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## 1 Introduction

Various metals have been used as battery anodes in electrochemical cells ever since the birth of the battery with Volta's pile. It was also true for the first primary (Zn/MnO<sub>2</sub>) and secondary (Pb/acid) batteries introduced in the market. Almost all commercial technologies using metal anodes are either primary batteries, or operate through mechanisms avoiding both the need of transporting multivalent ion charge carriers across the electrolyte and the metal plating/stripping process. One example is Ni/Cd cells in which Cd oxidizes to Cd(OH)<sub>2</sub>. For more modern, twentieth century secondary/rechargeable batteries, safety issues related to dendrite formation from the metal plating/stripping process caused the withdrawal of lithium metal anode-based batteries from the market in the 1980s - which also paved the way for the lithium-ion battery (LIB) in the 1990s. This issue seems to be mitigated only through the use of polymer electrolytes and cells operating at moderate temperatures (70–80 °C), and such batteries have a limited presence in the market. Another alternative is to use liquid metal anodes, as in the Na/S battery technology, which however entail other risks and only is viable for large-scale stationary applications. Indeed, smooth plating of a metal is a general problem well-known from classical electrochemistry to be a complex issue influenced by the current distribution, the fluid dynamics, and the crystal growth, with the presence of a possible surface layer on the electrodes being an additional issue to master. Yet, the studies aiming to solve this bottleneck are well worth the effort as there is a huge advantage in terms of energy density when using metal anodes as compared to other electrodes with "inactive elements" present, adding significant dead weight to the cell. The differences between "metal anode" and "metal-ion" battery concepts are schematized in Figure 1.

The density and redox potential of the metal are the keys to promising theoretical electrochemical performance and therefore the largest figures of merit clearly correspond to the very light and electronegative lithium metal. However,



**Figure 1** Schematic representation of battery concepts using a metal anode (a) or an insertion type anode (b). Source: Ponrouch and Palacin [1]. Licensed under CC BY 4.0.

other metals such as the here considered magnesium, calcium, and aluminum are also of interest despite their larger atomic weight as they are able to exchange two and three electrons per M-ion as compared with only one electron for lithium. In practice, their competitiveness will totally depend on if they can be cycled and the conditions required to avoid dendritic growth, if any. But the theoretical figures of merit (Table 1) show, for example the volumetric capacity of calcium metal to be on par with lithium, and the capacities of magnesium and aluminum to be approximately two and four times larger(!), respectively. Plating/stripping of these metals all require non-aqueous electrolytes (zinc is the most electropositive metal, which is relatively stable in alkaline solutions), but this also opens for higher voltage cells and both this and the attainable energy densities are required to build modules and packs with a certain energy density

Metal	Abundance Earth's crust (ppm) [2]	Density (g cm <sup>-3</sup> )	—E° vs. SHE (V) [3]	Gravimetric capacity (Ah g <sup>-1</sup> )	Volumetric capacity (Ah cm <sup>-3</sup> )	lonic radius (Å) [4] <sup>a)</sup>	Cost (\$/ton) [5] <sup>b)</sup>	LC <sub>50</sub> (µg L <sup>-1</sup> ) [6] <sup>c)</sup>
Li	18	0.53	3.04	3.86	2.05	0.76	20745	650
Na	22700	0.97	2.71	1.17	1.13	1.02	419	-
Mg	27 640	1.74	2.37	2.21	3.85	0.72	4740	-
Ca	46 600	1.54	2.87	1.34	2.06	1.00	177	_
Al	83 000	2.7	1.66	2.98	8.05	0.53	2 1 6 0	182
Fe	62 000	7.86	0.45	0.96	7.55	0.61	75	>1000
Zn	76	7.14	0.76	0.82	5.85	0.74	2 950	70
Cd	0.16	8.64	0.4	0.48	4.15	0.95	1700	0.57

 Table 1
 Selected properties for some metals of interest as battery anodes.

a) Values for M<sup>2+</sup> – except for Li<sup>+</sup>, Na<sup>+</sup>, and Al<sup>3+</sup>.

b) Per ton of metal equivalent.

c) Toxicity to Hyalella azteca (amphipod crustacean).



Figure 2 Spider graph for the properties of Table 1 (except for toxicity) for all metals except lithium.

and a specific voltage with as few cells as possible. Here some know-how from the LIB technology may help accelerate the development.

From a spider graph of technologically relevant magnitudes (Figure 2), aluminum clearly emerges as the most attractive metal anode option by its combination of abundance to high theoretical capacity, despite the somewhat moderate potential, at seemingly affordable cost. Calcium and magnesium are also appealing, the former exhibiting very low potential vs. the standard hydrogen electrode (SHE), high abundance and low cost, and the latter suffering from somewhat higher cost, but theoretically enabling higher volumetric and gravimetric capacities. In contrast, iron, zinc, cadmium, and lead all suffer from too low gravimetric capacities, which are compensated by their high density to result in attractive volumetric capacity values, and toxicity is very much another factor to seriously consider to discriminate these metals. All these enable operation using aqueous electrolytes and the different battery concepts are dealt with in other articles.

Despite a myriad of primary battery concepts developed, including Al/air and thermal batteries, research in secondary/rechargeable non-aqueous multivalent battery chemistries has only recently attracted the interest of the scientific community. Most of the studies involve coupling metal anodes to inorganic cathodes, mostly containing a transition metal, in which the redox mechanism is based on  $M^{n+}$  ion insertion coupled to reduction/oxidation of the transition metal. Yet, for some cases, such as Mg, efforts are made to use organic-based cathodes. Moreover, coupling the metal anodes to sulfur or air has also been suggested, with different degrees of progress. While these concepts hold promise for low cost and potentially could be an option for large-scale energy storage, significant bottlenecks remains, and again, know-how from the development of Li metal electrodes (Articles Li/S and Lithium-Oxygen Batteries) will most certainly contribute to accelerate the progress.



**Figure 3** Number of Web of Science records (accessed February 2019) related to magnesium, calcium, and aluminum batteries vs. year showing the extreme intensification of research in recent years. As a comparison, the number of records for lithium and sodium batteries in 2018 are ~12.000 and ~2.500, respectively. The inset displays the percentage for each of the three metals vs. the total for all years accumulated.

Intercalation chemistry was developed in the 1970s and studies involving Li<sup>+</sup> turned out to be a cornerstone in the development of the LIB technology. In contrast, insertion of multivalent cations remained an academic curiosity (Figure 3), with the exception of some continued efforts on Al/air primary concepts and a significant amount of research being devoted to Mg-based secondary systems after that proof of concept being shown in 2000 [7].

The M-ion battery technologies mimicking the LIB concept pay an obvious penalty in energy density, but some advantages may result from avoiding issues related to plating/stripping. The main parameter to consider for both concepts is that the lowest negative electrode potential limit is set by the standard redox potential of the metal itself, which is only somewhat higher than lithium for calcium, sodium, and magnesium (~170, ~330, ~670 mV, respectively), but significantly higher for aluminum (~1.38 V). Any electrode material should, whether based on insertion, alloying, or any other redox mechanism, ideally: (i) be able to reversibly react with the largest possible amount of ions at high/low potential for the positive/negative electrode, respectively, to create cells of large energy density and (ii) exhibit large multivalent cation diffusion rates, to enable cell operating at high power densities.

Regardless of whether used as positive or negative electrode, and of the counter electrode used, the theoretical capacity of intercalation materials depends on

the total number of electrons that can be transferred to the cations of the host and does not depend on the guest ion itself. It though depends on the maximum concentration of guest ions that can be intercalated in the host structure and to what degree these guest cations affect the structure, where multivalent cations are causing larger perturbations as compared to Li<sup>+</sup> or Na<sup>+</sup>. The number of divalent cations that needs to be intercalated in the host, however, is only half the number of lithium ions necessary for an equivalent charge transfer. And of course for  $Al^{3+}$ , only one-third is needed. Hence, should the host be able to accommodate these more polarizing guest ions and reversibly at appreciable speed, high capacities would be achievable for multivalent M-ion batteries. The ionic radius of  $Mg^{2+}$  (0.72 Å) is close to that of Li<sup>+</sup> (0.76 Å), and ionic radius of  $Ca^{2+}$  (1.00 Å) is close to that of Na<sup>+</sup> (1.02 Å), and hence the existence of suitable structural frameworks for reversible lithium and sodium ion intercalation may serve as a background for the development of multivalent magnesium or calcium ion hosts. The main challenge for multivalent ions is their sluggish solid-state diffusion and the desolvation of solvent ligands at the electrolyte/electrode surface related to their high charge to radius ratio. Covalent electrode host materials would be more promising due to the decreasing Coulombic interactions. The case of aluminum is specifically challenging since its higher charge and smaller radius (Al<sup>3+</sup> at 0.53 Å) may be inconvenient for the development of successful insertion hosts - the small radius is arguably easily accommodated, but the strong Coulombic interaction is prohibitive, and hence, as described below, alternative concepts have been developed instead.

Experimental research aiming at developing new battery chemistries is far from being easy. It involves simultaneous development of electrodes and electrolyte, and the absence of any reliable standard for multivalent batteries makes the process cumbersome and non-trivial. For proper electrochemical studies, the use of a reference electrode is compulsory to be able to independently monitor the behavior of both electrodes, but the choice of the most suitable reference is not obvious [8]. While pure metals may not be the most reliable option, especially if a passivation layer is formed in contact with the electrolyte [9], silver wires have often been used as pseudo-reference electrodes. Yet, their potential is dependent on the anion present in the electrolyte and calibration against a well-known standard such as the ferrocene couple Fc<sup>+</sup>/Fc is therefore advisable. The choice of the other components, counter electrode and electrolyte, is not straightforward either. While again the pure metals would seem to be the obvious counter electrode, the fact that plating/stripping is only viable under very specific conditions casts severe restrictions on their applicability and therefore activated carbon (operating through a capacitive redox mechanism) has more often been used. Due attention must then be paid to electrode balancing to ensure oversizing of the capacitive counter electrode (typically exhibiting low specific capacity) vs. the electrode material at the working electrode. For the choice of electrolyte, care must be taken to make sure that any parasitic reactions due to degradation or aging are kept under control to assure to report data originating in the redox reaction aimed at. This is especially cumbersome when expanding the work on novel electrodes and electrolytes simultaneously for a new battery concept such as the multivalent chemistries.

## 2 Magnesium-Based Batteries

As described in the previous section, magnesium is a highly abundant element with relatively low redox potential of -2.37 V vs. the SHE, which makes it less reactive than lithium, calcium, and sodium toward ambient atmosphere and easier to manipulate, despite involving a decrease in the potential at the cell level. Due to the possibility to exchange two electrons and its relatively high density  $(1.74 \text{ g cm}^{-3})$  as compared to alkali metals (Table 1), magnesium anodes could enable high gravimetric (2206 mAh g<sup>-1</sup>) and volumetric (3834 mAh cm<sup>-3</sup>) capacities. In combination with a suitable cathode, this offers promising cell energy densities (Table 2) – where the more remarkable is sulfur, possibly leading to a theoretical energy density of 1684 Wh kg<sup>-1</sup> only based on active materials. The Mg-S cell concept is indeed sometimes referred to as a "Holy grail" battery, due to its expected impact on both sustainability and price, derived from the high abundance of both elements in the Earth's crust.

Stripping and plating of magnesium metal was reported for the first time in the early twentieth century [14], but the electrolyte, based on solutions of PhMgCl and PhMgBr, had too low conductivity and inadequate oxidative stability to be used in magnesium batteries.

Much later, magnesium stripping and plating was demonstrated in a first generation of battery relevant electrolytes, consisting of Lewis acids and a Grignard reagent (R—MgX, X=Br, Cl) mixture or magnesium salts dissolved in ether solvents, mostly tetrahydrofuran (THF). These enabled a realization of the first Mg battery prototype by using  $Mo_6S_8$  Chevrel phase as insertion cathode in 2000. The cell sustained >2000 cycles at a moderate rate with low capacity fading, but the specific capacity was rather low (ca. 60 mAh g<sup>-1</sup>), which coupled to the relatively low cell potential rendered it less interesting for practical application [7]. The low stability of the electrolyte toward oxidation coupled to its nucleophilic nature, prevented usage with both high voltage cathodes and sulfur or redox active organic molecules, being electrophilic materials.

Cathode	Theoretical capacity (mAh g <sup>-1</sup> )	Cell voltage (V)	Theoretical gravimetric cell energy density (Wh kg <sup>-1</sup> )
Mo <sub>6</sub> S <sub>8</sub> Chevrel phase [7]	129	1.1	134
Ti <sub>2</sub> S <sub>4</sub> thiospinel [10]	239	1.2	259
Poly(anthraquinone) PAQ [11]	260	1.5	349
Poly(benzoquinonyl sulfide) PBQS [12]	388	2.0	660
S [13]	1672	1.77	1712

 Table 2
 Theoretical cathode capacities and theoretical gravimetric cell energy densities for different battery concepts using magnesium metal anodes.

#### 2.1 Anodes and Electrolytes

The magnesium metal anode is interesting from different points of view. A major advantage is its high energy density, but this became really attractive only after the reports on plating of magnesium being non-dendritic [15, 16]. A general discussion on the importance and role of dendritic growth can be found in the section titled "Technological Prospects". Magnesium anodes are highly sensitive to all kinds of impurities in the electrolyte and the surface is stable only toward a few known solvents and salts. Impurities in the electrolyte can be easily reduced on the surface due to the low redox potential of magnesium metal and only a few ppm of impurities can form a passive (blocking) film on the surface, which prevents, or at least introduces large overpotentials for, the stripping and plating processes. For example, water impurities lead to a significantly increased overpotential for magnesium stripping and a decrease in Coulombic efficiency, while chlorine can in fact mitigate magnesium surface passivation [17].

As an alternative to magnesium metal, different p-block metals (Bi, Sn, Sb, In) have also been tested as anodes [18–21], but these concepts are less interesting as their reduced voltages and capacities would significantly lower the cell energy density.

The preparation of an Mg battery electrolyte requires use of highly purified solvents that are stable toward magnesium, i.e. which are not reduced on the surface of magnesium metal. Currently only a few solvents are known to fulfil this demand, most often glymes and THF are employed [22], but also the use of sulfones and ionic liquids has been reported [23, 24]. Likewise, the salts used for the electrolytes must have very high purity and electrochemical stability – both toward the anode (reduction) and cathode (oxidation). Furthermore, the ionic conductivity of the surface films formed on the Mg metal electrodes is a crucial difference as compared to Li metal, whereas Li ions can easily be transported through the surface film the Mg surface films are blocking in their nature.

Different electrolyte generations have been developed to bring magnesium batteries closer to commercialization. As mentioned above, the first generation of Mg battery electrolytes was based on Grignard reagents, which limited their applicability [25], but they acted as scavengers for impurities and maintained an active magnesium metal surface. The most common electrolyte composition was Bu<sub>2</sub>Mg and EtAlCl<sub>2</sub> in THF, known also as a DCC (di-chloro-complex) electrolyte [7]. The chloride ions were found to play an important role, as alternatives, fluoride or cyanide, lead to a decreased working voltage and/or passivation of the magnesium surface [22]. An improvement in operational voltage window, >3.3 V vs. magnesium, was achieved by using a mixture of PhMgCl and AlCl<sub>3</sub> ("all phenyl complex", APC) [26]. For all these electrolytes, high reversibility of magnesium stripping and plating was achieved regardless of the impurities present in the electrolyte, but compatibility with high capacity or high voltage cathode materials is questionable. Non-organometallic electrolyte formulations enabling efficient magnesium stripping/plating such as MgCl<sub>2</sub> and AlCl<sub>3</sub> in THF and dimethoxyethane (DME) ("MACC electrolytes"), were developed later [27, 28]. As compared to the anions commonly used in

LIB electrolytes, only the TFSI (bis(trifluoromethane)sulfonylimide) anion in Mg(TFSI)<sub>2</sub> has been successful, despite often a limited Coulombic efficiency, likely due to lacking quality (purity) of the salt and/or the solvent [17, 29, 30]. The best results have been achieved using DME, with the Coulombic efficiency being significantly improved by the addition of MgCl<sub>2</sub>. Other magnesium salts based on  $ClO_4^-$ ,  $PF_6^-$ , or  $BF_4^-$  as anions cannot be used due to high reactivity and formation of ionically non-conductive passive films on the Mg metal. Addition of chlorides to PF6-based electrolytes renders improved reversibility, again connected with the role of adsorbed chlorine species on the surface of metallic magnesium, which prevent the reduction of  $PF_6^-$  and formation of a passivating film [31]. Some more attempts to develop non-nucleophilic electrolytes, which deserve to be mentioned are those based on the magnesium hexamethyldisilazane (Mg(HMDS)<sub>2</sub>) salt with different co-salts such as MgCl<sub>2</sub> and AlCl<sub>3</sub>, which forms stable electrolytes useful in combination with sulfur cathodes - and this combination enables almost fully reversible stripping and plating of magnesium with an oxidative stability of up to 3.2 V [32, 33]. Overall, electrolytes containing chlorides enable improved properties on the Mg metal side, but their corrosive nature toward inactive parts of the battery, such as current collectors, current leads, cell housing, and also cathode materials, mainly transition metal oxides, limit their practical use [22]. Addition of chloride is also questionable from the point of view of magnesium metal since it can lead to non-uniform corrosion by formation of pits and Mg deposits, which with time can grow through the separator [34]. For that reason, much effort is focused on the development of non-chlorine-containing electrolytes - with pioneering work carried out by Mohtadi et al. [35] using Mg(BH<sub>4</sub>)<sub>2</sub> in DME and THF. Unfortunately, due to low oxidation stability and low Coulombic efficiency, this electrolyte has limited applicability. It however inspired further development of magnesium salts with carborane-based anions  $[CB_{11}H_{12}]^{-}$ , which enabled highly efficient magnesium stripping and plating combined with a high stability toward oxidation [36].

Another, simpler, salt is  $Mg[B(hfip)_4]_2$  (hfip being hexafluoroisopropoxide), which can be used without  $MgCl_2$  [37]. This compound satisfies all requirements for an electrolyte salt since it possesses high anodic stability (>4.5 V), high ionic conductivity, excellent long-term Mg cycling stability with a low polarization, and is much simpler to synthesize than the carborane salt and hence also much cheaper.

Recent studies demonstrated that in cells with chloride-containing electrolytes, coordination or insertion of MgCl<sup>+</sup> instead of Mg<sup>2+</sup> can be the dominant energy storage mechanism, both for organic [38] and inorganic materials (interlayer expanded TiS<sub>2</sub>) [39]. The chloride content in the electrolyte is then the capacity limiting species, which is especially troublesome when most research efforts are focused on avoiding chloride for corrosion issues. However, work on an Mg(TFSI)<sub>2</sub>-MgCl<sub>2</sub> electrolyte vs. an organic cathode shows that in this case both MgCl<sup>+</sup> and Mg<sup>2+</sup> taking part in the redox mechanism, with the charge transport being dominated by Mg<sup>2+</sup> [40].

#### 2.2 Cathodes

As outlined above, the motivation behind the development of different generations of electrolytes was partly the feasibility of using different types of cathode materials: inorganic, or sulfur – each treated separately below.

Starting with inorganic cathodes, even before first successful demonstration of an  $Mg//Mo_6S_8$  prototype, different groups worked on Mg insertion [41], into metal oxides as well as sulfides [42-45], but without any significant progress or practical use. Mo<sub>6</sub>S<sub>8</sub>, however, enables a facile extraction of the first Mg from  $Mg_2Mo_6S_8$  at room temperature, whereas it is more or less impossible to extract the second Mg. Replacing S with Se allows a full capacity utilization of the Chevrel phase [46, 47], despite inducing a weight penalty. After the successful demonstration of Mg insertion into Mo<sub>6</sub>S<sub>8</sub>, different inorganic materials have been proposed, mainly based on chalcogenide, oxide, and polyanionic structures. In contrast to oxides, sulfides or selenides such as Mo<sub>6</sub>S<sub>8</sub> are materials with small electrostatic interactions between the sulfide/selenide-based anion framework and the inserted magnesium cation - why also other transition metal sulfide compounds have been evaluated as potential cathodes. Different structural dimensionalities, for instance 1D MS<sub>2</sub> nanotubes, 2D layered materials, and 3D thiospinels, have been tested [10, 48-50]. While some of them show good reversibility at low, non-practical voltage ranges, others must be operated at elevated temperatures. The most interesting material in terms of energy density from this group,  $Cr_2S_4$  [51], was proposed by computational studies, but has not yet been synthesized. Again, electrochemical properties of this group of materials are expected, not proven, to be improved by the substitution of sulfur by selenium, but this would also considerably decrease the specific capacity due to the heavier Se atoms as compared to S atoms.

Much larger interest has so far been given to the oxides, due to their higher oxidation potentials - despite this also significantly limits the number of electrolytes available. Moreover, most show poor electrochemical characteristics, mainly attributed to poor magnesium mobility within the lattice as a result of strong Coulombic interactions [52, 53] and irreversible conversion reactions [54, 55]. Additionally, corrosion of transition metal oxides in the presence of chloride-based electrolytes cannot be avoided, which again calls for further progress in the electrolyte development. Nevertheless, some oxides like  $MoO_3$ [44, 56], Mo<sub>2.48</sub>VO<sub>9.93</sub> [57], and V<sub>2</sub>O<sub>5</sub> [56, 58] have shown reversible magnesium insertion, but only in electrolytes passivating magnesium anodes and thus not enabling reversible plating/stripping. Solvent co-intercalation or intercalation from electrolytes containing water have been reported to favor magnesium insertion into different MnO<sub>2</sub>-based (birnessite [59, 60] spinel [61]) and V<sub>2</sub>O<sub>5</sub> materials [62]. However, significant capacity contributions from side reactions involving protons/water cannot be excluded [45, 58, 63, 64]. Due to the similar ionic radii of magnesium and manganese cations, the formation of inverse spinel is energetically favored and the inverse spinel also has very sluggish electrochemical kinetics. Several attempts of magnesium insertion into polyanionic materials have been carried out as these exhibit stable crystal structures due to the covalent bonding of oxygen atoms to different non-metal atoms. Although

some early reports claimed promising performance [65], recent studies showed that most of the electrochemical activity results from side reactions [55]. Other candidate compounds are Prussian Blue Analogues (PBAs), which are able to intercalate several different multivalent ions but exhibit poor performance in magnesium electrolytes [66], and conversion cathodes, for instance sulfides [67], possessing similar operating voltages as insertion cathodes and much higher specific capacities, but with a large potential hysteresis between the oxidation and reduction processes and hence a large penalty in energy efficiency. Overall, for the inorganic cathodes,  $Mo_6S_8$  and some other chalcogenides remain the best candidates in terms of assessed performance, while oxides and polyanionic materials, more attractive from the point of view of energy density, suffer from sluggish kinetics and structural transformations.

Moving to organic cathodes, the limitations for inorganic cathodes, energy penalized Mg<sup>2+</sup> desolvation, and sluggish solid-state diffusion, can be effectively circumvented by operating via a redox mechanism based on a coordination reaction at a specific site. Reversible electrochemical activity for organic electrodes has been demonstrated with various monovalent and multivalent cations [68–73], and these materials can in most cases be produced from renewable and sustainable feedstock at low synthesis temperatures, which in the end would lower the carbon and the environmental footprints of battery production. They do, however, suffer from dissolution of the active material from the cathodes into the electrolyte, leading to rapid capacity fading, low volumetric energy densities, and inherent low electronic conductivities. Dissolution can be prevented through grafting of organics onto a solid support [74], use of selective separators [75], or by preparation of insoluble polymers from the electroactive monomers [76]. Unfortunately, all three approaches decrease the cell energy density via adding inactive material or an increased molecular weight.

As the organic materials often contain electrophilic centers, this rendered them incompatible with the first-generation nucleophilic electrolytes [77, 78]. The first organic cathode with electrochemical activity, confirmed by *ex situ* X-ray diffraction (XRD) [79], at ca. 1 V demonstrated was 2,5-dimethoxybenzoquinone (DMBQ) using an Mg(ClO<sub>4</sub>)<sub>2</sub> in  $\gamma$ -butyrolactone (GBL) electrolyte, but with no reversible Mg stripping/plating. Further attempts to cycle DMBQ in Mg metal passivating electrolytes lead to poor electrochemical performance [80, 81].

Development of non-nucleophilic electrolytes, to enable reversible Mg stripping/plating, opened for the development of practical Mg metal–organic batteries and this was first demonstrated using a polymeric cathode poly(anthraquinonyl sulfide) (PAQS) and an Mg<sub>2</sub>Cl<sub>3</sub>-HMDSAlCl<sub>3</sub> electrolyte [82], resulting in a reasonable overpotential for Mg stripping/plating at the Mg metal anode. The average discharge voltage for the cell was 1.5 V and 100 cycles were obtained. The high initial polarization was alleviated by the use of a powder anode, but still significant capacity fading was observed for both Mg foil and powder anodes [69]. The reaction mechanism of PAQS was investigated through *operando* IR spectroscopy and was found to be similar to that observed in lithium cells, involving reduction of a carbonyl bond on reduction, accompanied by some minor structural differences of the cathode (Figure 4) [83].



**Figure 4** (a) Discharge capacity and Coulombic efficiency of the Mg–PAQS cell, (b) selected galvanostatic cycles, and (c) corresponding *operando* ATR-IR spectra of the PAQS cathode. Source: Vizintin et al. [83]. Licensed under CC BY 4.0.

A significant improvement in the electrochemical performance was achieved through the application of another anthraquinone (AQ)-based polymer, poly(anthraquinone) (PAQ) [84] whereby >1000 cycles were made possible using an Mg(HMDS)<sub>2</sub>-4MgCl<sub>2</sub> in THF electrolyte, despite not reaching more than 50% of the theoretical capacities at 0.5 C [85]. It was demonstrated that this can be improved further on by making judicious choices of salts and solvents for the electrolytes, with Mg(TFSI)<sub>2</sub>-2MgCl<sub>2</sub> in DME delivering 63% of the theoretical capacity at 1 C (which is 75% of the capacity observed in lithium cells) [11].

Significant improvements in the energy densities can be achieved by using active materials with higher redox potentials and/or higher capacities, such as benzoquinone (BQ). A DMBQ cathode together with a  $Mg(TFSI)_2$ -2 $MgCl_2$  electrolyte resulted in redox activity at 2.0 V vs. Mg with an initial discharge capacity of 226 mAh g<sup>-1</sup> (71% of the theoretical). Unfortunately, solubility issues resulted in rapid capacity fade – only 74 mAh g<sup>-1</sup> remained in the 30th cycle [86]. This specific cathode material also assisted in revealing that the overpotential for Mg stripping/plating has a big influence on the cycling of practical two-electrode Mg cells; using an Mg(TFSI)<sub>2</sub> in diglyme electrolyte, where the overpotentials were significantly larger, the discharge voltage of DMBQ was significantly lower than 1 V. Furthermore, in an attempt to reduce the solubility, a sulfur bridged polymer – poly (hydroquinoyl-benzoquinoyl sulfide) – was synthesized, which delivered 240 mAh g<sup>-1</sup> in lithium cells, but only 160 mAh g<sup>-1</sup> in magnesium cells,

with much lower coulombic efficiency and poorer capacity retention [12]. Given the, for this chemistry, high operation potential (2.0 V), and the high theoretical capacity (>400 mAh  $g^{-1}$ ) further research in BQ-based polymers is expected.

Polyimides have also been tested as cathodes in non-aqueous Mg metalorganic batteries [72, 87], but also as anodes in both aqueous and non-aqueous Mg-ion batteries [88, 89]. For the former, a naphthalene-hydrazine (NH)-based polymer exhibits a well-defined voltage plateau on reduction at 1.7 V in an MgCl<sub>2</sub>-Mg(TFSI)<sub>2</sub>-based electrolyte with very good capacity retention [87]. Yet, the initial capacities are quite modest, a long capacity activation process was observed, attributed to wettability issues, and overall the maximum capacity was <50% of that observed for lithium cells. Higher capacity utilization was achieved for polyimides based on pyromellitic ethylenediamine (PMEDA) nanostructured using MWCNTs [72]. Although, pseudo-capacitive behavior was claimed, the large amount of carbon nanotube and the low sweep rates employed during cyclic voltammetry measurements do not allow for reliable conclusion on the charge storage mechanism. More than 2000 cycles were achieved using naphthalene-ethylenediamine (NEDA) polymer in aqueous electrolytes with low capacity fading [88]. Fullerenes were also tested as organic cathodes but could deliver only 50 mAh  $g^{-1}$ , far from their theoretical capacities (223 mAh  $g^{-1}$ ) although with well-defined voltage plateaus [54]. Overall, organic cathodes offer long-term cycling performance and practical voltages, which combined largely outperform inorganic cathodes. However, there are still several challenges to be resolved - both more fundamental such as to stabilize the electrochemical performance of electrochemical groups that offer the higher redox potentials and capacities, and more technical - the practical application will depend on the volumetric energy density, areal loadings, and electrolyte amounts required.

Finally, we turn to sulfur cathodes with their high theoretical capacity  $(1672 \,\text{mAh}\,\text{g}_{\text{S}}^{-1})$  and high abundance coupled with low cost making them promising cathodes for several battery systems (Li–S, Na–S, Mg–S and Ca–S). The obvious disadvantages are the low redox potential, the isolating nature of sulfur, and the relatively low volumetric capacity, but the latter can for Mg batteries be effectively compensated for by the high volumetric capacity of the Mg metal anode. The theoretical cell voltage is only 1.77 V, but still the theoretical gravimetric (1684 Wh kg<sup>-1</sup>) and volumetric (3221 Wh l<sup>-1</sup>) energy densities are appealing, despite these values being calculated for electrodes containing 100% of sulfur [90]. Again, the development of Mg–S batteries was hindered by the electrophilic character of sulfur, hence incompatible with the first generation of electrolytes. This was overcome by the development of Mg<sub>2</sub>Cl<sub>3</sub>-HMDSAlCl<sub>3</sub> electrolyte enabling the first Mg-S cell [82]. Unfortunately, THF as electrolyte solvent caused rapid dissolution of sulfur from the cathode, as confirmed by ex situ XPS and this also enabled identification of the Mg polysulfides and MgS species created, and only a few cycles were achieved with a discharge voltage below 1 V and poor coulombic efficiency. Sulfur species dissolved in the electrolyte can in general react directly with any metal anode and deposit on the surface – leading to rapid capacity fade due to loss of active material and by blocking the anode. However, according to the coulombic efficiencies

in general observed, this "polysulfide shuttle effect" is not a large problem for Mg–S batteries, in contrast to Li–S batteries.

A new electrolyte family based on  $MgCl_2$ ,  $Mg(HMDS)_2$  and  $AlCl_3$  combined with ionic liquids allowed two well defined voltage plateaus at 1.6 and 1.2 V with improved reversibility to be observed upon sulfur reduction. However, the practical capacity did not exceed 800 mAh g<sup>-1</sup> – and was shown by *ex situ* XPS to be due to a kinetically limited reduction reaction – proceeding only to  $MgS_2$ and not to MgS.

A higher discharge capacity, 1320 mAh  $g^{-1}$ , was obtained using an Mg(TFSI)<sub>2</sub>-MgCl<sub>2</sub> tetraglyme : dioxalane (TEG : DOL) electrolyte, again rendering the sulfur two discharge plateaus, now at 1.4 and 1.2 V (Figure 5a). Employing XANES and RIXS confirmed the transformation of sulfur into different Mg polysulfides



**Figure 5** (a) Capacity and Coulombic efficiency of the Mg–S cell using 0.4 M MgCl<sub>2</sub><sup>-</sup>Mg(TFSl)<sub>2</sub> in TEG:DOL electrolyte at C/60 rate, and (b) first discharge of Mg–S cell under the same conditions and with the relative amounts of the different sulfur compounds as determined by *operando* RIXS. Source: Bitenc and Dominko [91]. Licensed under CC BY 4.0.

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during the first plateau and the reduction of the polysulfides to MgS during the second lower voltage plateau (Figure 5b).

The rapid capacity fade due to sulfur and polysulfide solubility was improved on by using a more concentrated  $Mg(TFSI)_2-2MgCl_2$  in DME based electrolyte – with >600 mAh g<sup>-1</sup> of capacity after 100 cycles [92].

Using a chloride-free electrolyte, based on the  $Mg[B(hfip)_4]_2$ , salt in diglyme/tetraglyme an Mg-S cell was made exhibiting two plateaus, one flat at ca. 1.5 V and a second sloping below 1.2 V [37]. The initial cycling showed rapid capacity fade and relatively low capacity utilization with a maximum capacity of  $500 \text{ mAh g}^{-1}$ , but  $930 \text{ mAh g}^{-1}$  could be achieved by a binder-free cathode and activated carbon cloth with the same salt in DME [93]. Unfortunately, no long-term capacity improvement was achieved after 100 cycles. A stark contrast in electrochemical behavior was observed for similar Mg–S cells, due to the application of Cu current collectors [94–96] – as Cu reacts with sulfur species to form CuS, CuS is cycled rather than S [67, 97].

Overall, the Mg–S battery is attractive from the standpoint of high theoretical energy density and sustainability of electrode materials. The development of non-nucleophilic electrolytes opened a path toward practical testing of sulfur cathodes, but their initial performance was poor due to fast dissolution of sulfur and Mg polysulfides into the electrolytes. The recent development of more concentrated electrolytes has led to improved electrochemical cycling and >100 reversible cycles demonstrated – but more effort should be directed to understanding the Mg polysulfide to MgS mechanism and the protection of Mg anode since Mg stripping/plating in the presence of sulfur species leads to poor Mg cycling [98]. Another challenge is to decrease the overpotentials, as all cells demonstrated so far have practical discharge voltages well below the theoretical 1.77 V.

Current research efforts on Mg battery cells are paving the way for a practical Mg battery technology. Recent advances on electrolytes have resulted in important steps forward with the development of non-nucleophilic electrolytes with high oxidative stabilities and even being non-corrosive. On the cathodes, progress has been significantly slower and the performance of the original  $Mo_6S_8$ cathodes has only been slightly enhanced with the use of thiospinels and layered chalcogenides. However, the development of the non-nucleophilic electrolytes opened a path toward the use of organic and sulfur cathodes, which are showing promising early results, despite practical viability in a full cell setup still pending.

## 3 Calcium-Based Batteries

The first use of calcium as an electroactive metal was reported in the 1960s and related to thermal batteries [99, 100]. Other high-operating temperature battery concepts investigated at the time attempted to use solid electrolytes [101, 102] and even involved using oxygen counter electrodes [103]. Despite that a few cycles were reported, the redox mechanism was not unambiguously ascertained and no further studies were published. Later on, Staniewicz [104] reported on



**Figure 6** Volumetric (a) and specific (b) cell energy densities for LIBs (LFP/graphite and NMC/graphite, circles) and Li-S batteries (triangle). The straight lines are calculated energy densities of CaBs as a function of operation potential and capacities (denoted on the right of each line). Source: Adapted from [111].

the Ca-SOCl<sub>2</sub> system as an alternative to the Li-SOCl<sub>2</sub> primary cells, suggesting that the impossibility of calcium plating on cell reversal could be a safety advantage. Further studies attributed this to the formation of a passivation layer consisting mainly of CaCl<sub>2</sub> not permeable to  $Ca^{2+}$  ions [105]. Yet, the calcium alternative did never provide enough advantages as compared to Li-SOCl<sub>2</sub> to ever reach the market. The issues related to electrochemical calcium plating also prevented any investigation of secondary battery technologies based on using calcium metal anodes [106], hence the need for activated carbon counter electrode to evaluate possible cathode materials [107]. The topic of rechargeable Ca batteries has, however, recently reemerged as part of the worldwide quest for new battery technologies, which can fulfill the needs of the vast diversity of potential applications, and progress is reported in recent reviews [108, 109]. Indeed, quantification of the figures of merit attainable at the cell level, using a simple energy-cost model [110], indicates that the theoretical energy densities for rechargeable calcium batteries could easily top the state-of-the-art LIB, while cost most likely being much lower [111]. Overall cells with only moderate operating voltages of ca. 2.0-2.5 V and cathode capacities of 250 or 200 mAh g<sup>-1</sup> would result in specific energy densities higher than for LIBs, while for  $3.0 \text{ V}/250 \text{ mAh g}^{-1}$  or  $3.5 \text{ V}/200 \text{ mAh g}^{-1}$ , the volumetric energy densities would be >1000 Wh  $l^{-1}$  (Figure 6).

## 3.1 Cathodes

Calcium ion intercalation in transition metal compounds was studied in the early days of intercalation chemistry research during the 1960s and 1970s [112]. Despite most of the investigations involved lithium and other alkali ions, attempts to chemically intercalate multivalent ions were not uncommon. The characterization of intercalates formed was, however, limited, and co-intercalation of the solvent rather common. The advent of the LIB technology

in the 1990s concentrated most research efforts in the battery field there, and alternative concepts were more or less forgotten. Indeed, even if there was some further interest from the materials science perspective, the absence of suitable electrolytes rendered any electrochemical testing very challenging.

The field started to re-emerge in the early 2000s, probably linked to the establishment of proof of concept for the Mg-based technology at the time, with publication of a few reports dealing with the feasibility of calcium intercalation in a few materials. These included hexacyanoferrates (PBAs) using either aqueous [113] or organic electrolytes [114] and studies of  $V_2O_5$  [115]. The former seem to exhibit good performance at high rates, despite the interpretation of the redox mechanism being very difficult. Indeed, these materials are known to exhibit variable amounts of water in their crystal structure, which are sometimes difficult to remove, and very limited structural modifications, if any, have been observed during operation. V<sub>2</sub>O<sub>5</sub> has so far attracted most attention, but here the interpretation of results is even more controversial, as changes in the diffraction pattern might be related to the presence of water/protons in the electrolyte [64], which does not come to a surprise as related findings have been reported for magnesium cells [62]. Electroactivity has also been reported for NaFePO<sub>4</sub>F [116] and MoO<sub>3</sub> [117], despite that the crystal structures of the calcium-containing phases have not been unambiguously assessed. Finally, while electrochemical extraction of calcium in Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub> is feasible [118], the only compound for which reversible electrochemical calcium insertion/extraction has reliably been shown to date is  $TiS_2$  [119], despite the process being complex and non-practically viable as a result of solvent co-intercalation and high cell overpotential (Figure 7). At present, most efforts have thus focused on positive electrode materials with intercalation reactions, similar to those of the LIB technology. To the best of our knowledge, organic cathodes and other alternatives such as sulfur or air/oxygen electrodes have been only marginally considered [120, 121]. Overall, it is clear that there is a long way to go before reliable proof of concept can be achieved and technological prospects evaluated. In this sense, development of reliable experimental setups, including reference and counter electrodes, coupled to complementary characterization techniques, with attention given to precision and reliability for each technique [122], as well as computational tools, is mandatory if steady progress is to be achieved. Indeed, density functional theory (DFT) computational studies have enabled forecasting not only phase stability for given compositions and ion content but also intercalation voltages and energy migration barriers [123, 124], the latter probably being the main hurdle in developing cathodes for CaBs [125].

## 3.2 Anodes

As stated above, the viability of calcium anodes is critical if energy densities outperforming current figures of merit for the LIB technology are to be achieved. Yet, calcium plating has for long been elusive, as passivation layers formed in conventional solvents were believed not to enable transport of  $Ca^{2+}$  and no calcium analogues to magnesium Grignard-based electrolytes are available [126]. By the end of 2015, the feasibility of reversible calcium metal plating/stripping



**Figure 7** (a) Synchrotron X-ray diffraction (SXRD) patterns collected at different stages of  $Ca_3Co_2O_6$  oxidation in Ca cells, (b) the associated refined structural model, (c) SXRD collected at different stages of  $TiS_2$  reduction in Ca cells, and (d) three-dimensional Ca distribution representation obtained by differential absorption tomography at the Ca L<sub>2</sub> edge – with three Ca regions identified: "high absorption external Ca" (red), "low absorption external Ca" (orange), and "intercalated Ca" (pink) inside the  $TiS_2$  particle. Source: Berg et al. [110], Monti et al. [111]. Reproduced with permission of American Chemical Society and Royal Society of Chemistry.

in alkyl carbonate–based electrolytes, forming a passivation film on calcium was achieved, but with moderate Coulombic efficiency and a need to raise the temperature somewhat (>75 °C) to improve ion mobility within the electrolyte [127]. Further research has mostly focused on improving the electrolyte formulation (next section) and to unravel suitable cathodes. Yet, some attempts have been made to develop alloy-based anodes of high theoretical energy density, with either Sn [114] or Si [128], both using alkyl carbonate–based electrolytes, however without any successful performance shown [129]. Formation of crystalline  $Ca_7Sn_6$  after 300 cycles was recently reported on using Sn foil as the anode coupled to a graphite cathode (most likely involving anion intercalation in the redox process), also this using alkyl carbonate–based electrolytes, calling for further investigations [130]. For carbonaceous anodes, the first-stage calcium

graphite intercalation compound  $(CaC_6)$  can be prepared chemically [131], but has not yet been reported electrochemically.

## 3.3 Electrolyte

Very few calcium salts are commercially available, which has also contributed to delaying any investigations of calcium-based systems. The most commonly used Ca salt is  $Ca(ClO_4)_2$ , which typically is hydrated and difficult to obtain anhydrous due to its explosive nature. Thus, the literature may in some instances involve electrolytes with non-negligible amounts of water – and this has furthermore seldom been reported in the experimental sections, until very recently. The water contained can trigger unwanted side reactions, proton/water intercalation or water reduction/oxidation, which may result in some additional electrochemical capacity and hence misleading conclusions with respect to the electrochemical reactivity of electrode materials tested. While the Ca(TFSI)<sub>2</sub> and the Ca(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> salts also are commercially available, the synthesis of Ca(PF<sub>6</sub>)<sub>2</sub> has only recently been reported [114, 132], and there are still purity issues related to a very high tendency of hydrolysis connected to anion decomposition.

As mentioned above, the feasibility of reversible calcium metal plating/stripping has only recently been demonstrated (Figure 8), both in alkyl carbonates forming a passivating layer provided that the temperature is moderately raised (>75 °C) to favor cation mobility [127], and more recently also at room temperature by using an electrolyte of  $(CaBH_4)_2$  in THF, by which a CaH<sub>2</sub>-containing passivation layer was obtained [133]. Notable is the very high salt concentration in the latter study (1.5 M) – in addition to ion-pairing issues, reducing the effective number of charge carriers, there is often a limited solubility, where the optimal salt concentration is more often close to 0.5 M rather than 1.0 M as for the LIB technology electrolytes. Other crucial parameters hindering  $Ca^{2+}$  migration and hence impacting on the plating rate and efficiency are: (i) the energy barrier associated with the cation desolvation at the anode/electrolyte interface and (ii) the transport of Ca<sup>2+</sup> across the passivating layer (if any). Hitherto, most studies on multivalent cation-based batteries have focused on the solid-state diffusion, while less attention has been given to the interfacial and migration processes within the electrolyte. As divalent cations naturally induce much stronger Coulombic interactions on the electrolyte solvent and salt anions than monovalent cations such as lithium or sodium [9], more efforts are needed in this direction. Indeed, unraveling electrolyte concepts with low desolvation energies may have also an impact on the reversibility of calcium insertion/deinsertion in the cathodes (section titled "Cathodes").

## 4 Aluminum-Based Batteries

If we would be able to turn to using aluminum (Al) as the negative metal anode and create Al metal-based batteries, then we would make efficient use of the third most abundant element in the Earth's crust and as mentioned above at the



Figure 8 (a) Cyclic voltammetry depicting calcium plating/stripping in 1.5 M Ca(BH<sub>4</sub>), in THF at room temperature (25 mV s<sup>-1</sup>, working, reference, and counter electrodes Au, Ca, and Pt, respectively) and using Ca(BF<sub>4</sub>)<sub>2</sub> in EC : PC at 100 °C (0.5 mV s<sup>-1</sup>, stainless steel working, and Ca counter and reference electrodes). (b) Charge/discharge curves (50 μA cm<sup>-2</sup>, 150 cycles) of symmetric Ca/Ca cells with 0.45 M Ca(BF<sub>4</sub>)<sub>2</sub> in EC : PC at 100 °C and Li/Li cells cycled at room temperature in 1 M LiPF<sub>6</sub> in EC : DMC. Source: Ponrouch et al. [127], Wang et al. [133]. Reproduced with permission of Springer Nature.

same time make use of not only two electrons per charge carrying cation as for  $Mg^{2+}$  and  $Ca^{2+}$ , but three for  $Al^{3+}$ . These obvious advantages, however, come together with a negative potential of "only" -1.66 V of the  $Al^{3+}/Al^{\circ}$  couple vs. the SHE – making high (or even medium) voltage cells rather cumbersome to create, and in addition the strongly polarizing  $Al^{3+}$  cation makes it difficult to obtain fast ion transport in active intercalation materials.

### 4.1 Anode

At a large scale of thinking of batteries for the future, and not only in terms of natural abundance, aluminum is both a very low cost material, not only in the bulk (Table 1) but furthermore also in the shape of high quality and very thin technologically relevant 16  $\mu$ m Al foil produced at <1 USD m<sup>-2</sup> [134]. It is also produced industrially at a rate annually exceeding 50 million tons, which ensures a ready supply of raw material needed for wide-scale commercialization of any realized next-generation battery technology. Alongside the low cost and large production capacity, Al is also a widely and efficiently recycled material, further emphasizing the green dimension of this battery chemistry. Of course, the Al metal foil will more or less always be covered by a thin very stable Al<sub>2</sub>O<sub>3</sub> passivation layer, but this layer can be controlled and limited in thickness and given a specific quality by careful etching, cleaning, and washing procedures.

Due to the lightweight and the possibility to exchange three electrons aluminum indeed has a theoretical specific gravimetric capacity higher than all alkali and earth alkali metals, except Li, at 2980 mAh g<sup>-1</sup>, but even more impressive is the volumetric specific capacity at 8046 mAh  $cm^{-3}$  – which is double than that of Mg being second best at 3850 mAh cm<sup>-3</sup> (Table 1). The much higher redox potential of aluminum compared to lithium, but also to magnesium, decreases the cell voltages possible to easily create substantially, but again the energy densities can partially be compensated for by virtue of the very high specific and volumetric capacities. An Al-based cell chemistry would then represent one take on a so-called "holy grail" battery - not in the usual terms of leapfrogging in the energy density, gravimetric or volumetric, but rather due to expected low impact on the environment – and hence a more profound sustainability aspect, and the low cost per kWh of effective storage - paving the way also for true large-scale implementation, when/if this chemistry will be commercialized. This can, however, only be perceived as practically feasible given much focused research efforts to achieve both novel Al-ion conducting electrolytes and novel active cathode materials enabling to effectively and not the least reversibly handle and transfer three electrons per Al charge carrying species transported across the electrolyte.

As mentioned above in general terms for all non-aqueous multivalent battery technologies is even more true for rechargeable Al metal batteries, it has only rather recently attracted the interest of battery researchers and is more or less in its very infancy. Yet research on re-chargeable batteries based on Al is not really new, it has been laden with numerous problems at least the last 30 years [135]. Indeed, a few rather covering studies and reviews on various Al-based batteries exist [136–140] and from these it is clear that the efforts to obtain electrolyte/electrode combinations and operating conditions for Al metal anode

based batteries to become feasible have also to some extent been accompanied by exploring other electrode choices. This is why various Al-ion battery chemistries, as opposed to Al metal batteries, have been explored – especially those using graphite, sometimes very special sparse graphite, based materials to intercalate different Al-containing complexes. These Al-ion batteries, sometimes labeled Al batteries, have been very successful in terms of cyclability and overall very impressive performance has been shown; >7000 cycles at a ca. 99% CE, and high rate capabilities, up to  $4 \text{ A g}^{-1}$  [135]. Even more impressive cells with up to 500 000(!) cycles have been shown and with the possibility of a discharge event in approximately 10 s [141]. However, none of these Al-ion batteries hold fundamental promise of high (or even moderate) energy density at the cell level as they are limited in their energy density by the amount of electrolyte employed. When the energy contained in the cell depends on this component rather than the electrodes employed, the resulting energy density is closer to 50 Wh kg<sup>-1</sup> at the cell level rather than the ca. 500 Wh kg<sup>-1</sup> aimed for with Al metal batteries.

### 4.2 Electrolytes

The start of reversible Al metal battery research focused on using different  $AlCl_3$ -based electrolytes to create the  $[AlCl_4]^-$  and  $[Al_2Cl_7]^{2-}$  electroactive anions and different inorganic intercalation host materials as the positive electrode. All early attempts to reversibly strip and plate aluminum were based on this first generation of Al-conducting electrolyte and also enabled a first rechargeable Al metal battery prototype using  $V_2O_5$  as an insertion cathode material [142] and the usage of an ionic liquid (IL)–based electrolyte (AlCl\_3-EMICl) was the key, as hinted at before [143], and perhaps this was the "expected" solution as seen by the use of ILs for Al metal plating in general [144]. Furthermore, the ratio of  $AlCl_3 : IL$  must always be >1 to render these electrolytes acidic and functional.

Indeed, most Al battery studies still employ electrolytes based on the concept of creating  $[AlCl_4]^-$  complexes, by ILs or other means, to transfer the  $Al^{3+}$  cation charge carriers – and hence Al is transported across the electrolyte as species which notably are negatively charged. This renders most Al battery cells low energy densities – as the anode effectively is not only Al metal but also Cl from the electrolyte, somewhat like a mixed anolyte system. Furthermore, the ubiquitous presence of Cl also adds the issue of cell corrosion. The latter is sometimes a cause of mistrust in the efficiencies reported for Al metal and Al-ion electrochemical cells if not proper precautions have been made to monitor the role/contribution from such side reactions. Hence, the two main obstacles to overcome from an Al electrolyte point of view are therefore to create electrolytes free from  $Cl^-$  ions and capable of fast cationic  $Al^{3+}$  transport – but still with maintained stripping and plating capability at the Al metal anode.

Some few attempts have been made to create this other type of electrolytes, including avoiding Cl chemistry and creating cationic  $Al^{3+}$  charge carrying complexes [145–147]. Ideally, the  $Al^{3+}$  ion should be transported the same way as other battery monovalent cations like Li<sup>+</sup>, Na<sup>+</sup>, and indeed also the divalent  $Ca^{2+}$ , i.e. in simple  $[Al(L)_n]^{3+}$  complexes, where L are neutral ligands of standard

organic solvent molecules. The very hard, in the Brønsted sense, nature of the Al<sup>3+</sup> cation would, however, make for rather sluggish kinetics of desolvation. But if  $Al^{3+}$  can be the sole electroactive species at the Al metal battery cathode as well, up to 10 times of increased energy density at the cell level becomes viable. One example we here highlight was based on stripping/plating from an solvated ionic liquid (SIL) concept electrolyte – by creating an  $[Al(BIm)_{\epsilon}]^{3+}$  complex, where BIm is a large imidazolium-based solvent and creating modest ion conductivity and electrochemical activity at room temperature, but functional at a somewhat elevated temperature (85 °C) [146]. Together with the other studies on using different glyme solvents to create Al-based SILs, this shows that it is possible to create cationic  $Al^{3+}$  complexes, possibly with some solvent dynamics – especially as their ion conductivities seem to not be limited by the viscosity – but rather showing decoupling. Compared to these efforts to construct electrolytes via rather odd and strange chemistries, no electrochemical activity has ever been reported for more classic organic electrolytes – such as those working for LIBs or SIBs – and thus this bears many similarities to the situation of Mg battery electrolytes.

### 4.3 Cathodes

Turning to the cathode-active materials employed – disregarding the sparse graphite/carbons employed for Al-ion batteries with  $[AlCl_4]^-$  intercalation concepts – there are in principle three main tracks followed in the Al battery research: (i) inorganic, (ii) organic, and (iii) sulfur cathodes. Starting with the latter – this mainly aims to balance the vast capacities of the Al metal anode and hence to reach a very high energy density cell overall, but special care must be taken to enable reversible operation. In contrast to both Mg and to less extent Ca batteries, sulfur-positive electrodes with their theoretical capacity of 1672 mAh  $g_s^{-1}$  have so far not been vastly explored and hence Al-S batteries is a largely unknown area of research. Early proof of concept of Al-S [148] was quickly developed further [149, 150], but nevertheless significant challenges with respect to charge/discharge kinetics remain. Among them the release of free Al<sup>3+</sup>, which was shown to benefit from changing from Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> to Al<sub>2</sub>Cl<sub>6</sub>Br<sup>-</sup> [151], was found extremely important.

The main track for Al metal battery cathode active materials has traditionally, however, been inorganic hosts such as  $V_2O_5$  and  $Mo_6S_8$ . The former was, as mentioned above, used as an aerogel to create a first proof-of-concept Al metal battery reaching ca. 240 Wh kg<sup>-1</sup> by the virtue of 273 mAh g<sup>-1</sup> and an OCV of 1.8 V, for a limited 20 cycles [142]. Yet, this cell has also been questioned; parts of the energy realized are rather suggested to originate from stainless steel current collector corrosion [152]. Also other groups have employed  $V_2O_5$  as cathodes, but in different morphologies – to try to remedy the capacity fading and the kinetics – but so far with limited success [153]. The situation is not better for the cells employing  $Mo_6S_8$  as cathode – they result in very low cell voltages of ca. 0.4–0.6 V and parts of the Al<sup>3+</sup> becomes irreversibly trapped inside [154]. This latter phenomenon, which seems intrinsic to the Al<sup>3+</sup> intercalation reaction, results in the capacity to be only ca. 80 mAh g<sup>-1</sup>. Furthermore, employing Mo should not really be considered due to the scarcity of this metal and hence resulting in a very unsustainable battery chemistry. A full three-electron transfer is a common problem for inorganic intercalation host materials and this fundamentally limits the concept in terms of efficiency and in fact makes it more of a worse type of Li-ion battery (if only a one-electron transfer is possible).

Organic cathodes hold promise to resolve many of the issues above; they are not limited as resource, they can be designed to not trap cations hard in any "lattice", and they can exhibit both high and tailorable capacities. The main problem of organic cathodes in general is that the active materials often are soluble in the electrolyte and hence capacity fade can be rapid. This can be circumvented by preparing polymers or oligomers of the organic redox active monomer, such as different quinones – as previously made for Mg-organic batteries [69]. This is conceptually rather new to the field of Al batteries with only a few studies known to date [155, 156]. Both these very recent studies basically show proof of concept for Al metal – organic batteries, the former present ca. 5000 cycles of appreciable stability with a reversible capacity of less than  $60 \text{ mAh g}^{-1}$  – but at a rate of 20 C (Figure 9), while the latter exhibits 500 cycles at about twice the capacity: 110 mAh g<sup>-1</sup>. Both studies use an AlCl<sub>3</sub>-EMImCl-based electrolyte, but with some differences in the exact composition. The organic active material, for the former a phenanthrene-quinone (PQ), is mixed with graphite flakes to achieve a better electronic conductivity and thereby areal loading possible. Judging from the field of Mg-organic batteries, these types of cathodes can be made inexpensively and by virtue of the vast possibilities of organic chemistry the basic limitations to tailor them are few. Oxocarbons and different (poly)-quinone derivatives seem very suited for many electron transfers with their multiple adjacent redox centers and possibly produced from precursors from agricultural resources and be biodegradable - and hence not at all resource limited. With respect to the cathode-Al<sup>3+</sup> interaction, we stress that these are coordination based and that the exact species originating from the electrolyte found at the interaction site, basically different  $[AlCl_x]^{3-x}$ , will determine the final theoretical cell energy density possible – why much work has been devoted to study the cells operando [156]. As compared to organic Mg batteries, the preferred potential voltage of cathode needs to be raised, due to the 0.7 V difference between the Al<sup>3+</sup>/Al° and Mg<sup>2+</sup>/Mg° couples, and accompanied by an electrolyte stable at these high oxidation potentials. Given this a promise of high cell energy densities remains - despite the PQ-based battery reported by Kim et al. [155] resulting in no more than 53 Wh  $kg^{-1}$  in practice at present.

## 5 Technological Prospects

While the main interest in multivalent cation-based battery technology development does arise from the possibility to use metal anodes, which are compulsory to achieve any leapfrog breakthroughs in energy densities, the use of Ca, Mg, or Al metal anodes indeed all involve significant technological challenges.

Cells with Li metal anodes having been commercialized using a polymer electrolyte [157], one might speculate that similar handling protocols could be



derivatives at a C-rate of 0.2 C. (b) Rate capability of best-performing phenanthrenequinone derivative (PQ-Δ) and (c) its long-term cycling performance at Figure 9 (a) Galvanostatic curves for different phenanthrenequinones-PQ (PQ-A triangle trimer, PQ-Lin linear trimer and PQ-Ref monomer compound) 20 C. Source: Kim et al. [155]. Reproduced with permission of Springer Nature.

adapted to Ca, Mg, or Al. Atmosphere control during cell assembly is compulsory to avoid any traces of oxygen, water, or any other kinds of contaminants, which could react at the electrode surface and completely block (or at least significantly lower) the plating/stripping kinetics. Two scenarios to address this issue can be envisaged: (i) development of prepassivation methods allowing for easier handling in conventional dry rooms as today used for LIB cell assembly or (ii) use of chambers with an ultra-high purity atmosphere. The latter would most likely result in a significant impact on the overall cost of the cells (in \$/kWh).

Another issue relates to the mechanical properties of the metals - the difference in terms of stiffness between Li and Mg or Ca, with the Young's modulus being 4.9 GPa for Li and 45 and 20 GPa for Mg and Ca, respectively, alternative production strategies will be needed to produce suitable anode shapes. If foils are to be used, evaporation methods leading to high purity Ca and Mg may have to be implemented and this cost to be taken into account for the overall cell production. For Al, the situation is very different; although the pure metal also presents a high Young's modulus (70 GPa) the assembly of commercial cells would likely benefit from the vast knowledge available from the Al industry. Indeed, pure and thin Al foils are already commercially available, although price can be rather high and strongly depending on metal purity. In contrast, given the significant increase in terms of energy density at the cell level for multivalent metal anode concepts, when compared with LIBs, production costs (in \$/kWh) may decrease if the number of cells needed for a module/pack is reduced. However, this will ultimately depend on the balance between high voltage (cells placed in series) or high capacity (cells placed in parallel) needed for the specific application. One could also assume that a lower tendency to dendrite formation could ease the safety requirements and lower the level of complexity of the battery management system.

However, smooth plating of metals is well known from classic electrochemistry to be a complex issue. Dendritic plating results from a diffusion-limited process and Mg cells appear to be less prone to dendrite formation than Li cells. Indeed, even for plating at relatively high current density  $(2 \text{ mA cm}^{-2})$  no evidence of irregular, dendritic growth was observed [15], rationalized by lower diffusion barriers of magnesium ad-atoms on the metal as compared to lithium and sodium, which should promote a growth of smoother structures [158, 159].

But in contrast to the major perception that magnesium plating is dendrite free, recent experiments showed dendrites to form under certain conditions [160, 161]. Indeed, in many reports from different authors proposing non-dendritic growth of magnesium, platinum, or copper, but not actual magnesium working electrodes, were used. While an actual Mg working electrode was used in the work of Davidson et al. [160], a reliable value of the critical current density at which Mg dendrites start to form could not be concluded since the Mg electrode presented very sharp edges and was most likely, at least partially, passivated, significantly enhancing the inhomogeneity of the Mg plating. Extensive calculations, taking into account the five most stable surface orientations for magnesium crystals, showed that the morphology evolution during plating is dependent on the surface orientation and thus emphasizes the need to include all commonly present facets and not only the most stable magnesium surfaces [162]. This

as different surface orientations vary in density of surface packing, adsorption, surface energies, and diffusion barriers – all factors which likely have large impact on the growth mechanism – and most of all; the study showed that magnesium plating can result in dendrite formation. While it can be a result of simply being much less researched concepts, Ca and Al dendrite formation resulting from cycling these metal anodes is not reported as far as we know.

## 6 Conclusion

Efforts to develop battery technologies alternatively or complementary to the prevalent LIB technology have recently intensified due to both batteries embracing larger fields of application, with a wider distribution of requirements, and also due to supply risk considerations. This has attracted the academic community, which sees an opportunity for rapid alternative developments stemming from the knowledge gained in the field of LIBs. A vast diversity of alternative strategies is pursued in the quest for high performance: magnesium, calcium, and aluminum batteries all hold promise for applicability of metal anodes and hence very large capacities, but the development of suitable cathodes is a must for the advent of a breakthrough in cell energy density, and in turn, this requires novel electrolyte formulations enabling wider electrochemical stability windows.

The power density performance for the multivalent concepts outlined will likely not be comparable to any monovalent concepts, due to the (inevitable?) sluggish multivalent ion diffusion in the cathode materials. Nonetheless, these limitations should not necessarily hamper implementation in application niches not requiring large power density, especially if an efficient and cost-effective concept can be developed.

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