Hirayama M and Kanno R 2025 High-capacity, reversible hydrogen storage using H—conducting solid electrolytes *Science* **389** 1252–5
- [17] Liu L *et al* 2026 Coordination engineering of ion highways for ultrahigh flux and interfacial stabilization in MOF-based solid electrolytes *Nano Energy* **154** 111986
- [18] Hu F, Yang H, Zhou X, Zhao S, Qiu L, Wei S, Hu J, Chen Y, Hu H and Zhou H 2026 Spatial dynamics of lithium battery recycling enterprises in China: implications for smart waste management and public health *Front. Public Health* **13** 1729413
- [19] Zhang Y, Li J, Yu M, Chen X, Chen X and Shen J 2025 Dominant factor identification and fast optimization of carnot battery by integrating SHAP and physics-guided neural network *Appl. Energy* **401** 126641
- [20] Martha S K, Nanda J, Zhou H, Idrobo J C, Dudney N J, Pannala S, Dai S, Wang J and Braun P V 2014 Electrode architectures for high capacity multivalent conversion compounds: iron (ii and iii) fluoride *RSC Adv.* **4** 6730
- [21] Zhou H, Ruther R E, Adcock J, Zhou W, Dai S and Nanda J 2015 Controlled formation of mixed nanoscale domains of high capacity Fe₂O₃—FeF₃ conversion compounds by direct fluorination *ACS Nano* **9** 2530–9
- [22] Inamoto J, Enoki S, Inoo A, Tamura N and Matsuo Y 2023 The promise of dual carbon batteries with graphene-like graphite as positive and negative electrodes
- [23] Holoubek J, Yin Y, Li M, Yu M, Meng Y S, Liu P and Chen Z 2019 Exploiting mechanistic solvation kinetics for dual-graphite batteries with high power output at extremely low temperature *Angew. Chem., Int. Ed.* **58** 18892–7
- [24] Zhao X, Ren S, Bruns M and Fichtner M 2014 Chloride ion battery: a new member in the rechargeable battery family *J. Power Sources* **245** 706–11
- [25] Gschwind F, Rodriguez-Garcia G, Sandbeck D J S, Gross A, Weil M, Fichtner M and Hörmann N 2016 Fluoride ion batteries: theoretical performance, safety, toxicity, and a combinatorial screening of new electrodes *J. Fluor. Chem.* **182** 76–90
- [26] Nowroozi M A, Mohammad I, Molaiyan P, Wissel K, Munnangi A R and Clemens O 2021 Fluoride ion batteries—past, present, and future *J. Mater. Chem. A* **9** 5980–6012
- [27] Wang Y and Wang H 2022 Intercalation of tetrafluoroborate anions into graphite electrodes from mixed sulfones *ACS Appl. Energy Mater.* **5** 2366–74

- [28] Kang J, Lee S, Hwang J, Kim S, Lee S, Yoo S, Han J W, Ryu J-H, Ryu J and Park S 2023 Azacyclic anchor-enabled cohesive graphite electrodes for sustainable anion storage *Adv. Mater.* **35** 2306157
- [29] Yang K, Jia L, Liu X, Wang Z, Wang Y, Li Y, Chen H, Wu B, Yang L and Pan F 2020 Revealing the anion intercalation behavior and surface evolution of graphite in dual-ion batteries via *in situ* AFM *Nano Res.* **13** 412–8
- [30] Han X, Jiang H, Mu P, Zhang W, Zhang H, Xu G, Chen Z, Han P and Cui G 2025 Helmholtz plane regulation empowers PF₆[−] permselectivity towards high coulombic efficiency dual ion battery of 5.5 V *Angew. Chem., Int. Ed.* **64** e202412753
- [31] Betz J, Bieker G, Meister P, Placke T, Winter M and Schmich R 2019 Theoretical versus practical energy: a plea for more transparency in the energy calculation of different rechargeable battery systems *Adv. Energy Mater.* **9** 1803170
- [32] Zhang X, Tang Y, Zhang F and Lee C 2016 A novel aluminum–graphite dual-ion battery *Adv. Energy Mater.* **6** n-a
- [33] Kravchik K V, Bhauriyal P, Piveteau L, Guntlin C P, Pathak B and Kovalenko M V 2018 High-energy-density dual-ion battery for stationary storage of electricity using concentrated potassium fluorosulfonylimide *Nat. Commun.* **9** 4469
- [34] Guo Z, Cheng G, Xu Z, Xie F, Hu Y, Mattevi C, Titirici M and Crespo Ribadeneyra M 2023 Sodium dual-ion batteries with concentrated electrolytes *ChemSusChem* **16** e202201583
- [35] Kravchik K V and Kovalenko M V 2020 Aluminum electrolytes for Al dual-ion batteries *Commun. Chem.* **3** 120
- [36] Huang Z et al 2021 Manipulating anion intercalation enables a high-voltage aqueous dual ion battery *Nat. Commun.* **12** 3106
- [37] Balabajew M, Reinhardt H, Bock N, Duchardt M, Kachel S, Hampp N and Roling B 2016 In-situ raman study of the intercalation of Bis(trifluoromethylsulfonyl)imid ions into graphite inside a dual-ion cell *Electrochim. Acta* **211** 679–88
- [38] Read J A 2015 In-situ studies on the electrochemical intercalation of hexafluorophosphate anion in graphite with selective cointercalation of solvent *J. Phys. Chem. C* **119** 8438–46
- [39] Heckmann A, Thienenkamp J, Beltrop K, Winter M, Brunklaus G and Placke T 2018 Towards high-performance dual-graphite batteries using highly concentrated organic electrolytes *Electrochim. Acta* **260** 514–25
- [40] Zhang L, Wang H, Zhang X and Tang Y 2021 A review of emerging dual-ion batteries: fundamentals and recent advances *Adv. Funct. Mater.* **31** 2010958
- [41] Heckmann A, Fromm O, Rodehorst U, Münster P, Winter M and Placke T 2018 New insights into electrochemical anion intercalation into carbonaceous materials for dual-ion batteries: impact of the graphitization degree *Carbon* **131** 201–12
- [42] Spotte-smith E W C, Petrocelli T B, Patel H D, Blau S M and Persson K A 2023 Elementary decomposition mechanisms of lithium hexafluorophosphate in battery electrolytes and interphases *ACS Energy Lett.* **8** 347–55
- [43] Zhang Z et al 2021 Cathode-electrolyte interphase in lithium batteries revealed by cryogenic electron microscopy *Matter* **4** 302–12
- [44] Tang B et al 2026 Ion-mediated carbon microdomain engineering boosting enhanced plateau capacity of carbon anode under high rate towards high-performance sodium dual-ion batteries *Nanomicro Lett.* **18** 161
- [45] Li P, Zhang H, Lu J and Li G 2023 Low concentration sulfolane-based electrolyte for high voltage lithium metal batteries *Angew. Chem., Int. Ed.* **62** e202216312
- [46] Degen F, Winter M, Bendig D and Tübke J 2023 Energy consumption of current and future production of lithium-ion and post lithium-ion battery cells *Nat. Energy* **8** 1284–95
- [47] Hu X et al 2023 Large interlayer distance and heteroatom-doping of graphite provide new insights into the dual-ion storage mechanism in dual-carbon batteries *Angew. Chem., Int. Ed.* **62** e202307083
- [48] Yang H, Liu F, Zou X, Jiang Z, Zhou X, Wu X, Qiao S, Zhang W and Zheng W 2025 B-doping tunes surface chemistry of graphite cathode interfaced at electrolyte for optimal anion storage and robust dual-ion batteries *Acta Mater.* **285** 120692
- [49] Shang L, Shi B-Y, Liu X, Zhang T-T, Liu H, Zheng Y, Dou W-D, Pan Q and Tang Y 2024 Directional guiding of mass and charge transfer via vertically aligned graphite nanosheets for high-rate and ultralong lifespan Dual-ion batteries *Chem. Eng. J.* **482** 149037
- [50] Li C, Yang H, Xie J, Wang K, Li J and Zhang Q 2020 Ferrocene-based mixed-valence metal–organic framework as an efficient and stable cathode for lithium-ion-based dual-ion battery *ACS Appl. Mater. Interfaces* **12** 32719–25
- [51] Mishra S B, Abhijitha V G, Ramaprabhu S and Nanda B R K 2021 Graphdiyne—a two-dimensional cathode for aluminum dual-ion batteries with high specific capacity and diffusivity *ACS Appl. Energy Mater.* **4** 7786–99
- [52] Peng S, Zhou X, Tunmee S, Li Z, Kidkhunthod P, Peng M, Wang W, Saitoh H, Zhang F and Tang Y 2021 Amorphous carbon nano-interface-modified aluminum anodes for high-performance dual-ion batteries *ACS Sustain. Chem. Eng.* **9** 3710–7
- [53] Wang H, Wang C and Tang Y 2021 Interface engineering toward high-efficiency alloy anode for next-generation energy storage device *EcoMat* **3** e12172
- [54] Jiang C, Xiang L, Miao S, Shi L, Xie D, Yan J, Zheng Z, Zhang X and Tang Y 2020 Flexible interface design for stress regulation of a silicon anode toward highly stable dual-ion batteries *Adv. Mater.* **32** 1908470
- [55] Fan Y, Liu X, Shang J, Liu B, Lei X, Zong H, Peng Z, Jiang C and Tang Y 2026 Interfacial phonon scattering enables ultrastable and high-power sodium-based dual-ion batteries with alloying anodes *Adv. Mater.* **38** e72848
- [56] Wang Y, Zhang Y, Wang S, Dong S, Dang C, Hu W and Yu D Y W 2021 Ultrafast charging and stable cycling dual-ion batteries enabled via an artificial cathode–electrolyte interface *Adv. Funct. Mater.* **31** 2102360
- [57] Kim S-H, Woo M-H, Omkar S, Javid A, Chang D-R and Park C-J 2025 Advanced PVDF-HFP-based composite quasi-solid polymer electrolyte for high-energy lithium-ion batteries with enhanced safety and durability *J. Power Sources* **640** 236716
- [58] Kravchik K V and Kovalenko M V 2020 Building better dual-ion batteries *MRS Energy Sustain.* **7** 36
- [59] Chen C-Y, Matsumoto K, Kubota K, Hagiwara R and Xu Q 2020 An energy-dense solvent-free dual-ion battery *Adv. Funct. Mater.* **30** 2003557
- [60] Pan X, Zhao Y, Deng X and Wu M 2026 Dual-ion batteries: efficient and environmentally friendly energy storage for the future *Korean J. Chem. Eng.* **43** 855–932
- [61] Xu W, Li L, Zhao Y, Li S, Yang H, Tong H and Wang Z 2025 Some basics and details for better dual-ion batteries *Energy Environ. Sci.* **18** 2686–719
- [62] Liu Q, Wang Y, Yang X, Zhou D, Wang X, Jaumaux P, Kang F, Li B, Ji X and Wang G 2021 Rechargeable anion-shuttle batteries for low-cost energy storage *Chemistry* **7** 1993–2021
- [63] Panja S, Miao Y, Döhn J, Choi J, Fleischmann S, Guddehalli Chandrappa S, Diemant T, Groß A, Karkera G and Fichtner M 2024 Synthesis, structural analysis, and degradation behavior of potassium tin chloride as chloride-ion batteries conversion electrode material *Adv. Funct. Mater.* **35** 2413489
- [64] Martello V G, Piovano A, Bonomo M, Dinç M, Bordiga S and Gerbaldi C 2026 A leap toward quasi-solid-state chloride-ion batteries with metal–organic frameworks *ACS Energy Lett.* **11** 419–25

- [65] Li T, Li M, Li H and Zhao H 2021 High-voltage and long-lasting aqueous chlorine-ion battery by virtue of “water-in-salt” electrolyte *iScience* **24** 101976
- [66] Karkera G et al 2023 A structurally flexible halide solid electrolyte with high ionic conductivity and air processability *Adv. Energy Mater.* **13** 2300982
- [67] Yin Q, Luo J, Zhang J, Zheng L, Cui G, Han J and O'hare D 2020 High-performance, long lifetime chloride ion battery using a NiFe-Cl layered double hydroxide cathode *J. Mater. Chem. A* **8** 12548–55
- [68] Gschwind F, Euchner H and Rodriguez-Garcia G 2017 Chloride ion battery review: theoretical calculations, state of the art, safety, toxicity, and an outlook towards future developments *Eur. J. Inorg. Chem.* **2017** 2784–99
- [69] Zhu Y, Yin J, Emwas A, Mohammed O F and Alshareef H N 2021 An aqueous Mg^{2+} -based dual-ion battery with high power density *Adv. Funct. Mater.* **31** 2107523
- [70] Li W and Sun Z 2025 Second hydration shell of Mg^{2+} : competition between ion–water interaction and hydrogen bonding interaction *J. Phys. Chem. Lett.* **16** 503–9
- [71] Lapidus S H, Rajput N N, Qu X, Chapman K W, Persson K A and Chupas P J 2014 Solvation structure and energetics of electrolytes for multivalent energy storage *Phys. Chem. Chem. Phys.* **16** 21941–5
- [72] Zhao X, Zhao-karger Z, Wang D and Fichtner M 2013 Metal oxychlorides as cathode materials for chloride ion batteries *Angew. Chem., Int. Ed.* **52** 13621–4
- [73] Zhao X, Li Q, Yu T, Yang M, Fink K and Shen X 2016 Carbon incorporation effects and reaction mechanism of FeOCl cathode materials for chloride ion batteries *Sci. Rep.* **6** 19448
- [74] Gao P, Zhao X, Zhao-Karger Z, Diemant T, Behm R J and Fichtner M 2014 Vanadium oxychloride/magnesium electrode systems for chloride ion batteries *ACS Appl. Mater. Interfaces* **6** 22430–5
- [75] Yu T, Li Q, Zhao X, Xia H, Ma L, Wang J, Meng Y S and Shen X 2017 Nanoconfined iron oxychloride material as a high-performance cathode for rechargeable chloride ion batteries *ACS Energy Lett.* **2** 2341–8
- [76] Gao P, Reddy M A, Mu X, Diemant T, Zhang L, Zhao-karger Z, Chakravadhanula V S K, Clemens O, Behm R J and Fichtner M 2016 VOCl as a cathode for rechargeable chloride ion batteries *Angew. Chem.* **128** 4357–62
- [77] Yin Q, Rao D, Zhang G, Zhao Y, Han J, Lin K, Zheng L, Zhang J, Zhou J and Wei M 2019 CoFe–Cl layered double hydroxide: a new cathode material for high-performance chloride ion batteries *Adv. Funct. Mater.* **29** 1900983
- [78] Luo J, Yin Q, Zhang J, Zhang S, Zheng L and Han J 2020 NiMn-Cl layered double hydroxide/carbon nanotube networks for high-performance chloride ion batteries *ACS Appl. Energy Mater.* **3** 4559–68
- [79] Li Z et al 2026 Dual vacancy-driven “Lattice softening” NiFeAl_x LDHs for high-rate and durable chloride ion storage *Adv. Mater.* **38** e17528
- [80] Zhao Z, Yu T, Miao Y and Zhao X 2018 Chloride ion-doped polyaniline/carbon nanotube nanocomposite materials as new cathodes for chloride ion battery *Electrochim. Acta* **270** 30–36
- [81] Kong H, Yang M, Miao Y and Zhao X 2019 Polypyrrole as a novel chloride-storage electrode for seawater desalination *Energy Technol.* **7** 1900835
- [82] Zhao X, Zhao Z, Yang M, Xia H, Yu T and Shen X 2017 Developing polymer cathode material for the chloride ion battery *ACS Appl. Mater. Interfaces* **9** 2535–40
- [83] Xia T, Zhu T, Miao Y and Zhao X 2022 Polyxylylviologen chloride as an organic electrode material for efficient reversible chloride-ion storage *ACS Appl. Energy Mater.* **5** 6980–5
- [84] Yang X et al 2023 Electrolyte design principles for developing quasi-solid-state rechargeable halide-ion batteries *Nat. Commun.* **14** 925
- [85] Zhao L, Inoishi A, Miki H, Motoyama M, Okada S, Asano T, Sakuda A, Hayashi A and Sakaebe H 2024 Super chloride ionic conductivity in CsSnCl₃-based perovskite compound and its application for solid-state chloride batteries *Adv. Energy Sustain. Res.* **5** 2400198
- [86] Yang H, Kim S, Lee S, Zhao L, Inoishi A, Sakaebe H, Albrecht K and Li O L 2025 Sn–carbon nanocomposite anode for all-solid-state chloride-ion batteries operating at room temperature *Chem. Commun.* **61** 1866–9
- [87] Chen F, Leong Z Y and Yang H Y 2017 An aqueous rechargeable chloride ion battery *Energy Storage Mater.* **7** 189–94
- [88] Chen C, Yu T, Yang M, Zhao X and Shen X 2019 An all-solid-state rechargeable chloride ion battery *Adv. Sci.* **6** 1802130
- [89] Sakamoto R, Shirai N, Zhao L, Inoishi A, Sakaebe H and Okada S 2023 Room-temperature operation of all-solid-state chloride-ion battery with perovskite-type CsSn_{0.95}Mn_{0.05}Cl₃ as a solid electrolyte *Electrochemistry* **91** 077003
- [90] Xia T, Li Q, Xue Z, Miao Y, Shen X and Zhao X 2024 Boosting the structural and electrochemical stability of chloride-ion-conducting perovskite solid electrolytes by alkali ion doping *Adv. Mater.* **37** 2411605
- [91] Xia T, Li Q, Zhao X and Shen X 2024 Bismuth and chlorine dual-doped perovskite chloride as a phase-structure-stable and moisture-resistant solid electrolyte for chloride ion batteries *Adv. Mater.* **36** 2310565
- [92] Panja S, Gopikuttan A P, Mundsinger M, Radwan A, Chen H, Biskupek J, Clemens O and Fichtner M 2026 Synergistic optimization of cathode composite architecture and stack pressure for high-performance all-solid-state chloride-ion batteries *Adv. Energy Mater.* (<https://doi.org/10.1002/aenm.71335>)
- [93] Shannon R D 1976 Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides *Acta Crystallogr. Sect. A* **32** 751–67
- [94] Ma D, Zhang R, Hu X, Chen Y, Xiao C, He F, Zhang S, Chen J and Hu G 2022 Insights into the electrochemical performance of metal fluoride cathodes for lithium batteries *Energy Mater.* **2** 200027
- [95] Rongeat C, Anji Reddy M, Witter R and Fichtner M 2014 Solid electrolytes for fluoride ion batteries: ionic conductivity in polycrystalline tysonite-type fluorides *ACS Appl. Mater. Interfaces* **6** 2103–10
- [96] Rongeat C, Anji Reddy M, Diemant T, Behm R J and Fichtner M 2014 Development of new anode composite materials for fluoride ion batteries *J. Mater. Chem. A* **2** 20861–72
- [97] Wang Z, Ju J, Wang Q, Chen J, Liang L, Kang W and Cheng B 2025 Advances and future perspectives of solid-state electrolytes for fluoride-ion batteries *Adv. Funct. Mater.* **36** e18061
- [98] Alshangiti O, Galatolo G, Rees G J, Guo H, Quirk J A, Dawson J A and Pasta M 2023 Solvent-in-salt electrolytes for fluoride ion batteries *ACS Energy Lett.* **8** 2668–73
- [99] Nakayama K et al 2024 Composite anode for fluoride-ion batteries using alloy formation and phase separation in charge and discharge processes *J. Mater. Chem. A* **12** 8350–8
- [100] Galatolo G, Alshangiti O, Di Mino C, Matthews G, Xiao A W, Rees G J, Schart M, Chart Y A, Olbrich L F and Pasta M 2024 Advancing fluoride-ion batteries with a Pb–PbF₂ counter electrode and a diluted liquid electrolyte *ACS Energy Lett.* **9** 85–92
- [101] Anji Reddy M and Fichtner M 2011 Batteries based on fluoride shuttle *J. Mater. Chem.* **21** 17059–62

- [102] Thieu D T, Fawey M H, Bhatia H, Diemant T, Chakravadhanula V S K, Behm R J, Kübel C and Fichtner M 2017 CuF₂ as reversible cathode for fluoride ion batteries *Adv. Funct. Mater.* **27** 1701051
- [103] Inoishi A, Setoguchi N, Hori H, Kobayashi E, Sakamoto R, Sakaebe H and Okada S 2022 FeF₃ as reversible cathode for all-solid-state fluoride batteries *Adv. Energy Sustain. Res.* **3** 2200131
- [104] Zhang D *et al* 2025 Cathode design based on nitrogen redox and linear coordination of Cu center for all-solid-state fluoride-ion batteries *J. Am. Chem. Soc.* **147** 5649–57
- [105] Liu E, Duan Y, Li Y, Peng C and Feng W 2025 Fluoride-ion batteries: a review of recent advances and future opportunities *Electrochem. Energy Rev.* **8**
- [106] Mezzadra G, Guo X, Ravalli M, Ritter C, Ceresoli D, Clemens O and Tealdi C 2026 The role of oxygen excess on fluoride intercalation in Ruddlesden–Popper electrodes for fluoride ion batteries: the case of LaSrMnO₄ *J. Mater. Chem. A* **14** 15446–55
- [107] Shimoda K, Morita Y, Noi K, Fukunaga T, Ogumi Z and Abe T 2023 Practical reversibility of CuF₂ in a bulk-type all-solid-state fluoride-ion battery *ACS Energy Lett.* **8** 2570–5
- [108] Schoonman J 1984 The dynamic behaviour of ions in fluorite and tysonite-type solid solutions *Solid State Ion.* **12** 525
- [109] Bhatia H, Thieu D T, Pohl A H, Chakravadhanula V S K, Fawey M H, Kübel C and Fichtner M 2017 Conductivity optimization of tysonite-type La_{1–x}Ba_xF_{3–x} solid electrolytes for advanced fluoride ion battery *ACS Appl. Mater. Interfaces* **9** 23707–15
- [110] Chable J *et al* 2017 Fluoride solid electrolytes: from microcrystalline to nanostructured tysonite-type La_{0.95}Ba_{0.05}F_{2.95} *J. Alloys Compd.* **692** 980–8
- [111] Mori K, Morita Y, Saito T, Kamiyama T, Otomo T, Abe T and Fukunaga T 2020 Structural and electrochemical properties of tysonite Ce_{0.95}A_{0.05}F_{2.95} (A=Mg, Ca, Sr, and Ba): fast-fluoride-ion-conducting solid electrolytes *J. Phys. Chem. C* **124** 18452–61
- [112] Molaiyan P and Witter R 2021 Synthesis and characterization of Ca_(1–x)Sm_xF_(2+x) (0 ≤ x ≤ 0.15) solid electrolytes for fluoride-ion batteries *Mater. Des. Process. Commun.* **3**
- [113] Düvel A, Bednarcik J, Šepelák V and Heitjans P 2014 Mechanochemical synthesis of the fast fluoride ion conductor Ba_{1–x}La_xF_{2+x}: from the fluorite to the tysonite structure *J. Phys. Chem. C* **118** 7117–29
- [114] Mohammad I, Chable J, Witter R, Fichtner M and Reddy M A 2018 Synthesis of fast fluoride-ion-conductive fluorite-type Ba_{1–x}Sb_xF_{2+x} (0.1 ≤ x ≤ 0.4): a potential solid electrolyte for fluoride-ion batteries *ACS Appl. Mater. Interfaces* **10** 17249–56
- [115] Liu J *et al* 2023 Construction and interfacial modification of a β-PbSnF₄ electrolyte with high intrinsic ionic conductivity for a room-temperature fluoride-ion battery *ACS Appl. Mater. Interfaces* **15** 36373–83
- [116] Liu L, Yang L, Liu M, Li X, Shao D, Luo K, Wang X and Luo Z 2020 SnF₂-based fluoride ion electrolytes MSnF₄ (M=Ba, Pb) for the application of room-temperature solid-state fluoride ion batteries *J. Alloys Compd.* **819** 152983
- [117] Molaiyan P and Witter R 2019 Crystal phase and surface defect driven synthesis of Pb_{1–x}Sn_xF₂ solid solution electrolyte for fluoride ion batteries *J. Electroanal. Chem.* **845** 154–9
- [118] Achary K R, Khatua S, Bai K D L, Sahoo G and Patro L N 2025 Exploring the structural and conductivity behaviours of mechanochemically and hydrothermally synthesized Ce³⁺-doped BaSnF₄ solid electrolytes for all-solid-state fluoride-ion batteries *Solid State Ion.* **431** 117032
- [119] Liu L, Yang L, Shao D, Luo K, Zou C, Luo Z and Wang X 2020 Nd³⁺ doped BaSnF₄ solid electrolyte for advanced room-temperature solid-state fluoride ion batteries *Ceram. Int.* **46** 20521–8
- [120] Zang Z, Liu L, Yang L, Luo K, Zou C, Chen X, Tao X, Luo Z, Chang B and Wang X 2021 Preparation and performance of Eu³⁺-Doped BaSnF₄-Based solid-state electrolytes for room-temperature fluoride-ion batteries *ACS Sustain. Chem. Eng.* **9** 12978–89
- [121] Zang Z, Liu J, Tao X, Zou C, Chen X, Yi L, Chang B and Wang X 2023 Mn²⁺ doped BaSnF₄-based solid state electrolyte for room-temperature fluoride ion batteries *J. Electroanal. Chem.* **930** 117145
- [122] Wang J, Hao J, Duan C, Wang X, Wang K and Ma C 2022 A fluoride-ion-conducting solid electrolyte with both high conductivity and excellent electrochemical stability *Small* **18**
- [123] Hao Y *et al* 2024 Effects of mixed phases on ionic conductivities for (LaF₃)_{1–x}(PbF₂)_x fast-fluoride-ion-conducting solid electrolytes *New J. Chem.* **48** 9196–207
- [124] Liu L, Yang L, Liu M, Wang X, Li X, Shao D, Luo K, Luo Z and Chen G 2019 A flexible tysonite-type La_{0.95}Ba_{0.05}F_{2.95}@PEO-based composite electrolyte for the application of advanced fluoride ion battery *J. Energy Storage* **25** 100886
- [125] Motohashi K, Matsukawa Y, Nakamura T, Kimura Y, Kuwata N, Uchimoto Y and Amezawa K 2022 Fast fluoride ion conduction of NH₄(Mg_{1–x}Li_x)F_{3–x} and (NH₄)₂(Mg_{1–x}Li_x)F_{4–x} assisted by molecular cations *Sci. Rep.* **12** 5955
- [126] Yu Y, Li G and Li C 2025 Polymer electrolyte based all-solid-state rechargeable fluoride ion batteries *Adv. Funct. Mater.* **35** 2410891
- [127] Cui H, Gao X, Guo K, Liu W, Ouyang B and Yi W 2025 Lewis acid–base synergistically enhancing practical composite electrolyte for fluoride-ion batteries at room temperature *Adv. Sci.* **12** 2502824
- [128] Bashian N H *et al* 2021 Electrochemical oxidative fluorination of an oxide perovskite *Chem. Mater.* **33** 5757–68
- [129] Andrews J L *et al* 2022 Room-temperature electrochemical fluoride (De)insertion into CsMnFeF₆ *ACS Energy Lett.* **7** 2340–8
- [130] Davis V K *et al* 2018 Room-temperature cycling of metal fluoride electrodes: liquid electrolytes for high-energy fluoride ion cells *Science* **362** 1144–8
- [131] Celik Kucuk A and Abe T 2020 Borolan-2-yl involving anion acceptors for organic liquid electrolyte-based fluoride shuttle batteries *J. Fluor. Chem.* **240** 109672
- [132] Konishi H, Minato T, Abe T and Ogumi Z 2018 Triphenylboroxine and triphenylborane as anion acceptors for electrolyte in fluoride shuttle batteries *Chem. Lett.* **47** 1346–9
- [133] Li D, Li G, Yu Y and Li C 2025 Construction of acceptor-multi-f state electrolyte to enable unprecedented long-life and high-capacity fluoride-ion batteries *Adv. Mater.* **37** 2415106
- [134] Yamamoto T, Matsumoto K, Hagiwara R and Nohira T 2021 Charge–discharge performance of copper metal positive electrodes in fluorohydrogenate ionic liquids for fluoride-shuttle batteries *J. Electrochem. Soc.* **168** 040530
- [135] Zou P, Wang C, He Y, Xin H L and Lin R 2024 A water-in-salt electrolyte for room-temperature fluoride-ion batteries based on a hydrophobic–hydrophilic salt *Nano Lett.* **24** 5429–35
- [136] Lütchefeld J, Hemmelmann H, Wachs S, Mayrhofer K J, Elm M T and Berkes B B 2022 Effect of water contamination on the transition metal dissolution in water-enriched electrolyte: a mechanistic insight into a new type of dissolution *J. Phys. Chem. C* **126** 17204–11
- [137] Ren T, Chen X, Zhang H, Zhang H and Xia W 2025 Humidity stability of halide solid-state electrolytes *J. Mater. Chem. A* **13** 38609–32
- [138] Xiao A W, Galatolo G and Pasta M 2021 The case for fluoride-ion batteries *Joule* **5** 2823–44

- [139] Li H, Li M, Zhou X, Li T and Zhao H 2020 A novel rechargeable bromine-ion battery and the induction of bromine ions on metal electrodes *Sustain. Energy Fuels* **4** 3871–8
- [140] Inoishi A, Hokazono M, Kashiwazaki E, Setoguchi N, Sakai T, Sakamoto R and Okada S 2021 An all-solid-state bromide-ion battery *ChemElectroChem* **8** 246–9
- [141] Wang L, Li J, Li M, Duan X, Weng H and Xu S 2024 Advancing bromine-ion batteries: a breakthrough in “Water-in-Salt” electrolyte for safe and sustainable energy storage *Chem. Phys. Lett.* **841** 141176
- [142] Kobayashi G et al 2016 Pure H-conduction in oxyhydrides *Science* **351** 1314
- [143] Zhang W, Cui J, Wang S, Cao H, Wu A, Xia Y, Jiang Q, Guo J, He T and Chen P 2023 Deforming lanthanum trihydride for superionic conduction *Nature* **616** 73–76
- [144] Cui J et al 2025 A room temperature rechargeable all-solid-state hydride ion battery *Nature* **646** 338–42
- [145] Tiam Kapen P 2026 Electrochemical modeling of solid-state hydride-ion batteries based on a $\text{CeH}_2 \mid 3\text{CeH}_3\text{@BaH}_2 \mid \text{NaAlH}_4$ architecture *J. Electroanal. Chem.* **1002** 119751
- [146] Liu Y, Zhou K, Wang R, Ma Q, Xiong P, Zhang L and Zhang C 2025 $\text{I}^+/\text{I}_2/\text{I}^-$ conversion toward energy-dense aqueous Zn-I₂ batteries: progress and perspective *Chem. Sci.* **16** 16381–91
- [147] Zou Y, Liu T, Du Q, Li Y, Yi H, Zhou X, Li Z, Gao L, Zhang L and Liang X 2021 A four-electron Zn-I₂ aqueous battery enabled by reversible $\text{I}^-/\text{I}_2/\text{I}^+$ conversion *Nat. Commun.* **12** 170
- [148] Liu L, Zhang L, Liu Y, Zhang S, Wang R, Li F, Li H, Hao J, Zhang C and Guo Z 2025 Enhanced redox kinetics of aqueous $\text{I}^-/\text{I}_2/\text{I}^+$ conversion chemistry in hydrated eutectic electrolyte over a wide temperature range *Adv. Energy Mater.* **15**
- [149] Liu T, Lei C, Wang H, Xu C, Ma W, He X and Liang X 2024 Practical four-electron zinc-iodine aqueous batteries enabled by orbital hybridization induced adsorption-catalysis *Sci. Bull.* **69** 1674–85
- [150] Gong J et al 2024 Cation engineering perovskite cathodes for fast and stable anion redox chemistry in zinc-iodine batteries *Adv. Funct. Mater.* **34** 2411137
- [151] Li X, Wang S, Zhang D, Li P, Chen Z, Chen A, Huang Z, Liang G, Rogach A L and Zhi C 2024 Perovskite cathodes for aqueous and organic iodine batteries operating under one and two electrons redox modes *Adv. Mater.* **36** 2304557
- [152] Jiang P, Du Q, Lei C, Xu C, Liu T, He X and Liang X 2024 Stabilized four-electron aqueous zinc-iodine batteries by quaternary ammonium complexation *Chem. Sci.* **15** 3357–64
- [153] Matsuo Y, Inoo A and Inamoto J 2024 Electrochemical intercalation of anions into graphite: fundamental aspects, material synthesis, and application to the cathode of dual-ion batteries *ChemistryOpen* **13**
- [154] Zafar Z A et al 2022 Reversible anion intercalation into graphite from aluminum perchlorate “water-in-salt” electrolyte *Electrochim. Acta* **404** 139754
- [155] Zheng Y, Deng T, Shi X, Zhang H, Liu B, Li X and Zheng W 2024 Decoupled design for highly efficient perchlorate anion intercalation and high-energy rechargeable aqueous Zn-graphite batteries *Adv. Sci.* **11**
- [156] Shpigel N et al 2020 New aqueous energy storage devices comprising graphite cathodes, MXene anodes and concentrated sulfuric acid solutions *Energy Storage Mater.* **32** 1–10
- [157] Jiang H et al 2019 An aqueous dual-ion battery cathode of Mn_3O_4 via reversible insertion of nitrate *Angew. Chem., Int. Ed.* **58** 5286–91
- [158] Zhang M, Cao X, Hao Y, Wang H, Pu J, Chi B and Shen Z 2024 Recent progress, challenges and prospects of electrolytes for fluoride-ion batteries *Energy Rev.* **3** 100083
- [159] Li X, Wen C, Qi J, Li A, Xu Z, Ding K, Meng Y, Wang M and Huang S 2026 Four-electron iodine conversion chemistry for high-energy rechargeable batteries *Coord. Chem. Rev.* **563** 218030
- [160] Chang X and Cabot A 2025 Insights on polyiodide shuttling of Zn-I₂ batteries by I_3^-/I^- electrolytes based on the dual-ion battery system *Nanomaterials* **15** 738
- [161] Ran L et al 2025 Stable four-electron zinc-iodine battery realized by polyacrylamide as catalytic binder *Angew. Chem., Int. Ed.* **64**
- [162] Zhao H et al 2024 Highly electrically conductive polyiodide ionic liquid cathode for high-capacity dual-plating zinc-iodine batteries *J. Am. Chem. Soc.* **146** 6744–52