The Challenge of Corrosion in Next-Generation Rechargeable Metal Batteries

Minkwan Kim,[1,†] Lea Pompizii,[2,†] Jihwan Byun,[1] Ali Coskun,[2,*] and Jang Wook Choi[1,3,*]

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[1]School of Chemical and Biological Engineering and Institute of Chemical Process, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

[2]Department of Chemistry, University of Fribourg, Chemin de Musee 9, Fribourg, 1700, Switzerland

[3]Lead Contact

*Correspondence: ali.coskun@unifr.ch, jangwookchoi@snu.ac.kr

†These authors contributed equally to this work.

The bigger picture

Challenges and opportunities

- Despite its profound impact on the calendar life, metal corrosion in emerging rechargeable metal-based batteries remains insufficiently understood.
- The limited understanding of corrosion phenomena across diverse battery systems originates from fragmented discussions and evaluation standards biased toward cycling reversibility.
- Integrating an in-depth mechanistic understanding with insights from existing corrosion suppression strategies can provide transformative opportunities to extend the calendar life of rechargeable metal-based battery systems and enhance their practicality.

SUMMARY

Rechargeable metal-based batteries, which offer the highest theoretical energy densities, stand as highly promising candidates for next-generation energy storage devices. However, despite substantial progress in their cycling reversibility, their calendar life remains critically undermined by persistent metal corrosion. This mismatch highlights corrosion as a distinct electrochemical process governed by an electron transfer pathway that differs fundamentally from that of operational cycling, particularly under non-operational (rest) conditions. Although corrosion-related studies have emerged across various battery chemistries, they have largely remained fragmented without a cohesive, in-depth understanding. In this Perspective, we highlight ongoing debates surrounding corrosion phenomena and their mechanistic understandings, with particular emphasis on their critical implications for the calendar life of diverse metal-based battery systems. Building upon this expanded discussion, we integrate insights from existing corrosion suppression strategies and propose a spectrum of promising design principles—spanning metal electrode fabrication, surface modification, and electrolyte engineering—with the aim of fostering further developments in this important area.

1. Introduction

Electrochemical principles have been harnessed throughout history, spanning applications such as galvanic protection, electroplating, and both primary and secondary batteries. Among the innovations, lithium-ion batteries (LIBs) have transcended their role as energy storage devices and have established themselves as a cornerstone of modern technological progress and transformation that has revolutionized our daily lives in ways that extend from portable electronics to electric vehicles.[1,2] However, the energy density limitations of LIBs present a critical hurdle to powering a wider range of applications with higher energy demands, imposed by their graphite anodes approaching their intrinsic capacity limit.[1]

In this context, metal anodes have re-emerged as a fundamental solution to the limited energy densities of current commercial LIBs.[3,4] The (de)plating process of metal anodes, in principle, offers the highest specific capacities and the lowest electrochemical potentials, positioning them as ideal candidates for the next-generation batteries with unparalleled energy densities. As recent investigations of the critical interfacial phenomena of metal anodes have elucidated their degradation mechanisms, there have been a variety of creative solutions to overcome these limitations to extend the cycle life. This remarkable progress has raised the practical viability of metal-based rechargeable batteries, including lithium metal batteries (LMBs),[4] aqueous zinc-ion batteries (AZIBs),[5,6] and rechargeable magnesium metal batteries (RMBs).[7,8]

Despite significant progress, the community is still confronted by a critical challenge that has impeded the advancement of rechargeable metal-based batteries: a poor calendar life stemming from uncontrolled metal corrosion.[9,10] Contrary to the early rationale that enhancing the (de)plating reversibility would inherently guarantee stability at the resting state, periodic intervals of intermittent rest or prolonged dormancy have been revealed to induce catastrophic premature failure of metal anodes—even in systems demonstrating exceptional reversibility over a large number of cycles.[11] This issue presents a fundamental challenge to one of the core prerequisites of rechargeable batteries: the reliable, on-demand utilization of stored energy. To ensure the practical viability of metal-based batteries, the community has increasingly recognized the need to suppress metal corrosion. Nevertheless, a thorough understanding of corrosion and its underlying mechanisms has remained largely elusive, hindering the development of groundbreaking strategies to suppress this detrimental process.

This perspective aims to offer comprehensive insights into metal corrosion in rechargeable metal-based batteries, structured into two key sections:

1) The first section presents an in-depth discussion on corrosion, including its detrimental impact on electrochemical performance, the underlying physicochemical factors, and broader discussions on corrosion mechanisms in rechargeable metal-based battery systems.
2) The second section explores strategic pathways for corrosion mitigation by proposing potential approaches that extend beyond existing suppression strategies, supported by mechanistic insights from the first section.

With this Perspective, we hope to provide a comprehensive framework that integrates the fundamental understanding of metal corrosion. We additionally aim to offer guidance for shaping future research trajectories in corrosion control towards the ultimate long-term stabilization of rechargeable metal-based battery systems.

2. Extensive Consideration of Corrosion and Calendar life

2-1. Metal Corrosion: A Hidden Yet Catastrophic Threat to Battery Performance

Corrosion is a thermodynamically driven decomposition reaction between a solid material and its surrounding medium. In the case of metal corrosion in an electrolyte, electrons generated by the oxidation of metal atoms are spontaneously transferred to electrolyte species that undergo reduction. Depending on the nature of the electrolyte, released metal cations either dissolve into the electrolyte via solvation or precipitate through various reactions with electrolyte components, while the reduced species can manifest themselves in different forms, including gaseous products (e.g., hydrogen gas on Zn metal surfaces in AZIBs), dissolved species, or solid products (e.g., byproducts on Li metal surfaces in LMBs).

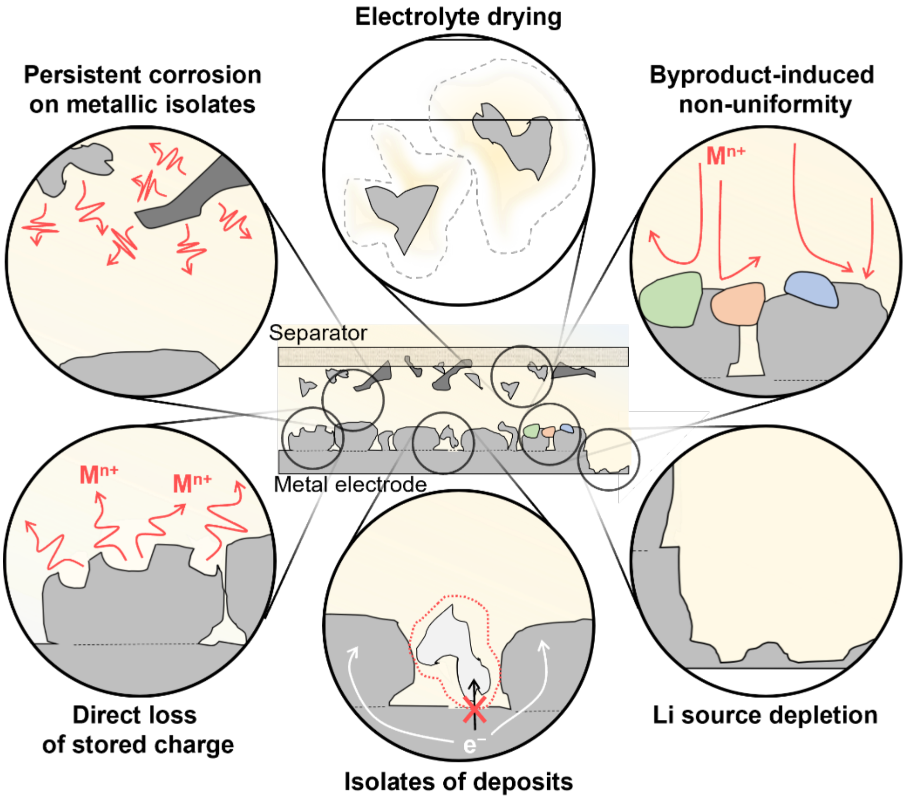

Figure 1. Corrosion-induced cell degradation pathways. The degradation occurs across the metal electrode and electrolyte, as illustrated in this schematic.

The detrimental impacts of metal corrosion on electrochemical performance are multifaceted and profound, as illustrated in Figure 1. The oxidation of deposited metal, in principle, corresponds to a loss of stored charge, which translates into capacity fade in subsequent discharge.[12] The most critical capacity loss stems from corrosion at the roots of the deposited metal, which can electrically isolate these deposits from the current collector to further exacerbate capacity loss.[13,14] Meanwhile, the agglomeration of corrosion-induced byproducts disrupts the charge transfer uniformity and accelerates the formation of dead (i.e., electrically disconnected) metal. This instability, in turn, intensifies dendritic growth in subsequent deposition cycles, resulting in a cascading cell degradation because of severely compromised (de)plating reversibility.[15]

Under practical cell conditions, particularly with regard to the specific energy density, this detrimental issue escalates into a significant challenge. To fully leverage the high energy density of metal-based batteries in practice, it is necessary to minimize both the metal anode loading (thickness) and electrolyte volume, as represented by a low N/P ratio (the ratio of the capacity of the negative electrode to that of the positive electrode) and low E/C ratio (the electrolyte-to-capacity ratio).[3] However, with the limited metal availability that is necessary for a low N/P ratio, irreversibility aggravated by corrosion directly translates into the rapid depletion of the initially loaded metal, which accelerates cell failure compared to scenarios with a high N/P ratio. Likewise, corrosion-driven electrolyte decomposition exacerbates electrolyte consumption, which in turn triggers severe de-wetting of the electrolyte from the porous framework of the cell, such as the separator, isolated dead metal/SEI layers, and the cathode.[16] This process causes progressive deterioration of the electrode reaction homogeneity and further amplifies cell degradation, thus resulting in a premature cell failure.

Finally, it is essential to recognize that isolated dead metal, which inevitably accumulates during cycling, further exacerbates premature cell degradation due to persistent corrosion. These metallic isolates, originating from dendritic growth, inherently have a large surface area with extensive electrolyte contact. Furthermore, as these metal fragments remain electrically disconnected, they are subjected to a perpetual non-operational state, even while the battery is actively cycling. Consequently, the corrosive degradation of dead metal, regardless of whether the battery is in operation or at rest, persists in undermining the performance through the accumulation of corrosion-derived byproducts and electrolyte depletion. This highlights that even subtle metal corrosion can exert a detrimental influence and poses a critical obstacle to the long-term stability of rechargeable metal-based batteries.

2-2. Decoupling Reversibility and Corrosion: Bridging the Gap between Operational and Non-operational Behaviors

A perplexing paradox is that improvements in the (de)plating reversibility of rechargeable metal-based batteries do not necessarily translate into corrosion mitigation and an enhanced calendar life (Figure 2A).[10] Rather, many electrolyte strategies aimed at improving the reversibility have at times been found to exacerbate calendar aging (Figure 2B). In LMB systems, fluorinated (co-)solvent-based electrolytes have been widely explored for their ability to enhance the Coulombic efficiency (CE) in each cycle of Li (de)plating. However, recent findings[10,15] revealed that these fluorinated solvents engage in pronounced reactivity with Li metal during non-operational periods to accelerate Li corrosion and severely decrease the calendar life. The similar phenomenon in AZIBs has a well-established consensus that the high reversibility of Zn (de)plating at fast rates does not necessarily increase the calendar life.[17] Likewise, although the RMB community has recently recognized methoxy-amine-type (co-)solvents as promising enablers of reversible Mg (de)plating,[8,18] Mg corrosion by these solvents is now emerging as a serious concern that stands in the way of their practical implementation.[19] These recurring discrepancies across different rechargeable metal-based battery systems highlight the urgent need to decouple corrosion reactions during periods of rest from our conventional understanding that focuses exclusively on (de)plating reversibility during cycling.

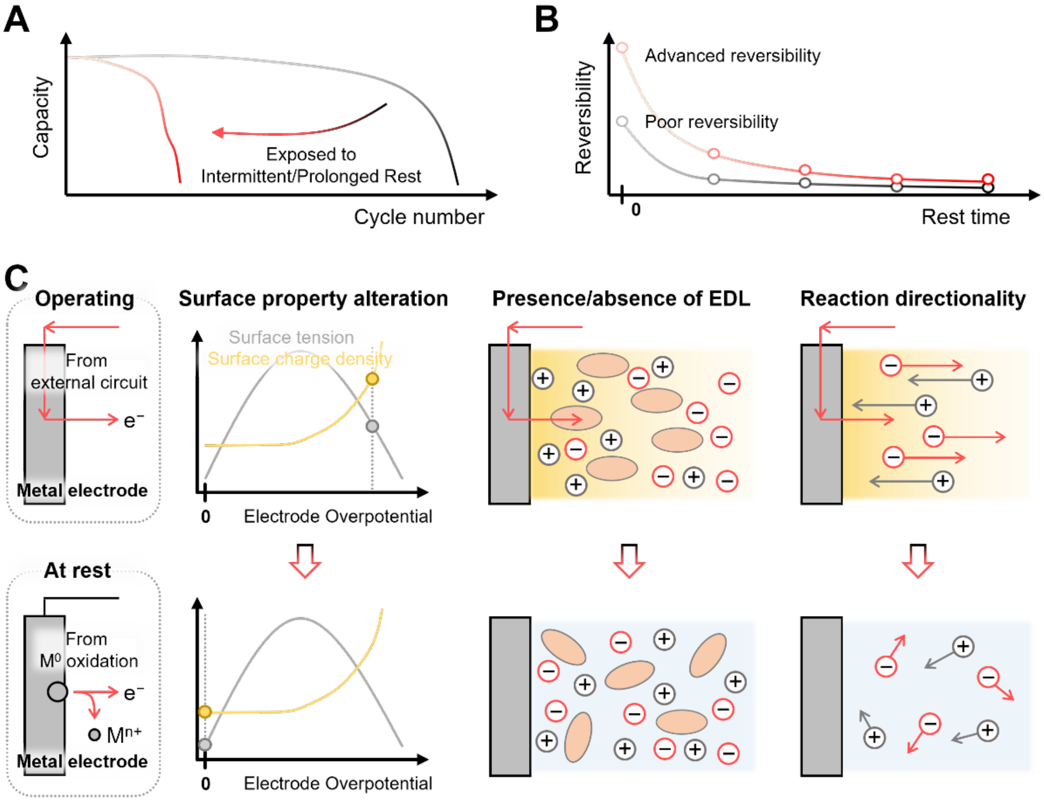

Figure 2. Disparity between operational and non-operational behaviors. (A) Drastic performance degradation upon rest exposure. (B) Reversibility loss with rest time. (C) Mechanistic distinction between operation and rest.

Indeed, such inconsistencies between operational and non-operational behaviors have been also observed in the context of the hydrogen evolution reaction (HER) and metal corrosion in aqueous environments. For instance, platinum (Pt) is an exceptional HER catalyst while simultaneously being a corrosion-resistant noble metal.[20] In contrast, zinc (Zn) is an unfavorable HER substrate yet is highly susceptible to corrosion, to the extent that it is commonly employed as a sacrificial anode to protect other metals. These contrasting reactivities, even within the same material, likely stem from the fundamentally distinct nature of electron transfer processes between the two reactions (Figure 2C). In other words, corrosion during rest periods is characterized by electron exchange between metal atoms and electrolyte species via a simultaneous redox process, in which oxidation of the metal supplies electrons to the reducing species. On the other hand, operational current flow involves electron transfer between the electrode and external circuit without necessitating direct metal oxidation.

This fundamental divergence in electron transfer pathways may suggest kinetic discrepancies in the electrolyte decomposition, depending on whether the system is in operation or at rest. Furthermore, the overpotential induced by external current (or voltage) control imposes a significant deviation in the characteristics of the metal electrode from its intrinsic properties in the rest state, including the surface charge density, surface tension, and surface capacitance.[21,22] Additionally, the flow of external electrons through the metal body indicates excessive or deficient charge compared to the rest state, likely perturbing its electronic properties, such as the Fermi level or electronic orbital distribution, to ultimately give rise to distinct characteristics compared to those in the non-operational state.

Another critical factor underlying this disparity is the presence of an externally induced electric field during operation and the consequent modulation of the electric double layer (EDL) structure at the interface. The exertion of surface potentials during operation generate an electric field, which reconfigures interfacial molecular interactions, thereby influencing the reactivity of electrolyte species with the metal surface.[23,24] Beyond molecular realignment, the applied current flow dictates the directionality of net charge transfer and ion transport dynamics at the interface,[25] and this governs the reaction pathways, which may diverge from those in corrosion processes.

These interconnected phenomena collectively contribute to the stark behavioral differences between operational and non-operational states, and ultimately explain the observed inconsistency between (de)plating reversibility and corrosion behavior. Unfortunately, it remains challenging to directly observe and substantiate these (non-)operational interfacial phenomena, primarily due to two intricately intertwined factors: the dynamic changes at the electrolyte-electrode interface and the internal transformations of the metal electrode. Nevertheless, by leveraging well-established electrochemical principles alongside experimental investigations, it becomes possible to systematically evaluate and understand the fundamental factors affecting corrosion behaviors.

2-3. Interfacial Determinants of Metal Corrosion

Metal corrosion occurs when the redox potential of a metal electrode extends beyond the electrochemical stability window (ESW) of the electrolyte, which makes spontaneous metal oxidation energetically favorable. In this context, the corrosion reactivity can be rationalized through a comparative assessment of the intrinsic properties of both the metal and the electrolyte. A common approach to estimate the reduction favorability of an electrolyte involves evaluating the lowest unoccupied molecular orbital (LUMO) energy of its constituent species, as lower LUMO levels generally indicate greater reducibility.[26] However, theoretical LUMO calculations for isolated molecules often fail to establish a comprehensive correlation with experimentally observed corrosion behavior. This discrepancy might arise from the fact that electrolyte species do not exist as discrete molecular entities but instead reside within dynamic solvation environments, where their electron density distribution and molecular orientation undergo substantial reorganization.

The simultaneous interfacial electron transfer between metal atoms and electrolytes involves direct molecular adsorption[27] or interaction with the metal surface, suggesting that effective interfacial interactions can facilitate metal corrosion. This extrapolates to broader implications, wherein steric hindrance effects or molecular dipole alignment may collectively modulate the chemical interaction landscape at the electrode-electrolyte interface, thereby exerting significant influence on the corrosion kinetics.[28,29]

In scenarios in which the continuous supply of reducible species to the interface is restricted, corrosion rates can become kinetically limited. This highlights the passivation capability of corrosion-induced byproducts as a decisive factor in determining whether corrosion remains self-limiting or progresses into catastrophic material failure. Thin oxide passivation layers on metals such as aluminum, zinc, and magnesium represent a general demonstration of this principle, wherein the oxide layers that formed through initial oxidation reactions generate a protective barrier that significantly impedes the subsequent diffusion of oxidizing species, thereby preventing deeper structural degradation. Analogously, the solid-electrolyte interphase (SEI) in LIB systems is regarded as a passivating layer that can stabilize the anode-electrolyte interface and suppress further undesirable reactions.[30]

The electronic and structural properties of the metal electrode itself can also play a pivotal role in the corrosion reactivity. The redox potential of a metal is governed by its Fermi level, implying that corrosion can be modulated by its band structure and electronic density of states (DOS). Additionally, the surface morphology and crystallographic orientation of the metal electrode could decisively affect the corrosion susceptibility. Corrosion processes tend to initiate preferentially at high-energy sites, particularly defect-rich regions and under-coordinated surface atoms that readily interact with electrolyte species.[31] In polycrystalline metal electrodes, grain boundaries have been well established to serve as preferential corrosion sites due to their high defect density and localized strain fields. The crystallographic dependence of corrosion resistance was clearly demonstrated in AZIB systems,[32,33] where the corrosion stability of hexagonal close-packed (hcp) Zn (002) facets is markedly enhanced compared to that of other crystallographic orientations. This observation emphasizes the critical role of surface energy variations and metal-electrolyte interactions (e.g., adsorption) in governing the corrosion reactivity. Meanwhile, micro- and nanoscale surface irregularities—including edge sites and kinks—can further intensify the corrosion susceptibility.

2-4. Persistent Metal Corrosion Even in a Stabilized SEI layer

Since the development of LIBs, the SEI layer has traditionally been perceived as an effective passivation layer that fully isolates the anode surface from the electrolyte. This led to the assumption that achieving Li metal reversibility through a stabilized SEI would ensure the effective suppression of corrosion. This rationale has driven extensive efforts to prioritize securing high reversibility by inducing inorganic-rich SEI layers via fluorinated (co-)solvent incorporation, without considering its relevance to corrosion reactivity. However, contrary to this initial assumption, fluorinated electrolytes—despite forming robust inorganic-rich SEI layers and demonstrating superior reversibility—exhibit even higher corrosion rates than conventional systems with less stable, organic-rich SEI layers. Given the greater chemical and structural integrity of these inorganic-rich SEI layers, they would have been expected to exhibit more corrosion-resistant metrics compared to organic-rich ones. This observation cannot be solely explained by SEI fracture and necessitates reassessment of the SEI model beyond its conventional passivation paradigm.

One proposed explanation for persistent Li corrosion, even in the presence of stabilized SEI layers, is SEI dissolution.[34,35] However, several experimental findings and practical electrochemical conditions have challenged this assumption. Boyle et al. reported that low-concentration electrolytes, despite their strong ability to dissolve organic SEI components, ironically exhibited lower corrosion rates.[10] In contrast, advanced electrolytes with weaker dissolving power induced far more severe corrosive degradation, even though they formed inorganic-rich SEI layers that, in principle, should have been more resistant to dissolution. Furthermore, in realistic cell configurations with their inherently limited electrolyte volume, SEI dissolution is likely to be further restricted due to solubility saturation effects—especially in advanced electrolytes with low intrinsic solubility and for inorganic SEI components.[36] These considerations collectively suggest that SEI dissolution alone is insufficient to explain the severe corrosion observed for metal anodes with stabilized SEI layers.

Rather than adhering to the conventional SEI model that assumes the complete exclusion of electrolytes, recent studies[30,37] revealed that the SEI layer can incorporate electrolyte species by swelling. This understanding suggests that highly corrosive fluorinated (co-)solvents can permeate the SEI and still reach the metal surface, thereby sustaining corrosion reactions. Moreover, the agglomeration of corrosion-induced byproducts may exacerbate SEI fracture, further promoting electrolyte infiltration alongside the expansion of the corroded surface. These insights indicate that, despite the presence of a stabilized SEI layer, corrosion can remain severe due to the continuous inward diffusion of reactive species, whereby metal degradation is perpetuated.

2-5. Cross Talk with the Cathode: Influence of Cathode Chemistry on Metal Corrosion

The influence of the cathode on metal corrosion is a critical yet underappreciated factor that governs the calendar life of metal-based batteries. In nickel-rich NCM cathodes, highly oxidized Ni species in the charged state are inherently catalytic and highly susceptible to dissolution.[38,39] Prolonged exposure to elevated voltage levels not only accelerates electrolyte oxidation but also intensifies Ni dissolution and allows the migration of oxidized species and dissolved Ni cations toward the metal anode.[40] Upon reaching the metal surface, these species can undergo reduction, where they contribute to SEI thickening and to exacerbating its structural inhomogeneity. Furthermore, deposited transition metal ions can serve as catalysts for electrolyte decomposition by disrupting the SEI layer and promoting dendritic growth to ultimately aggravate metal corrosion and interfacial instability. Given that these effects are strongly dependent on the voltage state of a full-cell, metal corrosion may depend on the state-of-charge (SOC) in full-cell configurations.

Metal corrosion becomes even more severe in dissolution-prone conversion-type cathodes, such as sulfur, iodine, and organic cathodes across various battery systems.[41-43] When these materials generate liquid-phase intermediates or exhibit intrinsically high solubility, prolonged equilibration times in the non-operational state could intensify the dissolution of species, which would enable unrestrained shuttling across the electrolyte. This process ultimately leads to anode poisoning and accelerated interfacial degradation, a phenomenon that is well documented as a key driver of metal corrosion,[44,45] and which poses a formidable challenge to the long-term electrochemical stability of conversion-based battery systems.

These insights underscore the necessity of evaluating metal corrosion within the broader framework of cathode-anode interdependence, particularly in systems where active cathode species undergo substantial dissolution. This intricate interplay, which highlights the performance disparity between metal corrosion observed in isolated anode studies and calendar life manifested in full-cell configurations, emphasizes the necessity to incorporate the effect of the cathode into assessments of the stability of the metal anode during rest periods.

3. Toward Extension of the Calendar Life by Anti-corrosive Strategies

3-1. Metal Electrode Fabrication for Corrosion Mitigation

Metal anodes can have two primary configurations: foil-type and powder-type. Foil-type configurations offer a distinct advantage over their powder-based counterparts by restricting the surface area exposed to the electrolyte,[46] thereby inherently limiting their susceptibility to corrosion (Figure 3). However, to fully leverage this advantage, it is essential to minimize structural irregularities, exposed edges, and fabrication-induced defects (e.g., scratches), all of which are known to exacerbate metal corrosion.

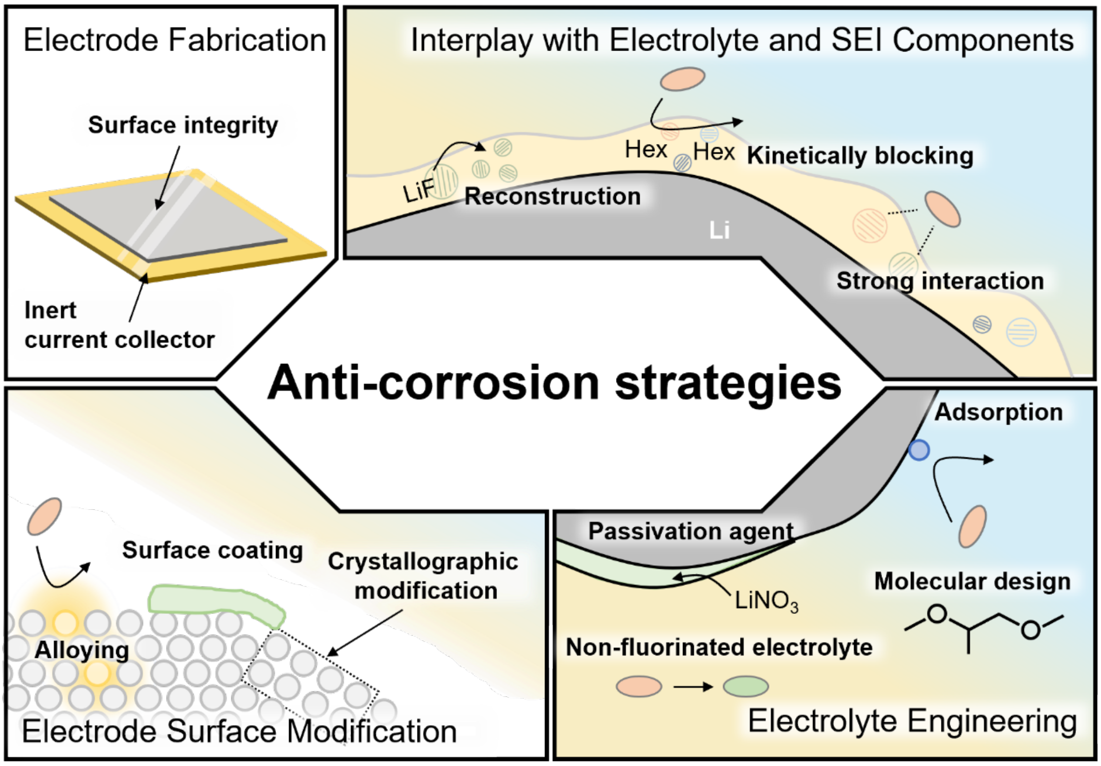

Figure 3. Multifaceted design strategies for suppressing metal corrosion. These strategies include the proper selection of current collector, SEI reconfigurations, surface modifications, and electrolyte engineering.

In pursuit of high energy density, rechargeable metal-based batteries often require a low N/P ratio, which necessitates the use of thin metal electrodes. To maintain their structural integrity, current collectors are typically employed; however, these components can inadvertently trigger galvanic corrosion of the metal electrode.[12,46,47] This phenomenon becomes particularly problematic when the current collector—despite being stable within the ESW of the electrolyte—facilitates electron transfer more readily than the metal alone, thereby promoting localized corrosion. Accordingly, rational current collector design must be considered. The introduction of electron transfer-inhibiting materials could effectively suppress the undesired galvanic corrosion, thus reinforcing the calendar life of metal-based battery systems.

3-2. Shifting the Perspective Beyond the Chemical and Structural Integrity of the SEI

Even though the prevailing view of LMBs has long emphasized the chemical and structural integrity of the SEI as the critical element for suppressing metal corrosion, recent findings indicated that SEI robustness alone does not necessarily ensure long-term corrosion stability. This would necessitate a fundamental shift in perspective to move beyond conventional strategies of SEI optimization toward a more comprehensive understanding of interfacial dynamics and its role in mitigating corrosion.

The interaction between SEI components and electrolytes may offer a useful guideline for designing intrinsically anti-corrosive electrolyte systems, as demonstrated by the interaction between $LiBF_4$ and ether-based solvents within a swollen SEI, which has been shown to facilitate LiF reconstruction.[30] In line with this concept, our group has demonstrated that the strategic incorporation of inert hexane within a swollen SEI kinetically shields the Li metal to significantly extend the calendar life.[15] This work highlights the potential of tailoring the interfacial dynamics through electrolyte engineering to suppress metal corrosion. Based on this rationale, a compelling approach would be to modulate the hydrogen-bonding interaction in fluorinated (co-)solvents, which would otherwise be severely corrosive owing to their low LUMO levels. By strategically tuning their interaction with hydrogen bond donors, it may be possible to attenuate their aggressive reactivity or diffusion through the swollen SEI layer to mitigate corrosion without directly altering the SEI composition.

Notably, the limitations of the SEI integrity in preventing corrosion need to be considered in AZIB systems, as either artificially constructed or in situ-formed SEI layers may not necessarily markedly suppress Zn corrosion.[9] This viewpoint suggests the need to transcend conventional SEI-centric approaches and explore broader interfacial strategies that comprehensively take into consideration the dynamic interplay between the electrolyte, SEI layer, and metal anode when analyzing and designing battery systems.

3-3. Surface Modification of Metal Anodes

Across various rechargeable metal battery systems, electrode modification via alloying with other elements has been widely explored to regulate metal deposition behavior by having these elements serve as nucleation seeds.[48-50] Indeed, in the field of metallurgy, corrosion inhibition by substitutional alloying has long been established.[51] Inspired by this historic approach, introducing anti-corrosive metal dopants—even in trace amounts—into the metal electrode could represent a viable strategy to enhance both the reversibility and calendar life.

The application of an artificial surface coating points to another compelling avenue for controlling corrosion reactivity.[52] Such protective layers can function either by physically preventing exposure of the metal to the electrolyte or by actively modulating interfacial interactions. However, the design of these protective coatings would have to be meticulously optimized to avoid undesirable trade-offs that could compromise key electrochemical performance parameters such as the electrode reversibility, ionic transport, and deposition uniformity.

Given the pronounced influence of the crystallographic orientation and defective sites—particularly at grain boundaries—on the corrosion susceptibility, the implementation of corrosion-resistant surface structures constitutes an effective strategy for minimizing corrosion without sacrificing the key properties of cell operation. This can be realized through epitaxial control, wherein the deposition of a metal onto a substrate with high lattice coherence facilitates the growth of well-oriented, corrosion-resistant surfaces.[53] In a similar line, the adoption of single-crystalline metal could also improve the corrosion resistance by eliminating defective grain boundaries as well as promoting the preferential exposure of anti-corrosive surfaces.

3-4. Electrolyte Engineering

As the corrosion of a metal fundamentally originates from its reaction with reducible electrolyte species, electrolyte engineering could be one of the most effective approaches for mitigating corrosion. Among the most prominent strategies along this direction is the incorporation of preferential adsorption additives,[5,27] which selectively bind to reactive defect sites on the metal surface that would otherwise serve as corrosion initiation points. By effectively deactivating these highly active dangling bonds, these additives—even in minimal amounts—can significantly suppress metal corrosion. This approach has already demonstrated substantial success in AZIB systems, suggesting that similar principles could be applied to other metal battery chemistries.[5,54]

A complementary strategy would involve rational molecular design aimed at eliminating or sterically shielding functional groups with high reactivity toward metal surfaces. Functional moieties such as amine and nitrile groups, which are severely reactive towards Li metal, could be systematically excluded from electrolyte formulations. Moreover, introducing steric hindrance around highly reducible sites could further impede corrosion pathways by providing an additional level of control over the electrolyte stability.

Despite their widespread adoption in LMBs due to their low coordination strength and superior oxidative stability, fluorinated (co-)solvents are intrinsically challenging in terms of Li corrosion. As described above, fluorination lowers their LUMO energy levels, and renders them more susceptible to engage in corrosive degradation. An alternative strategy would be to develop non-fluorinated electrolytes that are less inclined to be corrosive, while preserving the advantageous characteristics of weakly solvating solvents and diluents.[4,55-57] This can be achieved by extending non-coordinating carbon chains or by structurally tuning molecules to sterically hinder coordination.[58] Another viable approach could be to utilize electrolyte systems with elevated LUMO levels. As noted above, this concept is exemplified in hydrocarbons such as hexane and polypropylene, which demonstrate exceptional inertness toward highly reactive metals. Additionally, ionic liquid-based electrolytes, known for their wide ESWs due to their strong ionic interactions, might offer another compelling avenue for designing anti-corrosive electrolyte systems.

In the context of conversion-type cathodes, where shuttling-induced anode poisoning remains a pervasive issue, $LiNO_3$ has been broadly employed as a passivation agent to suppress cell degradation.[42,59] Inspired by this approach, the introduction of electrolyte components capable of forming a protective interphase to selectively passivate sites and faces that are prone to corrosion could serve as a viable strategy for corrosion suppression in metal-based battery systems.

Conclusion and Outlook

Although significant progress has been made towards enhancing the cyclability of rechargeable metal-based batteries, the issue of calendar aging has only recently been recognized as a critical concern. To effectuate the practical adoption of these systems, metal corrosion must be seen as a formidable challenge matching in significance with the (de)plating reversibility. This recognition necessitates a deeper understanding of the fundamental distinctions between operational and non-operational electron transfer processes, wherein subtle differences in the interfacial dynamics may govern divergent degradation pathways.

Investigations such as these would broaden the current understanding of interfacial corrosion phenomena by unveiling latent interfacial factors, and would play a crucial role in establishing a scaffold for the formulation of systematic, mechanism-driven mitigation strategies. In this context, the conventional perspective that views the SEI as a structurally inert and chemically passivating barrier must be critically re-evaluated; instead, the thermodynamic and kinetic interactions between SEI components and electrolyte species, particularly within the swollen SEI layer, could offer transformative yet effective insights into corrosion control. Furthermore, the role of the cathode chemistry warrants more attention as the crossover of dissolved cathodic species can profoundly influence the metal corrosion by perturbing the anode interface.

These insights compel a comprehensive portfolio of approaches, wherein metal electrode fabrication, interfacial surface engineering, and advanced electrolyte design are pursued as integrated pillars of corrosion-resilient battery architectures. Crucially, given the inevitability of dead metal formation during extended cycling, the development of inherently anti-corrosive electrolyte systems would be a meaningful direction—these electrolytes would have to suppress metal corrosion not only at active metal surfaces but also over electrically disconnected metal residues that persist in perpetually non-operational states.

As the calendar life becomes an increasingly important performance metric in relatively mature systems such as LMBs and AZIBs, the proactive advance adoption of analogous considerations in other emerging systems would be beneficial. Beyond optimizing the reversibility, future research would need to embrace corrosion not as an ancillary degradation mechanism but as a foundational electrochemical phenomenon that demands equal intellectual rigor and technological innovation.

Conflicts of interest

The authors declare no competing interests.

Acknowledgements

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