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ROADMAP

Roadmap on multivalent batteries

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Abstract

Battery technologies based in multivalent charge carriers with ideally two or three electrons transferred per ion exchanged between the electrodes have large promises in raw performance numbers, most often expressed as high energy density, and are also ideally based on raw materials that are widely abundant and less expensive. Yet, these are still globally in their infancy, with some concepts (e.g. Mg metal) being more technologically mature. The challenges to address are derived on one side from the highly polarizing nature of multivalent ions when compared to single valent concepts such as Li^+ or Na^+ present in Li-ion or Na-ion batteries, and on the other, from the difficulties in achieving efficient metal plating/stripping (which remains the holy grail for lithium). Nonetheless, research performed to date has given some fruits and a clearer view of the challenges ahead. These include technological topics (production of thin and ductile metal foil anodes) but also chemical aspects (electrolytes with high conductivity enabling efficient plating/stripping) or high-capacity cathodes with suitable kinetics (better inorganic hosts for intercalation of such highly polarizable multivalent ions). This roadmap provides an extensive review by experts in the different technologies, which exhibit similarities but also striking differences, of the current state of the art in 2023 and the research directions and strategies currently underway to develop multivalent batteries. The aim is to provide an opinion with respect to the current challenges, potential bottlenecks, and also emerging opportunities for their practical deployment.

Contents

Introduction

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Regardless of whether we use the United Nations Sustainable Development Goals [1], the EU Green Deal [2], or some other source of arguments to advocate for the need of a green energy transition, it is clear that a way to store large quantities of energy with high quality (*i.e.* exergy) is utmost needed. Only this will enable the decarbonization of our energy ecosystem at the speed necessary to in time combat the climate changes caused by us humans. Here enters electrochemical energy storage (EES), which means rechargeable batteries and/or supercapacitors and the former today primarily manifested as lithium-ion batteries (LIBs) that are adopted in a wide range of usage cases and applications—most notably consumer electronics and electromobility. And the industry is now globally vividly building capacity to meet the rapidly increasing demand for LIBs for a variety of sectors [3].

Our prime interest in using batteries in our energy system is to get the electrons we need to store back as efficiently as possible and for as many needs as possible—we should be agnostic and not really care about by what technology/technologies this is accomplished. However, cost, environmental impact, sustainability, *etc.* must all be taken seriously into account to ensure responsible competitiveness long-term. Multivalent batteries with ideally two or three electrons transferred per cation moved between the electrodes have large promises in raw performance numbers, most often expressed as high energy density, and are also ideally based on raw materials that are widely abundant and less expensive [4]. A notable misconception is that these technologies will only be suited for large-scale energy storage, such as grid-coupled or off-grid applications, and that for these uses weight and volume measures do not matter—clearly not the full truth when techno-economic analyses are made [5].

The potential is obvious, but the challenges are still more plentiful and hence we have at present many active research directions. The multivalent battery chemistry is in addition very diverse, as should be clear from this Roadmap on multivalent batteries that cover magnesium (Mg), calcium (Ca), aluminium (Al) and to some extent zinc (Zn) (-ion) batteries. To limit the scope somewhat it only covers non-aqueous technologies, hence emphasizing the common strive for medium to high voltage cells.

The Roadmap has contributions from a global set of researchers, with an emphasis on European academic groups. The true purpose of the Roadmap is to highlight the active research directions and areas efficiently and constructively and where the more urgent needs of progress are to be found, not the least to guide early-stage researchers, while in contrast the purpose is clearly not to do any exhaustive review.

'Technology is always limited by the materials available' the adage at Defense Advanced Research Projects Agency from the 1960's [6] is still true and not the least for EES and explains why battery R&D to a very large extent is battery *materials* R&D. This is also why battery Roadmaps often, and a strategy that we adopt also here, are based on sections of anode, cathode, electrolyte and sometimes other cell components and materials. Here we do this in four separate themes, one for each multivalent battery technology. There are clear similarities that are acknowledged, but also many differences which are reflected in the way that the research emphases differ. This has also been the case in the past, leading to the different maturity levels present, often given as TRLs—even if that is sometimes tricky to speak about for some concepts.

Picking a few unique features of multivalent batteries that are high-lighted in this Roadmap is not easy, but surely the rather sluggish nature of both cation transport and charge transfer at the electrolyte/electrode interfaces/interphases [7] is one. In particular challenges with electrolytes enabling a reversible plating and stripping of multivalent ions on metallic anodes as well as better intercalation hosts for the multivalent ions are key. As a second, the sometimes largely unknown (active) charge carrying species in the electrolytes, originating in the rather unconventional chemistries applied. The third is the prominent role/place of organic cathodes, as compared to the more conventional and well-known inorganic chemistry based, even if the latter often hold large promise—just as for LIBs. All choices of concepts, designs and material should also, but is far too seldom, be combined and assessed for (possible) real battery performance, and the latter also beyond the materials and cell levels—which here is made for a few technologies.

Finally, while the present reality and proven, often rather limited, performance should never hamper creativity, we stress that a dose of scepticism towards fantastic results [8] and applying checks *vs.* true needs, that can be learnt *e.g.* by applying a proper LIB industry perspective [9], are nevertheless very useful. This serves to avoid adding to the hype and ultimately to keep the surrounding society to also long-term trust that we as scientists carefully *do* strive to develop more sustainable batteries. This is especially important when we are at a stage when no commercialization is evident, such as for the present battery technologies.

1. Advantages and pitfalls of magnesium metal electrodes

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Status

As of today, LIBs continue to dominate the battery market across various sectors. Several efforts are being made to further improve their energy density by exploring alternatives. One potential solution involves replacing graphite electrodes with metallic lithium electrodes. This approach, combined with the use of all solid-state electrolytes, is currently considered the most viable option. However, the concerns arise from the limited resources of lithium and its uneven geographical distribution. Efforts are underway to develop and commercialize alternative battery chemistries, such as other types of alkali metal or multivalent batteries, which can potentially offer comparable or even improved performance to Li-ion batteries while reducing reliance on lithium.

Magnesium metal batteries are gaining attention as potential next-generation batteries, due to their high energy density, abundance, and potential low cost. Magnesium metal electrodes are considered a safer option due to the high melting point of metallic magnesium compared to other possible metal electrodes used in aprotic electrolytes. Although the magnesium metal combined with 3 V oxides cathodes or with sulphur can deliver values of energy density that are comparable with today's state of the art Li-ion battery technology [10], its commercial use in rechargeable batteries is still under debate due to several challenges. This short contribution aims to discuss those challenges while the reader if needed can access more comprehensive review papers published recently [11–13].

Current and future challenges

The use of magnesium metal for batteries does present several significant challenges:

(a) Poor reversibility of magnesium deposition and dissolution is one of the main challenges causing the limited cycling stability. This leads to capacity loss and reduced overall performance of magnesium batteries.
(b) During the charging and discharging cycles of a magnesium-based battery, the deposition and dissolution of magnesium can be uneven. This uneven growth can lead to the formation of dendrites or uneven electrode surfaces, which can cause short circuits, reduced capacity, and decreased battery lifespan.
(c) Magnesium has low ductility, which makes it difficult to process thin electrodes required for high-energy-density batteries. Thin electrodes are desirable to maximize energy density.
(d) Magnesium is highly reactive, and when exposed to the electrolyte, it forms a passivation layer that hampers the transport of ions. This passivation layer typically exhibits poor ionic conductivity due to the high polarizability of magnesium cations, which further affects the battery's performance. Finding ways to mitigate the reactivity and improve the formation and properties of the passivation layer are important research directions for magnesium-ion batteries.

Challenges are to a large extent connected with the choice of electrolyte, additives, and potential cross-contamination with degradation products from the cathode. Early-stage electrolytes based on Grinard reagents or chlorine complexes possessed higher reversibility for the stripping and deposition, however, their drawback was low oxidative stability and incompatibility with some potential cathode materials. Due to the nature of the passivation layer on the metallic magnesium use of approaches known from Li-ion batteries leads to a highly passivated surface with limited electrochemical activity. New salts based on weakly coordinating salts and the use of additives recently proposed lead to improvements in the reversibility and enable the use of different cathode materials.

Advances in science and technology to meet challenges

The poor reversibility of magnesium metal electrodes is evident in the Coulombic efficiency (CE), which falls significantly below the desired value close to 100%. Currently, this issue is rarely addressed in laboratory research, as most results are obtained using thick Mg metal anodes and a substantial excess of electrolyte. The reversibility of the stripping and deposition process depends on various factors, with the magnesium-electrolyte interface and impurities being the most critical. Impurities, such as native passive film and electrode doping, play a significant role in the reversibility of the process. Although the initial generation of electrolytes showed higher CE, they exhibited drawbacks such as low oxidative stability and corrosiveness. Efforts have been made to develop weakly coordinating anions (WCA), such as carbaboranes [14] and hexafluoro iso-propyl-based [15] magnesium salts, to address the issues of corrosion and oxidative stability. However, these electrolytes often result in lower reversibility of the stripping and deposition process, especially in the presence of impurities, as they are unable to act as scavengers. To make further progress, various additives [16] have been developed to enable CE above 99%. Additionally, the formation of protective layers that prevent direct contact between magnesium and electrolyte are considered a promising approach for all metal-based batteries [17, 18].

The uneven growth of magnesium deposits can result in the formation of uneven deposits or dendrites which can grow through the separator and eventually cause a short circuit in the cell. Several factors contribute to the uneven growth of magnesium deposits. These include variations in the current density, impurities in the electrolyte, and electrode/electrolyte interface properties. According to theoretical prediction, the diffusion barrier for the most stable Mg surface (0001) is high enough to prevent the formation of dendrites [19]. However, the most stable surface is not the one with the highest area fraction, and that changes with the chemical environment and kinetics of the deposition process [20]. Other crystal surfaces have lower diffusion barriers and, due to their higher fraction or higher current densities, the deposition of magnesium can occur in the form of dendrite [21].

The kinetics of magnesium deposition are often hindered by the use of metal foil electrodes with a surface area close to their geometrical surface area. This limitation affects the kinetics, resulting in high overpotential during the formation cycles required for activation amplified with the presence of a native passivation layer. An alternative approach is to utilize magnesium powder, although this is an attractive approach it requires additional electrode processing with a solvent and binder that are stable with highly reactive magnesium particles.

Another issue with using magnesium metal foil is its ductility. Since batteries typically operate with an areal capacity per electrode layer of a few mAh cm^{-2}, the thickness of the magnesium metal electrode is limited to a few tens of micrometers (10 μm approximately corresponds to 4 mAh cm^{-2}). Alloys such as AZ31 [22] can be processed to much thinner dimensions and offer potential solutions for matching the areal capacities of positive and negative electrodes. The pitfall of introducing alloys is decreased energy density [10] and this effect becomes more pronounced when employing alloys with a higher ratio of inactive metal i.e. bismuth (Bi) or tin (Sn) [23].

One of the most challenging aspects of batteries is the interface between the metal anode and electrolyte. It is crucial to understand the electrochemical reactivity of solvents and salts near the electrode surface to predict and identify stable solvents and salts. One alternative approach to developing new electrolyte components is the creation of an artificial layer that mimics the solid electrolyte interface. Although a well-designed artificial layer can address the conductivity issues associated with highly polarizable magnesium cations, it introduces additional non-active mass and volume, thereby reducing the advantages offered by magnesium metal in batteries.

Concluding remarks

Nowadays, it is clear that LIBs will not be able to cover all needs induced by the electrification of different sectors. One or several technologies will compete with them and there will be several winners. Mg metal batteries have several advantages and considering that the majority of research efforts have started just recently, they can be found in applications in some sectors where the use of sustainable and cheap materials will be demanded.

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2. The evolution of non-aqueous electrolyte solutions for rechargeable Mg batteries

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Status

Extensive work was done in 1957 by Connor *et al* [24] about Mg deposition from Grignard reagents' solutions comprising RMgX compounds (R = alkyl groups, X = halide anions like Cl^-, Br^-) in ether solvents (THF, glymes like dimethoxy-ethane, DME). Based on this work Muldoon *et al* [25] tested several types of electrolyte solutions. They realized that $Mg(BF_4)_2$, and $Mg(ClO_4)_2$ solutions in THF may support partially reversible Mg deposition-dissolution, however their side reactions with Mg form passivation layer that blocks the Mg electrodes. Ethereal solutions of Grignard reagents which can allow fully reversible Mg deposition have a very limited anodic stability, being oxidized below 1.5 V vs. Mg, what means that they are not suitable to any relevant cathodes. In turn, solutions comprising THF, and $Mg(BR_4)_2$ species (R = aryl or alkyl groups) showed reversible magnesium stripping-plating processes and anodic stability approaching 2 V vs. Mg [25]. In 2000, Aurbach *et al* reported on the first prototype of rechargeable Mg batteries. These cells included Mg foil anodes, $Mg_xMo_6S_8$ Chevrel phase (CP) cathodes ($0 < X < 2$) and 0.25 M $Mg(AlCl_2BuEt)_2$ in THF electrolyte solution [26]. Replacing the organoborate with aluminum-based Lewis-acid presented higher anodic-stability (2.5 V vs. Mg), almost 100% magnesium deposition-dissolution reversibility, and good Mg^{2+} ions intercalation kinetics into CP cathodes [27]. A further work, demonstrated a better solution, replacing the alkyl ligand with a phenyl group [28]. The goal of widening the electrochemical window (EW), and still supporting 100% Mg deposition reversibility, pushed research groups to develop more organo-halo-aluminates based electrolyte solutions (in ethers), demonstrating anodic stability up to 3.7 V [29]. Despite the advantages which these solutions have, they are still problematic due to several issues. The above-described solutions contain chlorides. It is known that chlorides have corrosive nature, preventing from working with non-noble metals for the cathode's current collectors and for other cells' components [30]. In addition, THF is a very volatile solvent and tend to form peroxides [31]. Shterenberg *et al* developed electrolyte solutions based on $MgTFSI_2$ salt, using the less volatile DME solvent [32]. $MgTFSI_2$ is the only ether-soluble 'simple' magnesium salt. In DME/$MgTFSI_2$ solutions, $Mg(DME)_3^{2+}$ cluster cations are formed due to strong DME-Mg^{2+} interactions [33]. Because of these strong interactions, processes like Mg deposition or Mg^{2+} ions intercalation are not reversible. When $MgCl_2$ is introduced, the interactions of the Cl^- species with the Mg ions soften the $Mg(DME)_3^{2+}$ clusters leading to the formation of DME solvated cations like $[Mg_2Cl_2(DME)_4]^{2+}$ and $[Mg_3Cl_4(DME)_5]^{2+}$ (see figure 1). The formation of such Mg-Cl cations complexes enables to obtain reversible Mg deposition and reversible Mg cations intercalation (into CP cathodes) [34]. This solution avoids the use of THF, but still contains chlorides, what is causing corrosion to the cells' components. In addition, Attias *et al* [35] showed that chlorides have a major role in facilitating Mg ions intercalation into cathodes like CPs, via the formation of adsorbed surface layer—chloride anions interacting with the surface of the cathode material, enabling an easy transfer of Mg cations from the solutions' structures to the intercalation sites on the surface.

In recent years, new classes of non-corrosive electrolyte solutions for secondary Mg batteries were intensively investigated. Magnesium borohydride, $[Mg(BH_4)_2]$, was reported as the first inorganic compound supporting Mg deposition-dissolution in aprotic solutions by Tutusaus *et al* [36] However, this electrolyte shows low anodic stability.

The same group developed further Mg organo-borate electrolytes that are soluble in ethers. They demonstrated electrolyte solutions without chloride species, in which Mg electrodes behave reversibly and their anodic stability may reach values >3 V vs. Mg [36]. Etheral solutions of these solutions seem promising for use in rechargeable Mg batteries, but nevertheless, there are not yet reports on secondary Mg batteries based on these solutions.

Zhao-Karger *et al* [15] reported on fluorinated alkoxyborate-based electrolytes, $Mg[B(HFIP)_4]_2$ (HFIP—Hexafluoroisopropanol), synthesized in ethereal solvents, which is capable of reversible Mg deposition and intercalation without the presence of chloride ions (See figure 2). Dlugatch *et al* [37] showed that the $Mg[B(HFIP)_4]_2$/DME solutions require pre-treatments (denoted as 'conditioning' processes) for improving their performance (see figure 2),

$$2MgCl_2 + MgTFSI_2 + 5DME \rightarrow [Mg_3Cl_4](DME)_5{}^{2+} + 2TFSI^- \quad (1)$$

$$MgCl_2 + MgTFSI_2 + 4DME \rightarrow [Mg_2Cl_2](DME)_4{}^{2+} + 2TFSI^- \quad (2)$$

1. $2MgCl_2 + MgTFSI_2 + 5DME \rightarrow [\mathrm{Mg_3Cl_4}](DME)_5{}^{2+} + 2\mathrm{TFSI}^-$
2. $MgCl_2 + MgTFSI_2 + 4DME \rightarrow [Mg_2Cl_2](DME)_4{}^{2+} + 2TFSI^-$

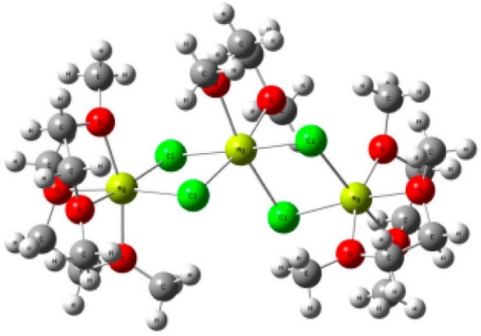

Figure 1. The chemical reactions of $MgTFSI_2$ with $MgCl_2$ in DME at different ratios, followed by a refined structure of $Mg_3Cl_4(DME)_5](TFSI)_2$recrystallized from solutions of $MgTFSI_2/MgCl_2$ at a 1:2 molar ratio in DME. Reprinted with permission from [34]. Copyright (2017) American Chemical Society.

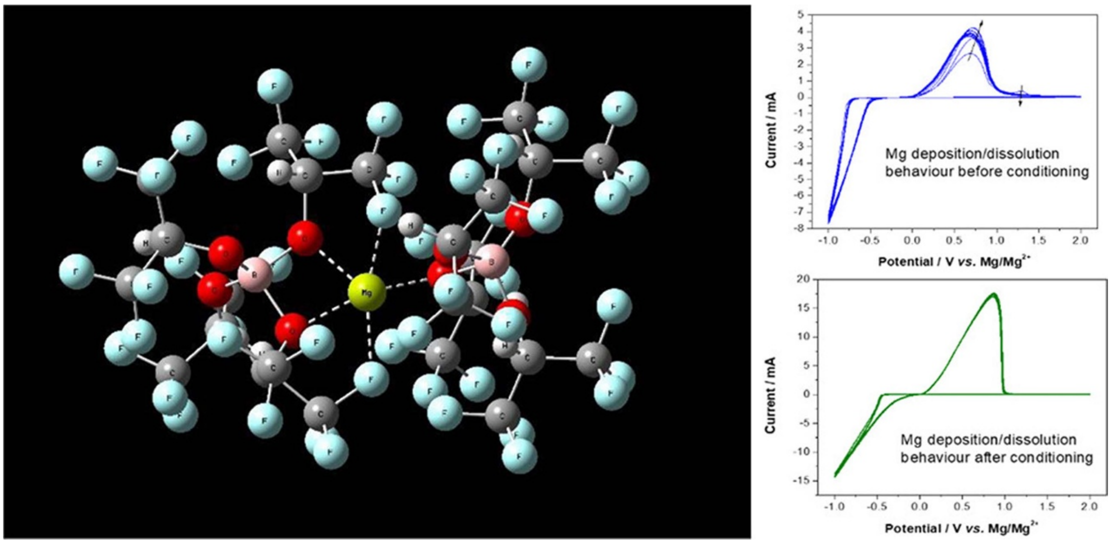

Figure 2. The solution structure of $Mg[B(HFIP)_4]_2$/DME followed by CV voltammograms before (upper) and after (lower) 'electrochemical conditioning process' of 0.3 M $Mg[B(HFIP)_4]_2$/DME, using Mg foil as counter and reference electrodes, and Pt rod as working electrode, at 0.5 mV s^{-1}.

Current and future challenges

It is important to emphasize that the major advantage of Mg batteries is the possible use of very thin Mg foils anodes, what may enable to reach high capacity and high energy density with them. The formation of fully blocking passivation layers on the Mg anodes surface while being in touch with all protic solvents and polar aprotic solvents like alkyl carbonates and esters, forces us to use only ether solvents like THF, DME and heavier glymes in rechargeable Mg batteries. Mg anodes in touch with even small traces of protic species, oxygen, certain commonly used salt anions like BF_4^-, PF_6^-, ClO_4^- etc, in ether solvents also develop fully blocking surface films. Thereby, metallic Mg surface must be passivation free, with no side reactions. There are only a few electrolyte solutions that support reversible Mg deposition/dissolution with a decent kinetics at room temperature. Most of them contains Grignard reagents. High enough reversible Mg deposition and dissolution, which is critical for rechargeable battery technology, was demonstrated so far mostly with electrolyte solutions with relatively low anodic stability ($<$3 V vs. Mg/Mg^{2+}), that limits the use of high voltage cathodes [30].

The limited EW prevents us to use high potential cathodes since by using them we will exceed the window and oxidize the electrolyte solution.

Most of these electrolyte solutions contain corrosive chlorides that pose compatibility issues with non-noble metals, prevents us from using simple, cheap, abundant metals as current collectors and other components.

Chlorides has two major roles. (1) Form Mg-complexes that facilitates the de-solvation of Mg^{2+} ions [32]. (2) Form adsorbed layer on sulphides-based cathodes' surface that reduces the activation energy of Mg^{2+} ions intercalation [35]. These roles are crucial for power sources related magnesium electrochemistry. However, the new class of non-corrosive, Cl-free electrolyte solutions supposed to provide the solution for the corrosion problem of these systems [15]. Although, Cl-free electrolyte solutions enable reversible Mg deposition-dissolution, the efficiency is much lower, the over-potential for magnesium deposition is higher, and in general, these solutions perform better when containing chlorides.

Magnesium, in contrast to lithium, is safe in ambient air, but Mg-based electrolyte solutions contain problematic materials such as THF, chlorides, and Grignard reagents that have high corrosive nature, air sensitivity, and volatile solvents are used.

The sensitivity to atmospheric components is a critical challenge to address. It is critically important to demonstrate cycling efficiency of Mg anodes approaching to 100% during prolonged cycling tests and to examine compatibility with full cells, comprising Mg foil anodes and high voltage (2–3 V vs. Mg) cathodes.

Advances in science and technology to meet challenges

Developing electrolyte solutions for rechargeable batteries are always facing great challenges. Formation of passivation layers on Mg anodes restricts the solutions components to ethers and ether soluble Mg-salts. The main effort since the nineties was to establish high anodic stability, so it will be possible to work with high-potential cathode materials. The goal was achieved with electrolyte solutions stable up to 3.5 V vs. Mg. However, those solutions consist of organohalo-aluminates, which are corrosive, unstable in air, highly nucleophilic, and include volatile solvents. The active species in the best solutions developed so far are ether solvated Mg-Cl complex cations with several optional stoichiometries. The corrosive properties of the chlorides containing solutions are forcing development of alternative electrolyte solutions. Examples are ethereal solutions based on $Mg(CB_{11}H_{12})_2$, [36] and later $Mg[B(HFIP)_4]_2$ [15]. Aurbach *et al* showed that the electrochemical performance of DME/$Mg[B(HFIP)_4]_2$ solution is far from that obtained with solutions comprising Mg—organohalo-aluminate electrolytes, showing only 96.5% efficiency (compared to almost 100% with the latter ones). From preliminary studies it appears that only addition of chloride moieties to the borates-based solutions can really improve their performance.

To develop further non-corrosive, stable, safe, non-hazard electrolyte solutions, we should strengthen understanding the mechanistic differences between Mg deposition/stripping processes in Cl-free and Cl-containing solutions. We may decide to concentrate on chlorides containing solutions but develop compatible cathodes, like redox organic compounds and use cells based on corrosive resistant components. We will struggle to improve the boron-clusters based electrolyte solutions by most effective 'conditioning' processes.

It is not clear yet whether Mg rechargeable batteries will ever become a practical, competitive post-lithium batteries technology. We know that the key for such an achievement still depends on the availability of most effective electrolyte solutions (to be developed considering the above discussion).

Concluding remarks

Magnesium seems as an ideal active metal for use as an anode material in high energy density, cost effective rechargeable batteries. However, its reactivity and the bivalent nature of Mg ions are very challenging, because any type of side reactions between Mg metal and the environment (reactive solutions species, atmospheric contaminants) form surface films that fully block Mg ions transport. Thereby, it is mandatory to use in secondary Mg batteries only electrolyte solutions in which Mg anodes are bare, fully passivation free. It is important to emphasize that these systems may be advantageous only if the anodes are very thin Mg metal foils. Only ether solvents are compatible with Mg metal anodes, but they form very strong complexes with Mg^{2+} ions, what slows down their transport kinetics in all kinds of redox processes. Several families of relevant electrolyte solutions for secondary Mg batteries were developed during the last 2 decades. Most important are THF/PhMgCl/$AlCl_3$, DME/$MgTFSI_2$/$MgCl_2$ and DME/$Mg[B(HFIP)_4]_2$ solutions (reversible Mg deposition, wide electrochemical window). Their structure is understood thanks to intensive analytical and theoretical studies. It seems that the best starting point for a further development and improvement are solutions comprising ultra-pure glyme solvents (like DME, but not only) and electrolytes like $Mg[B(HFIP)_4]_2$.

3. Mg based batteries—inorganic cathodes

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Status

Rechargeable batteries with magnesium (Mg) metal anodes offer an opportunity to expand the energy storage landscape towards safer and more sustainable options. In addition, Mg metal anode provides a high theoretical capacity (3833 mAh cm^{-3} and 2206 mAh g^{-1}) and a low redox potential (-2.37 V vs SHE). As a result, the exploration of viable cathode materials for Mg batteries could foresee a significant improvement in energy density even exceeding that of the current Li-ion technology.

In 2000, Aurbach *et al* demonstrated the first prototype Mg batteries by reporting a CP Mo_6S_8 cathode with superior ionic conductivity, which provided a capacity of $\sim$70 mAh g^{-1} at an average voltage of $\sim$1.1 V vs. Mg for more than 2000 cycles [26]. The excellent cycling performance and Mg kinetics of the CP structure inspired considerable efforts on the discovery and evaluation of new compounds that provide redox reactions at high voltages [38]. However, most of the host structures, which have been successfully developed in monovalent systems, did not show comparable storage capability in Mg batteries, such as layered oxides or polyanionic frameworks [39]. Mg storage in these materials typically suffers from sluggish ion mobility, resulting in low reversibility and large hysteresis. This indicates completely different insertion chemistry of Mg when compared to the monovalent systems. Further theoretical investigations revealed site preference of the intercalant as a key factor for lowering diffusion kinetic barrier: while Li^+ favors a four-coordination in the host structure, Mg^{2+} prefers a six-coordination environment [40]. Based on these findings and stepping back to softer lattice, thiospinel Ti_2S_4 was developed, providing an energy density of 230 Wh kg^{-1} at material level, which is twice as high as the benchmark of the Mo_6S_8 cathode [41].

Till now, the development of Mg cathodes is largely restricted to sulfide materials, which can be charged at an acceptable rate, yet offering only moderate redox potentials. Some of the transition metal sulfides (e.g. MoS_2 and VS_4) provide energy densities in the region of 300–400 Wh kg^{-1} at material level, by delivering a high capacity (figure 3 left) [42, 43]. Despite that, their fast capacity fading due to parasitic conversion processes calls for structural optimization strategies in order to achieve a long-term cycling stability. In a practical scenario, the spinel Ti_2S_4 cathode may reach energy density of $\sim$130 Wh kg^{-1} at cell level (figure 3 right), given a dense cathode, lean electrolyte condition and highly efficient anode reactions can be realized [44]. Further pushing the energy density to the target of 350 Wh kg^{-1} or 750 Wh l^{-1} requires a well-functioning cathode that operates at 3.1 V vs. Mg and provides a capacity of 165 mAh g^{-1} or more.

Current and future challenges

A major roadblock that impedes the development of high-voltage Mg cathodes is the sluggish diffusion kinetics of Mg^{2+}. The bivalency and high charge density of Mg^{2+} induce a strong interaction with the host lattice, which builds up a significantly higher kinetic barrier than required for Li^+ migration [45]. Worse is that the strong interaction leads to severe structural distortion both crystallographically and electronically, which often results in either parasitic conversion reactions or detrimental phase transitions along with Mg intercalation. In case of high-voltage layered oxide (e.g. MnO_2), the undesired conversion reactions can be the dominant process, due to their thermodynamic preference over intercalation [46]. Even for transition metal sulfides with softer structures, the conversion process may take place at a similar voltage to Mg^{2+} insertion [47]. Layered sulfides show better structural stability upon Mg intercalation, without triggering conversion reactions [48]. Nevertheless, they undergo multistep phase transition, which limits the reversibility of the reaction in long-term cycling. To enhance the Mg storage performance in layered compounds, structural engineering strategies were also attempted to tailor the diffusion kinetics, which however normally have to compromise with the energy density [49]. Despite valuable fundamental insights into the charge storage mechanism gained during the past years, viable host structures that provide energetically favorable diffusion pathways for Mg^{2+} are still lacking. In search for cathode materials with high polarizability, the interplay between crystallographic geometry and charge compensation (redox reactions) during de-/magnetization remains to be explored.

In addition to solid diffusion, interfacial charge transfer and mass transport is a combinatory issue that disturbs the evaluation of cathode materials, leading to controversial results. This issue relates closely to

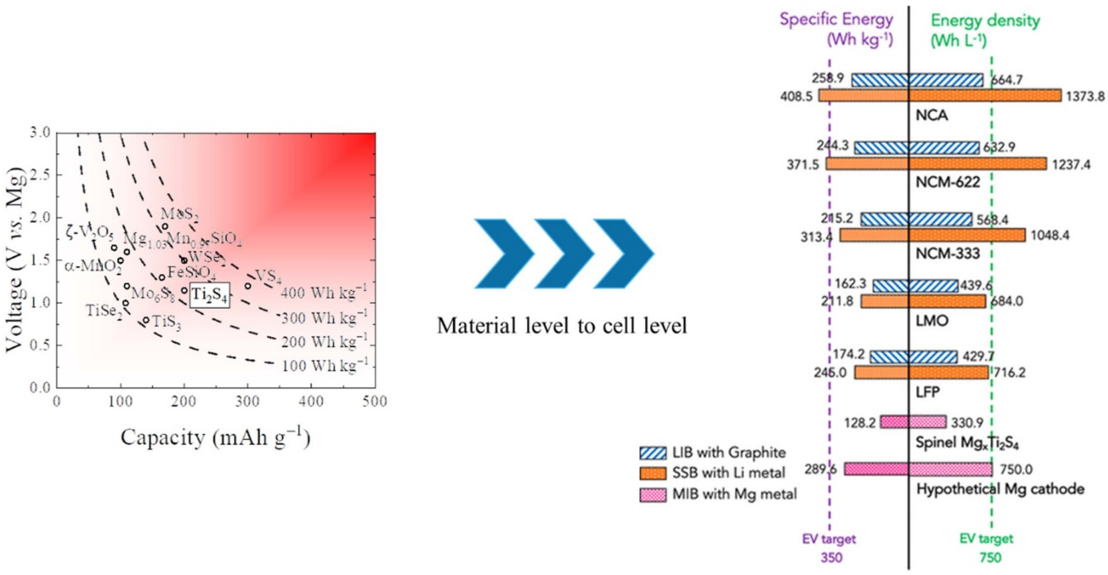

Figure 3. Left: experimental performance of representative cathode materials for Mg storage. Reproduced with permission from [43]. © 2020 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. CC BY-NC 4.0. Right: a comparison of specific energy and energy density between lithium ion batteries (LIBs), all solid-state batteries (ASSBs) and Mg batteries (MIBs) using selected cathode materials. Reprinted with permission from [44]. Copyright (2021) American Chemical Society.

solution environment of the electrolyte, where Mg^{2+} is in most cases coordinated strongly by the ligands (either anions or solvent molecules) [11]. Based on theoretical investigations, desolvation process for Mg^{2+} requires to overcome an energy barrier that is more than twice the value for Li^{+} in common organic solvents, and can be even higher than that for the subsequent solid diffusion [50]. The desolvation process with large energy barrier in turn may lead to decomposition of electrolyte and the possible formation of passivation layer on the cathode surface. Furthermore, the decomposition of even non-aqueous electrolyte could produce proton, which might be (co)-intercalated into the cathode due to its faster kinetics than Mg^{2+}, and thereby contributing to the measured capacity, which may mislead the evaluation of Mg^{2+} storage in the cathode [51].

Advances in science and technology to meet challenges

To tackle the abovementioned issues, controlling the Mg^{2+}-cathode interaction is a primary goal. This requires to take into account crystal structures of the host materials for accommodating highly polarizing Mg^{2+}, but also their electronic structures to balance the multi-electron transfer. In this regard, cathode materials that support multiple kinetic transition states are desirable, e.g. by providing multi-electron reactions. As most of the transition metal elements only offer single-electron redox, triggering anionic redox in addition to cationic redox can be a feasible solution to realize multi-electron redox. From the crystallographic perspective, most of the well-developed lattice frameworks for monovalent ions did not show satisfactory Mg storage capability. To unlock their kinetic limitations, constructing percolating networks in addition to the existing diffusion channels may open the avenue for fast Mg mobility in known structures. The percolating networks could be built by introducing highly ordered defects with high concentration [52]. On the other hand, a number of studies on co-intercalation have demonstrated that monovalent ions could act as assisting ions for lowering the diffusion barrier for Mg^{2+} [53], which calls for further efforts in this research direction. An extreme scenario of co-intercalation is hybrid Mg batteries where the fast-kinetic monovalent cathode chemistry is coupled with Mg metal anodes [54]. Under sustainability aspects, the selection of assisting cations for Mg-based co-intercalation should preferably be made from alkali metal ions beyond Li^{+}.

Beyond intercalation, unique interfacial properties were also observed in Mg systems, which largely affect the transport kinetics at cathode-electrolyte interfaces. To circumvent the desolvation process, intercalation of solvated Mg^{2+} has demonstrated a clear path towards fast-charging cathode chemistry [55]. By forming a ternary intercalated compound, Mg-solvent co-intercalation strategy offers an additional opportunity to design the energetic reaction pathway. Moreover, surface coating is a promising approach that may enhance the compatibility between cathode and electrolyte, but also promotes interfacial charge transfer through surface regulation. In spite of concerns on the migration kinetics through the coating layer, this approach deserves further efforts if a proper selection of the coating materials (e.g. disordered materials) with a desirable coating thickness can be made. Besides, as the interfacial processes are accompanied by various side reactions that can contribute largely to the measured capacity, a careful evaluation of the storage mechanism by combining elemental, redox and structural analysis is highly recommended [56].

Concluding remarks

Inorganic cathode materials with rigid crystal structures represent a grand challenge for allowing sufficient Mg^{2+} mobility. However, the compact structures exhibit the potential of significant gains in energy density, which could be further enhanced by coupling with high-capacity Mg metal anodes. The major issue associated with complex interactions between divalent Mg^{2+} and the polar moieties of the host materials need to be carefully addressed. This requires a robust fundamental understanding of the storage mechanism, which enables material developments through combinatory consideration of crystal structures and electronic configurations. Cathode materials with either high-voltage or high-capacity provide two pathways towards high-energy density, both of which require unconventional strategies to unlock the kinetic limitations.

Acknowledgements

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4. Mg based batteries—organic cathodes

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Status

The Mg^{2+} ion size is quite similar to the size of the Li^{+} ion. However, due to the double charge, its insertion inside inorganic structures is extremely difficult and is plagued by irreversible conversion reactions, poor ion mobility and solvent co-intercalation [38]. Hence, researchers are actively investigating alternative electrode materials such as organic-based ones. Organic cathodes can accommodate various cations through coordination mechanism due to their adaptable structures, which makes them suitable to circumvent the limitations of inorganic hosts. Additionally, organic chemistry offers a multitude of possibilities for tuning both the capacity and redox potential of organic active groups. However, organic materials also have some inherent limitations. Small organic molecules suffer from dissolution issues while most organic materials have low conductivity (higher amounts of carbon black needed in electrode formulation) and low tap density, which might compromise their volumetric capacity and the energy density of the cells. The low volumetric capacity of organic cathodes can be effectively compensated by the high volumetric capacity of Mg metal anode.

A significant limitation of the application of organic materials in the past was the chemical nature of Mg electrolytes, which were in the first generation based on organometallic compounds (Grignard reagents). Organometallics, as strong nucleophiles, can react with certain functional groups (carbonyls, sulfur groups) within organic materials and lead to irreversible reactions. The earliest attempt to apply organic materials into Mg metal anode cell setup was reported in 2007 when different organosulfur compounds containing S-S bonds were investigated as cathodes [57]. However, due to the use of highly reactive nucleophilic electrolyte, reversibility was quite limited. The reversible electrochemical activity of conjugated carbonyl compounds upon storing Mg^{2+} ions was observed and confirmed using *ex situ* x-ray diffraction (XRD) on the 2,5-dimethoxybenzoquinone in Mg metal passivating electrolyte, $Mg(ClO_4)_2$ in γ-butyrolactone, which meant that 3-electrode setup had to be utilized to achieve reversible cycling [58]. Significant progress was enabled by the advent of non-nucleophilic electrolytes (absence of organometallic compounds), which allowed broad exploration of organic compounds [59]. Non-nucleophilic electrolytes enabled good reversibility, and many different organic compounds were successfully employed in Mg metal anode-organic cathode setups, displaying several hundreds of reversible cycles with relatively high rates, opening the path towards practical high-performance Mg-organic batteries [60]. Among organic compounds, the most promising are n-type compounds, which become negatively charged during discharge and can store Mg^{2+} ions, enabling high-energy density Mg batteries upon pairing with Mg metal anode. Such an example would be the Mg metal-benzoquinone cathode, which could, on the level of electrode materials, enable a theoretical energy density of 810 Wh kg^{-1}. This value is above the theoretical energy density of the graphite-NCA Li-ion cell [61].

Current and future challenges

The electrochemical cell setup in Mg batteries is typically a two-electrode one, which is transferred from the Li battery research. However, the overpotential of the Mg metal anode is significantly larger than in the case of the Li metal anode, which makes it quite difficult to separate between the metal anode and working electrode (WE) contributions. An alternative option is the use of a three-electrode cell, but Mg metal as a reference exhibits unstable potential and is prone to passivation. Hence, different cell setups have been proposed, such as symmetric cells or alternative setups with capacitive carbon black electrodes serving as counter electrodes [62, 63].

Among different organic compounds, most of the early studies have focused on anthraquinone (AQ) type compounds, which exhibit moderate redox potential and specific capacity. While redox potential (around 1.5 V *vs.* Mg/Mg^{2+}) fits well into the electrolyte stability window of most Mg electrolytes, future research should aim for both higher voltage and capacity compounds to be able to achieve competitive energy densities of full cells. However, when moving towards higher voltage compounds, the oxidative stability of electrolytes might become an issue. The majority of Mg electrolytes are based on ether-type solvents (glymes and tetrahydrofuran), whose oxidative stability is limited to around 3 V vs. Mg/Mg^{2+}. This presents a major challenge in targeting higher voltage compounds since operating voltage windows can easily exceed this limit,

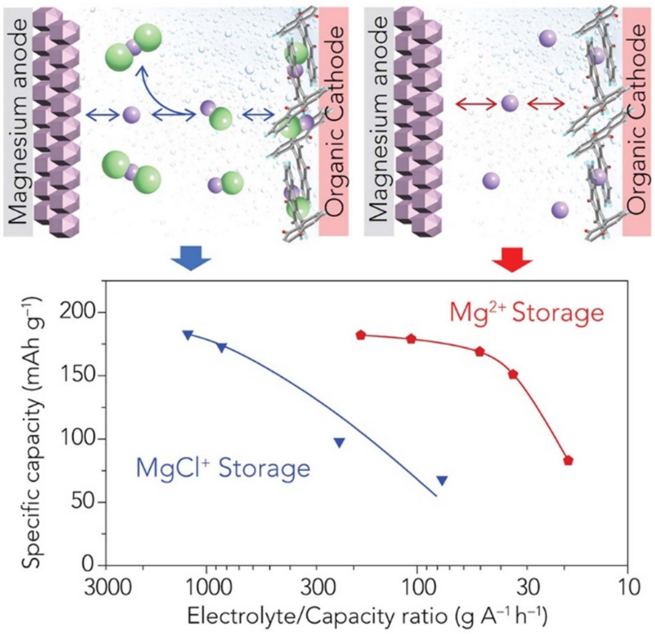

Figure 4. Schematic representation of $MgCl^+$ and Mg^{2+} ion storage in Mg metal-organic battery and effect of electrolyte amount on the capacity of the organic cathode for $MgCl^+$ (blue) and Mg^{2+} (red) ion storage. Reprinted from [64], Copyright (2019), with permission from Elsevier.

especially given the larger overpotential present in Mg metal anode cells and less favorable kinetics. High amounts of carbon blacks typically used in organic electrode formulation can also accelerate side reactions.

Another key issue of organic materials is a capacity utilization drop when moving from the Li cells to Mg cells. Incomplete capacity utilization of active material is not yet well understood and is most likely connected with aggravated accessibility of electrolyte species towards electroactive groups of organic compounds. Additionally, electrolyte speciation in Mg electrolytes is much more complex than in monovalent electrolytes due to the capability of Mg to form various complexes. Studies of discharged cathodes have also shown that in certain Mg electrolytes, the dominating Mg species inside discharged cathodes are not Mg^{2+} ions but cation-anion pairs, MgA^+, especially in $MgCl_2$-based electrolytes (figure 4) [64]. While this does not have serious consequences in laboratory testing setups, where flooded electrolyte setups are utilized, it would seriously limit the energy density of the practical Mg batteries due to electrolyte participation in the electrochemical mechanism. Additionally, electrochemical experiments should be supported by theoretical calculations, aiming to understand the effects coordination with monovalent ionic complexes and multivalent ions have on functional group rearrangement and interactions with neighboring molecules.

Advances in science and technology to meet challenges

In recent years, organic compounds that go beyond the energy density of AQ-based compounds were pursued, with various groups focusing on benzoquinone-based compounds [65, 66], polyimides [67] and hybrid polymers incorporating multiple electroactive groups [68]. The use of organic polymers has proven to be a good strategy for limiting active material dissolution and achieving long-term cyclability (figure 5). However, practical capacity utilization is often quite low. A study on the comparison of linear polymers with flexible porous polymer has shown an important correlation between practical capacity utilization and the degree of electrochemical swelling [69]. Additionally, large pore volume and flexible polymer nature were shown to aid swelling. An alternative approach to increase utilization is the use of solid particles to nanostructure organic compound composites with various carbon supports like graphene-based materials or carbon nanotubes (CNTs) [60, 70, 71]. However, it is important to take into account the capacitance contribution of the carbon support and subtract it properly, as this contribution can be quite significant.

According to our knowledge, all studies of the electrochemical mechanism through various *ex situ* and *operando* characterization techniques have confirmed that the electrochemical mechanism of organic materials does not change when moving from Li to Mg electrolytes [68, 70, 72], which provides a strong incentive to further develop organic materials for Mg batteries. At the same time, the development of Mg electrolytes has been directed into the field of non-corrosive and non-nucleophilic electrolytes, which should ensure good electrochemical compatibility with different organic compounds. The new generation of Mg

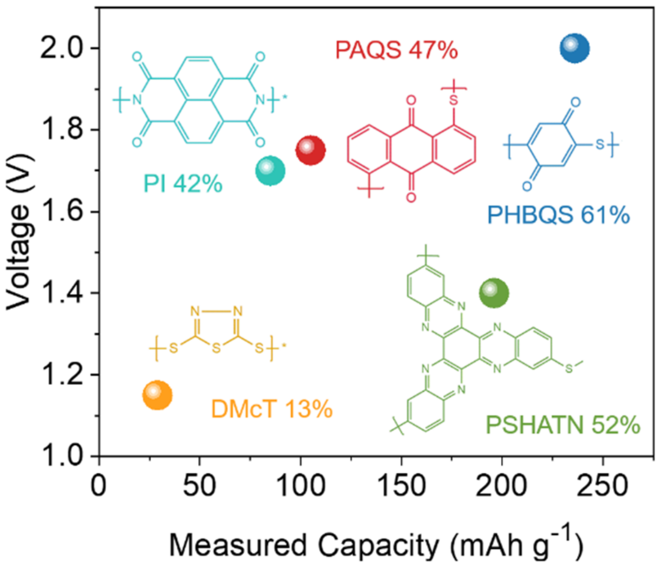

Figure 5. Voltage versus measured capacities of some organic polymer compounds (PI-naphthalene-hydrazine diimide polymer, DMcT-2,5-dimercapto-1,3,4-thidiazole, PAQS-poly (anthraquinonyl sulfide), PHBQS-poly (hidroquinonyl-benzoquinonyl sulfide), and PSHATN-poly (hexaazatrinaphthalene sulfide)) in Mg half-cells with percentage of capacity utilization calculated as obtained capacity divided by theoretical capacity value. Values were obtained from references [57, 59, 65, 67] and [69].

electrolytes is based on salts incorporating WCA, which enable simpler dissociation of cation-anion pairs. Indeed, it was shown that the number of ion pairs in the case of electrolytes based on WCA salts is lower compared to chloride-containing salts. However, a certain number of ion pairs was still detected in certain electrolytes [70], while in other electrolytes presence of ion pairs in discharged cathodes could not be detected [64]. Another important consideration is the fact that currently all the electrochemical testing is performed in laboratory half-cells operating with big excess of Mg metal anode and electrolyte with relatively low areal loadings of active materials. Thus, future research should also aim to address these challenges by prototype testing, where the effects of electrolyte amount, areal loading and carbon black in electrode formulation should be investigated to give some additional guidelines for future battery research.

Concluding remarks

Organic cathode electrochemical performance in Mg batteries by far surpasses the performance of inorganic cathode materials and offers an alternative pathway for the practical realization of rechargeable Mg batteries. However, organic cathodes still suffer from general Mg electrochemical issues connected with large electrode overpotentials, Mg metal passivation and limited electrolyte stability windows. Hence, electrochemical results should be evaluated with sufficient rigor to prevent misinterpretation. Future research should be directed towards improving the cation-anion pair dissociation and achieving both higher voltage and capacity of organic compounds coupled with good capacity utilization and long-term cycling stability. This can be successfully achieved only through the synthesis of new organic compounds as well as tailoring of Mg electrolytes to improve the performance of organic materials.

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5. Mg based batteries—solid electrolytes

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Status

Solid-state electrolytes have attracted ever-increasing research interest owing to the intrinsic safety merits compared to the flammable organic liquid electrolytes. In addition, the superior mechanical properties of the solid electrolyte play a significant role in avoiding dendrite growth and suppressing the bidirectional crosstalk phenomenon between cathode and anode. Furthermore, inorganic solid electrolytes (SE) are single-ion conductors, and therefore, concentration polarization at high current densities does not occur. However, the sluggish diffusivity of the Mg^{2+} ion, originating from its high charge density gives rise to difficulties in designing Mg SE with high ionic conductivity. Along with this, it is of course difficult to explore the function of potential Mg solid-state cells. Nevertheless, successful cases have been reported utilizing different types of anion chemistry. In the 1980s, $Mg_{0.5}Zr_2(PO_4)_3$ with β-$Fe_2(SO_4)_3$-type structure was synthesized, which achieved ionic conductivities of $6.1 \cdot 10^{-3}$ S cm^{-1} and $2.9 \cdot 10^{-5}$ S cm^{-1} at 800 °C and 400 °C, respectively, with an activation energy of 0.82 eV [73]. The Mg-ion conduction was validated by a modified Tubandt method, where the detected mass transfer during electrolysis through $Mg_{0.5}Zr_2(PO_4)_3$ corroborates the assumption of Mg^{2+} ion conduction. Based on the same structure, replacing Zr^{4+} by various aliovalent dopants, such as Al^{3+}, Zn^{2+} and Fe^{3+}, to increase the Mg^{2+} concentration, has been attempted to further enhance the ionic conductivity [74, 75]. In recent years, inspired by the superionic Li^+ and Na^+ conductivity of several phase, mostly the Li-argyrodite and Na_3PS_4 phases with face-centered cubic anion arrangement, a Mg-based sulfide was also prepared in the form of glasses in the quasi-ternary system MgS-P_2S_5-MgI_2 [76]. The conductivity of as-prepared glass achieved $2.1 \cdot 10^{-7}$ S cm^{-1} at 200 °C when composition is $48MgS{\cdot}32P_2S_5 \cdot 20MgI_2$. However, the activation energy is unspecified, and the transport mechanism is not yet investigated so that further optimization is still waiting. Additionally, a series of Mg halides were also successfully synthesized, with the highest ionic conductivity of $1.3 \cdot 10^{-6}$ S cm^{-1} at 127 °C for $MgAl_2Cl_2Br_6$ [77]. Theoretical work suggests that the migration barriers of spinel-structured magnesium selenides of the type $MgRE_2Se_4$ (RE = rare earth metal) are relatively small (0.36–0.53 eV) due to the favorable Mg hopping via the tet-oct-tet path in the spinel structure [78]. Experimentally, $MgSc_2Se_4$ has been successfully prepared, with a high room-temperature ionic conductivity of $\sim 10^{-4}$ S cm^{-1}. However, the relatively high electronic conductivity (0.04% of the ionic conductivity) is of concern as it is higher than that of common SE (10^{-4}%–10^{-6}%). Moreover, the considerable electronic conductivity makes the reliable identification of the partial ionic conductivity rather challenging. Nevertheless, the encouraging result showing Mg-ion conductivity at room temperature has stimulated more research investigating other phases for Mg^{2+} conduction. In spite of the lower ionic conductivity compared to lithium counterparts, the possibility of using thinner SE layers to increase the conductivity across the pellet in the full cell still makes them worth of further exploration.

Apart from SEs composed of rigid inorganic anion sublattices, another category of crystalline candidate comprises the coordination of Mg-ions with more ‘flexible’ complex functional groups. A typical successful example is magnesium borohydride, in which the complex hydride structure can be tuned for an energetically more favorable migration pathway for the Mg^{2+} ion [79]. To name a few, $Mg(BH_4)(NH_2)$ with shorter Mg-Mg distance in the Mg zigzag chain exhibits an ionic conductivity of $1.0 \cdot 10^{-6}$ S cm^{-1} at 150 °C [80]. $Mg(BH_4)_2(CH_3NH_2)$, with a 1D chain-like structure interconnected by weak dihydrogen bonds, shows a conductivity of $1.5 \cdot 10^{-4}$ S cm^{-1} at room temperature and an activation energy of 0.6 eV [81]. Moreover, metal-organic frameworks (MOFs) with an open porous framework and adaptable organic ligands also hold great promise for multivalent-ion conduction by providing highly-selective ion pathways in the porous structure [82, 83]. Indeed, most MOF materials deliver relatively high room-temperature Mg^{2+} ion conductivity, probably allowing conductivities in the mS cm^{-1} range [84, 85]. Along this line, encouraged by the successful application as lithium-ion solid-state separators [86–88], covalent-organic frameworks are also believed to be feasible as platform to design Mg^{2+} ion solid-state conductors with high ionic conductivity.

Current and future challenges

To be a potential candidate as SE for battery cells, ionic conductors need to fulfill certain requirements (summarized in figure 6), including, but not limited to high ionic conductivity, high electronic resistance, sufficient chemical/electrochemical stability and suitable mechanical properties. The development of Mg SE

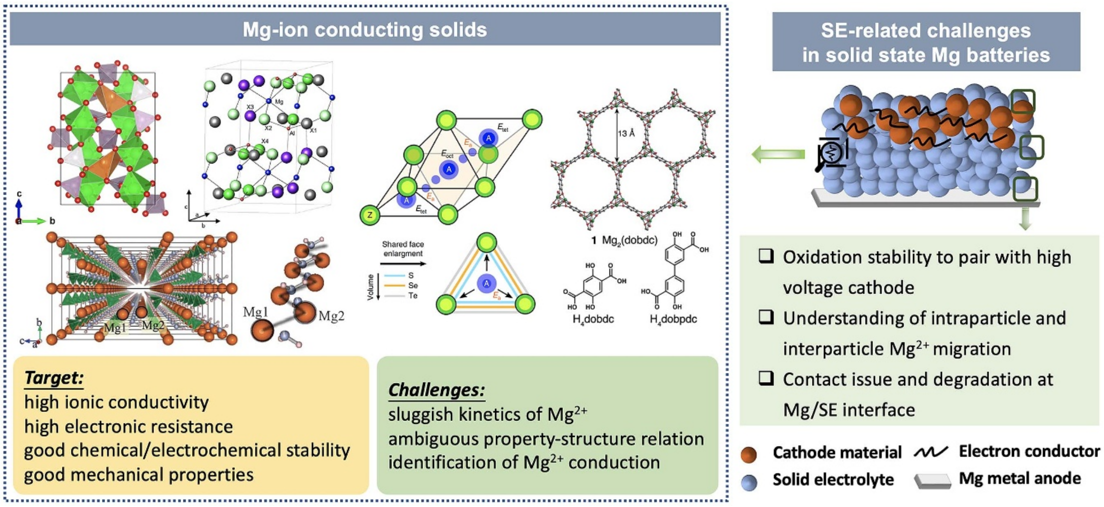

Figure 6. Summary of the crystal structures being used for the design of Mg^{2+} solid electrolytes and the key challenges for the development of Mg solid electrolytes. Reprinted from [77], Copyright (2021), with permission from Elsevier; Reproduced from [78]. CC BY 4.0; Reproduced from [80] with permission from the Royal Society of Chemistry; Reproduced from [82] with permission from the Royal Society of Chemistry.

is still in its early stage. Among the reported structure types, there is always a tradeoff between ionic conductivity and the electrochemical stability window. For materials with high room-temperature conductivity such as borohydrides, the threshold of the upper cutoff potential is as low as 1.2 V (vs. Mg^{2+}/Mg) [89, 90], which raises challenges for pairing with suitable cathode materials. As for selenides, no study of the electrochemical stability window (EW) was experimentally reported, although, theoretical studies suggest that the anodic cutoff potential of ternary spinels is also below 2.0 V (vs. Mg^{2+}/Mg) [91].

The future R&D of Mg^{2+} SEs still encounters the challenges caused by the specific physical properties of magnesium: (i) *the di-valency of the Mg ions*. As discussed above, the designing principle of Li/Na-ion superionic conductors cannot be directly transferred into the exploration of Mg-ion electrolytes. Just like the finding of the feasible Mg^{2+} conduction in spinel structures, new structure-property relationships need to be established. Besides, the existing studies could not differentiate bulk resistance and grain boundary resistance, which are largely dependent on the crystal structure and synthesis procedure, respectively, posing additional difficulties in understanding Mg^{2+} migration in solids. (ii) *The small ionic radius of Mg ions*. Compared to typical anions in the solid state, the ionic radius of Mg^{2+} is much smaller (0.72 Å *vs.* 1.40 Å of O^{2-}, 1.84 Å of S^{2-} and 1.81 Å of Cl^{-}), meaning that the electrons more densely distributed around the atomic nucleus, making their migration kinetically unfavorable due to the increased Coulomb interaction with the host anion lattice. As a consequence, it is of great significance to determine whether the charge carrier is Mg^{2+}, or anions with 'relatively' more facile migration capability. In other words, the transportation of Mg^{2+} in the solid needs to be unequivocally proven, instead of anion conduction, or electron conduction in case of the mixed ion-electron conductors. (iii) *The high Young's modulus of Mg*. The Young's modulus of Mg is 44.3 GPa, which is much higher compared to lithium (4.9 GPa) and sodium (10 GPa) [326], indicative of poorer contact between SE and magnesium metal anode (MMA) in a practical solid-state Mg cell. Moreover, the interface between SE and MMA derived from the degradation of SE has been rarely studied [327]. An appropriate method to enhance the wettability of MMA, such as artificial interphases and lattice plane orientation, needs to be addressed to approach the high volumetric energy density of solid-state Mg batteries (SSMB).

Advances in science and technology to meet challenges

Due to the limited understanding of the Mg migration behavior, theoretical calculations are important to predict the properties of new materials, and guide further experimental investigations. A successful example are the Mg sulfide and selenide spinels, which have been studied systematically in depth. Großʼs group used ASc_2S_4 and ASc_2Se_4 spinel compounds as platform to understand the migration barriers of different cations (including Mg^{2+}) *via* DFT calculation [328]. From the derived correlation between activation barriers and the site preference, a descriptor was proposed as a universal parameter to explore the Mg migration behavior in a variety of d_0-metal-based spinel chalcogenides, which saves considerable amount of effort in the selection and preparation of SE materials. Moreover, the stability of the ternary spinel compounds (MgB_2S_4) was investigated by the same group. It is suggested that, if the ionic radius of the B-cation is smaller than

1.1 Å, the compound is supposed to be chemically stable, and thus be able to be synthesized [91]. The stability of the Mg binary compounds was also calculated, from which the Mg halides appear to exhibit good stability against both reduction and oxidation, making them good candidates as coating material.

As for the identification of the charge carrier, Ikeda *et al* used a modified Tubandt method to verify the Mg-ion conduction in their report of the $Mg_{0.5}Zr_2(PO_4)_3$ material [73]. Specifically, a SE pellet was sandwiched between two Pt foils and electricity was driven through the cell. After electrolysis for 20 coulombs at 800 °C, the electrodes were taken out and weighed to measure the change in mass. As a result, the weight loss of anode and weight gain of cathode corroborates well with the theoretical value considering Mg^{2+} as charge carrier, successfully proving the Mg-ion conduction. Along with the further exploration of new SE materials for Mg, convincing characterization techniques to identify the Mg^{2+} conduction also needs to be developed.

Concluding remarks

Thanks to the effort in both theoretical study and experimental synthesis, the development of Mg SEs, although still with grand challenges, is on a solid track, with selenide spinels, borohydrides and MOFs showing satisfactory ionic conductivity at room temperature. However, drawbacks such as the low electronic resistivity and low oxidation stability of the existing SE materials push the field to explore optimization strategies and new possible structures to realize practical solid-state Mg cells. Other than that, better fundamental understanding of the current SE materials needs to be established, including the ion conduction mechanism and degradation mechanisms. The challenge in developing the SSMB technology also lies in the control of interfaces between SE and MMA. Fortunately, the well-developed characterization techniques for lithium batteries can help to accelerate the establishment of knowledge fundations of interfaces in SSMBs. Last but not least, once the issue of the SE/MMA interface gets solved, suitable cathode materials are also called for, with the aim of designing high-energy-density and long-term-stable SSMB.

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6. Challenges and perspectives towards practical rechargeable Mg batteries

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Status

Nowadays, LIBs are the main battery technology for many emerging markets such as electric mobility or stationary storage for renewable energy. However, regardless of the proper performances of LIBs, they are supposed to deal with resource supply-chain challenges due to lithium relatively low natural abundancy and its geographical uneven distribution worldwide, especially if LIBs are used as the only solution for EES in both, the mobility and stationary storage sectors. This concern has led scientists to search for alternative and sustainable rechargeable battery technologies to overcome these challenges.

In this context, the competitive advantages of rechargeable magnesium batteries (RMBs) make it a promising candidate as a non-Li energy storage system [26, 92, 93]. The use of metallic Mg as anode leads to important benefits concerning, safety, cost, sustainability, recyclability, and lower material supply risk due to the natural abundancy of Mg. Moreover, due to its bivalency, Mg presents high volumetric capacity (3832 mAh cm^{-3}), high specific capacity (2205 mAh g^{-1}), and low reduction potential (−2.37 V vs SHE) [94].

Despite the potential of RMB, research is still limited at coin-cell configuration and laboratory scale neglecting many practical aspects of RMB [64, 95–97]. In that respect, pouch cells are an appropriate configuration to optimize components and constitute a crucial step towards an application-ready battery. Accordingly, to the best of our knowledge, Blázquez *et al* [22], for the first time have demonstrated the feasibility of RMB at pouch-cell level for cell optimization toward industrial use. This pouch cell contained the reference state-of-the art materials, a CP Mo_6S_8 cathode on a nickel current collector, thick pure magnesium anode (100 μm) and all-phenyl complex (APC) electrolyte. The electrochemical performance was analyzed by galvanostatic cycling at C/10, demonstrating an specific energy of 18 Wh kg^{-1} and 100% specific energy retention after 200 cycles. Although manufacturing the first RMB prototype has constituted a breakthrough in the technological maturity of the technology, these specific energy values are still far from reaching accepted industry standards.

Current and future challenges

RMB have suffered from low degree of development with drawbacks that limit their practicability and commercialization. Some of these challenges consist of low compatibility and durability between the cell components (anode, cathode and electrolyte) with the required conditions for a feasible rechargeable battery operation. In this regard, the main drawback of RMB is the development of advanced electrolyte solutions which lead to a fully reversibly Mg plating/stripping behavior, with wide EW [98, 99]. In this context, in 2000, Aurbach *et al*, developed a novel APC electrolyte which exhibited an impressive anodic stability and a fully reversible Mg metal anode behavior [26]. However, the presence of corrosive chloride ions affects the stability and the compatibility with conventional light aluminum current collectors, requiring the use of heavier materials that reduce the specific energy of the battery [100]. Therefore, it is necessary to develop chloride-free magnesium electrolytes with high conductivity and which promote fully reversible Mg plating/stripping processes, allowing the use of lighter current collector and the development of high specific energy cathode materials [95, 101].

On the other hand, another challenge is the poor mechanical properties of pure Mg foils caused by its limited intrinsic ductility [102], brittleness and mechanical weakness, especially for ultrathin foils ($<$100 μm) [103]. However, to obtain high specific energy Mg batteries, it is mandatory to use thin Mg metal foils anodes (15 μm), by means of Mg alloys [103–105].

Consequently, novel and suitable anode, cathode and electrolyte materials are needed to achieve a fully compatible and advanced RMB technology [15, 103].

Advances in science and technology to meet challenges

Reference [103] demonstrated the feasibility of processing ultrathin Mg anodes (25 μm) by using the ductile AZ31 Mg alloy (3% Al; 1% Zn). It was found that the Mg plating/stripping process of AZ31 magnesium alloy is equivalent to that of pure Mg metal anode. Furthermore, thin AZ31 foil presents high mechanical stability during processing and cell manufacturing while maintaining comparable electrochemical behavior to that of

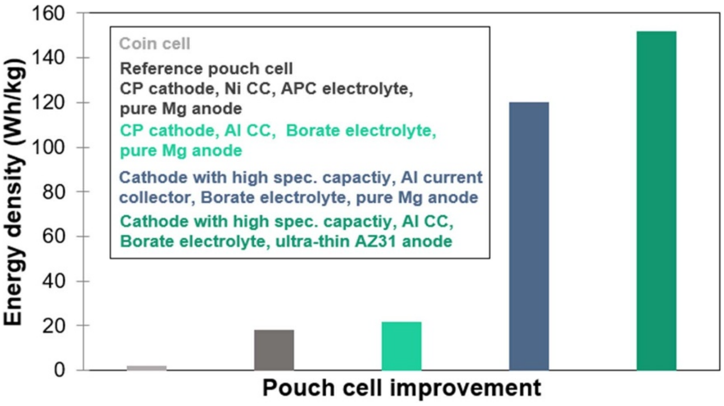

Figure 7. Pouch cell specific energy improvement.

low ductile pure Mg anodes, even after 500 cycles [103]. The possibility of using ultrathin processable Mg metal anodes is an important step in the development of rechargeable Mg batteries.

In 2017, an important breakthrough was achieved by Zhao-Karger *et al* [15], who developed the non-corrosive magnesium tetrakis(hexafluoroisopropyloxy) borate ($Mg[B(hfip)_4]_2$)/glyme based electrolyte. This novel chlorine free electrolyte fulfills most of the requirements for RMB such as high oxidative stability ($>$4.5 V on Al), high ionic conductivity ($\sim$11 mS cm^{-1}), high CE for reversible Mg deposition and compatibility with conventional lightweight aluminum current collectors. Besides, the electrolyte composition was further optimized adding new additives and leading to a reduced Mg plating/stripping overpotential and enhanced Mg cycling performance [95].

Above all, the development of this novel electrolyte has allowed the synthesis of a promising and compatible cathode material, VS_4, for reversible two-electron reaction with synergetic cationic-anionic contribution. Besides, in terms of electrochemistry, VS_4 has shown a high specific capacity of 330 mAh g^{-1} at 100 mA g^{-1} current density, resulting in specific energy greater than 300 Wh/$kg_{VS4,}$ three times higher than reference materials [43].

As stated above, in order to obtain a high specific energy RMB, it is necessary to replace the reference components by the novel and advanced RMB materials. Accordingly, Blázquez *et al* [22], estimated a RMB composed by an ultrathin AZ31 Mg alloy anode, an aluminium current collector, a VS_4 cathode and the $Mg[B(hfip)_4]_2$/DME electrolyte solution. RMB will be able to present promising performances, with energy densities up to 200 Wh kg^{-1} (figure 7).

Additionally, if the VS_4 cathode is replaced by high voltage/capacity cathodes these energy densities could be further enhanced. These performances will guarantee the feasibility and competitiveness of RMB technology compared to current LIBs, lead acid batteries (LABs) and other promising EES systems such as Ni–Zn, redox flow batteries or Na-ion for stationary applications.

Therefore, further research efforts are needed to develop high-energy and high voltage cathodes, as well as to develop cost-effective synthetic routes of these novel battery components to produce enough amount of the materials to build high-capacity industrial prototypes.

Concluding remarks

RMBs are one of the most promising alternatives to the post-lithium technologies for the future of sustainable stationary energy storage. In fact, the technological feasibility of the technology has been demonstrated by means of the first non-aqueous multilayer RMB pouch cell prototype, constituting a breakthrough in the maturity of the technology. Despite having obtained robust pouch cells, RMB still present some limitations that need to be improved, such as the low electrochemical properties in terms of specific energy. In that sense, the roadmap reveals a promising RMB based on novel and most advanced materials reported in the literature with the potential to achieve a competitive specific energy up to 150 Wh kg^{-1}, although it could be even further enhanced, by means of employing high voltage cathodes.

Therefore, more research is needed to go one step further for the development of cost-effective synthetic routes of these novel battery components and to produce enough amount of the best materials to build high-capacity pre-industrial cell prototypes and demonstrate the potential of RMBs.

Acknowledgements

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7. Ca based batteries—anodes, liquid electrolytes and interfaces

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Status

Among the different post-Li batteries, calcium based technology is the object of growing interest mostly due to the abundance of raw materials and expectations for outperforming Li-ion in terms of energy density. The latter will solely be possible if Ca metal anode is used [106], owing to the promising standard redox potential (−2.87 V vs. SHE) and theoretical specific capacity (1340 mAhg^{-1}). Currently, only a handful of electrolyte formulations have been reported allowing for Ca electrodeposition: calcium tetrafluoroborate ($Ca(BF_4)_2$) in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) [107], calcium borohydride ($Ca(BH_4)_2$) in tetrahydrofuran (THF) [108], calcium tetrakis(hexafluoroisopropyloxy)borate ($Ca[B(hfip)_4]_2$) in glymes with or without tetrabutylammonium chloride (Bu_4NCl) [109, 110], calcium monocarborane ($Ca(CB_{11}H_{12})_2$) in a mixture of THF and dimethoxyethane (DME) [111], and more recently calcium bis(trifluoromethanesulfonyl)imide ($Ca(TFSI)_2$) in EC:PC with boron functional additives [112, 113]. Table 1 summarizes key electrochemical properties and comments on the characterization of the deposits and surface layer for each of these electrolytes.

Although the electrolyte speciation and the interphase formed onto the Ca deposits are sometimes investigated, the electroactive species and the exact surface layer composition and properties remain unknown. Accordingly, the Ca electrodeposition mechanism is poorly understood and the lack of reliable electrochemical setups [63] significantly complicates systematic investigation and comparison of results from different groups. For instance, assessment of the anodic stability can sometimes be questioned when evaluated using a WE previously polarized to negative potential values (for Ca plating). Indeed, the formation of any kind of passivation layer can result in a significant overestimation of the anodic stability.

Current and future challenges

Many of the current and future challenges are linked to the development of calcium metal anode able of long-term cycling with 99.99% CE. Success for industrial application of calcium rechargeable batteries would require either (i) exceptional electrolyte reductive stability or (ii) engineering of stable and fully covering solid electrolyte interphase (SEI), either ex-situ or operando, supporting Ca^{2+} transport while being electronically insulating. The low standard potential of the Ca metal in conjunction with the facile reduction of the Ca^{2+} solvation shell due to strong coordination to the divalent cation, explain why route (i) is arduous and no such electrolyte has been reported to date. Indeed, all liquid electrolytes reported to support Ca plating undergo parasitic reactions, leading to formation of surface layers of different composition on the Ca anode prior to the plating reaction—reported compounds detected on the Ca surface are listed in 'Characterization of interphase' in table 1. On the cathode side, the current understanding of anodic stability of different electrolytes remains limited. While anodic stability of/above 4 V *vs.* Ca^{2+}/Ca is often reported (see table 1), it is worth stressing that such values are obtained using linear sweep voltammetry on inert and low surface area electrodes. Such set-ups are far from being representative in realistic battery conditions, with composite electrodes potentially including components catalyzing electrolyte oxidation. Additional factor for applicability is establishment of a standard for current collectors. Pt is currently the best option for Ca plating, but Ca batteries will only remain a laboratory curiosity if an electrolyte compatible with a less expensive current collector is not identified.

From a fundamental viewpoint, achieving highly reversible Ca electrodeposition requires a fine control of several processes: transport of cation species to the electrode, cation desolvation from its shell, cation transport through the surface layer, adsorption and surface diffusion of the adatoms, charge transfer and nucleation. Each step is associated with an activation energy barrier [7] and it is still not clear which process is the main limiting step during electrodeposition and how it changes with electrolyte composition. Thus, methodical determination of two key properties is required:

(i) Cation species in solution and its (their) transport properties, presently not completely characterized. For instance, in $Ca(BH_4)_2$/THF electrolyte rather weak cation-anion interactions were suggested even at 1 M, Ca^{2+} being mainly surrounded by solvent molecules [116], opposite to formation of neutral aggregates, $[Ca(BH_4)]^-$ and $[Ca(BH_4)_3]^-$ in [118]. The extremely low ionic conductivity measured (0.09–0.6 mS cm^{-1}, see table 1) points at significant degree of CIP formation and/or poor ions mobility.

Table 1. List of electrolytes reported to allow for Ca electrodeposition and brief description of electrochemical performances, along with deposit morphology as well as type of passivation layer, when available. Acronyms used in the table: VH = Voltage hysteresis, CE = Coulombic efficiency, SS = Stainless steel, WE = Working electrode.

Electrolyte	Anodic stability	VH and CE	Morphology of Ca deposit	Characterization of interphase	Comments
0.3–0.5 M $Ca(BF_4)_2$/EC:PC at 100 °C [107]	~4 V *vs.* Ca^{2+}/Ca	VH ~520 mV at 0.5 mV s^{-1} and 70% CE on SS WE	Compact homogeneous granular deposit (~15 nm crystallite size from XRD)	~80 nm layer: ~15% CaF_2; ~8% $CaCO_3$; ~14% of B in oxygenated environment; ~35% of C including polymeric species [114].	Best plating/stripping kinetics obtained at 0.45 M salt concentration (correlated with maximum ionic conductivity ~5.5 mS cm^{-1} at 25 °C).
0.4 M $Ca(TFSI)_2$/ EC:PC + 2 wt.% of BF_3.DE (100 °C) [112, 113]	~4 V *vs.* Ca^{2+}/Ca	VH ~520 mV at 0.5 mV s $^{-1}$ and 80% CE on SS WE	Compact homogeneous granular deposit	Similar components and thickness as for $Ca(BF_4)_2$ based electrolytes [113].	The composition of the interphase is dependent on the lower cutoff potential in CV [113].
0.5–1.5 M $Ca(BH_4)_2$/THF at RT [108, 115, 116]	~2.5 V *vs.* Ca^{2+}/Ca	VH ~250 mV and 90% CE Increase of CE with salt concentration [116]	Granular-like Ca deposit. Cracks form upon cycling [108]. Dendrite at or above 10 mA cm^{-2} with in situ TEM flow cell, but at 5 mA cm^{-2} in electrolytic cell [115]. Different deposit morphology with Pt or Au substrates [116].	Porous CaH_2 film growing upon cycling. XRD and FTIR show no other decomposition products [108] Presence of heterogeneous CaO reported [117].	CaH_2 acts as passivation layer, not a SEI. Extremely low ionic conductivity: 9×10^{-2} mS cm^{-1} at 1.0 M in [116], 0.6 mS cm^{-1} at 1 M in [118].
0.25 M or 0.5 M $Ca[B(hfip)_4]_2$ in DME or Diglyme with or without 100 mM Bu_4NCl at RT [109, 110, 119]	Between 3.0 and 4.8 V *vs.* Ca^{2+}/Ca (substrate dependent, Al being the best)	VH ~ 300 mV, CE ~80% (25 mV s^{-1} [109]) VH ~ 500 mV, CE ~90% (80 mV s^{-1} [110]) Best results with Pt substrate [110]	Deposition on Pt substrate (0.2 mA cm^{-2}, RT for 20 h): micro-sized Ca-agglomerates [109]. Au substrate in similar condition lead to dendritic growth [110].	CaF_2 identified (with EDX and XRD) Higher anion decomposition at low cycling rates	Discrepancy in ionic conductivities between [109] (8.3 mS cm^{-1} for 0.25 M solution) and [110] (3.2 mS cm^{-1} for 0.5 M solution or 6.7 mS cm^{-1} with 100 mM Bu_4NCl).
0.5 M $Ca[CB_{11}H_{12}]_2$ in DME:THF (1:1 vol) at RT [111]	~3.5 V *vs.* Ca^{2+}/Ca on Au WE	VH ~300-400 mV (20 mV s^{-1}) and ~88% CE on Au or Pt WE (after initial conditioning cycles)	Globular-like deposit (~10 μm) not fully covering the Au WE. Relatively poor adherence of Ca deposit.	CaH_2 detected in XRD. No further characterization of surface film.	Ionic conductivity ~4.0 mS cm^{-1}. Solubility of $Ca[CB_{11}H_{12}]_2$ drastically improves in solvents mixture instead of single-solvent formulation.

In fact, it is surprising that Ca electrodeposition is achievable in such low ionic conductivity electrolyte. The cation solvation shell in Ca[$CB_{11}H_{12}$]$_2$ based electrolytes is even less studied. It is notable that use of a solvent mixture (DME:THF), instead of single solvent, has a dramatic positive impact on the salt solubility and ionic conductivity (see table 1) [111]. For Ca[B(hfip)$_4$]$_2$ based electrolytes, using diglyme [119] instead of THF or DME seemingly improves the current density and CE as less CaF_2 precipitated, possibly due to fewer contact ion pairs (CIPs). Yet, triglyme based electrolytes, where no CIPs are present, were reported to not enable reversible electrodeposition [120], likely because of high desolvation energy barrier or passivation.

Another facet relates to the transport properties in electrolytes and at interface, but Ca transference numbers are unexplored, partly due to lack of a reliable experimental evaluation technique. Nonetheless, extremely low cation transference numbers are expected (well below 0.2) as Ca^{2+} complexes are much bulkier compared to monovalent cations [7, 114]. Thus, consistent experimental method for evaluating transference numbers, and a modeling approach to rationalize results are much needed.

(ii) The composition and properties of the surface layer formed onto Ca metal. For instance, while the presence of CaH_2 has clearly been identified in XRD of Ca deposits from $Ca(BH_4)_2$/THF in the original work [108], recent findings [117] demonstrated that CaH_2 is rather present as inclusions between electrodeposited Ca metal grains, its participation in the surface layer not being clearly identified. The Ca surface layer resemble a heterogeneous film, mainly composed of CaO mixt with B-compounds, carbonate and traces of Na^+ containing species. Regarding the Ca[B(hfip)$_4$]$_2$ in DME or diglyme electrolytes, CaF_2 was reported as part of the surface layer, but the presence of other components (amorphous and/or organic) was not investigated. For $Ca(BF_4)_2$ based electrolytes, although several characterization techniques were combined to fully assess the composition and morphology of the SEI and presence of borate based cross-linked polymers was identified as the potential Ca^{2+} conducting species [121], the exact structure of such polymer remains to be ascertained.

Advances in science and technology to meet challenges

Complete characterization of Ca species in solution should be routinely performed by combining several techniques, given the complexity of the Ca^{2+} solvation. Associating conductivity and viscosity measurements with vibrational, mass and NMR spectroscopies could provide a basis for understanding the electrolyte physicochemical properties. An effective approach to complement such analysis would integrate insight from modeling realistic systems, with salt concentration being always considered. The most adequate and used method presently is based on classical molecular dynamics (MD) simulations, however it is less accurate compared to density functional theory (DFT) and also suffers from limited availability of force fields adapted to the Ca electrolytes. Ab initio MD studies can circumvent these issues to the expense of computational time, or machine learning (ML) approaches could be applied, but are currently underused with liquid electrolytes.

Regarding transport properties, combining experimental and modeling methods to investigate Ca^{2+} transference number appears as a crucial step forward. MD simulations previously applied to Li polymer electrolytes [122] could be valuable for Ca electrolytes, but also in the exploration of promising polymeric compounds for Ca SEI. Indeed, DFT calculations of several Ca-inorganic phases [121, 123, 124] demonstrated generally very high barriers for Ca^{2+} diffusion. Focus should thus be placed on the Ca^{2+} transport in organic compounds and the possibility of engineering composite SEI (synergy between components) for optimal Ca^{2+} mobility.

Finally, this brings the need for comprehensive characterization of the interphase, and techniques allowing to decipher the organic components are of particular interest, such as: x-ray photoelectron spectroscopy (XPS), IR spectroscopies and time-of-flight secondary ion mass spectrometry (TOF-SIMS) [121]. Although challenging for the study of thin interphases, the use of NMR would also be very informative. Besides, the nature of such layers can be affected by impurities and/or they could evolve upon cycling, various conditions (including temperature) having a significant influence. Also in some cases they can evolve during preparation for characterization, interfering with a reliable analysis and highlighting the importance of operando measurements whenever it is feasible.

Concluding remarks

The Ca metal anode battery is still in its infancy. While many challenges are slowing down the development of each individual component (anode, cathode and electrolyte), the major difficulty will most likely originate from uncertain compatibility between them. With respect to the metal anode, the reversibility of Ca electrodeposition is closely related to the composition of the electrolyte and in particular to the nature of the cation solvation shell. The latter determining the mobility of the cation species, the formation of surface layer and its properties (cation and electronic conductivities). None of the electrolyte formulations designed during the last decade, albeit a handful, allow for highly reversible electrodeposition and, in most cases, the use of Pt current collector is required. While the realization of a practical Ca battery is an intricate journey, current research efforts already identified promising strategies, such as the engineering of the cation solvation shell and the exploration of organic based SEI components to favor Ca^{2+} transport.

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8. Ca based batteries—inorganic cathodes

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Status

Ca reversible intercalation (extraction) has been attempted in several materials chemistries [124]. Figure 8 surveys the Ca-host materials investigated as potential positive electrode materials in terms of two main figures of merits: (i) the x-axis shows the Ca-ion migration barrier (derived from first-principles simulations), and (ii) the y-axis reports the estimated specific energy of these materials.

The research team led by Palacin, tested experimentally the possibility of reversible Ca insertion in 'compact' oxide materials. Preliminary theoretical work suggested low migration barriers ($E_m \sim 200$ meV) for Ca intercalation in δ-V_2O_5, and prohibitively high barriers ($E_m \sim 1800$ meV) for Ca intercalation in the α-polymorph of V_2O_5 [126]. An in-depth experimental analysis demonstrated the absence of electrochemical and chemical Ca extraction (oxidation) from α-V_2O_5 [51]. Cabello *et al* [127] reported Ca insertion into the hydrated layered α-MoO_3 with a gravimetric capacity of ~100 mAh g^{-1} at a low voltage of ~1.3 V vs. Ca/Ca^{2+}. The team of Arroyo-de Dompablo investigated extensively Ca^{2+} intercalation and mobilities in oxides, such as $CaMn_2O_4$, $Ca_2Mn_2O_5$, $CaMn_4O_8$, $Ca_2Fe_2O_5$, $Ca_4Fe_9O_{17}$, $Ca_3Co_4O_9$, and $Ca_3Co_2O_6$.

Simultaneously, Black and Lu [125, 128], identified experimentally and computationally the post-spinel CaV_2O_4 as a fast Ca-ion conductor (with a computed migration barrier as low as ~654 meV), delivering a reversible capacity of ~60 Ah g^{-1} and an average voltage of 2.36 V vs. Ca/Ca^{2+} when cycled at 50 °C. Note that the extracted capacity accounts for 60% of the theoretical capacity of the post-spinel CaV_2O_4. Aside from the observed polarization [128], the high operation potential coupled to a its high theoretical capacity (260 mAh g^{-1} considering operation involving V(III)/V(IV) redox couple) makes this compact oxide a very promising positive electrode for Ca batteries. Lu *et al* predicted another promising oxide-based Ca-positive electrode [125], namely $CaNb_2O_4$, which is a layered framework with Ca occupying prismatic sites.

The electrochemical properties of Ca insertion and its mobility were investigated computationally in mixed anion and polyanion host materials, including CaFeSO, CaCoSO, CaNiN, Ca_3MnN_3, $Ca_2Fe(Si_2O_7)$, $CaM(P_2O_7)$ with M = V, Cr, Mn Fe and Co, $CaV_2(P_2O_7)_2$, $Ca(VO)_2(PO_4)_2$, and α-$VOPO_4$. Considering the polyanion chemical space, Kim *et al* demonstrated reversible Ca^{2+} extraction from a sodium-containing 'NaSICON'-$NaV_2(PO_4)_3$, delivering a gravimetric capacity of ~81 mAh g^{-1} at ~3.2 V vs. Ca/Ca^{2+} [129]. Notwithstanding the shear complexity of NaSICON-based materials, Tekliye *et al* [130] recently performed an extensive screening study with first-principles computations covering the wide chemical space of NaSICONs, with a chemical formula of $Ca_xM_2(ZO_4)_3$ (where M = Ti, V, Cr, Mn, Fe, Co, or Ni and Z = Si, P, or S) as Ca electrodes. This extensive survey indicated that $Ca_xV_2(PO_4)_3$, $Ca_xMn_2(SO_4)_3$, and $Ca_xFe_2(SO_4)_3$ Ca-NaSICONs are promising as positive electrodes in Ca batteries.

Albeit the lower reversible capacity (~72 mAh g^{-1}) and voltage (~2.9 V vs. Ca/Ca^{2+}) [129], claimed partial reversible Ca^{2+} insertion in olivine-$FePO_4$. Recently, the research team of Kang reported Ca intercalation in the high-voltage (~3.2 V vs. Ca/Ca^{2+}) vanadium fluorophosphate, with formula $Ca_xNa_{0.5}VPO_{4.8}F_{0.7}$ with a reversible capacity of ~87 mAh g^{-1} and 90% capacity retention over 500 cycles. Both polyanion materials, that are $Ca_xNa_{0.5}VPO_{4.8}F_{0.7}$ and $Ca_xNaV_2(PO_4)_3$ (see previous paragraphs) include Na^+ ions, which appears an important feature for these electrodes [129, 131]. While the presence of auxiliary active ions, such as Na^+ may stabilize these polyanion frameworks, currents monitored in electrochemical experiments may also originate from the extraction of these auxiliary species.

Current and future challenges

Besides challenges associated with designing electrolytes with high cathodic and anodic stabilities [124], understanding and optimizing the Ca-stripping and plating mechanisms at the metal negative electrode [107, 121, 124], and preventing spurious processes that can contribute to perceived electrochemical performance such as current-collector corrosion [132], identifying positive electrode materials with facile Ca transport represents the most pressing challenge in the development of Ca-batteries. The perceived poor mobility of Ca^{2+} as compared to monovalent ions such as Li^+ or Na^+, has precluded the exploration and development of a wide variety of material chemistries for positive electrodes, similar to the case of Li-ion or Na-ion batteries. A good positive electrode material for Ca batteries should also guarantee high specific capacities, intercalation voltage vs. Ca/Ca^{2+}, and be thermodynamically stable (both bulk electrode and

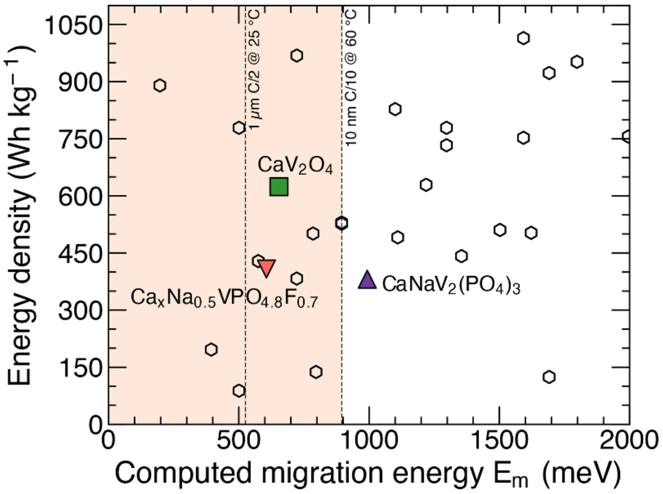

Figure 8. Computed migration barriers (in meV) vs. energy densities (in Wh kg^{-1}) of potential host chemistries. Two limits of maximum tolerable barrier are indicated by vertical lines, i.e. 525 and 895 meV at two specific (dis)charge conditions (including rate, temperature of operation and particle size). Adapted with permission from [125]. Copyright (2021) American Chemical Society.

interface with electrolyte), thus providing competitive energy densities, ease of synthesis, and possibly long cycle life. However, the optimization of energy density becomes of secondary importance in the absence of optimal Ca^{2+} mobility.

Good positive electrode materials for Ca batteries must display low migration barriers, E_m, for Ca^{2+}, which entails good Ca^{2+} transport. Therefore, it is important to demarcate the tolerable limits of E_m that make candidate materials viable Ca-ion conductors. A practical Ca^{2+} positive electrode operating at room temperature and a moderate discharge rate of C/2, must display migration barriers E_m ~525 meV or lower for micron-sized particles and 650 meV for nano-sized particles [45]. Higher values of Ca^{2+} migration barriers become acceptable if the rate of charge is decreased and/or the temperature of the experiment is increased. As an example, if the particles of the candidate materials are as small as 10 nm and are cycled at ~60 °C at a rate of C/10 (10 h of discharge) the upper limit on E_m can be increased up to ~985 meV [133].

Besides Ca-mobility, another factor that crucially determines the utility of any potential Ca-cathode is its thermodynamic stability and its resistance toward detrimental conversion reactions. In particular, several chalcogenide chemistries are susceptible to irreversible conversion reactions when reduced with Ca, which often leads to the formation of binary Ca-compounds (such as CaO, CaS, etc), trapping the Ca and, in turn, prevents a reversible electrochemical process to occur [134]. Additionally, estimating thermodynamic stability, especially using first-principles calculations is often difficult for polyanionic compounds since the chemical space (quaternary or higher) is significantly larger compared to simpler chalcogenides. This is certainly a challenge worth pursuing as there are large polyanionic chemical spaces that have not been explored yet as Ca-intercalation electrodes.

Advances in science and technology to meet challenges

In terms of discovering new electrodes (and possible solid/liquid electrolytes) for Ca-batteries, computational techniques have been of great utility, especially high-throughput first-principles-based screening approaches. One way the discovery of new materials can be accelerated even further is by the adoption of ML techniques, both at the computational screening level and at the experimental automation level. However, using ML along with materials science datasets must be done with care since dataset' sizes are often too small (few 100s–1000s). Furthermore, significant human supervision is often required for training reliable models.

One of the limitations in high-throughput screening approaches is the ease with which E_m can be predicted in novel materials. The state-of-the-art in calculating E_m is either using DFT-based nudged elastic band calculations or *ab initio* MDs simulations, with both approaches suffering from significant computational costs and/or convergence difficulties [135, 136]. Finding good Ca-conductors becomes easier if there are 'design rules' and descriptors that can be followed to identify candidate structures. Lu *et al* [125] adapted to calcium chemistry, the design rules originally postulated by Chen *et al* [133] for multivalent ions, these rules may need further refinement and/or validation. Formulating accurate criteria for designing facile Ca-conductors can accelerate enormously the discovery and implementation of new materials.

The evaluation of the stability of an electrode-electrolyte interface and designing coating materials for unstable/metastable interfaces computationally is a significant challenge as well, similar to E_m predictions. Constructing representative models of interfaces that meaningfully capture surface irregularities still appears an untreatable problem to approach with first-principles methods. One computational pathway to study interfaces is to construct machine-learned interatomic potentials (MLIPs), including some accuracy of first-principles calculations yet is computationally as inexpensive as classical force fields. MLIPs have been used for the construction and study of large-scale interfacial models before [137]. However, creating and validating MLIPs is still significantly human-time-intensive, and processes to automate MLIP creation and/or theoretical frameworks that are naturally simple to train [138, 139]are advances that can help in the study of interfaces.

Finally, standardization of testing cells and protocols, particularly for Ca-mobility evaluation is an important experimental advance that is required for the testing and validation of new materials, such as Ca-electrodes and/or electrolytes. From identifying reliable blocking electrodes for electrochemical impedance spectroscopy (EIS) measurements to standardizing galvanostatic intermittent titration technique setups, and cell construction to minimize side reactions, significant advances need to be implemented to experimentally study positive electrodes for Ca batteries with the appropriate accuracy [107, 121].

Concluding remarks

The last ten years of intense research in complementary battery technologies to the LIB platform spearheaded enormous progress in calcium-ion batteries. While prototypes of Ca full cells are currently unavailable due to intrinsic limitations of the existing electrolytes, here we surveyed the state-of-the-art positive electrode materials for this technology. We demonstrated that the discovery of host materials, with adequate topologies enabling sufficient ion transport for Ca-reversible extraction, could only be achieved by combining experimental and theoretical efforts. There are still several limiting factors in the search for positive electrode materials for Ca batteries, and multivalent batteries, in general. These limitations range from fundamental aspects, including the lack of accurate design rules facilitating ion transport in host materials to the availability of rigorous electrochemical protocols.

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9. Ca based batteries—organic cathodes

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Status

High charge density and increased size of calcium cation in comparison with lithium cation leads to difficult insertion into inorganic hosts. Organic electrodes have recently emerged as viable alternatives, owing to their weak intermolecular forces that result in more flexible structures enabling better electrochemical accessibility than more rigid inorganic structures. On top of that, the potential and specific capacity of organic materials can be tuned by the addition of different functional groups, allowing for tailoring the electrode materials for the particular application and better fitting in the operating window of the electrolyte [140]. Despite the apparent advantages, simple redox-active organics suffer from several drawbacks. The most prominent ones are high solubility in common aprotic solvents, low tap density, and low intrinsic conductivity. Dissolution can be mitigated by polymerization, which often comes with the penalty of a slight reduction in capacity owing to the increased mass due to inactive linkers [141]. On the cell level, low tap density can be alleviated by pairing organic electrodes with an energy-dense Ca metal anode. The low electronic conductivity implies the addition of a high amount of carbon black during electrode preparation or synthesis of hybrid polymers containing carbon fillers [142].

To this date, one of the main challenges in the field of Ca-metal batteries is the lack of suitable electrolytes that enable room-temperature and reversible plating and stripping. While $Ca(BH_4)_2$ in THF enabled room temperature Ca plating/stripping, the chemical reactivity of the salt combined with low oxidative stability hamper its application in cells with organic electrode materials (OEMs) [108]. Therefore, investigation of organic electrodes in non-aqueous electrolytes is very limited to electrolytes based on tetrakis (hexafluoroisopropyloxy) borate ($Ca[B(hfip)_4]_2$) [109, 110]. Considering substantial issues present on the Ca metal anode side, up to now, only a handful of organic cathodes have been reported in conjunction with organic electrolytes. Similar to Mg metal-organic batteries, reports are mainly focused on n-type carbonyl-based compounds that undergo reduction upon discharge with subsequent charge balancing with cationic species. The combination of n-type cathodes and Ca metal has the potential to enable high energy density due to the shuttle of Ca^{2+} ions [143–145]. In theory, Ca metal anode organic cell employing benzoquinone electroactive compound enables a theoretical density of 940 Wh/kg. Currently, the majority of the examples are focused on AQ-based compounds, poly(anthraquinonyl sulfide) (PAQS) [143] and 1,4 poly(anthraquinone) (14PAQ) [144] in state-of-the-art $Ca[B(hfip)_4]_2$-based electrolyte. However, a p-type cathode, polytriphenylamine (PTPAn), was also investigated in a dual-ion battery configuration [146].

Current and future challenges

In a typical two-electrode setup, where the Ca metal anode serves as both counter and reference electrode, the reversible operation of the cell is limited by the processes occurring on the surface of the Ca-metal anode. In this arrangement, the stability of the organic materials cannot be fairly assessed, as cell failure due to the passivation of metal anode occurs after a few charge/discharge cycles (figure 9) [62, 143, 144]. Additionally, investigation of the organic cathode performance at higher current densities is also precluded by the large overpotential of metal anode [63]. For this reason, devising an electrochemical setup that would allow proper electrochemical benchmarking of novel organic materials is a necessity. Recently, 14PAQ was tested versus Ca_xSn alloy as a counter electrode that enabled long-term reversibility [144]. For the first time, the cycling stability of organic polymer was assessed in non-aqueous electrolyte over 5000 cycles, demonstrating that organics can undergo long-term cycling with good capacity retention in Ca-based cells. However, certain stability issues were observed at the beginning of cycling and could not be unambiguously assigned to the anode or cathode degradation. To clearly distinguish between organic cathode and metal anode contributions to the phenomena observed in electrochemical experiments, the use of three-electrode setups or two-electrode symmetric setups is necessary. This way, organic materials and their interactions with organic electrolytes can be assessed without limitations imposed by the anode/electrolyte interface. However, even three-electrode setups might experience certain limitations due to the instability of Ca metal reference [63].

Another challenge organic materials face in Ca batteries is a sharp decrease in active material utilization compared to the values obtained in Li half-cells [147]. Focus in the field of organic cathodes has thus far been on the design of new materials that can offer high capacities and voltages, but it is necessary to gain a

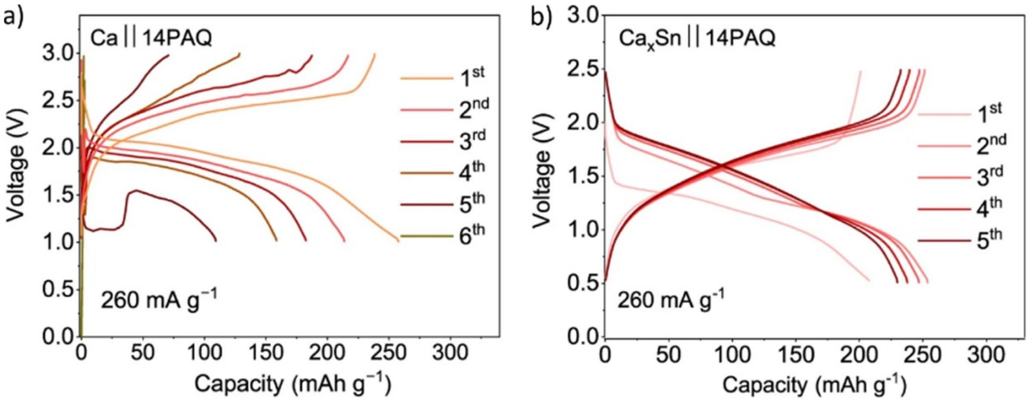

Figure 9. Organic electrode (1,4-poly anthraquinone) performance versus Ca metal anode (a) and Ca–Sn alloy (b) demonstrating the importance of counter electrode consideration when performing electrochemical characterization of organic electrodes in Ca-based batteries. Reproduced from [144]. CC BY 4.0.

fundamental understanding of organic material interactions with Ca^{2+} ions so main culprits for the inferior performance can be identified and potential changes in material or electrode design can be made.

Another issue common to several multivalent electrolytes (Ca, Mg, Al) is the tendency of Ca to form ion pairs and difficult cation and anion dissociation. In a case study of PAQS, energy-dispersive x-ray spectroscopy (EDS) analysis showed that around 25% of coordinating ions are monovalent cationic complexes and not Ca^{2+} ions [143]. Similar ratios are observed in Mg-based organic batteries [70]. Although at the laboratory stage of research monovalent coordination does not represent a major concern, the issue needs to be addressed in the future through electrolyte design, as the presence of cation-anion pairs can severely affect the final cell energy density due to electrolyte utilization.

Advances in science and technology to meet challenges

Certain issues like accessibility of the organic active sites are not yet properly understood as these phenomena are strongly affected by the complex interplay of various factors such as solvent swelling and solid-liquid interfaces. For the future development of Ca-organic batteries, a deeper understanding of these factors is essential. Understanding the processes involved in charge transfer and ion transport will require advanced electrochemical investigation of organic materials and also a combination of electrochemical analysis with other characterization techniques. New insight into the performance of organic cathodes was already obtained by the use of symmetrical cells and the application of EIS. Symmetrical cell cycling has shown good long-term capacity retention in the case of PAQS and significantly smaller resistance contribution for charge storage of Ca species in comparison with Mg species in electrolytes based on $[B(hfip)_4]^-$ anion in dimethoxyethane solvent (figure 10). These findings point to the fact that Ca-organic batteries might enable less impeded ion storage within organic materials than Mg-organic batteries. The combination of EIS with tracking of chemical and morphological changes in materials both post-mortem and during cycling could bring a fundamental understanding of processes limiting the charge transfer reaction and guide the future synthesis of organic materials.

On the organic cathode side, new materials with higher voltages are being introduced. A recent report on polytriphenylamine (PTPAn, p-type material) composite cathodes with an average operating voltage of around 3.5 V and energy density of about 300 Wh kg^{-1} (on a material level, not taking into account salt anion utilization) paved the way for the further exploration of higher voltage cathodes for Ca batteries [146]. After solving fundamental issues on a material level, considerations such as electrode design should be taken into account, including increasing the areal loading of active material, moving away from flooded electrolyte conditions, etc [148].

Concluding remarks

The field of Ca-organic batteries is still very young, and only a handful of organic materials have been explored so far. Future research should move in the direction of higher voltage and capacity compounds, enabling competitive energy densities with other novel battery systems. At the same time, joint electrolyte and organic cathode material research should be directed at increasing the active material utilization and improving the kinetics while ensuring the utilization of Ca^{2+} cations in the charge storage mechanism. These efforts should be accelerated by a preceding investigation of the governing parameters decreasing the performance of organic electrodes upon switching from Li-organic batteries to Ca-organic ones.

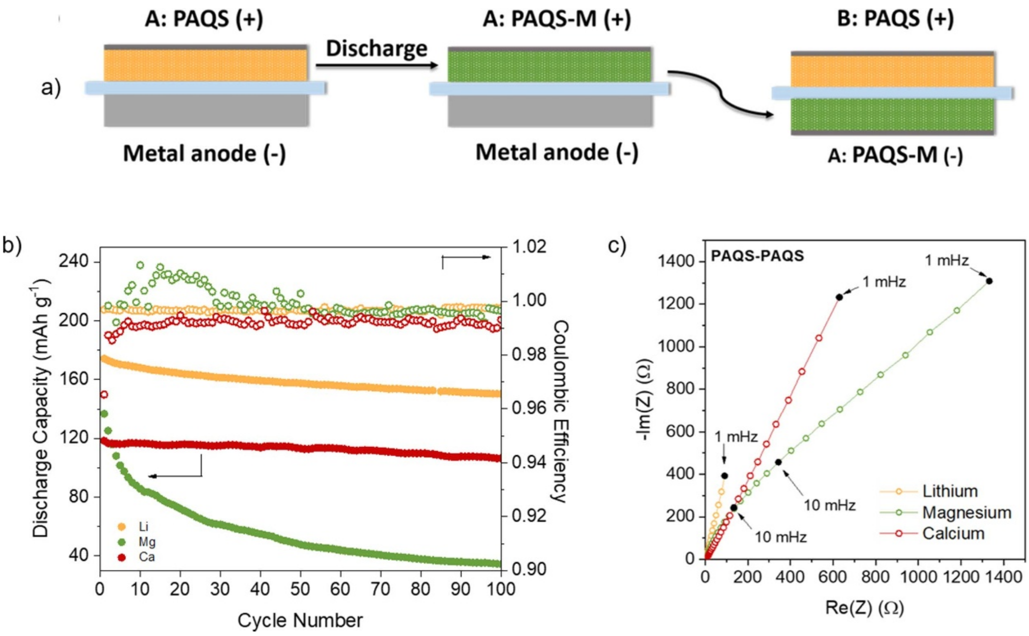

Figure 10. Schematics of symmetric organic cells preparation (a). Cycling stability and Coulombic efficiency of symmetric PAQS(+)-PAQS-M(−) cells with lithium (orange), magnesium (green), and calcium (red) displaying much better capacity retention of organic cathode in Ca electrolyte than in Mg. (b). Electrochemical impedance spectroscopy was obtained on symmetric Li, Mg, and Ca cells at 0.5 SOC (c). Reproduced from [62]. CC BY 4.0.

Development of Ca organic batteries will also benefit from the knowledge and experience obtained in the application of organic cathodes in Mg batteries and other monovalent batteries, providing a boost to the research efforts in the field.

Acknowledgments

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10. Calcium-conducting polymer electrolytes

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Status

Pillot [149] forecasts a huge increase of the worldwide Li-ion battery market from 230 GWh in 2020 to 1.3 TWh in 2030. This is mainly ascribable to the market expansion from the 4C market to the electromobility and energy storage growing markets. From the battery manufacturer to the end-user, safety is both, the keyword and the main concern. Safety: (1) regarding the societal acceptance of electric vehicles and the concomitant banning of ICE-powered cars; (2) regarding the hazards e.g. flaming, explosion and toxicity; (3) regarding the supply of key materials (cobalt, lithium). The development of calcium-rechargeable batteries based on polymer electrolytes is at the confluence of two safety concerns, i.e. the highly flammable and toxic liquid organic electrolytes and the mid to long term scarcity of lithium resources. Regarding the latter, during the last decade a growing interest has arisen in post-Li batteries based on abundant alkaline metals (Na, K) and on alkaline-earth metals (Mg, Ca). All are, indeed, realistic alternatives to the relative scarcity of lithium resources. Owing to (1) the high abundance of calcium ores e.g. in limestone and gypsum, (2) its redox potential (close to Li/Li^+) and (3) its volume capacity, equal to the lithium one and (4) its markedly higher melting point ($T_m = 842\ ^\circ C$) when compared to alkaline metals and magnesium, it has been prioritized as a post-lithium technology. Indeed, Peled *et al* reported, roughly forty years ago, the high performance of a non-rechargeable calcium battery but also the cycling issues of calcium metal, Ca^0 [150, 151]. Regarding safety hazards, all-solid-state batteries, ASSB, based on inorganic materials e.g. ceramic electrolytes, are not flammable and safer than current Li-ion batteries. Nonetheless, while alkaline-based ceramic electrodes exist and often exhibit a high cationic conductivity, the very low mobility of divalent cations in alkaline-earth based ceramic electrolytes hinders the development of magnesium or calcium based ASSB. Whether solid inorganic calcium electrolytes are unsuitable, a rechargeable calcium battery based on solvent-free calcium conducting polymer electrolytes meets most of the safety requirements of a state of art ASSB. Calcium ionomers is an option and can be considered [107] as both polymer electrolyte and binder of composite positive electrodes. Endowed with high Flash Point and a T^+ (cationic transport number) equal to 1, the calcium ionomers should avoid the formation of salt concentration gradients during the battery operation and, possibly, the formation of dendrites when mechanical properties are promoted.

Current and future challenges

The first proof of Ca^0 cycling was reported using an EC-PC solution of $Ca(BF_4)_2$ [107]. Then, a THF solution of $Ca(BH_4)_2$ allowed cycling Ca^0 over 50 cycles [108], forming CaH2 both at the surface and in the bulk of the Ca^0 electrode. A bulky calcium salt $Ca[B(hfip)_4]_2$ was found to significantly increase the anodic stability vs $Ca(BH_4)_2$, while allowing Ca^0 cycling [109]. Despite allowing a promising Ca^0 cycling, $Ca(BH_4)_2$ and $Ca[B(hfip)_4]_2$ utilization in batteries remains questionable. In this sense, if an efficient SEI is one of the routes to reversibly cycle Ca^0, another route is the design of a stable electrolyte. Although intrinsically stable in reduction, halides salts are poorly conductive. About anions having dative bonds e.g. BF_4^- or PF_6^- that disproportionate in BF_3 or PF_5, prone to chain breakings, they are unsuitable in polymer electrolytes. Remain triflate or imide calcium salts intrinsically unstable vs metal anodes but whose anodic stability matches with most cathodes. Figure 11 compares liquid electrolytes (Ca-LE), solvent-free polymer electrolytes (Ca-SFPE) and networked ionomer electrolytes (Ca-NIONO) [152].

Solvents and perfluorinated anions of Ca-LE are intrinsically unstable vs Ca^0, their continuous renewal on Ca^0 contributing to electrode degradation. In case of Ca-SFPE, the low or inexistent reptation of entangled chains impedes chain renewal on Ca^0; the main source of degradation lying in anion renewal. Regarding Ca-NIONIO, the renewal of infinite chains and of the anions is impossible, minimizing the impact of the ionomer electrolyte on the electrode. Moving from liquid to polymer and ionomer therefore improves the electrolyte cathodic stability vs alkaline-earth metals. Host polymers [153] to be selected have heteroatoms as polysulfides, polyamines or polyethers. The first two have a limited anodic stability. Main Ca-PE challenges are (i) to allow cycling reversibly over hundreds cycles, currently, then over thousands cycles Ca^0 (ii) to provide high cationic conductivities and (iii) to guarantee their thermomechanical stability thanks to crosslinking. Nonetheless, if electrolyte stability is a pledge of safety, it does not guarantee a

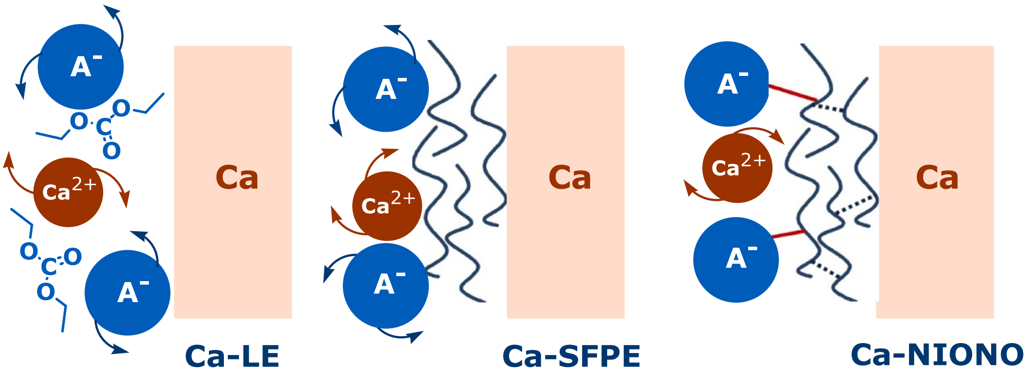

Figure 11. Comparison of calcium metal interfaces with calcium-conducting electrolytes. From left to right liquid electrolyte, Ca-LE, solvent-free polymer electrolyte, Ca-SFPE, and networked ionomers, Ca-NIONO.

reversible cycling of Ca^0. Therefore, a synergic effect resulting from highly stable electrolytes and the incorporation of additives forming a stable and efficient SEI might be an option. A Ca-SFPE battery imposes to use it as a binder of the cathode, endowing it with ionic conductivity and mechanical integrity in view of increasing its thickness and, therefore, its areal capacity. Thanks to the polyether anodic stability Ca-vanadates and sulphur cathodes can be considered.

Advances in science and technology to meet challenges

Vincent [154] compared the mobility of Mg^{2+}, Li^+ and Ca^{2+} in SFPE based on oligo(oxyethylene), PEG, and poly(oxyethylene), POE, concluding that Mg^{2+}, conversely to Li^+, does not move in entangled SFPE. DC polarization, performed on Mg and Ca-based amalgam electrodes, confirmed the lack of mobility of Mg^{2+} (rapid current drop) and concluded to Ca^{2+} mobility (current flowing after 20 h). Prior to select a host polymer for SFPEs, obtaining stable macromolecular solutions is indispensable as, for instance, poly(oxypropylene), although similar to POE, leads to microphase separations [155]. The phase diagram of POE/$Ca(CF_3SO_3)_2$ revealed salt precipitation [156]. Using 300 000 $g.M^{-1}$ POE, without unentangled oligomers, we confirmed a salt precipitation starting at 270 °C [157–159]. However, on the one hand, this precipitation occurs well beyond the operating temperature of a Ca polymer battery and, on the other hand, x-ray mapping (EDS) demonstrates a homogeneous distribution of calcium salts (iodide, triflate, TFSI). Figure 12(a) compares the Arrhenius plots of various G4/$Ca(TFSI)_2$ [160], G4, tetraglyme that mimics POE chains. The conductivity drop from roughly 55 °C, mitigated for concentrations exceeding 0.5 $M.l^{-1}$, is also observed with $Mg(TFSI)_2$ but not with LiTFSI. Figure 12(B) reveals a different behavior of Ca-POE electrolytes, whatever the salt, doubling conductivity of POE/$Ca(TFSI)_2$ from 70 °C to 90 °C. We hypothesize a higher solvating ability of POE: a higher DN. This means G4 is not a model oligomer of POE.

Among the few contributions on Ca-SFPE, we can cite networked poly(oxytetramethylene) poly(THF) [161], poly(oxyethylene-methacrylate) POEM [162] and miscible blends of poly(vinyl alcohol) and poly(vinyl pyrrolidone), PVA/PVP [163] hosting $CaCl_2$. PVA/PVP/$CaCl_2$ conductivities are surprisingly high but as the films were cast in water, we suspect remaining water plasticizing the high T_g blends. Even though LiTFSI in a POE network presents a ten times higher ionic conductivity when compared with cross-linked PTHF [164] in the form of Ca-SFPE, it could be an attractive alternative if stable solutions are obtained. Indeed, the lower solvating ability of PTHF vs POE, should favor Ca^2 mobility. However, the reported Ca-PTHF conductivities are not conclusive, as the electrolyte is rich in unstable alcohol groups, i.e. OH concentration ~4 $M.kg^{-1}$, knowing that OH groups strongly interact with anions. Due to the questionable plating onto Ca^0 in Ca/SFPE/Ca cells and the no-response of calcium in NMR, the main concern in the understanding of Ca^{2+} conduction mechanisms is obtaining indisputable T^+. Beyond calcium electrolytes, vanadate electrodes based on Ca-SFPE binders are currently evaluated [165].

Concluding remarks and prospects

At this stage, the interest of a rechargeable calcium battery lies in the use of calcium metal, Ca^0, as negative electrode. This supposes reversibly cycling (with low overpotential) Ca^0 electrode over hundreds or even thousands of cycles. Nevertheless, the difficult plating/stripping on Ca^0 requires focusing on two research lines (1) the design and preparation of stable calcium ionomer-based electrolytes and (2) the selection of

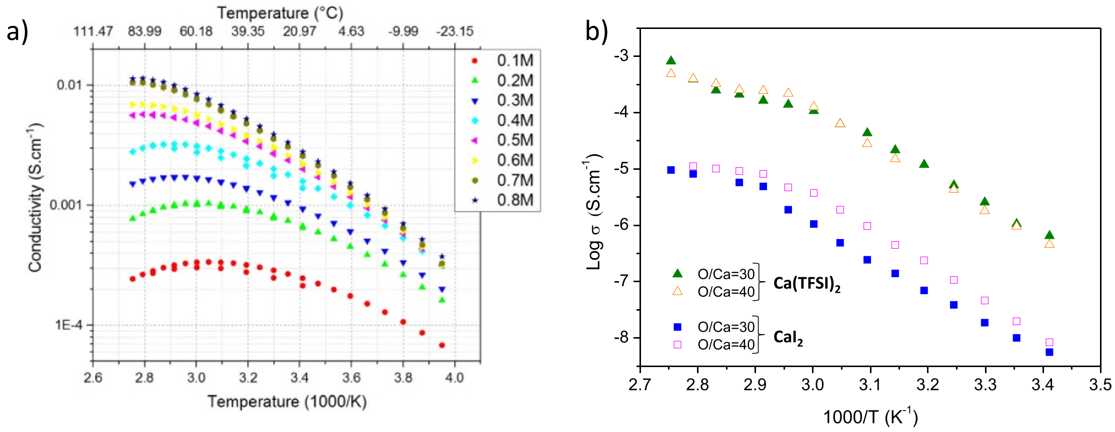

Figure 12. (a) Arrhenius plots of various G4/Ca(TFSI)$_2$ (reproduced with permission [160]); (b) Ionic conductivity as a function of temperature and O/Ca ratio for POE-CaI$_2$ and POE-Ca(TFSI)$_2$ electrolytes. O means the oxyethylene repeat unit. Reproduced from [160] with permission from the Royal Society of Chemistry.

additives able to form an efficient SEI that allows the Ca^0 reversible cycling. Despite both approaches seem competitive, they can be carried out concomitantly and, therefore, a synergy between them seems necessary. From now on, several calcium polymer electrolytes can be shaped into membranes by green elaboration processes i.e. either by extrusion or by film casting from aqueous solutions. The recent comparison of conductivity data [166] between calcium polymer electrolytes and calcium ionomers shows a significant gap with regard for instance to their lithium analogues. This suggests a complex conduction mechanism. Swelling the Ca ionomers with various solvent showed that a tremendous increase of conductivity is only obtained with highly polar solvents e.g. EC, suggesting that the low conductivities of the Ca-ionomers has to be mainly ascribed to the insufficient ion-pair dissociation.

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11. Introduction to Al dual-ion batteries

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Status

Aluminum dual-ion batteries (ADIBs) are currently gaining attention as an emerging stationary energy storage concept due to their relatively high theoretical gravimetric/volumetric energy densities of up to *ca.* 60 Wh kg^{-1}/100 Wh l^{-1}, long cycle life, high energy efficiency, and the potential to be manufactured at low cost [167–169]. They operate by the reversible insertion/de-insertion of $AlCl_4^-$ ions into the positive electrode with a concomitant aluminum electroplating/stripping reaction at the Al negative electrode (figure 13(a)). The very first reports on ADIBs date back to the 1970s, when Fouletier and Armand [170] demonstrated the intercalation of $AlCl_4^-$ ions into graphite from molten LiCl/$AlCl_3$ salts (at *ca.* 140 °C). In 1988, Gifford and Palmisano [171] extended the research on ADIBs by replacing molten salts with imidazolium-based room-temperature ionic liquids (RTILs). More recently, in 2015, ADIBs received renewed attention after the publication of Lin *et al* [172] who demonstrated an ADIBs composed of a pyrolytic graphite foil cathode, an Al foil anode, and an ionic liquid electrolyte [$AlCl_3$/1-ethyl-3-methylimidazolium chloride (EMIMCl)]. Dai's battery exhibited high reversibility of the intercalation/de-intercalation of $AlCl_4^-$ ions into pyrolytic graphite, delivering cathodic capacities up to 67 mAh g^{-1} over thousands of cycles. Following the publication of Lin *et al* [172], the past decade has seen extensive research on ADIBs, including the discovery of other active materials capable of reversibly accommodating $AlCl_4^-$ ions [173], the investigation of the electrochemical properties of ionic liquid electrolytes [174], and the elucidation of the mechanisms of intercalation and diffusion of the $AlCl_4^-$ ions into the cathode materials [175], the degree of cathode volume expansion [176–178], and so on.

Current and future challenges

The primary challenge of ADIBs is directly related to the fact that the composition and volume of the aluminum electrolyte changes during charge/discharge. This is because the electrolyte in dual-ion batteries not only acts as a carrier of the ions, but also contributes to the EES and can therefore be called anolyte. For this reason, the practical energy and power densities that can be achieved in dual-ion batteries are linked to the initial concentration of the' energy-storage' ions in the electrolyte [179]. In the case of ADIBs, considering the fact that the electrodeposition of Al occurs only in acidic compositions (in the presence of $Al_2Cl_7^-$, but not $AlCl_4^-$ ions) [180, 181], specifically the concentration of $Al_2Cl_7^-$ defines the charge storage capacity of the anolyte, since the charging of ADIBs proceeds through the depletion of $Al_2Cl_7^-$ according to the following reaction:

$$4Al_2Cl_7^- + 3e^- \leftrightarrow 7AlCl_4^- + Al.$$

Charging stops when only $AlCl_4^-$ anions remain in the anolyte (figure 13(b)). Considering that the concentration of $Al_2Cl_7^-$ ions in an ionic liquid anolyte is determined by the $AlCl_3$ (Lewis acid): ACl (Lewis base) molar ratio (r), the anolytes with low and high ratios have different capacities. For example, at $r = 1.3$ and $r = 2$, the volumetric and gravimetric capacities of $AlCl_3$:EMIMCl are 24 Ah l^{-1}, 19 mAh g^{-1} and 63 Ah l^{-1}, 48 mAh g^{-1}, respectively [182]. In this context, the cell-level charge storage capacity of ADIBs is severely limited by the low acidity and therefore low anolyte capacity, resulting in low energy density values of ADIBs. Importantly, the highest molar ratio (r) between $AlCl_3$ and Lewis base chlorides at which an ionic liquid will still form at room temperature is *ca.* 2:1. Higher molar ratios result in the formation of aluminum chloride precipitate [183]. It should be noted that completely different considerations apply to aluminum-ion batteries (AIBs), where the volumetric/gravimetric capacities of the Al anode (8046 mAh cm^{-3}/ 2980 mAh g^{-1}), but not the Al electrolytes, are used to evaluate the charge-storage capacity of AIBs [184]. This is because the chloroaluminate ionic liquid melt in AIBs acts solely as a carrier of the Al^{3+} ions and therefore does not contribute to the energy storage.

Advances in science and technology to meet challenges

Following the above considerations regarding anolyte as an 'active' charge-storage electrolyte medium, it is clear that the amount of anolyte must be at matched to the charge of the cathode active material (in mAh). For example, given capacities of graphite and anolyte of 100 mAh g^{-1} and 48 mAh g^{-1}, respectively, a graphite

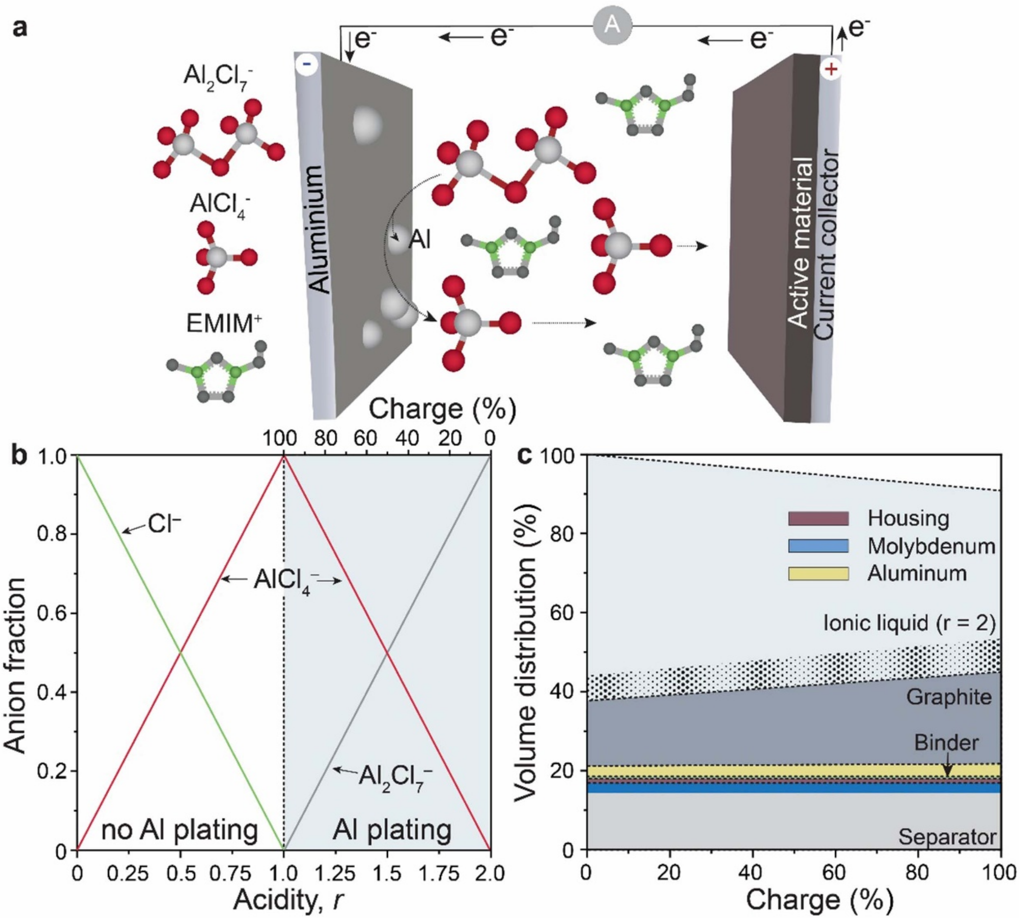

Figure 13. (a) Schematic of the charging process of ADIBs. (b) Fractions of Cl^-, $AlCl_4^-$ and $Al_2Cl_7^-$ ions in room-temperature chloroaluminate melts as a function of their acidity. Reprinted with permission from [185]. Copyright (1985) American Chemical Society. (c) Volumetric distribution of the different battery components in graphite based ADIBs *vs.* state of charge. Reproduced from [186]. CC BY 4.0.

electrode with a mass loading of 10 mg cm^{-2} must be coupled with an anolyte with a volume loading of 15 μl cm^{-2}. The excess of anolyte has a drastic negative effect on the energy densities of ADIBs. For example, the use of 50 wt% excess $AlCl_3$:EMIMCl anolyte ($r = 2$) leads to a sharp decrease in energy density of ADIBs to 30.4 Wh kg^{-1}/55.1 Wh l^{-1} (for a 1 mAh cm^{-2} graphite cathode). Doubling the amount of anolyte ($r = 2$) results in almost 40% lower values of gravimetric and volumetric energy densities (24.5 Wh kg^{-1} and 43.1 Wh l^{-1}) of ADIBs. These considerations indicate that research efforts should be focused on minimizing the excess amount of anolyte (relative to theoretical) while maintaining the high rate capability of ADIBs. To date, the issue of cell charge balancing has not been addressed. Reports on ADIBs present results obtained with highly unbalanced cells, typically with a large excess of anolyte. Such measurements are well suited for accessing the performance of novel cathode materials, but do not allow estimation of the achievable performance of ADIBs in respect to maximized energy and power density.

In addition to charge balancing the cells, further advances are needed to eventually commercialize this technology. These are associated with drastic fluctuations in electrolyte volume during battery operation. For example, in the case of an $AlCl_3$:EMIMCl anolyte with $r = 2.0$, its volume can decrease by up to 26%, corresponding to a complete depletion of $Al_2Cl_7^-$ ions from the anolyte, to reach neutrality ($r = 1$). The higher the molarity or acidity of the electrolyte, the greater the volume change. In addition, in contrast to the rather small volume increase of insertion-type active materials used in Li-ion batteries upon intercalation of Li^+ ions (up to 10%), the volume of the most common cathode material of ADIBs, graphite, can expand by up to 41% upon intercalation of $AlCl_4^-$ anions. Although the volume changes of the graphite cathode and the anolyte may partially overcompensate each other during the operation of ADIBs, the total cell volume changes significantly by up to 10 vol% (figure 13(c)). Therefore, radically new battery design, very different from that used in commercial Li-ion batteries, would be required to solve this issue.

Concluding remarks

While the literature on ADIBs has blossomed over the past few years, the development of commercially competitive prototypes has lagged considerably behind. This technology still requires further advances in several areas related to both the performance (energy and power densities, energy efficiency, and cycle stability) and overall cost competitiveness of ADIBs batteries. These are: (1) finding a battery design that can mitigate drastic volume fluctuations of the anolyte, cathode active materials, and cell during cycling, (2) optimization of amount of anolyte to maximize the energy density of ADIBs while maintaining their high power density, (3) increase the areal capacity of the cathodes to at least the level of 1 mAh cm^{-2}, (4) development of inexpensive and less corrosive anolytes that have high gravimetric/volumetric capacity, support non-dendritic plating of Al, and have a wide electrochemical voltage window of up to 0–2.5 V *vs.* Al^{3+}/Al, (5) search for low-cost cathode current collectors, which are oxidatively stable up to 2.5 V *vs.* Al^{3+}/Al. Research on ADIBs is therefore continuing. However, given the current technological immaturity of ADIBs, it is difficult to predict whether ADIBs will realize their low-cost potential and undergo a large-scale deployment in the near future.

12. Dual-ion Al batteries—electrolytes

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Status

The most widely used electrolytes for aluminium dual-ion batteries are RTILs, which are of interest in a variety of fields as a green alternative to conventional solvents. RTILs consist of a Lewis acidic metal salt and a Lewis basic organic salt which mix to form weakly coordinated complex ions that become liquid at room temperature. Typically, the RTILs for this application are made of $AlCl_3$ and an organic halide salt, often imidazolium chlorides. RTILs were first used in aluminium batteries in the form of $AlCl_3$-MEImCl [187], but since 2011 $AlCl_3$-EMImCl has become the most reported electrolyte, ahead of other imidazolium- and amine-based RTILs [172, 188–191].

The operating principle of aluminium dual-ion batteries relies on electroplating of metallic aluminium from $Al_2Cl_7^-$ at the anode and storage of $AlCl_4^-$ at the cathode. Both required aluminium anion species are present in RTILs in acidic conditions, at $1 < r < 2$, where r is the molar ratio of $AlCl_3$ to organic salt (figure 14(a)). Kravchyk *et al* [192] highlighted that, in the dual-ion configuration, the electrolyte acts as the anolyte to the cathode such that the capacity of the cell depends on both the quantity of cathode active material and electrolyte volume and acidity. It is therefore important to balance the electrolyte-cathode ratio to maximize the energy density. A significant benefit to these electrolytes is their wide liquids range (-90 °C–300 °C for $AlCl_3$-EMImCl) and negligible vapor pressure [193], resulting in low flammability and hence improved safety. However, only a small fraction of possible material combinations have been studied (figure 14(b)), leaving significant parameter space for further investigation.

Other materials, including deep eutectic solvents (DESs), inorganic molten salts (IMS), organic solutions, and aqueous solutions (2022 Roadmap on aqueous batteries [194]), have also been employed in aluminium batteries to varying degrees of success. DESs (such as $AlCl_3$-urea) are analogues to ILs, utilizing a metal salt and a hydrogen donor ligand to form a liquid with negligible vapor pressure, with lower cost than RTILs but with higher viscosity and lower ionic conductivity. IMSs typically consist of $AlCl_3$ with up to three other metal chloride salts, allowing effective aluminium plating/stripping but requiring elevated temperatures ($\sim$90 °C) to be in the liquid state [195]. Whilst aluminium plating is achievable from organic solutions [196], their toxicity and flammability has discouraged their use in aluminium batteries. However, limitations of Cl-based melts have recently motivated research into Cl-free organic electrolytes.

Current and future challenges

Despite their advantages of fast, reversible, and relatively safe charging, using chloroaluminate RTILs introduces several challenges (figure 15). Most critically, the acidic conditions required for electrodeposition result in high corrosivity. The concentration of $Al_2Cl_7^-$ anions in acidic RTILs, DESs, and molten salts is known to negatively affect the stability of both electrodes, as well as other battery components, which can lead to cell failure [198]. This limits the potential of aluminium batteries as a drop-in technology in its current state, and significantly impacts cycle and shelf life. Consequently, research is required to adapt cell designs to withstand electrolyte corrosion, and/or to modify the electrolyte to allow aluminium electrodeposition without degradation of cell components. Several materials have been studied to understand electrode corrosion and to identify suitable current collectors (see section 3.3), with preliminary efforts also directed towards alternative separator and cell casing materials. However, there is currently a lack of understanding of the fundamental corrosion mechanisms, the effect of possible SEIs, and their impact on cell performance.

Additional challenges of RTILs include their hygroscopic nature, high cost, and high viscosity, leading to low ionic conductivity [199]. An aspect that is often overlooked when discussing the safety of these electrolytes is their exothermic reaction with moisture, which is reported to form hydrochloric acid [200]. Other potential gas emissions, which would be expected from thermal and electrochemical decomposition of the electrolyte, also need further investigation to design appropriate safeguards. In addressing the cost of RTILs, DESs offer a cheaper alternative, with high CE, but their comparatively low conductivity at room temperature severely reduces the achievable discharge capacity. Research into organic solvent additives, such as dichloromethane [201], for both RTILs and DESs, has shown improved conductivity and reversible capacity.

Cl-free electrolytes are a potential solution to the instability of aluminium battery components. Experimental and computational approaches are being employed to select promising salt-solvent combinations. For example, trifluoromethanesulfonate in diglyme has allowed aluminium electrodeposition

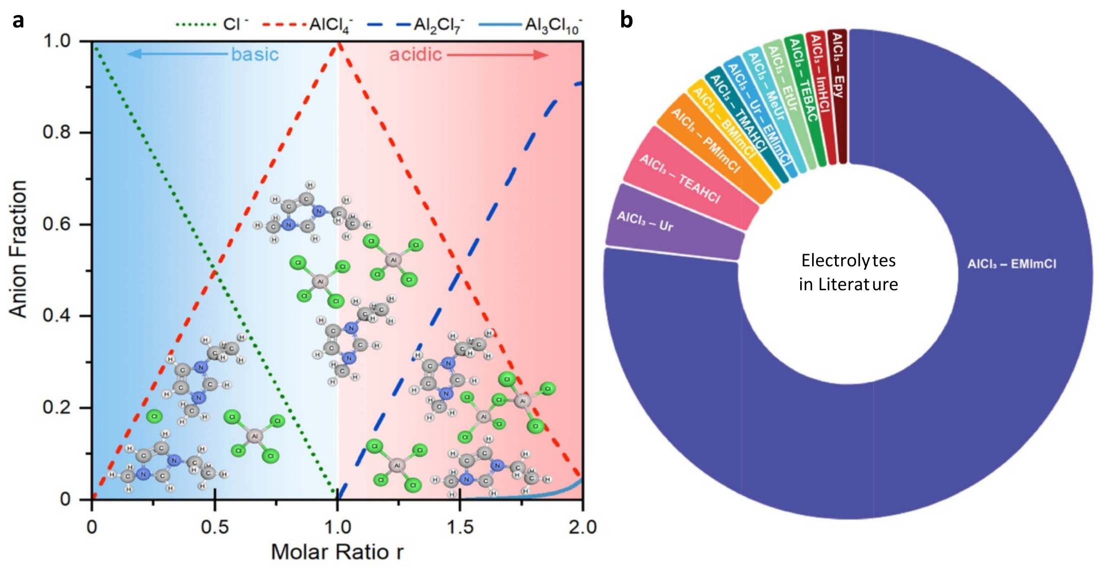

Figure 14. (a) The anion speciation diagram of $AlCl_3$–EMImCl at room temperature (data based on Shi *et al* [197]) illustrating the electrolyte compositions at $r = 0.5$, 1.0, and 1.5, and (b) the fraction of different electrolyte materials reported for room temperature full cell aluminium-graphite dual-ion batteries in 2015–2021, including EMImCl (1-ethyl-3-methylimidazolium chloride), TEAHCl (triethylamine hydrochloride), Ur (urea), PMImCl (1-propyl-3-methylimidazolium chloride), BMImCl (1-butyl-3-methylimidazolium chloride), ImHCl (imidazole hydrochloride), TMAHCl (trimethylamine hydrochloride), TEBAC (benzyltriethylammonium chloride), MeUr (N-methyl urea), EtUr (N-ethyl urea), and EPy (4-ethyl pyridine).

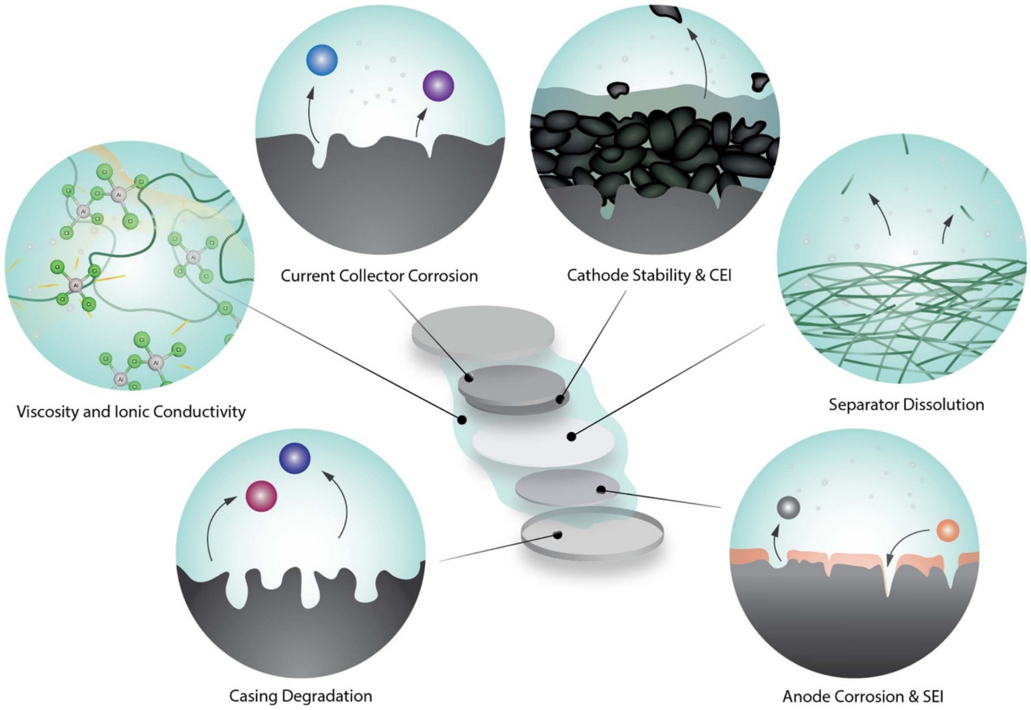

Figure 15. An overview of the challenges associated with the use of chloroaluminate based electrolytes in aluminium dual-ion batteries.

but has shown poor reversible capacity with copper hexacyanoferrate cathodes [202]. However, careful consideration is required of the overall benefit of the improved corrosion resistance, compared to the increased safety hazard that accompanies organic solvents, as well as the additional factor of performance gain/loss. It is imperative to balance the development of any higher performance electrolytes, especially Cl-free electrolytes and electrolyte additives, with considerations for the effect on device lifetime, safety, and the overall environmental impact.

Advances in science and technology to meet challenges

While the properties of aluminium electrolytes are well studied in isolation, in a battery system the electrolyte is most importantly understood in relation to its behavior at the interface with other components. Significant progress has been made within the last decade in understanding solid-liquid interfaces and their impact on overall battery performance. There has been increased attention to the effect of IL acidity on both energy density [192] and component stability [198], as well as the impact of the cationic species on reversible intercalation and electrodeposition [189]. Future progress should focus heavily on interdisciplinary understanding to best address the challenges of intercalation, electrodeposition, ionic conductivity, corrosion, and interphase formation through study of the solid–liquid interfaces under *in situ* conditions.

Advances in *operando* characterization techniques, such as liquid cell transmission electron microscopy and operando x-ray absorption spectroscopy, as well as cryo-techniques, such as cryogenic atom probe tomography and electron microscopy, are expected to significantly advance studies of solid-electrolyte interfaces by visualizing and assessing the reactions in real-time or by better preserving the system in the state of interest. However, the corrosivity of the electrolyte poses various challenges in adapting these techniques, in addition to the complexity of the methods themselves. Computational methods, such as classical, *ab initio*, and ML MDs, are also continuously improved to screen for suitable materials by expanding understanding of their properties [174] to diversify feasible electrolytes, while a variety of modeling approaches employed for other battery technologies [329] will provide invaluable insight into advancing understanding the electrochemical interfaces in aluminium systems. Similarly, a combination of automated high throughput methods and material databases, as seen for more established battery chemistries [203], particularly auto-generated ones [204], are expected to significantly aid new material discovery and general understanding of the system.

Concluding remarks

Significant progress has been made in developing and understanding electrolytes for reversible aluminium energy storage. Chloroaluminate RTILs and DESs have proven the most reliable material to facilitate electrodeposition and intercalation of aluminium species at room temperature, but there is extensive potential for future progress to address their limitations. Advances in experimental and computational methods are accelerating the exploration and tuning of electrolyte materials to optimize energy density and battery lifetime.

Acknowledgements

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13. ADIBs—current collector and anode corrosion issues

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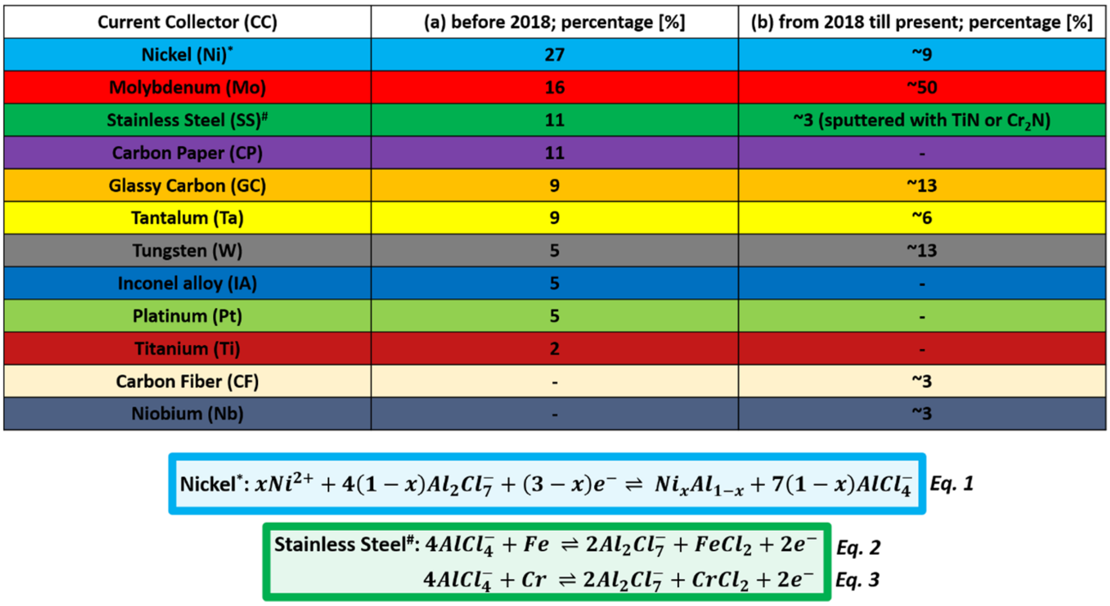
Status

ADIBs have attracted increasing attention in the battery research community because of the use of earth-abundant metal with high theoretical volumetric and gravimetric energy density and improved safety [182]. ADIBs with aluminum (Al) metal anodes have the potential to deliver breakthroughs in energy density besides the current established LIBs for specific applications like stationary energy storage systems. One main challenge of ADIBs is the electrode/electrolyte interface/interphase reactions, where poor ion-conducting passivation layers and slow ion solvation may significantly affect the ion kinetics [4]. Since the native-formed aluminum oxide (Al_2O_3) passivation layer is an insulator and is very stable, removing this film by using harsh and aggressive chemicals is fundamental. Indeed, the commonly used $AlCl_3$-based ionic liquid electrolytes (see section 12) are very acidic and can remove the Al_2O_3 layer, but as a drawback, they are also extremely sensitive to moisture and corrosive against metallic cell parts. Corrosion and re-passivation of the Al metal anode during the charging/discharging process cause unwanted side reactions (with the formation of hydrogen (H_2)) and consequent decay of capacity. These side reactions are mainly related to Al electrodes and other metals being susceptible to corrosion by chloride ions (Cl^-) or chloride-based complexes, like $Al_2Cl_7^-$. Recently, it was shown that corrosion of the Al metal anode results in an uneven distribution of the current on the electrode and an inhomogeneous amount of $AlCl_4^-$ at the interface [205]. In addition, metallic current collectors and cell-body parts suffer from severe corrosion when in contact with electrolyte anolytes [182]. Figure 16 presents a statistic of the current collector materials used before 2018 [206] and from 2018 until today; many of these materials are incompatible with the electrolyte, which could bring a misleading interpretation of the results (equations (1)–(3)). As a result, considering corrosion, passivation and side reactions, ADIBs are not yet ready for practical applications and commercialization. This section of the multivalent batteries' roadmap reviews the current challenges in developing ADIBs and describes possible routes to overcome the mentioned reactivity and corrosion issues. Finally, a summary and future perspectives on ADIBs research are given.

Current and future challenges

Two methods are reported to remove the insulating Al_2O_3 layer: electropolishing and surface etching. Electropolished foil results in higher specific energy compared to the etching method [205]. Due to the inhomogeneity of the oxide film, the electrochemical reaction is localized in a small area and the Al-Cl complex, $Al_2Cl_7^-$, has difficulties reaching the Al anode surface [207]. Therefore, the current will be localized and result in an increased impedance. It should be mentioned that the effectiveness of the Al_2O_3 layer depends on the thickness and on the microstructure of the Al-foil. For example, a thin oxide film with a porous structure may be beneficial for the metallic anode [207]. Several activation cycles are necessary for the electrochemical reduction of the oxide layer and for achieving reversible plating and stripping [207]. With a thicker Al_2O_3 layer, the current density peak is smaller. In addition, the reduction peak shifts to more negative potentials, while the oxidation peak shifts to a more positive potential, as shown in figure 17. This indicates that the oxide film thickness influences the electrochemical activity and polarization [207]. Apart from the problems with the metallic Al-anode, there are complications with the metallic current collectors. In LIBs and Sodium-Ion Batteries (SIBs), aluminum foil is considered an established current collector metal for the positive electrode. In the case of ADIBs, it is impossible to use Al metal because of its low anodic stability [182]. Besides Al, many other metals get corroded by Lewis acidic chloroaluminate electrolytes, like stainless steel (SS) and titanium (Ti) [167]. The use of stable metals as current collectors is essential for producing reliable results. For example, it is shown that the SS current collector and SS coin cell housing are responsible for the redox activity of Al/V_2O_5 cell, which can be attributed to the dissolution and shuttling effect of the iron (Fe) and chromium (Cr) ions contained in the SS [208]. In addition, it was demonstrated that choosing an unstable current collector material can generate false discharge capacities [209]. Despite these findings, researchers are still using unstable metals as current collectors (figure 16). Instead, anodically



Current Collector (CC)	(a) before 2018; percentage [%]	(b) from 2018 till present; percentage [%]
Nickel (Ni)*	27	~9
Molybdenum (Mo)	16	~50
Stainless Steel (SS)#	11	~3 (sputtered with TiN or Cr_2N)
Carbon Paper (CP)	11	-
Glassy Carbon (GC)	9	~13
Tantalum (Ta)	9	~6
Tungsten (W)	5	~13
Inconel alloy (IA)	5	-
Platinum (Pt)	5	-
Titanium (Ti)	2	-
Carbon Fiber (CF)	-	~3
Niobium (Nb)	-	~3

Nickel*: $xNi^{2+} + 4(1-x)Al_2Cl_7^- + (3-x)e^- \rightleftharpoons Ni_xAl_{1-x} + 7(1-x)AlCl_4^-$ **Eq. 1**

Stainless Steel#: $4AlCl_4^- + Fe \rightleftharpoons 2Al_2Cl_7^- + FeCl_2 + 2e^-$ **Eq. 2**

$4AlCl_4^- + Cr \rightleftharpoons 2Al_2Cl_7^- + CrCl_2 + 2e^-$ **Eq. 3**

Figure 16. Statistic of current collectors used so far for aluminum dual-ion batteries (ADIBS) with corresponding side reactions of Nickel (Ni) and Iron (Fe)/Chrome (Cr) from stainless steel (SS), in contact with $AlCl_3$:EMImCl ionic liquid electrolyte before (a) 2018 and (b) starting from 2018 till present.

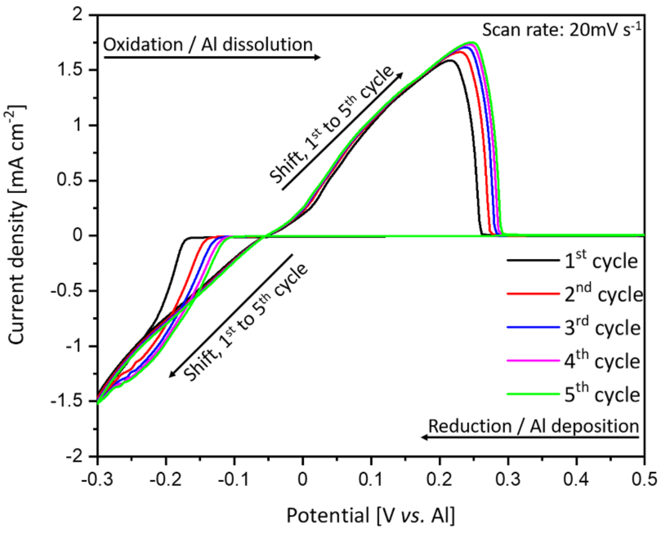


Figure 17. Cyclic voltammogram (CV) showing the influence of Al_2O_3 passivation layer on the Al dissolution/deposition in $AlCl_3$/EMImCl (1.5:1.0) ionic liquid electrolyte at 20 mV s^{-1} scan rate.

stable conductive materials such as tungsten (W) and tantalum (Ta) should be utilized. However, the high cost of those stable metals and their very high intrinsic density are huge disadvantages, the latter resulting in a high ratio of non-active and active components, leading to lower specific energy of the system [210].

Advances in science and technology to meet challenges

For material screening and correct electrochemical assessment, coin-type cells made of SS should be replaced by inert body parts, or experiments must be conducted in glass cells. For example, inert body cell parts can be made of Inconel alloy and polytetrafluoroethylene (PTFE). It is also possible to wrap unstable parts with Celgard [206]. The use of corrosion inhibitors like benzyl sulfoxide ($C_{14}H_{14}OS$) [206] or 1-octyl-3-methylimidazoliumhydrogen sulfate [211] is also a recommended strategy to reduce corrosion. Probably, the most straightforward way to avoid unwanted side reactions between electrolyte anolytes and metallic parts is to find new types of electrolytes. Ideally, chloride (Cl^-) based components should be avoided since Cl^-anions (and their complexes such as $Al_2Cl_7^-$) contribute immensely to the corrosion of metals [212, 213]. However, developing chloride-free electrolytes is very difficult due to various challenges, like poor stability associated with H_2 evolution [214]. A similar way to positively influence the ADIBS performance can be done *via* alloying the negative Al electrode. By this, it could be possible to modulate the formation of the SEI layer and/or influence the polarization or control the interfacial reaction on the anode surface [206]. Therefore, alloys of Al–Ga, Al–Ti, Al–Mo, and Al–Zr [215] were applied with promising results. The presence of a second metal could create an oxide layer with more defect sites, providing more pathways for the electrolyte to reach the fresh Al surface and enable dissolution/deposition of Al [216]. One way to minimize or reduce the oxide layer is surface pre-treatment of Al metal using procedures such as mechanical polishing, electrochemical polishing, and chemical etching, as mentioned in the 'Current and Future Challenges' section. However, Al metal is quickly re-passivated in contact with oxygen. Note that it is not urgent to remove the oxide film completely. It is more important to reconstruct the oxide structure to improve the ion/electron transfer during the charge/discharge process [216]. Last but not least, cheap current collector materials like SS can be sputtered with inert substrates, like titanium nitride (TiN) or chromium nitride (Cr_2N) [217]. Wang *et al* [217] proposed a current collector fabricated by sputtering TiN on SS or flexible polyimide (Kapton) substrates by using low-cost, rapid, scalable methods such as magnetron sputtering. TiN is highly corrosion resistant and allows a high anodic operation voltage limit [167]. Besides corrosion and side reaction issues, new and at the moment unexplored engineering challenges will occur on the way to fully realize metallic current collectors and anodes for ADIBs, such as the optimization of cathode-anode mass balance to build full cell systems.

Concluding remarks

The development of ADIBs is still at an infantile stage and faces at least one huge challenge: Namely, an insufficient plating/stripping of Al because the available electrolytes usually cause the corrosion of current collectors/metallic anode/cell parts and result in the formation of an inactive surface layer and 'dead-metal'. We emphasize the importance of current collector selection for ADIBs and explain several possibilities to modify metal-based anode. Unwanted electrochemical side reactions of the current collectors, cell-body, and anodes could lead to misinterpretation of the electrochemical reactions occurring on a given material. Indeed, the electrochemical oxidation of unstable metals leads to significant false discharge capacities from 150 mAh g^{-1} to 400 mAh g^{-1} [209]. The findings of Shi *et al* [209] indicate that the stability of the current collector is quite sensitive to experimental conditions. We suggest that researchers always test 'blank' current collector discs in the working system and avoid contact between the Lewis acidic ionic liquid electrolyte with unstable metals like SS (Fe, Cr-based compounds), Ni, platinum (Pt), Ti, etc [209].

Acknowledgments

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14. Al—organic batteries

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Status

Driven by the extensive knowledge developed in the fields of Li- and post-Li technologies, most of the cathode materials investigated in rechargeable aluminum batteries (RABs) are traditionally inorganic compounds [218]. Although aluminum (Al) is considered a safe and sustainable anode, typical inorganic intercalation and conversion cathodes hardly meet sustainability criteria. Moreover, one essential obstacle of RABs is the sluggish diffusion of Al ions within the inorganic cathode and the structural deformation that occurs during (de)intercalation of high charge-dense cations, which result in performance limitations such as insufficient rate and cycle stability in *cation-type RAB* [188, 218]. Interestingly, graphitic materials have demonstrated the ability to (de)intercalate $AlCl_4^-$ anions with enhanced cyclability and rate performance, thus introducing a new type of intercalation electrochemistry known as *anion-type RAB* (also known as *dual-ion* batteries) [172]. However, their practicability is still questionable because of lower capacities (compared to *cation-type* cathodes) and low energy density ($<$70 Wh kg^{-1}) and, sustainability [219].

In contrast, OEMs may provide an advanced and more sustainable storage solution because of their greater natural abundance, high resource availability and less toxicity. Furthermore, organic (macro)molecular engineering not only gives access to great structural diversity but also enables structure-property-performance paradigms, essential for the design of advanced OEMs with superior performances. In general, OEMs can be small molecular compounds with flexible crystal structures, linear polymers forming soft structures, or porous polymers with tunable porosity (figure 18(a)). Thanks to their unique redox ion-coordination mechanism and compatible topologies, the OEMs can accommodate high charge dense cations or bulky anions without much spatial hindrance. This guarantees high structural stability during battery operation and hence anticipates improved cyclability and enhanced performance [220]. Moreover, figure 18(b) illustrates the versatility of OEMs which can exhibit two distinct electrochemical storage mechanisms. One is characterized by anion charge compensation in p-type cathodes (e.g. pyrene, PANI, etc), resulting in *anion-type* RABs, and the other is characterized by cation compensation in n-type cathodes (e.g. quinone, imide, etc), resulting in *cation-type* RABs.

As depicted in figure 18(a), the first OEM assessment in RAB dates back to 1984 [221], and it was dedicated to the electrochemical characterization of polypyrrole in the $AlCl_3$:BuPyCl electrolyte in a half-cell. Then 1984–2018 was a dark period for the development of organic-RABs due to the mere incremental performance improvements and superiority of lithium chemistry that occurred at the same time, curtailing further development until recently. During the last years, despite the fact that significant progress has been made in the development of organic-RABs, their performance is still far from being competitive.

Current and future challenges

Table 2 compiles the electrochemical performance of selected organic-RABs reported in the literature. Noticeably, the examples reported in the last 5 years are mostly *anion-type* RABs (with p-type cathodes) that deliver enhanced overall performance with high voltage output (as high as 1.7 V), good cyclability, and fast kinetics, but limited capacities (typically below 150 mAh g^{-1}). Generally, the cyclability was not an issue in this battery configuration. For example, TpBpy COF (#4 in table 2) [222], PVBPX (#2) [223] and polythiophene (#3) [224] retained impressive capacities of 99%, 98%, and 76% over 13 000, 50 000 and 100 000 cycles, respectively. On the contrary, *cation-type* RABs (with n-type cathodes) featured higher capacities (100–240 mAh g^{-1}) but moderate cyclability and kinetics, and lower voltage output (below 1.35 V).

Despite the extensive investigations of n-type OEMs in various battery technologies, there are still many challenges associated with their use in RABs. For instance, the large radius of Al–Cl_x complexes sometimes induces sluggish kinetics and poor utilization of redox-active sites, causing decreased cyclability and capacity values. Furthermore, the solubility of small molecules mostly leads to poor capacity retention. For example, the phenanthraquinone reported by Bitenc *et al* [220] manifests an extremely fast capacity loss with only 20% retention after 20 cycles. Polymerization can limit the dissolution issue commonly encountered with small molecules. For example, the cycle stability of quinone-based linear polymers, PAQS (#5) [225] and pPQ (#6) [220] that retained 60% and 93% initial capacities after 500 cycles, respectively, has definitely improved compared to their related small molecules. However, linear polymers still lack the chemical robustness required for prolonged cyclability and/or high-rate output. To date, PANI(H^+)@SWCNT (#7) [226] not only delivered the best cyclability for an n-type polymer, maintaining 88% capacity over 8000 cycles, but also the best rate capability, maintaining 45 mAh g^{-1} at 40 A g^{-1}. Phenanthraquinone-based

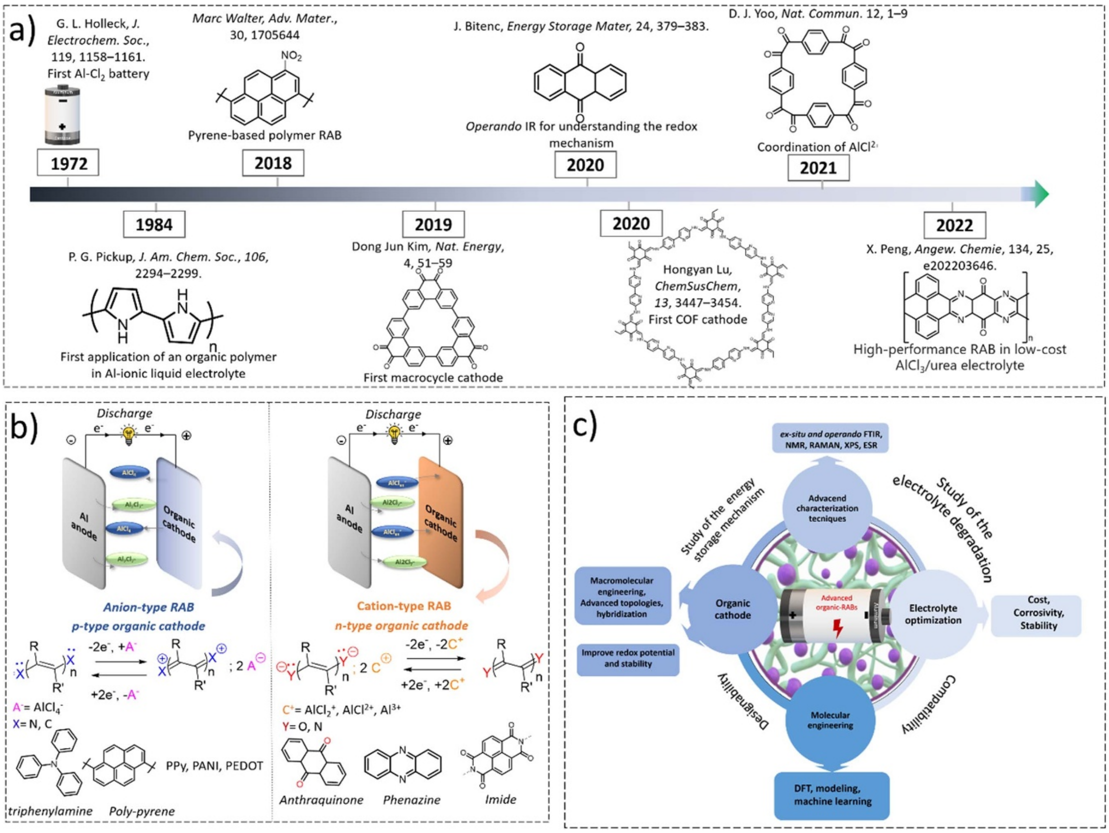


Figure 18. (a) Timeline of major developments of RABs. (b) Electrochemical discharge mechanism of *anion-type* RABs with p-type OEMs and *cation-type* RABs with n-type OEMs. (c) Research prospects in future work on RABs.

polymer (pPQ) (#6) [220] and macrocycle (#8) [227] attained the highest voltage output around 1.35 V, and PYTQ-CNT (#9) [228] delivered the highest specific capacity of 295 mAh g^{-1}. Interestingly, very recently Liu *et al* reported a *bipolar* covalent organic framework (COF) by combining n-type with p-type moieties, and applied as cathode in RABs for the first time [229]. Based on the unique redox-bipolar reaction involving both the anion and the cation coordination, the polyimide-triazine COF showed high capacity utilization (80.5%), a specific capacity of 132 mAh g^{-1} and impressive cycling stability over 4000 cycles (with 0.0007% decay per cycle). However, a challenge remains the moderate discharge voltage of 1.3 V.

Despite notable achievements, a critical challenge remains: advancing the electrochemical performance of organic RABs specifically with n-type cathodes, simultaneously enhancing voltage, capacity, rate, and cycling performances using a single class of OEM.

Moreover, from practicability aspects, it is first essential to carefully assess the corrosivity, cost and compatibility between conventionally used ionic liquid electrolytes and OEM. Then, strategies should be developed to maximize the OEM content and mass loading of the cathode to ensure optimal overall performance, as described in the next section.

Advances in science and technology to meet challenges

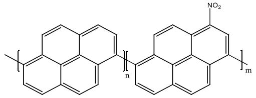
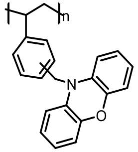
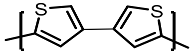
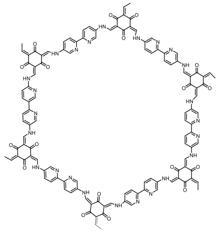
Performance: efforts must be focused on **(macro)molecular engineering**, preferably driven by simulation, **modeling,** and ML, in order to design OEMs presenting enhanced overall performance. For instance, by introducing electron-withdrawing chloride groups, the discharge voltage of base naphthoquinone was significantly boosted from 1.1 to record 1.5 V [233]. In another example, the self-adaptive re-organization mechanism from α-poly(thiophene) to β-poly(thiophene) (#3) during cycling, rendered superb rate and cyclability up to 100 000 cycles [224].

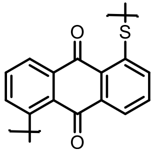
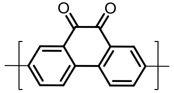
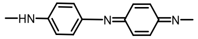
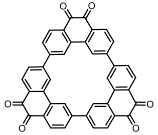
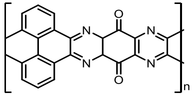
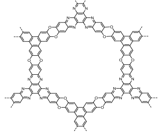
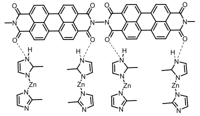
Furthermore, OEMs with **advanced topologies,** such as macrocycles with layered superstructures (#8) [227], COF (#4) [222], MOF (#11) [232] and hybrid COF (#10) [231] have been shown to significantly boost the overall electrochemical performance.

Hybridization of OEMs with carbon additives (e.g. carbon nanotubes) has proven to enhance material utilization and kinetics, owing to the improved interactions between the electrode components [226].

Mechanism: a better understanding of the charge storage mechanisms is crucial since electrochemical reactions are much more complicated in this technology which contains a high number of ion-complexes in

Table 2. A non-exhaustive list comprising the electrochemical performance of organic-RABs.

	p-type organic cathodes			
	# 1	# 2	# 3	# 4
Polymer structure	Poly(nitropyrene-co-pyrene) [230] 	PVBPX [223] 	Polythiophene [224] 	TpBpy COF [222] 
Capacity (mAh g^{-1})/current density (A g^{-1}) Capacity/current density /N° of cycle/capacity retention (%)	100/0.2 85/0.2/1000/70	133/0.2 133/0.2/50 000/98	180/2 106/10/100 000/75.5	245/0.1 150/2/13 000/99
Average voltage output (V)[a]	1.7	1.2	1.4	1.3

n-type organic cathodes						
# 5	# 6	# 7	# 8	# 9	# 10	# 11
PAQS/MWCNT [225] 	pPQ [220] 	PANI(H$^+$)@SWCNT [226] 	PQ- Δ [227] 	PYTQ-CNT [228] 	HATN-HHTP@CNT (40%) [231] 	PI-MOF [232] 
190/∼ 0.13 150/∼ 0.13/500/93	168/∼ 0.13 160/∼ 0.13/500/60	200/1 100/10/8000/87.6	110/0.1 94/∼ 2/5000/59	295/0.1 114/1/4000/77	128/0.01 110/0.5/350/80	83/1 83/1/1800/87
1.1	1.35	1	1.35	1.1	0.75	1.1

[a] Due to the considerable sloping nature of the charge-discharge voltage profiles, the average voltage output of the cell is approximately taken as the voltage value at 50% discharge capacity.

the electrolyte. *Ex-situ* ATR, Raman, and XPS of charged/discharged electrodes are commonly used for this purpose, but obtaining mechanistic information is challenging as the samples often degrade rapidly, especially in the discharge state. Furthermore, *ex-situ* SEM-EDS, XPS and TOF-SIMS are also helpful to qualitatively assess the nature of the charge carrier. Therefore, *in-situ* and *operando* techniques have been proposed recently for tracking all the electrochemical reactions. For instance, Bitenc *et al* used *operando* FTIR to evaluate reversible reactions between poly(anthraquinone) and $AlCl^{2+}$ complexes [220, 225]. Wang *et al* assessed the radical mechanism of triphenylamine cathodes using *in-situ* ESR [234], and multidimensional solid-state NMR spectroscopy was employed by Gordon *et al* to unveil the reversible enolization/$AlCl_2^+$ electrochemistry in indanthrone quinone [235].

Practicability: n-type cathodes able to operate at high voltages are preferred over p-type because they have the potential to store multivalent cations. While most of the reported n-type cathodes have been demonstrated to store monovalent $AlCl_2^+$, some compounds such as tetradiketone macrocycles store divalent $AlCl^{2+}$ owing to the presence of adjacent carbonyl groups. These groups form a stable chelate with $AlCl^{2+}$, as confirmed by both experiments and DFT calculations, guaranteeing high capacity (350 mAh g^{-1}) [236]. Indeed, the ability to store multivalent cations not only increases the capacity/energy density of the RABs, but also makes them more practical as they would require less quantity of electrolyte.

Urea-based deep eutectic electrolytes ($AlCl_3$: urea), proposed as a cost-effective and less-toxic electrolyte, have been also tested in organic-RABs [228]. Recently, a heterocyclic conjugated polymer cathode (#9) delivered an impressive high capacity of 295 mAh g^{-1} with reasonable stability over 4000 cycles using this electrolyte [228]. Unfortunately, the lower performance of the anodic reaction in this electrolyte limits the current/power density of the battery.

Concluding remarks

Although organic cathodes applied in RABs are still in their infancy, unlike inorganic materials, OEMs have demonstrated high versatility in storing both Al-Cl_x cations and anions. Moreover, they exhibit competitive or even better electrochemical performance compared to their inorganic counterparts. Further effort should focus on an integrated approach of (i) computer-driven molecular engineering to design advanced organic cathodes, (ii) *in-situ* and *operando* advanced characterization techniques for an in-depth understanding of charge storage mechanism and, (iii) electrolyte optimization to further elevate the potential of Al-organic batteries (as prospected in figure 18(c)).

For practicability, n-type cathodes are credible candidates for achieving the touted energy density of RABs, as they are projected to store multivalent cations in non-flooded electrolyte systems. However, identifying such innovative OEMs is still an ongoing challenge. Furthermore, urea-based solvents, which have been shown to be cost-effective and less toxic electrolytes, present a limited electrochemical stability window and ionic conductivity, hindering the performance of the RABs. Finally, the cost-performance analysis of organic-RABs should be done to evaluate their competitiveness. Since the specific areal capacity has a tremendous impact on battery cost, RAB will become viable only if practical level areal capacities ($>$3 mAh cm^{-2}) are achieved. Therefore, strategies to maximize OEM content and its mass loading in the cathode should be adapted, since they are currently typically below 70 wt% and 2 mg cm^{-2}, respectively.

Acknowledgements

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15. Zn based batteries—anodes

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Status

Research on Zn ion batteries (ZIBs) anodes has been a topic of significant interest due to the potential of ZIBs as large-scale energy storage devices [237]. The unique merits of ZIBs, such as intrinsic safety, low cost, and relatively high theoretical energy density, have positioned them as promising alternatives to LIBs for energy storage applications [238]. However, the development of ZIB anodes has been accompanied by several challenges that have hindered their commercialization. One of the primary challenges is the uncontrollable growth of Zn dendrites on the anode surface, which can lead to internal short circuits and reduced battery performance [239]. Additionally, the occurrence of the hydrogen evolution reaction (HER) and side reactions on the Zn anodes has been identified as a significant issue that deteriorates the CE and overall performance of ZIBs [240].

To address these challenges, extensive research has been conducted to understand the fundamental processes involved in Zn deposition and to develop rational strategies for improving the performance of ZIB anodes. Fundamental insights into Zn deposition, including nucleation, electro-crystallization, and growth of the Zn nucleus, have been systematically clarified to provide a solid foundation for further research [241–244]. In the quest for high-performance ZIB anodes, critical factors influencing Zn plating have been investigated. These factors include the utilization of Zn, dendrite growth, repeated plating/stripping processes, and the impact of Zn powder versus Zn flake anodes [245]. For example, Zn powder has been identified as having more industrial application prospects compared to Zn flake due to its adjustable loading quality and diversified processing technology, which can potentially address the challenges associated with Zn anodes [246].

Furthermore, rational strategies emphasizing coating structural design and interface engineering have been proposed to improve the performance of ZIB anodes. These strategies include the use of coatings on the Zn anode surface to inhibit HER and corrosion, as well as the development of advanced interface modification techniques to guide uniform Zn deposition and prevent dendrite formation [247–249]. Despite the progress in ZIB anode research, there are still challenges that need to be addressed for the practical application of ZIBs. These challenges include modulating the relationship between the depth of discharge (DOD) and CE of the Zn anode, selecting suitable types of Zn anodes for ZIBs, and improving the stability of Zn anodes under extreme operating conditions [250–252].

Current and future challenges

The widespread utilization of ZIBs (figure 19(a)) faces significant challenges arising from the interplay of Zn dendrites, the HER, and corrosion. Specifically, the first current challenge comes to the uncontrollable growth of Zn dendrites on the anode surface, which can lead to internal short circuits and reduced battery performance [249]. The non-uniform distribution of the electric field and Zn^{2+} induces uneven Zn deposition and dendrite growth. Due to weak adhesion to the Zn anode, these dendrites easily detach, leading to the issue of 'dead Zn.' Dendrite growth is a complex phenomenon that is influenced by several factors, including the electrolyte composition, current density, and anode morphology [253]. While several strategies have been proposed to mitigate dendrite growth, such as the use of additives in the electrolyte and the development of advanced interface modification techniques on anodes, there is still a need for further research to fully understand the mechanisms underlying dendrite growth and to develop effective strategies to prevent it.

Another challenge is the occurrence of the HER and side reactions on the Zn anodes, which deteriorate the CE and overall performance of ZIBs. HER is a parasitic reaction that occurs when the overpotential for Zn deposition is too low, leading to the evolution of hydrogen gas [254]. From a thermodynamic standpoint, the inevitable occurrence of the HER elevates local OH^- concentrations, promoting corrosion and generating inert by-products, such as $Zn_4SO_4(OH)_6 \cdot xH_2O$ (ZHS) [255]. This exacerbates interfacial concentration polarization and fosters Zn dendrite growth. Side reactions, such as the formation of ZnO and $Zn(OH)_2$, can also occur on the anode surface, reducing the capacity and stability of the ZIBs [256].

Anticipated future challenges in this domain encompass the imperative to enhance not only high-rate performance but also CE and overall stability, especially when confronted with extreme operating conditions. Addressing these challenges is pivotal for advancing the efficacy and reliability of the systems involved, propelling the field towards greater efficiency and resilience in the face of demanding operational

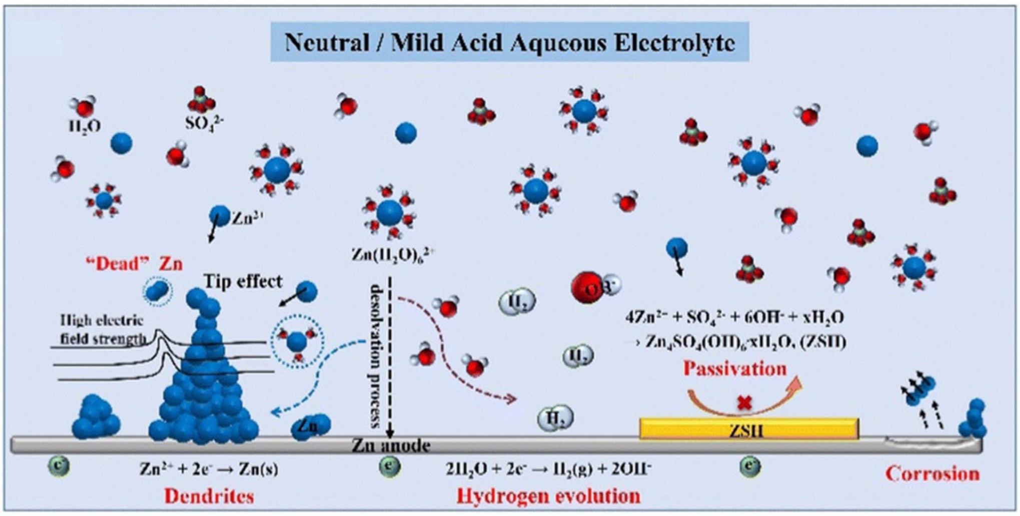

Figure 19. Scheme of the mechanism of dendrite growth, HER, and side reactions for the Zn anode. Reproduced from [246] with permission from the Royal Society of Chemistry.

scenarios. The pursuit of heightened high-rate performance involves optimizing the system's ability to deliver and absorb energy rapidly, responding effectively to dynamic requirements. Simultaneously, elevating CE remains a key objective, aiming to maximize the utilization of charge and discharge cycles with minimal losses, thereby contributing to the overall efficiency of the energy storage or conversion process [257]. Additionally, ensuring stability under extreme operating conditions entails fortifying the system against factors such as temperature fluctuations, mechanical stress, and other external variables that may adversely affect its performance. Another future challenge is the need to improve the energy density and cost-effectiveness of ZIBs. While ZIBs have a relatively high theoretical energy density compared to other battery technologies, such as lead-acid batteries, their practical energy density is still lower than that of LIBs. Additionally, the cost of ZIBs needs to be reduced to make them more competitive with other battery technologies. To address these challenges, there is a need for further research to develop advanced manufacturing processes to reduce the cost of ZIBs.

Advances in science and technology to meet challenges

To meet the challenges facing ZIBs anode research, significant advances in science and technology have been made in recent years. These advances have focused on developing new coating materials, optimizing manufacturing processes, and improving the understanding of fundamental processes involved in Zn deposition.

One of the key advances in ZIB anode research has been the development of advanced coating materials, such as Zn anodes with improved morphology [258]. For example, Dong *et al* proposed an anionic polyelectrolyte alginate acid (SA) coating on Zn anodes to initiate the *in-situ* formation of the high-performance SEI layer inspired by biomass seaweed plants [259]. This interface modification well inhibits the irregular growth of Zn dendrites and assists the uniform deposition of Zn on anodes, as shown in figure 20(a). The scanning electron microscopy (SEM) images presented in figure 20(b) provide additional support for the observation that the anionic polyelectrolyte-coated Zn anode demonstrates a consistently uniform and dendrite-free morphology, in contrast to the irregular and bumpy surface observed on the bare Zn anode. Additionally, the use of metal coatings on the Zn anode surface has been shown to inhibit HER and corrosion, improving the stability and performance of ZIBs.

Substituting the planar Zn foil with 3D porous electrodes offers a significant enhancement in charge distribution and interfacial electric field uniformity, resulting in an anode free from dendrite formation [250]. The scientific community has made notable strides in Zn anode development, introducing hierarchical porous structures that guide consistent Zn deposition, effectively inhibiting dendrite growth [260–262]. Another notable advancement in ZIB anode research involves refining manufacturing processes to lower costs and enhance overall performance. Examples of this are the creation of a scalable and cost-efficient method for producing Zn anodes through a straightforward electroplating process, roll-to-roll processing and 3D printing [238, 263, 264]. Furthermore, the integration of advanced characterization techniques, such as in situ microscopy and spectroscopy, has empowered researchers to deepen their

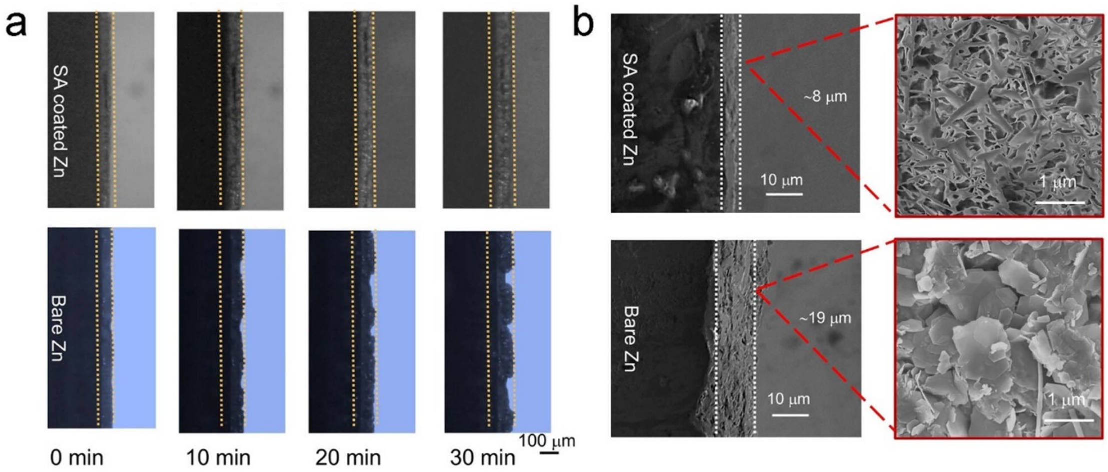

Figure 20. (a) Optical microscope images captured in situ depict the Zn^{2+} plating process on both the SA-coated Zn electrode and the uncoated Zn electrode, conducted at a current density of 10 mA cm^{-2}. (b) SEM images present cross-sectional and horizontal views of the Zn anode, showcasing both bare and SA-coated configurations after undergoing 50 cycles at 0.5 mA cm^{-2} with a capacity of 0.5 mAh cm^{-2}. Reproduced from [259]. CC BY 4.0.

understanding of the fundamental processes related to Zn deposition [265–267]. This knowledge has paved the way for more effective strategies aimed at improving the performance of ZIBs.

Concluding remarks

While significant progress has been made in ZIB anode research, there are still several challenges that need to be addressed for the practical application of ZIBs in large-scale energy storage systems. These challenges include dendrite growth, HER and side reactions, stability under extreme operating conditions, energy density, and cost-effectiveness. Addressing these challenges will require further research and development of advanced strategies and materials to improve the performance and competitiveness of ZIBs. Advances in science and technology have played a critical role in meeting the challenges facing ZIBs anode research. These advances have focused on developing new coating materials, optimizing manufacturing processes, and improving the understanding of fundamental processes involved in Zn deposition. While significant progress has been made, there is still a need for further research and development of advanced strategies and materials to improve the performance and competitiveness of ZIBs.

Acknowledgements

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16. Zn based batteries—cathodes

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Status

The development of cathode materials for ZIBs has been a subject of intense research in recent years, driven by the need for cost-effective and environmentally friendly energy storage solutions [268–270]. Current research progress in cathode research for ZIBs has focused on addressing the challenges associated with these materials, including low energy density, limited understanding of charge storage chemistry, dissolution of active materials, unsatisfactory electronic conductivity, and practical challenges associated with manufacturing and integration [238, 269, 271–273].

One of the key areas of research progress in cathode research for ZIBs is the development of new materials with improved electrochemical performance [274]. Researchers have been exploring a wide range of cathode materials, as shown in figure 21, including Mn-based oxides, V-based compounds, Prussian blue analogues (PBAs), organic compounds, layered chalcogenides, and polyanions, to identify materials that exhibit enhanced stability, higher capacity, and improved charge transfer kinetics. Zn^{2+}, H^+, active material dissolution/deposition, and conversion reactions are considered to be the energy storage mechanisms of cathode materials, which makes the energy storage mechanism of aqueous ZIBs complex [275–277]. Recent research has also focused on the development of cathode materials based on transition metal dichalcogenides (TMDs), which exhibit high theoretical capacity, excellent stability, and fast charge transfer kinetics. These materials have shown promising electrochemical performance, making them attractive candidates for practical application in ZIBs [278]. Another area of research progress in cathode research for ZIBs is the advancement of understanding of the charge storage chemistry and mechanisms of cathode materials. *In-situ* spectroscopy, operando XRD, and computational modeling, etc. have been employed to study the cathode structure [267, 279, 280]. This improved understanding has facilitated the rational design of new materials with tailored properties to meet the specific requirements of ZIBs.

Advances in the electronic conductivity of cathode materials have also been a focus of research progress in cathode research for ZIBs [274]. Researchers have explored various strategies to enhance the electronic conductivity of cathode materials, including the incorporation of conductive additives, nano-structuring, and the development of hybrid materials [281]. For example, recent research has focused on the development of cathode materials based on CNTs, which exhibit excellent electronic conductivity and high surface area, leading to improved electrochemical performance [275]. In the realm of manufacturing and scale-up, research progress has focused on the development of cost-effective and scalable production methods for ZIBs cathodes [282]. Advances in electrode fabrication techniques, such as roll-to-roll processing, inkjet printing, and spray coating, have enabled the production of ZIB cathodes with tailored microstructures and compositions [238]. These advancements have paved the way for the integration of cathode materials into practical battery systems, bringing ZIBs closer to commercialization.

Current research status in cathode research for ZIBs has focused on addressing the challenges associated with these materials, including low energy density, limited understanding of charge storage chemistry, dissolution of active materials, unsatisfactory electronic conductivity, and practical challenges associated with manufacturing and integration [283]. Advances in the development of new materials, understanding of charge storage chemistry, enhancement of electronic conductivity, electrolyte design, and manufacturing methods have collectively propelled ZIBs towards practical viability. Continued research and innovation in these areas will further accelerate the development and commercialization of ZIBs for diverse energy storage applications.

Current and future challenges

Cathode materials are a critical component of ZIBs and play a crucial role in determining the electrochemical performance and practical viability of these batteries. While significant progress has been made in the development of cathode materials for ZIBs, several current and future challenges must be addressed to enable their widespread commercialization and practical application.

One of the primary challenges facing cathode materials for ZIBs is the low energy density compared to LIBs [284]. The theoretical capacity of cathode materials for ZIBs is lower than that of LIBs, which limits the amount of energy that can be stored in a given volume or weight of the battery. This limitation is particularly significant for applications that require high energy density, such as electric vehicles and portable electronics [285]. Another challenge is the limited understanding of the charge storage chemistry and critical factors that

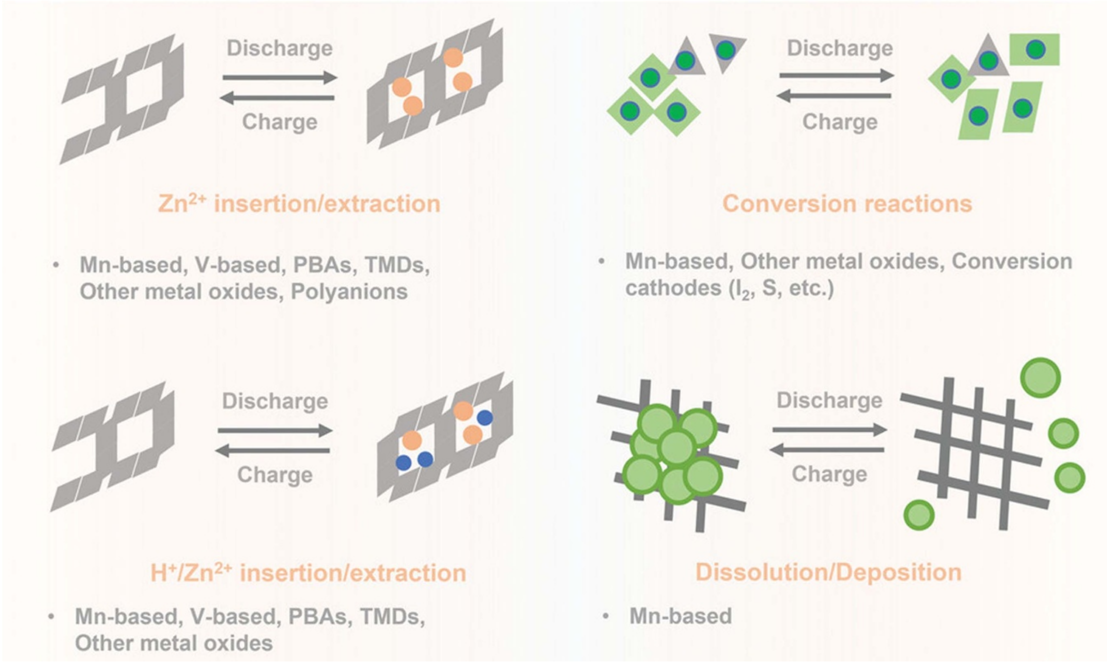

Figure 21. Scheme of the storage mechanism for commonly used cathode materials in aqueous ZIBs. [277] John Wiley & Sons. © 2023 The Authors. Advanced Functional Materials published by Wiley-VCH GmbH.

control electrochemical reactivity in cathode materials [286]. The complex redox chemistry of cathode materials for ZIBs makes it challenging to determine the genuine storage mechanism, including the inserted ions, inserted sequence, and structural changes [287]. A better understanding of the fundamental mechanisms of cathode materials is essential for the rational design of new materials with improved electrochemical performance.

Dissolution of active materials, especially Mn-based and V based cathode materials, is another significant challenge for cathode materials in ZIBs [277]. The mild-acid aqueous electrolytes used in ZIBs can degrade the electrochemical and chemical stability of cathode materials, leading to the dissolution of active materials into the electrolyte [288]. This can result in structural degradation and collapse of the cathode material, limiting the lifespan of the battery. Developing cathode materials with improved stability and resistance to dissolution is crucial for the practical application of ZIBs.

Enhancing the electronic conductivity of cathode materials is imperative for advancing ZIBs. Many cathode materials exhibit suboptimal electronic conductivity, necessitating the inclusion of numerous conductive species, albeit at the expense of active mass loading [289]. Developing cathode materials with improved electronic conductivity becomes essential to bolster the overall efficiency and performance of ZIBs. The critical role of active material loading in ZIB cathodes directly influences energy storage capacity and overall battery performance. Optimization not only boosts individual battery energy density but also enhances economic efficiency. Strategies like roll-to-roll coating and self-supporting approaches aim to increase cathode active material mass loading [275, 290–292]. Overcoming practical challenges in scalable synthesis, efficient manufacturing, and seamless integration into battery systems necessitates collaborative efforts from researchers, manufacturers, and policymakers. This multifaceted approach aims to create new materials, optimize processes, and establish performance and safety standards for ZIBs.

Advances in science and technology to meet challenges

In response to the challenges facing cathode materials for ZIBs, significant advances in science and technology have been made to address these issues and pave the way for the practical application of ZIBs.

One of the key areas of advancement is the development of new cathode materials with improved electrochemical performance. Researchers have been exploring a wide range of cathode materials, including Mn-based oxides, V-based compounds, PBAs, organic compounds, layered chalcogenides, and polyanions, to identify materials that exhibit enhanced stability, higher capacity, and improved charge transfer kinetics [290–292]. These efforts have led to the discovery of novel cathode materials with promising electrochemical properties, bringing ZIBs closer to practical viability. Advances in understanding the charge storage chemistry and mechanisms of cathode materials have also been instrumental in addressing the challenges associated with ZIBs. Researchers have employed advanced characterization techniques, such as in situ spectroscopy, operando XRD, and computational modeling, to gain insights into the redox processes, structural changes, and ion insertion/extraction mechanisms in cathode materials [267]. This improved understanding has facilitated the rational design of new materials with tailored properties to meet the specific requirements of ZIBs. In the quest to enhance the electronic conductivity of cathode materials, significant progress has been made through the incorporation of conductive additives, nano-structuring, and the development of hybrid materials [293]. These advancements have led to the improvement of the overall electronic conductivity of cathode materials, reducing the need for a large number of conductive species and enabling higher active mass loading in the cathode electrode. Additionally, the use of advanced manufacturing techniques, such as electrodeposition and chemical vapor deposition, has enabled the precise control of the microstructure and morphology of cathode materials to optimize their electronic conductivity.

On the other hand, research on cathode materials also aims to inhibit the dissolution of active materials by addressing the underlying mechanisms and employing various strategies to enhance the stability and integrity of the cathode [294]. Several approaches have been explored to mitigate the dissolution of cathode materials in ZIBs, including electrolyte modification, new cathode material development and surface modification techniques [295]. By optimizing the composition and pH of the electrolyte, researchers aim to minimize the corrosive impact on the cathode materials, thereby reducing the dissolution of active species into the electrolyte [242]. Additionally, the exploration of new electrolyte additives and the optimization of electrolyte compositions have contributed to enhancing the compatibility between cathode materials and the electrolyte, thereby improving the overall stability of ZIBs [296]. Advances in new cathode material development have played a crucial role in inhibiting the dissolution of cathode materials. Researchers have been exploring new cathode materials with enhanced chemical and structural stability to minimize the dissolution of active species. For example, the development of cathode materials based on TMDs has shown promise in inhibiting dissolution due to their excellent stability and resistance to chemical degradation [172]. By identifying materials that are less prone to dissolution and degradation, researchers aim to improve the long-term stability and cycling performance of ZIB cathodes. Surface modification techniques have been employed to create protective layers or coatings on the cathode materials, inhibiting the dissolution of active species [297]. For instance, the application of thin film coatings, such as polymer coatings or inorganic protective layers, has been investigated to create barriers that prevent the dissolution of active materials into the electrolyte [298]. These surface modification techniques aim to enhance the chemical and structural stability of the cathode materials, thereby reducing the propensity for dissolution and improving the overall performance of ZIBs.

Concluding remarks

Cathode materials for ZIBs face several current and future challenges that must be addressed to enable their widespread commercialization and practical application. These challenges include low energy density, limited understanding of charge storage chemistry, dissolution of active materials, unsatisfactory electronic conductivity, and practical challenges associated with manufacturing and integration. Addressing these challenges requires a collaborative effort from researchers, manufacturers, and policymakers to develop new materials, optimize manufacturing processes, and establish standards for the performance and safety of ZIBs. The development of new cathode materials, improved understanding of charge storage chemistry, enhancement of electronic conductivity, electrolyte design, and manufacturing advancements have collectively propelled ZIBs towards practical viability. Continued research and innovation in these areas will further accelerate the development and commercialization of ZIBs for diverse energy storage applications.

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17. Zn based batteries—electrolytes

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Status

One of the key components that significantly impacts the performance of ZIBs is the electrolyte, which plays a critical role in facilitating the transport of ions between the cathode and anode, thus influencing the battery's electrochemical performance, safety, and overall efficiency [299]. The battery's capacity, power capability, cycle life, safety, and stability, are markedly determined by the key properties of the electrolyte, such as ionic conductivity, electrochemical stability window, viscosity, and compatibility with other battery components [300]. Low ionic conductivity of electrolytes can limit the rate of charge and discharge, leading to reduced power capability [301]. Electrolytes with narrow electrochemical stability windows may limit the battery's operating voltage range, reducing the capacity and overall energy density [296]. Moreover, safety concerns such as electrolyte decomposition or formation of solid-electrolyte interphases (SEIs) can compromise the battery's safety and stability [302].

To overcome these challenges and improve the performance of ZIBs, there is an essential need to develop novel electrolytes with favorable properties. Commonly used electrolytes for ZIBs include aqueous and non-aqueous solutions of zinc salts such as zinc sulphate, zinc chloride, zinc triflate, etc. Traditional electrolytes used in ZIBs suffer from limitations such as limited voltage stability, low ionic conductivity, and safety concerns. Therefore, there is a growing interest in exploring electrolyte strategies that can address these issues and enhance the performance of ZIBs.

Current and future challenges

In ZIBs, aqueous electrolyte challenges encompass water decomposition, Zn dendrites, and corrosion (self-discharge) [303]. Water decomposition in aqueous media involves oxygen evolution reaction (OER) and HER, each requiring specific electron transfers [304]. The reaction pathway is influenced by electrolyte pH and electrode surface structure. An ideal electrolyte solvent should possess a wide stable EW. Commonly, the energy level difference between the lowest unoccupied molecular orbital and highest occupied molecular orbital is used to estimate EW [305]. Various methods, including thermodynamic cycles, are employed for more accurate estimates. The inherent thermodynamic oxidation potential (OER) and reduction potential (HER) with a voltage window of 1.23 V between them, and its narrow EW limits the operating voltage, resulting in a lower energy density, as shown in figure 22 [302]. OH^- formation during reactions degrades electrolyte and forms by-products on electrodes, diminishing battery performance. Suppressing water splitting and expanding the operating voltage window are vital for aqueous battery development. Strategies like water-in-salt, pH control, isotope effects, SEI modification, electrolyte additives, artificial protective layers, polymer coatings, and ionic liquids aim to broaden the stable EW, ensuring stable and extended output voltage in aqueous batteries [242, 306–308].

Zn dendrite formation is another side reaction that can occur in ZIBs. Zn metal is relatively abundant and can be directly used as anodes, which is one of the reasons why aqueous ZIBs have attracted much attention. But repeated deposition/stripping can also cause uneven deposition, resulting in dendrites [258, 309, 310]. Dendrites are small, flower-like structures that form on the surface of the Zn anode during battery operation. These structures can pierce the separator and cause a short circuit, leading to reduced battery performance and safety. The strategies of inhibiting Zn dendrites from the electrolyte perspective have the following aspects: adding inert components, pH buffer, Zn deposition aid, etc. to the aqueous electrolyte solution. Side reactions such as corrosion and passivation while charging and discharging have a strong relationship with CE and cycle stability [311]. Furthermore, corrosion, or self-discharge, is a side reaction that occurs in strong acid or strong alkaline aqueous solutions, which not only affects the CE but also causes irreversible water consumption and electrolyte concentration changes, often at the electrode-electrolyte interface [312]. Hence, limiting the chemical interaction at the electrode-electrolyte interface is essential for preventing electrode corrosion. Addition of inorganic or organic corrosion inhibitors to electrodes or electrolytes is the most often described strategy for reducing the corrosion rate of electrode materials at this time [313].

Future challenges in ZIBs electrolytes will center on the strategic development of cost-effective formulations. This involves the intricate task of designing electrolytes that not only meet the demanding performance criteria but also do so in an economically efficient manner. Researchers and engineers will need to explore innovative approaches, such as optimizing the selection and combination of electrolyte components, to strike a balance between performance, cost, and scalability. Additionally, addressing the

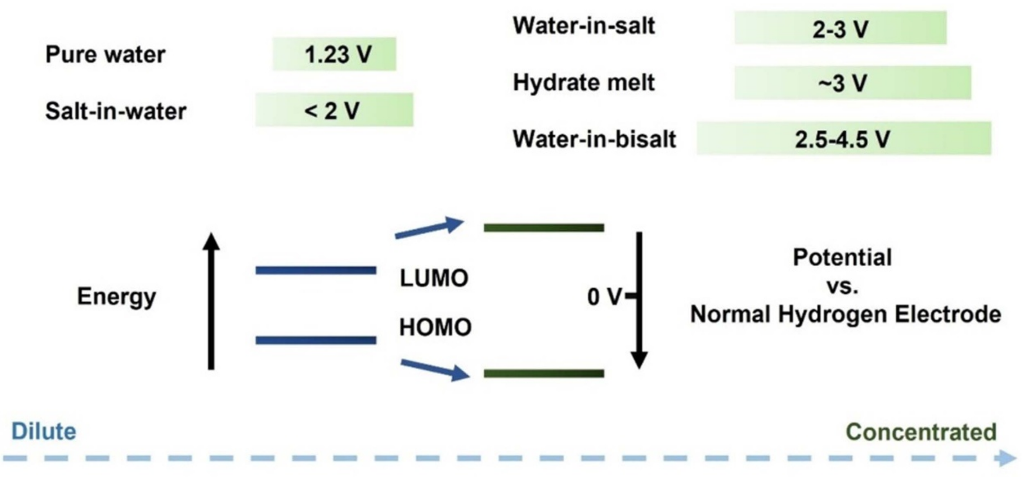

Figure 22. Illustration of output voltage extension from the standpoint of overpotential using water-in-salt or hydrate-melt electrolytes. Traditional aqueous electrolyte is referred to as the salt-in-water electrolyte. Reproduced from [302]. CC BY 4.0.

challenges associated with large-scale production and ensuring the stability and safety of these cost-effective electrolyte formulations will be pivotal for the widespread adoption and success of ZIBs in various applications.

Advances in science and technology to meet challenges

The influence of side reactions and Zn dendrites on battery performance and safety cannot be understated, which further reflects the importance of electrolyte strategy [314]. Both HER and OER divert electrons that could otherwise contribute to charging the battery, resulting in decreased performance. Furthermore, the production of hydrogen gas and hydroxide ions can lead to battery swelling and rupture, posing safety concerns [302]. Various strategies have been devised to mitigate these side reactions, including the use of additives in the electrolyte to suppress water decomposition and dendrite formation. However, the incorporation of additives may introduce new challenges such as decreased battery performance or increased costs, which can vary depending on concentration [315].

Additives play a crucial role in stabilizing electrolytes by suppressing unwanted side reactions or forming a passivation layer on the electrode surface. For instance, organic additives like sorbitol have been employed to curb undesired effects in the electrolyte. Some pH stabilizers effectively alleviate uneven Zn deposition on anodes. In 2023, Zhang *et al* introduced $NH_4H_2PO_4$ (NHP) to stabilize pH during ZIBs cycling, suppressing dendrite generation and side reactions, thus enhancing battery performance [242]. NH_4^+ forms a protective layer on the Zn surface, preventing direct contact with water, while the combination of NH_4^+ and $H_2PO_4^-$ maintains a favorable pH at the electrode-electrolyte interface, facilitating highly reversible galvanization and stripping processes in ZIBs. The interface between the electrolyte and electrode significantly impacts battery performance and stability. Protective coatings like carbon, metal oxides, or polymers applied to the electrode surface enhance adhesion, reducing crack or gap formation that may trigger unwanted reactions. Another approach involves modifying the electrolyte, with gel polymer electrolytes (GPEs) inhibiting Zn dendrite formation and mitigating parasitic reactions by restricting ion migration and water content [316]. Qin *et al* introduced a chemical welding approach that uses *in-situ* creation of a gel electrolyte, allowing ZIBs to achieve an ultralong life and reversibility [317]. The resulting well-bonded and water-poor interface between the electrode and electrolyte, achieved through the direct inclusion of the Zn anode in the chemical production of the gel electrolyte, reduces side reactions and facilitates preferential Zn deposition, resulting in an *in-situ* symmetric cell with an extremely long lifetime of 5100 h and a hybrid capacitor operating smoothly for over 40 000 cycles at 20 $A\,g^{-1}$.

An effective strategy for improving battery performance involves optimizing the electrolyte composition, as it plays a crucial role in controlling ion transport, chemical reactions, and thermal properties, thereby influencing overall battery stability [318–320]. For instance, the addition of salts like $Zn(TFSI)_2$ enhances electrolyte conductivity and stability by promoting the dissociation of Zn^{2+} [321–323]. Parameters subject to optimization include the choice of solvent, salt concentration, pH, and the inclusion of additives [310, 324, 325]. In 2023, Gao *et al* introduced the electrochemical effect of isotopes (EEI) of water into ZIB electrolytes, mitigating severe side reactions and extensive gas generation, as shown in figure 23 [296]. The use of D_2O results in a larger EW, reduced pH changes, and diminished zinc hydroxide sulphate (ZHS) generation due to

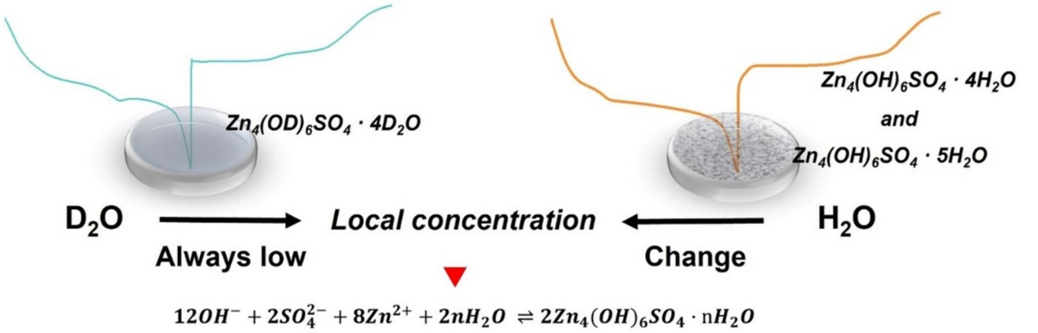

Figure 23. Scheme of the effect of D_2O-based and H_2O-based electrolytes on the formation of ZHS on the cathode surface based on the differences in local concentration. Reproduced from [296]. CC BY 4.0.

the low diffusion coefficient and high ion coordination in D_2O. In H_2O system, as the cycle proceeds and the electrolyte is consumed, the local concentration distribution of water molecules at the interface between the electrode and the electrolyte is uneven, thus forming a mixed phase of $Zn_2(OH)_2SO_4{\cdot}4H_2O$ and $Zn_2(OH)_2SO_4{\cdot}5H_2O$ is produced during the second discharge. However, due to the strong coordination and low diffusion brought by D_2O, D_2O-based electrolytes can keep the local concentration at a low level during charging and discharging. Therefore, for all D_2O-based full cells, it is difficult to find $Zn_2(OH)_2SO_4{\cdot}5H_2O$ on the cathode. D_2O-based electrolytes exhibit stable wide EWs and minimal gas generation, showcasing enhanced stability in full cells after 1000 cycles over a wide voltage range of 0.8–2.0 V and 3000 cycles over a typical voltage window of 0.8–1.9 V at a current density of 2 A g^{-1}, displaying approximately 100% reversible efficiency.

Concluding remarks

Aqueous electrolyte in ZIBs have gained considerable attention due to their affordability, safety, and the abundant availability of resources. However, the performance of ZIBs faces limitations due to side reactions like water decomposition, Zn dendrites, and corrosion occurring during electrochemical processes. These reactions induce irreversible changes in electrodes, reducing capacity and lifespan. Effective strategies to mitigate side reactions in ZIBs involve the use of additives, modification of the electrolyte-electrode interface, and optimization of electrolyte composition, enhancing their commercial viability. It is essential to recognize that these strategies are not mutually exclusive, and a combination may be necessary for optimal ZIBs performance. Despite notable progress, continuous research is needed to enhance ZIBs commercial viability, particularly in understanding the mechanisms behind side reactions. Identifying specific chemical reactions during electrochemical processes can guide the design of improved electrolytes and electrode materials. Additionally, comprehending the impact of various operating conditions, including temperature, current density, and cycling rates, is crucial for optimizing ZIB performance. Another research focus is developing cost-effective and scalable manufacturing processes for ZIBs, considering available electrolyte materials like Zn triflate. Despite Zn's low cost and abundant availability, large-scale ZIBs production remains challenging. Advancements in manufacturing processes for ZIBs can reduce production costs and enhance commercial viability. Continued research in this area is vital for improving ZIB performance and competitiveness with LIBs, especially in grid energy storage applications. Ongoing research may also unveil materials and electrolytes less prone to side reactions, further enhancing ZIB performance and viability.

Data availability statement

No new data were created or analysed in this study.

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