

Electrolytes for Rechargeable Magnesium Batteries

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Abstract

The accelerating global demand for rechargeable energy storage and the raw-material constraints associated with lithium-ion batteries (LIBs) have catalyzed the search for alternative battery chemistries. Among them, rechargeable magnesium batteries (RMBs) have emerged as a candidate due to their high volumetric capacity (3,833 mAh cm⁻³), natural abundance, and safety benefits of magnesium. However, the development of RMB remains hindered by the lack of viable electrolytes, as magnesium analogs of conventional LIB electrolyte formulations fail to support reversible magnesium deposition. In this Review, we examine the evolution of RMB electrolytes, from early Grignard-based complexes to emerging single-salt electrolytes, and discuss the fundamental design principles that have driven breakthroughs in electrolyte performance, stability, and compatibility. Electrolyte chemistry dictates interfacial behavior and dendrite formation, yet key knowledge gaps in understanding electrode-electrolyte interphases and magnesium plating mechanisms continue to limit battery performance. Addressing supply-chain vulnerabilities will improve RMB production reliability, whereas minimizing hazardous electrolyte components strengthens its viability as a next-generation clean energy storage technology. By articulating a clear roadmap grounded in both mechanistic understanding and materials innovation, future electrolyte development can be guided toward the commercialization of RMBs.

Introduction

Increasing energy demands coupled with limited lithium resources pose a challenge for lithium-ion batteries (LIBs) to meet future demands, driving focus toward post lithium-ion batteries (PLIBs)¹⁻³. The market share of PLIBs is projected to grow substantially, potentially reaching around 39% by 2040(ref.¹). More specifically, rechargeable magnesium batteries (RMBs) are emerging as a PLIB candidate, offering superior volumetric capacity (3,833 mAh cm⁻³ for Mg compared to 2,046 mAh cm⁻³ for Li), greater abundance (2.3% Mg in the earth's crust versus 0.002% for Li), and comparatively enhanced safety (lower reactivity and less dendrite formation)⁴. Nevertheless, the commercialization of RMBs remains constrained by electrolyte-related challenges. As electrolytes are central to battery functionality, enabling efficient charge transport between electrodes, their optimization is needed for advancing RMBs⁵.

Conventional electrolyte salts and solvents, widely employed in LIBs, induce severe passivation on Mg anodes when adapted for RMBs, highlighting the need to develop electrolyte design principles specifically tailored for RMBs instead of replicating the frameworks established for LIBs⁶. Non-aqueous Grignard reagents⁷ and derivatives such as dichloro complex (DCC)⁸ and all-phenyl complex (APC)⁹ have been proposed as electrolytes for RMBs (**Fig. 1**). However, their nucleophilicity and high reactivity has limited further development. Alternatively, a Grignard reagent-free electrolyte, magnesium aluminum chloride complex (MACC) has also been developed, but it still exhibited severe constraints including limited electrochemical stability voltage window and aluminum co-deposition^{10,11}.

Due to the limitations of early complex electrolytes systems like DCC and MACC, RMB electrolytes have shifted towards simpler single-salt formulations. This transition included the adoption of commercially available, non-nucleophilic Mg salts like magnesium bis(hexamethyldisilazide) (Mg(HMDS)₂) to develop effective non-aqueous electrolytes¹²⁻¹⁴. However, these salts still induced passivation at the Mg anode, requiring strategies such as additive modification and solvent engineering to achieve reversible Mg deposition. Rather than tailoring electrolytes based on passivating commercial Mg salts, an alternative has emerged through the direct synthesis of Mg salts with weakly coordinating anions (WCAs). This advancement has resulted in an improved electrolyte performance to levels approaching those of established PLIBs. For example, the WCA-based electrolyte magnesium tetrakis(hexafluoroisopropoxy)borate (Mg[B(hfip)₄]₂), exhibits a high ionic conductivity of 11 mS cm⁻¹, wide anodic stability of 4.5 V vs Mg/Mg²⁺, and high coulombic efficiency of 99.59%, along with excellent compatibility with a variety of cathodes¹⁵⁻¹⁷ (**Table 1 and Fig. 2**).

In this Review, we discuss the evolution of non-aqueous electrolyte systems for RMBs from early complex nucleophilic formulations to non-nucleophilic single salt systems, with particular emphasis on general principles, interfacial chemistry, dendrite formation phenomena, and sustainability considerations. We begin by examining development strategies for non-aqueous electrolytes, which have been instrumental in addressing critical limitations in RMB performance. Subsequently, we discuss developments in aqueous and solid-state electrolytes (SSEs) for RMBs. Special attention is devoted to the electrode-electrolyte interphases, emphasizing their dynamic interplay with electrolyte solvation structures and interfacial reactions. Then, the long-standing notion of RMBs as dendrite-free systems is re-evaluated through emerging mechanistic insights into dendrite growth under varying testing conditions. We also assess the environmental and sustainability implications of Mg metal, RMB technologies, and their electrolytes offering a framework for the development of next-generation energy storage solutions. Finally, we provide forward-looking perspectives on the design and discovery of electrolytes to enable the deployment of RMBs in future energy storage applications.

Non-aqueous electrolytes

For RMBs, the direct translation of established non-aqueous LIB electrolyte formulations proves impractical¹⁸⁻²⁰. Consequently, research efforts have been focused on developing effective non-aqueous Mg battery electrolytes using alternative Mg salts. Nonetheless, the widespread adoption of RMBs has been hindered by the interfacial chemistry of the Mg metal anode²¹⁻²³. Unlike its lithium

counterpart, Mg readily forms ionically insulating passivation layers when exposed to conventional non-aqueous electrolytes, blocking Mg^{2+} ion transport (**Fig. 3a**)²⁴⁻²⁶. This challenge has steered electrolyte research toward the development of complex chemical systems specifically designed to circumvent passivation.

Nucleophilic systems

Early electrolyte systems for RMBs were predominantly complex formulations rich in MgCl^+ species (**Fig. 3b**). Reversible Mg deposition and stripping was achieved using Grignard reagents (RMgX), in which R is an alkyl or aryl group and X is a halide (typically Cl or Br), in ethereal solvents^{7,27}. However, low ionic conductivities ($<0.265 \text{ mS cm}^{-1}$) and anodic stability of ($<2.0 \text{ V vs. Mg/Mg}^{2+}$), severely hampered their implementation with intercalating cathodes^{28,29}.

To address these shortcomings, Grignard reagents-based complex electrolytes have been developed. The reaction of Grignard reagents with Lewis acids, particularly aluminum chloride and aluminum alkyl chlorides (for example, AlEtCl_2), lead to the formation of magnesium organohaloaluminate electrolytes called DCC⁸. DCC achieved a substantially improved anodic stability ($2.5 \text{ V vs. Mg/Mg}^{2+}$) and ionic conductivity (1.4 mS cm^{-1}), and more importantly enabled an RMB prototype with a Mo_6S_8 cathode^{8,24}. Building on this development, the APC electrolyte was introduced as a further advance by replacing alkyl groups with all-phenyl ligands, which offered better anodic stability ($\sim 3.3 \text{ V vs. Mg/Mg}^{2+}$) and ionic conductivity (4 mS cm^{-1})(ref.^{9,30}). However, the nucleophilic nature of Grignard reagent-based systems renders the electrolytes highly reactive, moisture-sensitive, and incompatible with cathode materials³¹.

To overcome the reactivity of organomagnesium species, inorganic MACC electrolytes (comprising MgCl_2 and AlCl_3 in ethereal solvents) were developed with a Cl-rich coordination environment that supports reversible Mg plating and stripping^{10,11,32}. Although MACC electrolytes showed improved chemical stability and reduced nucleophilicity, their anodic stability remained low ($<3.4 \text{ V vs. Mg/Mg}^{2+}$)³³.

Another complex system proposed as an alternative to Grignard reagent systems is the non-nucleophilic Hauser-base-derived hexamethyldisilazide magnesium chloride (HMDSMgCl) system, which showed reduced reactivity with cathode materials and greater chemical inertness^{34,35}. Even though HMDSMgCl -based electrolyte was employed in one of the earliest Mg-S battery prototypes³⁵, this group of electrolytes exhibited low anodic stability ($2.4\text{--}3.3 \text{ V vs. Mg/Mg}^{2+}$) and relatively low ionic conductivity ($\leq 0.58 \text{ mS cm}^{-1}$). Despite the performance limitations, this particular formulation demonstrated the feasibility and efficacy of excluding nucleophilic species from RMB electrolytes.

Non-nucleophilic systems

Advancing beyond the limitations of early nucleophilic complex electrolytes and guided by the exclusion of nucleophilic species, RMB electrolyte design has shifted toward chemically benign (for example, non-corrosive, low-reactive and cathode-compatible), non-nucleophilic formulations. The $\text{Mg}(\text{HMDS})_2$ (ref.¹²) electrolytes provided non-nucleophilic characteristics and resulted in improved compatibility with electrophilic cathodes^{36,37}. The magnesium bis(trifluoromethanesulfonimide) ($\text{Mg}(\text{TFSI})_2$) (ref.¹³) electrolytes offered additional benefits, including high solubility in ether solvents, moderate ionic conductivity (5.2 mS cm^{-1}), and enhanced anodic stability (exceeding $4.0 \text{ V vs. Mg/Mg}^{2+}$). Despite the favorable physicochemical properties of $\text{Mg}(\text{TFSI})_2$ -based electrolytes, their electrochemical performance remained suboptimal, as evidenced by the high anodic overpotentials ($\sim 2 \text{ V}$) and low coulombic efficiencies (CEs) ($<50\%$)^{13,38,39}. Moreover, the hygroscopic nature of the $\text{Mg}(\text{TFSI})_2$ salt poses challenges to the complete elimination of trace water impurities from electrolytes (often present at levels ranging from tens to thousands of ppm)^{40,41} even under rigorously anhydrous solvent conditions and meticulous electrolyte preparation protocols⁴². In response to these limitations, magnesium trifluoromethanesulfonate ($\text{Mg}(\text{OTf})_2$) emerged as an alternative, offering structural similarity to $\text{Mg}(\text{TFSI})_2$ while demonstrating improved anodic stability ($4.7 \text{ V vs. Mg/Mg}^{2+}$), enhanced CE (99.96%), and greater cost-effectiveness^{14,43,44}.

Despite their respective merits, single-salt-single-solvent⁴⁵ electrolytes formulated using these Mg salts ($\text{Mg}(\text{HMDS})_2$, $\text{Mg}(\text{TFSI})_2$, and $\text{Mg}(\text{OTf})_2$) commonly undergo strong Mg^{2+} -anion interactions, which limit effective ion-pair dissociation in conventional ether solvents such as 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF). This restricted ion-pair dissociation leads to the predominance of contact ion pairs (CIPs) in the electrolyte, wherein anions persist within the primary solvation shell⁴⁶. These CIPs are prone to reductive decomposition at the anode interface, leading to the formation of ionically passivating interphases that hinder reversible Mg plating and stripping (**Fig 3a**)⁴⁷⁻⁴⁹. General design strategies to mitigate this passivation include additive modification and solvent engineering, which are employed to suppress anode passivation by precisely tuning bulk electrolyte speciation and interfacial chemistry, and enable reversible Mg cycling (**Fig 3c-e**).

Conventional RMB electrolytes exhibit poor compatibility with Mg anodes due to interfacial instability arising from the higher chemical potential of Mg, which lies above the lowest unoccupied molecular orbital of electrolyte anions^{3,50}. Compounding this issue, the bivalency of Mg^{2+} fosters cation-anion clustering, further lowering the lowest unoccupied molecular orbital energy and exacerbating electrolyte decomposition on Mg anodes⁵¹. Furthermore, the strong ion-pairing effect limits the dissociation of Mg^{2+} -anion in the electrolyte, resulting in low ionic conductivity and high CIP concentration. These challenges are typically mitigated through additive modification and solvent engineering in non-nucleophilic systems employing $\text{Mg}(\text{HMDS})_2$, $\text{Mg}(\text{TFSI})_2$, or $\text{Mg}(\text{OTf})_2$ salts. Alternatively, the rational design of electrolyte salts with WCAs can be an effective strategy to minimize these interfacial and solvation-related challenges (**Fig. 3f**)⁵². The WCA design⁵³ has helped clarify key mechanisms in single salt non-nucleophilic electrolytes. Among WCA-based electrolytes, the $\text{Mg}[\text{B}(\text{hfip})_4]_2$ -based system offers enhanced ionic conductivity, wider anodic stability, and excellent interfacial compatibility with a wide range of cathode materials¹⁵.

The design strategies additive modification, solvent engineering, and WCA design for non-nucleophilic electrolytes are further examined in the following subsections. The first two strategies have been predominantly applied to non-nucleophilic systems based on $\text{Mg}(\text{HMDS})_2$, $\text{Mg}(\text{TFSI})_2$, and $\text{Mg}(\text{OTf})_2$ salts, which are prone to surface passivation at the Mg anode. Although the specific base salt and composition of the electrolytes vary, the mechanisms for co-solvent and additive incorporation show consistent and transferable principles for regulating Mg^{2+} solvation environments and interfacial dynamics. In contrast, WCA design elucidates how anion coordination strength, solvation structure, and interfacial reactivity synergistically govern reversibility in single-salt, non-nucleophilic electrolytes by suppressing Mg anode passivation while facilitating efficient Mg^{2+} transport. The persistent challenges in cycling stability and CE are pivotal targets for further electrolyte optimization towards practical deployment of RMB.

Additive modification. Introducing auxiliary anions (by additives) to partially occupy the Mg^{2+} solvation shell weakens the Mg^{2+} -anion interactions, and subsequently inhibits electrolyte induced passivation in non-nucleophilic systems (**Fig 3c**). However, not all electrolyte additives modulate the solvation shell; in some cases, the adsorption of additive cations or anions suppresses passivation by forming a protective, non-passivating interphase (**Fig 3d**).

An electrolyte for RMBs based on the commercially available non-nucleophilic salt $\text{Mg}(\text{HMDS})_2$ was developed by adding AlCl_3 (ref.¹²). The resulting electrolyte yielded a mixed solvation structure dominated by the electroactive $[\text{Mg}_2(\mu\text{-Cl})_3]^+$ species, along with the formation of undesired $\text{HMDSA}(\text{AlCl}_2)$ by-product. Additionally, adding MgCl_2 into the electrolyte activates the otherwise electrochemically inert $\text{HMDSA}(\text{AlCl}_2)$, converting it into electrochemically active species⁵⁴. This mechanistic insight highlights the role of MgCl_2 as an additive, enabling precise solvation structure engineering when combined with commercial Mg salts⁵⁵. In $\text{Mg}(\text{TFSI})_2$ electrolytes modified with MgCl_2 additive, the high Lewis basicity of Cl^- anion promotes the formation of $[\text{Mg}_x\text{Cl}_y(\text{solvent})_z]^{n+}$ complexes as electrolyte active species, which mitigates the strong Mg^{2+} -TFSI $^-$ and Mg^{2+} -solvent interactions^{39,56-58}. Additionally, the Cl^- anions tend to adsorb onto the anode surface acting as an adsorption layer that prevents free TFSI $^-$ anions reduction and shields the Mg anode from attacks by impurities in the electrolyte^{40,59}.

In addition, alternative Cl⁻-donating agents (for example, GeCl₄)⁶⁰ have been explored with Mg(TFSI)₂ electrolyte. However, the effect of the additive on solvation structure remains unknown, as these additives are mainly targeted to enable a cation rich protective layer on Mg anode to inhibit passivation. Building on the insights from Mg(HMDS)₂- and Mg(TFSI)₂-based systems, Cl⁻ additives for Mg(OTf)₂ electrolytes have evolved beyond the traditional MgCl₂ additive⁶¹⁻⁶³ to encompass a wider range of Cl⁻-donating organic and inorganic compounds^{43,64,65}. Even though the reported organic chloride additives function analogously to MgCl₂ by forming modulated solvation structures ([Mg_xCl_y(solvent)_z]ⁿ⁺), the employed inorganic chloride additives are mainly targeted towards interfacial modulation of the anode to enable reversible Mg cycling. This distinction highlights the influence of the additive cation in the functional role of Cl⁻ ion containing additives, and the need to understand both the solvation structure and interfacial regulation to effectively mitigate passivation.

Despite the positive results, inclusion of Cl⁻ containing additives to mitigate passivation brings in several disadvantages to the electrolyte including low anodic stability and corrosiveness. Furthermore, the strong Mg-Cl bonding and low migration barriers of electroactive species like MgCl⁺ and Mg₂Cl₃⁺ promote their preferential intercalation into cathodes over Mg²⁺, reducing operating voltage and compromising energy density^{66,67}. Beyond Cl⁻-based additives, other halide species, including bromide- and iodide-based additives also have been explored to mitigate Mg anode passivation in non-nucleophilic electrolytes, primarily by promoting the formation of ion-conductive Mg-halide interphases⁶⁸⁻⁷⁰. These strategies are aimed at interfacial regulation, and experimental evidence indicates that such additives do not participate in the electrolyte solvation shell⁶⁹.

BH₄⁻ has been proposed as an alternative Cl⁻ ions, as it can serve as an auxiliary anion in non-nucleophilic systems to counter anode passivation^{42,71,72}. The addition of Mg(BH₄)₂ into Mg(TFSI)₂-based electrolytes acts both as moisture scavenger and solvation shell modulator⁷¹. The BH₄⁻ anion, owing to its stronger coordinating ability compared with TFSI⁻, preferentially forms stable ion-associated complexes, such as Mg(BH₄)₂(diglyme). Moreover, BH₄⁻ preferentially adsorbs at the Mg anode interface during charge transfer, repelling TFSI⁻ to inhibit its reductive decomposition⁷¹. In contrast, the incorporation of the tetrabutylammonium borohydride (TBABH₄) additive into Mg(HMDS)₂ electrolytes primarily mitigates anode passivation through moisture scavenging, without altering the solvation shell⁷². In another case, the incorporation of TBABH₄ additive was found not to alter either the solvation structure or the interfacial composition; rather, adsorption of TBA⁺ cations onto the Mg anode surface resulted in a dynamic electrostatic shield that moderates Mg²⁺ reduction kinetics and facilitates uniform Mg deposition and dissolution⁷³. Nevertheless, electrolytes modified with BH₄⁻ additives generally exhibit low anodic stability (<2 V vs. Mg/Mg²⁺), which limits compatibility with high-voltage cathodes^{71,72}.

Molecular additives with selective adsorption affinity toward the Mg anode can also suppress passivation in non-nucleophilic electrolytes by finely modulating interfacial chemistry^{74,75}. For example, the introduction of reduced perylene diimide-ethylene diamine into Mg(TFSI)₂-based electrolytes results in its preferential adsorption within the inner Helmholtz plane of the Mg surface⁷⁴. The adsorbed molecular layer effectively blocks direct contact between the Mg anode and reactive TFSI⁻ anions, preventing the formation of passivation layers. Notably, this interfacial stabilization is achieved without perturbing the electrolyte's ionic conductivity or coordination environment. Despite its promise, molecular additive-driven interfacial regulation in non-nucleophilic systems is still at an early development stage, with only a few systematic investigations reported to date.

Solvent engineering.

Tuning Mg²⁺-solvent coordination by solvent engineering is another possible strategy to mitigate passivation of the anode in non-nucleophilic electrolytes. For instance, co-solvents can promote the formation of solvent-separated ion pairs and reduce the concentration of CIPs in the electrolytes. Furthermore, the decomposition of Mg²⁺ coordinated with co-solvents can enable beneficial passivation of free interphases (**Fig 3e**). In addition to coordination chemistry, the bulk physicochemical properties of solvents such as dielectric constant, viscosity, and polarity also influence electrolyte performance⁷⁶. High dielectric constants facilitate salt dissociation and mitigate

ion pairing yet must be carefully balanced against the chemical stability of the solvent toward Mg metal. For example, low-viscosity ethers such as THF or DME support rapid Mg^{2+} transport but show limited oxidative stability, whereas more viscous ionic liquids improve electrochemical stability but suffer from sluggish kinetics. The polarity of the solvent modulates the solvation structure and interfacial de-solvation. Highly polar solvents strengthen Mg^{2+} coordination, potentially impeding interfacial charge transfer, whereas less polar solvents facilitate de-solvation but can promote ion aggregation^{38,76,77}. Optimal electrolyte design requires a balance of these interrelated solvent properties in conjunction with salt chemistry to achieve both interfacial compatibility and bulk transport.

Incorporating a non-ether solvent (sulfone) into Cl-containing $\text{Mg}(\text{HMDS})_2$ electrolytes prepared in an ether solvent (THF) can enable Mg metal electrodeposition by facilitating the partial integration of sulfone molecules into the primary Mg^{2+} solvation shell⁷⁸. This sulfone and THF solvent mixture also markedly enhances Mg deposition quality by altering the interfacial chemistry. The sulfone adsorption at the electrode-electrolyte interface is hypothesized to form a boundary layer that thermodynamically governs deposition⁷⁹. The optimization of Cl-based electrolytes through modulating Mg^{2+} -solvent coordination has extended full-cell cycling lifespans from hundreds to several thousand cycles⁸⁰⁻⁸².

To circumvent Cl-modification, an additive-free and non-corrosive electrolyte was developed by incorporating dimethylamine as a co-solvent to the $\text{Mg}(\text{TFSI})_2$ -THF electrolyte, demonstrating the direct involvement of dimethylamine molecules in the primary solvation shell of Mg^{2+} and offering an alternative strategy for tuning solvation structures⁸³. Further validation emerged when a series of methoxyethyl-amines were employed to modulate the solvation sheath of the $\text{Mg}(\text{TFSI})_2$ -DME electrolyte, in which the amine co-solvents disrupted the $[\text{Mg}^{2+}\text{-TFSI}^-]$ coordination⁸⁴. Among amine-ether co-solvent electrolyte systems, the bivalent complex $[\text{Mg}(\text{amino})_6]^{2+}$ has been identified as the electroactive species⁸⁵.

Although the integration of amines as co-solvents can help modulate Mg^{2+} -solvent coordination, rigorous selection criteria are still needed. Parameters such as donor number and dielectric constant are key descriptors of a solvent's ability to stabilize Mg^{2+} solvation and govern ion-pair dissociation dynamics⁴⁸. Commonly used ether solvents such as DME and THF exhibit relatively modest donor numbers of 20 and 21 kcal mol^{-1} , and low dielectric constants of 7.2 and 8, respectively. In contrast, 1-methylimidazole, characterized by a substantially higher donor number of 47 kcal mol^{-1} and a dielectric constant of 39, was used as a co-solvent in chloride-free $\text{Mg}(\text{TFSI})_2$ - and $\text{Mg}(\text{HMDS})_2$ -based electrolytes in DME and THF, respectively. The superior coordinating affinity of 1-methylimidazole toward Mg^{2+} disrupts the formation of CIPs by weakening electrostatic Mg^{2+} -anion interactions, suppressing the formation of a passivation layer. Additionally, 1-methylimidazole enhances salt dissociation, improving overall ionic conductivity (up to 30-fold). In the case of $\text{Mg}(\text{OTf})_2$ -based electrolytes, the more localized negative charge of OTf^- anion compared to TFSI^- reduces its decomposition tendency and results in low solubility. Leveraging the high dielectric constant (>20), 2-methoxyethylamine has also been used as a co-solvent in $\text{Mg}(\text{OTf})_2$ -ether electrolytes^{49,86}.

Amines have been investigated both as co-solvents of ethers and as primary solvents^{87,88}. Notably, electrolytes exhibiting fully solvent-separated ion pairs are more susceptible to reductive decomposition at the Mg anode, primarily due to the poor reduction stability of strong cation-solvent coordination, particularly involving NH_2 functionalities⁸⁷. Additionally, hydrogen evolution resulting from the reduction of amine groups has been identified as a major contributor to parasitic reactions. Gas evolution at battery anodes is typically attributed to solvent reduction^{89,90}. The gas that evolves during cycling of an $\text{Mg}(\text{TFSI})_2$ electrolyte with 2-methoxyethylamine as solvent was confirmed as hydrogen by gas chromatography, resulting from the reduction of NH_2 by the metallic Mg anode⁸⁷. Furthermore, the higher binding energy and lower vibrational wavenumber of the amino group, relative to commonly used ether groups, facilitate N-H bond breaking, promoting H_2 evolution. Incorporating anions into the solvation structure with less-coordinating solvents and weakly dissociating salts can reinforce the N-H bond within amine groups by attenuating their direct

interaction with Mg^{2+} cations. These findings underscore that the use of amines, whether as solvents or co-solvents, imposes strict requirements on anion selection. In contrast, phosphate-based co-solvents, which are also characterized by high donor numbers and dielectric constants, can help modulate Mg^{2+} -solvent coordination in ether-based electrolytes^{44,91,92}. Representative phosphate-based co-solvents such as trimethyl phosphate (TMP)⁹¹ and triethyl phosphate (TEP)^{44,92} have donor numbers of 23 and 23.4 kcal mol⁻¹, and dielectric constants of 20.6 and 13.1, respectively. These values demonstrate their strong electron-donating capability and moderate polarity, which are critical for modulating Mg^{2+} solvation. However, strongly solvating co-solvents (amines and phosphates) in multivalent electrolytes can also hinder cation de-solvation and charge-transfer processes⁹³. Furthermore, co-solvents might induce self-corrosion and compromise anodic stability^{80,85,87}.

Weakly coordinating anion design.

A WCA electrolyte with an aromatic caged anion ($\text{Mg}(\text{CB}_{11}\text{H}_{12})_2$) demonstrated exceptional CE (>99%) and high oxidative stability (>3.8 V vs. Mg/Mg^{2+}). However, its complex synthesis and high costs severely limit practical viability⁵³. Alternatively, a fluorination strategy was used to achieve a similarly delocalized electronic structure, which resulted in a $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -based electrolyte¹⁵. The $[\text{B}(\text{hfp})_4]^-$ anion has an electropositive boron center tetrahedrally coordinated by oxygen atoms, each bridging $-\text{CF}_3$ terminal groups. The strong electron-withdrawing effect of $-\text{CF}_3$ induces charge delocalization, ensuring elevated dissociation in ethereal solvents and high ionic conductivity (up to 11 mS cm⁻¹)(ref.¹⁶). Density functional theory calculations have shown that the reduction decomposition of free $[\text{B}(\text{hfp})_4]^-$ anions occurs at -2.04 V vs. Mg/Mg^{2+} , indicating good compatibility with Mg metal anodes⁹⁴. Due to the strong C-F bonds, $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -based electrolytes also have a high oxidative stability > 4.5 V vs. Mg/Mg^{2+} , which enables coupling with high-voltage cathodes¹⁶. Thus, $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -based electrolytes have been integrated with diverse cathodes, including transition metal sulfides⁹⁵⁻⁹⁷, high-voltage oxides⁹⁸, electrophilic sulfur^{16,99}, and organic cathodes^{100,101}, showcasing broad compatibility and versatility.

Theoretical investigations on alkoxyborate anions with varying substitution and fluorination levels in $\text{Mg}[\text{B}(\text{hfp})_4]_2$ electrolytes revealed a direct correlation between coulombic interactions and redox stability, dictated by the extent of charge delocalization in magnesium borate salts⁹⁴. To enhance charge delocalization, ligands with strong electron-withdrawing groups are preferred, however, they also lower the reduction potential of electrolyte, facilitating decomposition. One approach involves optimizing the number of withdrawing groups ($-\text{CF}_3$) through partial substitution at the alpha carbon, exemplified by the design of $\text{Mg}[\text{B}(\text{hfp})_4]_2$. Further experiments with representative Mg borates with the abovementioned fluorinated alkoxy ligands, confirmed the effectiveness of $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -based electrolyte¹⁰². Following this boron-centered WCA design principle, other Mg electrolytes with a similar structure were also developed. For example, Mg perfluorinated pinacolatoborate $\text{Mg}[\text{B}(\text{O}_2\text{C}_2(\text{CF}_3)_4)_2]_2$ with bidentate alkoxy ligands and Mg tetrakis(hexafluoroisopropoxy)aluminate $\text{Mg}[\text{Al}(\text{hfp})_4]_2$, an aluminate analogue of $\text{Mg}[\text{B}(\text{hfp})_4]_2$, exhibited comparable performances^{103,104}.

The reaction pathway and kinetic behavior of Mg plating and stripping processes in an $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -based electrolyte showed that $\text{Mg}[\text{B}(\text{hfp})_4]_2$ is highly dissociated in DME, generating $[\text{Mg}(\text{DME})_3]^{2+}$ cations as the major electrochemically active species¹⁰². Furthermore, the de-solvation of the solvated cations is the rate-limiting step during the deposition process¹⁰⁵. Specifically, the initial de-solvation of $[\text{Mg}(\text{DME})_3]^{2+}$ to free the first coordination site was determined as the most energy-consuming step, contributing to the voltage hysteresis. Moreover, decomposition of the strongly chelated $[\text{Mg}(\text{DME})_3]^{2+}$ complex leads to unstable and non-uniform electrode-electrolyte interphases. Adding THF as co-solvent to DME solvent promotes semi-chelation solvation and stabilizes interphases formation¹⁰⁶. In a complementary approach, a generative artificial intelligence model was applied to screen 823 potential solvent molecules for $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -based RMB electrolytes, ultimately identifying 18 candidates as possible alternatives to conventional DME solvent¹⁷. Notably, experimental validation demonstrated enhanced electrochemical performance for 1,3-dioxane, including higher CE (99.59%) and extended cycling life (5200 cycles). However, the electrolyte

showed drastically lower anodic stability (~ 3 V vs Mg/Mg^{2+}) and increased Mg plating overpotential. Although $\text{Mg}[\text{B}(\text{hfp})_4]_2$ electrolytes exhibit a high concentration of solvent-separated ion pairs, a residual amount of CIPs such as $\text{Mg}[\text{B}(\text{hfp})_4]^+$ and $\text{Mg}[\text{B}(\text{hfp})_4]_2$ remains detectable (for example, $\sim 1.5\%$ in 0.5 M solution)¹⁰². Owing to their higher reduction potential relative to the free $[\text{B}(\text{hfp})_4]^-$ anion, these CIPs are susceptible to partial electrochemical decomposition at the Mg anode interface⁹⁴.

Although promising, $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -based electrolytes are still facing several challenges. For example, the cycling performance in the borate electrolyte seemed to be dependent on the thickness of separators¹⁰⁷. This issue originates from insufficient removal of the native oxide layer (for example, by scratching), that causes uneven deposition of Mg. Upon cycling, this leads to isolated Mg deposits towards the separator and triggers soft short-circuits. Uneven Mg deposition is also influenced strongly by the water content in the electrolyte¹⁰⁸. Adding the water scavenging additive $\text{Mg}(\text{BH}_4)_2$ removes the native oxide layer and promotes the formation of an interphase layer on Mg surface¹⁰⁹. Other additives, such as MgCl_2 (ref.¹¹⁰) and I_2 (ref.¹¹¹) also have been proved effective in enhancing interfacial properties but largely compromise the anodic stability of the electrolyte.

Dual-salt hybrid systems

Dual-salt hybrid non-aqueous electrolytes are designed to leverage the advantages of Mg^{2+} (for example, dendrite-free cycling and high volumetric capacity) while addressing key limitations (for example, sluggish kinetics and anode passivation), through the incorporation of monovalent salts (Li^+ or Na^+)¹¹²⁻¹¹⁴. The dual-salt hybrid concept was demonstrated with the addition of LiCl to a Mg organohaloaluminate electrolyte, in which co-insertion of Li^+ alongside Mg^{2+} enhanced the capacity of Mo_6S_8 cathodes¹¹⁵. The dual-salt concept was then extended to a broader range of complex electrolytes, including APC^{116,117} and MACC^{118,119} systems. Given the limitations associated with Cl⁻ dependency in these complex electrolytes, Cl⁻-free hybrid systems were developed by integrating $\text{Mg}(\text{BH}_4)_2$ with monovalent borohydrides (LiBH_4 and NaBH_4)^{120,121}. This dual-salt strategy was further advanced in non-nucleophilic electrolytes based on $\text{Mg}(\text{HMDS})_2$ and $\text{Mg}(\text{TFSI})_2$ salts^{122,123}. The incorporation of monovalent salts is designed to enhance the electrolyte performance by promoting cation mobility and mitigating interfacial passivation at the Mg anode¹²⁴. Alternatively, rather than directly combining Mg and monovalent salts, Mg^{2+} can be generated in situ within a Li-based electrolyte during the initial electrochemical cycles with a Mg anode, forming a Mg-Li hybrid electrolyte¹²⁵.

Although dual salt hybrid systems have been evaluated with diverse cathodes and shown improvements in full-cell performance, the underlying mechanisms remain unclear, as the electrochemical behaviour might be predominantly governed by the added monovalent salts rather than directly advancing the primary goal of realizing RMBs^{126,127}. Moreover, hybrid electrolytes introduce several limitations, including the restricted solubility of monovalent salts in magnesium electrolytes and a narrowed electrochemical stability window^{112,128}. The use of Mg metal anodes in hybrid electrolytes also faces severe limitations, most notably the continuous changes in electrolyte concentrations caused by ion depletion during the cycling, which alter key electrolyte properties (for example, ionic conductivity) that subsequently impact the overall battery performance^{6,129}.

Aqueous electrolytes

Aqueous electrolytes are appealing for batteries due to their safety, low cost, and facile production, which stem from the properties of water as a solvent^{4,130,131}. However, challenges such as small electrochemical stability window of 1.23 V, and side reactions like hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) hinder their adoption in battery systems¹³²⁻¹³⁴. Although there have been rapid developments on aqueous electrolytes for other battery chemistries, such as Li, Na and Zn, efficient aqueous electrolytes for RMBs are still lacking¹³⁵.

A study on aqueous electrolytes for RMBs was conducted in 1993, exploring a limited number of metal oxides and sulfides as cathode materials in $\text{Mg}(\text{ClO}_4)_2$ -based aqueous electrolyte¹³⁶. However, further advancements remained muted for more than 20 years until reversible Mg^{2+} cycling

was achieved using $\text{Mg}(\text{ClO}_4)_2$ -based aqueous electrolytes with MnO_2 cathodes. Yet, the electrochemical stability window of such electrolytes remained low (<1.2 V)(ref.¹³⁷⁻¹³⁹). A proof-of-concept for aqueous RMBs was presented in 2017 using a Cl-free MgSO_4 aqueous electrolyte using Mg^{2+} host materials as anode and cathode^{140,141}. However, these experiments predominantly emphasized host material optimization, with limited attention to electrolyte engineering, constraining the electrochemical stability window to a modest ~ 1.8 V.

To achieve high-voltage aqueous electrolytes for RMBs, a range of strategies have been explored including super-concentrated electrolytes¹⁴², additive engineering¹⁴³ and hybrid electrolytes^{144,145}. For example, the incorporation of polyethylene glycol into dilute $\text{Mg}(\text{TFSI})_2$ -water systems yields an aqueous electrolyte with an expanded electrochemical stability window of 3.7 V, attributed to polyethylene glycol-induced modulation of the Mg^{2+} solvation structure¹⁴³. Another strategy generally employed to broaden the electrochemical stability window of aqueous electrolytes across diverse battery chemistries is the water-in-salt electrolyte concept¹⁴⁶, which has also been demonstrated effective for RMBs¹⁴⁷.

Hydrated eutectic electrolytes have also been used in aqueous RMBs, owing to their ability to finely tune the Mg^{2+} solvation structure through precise control of the primary salt-to-additive molar ratio^{148,149}. This tunability enables competitive solvation dynamics and supports an expanded electrochemical stability window of up to ~ 4.14 V (ref.¹⁵⁰).

Solid-state electrolytes

Progress in SSEs for RMBs has remained largely hindered by the low Mg^{2+} mobility within solid electrolyte frameworks. Among the SSE compositions explored, $\text{MgZr}_4(\text{PO}_4)_6$ exhibited exceptional Mg^{2+} ionic conductivity ($2.9 \times 10^{-5} \text{ S cm}^{-1}$ at 400°C), attributed to its crystal structure, which closely mirrors that of $\text{NaZr}_2(\text{PO}_4)_3$ (NASICON - Na Super Ionic Conductor) (ref.¹⁵¹). Subsequently, strategies like modulating the cation ratio and anion doping were employed to further improve the ionic conductivity of Mg-Zr- PO_4 based SSEs¹⁵²⁻¹⁵⁴. Alternatively, the implementation of new synthesis strategies (for example, sol-gel route) facilitated precise control over the formation of the $\text{MgZr}_4(\text{PO}_4)_6$ phase, enhancing its crystallographic purity and yielding superior ionic conductivity¹⁵⁵. Despite these advancements, many of these experiments focused on conductivity improvements, whereas comprehensive battery performance evaluations and interfacial characterizations remain largely unexplored.

$\text{Mg}(\text{BH}_4)_2$ was envisioned as another inorganic SSE for RMBs, due to its potential for efficient Mg^{2+} conduction in the liquid electrolyte phase¹⁵⁶ and the renewed prominence of hydride materials in energy research¹⁵⁷. However, in $\text{Mg}(\text{BH}_4)_2$, Mg^{2+} is encapsulated within a tetrahedral framework of BH_4^- units, leading to exceptionally low ionic conductivity ($<10^{-9} \text{ mS cm}^{-1}$ at 30°C) in the solid state^{158,159}. To enhance ion transport in $\text{Mg}(\text{BH}_4)_2$ -based SSEs, crystal engineering such as partial substitution of BH_4^- with larger anions or neutral species has been employed^{160,161}. Among these $\text{Mg}(\text{BH}_4)_2$ -based SSEs, $\text{Mg}(\text{BH}_4)(\text{NH}_2)$, which was formed by substituting BH_4^- with NH_2^- , exhibited enhanced ionic conductivity but predominantly at elevated temperatures^{160,161}. As an alternative approach to achieving ambient-temperature ionic conductivity, amine groups were incorporated through additive modification rather than partial anionic substitution. For example, ethylenediamine modified $\text{Mg}(\text{BH}_4)_2$ exhibited an ionic conductivity of $5 \times 10^{-5} \text{ mS cm}^{-1}$ at 30°C , but the electrochemical stability window narrowed due to the presence of the coordinating ligand¹⁵⁸. Further efforts involved the reaction of solid $\text{Mg}(\text{BH}_4)_2$ with ammonia gas, in which defect engineered variant exhibited the highest ionic conductivity at room temperature (0.296 mS cm^{-1}) for RMB SSE^{162,163}. Despite this advancement, the ionic conductivity remains considerably low for applications, and the electrochemical stability window of these electrolytes continues to be a limiting factor. Notwithstanding these challenges with the ionic conductivity and electrochemical stability window, $\text{Mg}(\text{BH}_4)_2$ -based SSEs have enabled an all-solid-state RMB prototype¹⁶⁴.

In parallel, theoretical predictions of high Mg^{2+} mobility at ambient temperature in spinel-type compounds (MgX_2Z_4 , where $\text{X} = \text{In, Y, Sc}$; $\text{Z} = \text{S, Se}$) have generated interest in these materials as solid-state electrolyte candidates for RMBs¹⁶⁵. However, these spinel structures suffer from

undesired high electronic conductivity, arising from defects and electron-conducting secondary phases. A refined solid-state synthesis such as incorporating Se-excess phases and aliovalent doping of Sc^{3+} with Ti^{4+} and Ce^{4+} were employed to decrease the electronic conductivity¹⁶⁶. However, both approaches failed to suppress the electronic conductivity of MgSc_2Se_4 , and instead, it was repurposed as a cathode material for Mg-ion insertion using a non-aqueous electrolyte¹⁶⁶. The high electronic conductivity in MgSc_2Se_4 arises from conductive regions of Sc^0 and ScSe , which were mitigated (from $10^{-6} \text{ S cm}^{-1}$ to $10^{-12} \text{ S cm}^{-1}$) through controlled heating rates and precursor processing¹⁶⁷. Despite improved overall Mg ion mobility, achieving reversible Mg plating using spinel structure SSEs requires an ion conducting interlayer¹⁶⁸⁻¹⁷⁰.

Unlike the previously mentioned inorganic SSEs, polymer-based electrolytes offer an added advantage, as they can be prepared to be solid and quasi-solid (gel) physical states¹⁷¹. Using polymers in electrolytes also holds advantages like structural flexibility, easy processability, and light weight nature¹⁷². Polymer based SSE for RMBs, reported as early as 1986, showed limited Mg^{2+} migration with unknown mechanism of Mg^{2+} transport^{173,174}. In general, polymer-based SSEs comprised of organic polymers complexed with passivating Mg salts results in slow Mg^{2+} ion migration¹⁷⁵⁻¹⁷⁷. To address this problem, approaches such addition of nanofillers¹⁷⁸, and mixed polymeric matrix¹⁷⁹ have been employed.

Quasi- solid-state electrolytes (QSSEs) or gel electrolytes, composed of a polymer matrix and liquid components, combine the high ionic conductivity and interface stability of liquids with the mechanical robustness and structural adaptability of solids¹⁸⁰. QSSEs for RMBs have been synthesized using Grignard reagents and poly(ethylene oxide), with trace tetrahydrofuran or dibutyl ether per Mg^{2+} to optimize conductivity and stability¹⁸¹. Challenges such as low ionic conductivity and poor cycling performance with pristine Mg salts are key limitations of QSSEs often addressed through the incorporation of plasticizers^{182,183} and ionic liquids^{184,185}. Despite these efforts, improvements in ionic conductivity remained modest, and the development was halted for a while. However, with the adoption of strategies such as in-situ polymerization^{186,187} and anion modification¹⁸⁸, and emergence of non-nucleophilic ($\text{Mg}(\text{OTf})_2$)(ref.¹⁸⁹) and non-passivating $\text{Mg}[\text{B}(\text{hfp})_4]_2$ electrolyte salts¹⁹⁰, the performance of gel-type polymer electrolytes for RMBs has been improved to rival that of non-aqueous liquid systems¹⁹¹. Further, given the vast potential of formulations, including MOF-based^{192,193} and aqueous QSSEs¹⁹⁴, a deeper understanding of design principles will help develop long-cycle, high-performance QSSEs for RMBs.

Electrode-electrolyte interphases

The composition and structure of the electrode-electrolyte interphases are linked to the battery performance, making it essential to elucidate the mechanisms underlying its formation. During electrochemical cycling, two distinct interphases typically emerge, the solid-electrolyte interphase (SEI) forms at the interface between anode and electrolyte, and the cathode-electrolyte interphase (CEI) forms at the interface between cathode and electrolyte.

Solid-electrolyte interphase

Both anode passivation and SEI formation result from electrolyte decomposition at the surface of the anode. Elucidating the mechanism of Mg metal deposition is important for distinguishing the mechanisms passivation from those of SEI formation. Such insights can guide electrolyte design toward a stable, ion-conductive SEI while avoiding undesired passivation. The deposition of divalent Mg ions onto metal anode is controlled by four sequential and interdependent steps (**Fig 4a**)^{3,195}. Initially, solvated metal ions migrate through the electrolyte, where cation-anion interactions influence dissolution and solvent-metal ion coordination dictates mobility. Subsequently, these solvated ions undergo de-solvation at the electrolyte-SEI interface, a step critically impacted by anode passivation. Thirdly, the de-solvated ions traverse the SEI, demanding a composition optimized for high Mg^{2+} mobility and low electronic conductivity. Finally, metal nucleation and subsequent deposition growth

occur on the anode surface. Notably, though the SEI influences all four stages, its formation is predominantly determined by the electrolyte's intrinsic structure.

The low reduction potential of Mg metal drives electron transfer to the unoccupied orbitals of the electrolytes, inducing intrinsic reductions and accumulating decomposition products during cycling. The formation of these passivating films on the Mg anode hinders Mg^{2+} ion diffusion, contrasting with LIBs, in which surface films from side reactions often function as SEI^{25,196}. For stable metal stripping and plating, the anode-electrolyte interphases formed in RMBs should act like the SEI in LIBs, which must ensure efficient metal ion conduction, whereas a broad electrochemical stability window is essential for electrolyte compatibility. Theoretical Mg^{2+} migration energy barriers and electrochemical stability window values for common interfacial inorganic Mg species (**Fig. 4b**) provide a valuable guide for future selection of suitable SEI species^{197,198}.

Early Grignard-based electrolytes enabled reversible Mg cycling by employing reactive organometallics to scavenge contaminants and prevent passivation, though the interfacial chemistry and passivation mechanisms remained unclear⁸. However, the interfacial chemistry in DCC electrolyte showed that the surface passivation species comprises of MgO and $\text{Mg}(\text{OH})_2$ (**Fig. 4c**)²¹. Additionally, interfacial species containing C, Al, and Cl were found to contribute to the inhibition of passivation. Nucleophilic complex systems are generally dominated by highly coordinated $[\text{MgCl}]^+$ species, which give rise to $[\text{Mg}_x\text{Cl}_y\text{solvent}]^+$ as the principal electroactive entities. Consequently, Mg deposition and stripping proceed through the interfacial adsorption of $[\text{MgCl}]^+$ intermediates, resulting in the formation of a Cl-rich protective interphase (**Fig. 4d**)⁶.

Despite the transition from nucleophilic systems to non-nucleophilic systems in RMB electrolytes, passivation issues persist. Notably, similar passivation species, such as MgO and $\text{Mg}(\text{OH})_2$, observed in Grignard-based systems, also form at the Mg anode-electrolyte interface in non-nucleophilic electrolytes^{40,69}. The pioneering strategy employed to encounter passivation in non-nucleophilic systems involved the addition of Cl^- containing additives. Analogous to nucleophilic complex electrolytes, these Cl^- -modified non-nucleophilic systems generate adsorbed Mg-Cl as part of the SEI layer. However, in contrast to the nucleophilic systems, the SEI in Cl^- modified non-nucleophilic electrolytes additionally incorporates inorganic Mg species originating from the decomposition of the electrolyte anion and auxiliary anion. For example, the SEI analysis of Mg anodes exposed to Cl^- -modified $\text{Mg}(\text{TFSI})_2$ electrolytes revealed that while pre-adsorbed Mg-Cl species suppress initial passivation, the progressive cycling induced formation of MgF_2 as dominant SEI component⁵⁶. Commonly these Cl^- -modified non-nucleophilic electrolytes exhibited in-situ formed SEI layers with an organic-rich surface and an inorganic-dominant bulk structure^{43,62}. The organic components within the SEI typically originate from the reductive decomposition of commonly employed ether-based solvents at the Mg anode surface, whereas the inorganic constituents predominantly derive from the decomposition of electrolyte anions and additives. Occasionally, other Mg halide-based SEI components with superior Mg^{2+} conductivity, like MgI_2 (ref⁶⁸) and MgBr_2 (ref⁷⁰) have been formed in-situ through electrolyte additive strategies aimed at mitigating passivation.

The SEI layers formed in additive-modified non-nucleophilic electrolytes comprise inorganic nanocrystalline domains (for example, halides, oxides and sulfides) randomly dispersed within an organic matrix, resulting in an organic-inorganic hybrid architecture (**Fig. 4e**). In systems employing BH_4^- -based additives, BH_4^- anions preferentially adsorbs onto the Mg surface during charge transfer, forming a protective layer that suppresses passivation⁷¹, whereas in another case, additive cation adsorption establishes a dynamic electrostatic shield layer on the anode⁷³. Although the classification of such adsorption layers as true SEIs remains debated, certain BH_4^- additive-modified non-nucleophilic systems still yield organic-inorganic hybrid SEI layers⁷².

Another strategy employed in mitigating passivation is the regulation of Mg^{2+} -solvent coordination by adding co-solvents containing a high donor number and dielectric constant (amines and phosphates) to commonly used ethers. Decomposition of co-solvent coordinated with Mg^{2+} cations forms inorganic SEI species on anode surfaces, which protects the anode from passivation and results in improved Mg conducting properties. The SEI layers in ether-based solvents generally possess high concentration of solvent-derived organics, which are also drastically reduced when

using amine and phosphate as co-solvents^{85,199}. Similarly, the formation of low-ion-mobility inorganic species, such as MgF_2 and MgS_2 , arising from anion reduction at the Mg surface, is markedly suppressed in co-solvent-modulated non-nucleophilic electrolytes⁹². Moreover, SEI layers formed in co-solvent systems are considerably thinner than those in ether-based counterparts, which helps enhance ion transport⁸⁶. These combined effects yield thin, inorganic-rich SEI layers in co-solvent-based non-nucleophilic electrolytes (**Fig. 4e**). Introducing phosphates (for example, TMP) as a co-solvent with ether induces in-situ formation of $\text{Mg}_3(\text{PO}_4)_2$ and $\text{Mg}(\text{PO}_3)_2$ on the anode, ensuring electronic insulation while enabling Mg^{2+} transport⁹¹. The commonly employed 2-methoxyethylamine co-solvent with ethers enabled N-containing SEI species (for example, Mg_3N_2) on the surface of Mg anode that shortened the ion transport path and eliminated electronic leakage from the Mg anode^{49,86}. Additionally, amine-ether co-solvents found to enable a thin (~5 nm) monolithic MgH_2 enriched SEI²⁰⁰. Despite exhibiting low Mg^{2+} migration barriers (647 meV for MgH_2 and 655 meV for Mg_3N_2) enabling fast ion transport, their narrow electrochemical stability windows (0.42 V for MgH_2 and 0.8 V for Mg_3N_2) pose substantial limitations to their viability as practical SEI components.

In contrast to other non-nucleophilic non-aqueous electrolytes that rely heavily on electrolyte modifications, WCAs based single salt systems (for example, $\text{Mg}[\text{B}(\text{hfp})_4]_2$) enables reversible Mg cycling inherently, with SEI layers formation governed predominantly by the controlled decomposition of the electrolyte itself rather than exogenous additive or co-solvent contributions. A pioneering, experimental interrogation of the anode-electrolyte interface in the most representative WCAs based electrolyte ($\text{Mg}[\text{B}(\text{hfp})_4]_2$ in DME) revealed that the in situ-formed SEI layer predominantly composed of F-rich species, including $-\text{CF}_x$ and MgF_2 derived from electrolyte decomposition²⁰¹. In specific, organic $-\text{CF}_x$ species distributed throughout the SEI layer, whereas the inorganic MgF_2 concentrated in the deeper regions, resulting in an overall organic-rich SEI layer (**Fig. 4e**). Subsequent investigation demonstrated that the organic fraction of the SEI is not limited to organofluorides, but also includes C-O and B-O species, while the inorganic component encompasses not only MgF_2 but also Mg-O, formed via decomposition of Mg^{2+} -DME coordination¹⁰². Additional investigations confirmed that DME decomposition generates C_2HO^- and C_2H^+ species and the decomposition of $[\text{B}(\text{hfp})_4]^-$ anion results in the formation of inorganic MgB_xO_y and MgF_2 in the SEI layer¹⁰⁶. Furthermore, partial substitution of DME with THF has been shown to enhance the organic content of the SEI, which correlates with the improved electrochemical performance of DME-THF mixed-solvent electrolyte. These observations further confirm that SEI layers in $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -ether electrolytes follow an organic rich model (**Fig. 4e**).

Although the suitability of MgF_2 as a solid SEI component remains debatable due to its poor Mg^{2+} conductivity, its wide electrochemical stability window protects the Mg metal anode from further electrolyte-induced degradation¹⁹⁸. A thin MgF_2 coating layer on Mg is sufficient to enhance the interfacial stability²⁰². Notably, the limited formation of MgF_2 from the decomposition of $\text{Mg}[\text{B}(\text{hfp})_4]_2$ appears to contribute positively to the long-term cycling stability of Mg anodes. However, despite enabling additive-free reversible Mg cycling, this electrolyte requires extensive activation cycles to reach optimal capacity attributable to the initially sparse adsorption of electrolyte species on the Mg surface, which increases charge transfer resistance and the initial plating overpotential. The incorporation of additives such as $\text{Mg}(\text{BH}_4)_2$ and I_2 can accelerate SEI formation by removing the native oxide layer^{109,111}. Nevertheless, the structure of SEI layers followed the same organic rich model observed in additive free counterparts. This strategy presents an opportunity to engineer tailored SEI components with superior Mg^{2+} conductivity through strategic additive or solvent modifications. However, such approaches must be carefully balanced to preserve the intrinsic properties such as high anodic ability and non-corrosive nature of the $\text{Mg}[\text{B}(\text{hfp})_4]_2$ electrolyte.

One such strategy is employing amine and phosphate co-solvents to ether-based $\text{Mg}[\text{B}(\text{hfp})_4]_2$ electrolytes. This strategy can mitigate passivation in non-nucleophilic systems by enabling thin, inorganic rich SEI layers for good electrochemical performance. As the ether-based $\text{Mg}[\text{B}(\text{hfp})_4]_2$ electrolytes commonly yield organic rich SEI with random distribution of inorganics rather than conformal SEI layers¹⁰², the amine and phosphate co-solvents will enable a thin, inorganic

rich interphase and shorten the ion diffusion pathway for highly reversible Mg cycling, improved coulombic efficiency and reduced overpotential.

In hybrid electrolytes, monovalent salts are typically incorporated to enhance full-cell performance. However, mechanistic understanding of SEI formation is limited. In a dual-salt hybrid electrolyte comprising $\text{Mg}(\text{TFSI})_2$ and LiBH_4 , even though the surface of SEI layer is composed of organic species, the bulk is composed mainly of Mg and Li based inorganic species, yielding a hybrid cation SEI layer (**Fig. 4e**)¹²⁴. A hybrid electrolyte formed in-situ by cycling Li salt in a Mg anode also yielded a hybrid cation SEI layer¹²⁵. The decomposed Li salt precipitates on Mg anode surface and forms Li containing SEI species such as Li_2CO_3 , Li_2O , and LiF along with formation of Mg based SEI species. The in-situ formed Li based SEI species prevent the further parasitic reaction between the remaining electrolyte and Mg anode.

Aqueous electrolytes require a more resilient SEI due to the reactivity of water (H_2O) as solvent, which easily passivates the Mg anode. Even trace level H_2O (≤ 3 ppm) in $\text{Mg}(\text{TFSI})_2$ -based non-aqueous electrolyte was found to induced passivation, that was countered by integrating Mg-Cl species into the SEI⁴⁰. However, comprehensive investigations into SEI formation in many aqueous electrolytes remain largely unexplored, primarily because of the focus on Mg^{2+} insertion into Mg host materials rather than using Mg metal as anode, often neglecting the intricate chemistries at the anode interface. Another important reason to prioritize understanding SEI behavior in aqueous systems lies in its potential to suppress surface side reactions (HER and OER)¹⁴⁷. Currently, Mg-Cl based species are well-known SEI components that provide interfacial stabilization in aqueous electrolytes for RMBs. Identifying other SEI components that offer enhanced Mg^{2+} ionic mobility and a broader electrochemical stability window could help improve the performance of aqueous RMBs.

Formation of SEI in SSEs has remained largely unexplored as research has primarily focused on enhancing Mg^{2+} ion conductivity. Emerging findings on the Mg anode interface in QSSEs have begun to shed light on SEI composition and structure¹⁸⁷. However, the SEI formation in QSSEs seems to be similar to that observed in non-aqueous Mg electrolytes, as QSSEs represent a distinct physical state of the same electrolyte composition. Another factor that needs to be considered regarding the SEI in QSSEs is the effect of polymer additives on the SEI composition and spatial arrangement, as these elements can shape its formation and functional efficacy.

Cathode-electrolyte interphase

The compatibility between cathodes and electrolytes is increasingly recognized as a decisive factor in RMBs. Although early efforts focused largely on overcoming surface passivation at the Mg metal anode, progress toward full cells requires equal attention to the interfacial reactions at the cathode. Indeed, electrolyte formulations that effectively activate the anode often prove chemically or electrochemically unstable against cathodes, limiting the development of high-energy RMBs.

In Cl-containing electrolytes, their Lewis acidic moieties enable the removal of passivation layers on Mg metal and the reversible Mg plating and stripping. However, the same reactivity renders them strongly nucleophilic toward cathodes. As a result, electrophilic frameworks of oxide hosts containing S-S bonds or redox-active organics undergo undesirable side reactions in such electrolytes²⁰³. Therefore, research focus has shifted toward non-nucleophilic Mg salts that can provide both chemical inertness and wide electrochemical windows. Among the candidates, salts with WCAs have emerged as model electrolytes for probing compatibility with higher-voltage cathodes, offering a foundation for systematic benchmarking^{15,53}.

In addition to anions, the role of the solvent is equally critical on cathode-electrolyte compatibility. In contrast to Li-ion systems, in which carbonate solvents combine high anodic stability with good interfacial behavior, magnesium electrolytes remain largely restricted to ether solvents. Even though electrolytes formulated using ethers can enable reversible Mg plating and stripping, their intrinsic oxidative stability (~ 3.5 V vs. Mg as free molecules) places limits on long-term cycling, especially under lean electrolyte conditions⁶. Coordinating interactions with Mg^{2+} can kinetically extend stability, but degradation processes remain a concern. Identifying new solvent classes for RMB electrolytes remains challenging due to the competing demands of Mg^{2+} solvation, oxidative

stability, and interfacial compatibility. Co-solvent systems with balanced hybrid formulations can reconcile these requirements, by offering enhanced ionic conductivity and anodic stability while expanding electrolyte design beyond conventional ether frameworks⁸⁴.

Parallel to bulk electrolyte design, attention is being directed toward controlling cathode-electrolyte interfacial chemistry. In analogy to the CEIs in Li-ion batteries, in-situ interphase formation has been explored in Mg systems. However, conventional decomposition products typically generate passivating layers with poor Mg^{2+} permeability, underscoring the challenge of achieving a functional CEI layer. The controlled decomposition of Cl-free borate salts or amine-modified electrolytes can yield nanometric boron- and nitrogen-rich interphases that actively facilitate Mg^{2+} de-solvation and accelerate charge transfer^{86,204,205}. These findings redefine CEI layers from inert transport barriers into chemically tunable mediators of interfacial kinetics. The broader implication is that electrolyte decomposition is not exclusively parasitic and can be used as a design strategy. Boron- and nitrogen-rich species can also be used as CEI layer components, as demonstrated with Mo_6S_8 cathodes²⁰⁶. Extending these insights into high-voltage cathodes can help develop next-generation RMBs, but systematic investigations are still required to clarify the structural and chemical requirements.

Dendrite formation

Dendritic structures can develop on Mg anodes in non-aqueous electrolytes²⁷. However, the potential for dendrite formation in RMB electrolytes is often underestimated and Mg battery chemistries are assumed to be unaffected by dendrite growth. Moreover, many reported systems operate within a restricted current density range, often neglecting the implications of high-current-density applications, in which dendrite formation might be exacerbated.

Fundamentals of dendrites formation

The electrochemical reaction rate and diffusion rate are the two main factors influencing plating morphology. The high charge density of Mg ions makes de-solvation and dissociation difficult, keeping the electroplating reaction in a kinetically controlled state and promoting uniform plating until a limiting current is achieved (**Fig. 5a**)²⁰⁷. However, when the reaction shifts to diffusion-controlled under high current densities, exceeding ion transport limit leads to dendrite-like deposits over time, as explained by Sand's time model²⁰⁸. Furthermore, the growth of porous Mg morphologies has been observed in less passivating electrolytes, arising from uneven formation of anode-electrolyte interface^{22,209}. These uneven anode-electrolyte interfaces disrupt ion flux and cause electron leakage during the Mg plating and stripping process. Over continuous cycling, this electron leakage leads to the formation of a porous Mg anode covered by a large accumulation of dead Mg, which usually initiates the dendrites formation (**Fig. 5b**).

Atomic-scale density functional theory simulations suggest that Mg, unlike Li, forms crystalline layers during deposition due to its thermodynamic traits, improving energy density while preventing dendrite formation²¹⁰. Metal deposition on Mg(0001) yields smoother structures compared to Li(001) and Na(001), owing to enhanced self-diffusion rates and stronger adatom interaction energies that promote stable nucleation²¹¹. However, some theoretical studies of dendrite formation during Mg electrodeposition, often using Li as a comparative model system, have uncovered unexpected phenomena that challenge prevailing assumptions²¹²⁻²¹⁴. For example, the diffusion barrier on the most common Mg surface under standard battery conditions is sixfold higher than that of Li under analogous conditions. If diffusion barriers would serve as predictors of dendrite formation, this observation would indicate that Mg is more prone to dendrite growth than Li. However, this apparent contradiction suggests that diffusion barriers alone are insufficient as a descriptor of dendrite formation mechanisms, or alternatively, that the models employed in these theoretical findings might be overly simplistic and fail to capture the complexity of real-world systems²¹².

Dendrite types

Initially, the role of electrolytes in dendrite formation was underestimated, with the absence of dendrites assumed to be an intrinsic feature of Mg chemistry. However, this assumption is now being challenged. As a result, experimental evidence of dendrite growth in various Mg electrolytes

has emerged, as for example globular dendrites (**Fig. 5c**) observed in Mg symmetric cells in Mg(TFSI)₂-glyme electrolyte²¹⁵. However, ambiguity remains regarding whether the globular formations observed in Mg cells qualify as true dendrites, as dendrites in Li batteries are conventionally characterized by their distinct branch-like morphology.

Further concerns over dendrite formation on Mg anodes have driven investigations into classical Grignard reagent-based electrolytes, revealing the direct emergence of branched dendritic structures (**Fig. 5d**)^{216,217}. Moreover, operando visualization of the morphological evolution of Mg metal anodes in APC electrolyte revealed the formation of needle-like dendrites (**Fig. 5e**), which were identified as the primary cause of internal cell shorting²¹⁸. To mitigate dendrite formation in APC electrolytes, strategies such as leveraging magnesiophilic sites²¹⁹ and incorporating lithium-based additives²²⁰ have been explored to promote uniform Mg deposition. Apart from these complex electrolyte systems, dendrite formation is also observed in non-nucleophilic single-salt electrolytes^{65,215}. For example, in Mg(OTf)₂ based electrolytes, whisker-shaped Mg dendrites (**Fig. 5f**) are observed, but they can be suppressed by adding organic additives to the electrolyte that enable planar deposition⁶⁵.

Sustainability considerations

The viability of RMBs for specific applications largely depends on overcoming their current technical challenges such as electrode compatibility and overpotentials²²¹. If these are resolved, the potential of RMBs for high energy densities and improved safety, primarily due to a lower risk of dendrite formation²²² could make them appealing for portable electronics, e-mobility, and the aerospace industry²²³. Even with modest performance, if the cost advantage of abundant Mg holds true, this technology could become a candidate for stationary applications, such as large-scale energy storage and renewable energy grid support²²⁴.

Benefits and challenges of magnesium

A key advantage is the use of magnesium metal, a geographically widespread and highly abundant element in the Earth's crust, that can even be extracted from seawater^{225,226}. However, production is concentrated only in a few regions, particularly in China, which controls about 86% of the global supply²²⁷. Other suppliers such as United States (US) and Russia own respectively only about 3% and 3.9% of the market, followed by Brazil, Iran, Israel, Kazakhstan, and Turkey, accounting worldwide for about two million metric tons of Mg produced per year²²⁷.

Unequal resource distribution has raised concerns about potential supply-chain bottlenecks and excessive dependency on a single importer in some regions. Mg has been included in the European critical raw material lists since 2011^{227,228}, (as the European union (EU) relies entirely on imports²²⁹) and it is currently part of the Critical Material List in the US²³⁰ (importing over 50% of its domestic consumption)²²⁷. An eventual large-scale rollout of RMBs could add pressure on the supply chain of Mg and aggravate the existing supply risks. These risks could be mitigated through Mg market diversification, achieved with the introduction of new players, re-establishing the industry in regions where it was previously produced, and with the increase of secondary material production²³¹. Ongoing research efforts and industry initiatives already seek to develop alternative cost-effective and low environmental impact sourcing techniques for Mg. Extracting Mg from seawater and desalination brines^{225,226,232} could incentivize domestic Mg production with smaller environmental impacts than the traditional industry standard and fossil fuel intensive Pidgeon process.

Increased secondary production from scrap material, incentivized through the definition of recycling targets and economic benefits, could also supply considerable amounts of Mg to the market²³³. The stability and low reactivity of Mg make it fully recyclable via simple separation methods without compromising quality²³⁴. This poses a critical advantage over the recycling of other metals such as Li, often achieved through advanced hydrometallurgical and pyrometallurgical techniques^{235,236}. Moreover, the energy requirements for Mg recycling from scrap materials can be as little as 5% of the energy demand for primary material production²³⁷. However, recycling can

become an inefficient and economically unattractive task if the scrap composition is very heterogeneous, hampering the separation steps²³⁸, or if there is a substantial amount of impurities in the Mg-alloys²³⁴. Due to such inefficiencies, it is estimated that only about 7% of the total Mg imports in Europe would originate from secondary sources and that the equivalent of about 18% of imported material would end up yearly in the landfill²³⁹.

Environmental sustainability

Due to their early stage of development, only a few assessments of the environmental profile of Mg batteries have been done so far. Life cycle assessments based on prototypes and theoretical modelling have been conducted for magnesium-sulfur (Mg-S) systems^{221,224,240,241}. The general life cycle stages of RMBs evaluate the potential effects on the environment from battery pack production and from their theoretical use in stationary and mobile applications (**Fig. 6**). The assessments are conducted based on theoretical values, expert judgement and scenario analysis to identify the most relevant factors that could influence the ecological footprint, while acknowledging the technological challenges that hinder battery performance. For example, Mg production for the anode is a main contributor to the environmental impact of the cell^{240,241}, mostly due to the pollutant and energy intensive nature of the Pidgeon process. Nevertheless, the life cycle assessment results support the premise that the resource depletion potential (based on reserves on the Earth's crust) of Mg-based batteries is lower than that of other benchmark systems such as LIBs^{224,241}.

Other impact categories such as climate change and toxicity also display favorable results, comparable to reference technologies. With respect to the electrolyte, a solution of $\text{Mg}[\text{B}(\text{hfip})_4]_2$ with DME as organic solvent⁹⁴ can contribute up to about 10% of the total environmental impacts of battery pack production in categories such as climate change and acidification potential. These contributions are mainly due to the energy intensiveness of the pre-chain and production process of sodium borohydride (NaBH_4), necessary for the synthesis of the precursor $\text{Mg}(\text{BH}_4)_2$. The relative contributions from the electrolyte in other categories such as resource criticality are less prominent, representing between 2-4% of the total impacts. Hexafluoroisopropanol, a precursor for the electrolyte, bears little direct impacts with respect to other cell components, but belongs to the broader family of per-fluoro alkyl substances (PFAS), known as forever chemicals due to their bioaccumulation capacity and persistence on the environment²⁴². Presence of this PFAS in the electrolyte [A1] preparation process has raised concerns associated with the potential effects on human health and on the biosphere from long-term exposure²⁴³, which could occur as a consequence of improper handling during the end-of-life phase of the battery. The production of these halogenated compounds, found in other common Mg salts, could also lead to the release of toxic fluorinated by-products and potent greenhouse gases²⁴⁴. Moreover, the use of organic solvents such as DME is also associated with safety concerns due to their flammable and volatile character, which could lead to risks of fire during battery failure or damage²⁴⁵.

Damage of the batteries during operation or improper disposal could also contribute to the leakage and exposure of potentially toxic compounds within the electrolytes such as solvents and PFAS to local environments or landfills. Though some of the negative impacts of production and hazards from direct exposure to these compounds have been documented (for example, via register of chemical substances in the European chemicals agency (ECHA)), further research is still necessary to quantify the adverse effects on the environment and human health over their entire life cycle, from resource extraction to end-of-life and with special attention to their final disposal.

In terms of battery recycling, as RMBs are still in their early stages of development, there is a chance to incorporate design-for-recycling strategies to ease material recovery at the end of battery life. For example, using magnesium foil as the anode material could simplify cell separation and improve the cost-effectiveness of recycling. This aspect becomes particularly relevant given the potentially lower financial incentive to recover abundant and inexpensive magnesium, in contrast to the more valuable cobalt, nickel, and lithium in LIBs. At the same time, novel cathode and electrolyte chemistries in RMBs might complicate recycling and involve potentially hazardous materials, such as fluorinated organic compounds³¹, but the presence of valuable compounds could also increase

the incentive for material recovery. In such cases, hydrometallurgy could become a viable recycling route, analogous to its application in LIBs²⁴⁶. Ultimately, more research is needed to develop cell designs that are economically attractive to recycle and to promote circularity for Mg batteries.

Costs and technical viability

Though magnesium is more abundant and cheaper than lithium²²⁷ the costs of purifying and processing it into battery-grade product⁶ still need to be analyzed. The low ductility of pure magnesium presents a major processing challenge, particularly for fabricating thin foils required to achieve high energy densities. To overcome this limitation, magnesium alloys incorporating elements such as aluminum and zinc²⁴⁷ have been explored, which would add further processing costs. Parallel efforts have focused on engineered alloy systems containing bismuth or tin²⁴⁸, designed to enhance surface charge-transfer kinetics, along with advanced surface modification strategies aimed at stabilizing magnesium metal anodes²⁴⁹. Nonetheless, the economic implications of these materials and design strategies on overall cell cost remain insufficiently quantified.

At the battery level, some investigations have reported progress toward cost-effective chemistries²⁵⁰⁻²⁵², but a comprehensive economic picture for large-scale RMB production is still lacking. Initial cost estimations of magnesium-sulfur batteries indicate that liquid organic magnesium borate-based electrolytes could represent a major cost barrier, whereas solid-state electrolytes might offer a more viable and scalable alternative²⁵³. From a technical feasibility perspective, the adaptation of existing LIBs manufacturing infrastructure for RMBs remains uncertain and would likely require substantial process modifications. Although some processes, like mixing slurries for cathode materials²⁵⁴, could be partially transferable, other processes, including electroplating of Mg anodes²⁵⁵ need entirely new protocols and dedicated equipment. Moreover, the high environmental sensitivity of Mg-based electrodes and electrolytes²⁵⁶ could require more stringent production protocols than those used for LIBs¹⁴².

Beyond cell fabrication, system-level integration introduces further complexities. Although battery management systems developed for LIBs could serve as an initial reference, their direct translation to RMBs remains uncertain. The distinct electrochemical characteristics of Mg batteries, such as narrower operational temperature ranges²⁵⁷ and shorter operating voltages⁶, necessitate specialized monitoring protocols and customized battery management system parameters. Furthermore, parameters governing charging behavior, cell balancing, and algorithms for estimating state of charge and state of health must be redesigned and optimized to accommodate the sluggish ion transport kinetics and characteristic voltage profiles.

Summary and future perspectives

The evolution of non-aqueous electrolytes for RMBs from early complex nucleophilic systems to simplified single-salt non-nucleophilic systems has been driven by a deeper understanding of solvation dynamics and ion-pairing behavior. This mechanistic insight has facilitated the development of design strategies that have substantially mitigated key challenges such as Mg anode passivation, low anodic stability and low ionic conductivity. In specific, the WCAs-based non-aqueous electrolytes show that precise modulation of Mg²⁺ coordination within both the salt and electrolyte is needed for constructing optimal solvation environments. These optimized solvation environments in WCAs based electrolytes facilitate charge transfer, rapid desolvation, and reduce parasitic reactions. In contrast to non-aqueous systems, aqueous electrolytes and SSEs for RMBs remains in early development nascent stages, necessitating a broadened research focus to address their fundamental limitations. The path forward for RMBs involves tackling several interconnected challenges including elucidating the mechanisms of electrode-electrolyte interphases formation through interdisciplinary research and comprehensive reporting of dendrite formation phenomena. Furthermore, solidifying RMBs as an economically viable and environmentally clean technology requires addressing geographical supply of magnesium metal and eliminating hazardous components from their electrolytes.

Aiming for practical RMBs, the current state-of-the-art non-aqueous electrolytes based on Mg[B(hfip)₄]₂ offer a combination of high ionic conductivity, wide anodic stability, and excellent

cathode compatibility, even in single-salt-single-solvent electrolyte configuration. Translating this laboratory success to large-scale application calls for cost-effective and scalable production. For instance, the $\text{Mg}[\text{B}(\text{hfp})_4]_2$ salt can be synthesized via a one-step reaction involving $\text{Mg}(\text{BH}_4)_2$ and fluorinated alcohols, providing a potential streamlined and scalable manufacturing route. Moreover, replacing $\text{Mg}(\text{BH}_4)_2$ with the cheaper $\text{Zn}(\text{BH}_4)_2$ precursor could decrease the materials cost to approximately 92.96 USD kWh^{-1} , which is in the same order of magnitude to that of the commercial LIBs¹⁰². Looking ahead, $\text{Mg}[\text{B}(\text{hfp})_4]_2$ -based electrolytes will encompass two primary directions. Firstly, continued efforts towards the further simplification of synthetic routes and ongoing cost optimization. Secondly, performance enhancement of these commercially available salts might be achieved through rational design strategies, particularly the fine-tuning of Mg^{2+} solvent coordination and advanced interfacial engineering.

Despite efforts, aqueous electrolytes remain limited by challenges such as narrow electrochemical stability window, low ionic mobility, and poor Mg plating reversibility. Future investigations should encompass a broader spectrum of experiments, such as Mg plating and stripping dynamics, anodic stability assessments, and detailed interphase characterization. For SSEs, although theoretically viable systems exist, research remains mainly focused on enhancing Mg-ion transport in solid state. Exploring their operational voltage ranges and compatibility with cathodes would also be important for SSEs development. For QSSEs a deeper understanding of design principles is needed, including going beyond conventional strategies (such as inclusion of plasticizers and ionic liquids) to fully leverage strategies such as in-situ polymerization, anion modification, and the integration of non-passivating Mg salts.

Electrolytes for RMBs should be designed holistically enabling reversible Mg deposition while simultaneously maintaining cathode integrity under high-voltage operation. Progress will depend on approaches that bridge solvation chemistry, anion and solvent engineering, and interfacial design, supported by advanced in situ characterization and modeling. Addressing these interlinked challenges will be essential for translating laboratory advances into durable, high-energy Mg-based full cells. Employing advanced characterization techniques such as electrochemical liquid phase transmission electron microscopy (ELP-TEM)²⁵⁸, ambient pressure X-ray photoelectron spectroscopy (AP-XPS)²⁵⁹, cryogenic electron microscopy (cryo-EM)²⁶⁰, and other operando methodologies²⁶¹ will be important for rational interphase understanding and design. Though some progress has been made in characterizing interphases in non-aqueous RMB systems, there is still a knowledge gap for aqueous and all-solid-state electrolytes. Therefore, a comprehensive understanding of interphase dynamics across all electrolyte classes is needed. Furthermore, a deep knowledge of electrode-electrolyte interfaces will help clarify the fundamental causes of dendrite growth, and contribute to the development of electrolyte engineering strategies for RMBs operating under high-current conditions.

From a sustainability perspective, though magnesium's abundance presents an important advantage, streamlining production requires consistent global availability. Environmentally, RMBs already demonstrate competitive performance, positioning them as a promising alternative to LIBs. Nevertheless, minimizing the use of hazardous chemicals, particularly in the electrolyte, will be essential to establish RMBs as a truly cleaner and more sustainable option among next-generation secondary battery technologies. In this context, the development of fluorine-free magnesium salts is especially important, as many high-performance electrolytes rely on fluorinated anions associated with environmental concerns³¹. Ongoing regulatory discussions on a potential class-wide restriction of PFAS further underscore this issue²⁶².

Artificial intelligence (AI)²⁶³ and machine learning (ML)²⁶⁴ have emerged as tools in battery research. The strategic integration of advanced ML algorithms into areas such as electrolyte design, SEI dynamics, and dendrite suppression could help improve RMBs performance. For example, generative AI/ML can enable property-to-structure prediction for inverse design of RMB electrolytes and SEI components. It is hoped that established theoretical frameworks and experimental methodologies from monovalent battery research^{265,266} could be adapted and leveraged to accelerate the understanding and development of RMBs.

Key points

Rechargeable magnesium batteries (RMBs) are well positioned as an alternative post lithium-ion battery technology; however, their commercial viability is constrained by electrolyte limitations.

Complex electrolytes (mostly Grignard reagents-based) dominated early RMB research but their nucleophilicity presents safety risks and limits their applicability.

RMB electrolyte design has transitioned from bulky Grignard-based complex systems to efficient single-salt formulations.

Though non-aqueous electrolytes show potential, advancements in aqueous and solid-state variants remain in the early stages of development, highlighting the need to adapt proven design frameworks to accelerate their progress.

Fundamental understanding of electrode-electrolyte interphases and dendrite formation mechanisms is critical for advancing RMBs from laboratory prototypes to commercially viable and low-environmental impact batteries.

Mitigating existing supply-chain risks would enhance production reliability, whereas further reducing hazardous components in RMB electrolytes would cement their viability as sustainable next-generation energy storage solutions.

Illustrative elements

Table 1 | **Properties and performance of electrolytes for Mg plating/stripping.**

Electrolyte salt	Additive/Solvent	Ionic conductivity at RT (mS cm ⁻¹)	Anodic stability (V vs. Mg/Mg ²⁺)		Coulombic efficiency (%)	Cycling life (number) ^b	Overpotential (mV) ^b	Ref.
			on Pt	on non-noble metals				
Non-aqueous electrolytes								
Grignard reagent	-/THF	0.265	2.0	-	~100	-	-	29
DCC	-/THF	1.4	2.5	-	~100 ^a	-	-	8,24
APC	-/THF	4	3.3	2.1 (SS)	~100 ^a	-	-	9,30
MACC	-/THF, DME	2	3.1	-	98.8	-	-	32
	-/THF	0.26	3.4	2.1 (SS)	~100 ^a	-	-	30,33
Mg(HMDS) ₂	AlCl ₃ /G2	1.70	3.9	2.60 (SS)	99.00	-	-	12
	TBABH ₄ /DME	0.5	1.98	3.18 (SS)	98.60	1000	250	72
	TBABH ₄ +MgBr ₂ /DME	0.46	3.1	2.78 (Mo)	99.26	1000	260	70
	OctylBr/DME	0.11	2.95	2.33 (Mo)	99.34	1800	45	69
Mg(TFSI) ₂	AlCl ₃ + MgCl ₂ /DME	6.82	3.2	2.2 (SS)	97.00 ^a	2000	120	57
	-/DME+G2+BTfE+TEP	2.8	-	4.16 (Al)	95.20	3500	500	92
	-/DME+MeIm	8.31	-	3.0 (SS)	90.65	110	400	48

Mg(OTf) ₂	MgCl ₂ +AlCl ₃ +PP ₁₄ TFSI/THF	5.83	3.1	2.20 (SS)	97	-	-	63
	-/G2+MOEA	0.67	-	3.00 (SS)	98.3	5000	100	86
	-/G2+TEP	-	4.7	4.50 (SS)	99.96	250	600	44
Mg[B(hfip) ₄] ₂	-/DME	6.8	3.5	4.3 (SS)	98	-	-	15
	-/DME	11	4.5	4.0 (SS)	-	1000	180	16
	-/DME	8.0	-	-	99.04	860	1700	102
	-/DOX	-	-	3.5 (SS)	99.59	3000	500	17
Aqueous electrolytes								
Mg(ClO ₄) ₂	adiponitrile / H ₂ O	-	-	-	94.20	300	50	150
Mg(NO ₃) ₂	Acetamide/H ₂ O	5.5	-	-	-	-	-	148
SSEs								
Mg(BH ₄) ₂	TiO ₂ +NH ₃ /-	0.296	-	1.3 (SS)	-	300	150	162
MgSc ₂ Se ₄	Ti, Ce/-	0.092	-	-	-	-	-	166
QSSEs								
n-BuMgCl	GDAE+AlCl ₃ +DODT+DMPA/THF	0.119	-	3.1 (SS)	95.20	1000	370	188
Mg(OTf) ₂	PVdF-HFP+SN+EMITF/Acetone	4.0	-	4.1 (SS)	-	-	-	189
Mg(BH ₄) ₂	MgCl ₂ +FTGB/THF	0.045	4.8	-	100	600	200	191

Best reported performance metrics for each electrolyte category are presented. Note that not all the electrolytes were measured under the same conditions, and direct one-to-one comparison between different electrolytes is not possible. Coulombic efficiency values were determined by galvanostatic cycling of asymmetric cells, except those marked with ^a, which were obtained via cyclic voltammetry. ^bCyclic life and overpotential values were measured using galvanostatic cycling of Mg//Mg symmetric cells. The current density used to measure cycling life and overpotential for ref.⁵⁷ is 0.025 mA/cm², for ref.¹⁹¹ is 0.05 mA/cm², for ref.^{16,150,162,188} is 0.1 mA/cm², for ref.^{48,69,70,72,86} is 0.5 mA/cm², for ref.⁴⁴ is 1 mA/cm², for ref.^{17,92} is 2 mA/cm², for ref.¹⁰² is 25 mA/cm².

Figure 1. Timeline of the development of electrolytes for RBMs. The coloured boxes distinguish the three major electrolyte classes: aqueous (blue), non-aqueous (orange), and solid-state (green). Relevant developments for each electrolyte class illustrate the evolution of electrolytes for RBMs over time. For non-aqueous electrolytes, the main development was the transition from nucleophilic complex systems to single-salt non-nucleophilic systems.

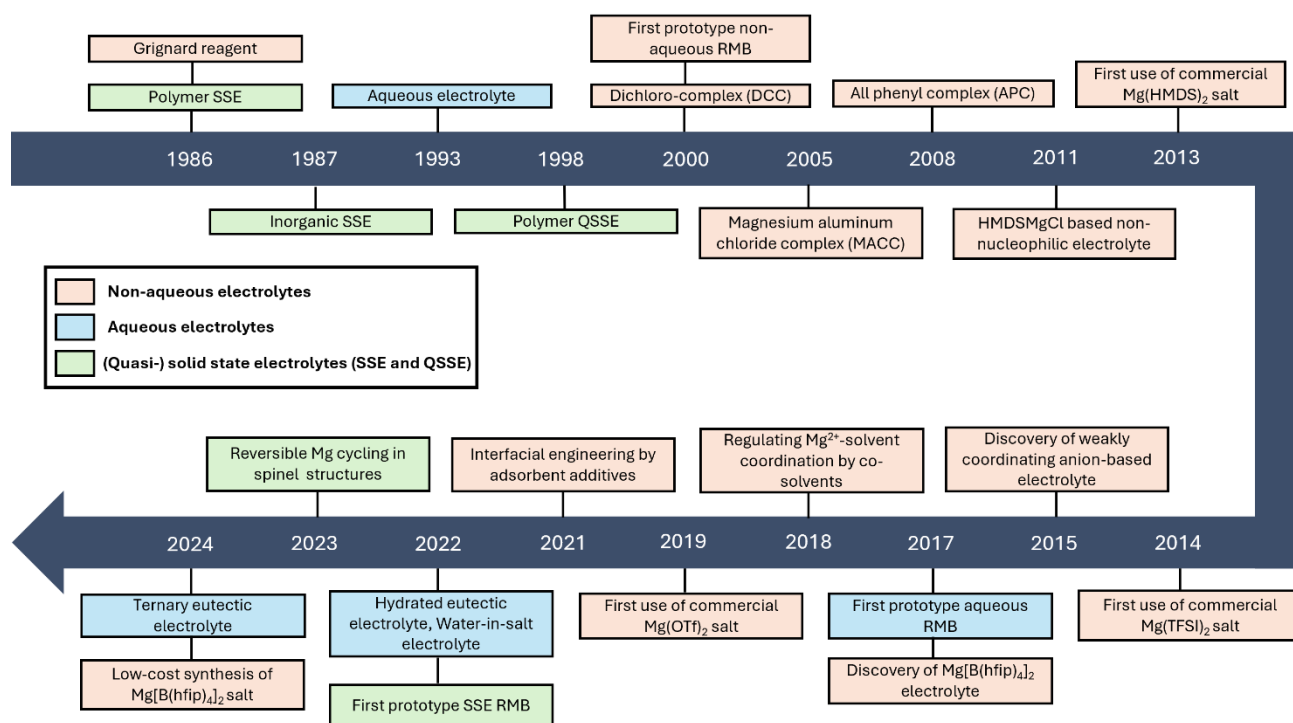


Fig 2. **Properties and performance of electrolytes for RMBs.** Best reported ionic conductivity, anodic stability, coulombic efficiency, cycling life and overpotential properties of (a-c) complex non-aqueous electrolytes, (d-g) simple salt-based non-aqueous electrolytes, (h) an aqueous electrolyte, and (i) SSE and QSSE. The data used in the figure are provided in Table 1 and was plotted in incremental values except for overpotential which is plotted in decremental order. The scale bar and units shown in part a apply to all panels.

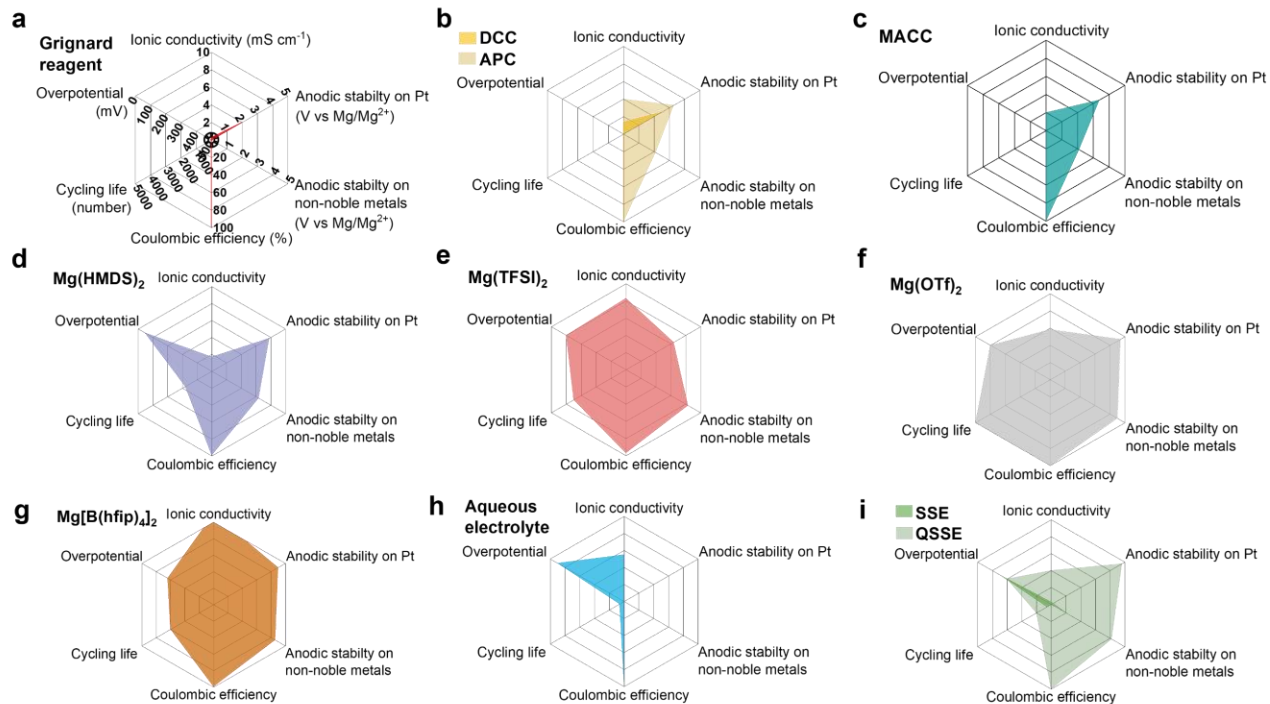
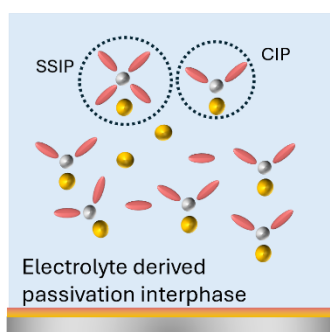
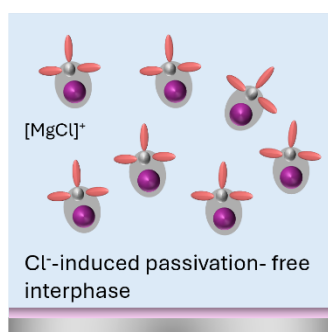


Figure 3. **Challenges and general design strategies of non-aqueous electrolytes for RMBs.** **a** | Conventional electrolyte design, in which Mg analogous of LIB electrolyte salts dissolved in commonly employed LIB solvents, tends to results in higher CIP concentration and an electrolyte derived passivation interphase. **b** | Early nucleophilic complex electrolytes enriched with $[\text{MgCl}]^+$ electroactive species and Cl-induced passivation-free interphase. **c** | Solvation shell reorganization by auxiliary anion incorporation to weaken cation-anion interactions and form auxiliary anion derived non-passivating interphase in non-nucleophilic systems. **d** | Interfacial engineering using additives for passivation-free and anion repelling anode-electrolyte interface in non-nucleophilic systems. **e** | Mg^{2+} -solvent interaction regulation through a co-solvent strategy to improve salt dissociation and solvent-separated ion pairs (SSIPs) concentration in non-nucleophilic systems and subsequently enabling co-solvent derived non-passivating interphase. **f** | WCA based non-nucleophilic electrolytes with enriched SSIPs and WCA derived non-passivating interphase.

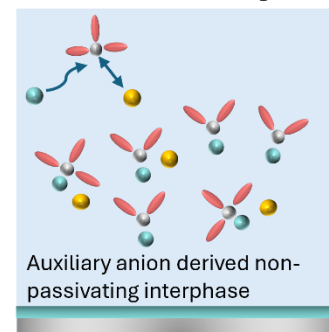
a Conventional electrolytes



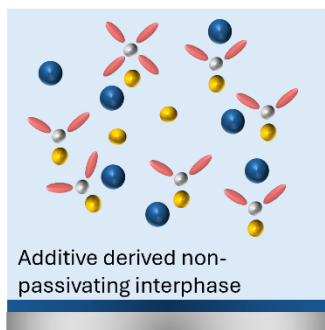
b Nucleophilic systems



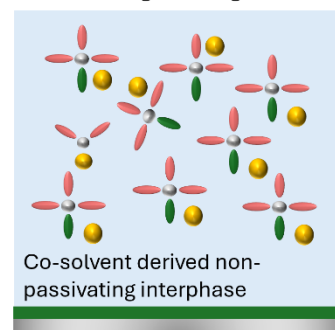
c Non-nucleophilic systems
– solvation modulating additives



d Non-nucleophilic systems
– interface modulating additives



e Non-nucleophilic systems
– solvent engineering



f Non-nucleophilic systems
– WCA design

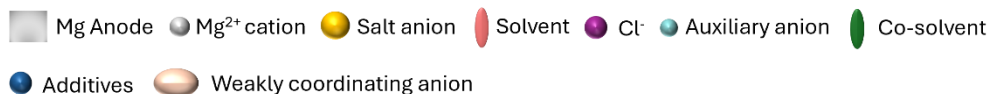
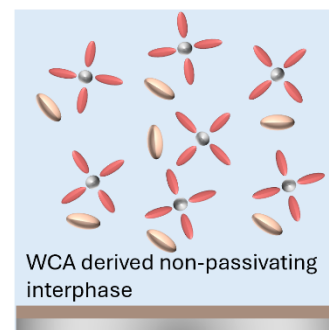


Figure 4. Solid-electrolyte interphase. **a** | Key sequential steps in the electrodeposition process of divalent Mg metal onto an anode surface in the presence of solid-electrolyte interphase (SEI). The low reduction potential of Mg metal promotes intrinsic electrolyte reduction and the accumulation of decomposition products during cycling. The resulting passivating films impede Mg^{2+} transport across the interface, in contrast to LIBs, where surface films formed from side reactions often function effectively as SEI. For stable Mg plating and stripping, anode-electrolyte interphases in RMBs must emulate the SEI in LIBs by enabling efficient Mg^{2+} conduction **b** | Theoretically calculated Mg^{2+} ion migration barrier and electrochemical stability window of various SEI forming Mg compounds. **c** | Typical passivation interphase observed in conventional electrolytes. **d** | Cl⁻-rich protective interphase observed in nucleophilic electrolytes. **(e-g)** Different SEI layer architectures observed in various non-nucleophilic systems. **e** | Organic-inorganic hybrid SEI observed in additives modified non-nucleophilic electrolytes. **f** | Inorganic-rich thin SEI observed in solvent engineered non-nucleophilic electrolytes. **g** | Organic-rich SEI observed in WCAs based non-nucleophilic electrolytes. **h** | Hybrid cation SEI observed in dual-salt hybrid electrolytes.

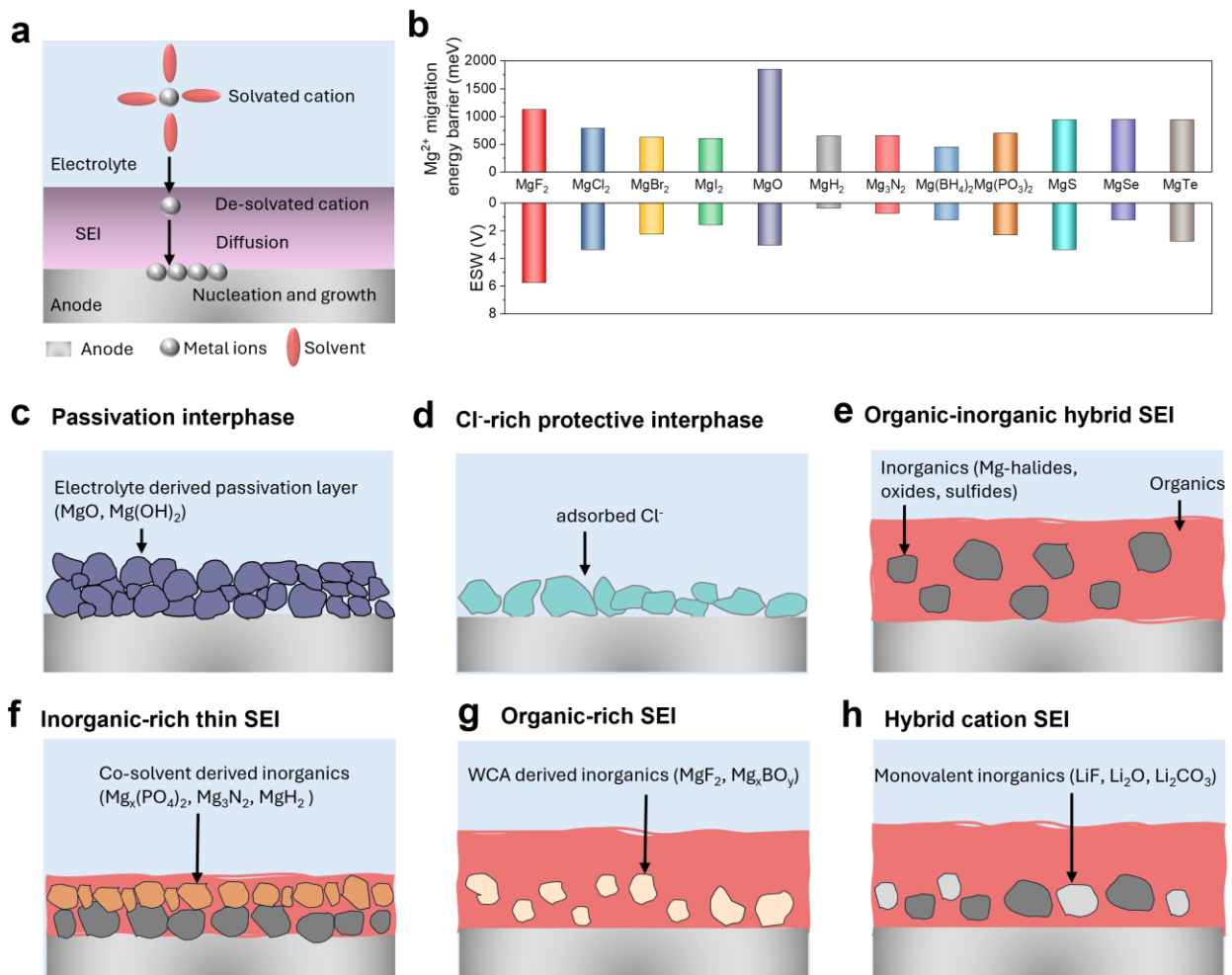
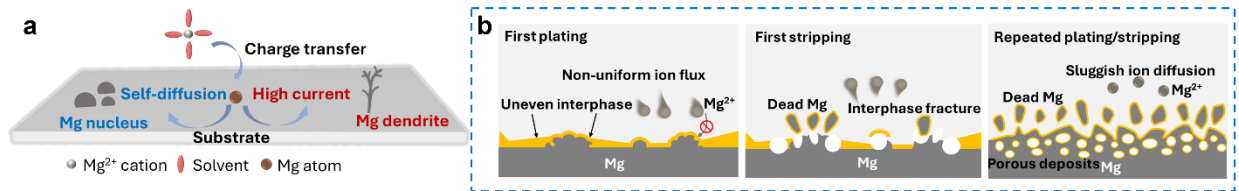


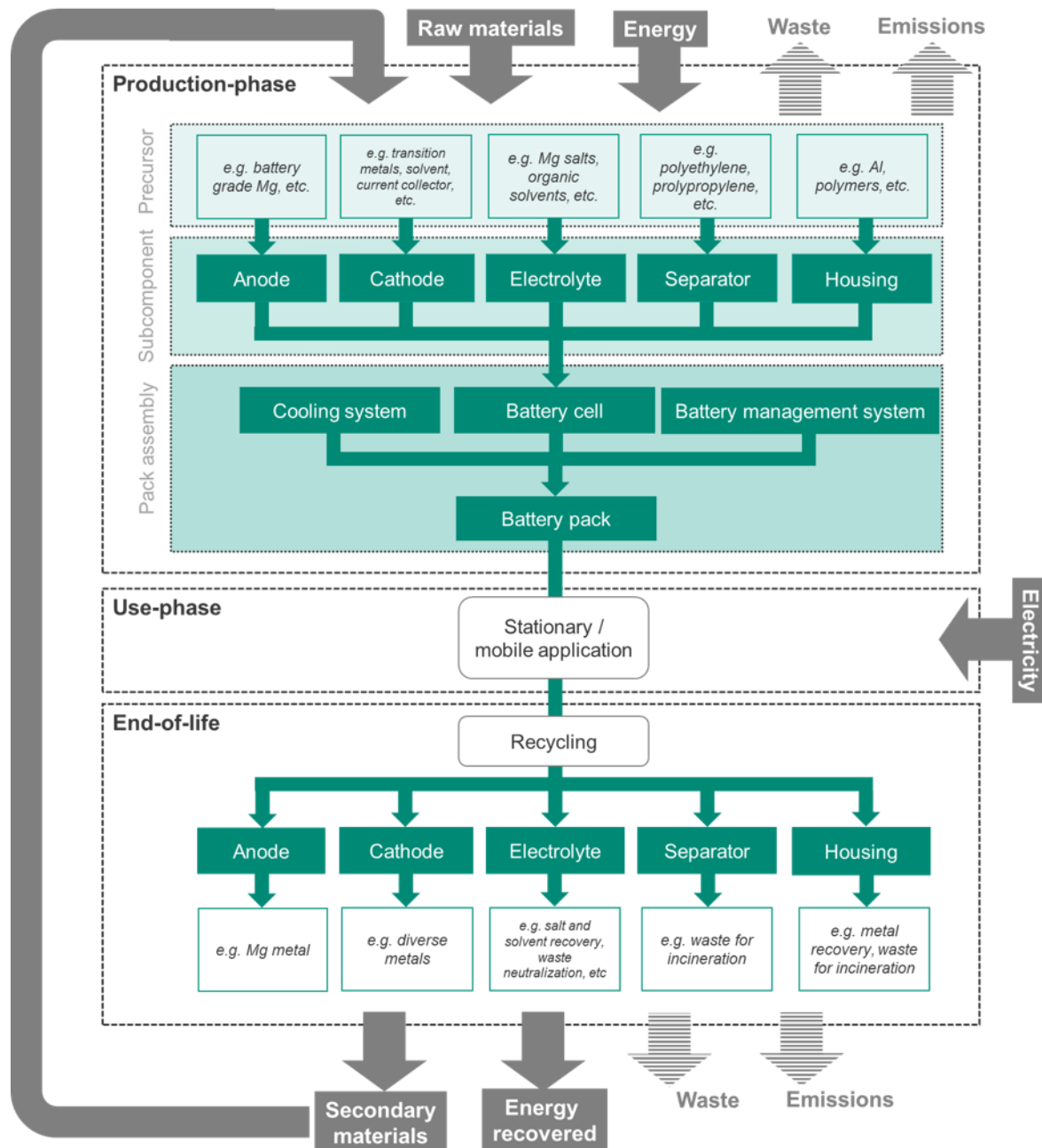
Figure 5. **Dendrite formation.** **a** | Charge transfer mechanisms during Mg plating. **b** | Influence of uneven anode-electrolyte interface on Mg ion flux and deposition morphology. Types of dendrites observed in RMBs, including **c.** globular dendrites, **d.** branch-like dendrites, **e.** needle-like dendrites, and **f.** whisker-shaped dendrites.



c Globular dendrites **d** Branch-like dendrites **e** Needle-like dendrites **f** Whisker-shaped dendrites



Figure 6. Life cycle stages of RMBs. Theoretically constructed life cycle of a prototype RMB, encompassing three principal phases: production, use, and end-of-life. From an electrolyte perspective, the production phase is critical, as environmentally conscious electrolyte design can be implemented with appropriate system-level knowledge. Regarding the end-of-life phase, given the early development stage of RMBs, there is an opportunity to integrate design-for-recycling strategies to facilitate material recovery and promote circularity.



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Competing interests

The authors declare no competing interests.

Author contributions

All authors contributed to discussion of the content and writing of the article. All authors reviewed and/or edited the manuscript before submission.

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