Multivalent rechargeable batteries

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A B S T R A C T

Rechargeable battery technologies based on the use of metal anodes coupled to multivalent charge carrier ions (such as Mg²⁺, Ca²⁺ or Al³⁺) have the potential to deliver breakthroughs in energy density radically leap-frogging the current state-of-the-art Li-ion battery technology. However, both the use of metal anodes and the migration of multivalent ions, within the electrolyte and the electrodes, are technological bottlenecks which make these technologies, all at different degrees of maturity, not yet ready for practical applications. Moreover, the know-how gained during the many years of development of the Li-ion battery is not always transferable. This perspective paper reviews the current status of these multivalent battery technologies, describing issues and discussing possible routes to overcome them. Finally, a brief section about future perspectives is given.

1. Introduction

Recent visionary words by battery pioneer J.B. Goodenough: “Today’s challenge is the design of an electrochemical technology that can perform safely the task of electrical-energy storage and recovery at a rate and cost that are competitive with the performance of the well-established fossil fuel technologies.” [1] While lithium-ion batteries (LIBs) clearly have delivered this to the extent that hybrid and fully electric vehicles (XEVs) today penetrate the car market at an ever-increasing rate, there are still issues with cost, energy and power density, life-length, resources, safety, etc. All these requirements (and more) are also to be re-valued and re-balanced when we look at other possible markets such as commercial vehicles, large-scale storage of renewable variable energy from solar and wind, etc. All these requirements combined are also difficult to solve in a combined manner and can therefore only be fulfilled through really high-risk forward looking research. Targeting to leap-frog in performance involves to directly deviate from incremental research, which for LIBs can be exemplified by adding minor amounts of Si to the graphite electrode – raising the energy density of an LIB at the cell level by max. ca. 10–20%. Instead we must go beyond the beaten track and investigate a vast array of next generation battery (NGB) concepts in parallel, even if it is clear that only a limited number of these will finally make it to the market. In comparison to the incremental path, some of these concepts have promises of energy density increases of up to 100%. For instance, considering the active materials only, theoretical specific energy density of ca. 950 Wh/kg can be calculated for a Ca/(hypothetical new 4 V cathode with 200 mAh/g capacity) cell. Taking into account the weight of all battery components (casing, electrolyte, separators, etc.) and using BatCap v1.0 software from Argonne National Laboratory [2], specific energy densities as high as ca. 450 Wh/kg are estimated. For sake of comparison, 260 Wh/kg currently constitute the highest values for state of the art LIBs.

Furthermore, as the wide variety of applications in which electrochemical energy storage can be applied comes with a significant diversity in technical and other requirements, a silver bullet technology is unlikely and rather a solid progress in very diverse technologies is probable, that ultimately will find specific niches of application within the vast energy storage landscape. There will of course be advantages by economics of scale which then finally will lead to convergence to not one and not unlimited NGB concepts available – but a foreseeable market place can display a handful or less.

One of the main challenges related to the LIB technology is materials availability and supply related to their domain of use extending from portable electronics to embrace large-scale applications [3]. This has prompted the scientific community to explore more sustainable NGB alternatives based on more abundant materials. To avoid using Li, natural...
graphite, Co, as well as Cu in the cells – all used in LIBs and either limited or expensive elements/minerals, concepts such as Na-ion batteries are currently rapidly making their way to proper commercialization [4]. Other NGB concepts are very much still in their infancy – and within these we find more or less all multivalent ion based rechargeable battery technologies [5,6]. Just using the very simple measure of the Earth’s crust abundance we find Mg to be 7th, Ca 5th and Al 3rd – and this can be contrasted to the very low levels of Li (being 33rd) at 18 ppm. In contrast, Zn, which is the anode used in alkaline primary batteries and may also appear as interesting for rechargeable batteries at first sight, can also be considered relatively scarce (76 ppm) and while its density is high, its standard potential is rather moderate, being the most electropositive metal that can be plated and stripped in aqueous solutions – leading to low voltage battery cells with limited energy density.

Briefly returning to the very basics, any battery/electrochemical cell is made of two electrodes containing electrochemically active materials separated by an electrolyte – an ion conductive electronically insulating medium (Fig. 1). The electrochemical capacity of a given electrode active material basically depends on the number of electrons exchanged and its formula weight, while the electrochemical cell voltage will depend on the difference in potential between the redox couples at each electrode. In order to maximize cell voltage, materials operating at high/low potential are required for the positive/negative electrode, respectively, and complemented by an electrolyte with a wide enough electrochemical stability window (ESW).

Moving from LIBs as well as Na-ion batteries to multivalent NGBs means that within the electrolyte we substitute $M^n$ by $M^{n+}$ (n = 2,3) charge carriers, which result in a reduced number of ions needed to react at the electrodes to achieve a certain electrochemical capacity by 1/2 or 2/3. Alternatively, doubled or tripled capacities would be achieved at the same amount of reacted ions, respectively. Moreover, although a recent study evidenced the possibility for Mg dendrites to grow [8] these multivalent metals overall seem less prone to dendrites growth upon plating/stripping at realistic current densities [9]. The latter opens for the possibility to use metal negative electrodes accompanied by significant enhancements in the theoretical energy density at cell level. This is in stark contrast to Li metal, why Li intercalated in graphite became the standard for the positive electrode insertion capacity of any intercalation compound depends on the total number of electrons that can be transferred to the host redox center(s) and does not depend on the guest cation itself. The maximum practical reversible capacity is controlled by the number of vacant sites accessible in the host and the structural changes occurring during the intercalation process. It therefore 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 – and multivalent cations often cause larger perturbations simply by their larger charge/radius ratios as compared to monovalent Li$^+$. This is indeed why rather conversion electrode reactions, such as with sulfur in Mg-S batteries, and redox reactions with the active groups of organic electrodes are utilized, as for Al-organic batteries [10,11].

Still, however, there are substantial efforts being directed to intercalation compounds for all the multivalent NGBs we here review [6]. As the number of Mg$^{2+}$/Ca$^{2+}$ needed to be intercalated in the host are only half the number of Li$^+$/Na$^+$ necessary (1/3 for Al$^{3+}$) for an equivalent charge transfer – much higher capacities would be achievable (as shown in Fig. 2). Indeed, the ionic radius of Mg$^{2+}$ (0.72 Å) is close to that of Li$^+$ (0.76 Å), while that of Ca$^{2+}$ (1.00 Å) is close to that of Na$^+$ (1.02 Å), and hence suitable structural frameworks should exist and serve as a background for the development of Mg and Ca hosts.

Furthermore, these hosts need to exhibit large cation diffusion rates to be able to operate under high power, and this is true both in the solid state, but also for the electrolyte. Suggish solid-state diffusion and desolvation of solvent ligands at the electrolyte/electrode surface are therefore large challenges for these NGBs. In the bulk of the electrolyte there is basically the same mechanisms at hand – the higher charge/radius ratios make the ions very stabilized by ligands, ions and solvents, of the electrolytes and indeed the solvation shells can be much larger.

![Fig. 1. Schematic illustration of a modern rechargeable battery; a LIB using LiCoO$_2$ and graphite as the electrode active materials and a Li$^+$ conducting electrolyte [7]. Reproduced with permission from ACS.](image1)

![Fig. 2. Standard reduction potential and gravimetric/volumetric capacities of metal electrodes compared to values for graphite, typically used in the Li-ion technology.](image2)
than for Li⁺/Na⁺ [6,7]. One of the main challenges is the electro-de/electrolyte interface where poorly ion conducting passivation layers and also slow ion (de-)solvation may significantly affect the overall power performance. The result is that rather awkward chemistries are employed, especially for Mg electrolytes, with additional problems of extreme sensitivity to moisture and corrosiveness vs. current collectors [12–15]. Aluminium is a particularly challenging case also for other reasons, due to its even higher charge and smaller radius (Al⁺¹ = 0.53 Å). The small radius ion is arguably easily accommodated in a host, but the strong Coulombic interactions resulting are highly prohibitive for both reversibility and fast diffusion – both in solids and liquids.

2. Battery concepts and state of the art

The multivalent ion battery technologies here treated are in many ways similar, but there are also significant differences and these are also further enhanced by the different maturities and history of research. Mg batteries, mainly Mg metal, has ca. 20 years of research efforts to date and a rather large active research community, including start-ups and large consortia focusing on the technology, while Al and especially Ca metal batteries are rather recent fields of research and more or less in their very infancy. The efforts in obtaining working negative metal electrode battery concepts are also to some extent accompanied by resorting to other electrode choices – hence also various M-ion batteries have been explored. Furthermore, in order to balance the vast capacities sulfur positive electrodes have also been explored; M-S batteries. Below we treat all these concepts grouped by the multivalent metal used.

2.1. Mg

Mg metal deposition from solution was demonstrated almost a century ago [16], however, the first report on the use of various Mg complexes and inorganic compounds suitable for rechargeable battery application was Gregory et al. in 1990 [17]. A decade later, a prototype magnesium battery was demonstrated by Aurbach et al. [18] by combining a Chevrel phase positive electrode with a Mg foil separated by an electrolyte containing Mg(AlCl₂BuEt)₂ as Mg-salt. Although the research of Mg metal batteries is rather recent, several large consortia focusing on the technology, while Al and especially Ca metal batteries are rather recent fields of research and more or less in their recent infancy. The efforts in obtaining working negative metal electrode battery concepts are also to some extent accompanied by resorting to other electrode choices – hence also various M-ion batteries have been explored. Furthermore, in order to balance the vast capacities sulfur positive electrodes have also been explored; M-S batteries. Below we treat all these concepts grouped by the multivalent metal used.

The proper choice of electrolyte is of large importance for Mg battery, as solvent and salts successfully used for development of LIBs most often are incompatible with Mg metal. Unlike in case of Li metal, passive film formation on Mg metal blocks both ionic and electronic transport and thereby increases the polarization between the reduction and oxidation reactions. Indeed, any presence of oxygen even at the ppm level, can lead to inactive MgO passivating films. The level and nature of impurities in the electrolyte is also crucial, especially water since even small amounts significantly increases the polarization for stripping and deposition of Mg [12,23], again due to the formation of a blocking passivating film, which is not conductive for magnesium cations. This can, however, be mitigated by using magnesium powder for the negative electrode, which can scavenge electrolyte impurities, and by doing so maintain an acceptable degree of Mg free surface to operate as counter electrode. One common electrolyte development direction is based on addition of Mg-chloride salts to any base electrolyte [23]. The chlorides help to maintain an active Mg surface by reducing the accessibility of reactive anions and impurities to it and additionally by assisting in the formation of various Mg₂Cl₂ species that diminish the high solvation energy associated with free Mg⁺². These electrolytes, however, are corrosive to current collectors based on Al, stainless steel, Cu and Ni. Recently, a couple of chloride-free electrolytes were made based on Mg salts containing complex boron anions; magnesium monocarbaborane (Mg(CB₁₁H₁₄)₂) in tetraglyme [24] and magnesium bis(hexafluorosopropoxide)borate (Mg(BHF₄)₂) in DME [25]. Both electrolytes exhibit high oxidative stabilities and compatibility with various non-noble current collectors. Also, the large majority of electrolytes developed for Mg based batteries currently involve the use of ether solvents. Such low dielectric constant solvents cause a number of new problems, the most important being the formation of relatively strong ion-ion interactions and poor salt solubility, why typically concentrations below 0.3 M are used.

As mentioned above different positive electrode materials are used for Mg batteries, the most interesting being sulfur, redox active organic materials, and inorganic materials capable of reversible insertion and extraction of Mg cations.

Amongst the latter, several materials have been proposed recently.

Besides the Chevrel phases, used very early for proof of concept, chalcogenides offer possibilities for reversible insertion of Mg due to anion lattices offering low electrostatic interactions [26]. One of the most researched materials is titanium sulfide with spinel [27] or layered [28, 29] structure, both displaying good reversibility, but the low operating voltages of the resulting cells decrease their commercial potential. Another large group is molybdenum based chalcogenides [30–32] and different transition metal selenides [33,34]. Much higher practical interest is attracted by oxides, where increased cell voltages result in higher energy densities, but in combination with the current generation of electrolytes they suffer from poor Mg mobility within the structures [35, 36] and structural conversion [37]. Some do show certain degree of reversible magnesium insertion [38–42], but sometimes it is difficult to differentiate between reversible intercalation and contributions from pseudo-capacitance due to nano-sized frameworks and electrolyte incompatibility. Hence, a lot of optimization in connection with novel electrolyte formulations is needed, particularly with respect to the interfaces between electrolyte and active cathode particles.

The combination magnesium and sulfur is highly attractive from a range of different perspectives. Sulfur has a high gravimetric capacity of 1672 mAh/g, much higher than chalcogenides, is highly abundant, and cheap. Although the resulting cell voltage is just above 1 V, a gravimetric energy density comparable to today’s LIB technology is possible. The major disadvantage is the low volumetric energy density of S, which is partly compensated for by the large volumetric density of Mg, a distinct advantage as compared to other sulfur based technologies such as Li-S or Na-S. An electrochemical characterization of a first Mg-S battery was performed in combination with the discovery of the first non-nucleophilic Mg conducting electrolyte, Mg₂Cl₂·HMDSAlCl₃ [10]. Recent literature reports on limited cyclic are connected with soluble polysulfides and their chemical reduction at the Mg metal surface. This can be mitigated at least partially, by use of carbon felts between the sulfur cathode and the separator as additional current collectors hindering polysulfide diffusion from the cathode to the metallic Mg electrode [43]. Classical electrolytes used in recent experimental studies are based on combining different glymes with Mg(TFSI)₂ and MgCl₂ salts. Reduction of sulfur to sulfide proceeds through two well-defined plateaus at 1.6 V and 1.2 V, which correspond to the formation of polysulfides and Mg₂S₈, respectively (Fig. 3) as studied by both XPS [10] and bulk techniques such as XAS, RIXS and ²⁵Mg NMR [45], showing that chemically and electrochemically prepared MgS crystallize in different structures.

Some recent reports show improved cycling stability, connected to improved electrolytes based on tris(hexafluorosopropyl) borate (R(BHF₄)₃), with a capacity >1000 mAh/g at ca. 1.1 V and with low cell polarization [46,47]. The use of a Cu current collector is crucial as applying the same electrolyte with an Al current collector leads to
electrochemical properties more comparable to other electrolytes. The reasonable explanation given is formation of CuS from soluble polysulfides and corroded Cu cations \[46\].

The use of redox active organic polymers as cathode materials show the most promise at present in terms of activity, stability, accessibility of materials, etc. It is also attractive since it represents a sustainable pathway with a lower carbon footprint as compared to inorganic cathode materials, mainly due to much lower energy consumption during the processing as much lower temperatures are needed. Again, as for S cathodes, the low volumetric energy density, polymers typically having densities below 1.5 g/cm³, is partly compensated for by the high volumetric energy density of Mg metal. Some of the proposed redox active compounds exhibit relatively fast capacity fading in their monomeric state, due to large solubility in the electrolyte, which can be mitigated by polymerization of the monomers, by use of ion selective membranes, or by grafting the monomers onto non-soluble substrates. The former path shows the most promise and when composites are prepared by in situ copolymerization with conductive additives, either carbons or electroconductive polymers, very good electrochemical properties result including power density, which often is problematic for multivalent batteries.

In the past the electrophilic centres (C, S) in the structures were not compatible with any of the at that time existing nucleophilic Mg electrolytes. Therefore the very first report showing reversible electrochemical reaction of dimethoxybenzoquinone (DMBQ) with Mg was demonstrated by using 0.5 M Mg(ClO₄)₂ in γ-butyrolactone \[48\], with the electrochemical reaction confirmed by XRD. Indeed, the exchange of electrons associated to parasitic reactions is more common than for LIB systems for which standard electrolytes are available. In this case, use of a three-electrode cell configuration with separate reference electrode, was mandatory in order to circumvent the impedance quickly building up on the Mg counter electrode due to passivation phenomena. As for Mg-S, also Mg-organic batteries have benefitted from the discovery of non-nucleophilic electrolytes \[18\]; and have demonstrated a highly reversible cycling of poly(anthraquinonyl sulfide) (PAQS) \[49\] with Mg metal in a two electrode cell set-up with a discharge voltage of 1.5 V \[50\], and electrochemical activity was demonstrated with three non-nucleophilic electrolytes which were state of the art \[50\]. Changing from anthraquinone (AQ) to benzoquinone (BQ), polymerized PHBQS, increases the operation voltage to 2 V (Fig. 4a) and such a battery can in theory deliver an energy density of up to 650 Wh/kg. Although this battery exhibits good cycling stability \[51\], the practically achievable capacity for BQ based polymers (160 mAh/g) are still far away from the theoretical capacities (400 mAh/g) (Fig. 4b).

Improved capacity retention was reported by using 1,4-polyanthraquinone (PAQ), while only 50% of the theoretical capacity was achieved with a Mg(HMDS)₂+4MgCl₂ (HMDS-hexamethyldisilazane) in tetrahydrofuran (THF) electrolyte \[52\], but still this combination demonstrated long term cycling at useful current densities; 1000 very stable cycles at 1C and 2C rates. Polymides is another group of conjugated carbonyl compounds with applicability in Mg batteries. A typical discharge voltage is around 1.7 V, while capacities are lower due to the higher molecular weight and as not all carbonyl groups are electrochemically active \[53\], which is the reason why the economic viability is relatively low. Practical capacities are lower than achieved in Li systems and the materials exhibit long activation periods – a property of all polymeric redox active organic materials. A proper electrolyte selection affects the activation period and the Coulombic efficiency. The electrochemical mechanism of organic cathodes has been discussed for a long time and the explanations predominately proposed are based on post mortem analysis and predictions. However, the long activation process and the practical capacity demonstrated being far from the theoretical stress the need for a characterization tool enabling operando visualization of the changes within the battery. Operando mode ATR-IR (attenuated total reflectance infrared) spectroscopy characterization was developed with a Si wafer pouch cell \[54\]. Reversible reduction of carbonyl bond upon discharge and its reappearance during charge was demonstrated, accompanied by the formation of new –C=O– band during discharge with some other changes in the polymer structure. Small differences between the lithiation and magnesiation processes were observed and further explained by DFT calculations. The lower capacities typically recorded in Mg cells are mostly due to the poor mobility of the large Mg complexes.
formed in the electrolytes. Nevertheless, it is still debatable whether two carbonyl groups interact with Mg$^{2+}$ or if each carbonyl group interacts with MgCl$^-$ formed in the electrolyte. In the latter case the battery capacity will depend on the concentration of MgCl$_2$ and on the electrolyte amount used in the cell [55].

2.2. Ca

As for Mg and all multivalent battery concepts the large promise for Ca batteries is in the application of a metal anode. In contrast to Mg, however, electrodeposition of calcium has for long been elusive, as no Ca analogues to Mg based Grignard reagent electrolytes are available [5]. Seminal studies by Aurbach et al. [56] using conventional aprotic organic electrolytes similar to those used for LiBs allowed them to conclude that the electrochemical behaviour of Ca metal anodes is surface-film controlled, as is the case for Li. Nonetheless, the lack of calcium ion permeability of the formed SEI was suggested to be the origin of the apparent impossibility to electrodeposition calcium using these electrolytes. It has, however, recently been demonstrated that Ca electrodeposition is indeed feasible, both from alkyl-carbonate based electrolytes forming an SEI layer, but provided that the operating temperature is moderately raised (>75°C) to favour the cation mobility [57], or by using an electrolyte of CaBH$_4$ in THF, creating a CaH$_2$ native SEI layer [58]. These findings for the metal negative electrode opened the quest for the other half of the Ca battery—potential positive electrode (intercalation) materials.

The first attempts to study electrochemical calcium intercalation in prospective positive electrode materials, which showed some electrochemical response, were published in the early 2000’s and were limited to either hexacyanoferrates using an aqueous electrolyte [59] or V$_2$O$_5$ using Ca(ONO$_2$)$_2$ in acetonitrile as electrolyte [60]. More recently, the former system has been re-investigated [61], using also organic non-aqueous electrolytes [62], which enabled to prove a very reversible electrochemical response and also enhanced capacity derived from water addition [63]. Despite some reports [64,65] indicating minor, if any, modifications of the host structure, the redox mechanism and the possible role of water is not fully elucidated.

As for Mg a major issue in the pursuit of novel positive electrode materials is that the know-how from the LIB field cannot be directly translated to Ca systems; the absence of reliable reference and counter electrodes is a significant bottleneck to overcome. While metal electrodes are widely used as counter/reference electrodes in so-called half-cell configuration for LiBs, the formation of an SEI impacts their trustworthiness as reference electrodes for in Ca systems [66].

Besides these issues, which are related to the stability of metal and counter/reference electrodes, the possible side reactions related to the presence of water, e.g. proton intercalation as for Mg intercalation in V$_2$O$_5$ [67], electrolyte decomposition or current collector corrosion [68], can lead to misleading conclusions/assumptions with respect to calcium intercalation [69]. The use of complementary characterization techniques [70,71] is thus compulsory to clearly assess reactivity. Computational studies are useful tools for screening potential positive electrode materials [71–74], but in silico design is not straightforward. Some compounds predicted to enable low migration barriers for Ca$^{2+}$, such as a hypothetical CaMn$_2$O$_4$ spinel, has never been achieved experimentally. In contrast a stable polymorph exhibits very large Ca$^{2+}$ migration barriers, in agreement with the impossibility to extract calcium ions from the structure experimentally [75]. Hitherto some electrochemical reactivity has been unambiguously proven related to calcium extraction for 1D Ca$_3$Co$_2$O$_6$ (Fig. 5) [76], but with lack of reversibility. In contrast, reversible intercalation and de-intercalation of calcium has been assessed for TiS$_2$, despite slow kinetics and solvent co-intercalation [77].

As for Mg, but with even less total effort put in, the use of a high capacity S positive electrode to balance the Ca metal negative in a Ca-S battery configuration is tempting and has indeed been attempted—but so far without any reversibility [78].

2.3. Al

The seemingly most obvious difference of Al to Mg and Ca would at a first glance be the triple-charged Al$^{3+}$ ion to be transported and active at the electrodes. But this is not really the case. The largest difference is rather that almost all functional Al batteries so far has been using an electrolyte with an anionic [AlCl$_4$] complex to transfer Al, and as this complex has been used for intercalation this has also resulted in low energy densities, corrosion by Cl$^-$ (as for the Mg batteries), and utmost a need for very special intercalation electrodes [79]. Another inherent large difference to both Mg, but in particular to Ca, is the relatively high standard potential of Al (−1.66 V) which most likely means that the cells created will end up being low to medium voltage as the cathode chemistry, and electrolyte stability window, cannot really be expected to be shifted by the same amount.

Fig. 5. a) Potential vs. capacity profile from potentiodynamic cycling of Ca/Ca$_3$Co$_2$O$_6$ cells at 100 °C and C/200 rate using 0.45 M Ca(BF$_4$)$_2$ dissolved in a 1:1 vol mixture of ethylene carbonate (EC) and propylene carbonate (PC) as electrolyte. b) Expanded region of synchrotron XRD showing changes upon oxidation/reduction (E corresponding to a sample fully reduced at 115 °C). c) 1D crystal structure of Ca$_3$Co$_2$O$_6$ consisting of infinite columns of face-shared CoO$_6$ octahedra and CoO$_6$ trigonal prisms forming a hexagonal lattice with Ca$^{2+}$ ions forming chains between the columns. Reproduced with permission from RSC [77].
Rechargeable AI metal based batteries, where the true promise is the fantastic theoretical volumetric capacity, may seem awkward, not the least due to the very stable Al2O3 oxide passivating the AI metal. Only a few reviews exists to date [80–82], and true proof-of-concept was presented as recently as in 2011 for an AI/V2O5 cell [83]. An ionic liquid (IL) based electrolyte ([AICl4]-EMICl) was the key to create the [AI2Cl7]- complex as hinted at before [84] and could perhaps even been "expected" by the replete use of ILs for AI electrodeposition [85]. In stark contrast no electrochemical activity whatsoever was demonstrated with conventional organic electrolytes. This AI-battery cell reached 20 stable cycles ending at 273 mAh/g, an OCV of 1.8 V, and ca. 240 Wh/kg. Even so, these results have been challenged in later studies, questioning the electrochemical reaction and suggesting corrosion of the stainless steel current collector to rather be the source [86].

Moving from V2O5, which also has issues of fast capacity fading [87], to Chevrel phase MoS8 as cathode came with a very low cell voltage of ca. 0.4–0.6 V, but the more problematic feature was the trapping of AI3+ rendering the capacity to be no more than ca. 80 mAh/g [88].

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In fact, research on re-chargeable batteries based on AI is not new, but they have been laden with numerous problems the last 30 years or more. In the article in Nature in 2015 where Lin et al. [79] presented a new AI-battery with considerable better efficiency and remarkably long cycle life (>7000 cycles) this was acknowledged. Despite the benefits presented, this AI-battery was based on a very special graphitic foam and resulted in a specific energy density of ca. 40 Wh/kg and is thus merely on par with Pb-acid and NiMH-batteries, and far from LiBs (or earlier AI-batteries). The overall problem resides in two designs of these batteries; 1) they (as most other AI-batteries) rely on the transport of AI3+ as a [AICl4]- complex, with concomitant issues of migration vs. diffusion, and 2) they intercalate this complex into a host, which obviously needs to be very sparse to accommodate the large complex. Another rather similar study using an AI/graphite system showed extreme performance in terms of cycle life and rate capability; half million cycles and discharge in 10 s. One of the main limitations was, however, consumption of electrolyte during cycling, why between 2 and 6 g of electrolyte (EMIMCl:AICl3) was required for each gram of carbon, and hence the battery is characterized by a very limited energy density [89]. There has recently been other advanced sparse hosts, 1-3D C3N, launched computationally for intercalation of the chloro-aluminate anion, but focusing on kinetics and voltage rather than capacity [90].

Starting with the problem of the electrolyte some few attempts to create Cl-free and cationic AI3+ complexes for more efficient transport in more fluidic systems have been reported [91,92]. Indeed, if the transport of AI3+ could be made the same way as for other cations, in cationic complexes [ML]2AI+3, where L is a ligand = neutral organic solvent, there is hope for more stability. If then AI3+ can be the electroactive species at the cathode as well, an up to 10-fold capacity increase as compared to the state-of-the-art is viable. No such electrolytes are, however, available (yet) - apart from those presented in some basic attempts, but as for the initial work on AI stripping/plating also these electrolytes, such as the "aluminium solvate IL", [AI(BIm)3][TFSI]3, a liquid at room-temperature with ion conductivity and some electrochemical activity, was made to function only at elevated temperature (85 °C) [93]. However, these studies have shown that it indeed is possible to create very weakly bound cationic complexes of AI3+, develop electrolytes where the conductivity is decoupled, not limited by the viscosity, and rationalize modify AICl3 into a variety of charge carriers by smart choices of ligands. The [AI(G3)2][AI(TIO)4(OH)2]-G3 structure (Fig. 6) shows very long AI-O distances (2.5–2.7 Å) in the [AI(G3)2]- part (left) and with only ca. 1/3 of the binding energy of the anionic [AI(TIO)4(OH)2]- complex (central) [93].

The figure below in turn shows the N-methylacetamide (NMA) + Urea + AI(Tf)3 deep eutectic solvents (DESs) based electrolytes to have an appreciable ion conductivity with the maximum not corresponding to the minimum in viscosity and with a non-linear behaviour. More recently an urea-based electrolyte, but using AlCl3 as the salt, have been used also by other groups [94]. On the positive side the state-of-the-art for AI-batteries has until now either: i) considered standard transition metal oxide materials like V2O5 (as shown above) with many problems, including that of a full 3-electron transfer and fundamentally limiting the efficiency and making it more of a worse type of LIB (as there is only a 1-electron transfer), and/or ii) been based on intercalating the entire [AlCl4]- complex from the electrolyte – again leading to the very low practical capacities reported.

Fig. 6. The cationic (left) and anionic (mid) AI complexes of a homometallic double complex salt flanked by co-crystallized G3 solvent (right) Reproduced with permission from RSC [94].

Fig. 7. Variation of ionic conductivity (σ) and viscosity (η) for ternary electrolytes as function of XNMA at 30 °C [93]. Reproduced with permission from RSC.
A more recent research direction for Al battery cathodes has been the use of organic active centra grafted onto polymers, such as those originally developed for Mg-batteries [95], also for Al-batteries. Very recently a proof-of-concept for an Al metal – organic battery was presented delivering 5000 stable cycles and a reversible capacity of 110 mAh/g, a battery wherein the organic part is mixed with graphite flakes [11].

3. Technical bottlenecks

While the development of multivalent cation based technologies would be mostly relevant in terms of energy density if metal anodes are being used [96], the use of Ca, Mg or Al metal implies significant technological challenges. Indeed, in contrast to Li metal that could be commercialized [97], Ca, Mg or Al would require drastic atmosphere control procedures during cell assembly. Any traces of oxygen, water, or any other kind of contaminant which could react at the electrode surface could completely block or at least significantly lower the kinetics of the plating/stripping process. Two possible avenues are foreseen to address this issue: 1) development of some kind of pre-passivation protocols for the metal anode, allowing for easier handling in conventional dry rooms as used for Li-ion battery cell assembly, or 2) use of ultra-high purity chambers for both metal anode preparation and cell assembly, which though most probably would have a significant impact on the overall cost of the cell (in $/Kwh).

Also, due to the difference in terms of material stiffness between Li and Mg or Ca (the Young's modulus of Li is 4.9 GPa and 45 and, respectively, 207 GPa for Mg and Ca) new anode production strategies will be needed. If foils are to be used, evaporation methods for high purity Ca - Mg might have to be implemented and its cost to be taken into account for the overall cell production. In contrast, production of Al foils is currently well mastered, despite the presence of the native aluminium oxide passivation layer possibly being an issue. On the other hand, a significant increase in terms of energy density at the cell level as compared to LIBs would also mean that production cost can be reduced by cutting on the cell packaging cost. One could also assume that the absence of dendrite formation for Mg and Ca could ease the safety requirements and perhaps lower the level of complexity of the battery management system (BMS).

Smooth plating of a metal is well known to be a complex issue from classical electrochemistry. Dendritic electrodeposition results from a diffusion limited process, the deposition potential being significantly shifted negative from the equilibrium potential of the M<Sup>+</Sup>/M couple. Under such conditions, an anisotropic growth is highly favored by the very limited surface diffusion of the adsorbed cations before charge transfer occurs, and the dendrite formation is facilitated by an improved hemispherical diffusion at the tip of the dendrite. Until very recently and unlike Li, Mg was thought not to be plagued by dendrite formation [98]. Indeed, even for plating at relatively high current density (2 mA/cm²) no evidence of irregular, dendritic growth can be observed. Several parameters could explain this difference between Li and Mg systems. Obviously, the absence of an SEI at the surface of Mg electrode is a significant factor improving the mass transport homogeneity towards the electrode. Theoretical investigations of the surface mobility of Li and Mg adatoms were performed and pointed at lower self-diffusion barriers of the Mg adatom than for Li [99].

However, two very recent studies have suggested formation of Mg dendrites. In one case, globular shape deposits were achieved [100], which closely resemble a non-uniform metal deposition, but could hardly be called dendrites. In contrast, the structures observed by Davidson et al. are unambiguously dendritic [8]. Nonetheless, even if Mg dendrites instead were growing when using a current density of ca. 1 mA/cm², the cell geometry and especially the shape of the Mg working electrode in these cells, presenting very sharp edges where dendrites always start to grow, is far from any real battery design and favour highly inhomogeneous current line distribution. Realistic tests on flat electrodes with reliable current density are thus mandatory in order to evaluate the exact current density threshold at which Mg dendrite start to grow.

4. Conclusion and perspectives

Looking for the holy grail combination of elements which can deliver cells of high energy density, multivalent ion metal anode based rechargeable battery technologies are clearly a research pathway to follow. At present it exhibits very different degrees of maturity for Mg, Ca and Al, and the bottlenecks and concepts are somewhat different, especially for the latter.

Several steps forward were done recently in the field of novel Mg based electrolytes, cathode materials and cell configurations. With respect to cathodes, both organic materials, and also sulfur (under some specific conditions) have demonstrated cells with long term cyclability being possible. While for the former there is a need to develop non-nucleophilic electrolytes with improved capability of polymer swelling, the Mg-S efforts should be directed towards suppressing the solubility of polysulfides. Inorganic cathodes are mostly chalcogenides, as use of oxides is still prevented by the lack of electrolytes with higher oxidative stability windows. Moreover, the (in)stability of interfaces is not fully yet explored and there are many open technological questions: anode composition, electrolyte additives, current collectors, separators, additives, cell casing, etc. Parallel efforts on several concepts in that direction by different groups should enable assessing conditions for practical viability and commercialization.

For Ca batteries, despite reversible plating/stripping being demonstrated with two different concepts, improvements are highly necessary for kinetics/efficiency and/or widening the electrochemical stability window of the electrolyte. On top of that, the road towards the development of a positive electrode material operating at high potential and enabling decent capacities with fast kinetics is clearly very long and winding. For the moment only inorganic materials have been considered, with organic materials and sulfur remaining interesting pathways to follow. Moreover, we can reasonably expect that efforts targeting electrolyte optimization may also result in performance benefits on the cathode side. Overall, a deeper understanding of the nature of cation complexes formed in the electrolyte, its transport properties and the interfacial processes such as adsorption, (de-)solvation, etc, will be key for further developments.

For Al batteries there are in principle two main (very) large obstacles to overcome. One is to develop functional electrolytes free from Cl- and capable of fast cationic Al<Sup>3+</Sup> transport, as this would render Al batteries both more performant and more stable including solving the corrosion problems, the latter today affect the reliability of tests made, but will in the future cause problems for encapsulation. The second is that there are no cathodes capable of either efficiently coordinating or even accommodating the 3 e<Sup>-</Sup>/Al<Sup>3+</Sup> in the framework, and this means to target different hosts and host-guest interactions than those employed at present. Here the path of organic cathodes seem to be the more promising with the large amount of flexibility in design.

Both these development must of course also be made without losing the Al plating/stripping capacity at the very advantageous Al metal anode.

While the global evolution prospects are relatively uncertain, it is clear that fundamental research is compulsory to assess viabilities for each of the concepts treated above and, if viable, realize the potential to transform them into reliable commercial products. Strategic materials design and selection are expected to play major roles in that respect and hence research should not only be done within academia, but also include industrial R&D departments with specific focus on accelerating progress through development of effective synergies.

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References


