



Current status and future directions of multivalent metal-ion batteries

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Batteries based on multivalent metals have the potential to meet the future needs of large-scale energy storage, due to the relatively high abundance of elements such as magnesium, calcium, aluminium and zinc in the Earth's crust. However, the complexity of multivalent metal-ion chemistries has led to rampant confusions, technical challenges, and eventually doubts and uncertainties about the future of these technologies. In this Review, we clarify the key strengths as well as common misconceptions of multivalent metal-based batteries. We then examine the growth behaviour of metal anodes, which is crucial for their safety promises but hitherto unestablished. We further discuss scrutiny of anode efficiency and cathode storage mechanism pertaining to complications arising from electrolyte solutions. Finally, we critically review existing cathode materials and discuss design strategies to enable genuine multivalent metal-ion-based energy storage materials with competitive performance.

Lithium-ion batteries are under widespread evaluation as an energy storage solution for grid applications and as major power sources for transportation. Nevertheless, the availability and potential price spike of lithium are under constant debate¹. Alternative battery technologies that use more abundant elements and may offer higher energy density and better safety features are therefore highly desirable. Among the top candidates for this purpose are multivalent metal-ion batteries; magnesium, calcium and aluminium are among the top ten most abundant elements in the Earth's crust. In these batteries, the charge carrier multivalent metal cations shuttle back and forth between the cathode and anode during the discharging and charging parts of a cycle without causing a drastic change in the electrolyte solution composition. This working principle resembles that of lithium-ion batteries in most ways, except for the replacement of monovalent lithium with divalent magnesium, calcium, zinc and trivalent aluminium. The similarity means much of the fundamental understandings and manufacturing experiences accumulated for lithium-ion batteries may be exploited for swift industry adaptation of multivalent metal-ion batteries. The development of multivalent metal-ion batteries also depends on whether the multivalent metals bring enough benefits over lithium to be worthy of being considered as alternatives.

In this Review, we first examine the strengths and weaknesses of multivalent metal-ion batteries in terms of energy density and safety features. We note that the anticipated direct use of multivalent metals as the anode materials is central to the safety promises and potential advantage in energy density of the technologies, but both aspects cannot be taken for granted and require thorough analyses and further research. We then critically review the status of anode materials, electrolyte solutions and cathode materials for the batteries with an emphasis on metal anode growth behaviour, coulombic efficiency and cathode storage mechanism. We recommend characterization practices that could help overcome the rampant confusion seen in the research of these aspects. Finally, we highlight material design strategies that could eventually lead to high-performance multivalent metal-ion batteries.

Conditional energy density advantages

The anticipated energy density of multivalent metal-ion batteries is sometimes confusing and needs clarification. A common assessment simply looks at the anode, particularly the promise of using pure metals, their high specific capacity, relatively high density and thus high energy density. This assessment does not address the generally less negative redox potentials of multivalent metals compared with lithium-based anodes (Fig. 1a) and could lead to an undue expectation of higher volumetric energy densities for multivalent metal-ion batteries than those of lithium-based ones, albeit somewhat lower gravimetric energy densities due to the higher atomic weights of multivalent metals.

In truth, the energy density of batteries is governed by both the anode and cathode. Thus, a proper evaluation of the impact that different multivalent metals have on energy density demands using identical cathode materials for each anode. At this stage, it is hard to provide a fully realistic universal cathode material, because optimal cathode materials for multivalent metal-ion batteries are not available yet. We can, however, provide a virtual comparison, using important representative hypothetical cathode materials available for practical lithium-ion batteries which have been also studied for multivalent metal ions experimentally and/or theoretically.

Here we consider the theoretical energy content of metal-ion batteries with two cathode materials—one with the high voltage, moderate-capacity Mn_2O_4 spinel, the other with the low voltage, ultrahigh-capacity sulfur (Fig. 1b)². Mn_2O_4 represents well many AO_2 oxide-type hosts (A = transition metal) in that its high operating voltage may be compatible with the anodic stability of the most relevant electrolyte solutions (ethereal solutions) for Mg and Ca batteries. This cathode material has been theoretically studied in detail³, even though reversible intercalation of all multivalent metal ions has not been experimentally demonstrated. Sulfur has shown encouraging performances when paired with several multivalent metals⁴. Graphite (C_6), the standard anode material for lithium-ion batteries, is also included for comparison.

Assuming a hypothetical $M_1Mn_2O_4$ (M = anode metal) composition of the discharge product of Mn_2O_4 (ref. ⁵), a hypothetical

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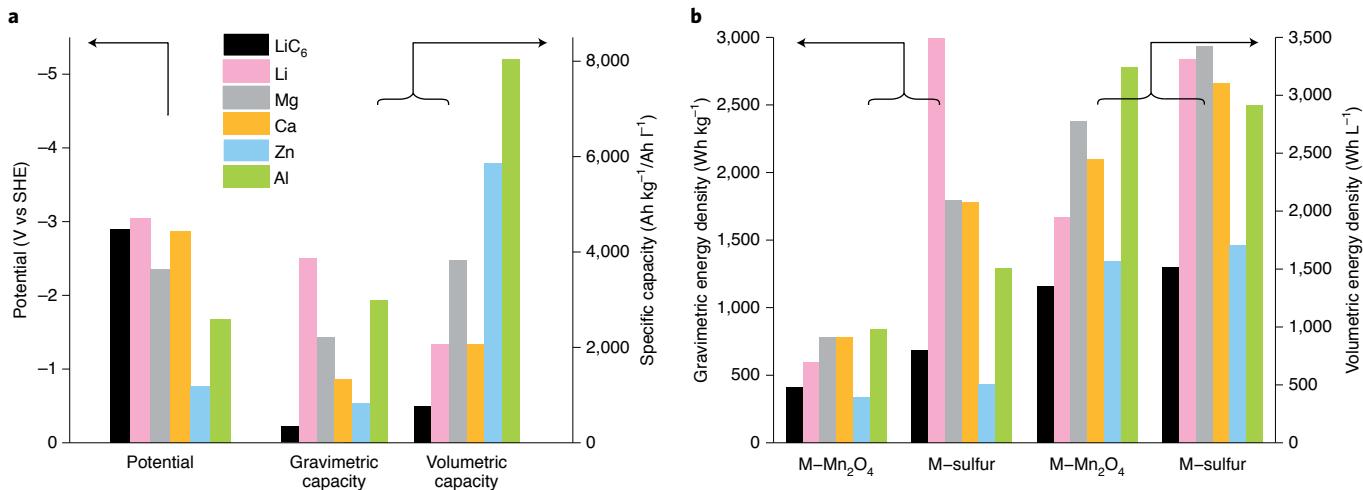


Fig. 1 | Electrochemical characteristics comparison. **a**, Redox potential and gravimetric specific capacities of lithiated graphite (LiC₆), lithium and the multivalent metals magnesium, calcium, zinc and aluminium. **b**, Theoretical gravimetric and volumetric specific energies of batteries with metal and LiC₆ anodes (M) and spinel Mn₂O₄ or sulfur cathodes calculated based on the weight of the cathode and the anode active materials. The theoretical specific capacities of Mn₂O₄ and sulfur are 154*n* (one intercalating ion per formula, *n* is the valence of the intercalating ion) and 1672 mAh g⁻¹ (two electrons per S), respectively. Theoretically predicted voltage values are used for multivalent metal based battery systems: M–Mn₂O₄, 2.9 (Mg), 3.1 (Ca), 1.5 (Zn), 2.1 (Al)^{3,5}. Typical experimental voltage values are used for Li systems: 4.0 (Li), 3.9 (LiC₆). The voltage values of M–sulfur is derived as the difference in standard reduction potentials between M ($M^{n+} + ne^- \leftrightarrow M(s)$) and sulfur (-0.476 V versus SHE). The only exception is Zn–sulfur, for which an alkaline cell¹⁰⁴ is considered and the potential of the Zn anode is -1.26 V versus SHE ($ZnO(s) + H_2O + 2e^- \leftrightarrow Zn(s) + 2OH^-$). The densities of Mn₂O₄ and sulfur are 4.14 and 2.07 g cm⁻³, respectively.

divalent metal–Mn₂O₄ battery may have higher gravimetric and volumetric energy densities than those of a LiC₆–Mn₂O₄ battery. The increased energy densities come in part from the relatively high cathode specific capacity, the result of a two-electron redox reaction per Mn₂O₄ unit. However, a major contribution comes from the possible option (maybe fully realistic) to use thin-film metal anodes. The metal thickness required to realize an areal capacity of 5 mAh cm⁻² is 13 µm for magnesium, 24 µm for calcium, 8.5 µm for zinc and 6 µm for aluminium (~24 µm for lithium). With a sulfur cathode that should show the same capacity when storing different metal ions, most multivalent metals still beat LiC₆ but fall behind metallic lithium in gravimetric energy density and may only match the latter in volumetric energy density. Zinc is the only anode that does not bring notable improvements in energy density over lithium-based systems, due to its 2.2-V higher redox potential than that of lithium metal and thus particularly low cell voltages.

The analyses above show that any energy density advantage of multivalent metal-ion batteries is highly conditional and greatly differs from what the performance parameters of the metal anodes alone suggest. Multivalent metal-ion batteries are better viewed as alternative solutions for large-scale energy storage rather than a direct competitor of lithium-based batteries in the race towards ever-rising energy density targets.

Uncertainty about the growth behaviour of multivalent metals

One of the biggest motivations of multivalent metal-ion batteries is the possibility to use the highly capacity-dense metals as safe anodes. The reputation was mainly earned by magnesium which has long been reported to show dendrite-free plating, compared to the almost ubiquitous dendritic/mossy morphologies of lithium. Metal dendrites are not only safety concerns, but also deteriorate cycle life. As more diverse electrolyte solutions are being experimented for using magnesium, however, the dendrite-free behaviour of magnesium is being challenged (vide infra). Furthermore, research activi-

ties on calcium, zinc and aluminium have grown rapidly in recent years, but the suitability of these metals as safe anodes has not been scrutinized as much as magnesium. As discussed below, there are reasons to believe that at least some of these metals could be safe anodes, but research efforts are necessary to make that a reality.

The safety in using a metal anode is best reflected by its plating morphology. Representative morphologies of multivalent metal deposits are summarized in Fig. 2. The favourable morphology for rechargeable battery applications is homogeneous, densely packed (small) crystals with high conformity (Fig. 2a) because it is the least likely to puncture separators or cause particles detachment upon cycling. Also, such a morphology ensures low specific surface area, thus minimum side reactions. Magnesium famously forms such morphologies in electrolyte solutions where the coulombic efficiency of deposition–dissolution approaches unity under a wide variety of conditions^{6–8}. This behaviour has been observed in the two main types of magnesium electrolyte solutions: those that contain chlorides where the solvation shell of Mg²⁺ includes both Cl⁻ and solvent molecules, and those that are chloride-free where Mg²⁺ is solvated only by the solvent molecules. The deposition mechanism is distinctive in the two solutions. The active cation species in the former undergo a two-step chemical–electrochemical deposition, while the latter a one-step electrochemical one⁹. Possible explanations of such an apparently universal deposition morphology have been theorized over the years, such as diffusion-controlled metal plating model, showing low self-diffusion barriers on magnesium metal leading to smooth surface growth,^{10,11} strong bonding between magnesium atoms resulting from the large free energy difference between high and low dimensional magnesium phases;¹² and suppression of local current hot spots caused by the high magnesium deposition overpotential and forming no solid–electrolyte interphase (SEI) layers on the magnesium surface⁶. A consensus is yet to be reached on which, if any, of the proposed mechanism(s) is/are dominant.

Magnesium does deposit into detrimental morphologies such as tree-like dendrites^{13,14} (Fig. 2b) and aggregates of random spheres¹⁵

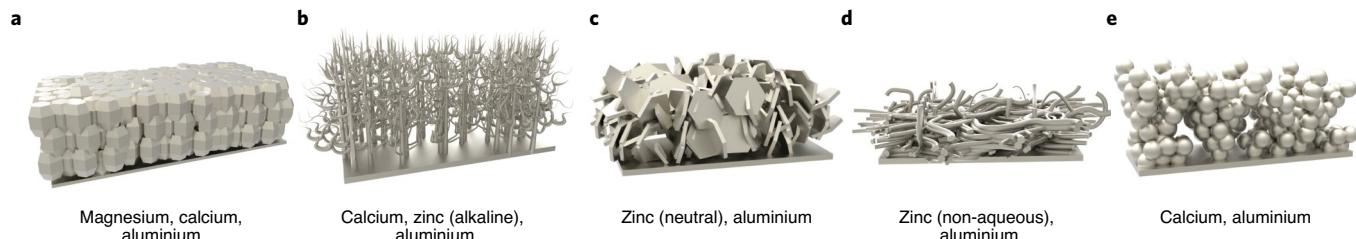


Fig. 2 | Typical plating morphologies of multivalent metal-ion metals. **a–e**, Compact crystals (**a**) are desirable and have established the reputation of multivalent metals as safe anodes. Tree-like dendrites (**b**) are directional structures that infamously penetrate separators and cause shorts, thus are actively avoided. Other morphologies such as connected platelets (**c**), random fibers (**d**) and connected spheres (**e**) do not cause shorts as quickly as dendrites do, but the impact of their large volume and surface area on coulombic efficiency and long-term stability deserves monitoring.

(Fig. 2e) in some uncommon electrolyte solutions. We note, however, that magnesium typically shows poor or questionable reversibility in these solutions, and the deposits are characterized with complicated surface chemical compositions instead of being pure magnesium. The undesirable morphologies are apparently the result of the magnesium surface being heavily modified by decomposition products of the electrolyte solutions. These studies nevertheless pointed to an important truth that magnesium is not guaranteed to plate universally in dendrite-free morphology, but only does so in selected electrolyte solutions where there are no side reactions, the active metallic surface is free of passivation, and the coulombic efficiency of magnesium deposition–dissolution is close to unity.

These findings bring to the question of how magnesium deposition morphology is regulated by the deposition mechanism as a function of the initial surface state (for example, the presence of native surface films) and the nature of the electrolyte solution (possible side reactions that form surface films). The answer is highly relevant to the safety promise of magnesium anodes as surface species may be formed even in efficient electrolyte solutions, leading to non-uniformity, uneven current distribution, and hence non-uniform deposition morphology. Real-world applications could also involve harsh operating conditions under which local structural changes of the electrolyte solution near the electrode surface lead to non-uniform electrochemical reactions, causing non-uniform current densities that can promote dendrite formation. Understanding the factors dictating dendrite formation and being able to manipulate them would be crucial for the realization of magnesium-ion batteries.

Calcium plates into various morphologies including the preferable dense and thick bulk^{16,17} and the undesirable tree-like dendrites¹⁸ and aggregates of spherical structures¹⁹. Note that in all electrolyte solutions where calcium deposits somewhat reversibly, surface films composed of electrolyte and/or solvent decomposition products were identified. Considering the studies on magnesium deposition discussed earlier, these morphologies may not reflect the intrinsic behaviour of calcium metal. Calcium metal could in fact be non-dendritic and an attractive anode material.

Zinc notoriously plates into tree-like dendrites in alkaline aqueous solutions, which are partially responsible for the short cycle life of alkaline rechargeable zinc batteries. Neutral solutions give rise to interconnected platelets (Fig. 2c)^{20,21}, a less detrimental morphology, but coulombic efficiency remains a major concern²². In non-aqueous solutions, random fibre-like structures (Fig. 2d) are formed²³. Similar structures for lithium are referred to as ‘mossy lithium’ or simply dendrites²⁴. Lithium anodes with these structures suffer from aggressive side reactions and ‘dead lithium’ formation, leading to low coulombic efficiencies and severe safety problems. Interestingly, zinc shows high coulombic efficiencies of >99% despite such structures²³, probably due to its much higher redox potential and hence low tendency to react with electrolyte solutions.

Aluminium metal anodes cycle in Al_2Cl_7^- -based ionic liquids with high coulombic efficiency, but their morphologies seem to be highly sensitive to the solution composition and plating condition. Morphologies of tree-like dendrites, interconnected platelets/spheres, random fibres and even dense crystals have all been reported in largely similar electrolyte solutions²⁵. The coulombic efficiency reported was generally high (>98%) regardless of morphology.

The diverse plating morphologies of multivalent metals calls for cautions when considering them as anode materials. Dendrite-forming multivalent metals are just as detrimental to battery performance and safety as uncontrolled lithium anodes are. Detailed characterization of the plating morphology under relevant test conditions is therefore indispensable for verifying the viability of suitable metal–electrolyte solution systems. High-resolution, very reliable surface and interface morphology imaging is possible today thanks to new microscopic techniques that enable operando measurements²⁶. Cross-sectional observation is equally important because the real deposits could be hidden underneath the metal–electrolyte solution interface, as was observed for aluminium dendrites covered by a smooth oxide top layer just 50 nanometres thick²⁷. Last but not least, characterizing the chemical nature of metal–electrolyte solution interfaces can help to understand the plating and stripping behaviour, since a major cause for dendritic plating morphologies is possible side reactions at the active metal surface. Formation of non-uniform surface films due to side reactions naturally promotes non-uniform metal deposition.

Vital but problematic non-passivating electrolyte solutions

The possible operation of multivalent metal anodes depends mostly on electrolyte solutions that enable their reversible behaviour. Magnesium, calcium and aluminium are all active metals which, very similarly to lithium, react easily with atmospheric components, any protic solvent, many polar aprotic solvents and salt anions to form interfacial species that passivate the active metal. In the case of lithium-based anodes, the surface films thus formed comprise ionic lithium compounds that behave like solid electrolyte interphase (the famous SEI model)²⁸, which avoid continuous side reactions but allow an easy migration of lithium ions through them. In contrast, surface films formed on multivalent metal anodes tend to block any possible transport of multivalent metal ions^{29–31}. Only a few reports have claimed multivalent metal-ion migration through such interfacial layers, but the nature of the interface and the transport mechanism in these rare cases are unclear^{27,32–34}. Protective coating materials that allow migration of Mg^{2+} while separating the magnesium anode and cathode active materials from the electrolyte solutions are theoretically predicted to be a viable solution but are yet to be demonstrated experimentally³⁵. Several types of all-solid-state electrolytes have been developed for Mg^{2+} conduction, which may also serve as protective coating materials. Among

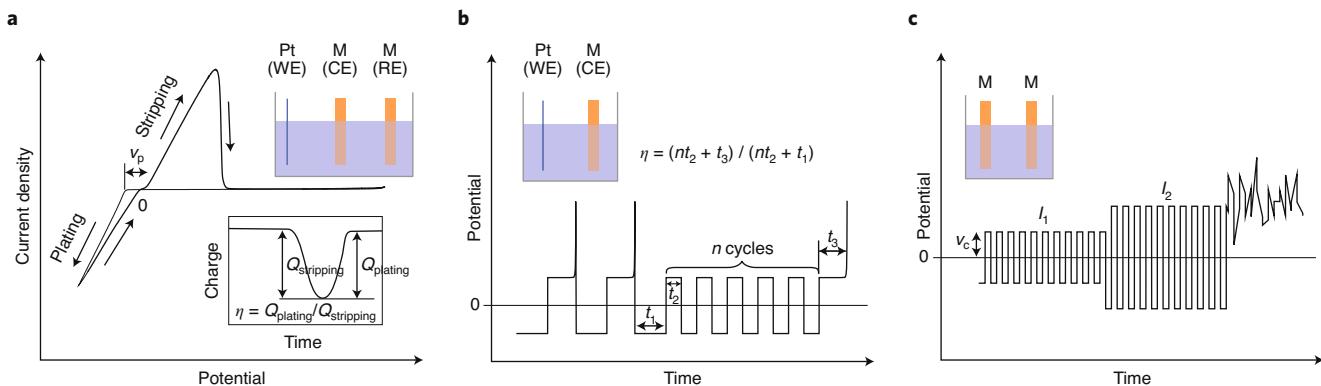


Fig. 3 | Electrochemical characterization methods for metal–electrolyte solutions systems. **a**, A typical cyclic voltammogram performed in a three-electrode cell (WE, working electrode; CE, counter electrode; RE, reference electrode) showing a cathodic loop and an anodic peak. Coulombic efficiency (η) is defined by the ratio of charges passed during the stripping ($Q_{\text{stripping}}$) and plating (Q_{plating}) processes. Plating overpotential (v_p) is measured as the delay of the cathodic current in the voltammogram. The stripping overpotential is often negligible in efficient electrolyte solutions. **b**, Galvanostatic measurements using two-electrode asymmetrical cells. A constant cathodic current is applied to the inert working electrode for a period of t_1 before being reversed for a completed stripping. The process is repeated as a substrate preconditioning measure. After a final plating, cycling is continued with a fixed plating/stripping time t_2 ($t_2 < t_1$) for n times before a final complete stripping that lasts for a period of t_3 . η is calculated using t_1 , t_2 , t_3 , and n as the inset equation shows. **c**, Galvanostatic measurement of two-electrode symmetrical cells. Plating and stripping are repeated at varying current densities for given time periods (I_1 , I_2 , and so on). The performance is gauged by the cell overpotential (v_c) and the total charge passed during the measurements. Increasing current densities can probe the electrodes' kinetics and current tolerance.

them, NASICON-type phosphates show low ion conductivities of $\leq 10^{-6}$ S cm $^{-1}$ even at 300 °C³⁶; Mg(BH₄)₂-derived complexes function at more practical temperatures but show narrow electrochemical stability windows and low coulombic efficiencies of $\leq 50\%$ at the magnesium anode³⁷; spinel chalcogenides show promising Mg²⁺ conductivities of up to 10⁻⁴ S cm $^{-1}$ at room temperature but also notable electronic conductivities even though they are computationally predicted to have extremely low electronic conductivities³⁸. Therefore, it is preferable for multivalent metal-ion batteries to use electrolyte solutions where the metal anodes are passivation-free with no tolerance to any side reactions that may form ion-blocking interfaces.

A variety of complex electrolyte solutions where multivalent metal anodes behave reversibly have been developed during the last two decades. They are composed of solvents and electrolytes that have relatively low electrophilic tendency and thus high cathodic stability, such as ethers. Some of them further contain chloride ions which help to dissolve passivating species. All magnesium electrolyte solutions that show high coulombic efficiencies of $> 98\%$ are based on ethers such as tetrahydrofuran and glymes since they are the only polar aprotic solvents in which magnesium metal is fully stable^{39–46}. Viable counter ions include weakly coordinating anions such as carborane anions and bulky borates and aluminates^{8,47,48}. Simple anions, notably bis(trifluoromethane)sulfonimide (TFSI $^-$), may also be used provided that the electrolyte solutions contain chloride anions^{49,50}. All of them have complex structures that are now reasonably well understood and the coulombic efficiency for magnesium plating/stripping in them can approach 100%. Calcium is also deposited/stripped in ethereal solutions of calcium salts with those anions that enable the high coulombic efficiency of magnesium plating and stripping, but the much higher reactivity of calcium than that of magnesium has led to notable cathodic decomposition of the anions^{17–19}. As a result, surface films do form on calcium, and the coulombic efficiencies are comparatively low (up to $\sim 95\%$) and constantly declining over cycles. Aluminium anodes can behave highly reversibly in Al₂Cl₇ $^-$ -containing ionic liquids with apparently little dependence on solution composition⁵¹. Zinc has the highest tolerance to electrolyte solution components, with

common polar organic solvents such as acetonitrile and carbonate esters and common anions such as TFSI $^-$, triflate and PF₆ $^-$ all being viable²³, probably a result of its high redox potential and low tendency of surface passivation.

While ethereal solvents and chloride anions are suitable for most multivalent metal anodes, they have limitations that could preclude many attractive high-voltage and high-capacity cathodes. Both ethereal solvents and chloride anions bind strongly to multivalent metal ions, causing a large energy penalty upon dissociation (desolvation) during intercalation reactions^{52,53}. Ethereal solvents have limited anodic stability, being oxidized as early as 3.4 V versus Mg²⁺/Mg on planar current collectors⁸. More anodically stable and less solvating solvents such as sulfones and nitriles have been computationally found to undergo cation-mediated reductive decomposition⁵⁴, agreeing with experimental observations that electrolyte solutions with these solvents give poor results^{51,55}. Chloride anions are also susceptible to oxidation, but their main limitation on the electrochemical window of electrolyte solutions is through corrosion of most relevant current collectors at moderate to low potentials⁵⁶. Among the weakly coordinating anions being considered, carborane anions such as CB₁₁H₁₂ $^-$ are probably the least coordinating and most anodically and cathodically stable, but they can be challenging to synthesize^{8,57}. Bulky fluorinated anions such as TFSI $^-$ and perfluorinated alkoxyborates and aluminates are easier and cheaper to synthesize, though ion pairs formation with cations and cathodic stability remain areas of concern^{48,50,58}. New electrolyte solutions are therefore still under intensive development.

It is important to note that for rechargeable batteries, the cycling efficiency of the electrodes must approach 100% (for example, 99.9%). Thereby, the development of new electrolyte solutions must include rigorous studies of the electrode interfacial chemistry, full understanding of possible side reactions, and their complete mitigation. The electrochemical characteristics of a multivalent metal–electrolyte solution system can be assessed by established methods. Cyclic voltammetry performed on inert substrates using a three-electrode cell configuration provides rich information including coulombic efficiency, plating–stripping potentials and overpotentials, electrode kinetics and even clues of nucleation–growth

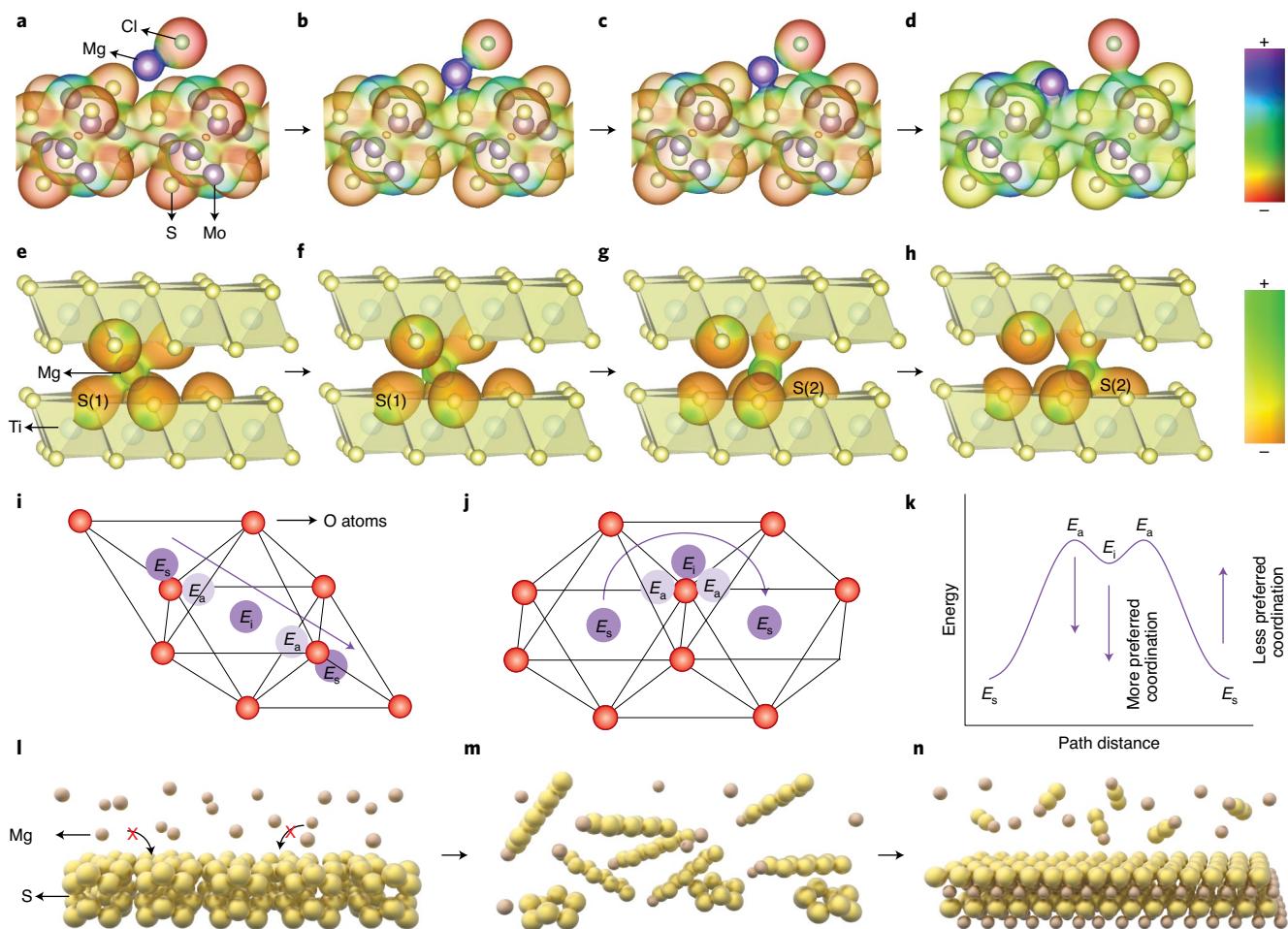


Fig. 4 | Schematic illustration of the mechanisms that enable multivalent metal-ion cathodes. **a–d**, Catalytic dissociation of MgCl^+ on the surface of Mo_6S_8 . When MgCl^+ approaches Mo_6S_8 , the electron clouds of surface S atoms are polarized (**a**) and S-Mg bonds form (**b**). Meanwhile, Cl^- is attracted by Mo cations (**c**), leading to the weakening and cleavage of the Mg-Cl bonds (**d**). **e–h**, Polarizable anions-assisted Mg^{2+} diffusion in TiS_2 . As Mg^{2+} migrates from a starting site (**e**), the electron clouds of the S atoms at the starting site (for example, S(1)) deform to stabilize Mg^{2+} at intermediate positions (**f**); the electron clouds of S atoms at a destination site (for example, S(2)) are then deformed to stabilize the incoming Mg^{2+} (**g**) before Mg^{2+} eventually settles (**h**). **i–k**, Coordination environment in spinel Mn_2O_4 and olivine FePO_4 affecting the diffusion of $\text{Mg}^{2+}/\text{Ca}^{2+}/\text{Zn}^{2+}$. M^{2+} diffusion in spinel Mn_2O_4 (**i**) starts from tetrahedral sites (E_s) to immediate octahedral sites (E_a) through oxygen planes (E_a), then to the next tetrahedral sites following a symmetrical path. The diffusion path in olivine FePO_4 (**j**) has E_s and E_a reversed. A schematic illustration of the energy change along the diffusion path is shown in **k**. **l–n**, Mg^{2+} storage in conversion-type sulfur. While direct Mg^{2+} insertion into sulfur is impossible (**l**), reduction of sulfur forms soluble polysulfides (**m**) that precipitate with Mg^{2+} as MgS_n (**n**).

mechanisms⁹ (Fig. 3a). This information would be essential for validating novel systems, especially those where plating/stripping of multivalent metals were not considered possible⁵⁹. Galvanostatic measurements using two-electrode asymmetric (inert substrate | electrolyte solution | multivalent metal) and symmetrical cell configurations (multivalent metal | electrolyte solution | multivalent metal) are gaining popularity due to their widespread use in lithium metal anodes studies. These methods have the advantage of operating under conditions more akin to those for full cells tests. Measurements in asymmetric cells accurately indicate the reversible metal plating coulombic efficiency, as well as evolution of impedance in any relevant electrolyte solutions (Fig. 3b)⁶⁰, while measuring symmetrical cells can assess rate capability, evolution of impedance, and cycle life (Fig. 3c).

Unlike the lithium electrochemistry which is relatively established in terms of the correlation between surface chemistry and electrochemical performance, with multivalent metals interfacial chemical aspects are not yet fully understood. Any possible side

reactions at the metal–electrolyte solution interface must be closely monitored, as the interfacial species formed can obscure the electrochemical activity of the multivalent active metal electrodes.

Cautions in deducing cathode storage chemistry

Although the concept of replacing lithium ions with multivalent ones in cathode hosts appears straightforward, the development of multivalent metal-ion cathode materials has been difficult. Multivalent cations have such high charge densities that their strong interactions with electrolyte solution species and cathode materials make dissociation and solid-state diffusion, the two essential events in an intercalation reaction, kinetically unfavourable. Low current densities and elevated temperatures are therefore employed to facilitate intercalation^{61,62}, under which conditions parasitic side reactions can contribute significantly to the observed capacities. The situation is further complicated by the complex composition of electrolyte solutions and in some cases corrosion of current collectors. Results from different studies were often inconsistent, as noted in a recent

Table 1 | The state-of-the-art of multivalent metal-ion batteries components

	Metal Anodes	Electrolyte solutions	Cathode materials
Areas of attention	Plating morphology after prolonged cycling. Both surface and cross-section observations are important.	(Electro)chemical stability, coulombic efficiency and overpotential.	Whether the stored cations are anion-bound, solvated, or, preferably, naked; mechanisms via which cations enter and diffuse in the materials.
Magnesium	Dendrite-free plating is widely documented in efficient electrolyte solutions.	Relatively established; some more reversible ones may be expensive, synthetically challenging, and of limited anodic stability.	Chevrel phase Mo_6M_8 is finally being challenged by more common chalcogenides, sulfur and organic carbonyl polymers, though most of the newcomers need to improve on cycling stability.
Calcium	Surface typically covered by electrolyte decomposition products, but non-dendritic deposition morphology seems plausible.	Compositions mimicking magnesium ones have shown decent reversibility albeit not as stable as their magnesium counterparts.	Viable options not yet available.
Zinc	Dendritic in both non-aqueous and aqueous electrolyte solutions; suppression via electrode architecture and surface film design being explored.	Common zinc salts in common organic solvents show high efficiency.	Reversible intercalation in high-potential oxides in non-aqueous electrolyte solutions; more options in aqueous electrolyte solutions but need stability improvement and scrutiny of the mechanism.
Aluminium	Depending on electrolyte solution composition and plating condition, morphologies of all sorts have been observed.	AlCl_3 -based ionic melts are the only options so far; they are corrosive, and the Al–Cl bonds are hard to break.	Al^{3+} -storing cathodes deliver low energy, efficiency and cyclability.
Lithium	Dendritic/mossy in most electrolyte solutions; improvement via surface modifications being explored.	Ethereal electrolyte solutions with fluorinated additives show high efficiency.	Established.
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review article⁶³. Characterizations were often not rigorous enough for unambiguous conclusions. In this section, we highlight the latest understandings of alternative reaction pathways and side reactions in multivalent metal-ion cathodes, based on which we have recommended practices that could facilitate truthful cathode study.

The reaction at a multivalent metal-ion cathode is often more complicated than a straightforward storage of multivalent cations. Transition metal oxides constitute a considerable body of literature on multivalent metal-ion cathodes, but recent studies revealed that proton intercalation was the dominant/sole reaction in many of these materials^{20,64–66}. The presence of H_2O in some electrolyte solutions and cathodes' crystal structure is understandably responsible for such reactions, but even in systems with anhydrous cathodes and thoroughly dried solvents, protons can still be generated via solvent decomposition⁶⁵. For cells with chloride-containing electrolyte solutions, intercalation of M^{n+} would require freeing the cation from the strong $\text{M}^{n+}\text{--Cl}^-$ bonds. This step is sometimes bypassed through direct storage of the complex ions (MgCl^+ , AlCl_2^+ , AlCl_4^- , and so on) instead of the bare M^{n+} (refs. ^{67–69}). Besides M–Cl bond cleavage, desolvation in strongly coordinating solvents is also energy-intensive⁵². Solvated ions are sometimes stored without stripping off the solvent molecules given that the cathode host can adapt to these large intercalants⁷⁰.

Due to the large variety of ion-storage chemistries, proper evaluation of cathodes requires unambiguous identification of the reaction mechanisms. Quantification of the elemental composition of discharged products is of utmost importance. Inductively coupled plasma spectroscopies, X-ray absorption spectroscopy, solid-state nuclear magnetic resonance, and so on, all provide such insights into the bulk composition of cathodes. Highly important is the capability to distinguish between bulk and surface phenomena, which has been developed in recent years for Li and Na ions

insertion electrodes using solid-state nuclear magnetic resonance (NMR) spectroscopy⁷¹. We may encounter situations in which the electrochemical measurements reflect charge transfer processes but multivalent metal ions form precipitates at the cathode surfaces instead of inserting into the bulk, thus making bulk analyses inconclusive^{20,66}. Therefore, quantitative compositional analyses often need to be complemented by tools that can provide spatial resolutions such as elemental mapping by energy-dispersive X-ray spectroscopy and electron energy-loss spectroscopy in conjunction with scanning electron microscopy, (scanning) transmission X-ray microscopy, and transmission electron microscopy (TEM). Such characterizations should also be quantitative, and the content of all relevant elements, including those related to components of the electrolyte solutions, should be reported, in order to provide conclusive data. Note that quantitative information from spatial characterizations does not replace dedicated compositional analyses that are more accurate. Storage of complex ions and solvated ions is usually accompanied by considerable change in the cathode lattice spacing, which can be qualitatively monitored by X-ray diffraction (XRD) and high-resolution TEM (HRTEM). In the cases where both the charged and discharged products are highly crystalline, structure refinement based on XRD, HRTEM and electron diffraction can provide additional valuable clues about the charge storage mechanisms.

In addition to direct identification of discharged products, running control cells with no multivalent metal ions in the electrolyte solutions was proposed to rule out proton reactions^{72–74}. Caution should be taken that accurately measuring and reproducing the pH in such reference experiments with the relevant non-aqueous solutions could be a great challenge.

The possible storage of complex species complicates the cell configuration compared to lithium-ion batteries. In the latter systems,

bare lithium ions move between the electrodes while the solution concentration remains invariant, enabling the use of a very small amount of electrolyte solution that serves solely as an ion-transfer medium. In contrast, rechargeable batteries based on the storage of complex species at the cathode but pure metal at the anode would suffer from material imbalance during charging–discharging which alters the concentration, pH value, ion species, and so on in the electrolyte solutions. In a practical cell where the amount of electrolyte solution is limited, these changes could impact electrodes' reaction mechanisms, cell stability and energy density^{67,75}. In fact, these batteries may not qualify as multivalent metal-ion batteries concerned herein, even though they may still be referred to as multivalent metal batteries as long as a multivalent metal anode is involved. The characterization methodologies described above are important for identifying cathode materials capable of genuine multivalent metal-ion storage, based on which the energy density estimates provided herein were made.

Design strategies for cathode materials

The vast majority of cathode materials for metal-ion batteries are based on intercalation chemistry. While the intercalation and solid-state diffusion of lithium ions are quite established, these processes become progressively problematic as the charge number of the migrating cations increases. Few materials that can intercalate lithium ions reversibly have shown proper performance in multivalent metal-ions storage.

For magnesium-ion batteries, Chevrel phase Mo_6S_8 (1.15 V versus Mg^{2+}/Mg , 129 mAh g⁻¹) has been an iconic cathode material since 2000⁷⁶. Recently emerged alternatives such as spinel Ti_2S_4 (1.2 V versus Mg^{2+}/Mg , 192 mAh g⁻¹), sulfur (1.1 V versus Mg^{2+}/Mg , 1247 mAh g⁻¹), and poly(1,4-anthraquinone) (1.37 V versus Mg^{2+}/Mg , 193 mAh g⁻¹) have shown higher energy densities than that of Mo_6S_8 but still fall short of stability^{47,67,77}. Higher-voltage oxide-based materials have long been pursued, but more solid evidence of actual magnesium storage in these hosts has only emerged recently, and their electrode kinetics and reversibility need significant improvement.

Cathode options for zinc-ion storage are relatively richer. Zinc ions reversibly intercalate into high-potential spinel compounds $\text{ZnAl}_x\text{Co}_{2-x}\text{O}_4$ (1.8 V versus Zn^{2+}/Zn , 120 mAh g⁻¹) and $\text{ZnNi}_x\text{Mn}_{2-x}\text{O}_4$ (~1.65 V versus Zn^{2+}/Zn , 180 mAh g⁻¹), representing a rare example of multivalent metal-ion storage in close-packed oxide hosts with evidenced naked cation storage, relevant energy density and decent cycling stability^{78,79}. There is not a universal explanation as for why the intercalation of zinc ions into inorganic hosts seems smoother than other multivalent metal ions, especially considering that zinc ions share the same charge number and ionic radius as those of magnesium ions. The chemical nature of zinc ions, generally categorized as ‘borderline’ cations in the hard–soft acid–base theory as opposed to the hard magnesium, calcium, and aluminium ions, could be responsible. Softer cations tend to form more-covalent bonds with host anions, which interactions in turn facilitate solid-state ion diffusion⁸⁰.

Calcium and aluminium ions have the least cathode materials options so far, and the relevant few cases typically show ill-shaped voltage profiles and large polarization. While the difficulty with aluminium ions is expected given their trivalent character, the case with calcium ions seems uncalled-for as it supposedly induces the weakest electrostatic interaction due to the large ionic radius. It has become evident that a significant advancement of cathode design strategies, different from the cathodes related to the lithium-ions era, is necessary for accomplishing multivalent batteries technologies.

The first challenge is that multivalent metal ions in the electrolyte solutions need to be freed from the strongly bound anions and solvent molecules before entering a host. The process is especially difficult for magnesium and aluminium ions where the

cations often exist as complexes with chloride ions. The energy cost to break $\text{Mg}-\text{Cl}$, for example, is calculated to be ~3 eV, which is too high for any practical application conditions. It is therefore intriguing that Chevrel phase Mo_6S_8 electrodes efficiently store bare Mg^{2+} and Al^{3+} in chlorides-containing electrolyte solutions even at room temperature⁸¹. Theoretical simulations found that the surface atoms of Mo_6S_8 could catalyse dissociation. In the case of the MgCl^+ complex, the electron-rich S anions coordinate to Mg ions and the electron-deficient Mo clusters attract Cl anions (Fig. 4a–d)⁸². These two interactions concertedly weaken the $\text{Mg}-\text{Cl}$ bond and reduce the cleavage energy from ~3 to 0.2–0.8 eV. Although such catalytic dissociation has been so far demonstrated only for Mo_6S_8 , many other materials may share similar capability. For example, two-dimensional transition metal disulfides are known to catalyse a wide range of reactions initiated with surface adsorption on exposed metal atoms. Many oxides also have active surface sites for anion adsorption, even though surface O atoms may not be as strong coordinating agents as S atoms to metal ions. Metal-free materials such as organic redox compounds can carry both electron-rich and deficient moieties that would interact with multivalent metal ions and complexing anions, respectively. Rational design of cathode materials with the necessary surface functions for complex-ion dissociation could turn out to be essential for any intercalation-based system.

The second challenge, solid-state diffusion of multivalent metal ions, is being approached from chemical and structural angles. The main chemical factor is the chemical hardness of the migrating cations and the host anions, to which the mobile cations coordinate to, in the diffusion path. Earlier in this section, the relatively good mobility of zinc ions in transition metal oxides hosts compared to magnesium cations was tentatively attributed to the softness of zinc ions. A parallel terminology may explain the relatively easy diffusion of Mg ions in Chevrel phases. The chalcogenide anionic framework, based on S^{2-} , is relatively soft compared to the O^{2-} -based frameworks in transition metal oxide hosts, thus allowing for good mobility of Mg^{2+} . Replacing S by Se in Chevrel phases increases the polarizability of their anionic framework (higher ‘softness’), thus enabling smoother Mg^{2+} diffusion and improving intercalation kinetics⁸³. The high polarizability of the chalcogenide anions helps to stabilize the intermediate states during cation diffusion between coordination sites. Similar mechanisms are believed to be partly responsible for the superionic conductivity of α -AgI and lithium thiophosphates^{84,85}. Figure 4e–h illustrate an example where a migrating cation in a framework made of soft anions is always partially coordinated by anions that are not immediately adjacent, which contributes to many temporarily stabilized configurations. Construction of frameworks with soft anions is reflected in several successful cathode designs. Spinel and layered chalcogenides, for instance, have polarizable/soft anionic frameworks similar to that of Mo_6S_8 (ref. 38,77,86). Drawbacks for these chalcogenides-based frameworks include generally lower redox potentials than what is possible with oxides as well as higher molecular weights. Organic compounds with conjugated/delocalized building blocks may be also considered soft and hence are viable cathode material candidates^{67,69}.

Structural factors may be equally important for designing solid hosts with improved solid-state ion diffusion capabilities. Multiple structural features including crystal system, cavity size, framework flexibility, and so on, come together to define the coordination environment of migrating ions, which, in turn, dictates the difficulty of their migration. The relationship between migration energy barrier, migrating ions' preferred coordination number, and their coordination environment in hosts has been demonstrated mainly via computational modelling of hypothetical systems.

Taking the theoretically modelled migration of Mg^{2+} , Ca^{2+} or Zn^{2+} in spinel Mn_2O_4 (Fig. 4i) as an example⁵, the ions migrate from a stable tetrahedral site (with energy E_s) through a 3-O plane (with

energy E_a) to an intermediate octahedral site (with energy E_i). The coordination number of the migrating ion changes accordingly from 4 (E_s) to 3 (E_a) to 6 (E_i). Among the three cations, Zn^{2+} which has the smallest average observed coordination number (AOCN)⁸⁷ of 4.98 in inorganic crystals is expected to prefer the less-coordinated starting site over the more-coordinated intermediate site. By contrast, Ca^{2+} with the highest AOCN of 7.31 is expected to prefer the intermediate site rather than the starting site. This difference in coordination environment preference was used to explain why Zn^{2+} has the largest difference between E_s and E_i and hence the highest migration barrier, while Ca^{2+} has the smallest ones. The stable and intermediate sites are predicted to be reversed for all three cations in olivine $FePO_4$ and layered NiO_2 (Fig. 4j)⁵. The calculated migration barrier in these latter hosts is therefore the lowest for Zn^{2+} while high for both Ca^{2+} and Mg^{2+} (AOCN 5.98).

This analysis shows that two structural characteristics could favour cation migration. First, structures with intercalation sites where the intercalating ions have an unfavourable coordination number (thus high E_s) and intermediate sites where the migrating ions have preferred coordination numbers (thus low E_a and E_i) will likely provide low migration barriers (Fig. 4k). Indeed, the migration barriers in several post-spinels for Mg^{2+} are even lower than those for Na^+ , which was attributed to the much lower stability of the magnesiated compounds than that of the sodiated ones⁸⁸. A higher E_s , however, means a smaller free energy change upon intercalation and thereby a somewhat compromised working potential⁵. Second, structures that provide migration paths where the coordination number of the migrating ions changes as little as possible could have a small difference between E_s and E_i , thus possibly low migration barriers. This characteristic was proposed to be responsible for the low energy barriers for Mg^{2+} migration in crystalline Mg_3Bi_2 (0.41 eV)⁸⁹ and $MgMo_3(PO_4)_3O$ (0.08 eV)⁹⁰. Structures with a certain degree of flexibility, such as rotating polyhedra in $MgMo_3(PO_4)_3O$ ⁹⁰, rippling layers in $\delta\text{-}V_2O_5$ ⁵, and polarizable anions in Li_3InBr_6 (albeit a Li^+ conductor)⁸⁵, are especially good for enabling such a migration path.

An alternative way to tackle cation dissociation and solid-state ion diffusion is to bypass them altogether. Conversion-type cathode materials such as sulfur, selenium, iodine and transition metal chalcogenides undergo dissolution–precipitation reactions that do not involve solid-state ion transport (Fig. 4l–n)^{91–94}. The most notable example is magnesium–sulfur batteries. They have delivered reversible specific capacities of up to 1200 mAh g_{sulfur}⁻¹ at 1.1–1.4 V versus Mg^{2+}/Mg with decent cycling stability (~100 cycles)⁴⁷. Their capacity decay has been attributed to the dissolution of polysulfides, but it remains unanswered why they show inferior stability compared to lithium–sulfur despite the relatively low solubility of magnesium polysulfides⁹⁵. A plausible explanation, though, is associated with the susceptibility of the Mg anode to passivation by dissolved polysulfides. Even trace amounts of polysulfides in the electrolyte solutions leads to precipitation of insoluble Mg–S species that impact the reversibility of magnesium anodes^{34,96}. Such passivation may also explain the low voltaic efficiency observed for all multivalent metal–sulfur batteries⁹⁷. Thereby, it seems that development of multivalent metal–sulfur batteries should include means to avoid even the slightest infiltration of polysulfides from the cathode to the solution phase. Interestingly, dissolved iodine was reported to reduce the magnesium deposition–stripping overpotential via surface film formation, although the coulombic efficiency of such modified anodes was not reported⁹⁸. Validation of the practicality of conversion cathodes for multivalent metal-ion batteries would require detailed characterization of the metal anode in these cathode-contaminated electrolyte solutions. The three types of electrochemical measurements described in Fig. 3 allow effective assessment for this purpose.

Conclusions and outlook

Multivalent metal-ion batteries may share the successful reversible operating mechanism with lithium-based batteries while using much more available elements as ionic charge carriers. Early evidence suggests plausibility to directly use at least some multivalent metals as safe anodes due to their dendrite-free plating behaviour. Calculations show that these batteries with metal anodes may deliver competitive energy densities compared to lithium-ion batteries, thus suitable for large-scale energy storage and even for some propulsion applications⁹⁹. As the metals of interest quickly expand from just magnesium to also calcium, zinc and aluminium, factors that established magnesium-ion batteries as promising systems will need to be validated for the new members using proven testing procedures. Cathodes development remains a major universal challenge for all multivalent metal-ion battery systems. A considerable portion of reported cathodes store in fact complex ions and protons instead of the desired naked cations. Cells based on these unintended alternative storage chemistries deliver inferior energy density and stability and may not qualify as multivalent metal-ion batteries as defined herein. Researchers would have to go the extra mile and make non-trivial characterization efforts to fully specify the nature of the stored ion species in any cathode materials of interest. Genuine multivalent metal-ion storage cathode materials, though still rare, do exist, from which useful design principles have been learned. Creative use of these principles combined with rigorous mechanistic studies would be essential to the search for successful cathodes.

Realization of competitive multivalent metal-ion batteries requires fully reversible multivalent metal anodes in very small-volume formats and high-voltage, high-capacity cathode materials that store non-complexed multivalent metal ions. The success of both electrodes is hinged on the electrolyte solution, because the solution composition subtly influences the morphology and coulombic efficiency of metal anodes, and the electrolyte anions and solvent species determine the electrochemical stability window and the ion dissociation energy which in turn limit the choice of cathode materials.

Table 1 summarizes the state-of-the-art of the three battery components. Efficient multivalent metal-ion electrolyte solutions by and large feature ethereal solvents, chloride and borohydride anions that are associated with sluggish dissociation and limited anodic stability. Therefore, the cathode material development is better directed to moderate-potential high-capacity types with a strong capability of dissociating complex ions. High-voltage materials such as V_2O_5 have been pursued as alternatives^{62,100}, but their potential cannot be fully unleashed until electrolyte solutions with compositions vastly different from what we have today are invented without compromising the metallic anodes performance.

Some alternative batteries utilize multivalent chemistries without fully adopting the typical multivalent metal-ion battery configuration, thus opening many possibilities for cathode materials and electrolyte solutions. There are attempts to replace multivalent metal anodes with anode materials, particularly alloying materials, for use of ‘conventional’ electrolyte solutions^{101,102}. These materials have higher redox potentials than those of pure multivalent metals, so that many common polar solvents and electrolyte anions are stable and do not decompose into cation-blocking surface films. Since these solvents and anions are relatively non-complexing, multivalent metal ions can intercalate reversibly into common hosts such as V_2O_5 and MoO_3 (refs. 52,62,103). Other attempts have been made to keep the multivalent metal anode and pair with established cathode materials from lithium- and sodium-ion batteries to form ‘dual ion’ batteries. The cathode reactions involve mainly monovalent metal ions that intercalate and diffuse much faster than multivalent ions, thus eliminating one of the greatest hurdles for multivalent metal-ion batteries. However, these batteries induce drastic

compositional changes in the electrolyte solutions and thus require a high amount of electrolyte solutions, compared to single-ion batteries. We do not discuss these directions in-depth because they lose some possible advantages of multivalent metal-ion batteries. The cycle life of many alloy anodes is limited; some alloying elements such as bismuth and lithium in the cathode of dual-ion batteries are not the most readily available elements; a gain in energy density due to the use of high-potential, high-capacity cathode materials may be largely offset by the relatively low-capacity, high-potential anode materials and the increased amount of electrolyte solutions.

Besides fundamental (electro)chemical questions, there are yet unexplored engineering challenges on the way to fully practical multivalent metal-ion batteries. These include electrode/cell design topics such as electrodes with high mass loading and optimal composite structure, cathode–anode mass balance, and optimization of the electrolyte solutions composition and content. Multivalent metal-ion batteries are at an early stage of development and there are many roadblocks to clear. Nevertheless, the increasing interests from the energy community and the encouraging progress already made are forging a clear path towards future success.

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References

- Weil, M., Zieman, S. & Peters, J. in *Behaviour of Lithium-Ion Batteries in Electric Vehicles: Battery Health, Performance, Safety, and Cost* (eds Pistoia, G. & Liaw, B.) 59–74 (Springer International Publishing, 2018).
- Salama, M. et al. Metal–sulfur batteries: overview and research methods. *ACS Energy Lett.* **4**, 436–446 (2019).
- Liu, M. et al. Spinel compounds as multivalent battery cathodes: a systematic evaluation based on ab initio calculations. *Energy Environ. Sci.* **8**, 964–974 (2015).
- Chung, S.-H. & Manthiram, A. Current status and future prospects of metal–sulfur batteries. *Adv. Mater.* **31**, 1901125 (2019).
- Rong, Z. et al. Materials design rules for multivalent ion mobility in intercalation structures. *Chem. Mater.* **27**, 6016–6021 (2015). **This work proposed the relationship between ion coordination environment and energy barrier for solid-state multivalent metal-ion diffusion.**
- Matsui, M. Study on electrochemically deposited Mg metal. *J. Power Sources* **196**, 7048–7055 (2011). **This work investigated the origin of the non-dendritic magnesium deposition in comparison with the dendritic lithium deposition.**
- Crowe, A. J., DiMeglio, J. L., Stringham, K. K. & Bartlett, B. M. Kinetics of magnesium deposition and stripping from non-aqueous electrolytes. *J. Phys. Chem. C* **121**, 20613–20620 (2017).
- Tutusaus, O. et al. An efficient halogen-free electrolyte for use in rechargeable magnesium batteries. *Angew. Chem. Int. Ed.* **54**, 7900–7904 (2015). **This work reported a non-corrosive, non-nucleophilic electrolyte solutions that enable reversible magnesium plating and stripping.**
- Ta, K., See, K. A. & Gewirth, A. A. Elucidating Zn and Mg electrodeposition mechanisms in nonaqueous electrolytes for next-generation metal batteries. *J. Phys. Chem. C* **122**, 13790–13796 (2018).
- Jäckle, M., Helmbrecht, K., Smits, M., Stottmeister, D. & Groß, A. Self-diffusion barriers: possible descriptors for dendrite growth in batteries? *Energy Environ. Sci.* **11**, 3400–3407 (2018).
- Jäckle, M. & Groß, A. Microscopic properties of lithium, sodium, and magnesium battery anode materials related to possible dendrite growth. *J. Chem. Phys.* **141**, 174710 (2014).
- Ling, C., Banerjee, D. & Matsui, M. Study of the electrochemical deposition of Mg in the atomic level: Why it prefers the non-dendritic morphology. *Electrochim. Acta* **76**, 270–274 (2012).
- Gregory, T. D., Hoffman, R. J. & Winterton, R. C. Nonaqueous electrochemistry of magnesium: applications to energy storage. *J. Electrochem. Soc.* **137**, 775–780 (1990).
- Davidson, R. et al. Mapping mechanisms and growth regimes of magnesium electrodeposition at high current densities. *Mater. Horiz.* **7**, 843–854 (2020).
- Ding, M. S., Diermant, T., Behm, R. J., Passerini, S. & Giffin, G. A. Dendrite growth in Mg metal cells containing Mg(TFSI)₂/glyme electrolytes. *J. Electrochem. Soc.* **165**, A1983–A1990 (2018).
- Ponrouch, A., Frontera, C., Barde, F. & Palacin, M. R. Towards a calcium-based rechargeable battery. *Nat. Mater.* **15**, 169–172 (2016).
- Wang, D. et al. Plating and stripping calcium in an organic electrolyte. *Nat. Mater.* **17**, 16 (2017). **This work reported calcium plating and stripping at room temperature in an organic electrolyte solution with low polarization and relatively high efficiency.**
- Shyamsunder, A., Blanc, L. E., Assoud, A. & Nazar, L. F. Reversible calcium plating and stripping at room temperature using a borate salt. *ACS Energy Lett.* **4**, 2271–2276 (2019).
- Li, Z., Fuhr, O., Fichtner, M. & Zhao-Karger, Z. Towards stable and efficient electrolytes for room-temperature rechargeable calcium batteries. *Energy Environ. Sci.* **12**, 3496–3501 (2019).
- Pan, H. et al. Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. *Nat. Energy* **1**, 16039 (2016).
- Zhao, Q. et al. High-capacity aqueous zinc batteries using sustainable quinone electrodes. *Sci. Adv.* **4**, eaao1761 (2018).
- Wang, F. et al. Highly reversible zinc metal anode for aqueous batteries. *Nat. Mater.* **17**, 543–549 (2018).
- Han, S.-D. et al. Origin of electrochemical, structural, and transport properties in nonaqueous zinc electrolytes. *ACS Appl. Mater. Inter.* **8**, 3021–3031 (2016).
- Qian, J. et al. High rate and stable cycling of lithium metal anode. *Nat. Commun.* **6**, 6362 (2015).
- Pradhan, D. & Reddy, R. G. Dendrite-free aluminum electrodeposition from AlCl₃-1-ethyl-3-methyl-imidazolium chloride ionic liquid electrolytes. *Metall. Mater. Trans. B* **43**, 519–531 (2012).
- Woods, J., Bhattachari, N., Chapagain, P., Yang, Y. & Neupane, S. In situ transmission electron microscopy observations of rechargeable lithium ion batteries. *Nano Energy* **56**, 619–640 (2019).
- Chen, H. et al. Oxide film efficiently suppresses dendrite growth in aluminum-ion battery. *ACS Appl. Mater. Inter.* **9**, 22628–22634 (2017).
- Peled, E. & Menkin, S. Review—SEI: Past, present and future. *J. Electrochem. Soc.* **164**, A1703–A1719 (2017).
- Aurbach, D., Skaletsky, R. & Gofer, Y. The electrochemical behavior of calcium electrodes in a few organic electrolytes. *J. Electrochem. Soc.* **138**, 3536–3545 (1991).
- Yu, J., McMahon, B. W., Boatz, J. A. & Anderson, S. L. Aluminum nanoparticle production by acetonitrile-assisted milling: effects of liquid- vs vapor-phase milling and of milling method on particle size and surface chemistry. *J. Phys. Chem. C* **120**, 19613–19629 (2016).
- Lu, Z., Schechter, A., Moshkovich, M. & Aurbach, D. On the electrochemical behavior of magnesium electrodes in polar aprotic electrolyte solutions. *J. Electroanal. Chem.* **466**, 203–217 (1999).
- Singh, N. et al. Achieving high cycling rates via in situ generation of active nanocomposite metal anodes. *ACS Appl. Energy Mater.* **1**, 4651–4661 (2018).
- Son, S.-B. et al. An artificial interphase enables reversible magnesium chemistry in carbonate electrolytes. *Nat. Chem.* **10**, 532–539 (2018).
- Gao, T. et al. Existence of solid electrolyte interphase in Mg batteries: Mg/S chemistry as an example. *ACS Appl. Mater. Inter.* **10**, 14767–14776 (2018).
- Chen, T., Ceder, G., Sai Gautam, G. & Canepa, P. Evaluation of Mg compounds as coating materials in Mg batteries. *Front. Chem.* **7**, 24 (2019).
- Tamura, S., Yamane, M., Hoshino, Y. & Imanaka, N. Highly conducting divalent Mg²⁺ cation solid electrolytes with well-ordered three-dimensional network structure. *J. Solid State Chem.* **235**, 7–11 (2016).
- Kisu, K. et al. Magnesium borohydride ammonia borane as a magnesium ionic conductor. *ACS Appl. Energy Mater.* **3**, 3174–3179 (2020).
- Canepa, P. et al. High magnesium mobility in ternary spinel chalcogenides. *Nat. Commun.* **8**, 1759 (2017).
- Pour, N., Gofer, Y., Major, D. T. & Aurbach, D. Structural analysis of electrolyte solutions for rechargeable Mg batteries by stereoscopic means and DFT calculations. *J. Am. Chem. Soc.* **133**, 6270–6278 (2011).
- Pour, N. et al. Multinuclear magnetic resonance spectroscopy and density function theory calculations for the identification of the equilibrium species in THF solutions of organometallic complexes suitable as electrolyte solutions for rechargeable Mg batteries. *Organometallics* **32**, 3165–3173 (2013).
- Kim, H. S. et al. Structure and compatibility of a magnesium electrolyte with a sulphur cathode. *Nat. Commun.* **2**, 427 (2011). **This work reported non-nucleophilic electrolyte solutions that enable reversible magnesium plating and stripping.**
- Doe, R. E. et al. Novel, electrolyte solutions comprising fully inorganic salts with high anodic stability for rechargeable magnesium batteries. *Chem. Commun.* **50**, 243–245 (2014).
- Carter, T. J. et al. Boron clusters as highly stable magnesium-battery electrolytes. *Angew. Chem. Int. Ed.* **53**, 3173–3177 (2014).
- Zhao-Karger, Z. et al. Toward highly reversible magnesium–sulfur batteries with efficient and practical Mg[B(hfip)₄]₂ electrolyte. *ACS Energy Lett.* **3**, 2005–2013 (2018).

45. Lipson, A. L. et al. Practical stability limits of magnesium electrolytes. *J. Electrochem. Soc.* **163**, A2253–A2257 (2016).
46. Liu, T. B. et al. A facile approach using MgCl₂ to formulate high performance Mg²⁺ electrolytes for rechargeable Mg batteries. *J. Mater. Chem. A* **2**, 3430–3438 (2014).
47. Du, A. et al. An efficient organic magnesium borate-based electrolyte with non-nucleophilic characteristics for magnesium–sulfur battery. *Energy Environ. Sci.* **10**, 2616–2625 (2017).
48. Luo, J., Bi, Y., Zhang, L., Zhang, X. & Liu, T. L. A stable, non-corrosive perfluorinated pinacolatoborate Mg electrolyte for rechargeable Mg batteries. *Angew. Chem. Int. Ed.* **58**, 6967–6971 (2019).
49. Cheng, Y. W. et al. Highly active electrolytes for rechargeable Mg batteries based on a [Mg₂(μ-Cl)₂]²⁺ cation complex in dimethoxyethane. *Phys. Chem. Chem. Phys.* **17**, 13307–13314 (2015).
50. Shterenberg, I. et al. Evaluation of (CF₃SO₂)₂N⁺ (TFSI⁻) based electrolyte solutions for Mg batteries. *J. Electrochem. Soc.* **162**, A7118–A7128 (2015).
51. Zhang, Y., Liu, S., Ji, Y., Ma, J. & Yu, H. Emerging nonaqueous aluminum-ion batteries: challenges, status, and perspectives. *Adv. Mater.* **30**, 1706310 (2018).
52. Attias, R., Salama, M., Hirsch, B., Gofer, Y. & Aurbach, D. Solvent effects on the reversible intercalation of magnesium-ions into V₂O₅ electrodes. *ChemElectroChem* **5**, 3514–3524 (2018).
53. Salama, M. et al. Unique behavior of dimethoxyethane (DME)/Mg(N(SO₂CF₃)₂)₂ solutions. *J. Phys. Chem. C* **120**, 19586–19594 (2016).
54. Seguin, T. J., Hahn, N. T., Zavadil, K. R. & Persson, K. A. Elucidating non-aqueous solvent stability and associated decomposition mechanisms for Mg energy storage applications from first-principles. *Front. Chem.* **7**, 175 (2019).
55. Senoh, H. et al. Sulfone-based electrolyte solutions for rechargeable magnesium batteries using 2,5-dimethoxy-1,4-benzoquinone positive electrode. *J. Electrochem. Soc.* **161**, A1315–A1320 (2014).
56. Yagi, S., Tanaka, A., Ichikawa, Y., Ichitsubo, T. & Matsubara, E. Electrochemical stability of magnesium battery current collectors in a grignard reagent-based electrolyte. *J. Electrochem. Soc.* **160**, C83–C88 (2013).
57. Hahn, N. T. et al. Enhanced stability of the carba-closododecaborate anion for high-voltage battery electrolytes through rational design. *J. Am. Chem. Soc.* **140**, 11076–11084 (2018).
58. Rajput, N. N., Qu, X., Sa, N., Burrell, A. K. & Persson, K. A. The coupling between stability and ion pair formation in magnesium electrolytes from first-principles quantum mechanics and classical molecular dynamics. *J. Am. Chem. Soc.* **137**, 3411–3420 (2015).
59. Attias, R., Salama, M., Hirsch, B., Gofer, Y. & Aurbach, D. Anode-electrolyte interfaces in secondary magnesium batteries. *Joule* **3**, 27–52 (2019).
60. Adams, B. D., Zheng, J., Ren, X., Xu, W. & Zhang, J.-G. Accurate determination of coulombic efficiency for lithium metal anodes and lithium metal batteries. *Adv. Energy Mater.* **8**, 1702097 (2018).
61. Sun, X., Bonnick, P. & Nazar, L. F. Layered TiS₂ positive electrode for Mg batteries. *ACS Energy Lett.* **1**, 297–301 (2016).
62. Yoo, H. D. et al. Intercalation of magnesium into a layered vanadium oxide with high capacity. *ACS Energy Lett.* **4**, 1528–1534 (2019).
63. Canepa, P. et al. Odyssey of multivalent cathode materials: open questions and future challenges. *Chem. Rev.* **117**, 4287–4341 (2017).
64. Sa, N. et al. Is alpha-V₂O₅ a cathode material for Mg insertion batteries? *J. Power Sources* **323**, 44–50 (2016).
65. Verrelli, R. et al. On the strange case of divalent ions intercalation in V₂O₅. *J. Power Sources* **407**, 162–172 (2018). **This work demonstrated the insuitability of α-V₂O₅ for magnesium and calcium storage despite the long-time belief of this material as a host for divalent metal ions, highlighting the importance of caution in deducing cathode storage chemistries for multivalent batteries.**
66. Zhao, Q. et al. Solid electrolyte interphases for high-energy aqueous aluminum electrochemical cells. *Sci. Adv.* **4**, eaau8131 (2018).
67. Dong, H. et al. Directing Mg-storage chemistry in organic polymers toward high-energy Mg batteries. *Joule* **3**, 782–793 (2019). **This work distinguished between complex-ion storage and pure metal-ion storage in magnesium battery cathodes and demonstrated the importance of the latter for practical cells performance.**
68. Lin, M.-C. et al. An ultrafast rechargeable aluminium-ion battery. *Nature* **520**, 324–328 (2015).
69. Kim, D. J. et al. Rechargeable aluminium organic batteries. *Nat. Energy* **4**, 51–59 (2018).
70. Li, Z. et al. Fast kinetics of multivalent intercalation chemistry enabled by solvated magnesium-ions into self-established metallic layered materials. *Nat. Commun.* **9**, 5115 (2018).
71. Haber, S. & Leskes, M. *What can we learn from solid state NMR on the electrode-electrolyte interface?* **30**, 1706496 (2018).
72. Kundu, D. et al. Aqueous vs. nonaqueous Zn-ion batteries: consequences of the desolvation penalty at the interface. *Energy Environ. Sci.* **11**, 881–892 (2018).
73. Wu, C. et al. Electrochemically activated spinel manganese oxide for rechargeable aqueous aluminum battery. *Nat. Commun.* **10**, 7 (2019).
74. Wang, R. Y., Wessells, C. D., Huggins, R. A. & Cui, Y. Highly reversible open framework nanoscale electrodes for divalent Ion batteries. *Nano Lett.* **13**, 5748–5752 (2013).
75. Kraychyk, K. V., Wang, S., Piveteau, L. & Kovalenko, M. V. Efficient aluminum chloride natural graphite battery. *Chem. Mater.* **29**, 4484–4492 (2017).
76. Aurbach, D. et al. Prototype systems for rechargeable magnesium batteries. *Nature* **407**, 724–727 (2000). **This work demonstrated reversible and reasonably fast magnesium-ion battery systems with the discovery of suitable complex ethereal electrolyte solutions and Chevrel phase cathodes such as Mo₆S₈.**
77. Sun, X. Q. et al. A high capacity thiospinel cathode for Mg batteries. *Energy Environ. Sci.* **9**, 2273–2277 (2016). **This work reported the first magnesium storage cathode material since the discovery of Mo₆S₈ that shows convincing performance.**
78. Pan, C., Zhang, R., Nuzzo, R. G. & Gewirth, A. A. ZnNi_xMn₃Co_{2-x}O₄ spinel as a high-voltage and high-capacity cathode material for nonaqueous Zn-ion batteries. *Adv. Energy Mater.* **8**, 1800589 (2018).
79. Pan, C., Nuzzo, R. G. & Gewirth, A. A. ZnAl_xCo_{2-x}O₄ spinels as cathode materials for non-aqueous Zn batteries with an open circuit voltage of ≤ 2 V. *Chem. Mater.* **29**, 9351–9359 (2017).
80. Yaghoobnejad Asl, H. & Manthiram, A. Mass transfer of divalent ions in an oxide host: comparison of Mg²⁺ and Zn²⁺ diffusion in hexagonal K_xW₃O₉ bronze. *Chem. Mater.* **31**, 2296–2307 (2019).
81. Geng, L. et al. Crystal structure transformation in Chevrel phase Mo₆S₈ induced by aluminum intercalation. *Chem. Mater.* **30**, 8420–8425 (2018).
82. Wan, L. W. F., Perdue, B. R., Apblett, C. A. & Prendergast, D. Mg desolvation and intercalation mechanism at the Mo₆S₈ chevrel phase surface. *Chem. Mater.* **27**, 5932–5940 (2015).
83. Levi, M. D. et al. The effect of the anionic framework of Mo₆X₈ Chevrel phase (X = S, Se) on the thermodynamics and the kinetics of the electrochemical insertion of Mg²⁺ ions. *Solid State Ionics* **176**, 1695–1699 (2005).
84. West, A. R. in *Basic solid state chemistry* Ch. 4 (John Wiley & Sons, 1988).
85. Adelstein, N. & Wood, B. C. Role of dynamically frustrated bond disorder in a Li⁺ superionic solid electrolyte. *Chem. Mater.* **28**, 7218–7231 (2016).
86. Mao, M. et al. Tuning anionic chemistry to improve kinetics of Mg intercalation. *Chem. Mater.* **31**, 3183–3191 (2019).
87. Brown, I. D. What factors determine cation coordination numbers? *Acta Crystallogr.* **B44**, 545–553 (1988).
88. Hannah, D. C., Sai Gautam, G., Canepa, P., Rong, Z. & Ceder, G. Magnesium ion mobility in post-spinels accessible at ambient pressure. *Chem. Commun.* **53**, 5171–5174 (2017).
89. Jung, S. C. & Han, Y.-K. Fast magnesium ion transport in the Bi/Mg₃Bi₂ two-phase electrode. *J. Phys. Chem. C* **122**, 17643–17649 (2018).
90. Rong, Z. et al. Fast Mg²⁺ diffusion in Mo₃(PO₄)₂O for Mg batteries. *Chem. Commun.* **53**, 7998–8001 (2017).
91. Zhao-Karger, Z. et al. Performance improvement of magnesium sulfur batteries with modified non-nucleophilic electrolytes. *Adv. Energy Mater.* **5**, 1401155 (2015).
92. Zhang, Z. et al. Novel design concepts of efficient Mg-ion electrolytes toward high-performance magnesium-selenium and magnesium-sulfur batteries. *Adv. Energy Mater.* **7**, 1602055 (2017).
93. Tian, H. et al. High power rechargeable magnesium/iodine battery chemistry. *Nat. Commun.* **8**, 14083 (2017).
94. Mao, M. et al. High-energy-density rechargeable Mg battery enabled by a displacement reaction. *Nano Lett.* **19**, 6665–6672 (2019).
95. Gao, T. et al. Reversible S⁰/MgS redox chemistry in a MgTFSI₂/MgCl₂/DME electrolyte for rechargeable Mg/S batteries. *Angew. Chem. Int. Ed.* **56**, 1326–13530 (2017).
96. Salama, M. et al. On the feasibility of practical Mg–S batteries: practical limitations associated with metallic magnesium anodes. *ACS Appl. Mater. Inter.* **10**, 36910–36917 (2018).
97. Gao, T. et al. Thermodynamics and kinetics of sulfur cathode during discharge in MgTFSI₂–DME electrolyte. *Adv. Mater.* **30**, 1704313 (2018).
98. Li, X. et al. Reducing Mg anode overpotential via ion conductive surface layer formation by iodine additive. *Adv. Energy Mater.* **8**, 1701728 (2018).
99. Liu, J. et al. Pathways for practical high-energy long-cycling lithium metal batteries. *Nat. Energy* **4**, 180–186 (2019).
100. Andrews, J. L. et al. Reversible Mg-ion insertion in a metastable one-dimensional polymorph of V₂O₅. *Chem* **4**, 564–585 (2018).
101. Arthur, T. S., Singh, N. & Matsui, M. Electrodeposited Bi, Sb and Bi_{1-x}Sb_x alloys as anodes for Mg-ion batteries. *Electrochim. Commun.* **16**, 103–106 (2012).

102. Yao, Z., Hegde, V. I., Aspuru-Guzik, A. & Wolverton, C. Discovery of calcium-metal alloy anodes for reversible Ca-ion batteries. *Adv. Energy Mater.* **9**, 1802994 (2019).
103. Gershinsky, G., Yoo, H. D., Gofer, Y. & Aurbach, D. Electrochemical and spectroscopic analysis of Mg²⁺ intercalation into thin film electrodes of layered oxides: V₂O₅ and MoO₃. *Langmuir* **29**, 10964–10972 (2013).
104. Licht, S. Zinc sulfur battery. US patent 6207324 (2001).

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Competing interests

Y.Y. has an equity interest in Polymax Energy Inc. Y.Y.'s relationship with Polymax Energy Inc. has been reviewed and approved by the University of Houston in accordance with its conflict of interest policies.

Additional information

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