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Side by Side Battery Technologies with Lithium-Ion Based Batteries

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In recent years, the electrochemical power sources community has launched massive research programs, conferences, and workshops on the "post Li battery era." However, in this report it is shown that the quest for post Li-ion and Li battery technologies is incorrect in its essence. This is the outcome of a three day discussion on the future technologies that could provide an answer to a question that many ask these days: Which are the technologies that can be regarded as alternative to Li-ion batteries? The answer to this question is a rather surprising one: Li-ion battery technology will be here for many years to come, and therefore the use of "post Li-ion" battery technologies would be misleading. However, there are applications with needs for which Li-ion batteries will not be able to provide complete technological solutions, as well as lower cost and sustainability. In these specific cases, other battery technologies will play a key role. Here, the term "side-by-side technologies" is coined alongside a discussion of its meaning. The progress report does not cover the topic of Li-metal battery technologies, but covers the technologies of sodium-ion, multivalent, metal–air, and flow batteries.

1. Introduction

In May 12–16, 2019, a dozen senior battery and supercapacitor scientists and approximately 30 PhD students and post doctorate fellows from Israel and Germany gathered in Berlin, Germany, in the frame of the 4th German-Israeli Battery School (GIBS4). The Berlin workshop was divided into two major sections; the first one consisted of invited talks delivered by leading scientists on their research, focusing on the state-of-the-art of electrochemical power sources technologies. The second part of the workshop was dedicated to thorough discussions focusing on four "burning topics", including the following themes: 1) Future after lithium; 2) fast charging; 3) will the future be liquid or solid; and 4) Fuel cells versus batteries—complementary or competitors.

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Here, we bring to the readers the outcome of Group 1 discussion: Future after lithium. The group has covered battery chemistries that are often being considered as "post-Li" battery technologies. After extensive deliberations, the group concluded that the current vibe about the need of future technologies after the lithium era and, thus, the quest for which new technologies can replace lithium-based battery technology, are somewhat inappropriate and misleading (partially incorrect), respectively. The discussion group reached the conclusion that it would be wise to approach and refer at these technologies as "side-by-side" to Li-based batteries. As such, we elaborate here in details on these "side-by-side" promising technologies.

Evaluation of the battery concepts depends on several aspects, among which performance is one of the key parameters. Hence, the performance comparison of different cell chemistry is everything, but immediate. As a matter of the fact, the European Commission, e.g., funded the ETIP Batteries Europe (https://batterieseurope.eu/) as the "one-stop shop" for the battery-related R&I ecosystem and aims to accelerate the establishment of a competitive, sustainable and efficient value chain and globally competitive European battery industry through Research and Innovation. Within this ETIP, several working groups have been established, including the one dealing with new and emerging cell technologies. This group, led by Prof. Edström, Dr. Steven and one of the co-authors of this manuscript (SP), is expected to identify the key performance indicators (KPIs) enabling a fair comparison of commercial, new and emerging cell technologies with respect to their applications. However, these KPIs have not been identified yet. Hence, the current study aims to provide insights into "side-by-side" new emerging technologies and also to report a comparative analysis to Li-ion batteries by using a simple approach (i.e., mainly considering cost, energy density, and cycle life). Nonetheless, due to the fact that most of the "side-by-side" technologies are at the early stage of development, a comparison among them is not trivial. Thus, we point out in this progress report only the possibly suitable applications of the new technologies without a comparison.

2. Sodium-Ion Batteries (Na-Ion)

2.1. Introduction

To relieve the environmental issues, solving the problem caused by intermittent availability of renewable energy resource, e.g., solar energy, wind energy and geothermal energy, is mandatory. Thus, energy storage systems, especially electrochemical energy storage (EES) systems including batteries, supercapacitors, etc., are in the focus of intensive research and development efforts.[1–3] In 1991, the Japanese Sony Corp. developed the first commercial lithium-ion batteries with $LiCoO_2$ and graphite as electrode materials.[4,5] With the blooming of portable electronic

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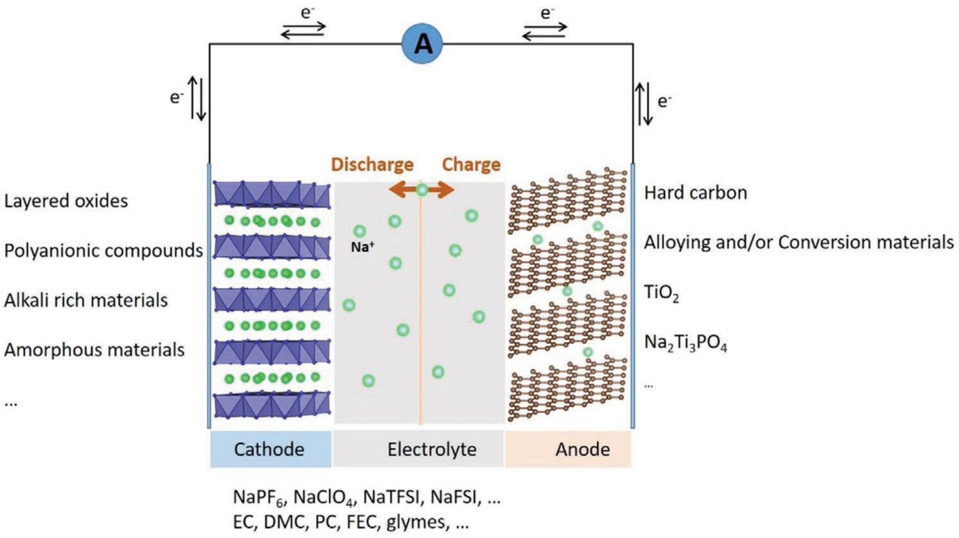

Figure 1. Schematic illustration of sodium-ion battery. The intensively studied materials are listed in the graph.

devices and electric vehicles, the lithium-ion batteries market has been developing very fast in last three decades, generating the societal change eventually recognized by the assignment of the Nobel Prize for Chemistry 2019 to Whittingham, Goodenough, and Yoshino. The increasing demand of electric and/or hybrid vehicles leads to the concern regarding the cost of lithium-ion batteries. However, the cost of these batteries has been decreased from around 1000 to almost 100 € kWh^{-1}, which is mainly due to the rapid, but effective large-scale industrial development.[6,7] This cost will further decline in the next several years following the increasing scale of production needed to fulfill the market requirements. Besides, the materials supply risk, especially for Co and, later, Ni, is the very recent concern for the sustainable long-term development of lithium-ion batteries. Sodium-ion batteries making use of more Earth abundant elements and, possibly, renewable carbonaceous sources are becoming promising for "side-by-side" energy storage systems. Indeed, the high-temperature Na–S battery technology, utilizing a molten Na metal and a sulfur cathode separated by a Na–aluminate solid electrolyte, has been already commercialized for grid-scale applications, but its cost is in the range of 445–555 $ kWh^{-1}.

As the lithium-ion batteries, sodium-ion batteries utilize the same ion storage principle, using the alkali ions only as charge carriers while energy is reversibly stored and released in intercalation and/or conversion electrodes, as illustrated in **Figure 1**. As per any generic alkali-ion-shuttling battery, Na-ion batteries normally consist of one positive and one negative electrode, the electrolyte, the separator, and the battery case. Upon charging a sodium-ion battery, sodium ions are extracted from the cathode material (positive electrode) and, shuttling through the electrolyte, transferred into the anode material (negative electrode, e.g., hard carbon). Allowing an external current to flow, the battery spontaneously discharge, i.e., the oxidation reaction on the anode occurs, corresponding to the sodium ions leaving the negative electrode host structure to go back into the cathode host structure, which is reduced by the electrons flowing in the external circuit. In spite of sharing the same principle, the different ionic radius of the shuttling ions ($r_{\mathrm{Na}^+} = 1.02$ Å, $r_{\mathrm{Li}^+} = 0.76$ Å, CN = 6) result in different physical properties of the ion storage materials and, even, the solvents and salts for electrolytes. Thus, more investigations are needed for sodium-ion batteries. Some intensively studied materials are listed as examples in Figure 1. This chapter discusses sodium-ion batteries by comparison to the well-developed lithium-ion batteries with regard to sustainability, safety, and performance.

Since both Li-ion and Na-ion battery technologies hold similar electrochemistry principles, the sodium-ion battery technology can track and adopt most of the knowledge gained through the extended and in-depth studies conducted with lithium-ion battery technology. Further breakthroughs regarding the energy density of sodium-ion batteries strongly rely on the development of high performance electrode materials.[8] Other cell components, including separators, binders, outer cases and, to some extent, the major components of the electrolyte (i.e., solvent and salt), may have a limited impact on further performance improvements and even cost reduction, especially when compared to lithium-ion battery, despite the ability to utilize an Al cathode current collector in sodium-ion batteries. Meanwhile, the synthesis of high purity battery grade sodium salt (i.e., $\mathrm{NaPF_6}$) as the electrolyte in Na-ion batteries requires more technical insight and price reduction.

2.2. Sustainability and Cost

The discovery of high Na-ion conductive materials in the 1930s opened the avenue to research investigation on high performance sodium-ion batteries.[9,10] After the discovery of lithium-ion batteries,[2,11] however, the research work on sodium-ion batteries suddenly declined. Yet, since 2008, the amount of publications on sodium-ion batteries is on a quick rise again.[12] This renaissance is not only because of the remarkably higher natural abundance of sodium compared with lithium, but also the ease availability even from seawater, see **Figure 2**a. The low price and unlimited available resources are thereby the major advantages of this technology. In fact, especially if shortage

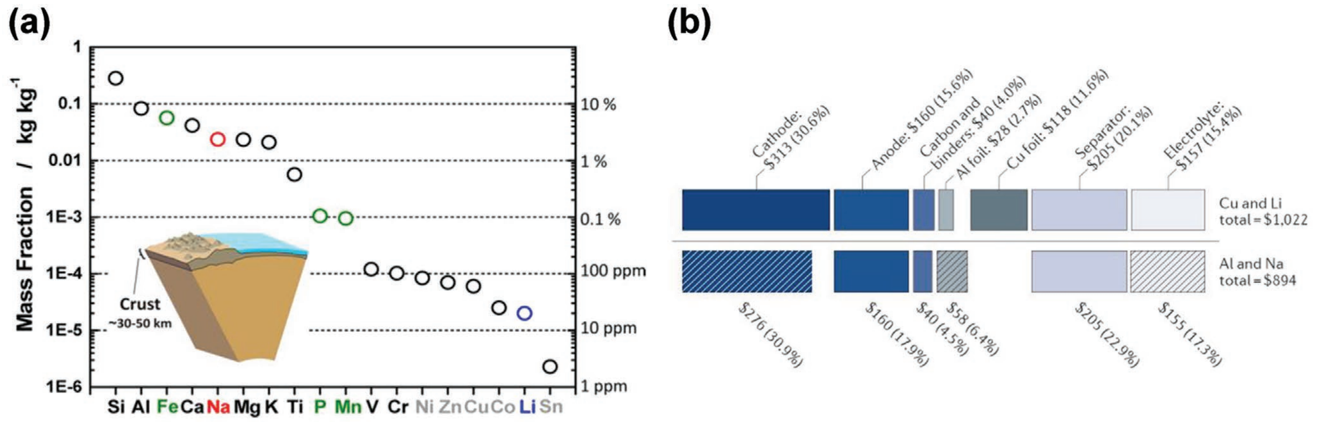

Figure 2. a) Earth crust elements abundance comparison, b) cost comparison of lithium-ion batteries with Cu as anode current collector and sodium-ion batteries with Al as current collector for both sides. Reproduced with permission.[17,13] Copyright 2014, American Chemical Society. Copyright 2018, Springer Nature.

of supplies or peaking prices of lithium and cobalt will occur, sodium-ion batteries could serve as an affordable complementary device.[13] Another advantage comes from the feasible use of aluminum foil as anode current collector instead of the expensive copper foil necessary in lithium-ion batteries. Considering that aluminum as current collector enables full discharge of the cell without anodic dissolution, its use could further decrease the materials and cell shipment costs substantially. The ease shipping could probably allow more efficient recycling of batteries at the end of life.[14] Finally, inexpensive transition metal-(TM) based cathode materials, like manganese and iron, appear feasible, thus relieving the tension caused by the Co and Ni, commonly used in lithium-ion batteries.[13,15,16] Actually, the cost and environmental friendliness of the layered oxide cathode materials proposed so far, appear to be the major advantages of sodium-ion batteries (Figure 2b).

2.3. Safety and Durability

The periodic table predicts that metallic Na is more active than Li. It is anticipated that Na metal might hold severe safety issues compared to Li metal. Na dendrite grows and forms faster than lithium dendrites upon metal plating because of the highest sodium ion migration barrier on the metal surface.[18] Although some recent reports have shown the beneficial effects of some electrolytes and/or electrolytes additives, preferentially leading to cubic Na crystal formation, against dendritic plating,[19] unwanted Na metal plating upon cell fast charging certainly represents a serious safety issue.

Traditional organic liquid electrolytes, similar to those adopted in Li-ion battery technology, are currently applied in Na-ion batteries. These include for example EC, DMC, PC, and ether solvents, though some challenges are posed with graphite-based anodes (the details will discuss in the following section).[20,21] These are all flammable organic compounds bearing the same safety concerns. Considering the operation voltage window, layered oxides (such as $Na_{2/3}Ni_{1/3}Mn_{2/3})O_2$[22,23] and vanadium-based polyanionic compounds are, so far, the best high voltage, candidate materials for the positive electrode[24,25] and hard carbon for the negative one. Thus, the cell voltage at 100% state of charge (SOC) is expected to be rather similar to that of Li-ion batteries, leading to similar safety concerns. Additionally, the use of hard carbons at the negative electrode, characterized by a large fraction of the Na-ion storage occurring at a potential near to Na plating, exacerbate the above-mentioned Na dendritic growth upon fast charging.[26,27]

On the other hand, Na-ion batteries are easier to ship than Li-ion batteries. These latter, in fact, have caused a few severe accidents during shipment due to their thermal and electrical instability under uncontrolled environments or mishandling during transportation, which may lead to release of hazardous gases, fire, and even explosion. The most critical reason for safety comes from the oxidation of the copper foil employed as negative electrode current collector. In fact, at high potential, i.e., when the cell is at 0% SOC, Cu is oxidized. To avoid the dissolution of Cu^{2+} ions in the electrolyte, which may result in internal short-circuiting upon the following charge, Li-ion batteries can only be shipped in a partially charged state. Thus, strict regulations have been established to ensure their safe transportation.[28,29] However, Na-ion batteries use Al foil as current collector for the negative electrode, which does not oxidize at high potentials allowing the full discharge of the batteries prior to shipment. This is certainly an additional advantage leading to lower costs for the shipment and delivery of Na-ion batteries. The long-term performance of O3 transition metal layered oxides and $Na_3V_2(PO_4)_3F_3$ has been compared in full-cell configuration using hard carbon as the negative electrode. The O3-based electrode outperformed the vanadium-based electrode, retaining 80% energy over 100 cycles between 4.4 and 1.2 V at C/20 rate.[30]

In light of all these aspects, it is concluded that Na-ion batteries hold similar safety issues of Li-ion batteries for large-scale applications, except for the ease shipment and shelf-storage. Similar to Li-ion batteries, the sodium-ion batteries have been proposed in several applications, such as large-scale energy storage. The durability of the battery has become also important parameter, in terms of liability, as well as the safety. The failure mechanisms can be ascribed to the degradation of the battery materials and the environmental conditions impact, as usually reported in LIBs.[31] Moreover, sodium compounds

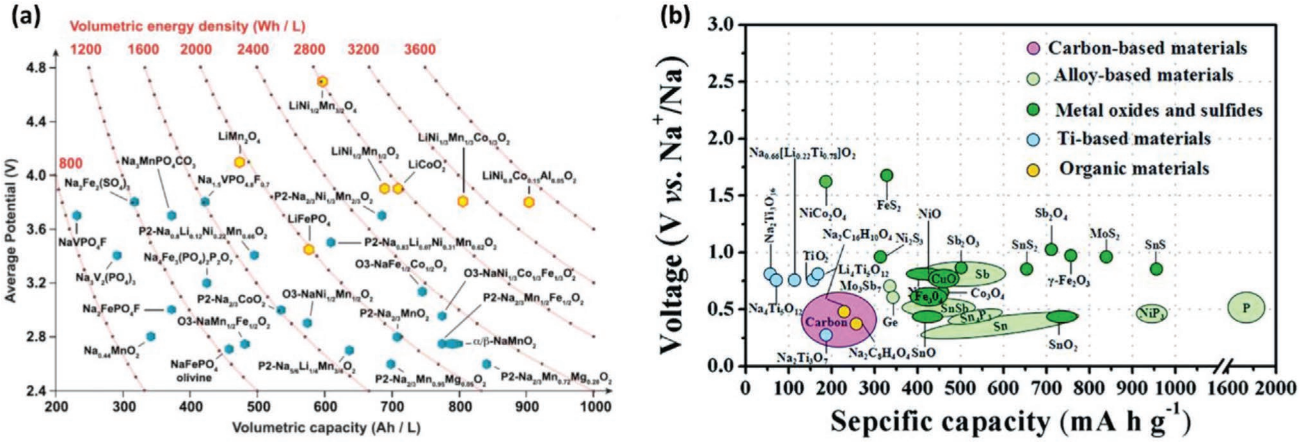

Figure 3. Comparison for selected cathode a) and anode b) materials for sodium-ion batteries. Reproduced with permission.[34,37] Copyright 2015, The Electrochemical Society. Copyright 2015, The Royal Society of Chemistry.

in principle, are more soluble than the counter-parents lithium compounds, reflecting on the instability of the SEI. However, due to the early stage of sodium-ion battery technology development, there is still an insufficient knowledge on failure modes, mechanisms, and analysis at the full cell level.

2.4. Performance

In order to discuss the performance of Na-ion batteries, it is wise to describe each electrode individually. Regarding the positive electrode (cathode) materials, as for Li-ion batteries, four different types can be easily identified, by their structures, namely: layered oxides, polyanionic compounds, alkali-rich materials, and amorphous materials.[32,33] **Figure 3**a compares the performance for some published lithium and sodium cathode materials.[34] With respect to layered compounds, Na-based materials incur in more structural changes upon (de-)sodiation than their Li-based counterparts. Because of this, they operate in larger voltage ranges with lower average voltages. An additional concern with Na layered oxides is that H_2O traces easily penetrate into these materials causing capacity degradation upon cycling. The need to reduce exposure to water obviously leads extra costs for material storage and handling and cell making requiring highly controlled environmental conditions.

Among the polyanionic compounds, the most famous one is certainly $LiFePO_4$ offering a rather stable working voltage of ≈3.5 V due to the two-phase reaction during charge and discharge.[35] However, the Na-counterpart can only be synthesized via electrochemical replacement of Li for Na. The intermediate phase $Na_{2/3}FePO_4$ forms for $NaFePO_4$ electrode during electrochemical process.[36]

Besides, Na-based cathodes display generally lower capacities than the analogous Li cathode materials. To achieve high energy density, more alkali ions need to be present in the structure. Researchers afforded to introduce additional Li-ions in the TM site in layered oxides. As a result, Li-rich material can really achieve high specific capacity of over 300 mAh g^{-1} thanks to the Li-ions located in the TM positions.[38] However, this approach is physically impossible for the Na-based materials due to the larger ionic size of Na ions. Instead of crystalline structures, amorphous materials, offering conversion storage mechanisms, are also viable options as Na-ion positive electrodes.

The concerns for the conversion materials are the rapid voltage decay and volume changes occurring upon charge–discharge cycling. It should be emphasize that in any cathode material for both Li- and Na-ion batteries, there is always a gradual voltage decrease upon prolonged cycle life, which leads to lower energy efficiency and density.[32] However, Na-based cathode materials face more challenges compared with lithium cathodes. Nonetheless, research and development efforts in this field should not be given up by the scientific and industrial communities. Li and especially Co supply issues may become more critical with the fast expanding market demands. Earth abundant and cheap elements, e.g., Mn, Fe, etc., are the leading promising materials for Na-ion battery positive electrodes that may lead to the commercialization of real less expensive and sustainable batteries.[39,40]

Regarding negative electrodes, carbonaceous materials are widely used in Li-ion batteries, especially graphite. However, graphite does not function as host material for Na ions in carbonate-based electrolytes, e.g., EC, DMC, PC etc.[41] On the other hand, ether-based electrolytes enable reversible Na ion storage into graphite via cointercalation mechanisms.[42] However, required additional amount of electrolyte's solvent and the lower storage capacity (about half of that for Li ions) makes graphite less interesting as negative electrode material for Na-ion batteries. Hard carbons, instead, show promising performance offering capacities exceeding 300 mAh g^{-1}, i.e., comparable with those of graphite.[43,44] Additionally, hard carbons can be efficiently produced from biowaste largely enhancing the sustainability of this battery chemistry.[45–47]

Alloying and conversion materials are also suggested as negative electrodes in sodium-ion batteries, e.g., Sn alloys, transition metal sulfides, and others.[48] They can work well with carbonates electrolytes, but the volume change and, sometime, the price are intrinsic drawbacks. Minimizing particle size and mixing with carbon materials are the two general strategies to relieve the electrodes expansion effect during cycling. Figure 3b compares the performance of some anode materials for sodium-ion batteries.[37] The performance of typical Li- and

Table 1. Comparison of the voltage of popular lithium-ion batteries and sodium-ion batteries. The voltage indicates the nominal operation voltage of the cells. Gravimetric energy density and volumetric energy density values are calculated at a cell level.

Cell type	Voltage [V]	Gravimetric energy density [Wh kg^{-1}]	Volumetric energy density [Wh L^{-1}]	Refs.
Lithium–ion				
$LiFePO_4$/graphite	3.3	80–150	120–300	[49]
$LiCoO_2$/graphite	3.7	160–210	340–580	
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/graphite	3.7	150–300	680–760	[50]
$LiMn_2O_4$/graphite	3.8	100–130	220–400	
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/graphite	3.7	150–220	580–750	
Sodium-ion				
$Na_xV_2(PO_4)F_y$/hard carbon	3.4	≈100	≈175	[30]
Na_xTMO_2/hard carbon	3.0	≈115	≈250	

Na-ion cells is listed in **Table 1** clearly proving the inferiority of the latter system. Dedicated work is needed on anode materials and electrolytes compositions (compared with the extended works dedicated to the cathode materials conducted thus far) in order to utilize a full sodium-ion battery system.

2.5. Applications

The relatively lower energy density of Na-ion batteries compared to their Li-ion counterparts (see Figure 3a, Table 1) cannot be overcome, unless of some breakthrough material discovery will occur. Therefore, the possible fields of application are narrowed to those where energy densities (both gravimetric and volumetric) are not the main requirements. Stationary energy storage systems and light-duty vehicles for short-range transportation of people and goods are suggested to be important market applications. Two examples of such applications have been already developed in China: a stationary energy storage plant with a capacity of 30 kW/100 kWh,[51] and a small vehicle.[52] However, expanding the portfolio of applications is quite difficult to achieve in the immediate future, i.e., before the Li-ion market will be fully exploited, because of the drawbacks and limitations related to fast charging and energy density. However, it is anticipated that new materials offering higher capacities and excellent conductivities, similar to those of the Li-based materials, will be developed enabling the introduction of Na-ion batteries into more fields.

2.6. Perspectives—Critical Opinion

Na-ion batteries have some advantages that may portrait them as complementary systems to Li-ion batteries, if certain conditions are met. The similarity of the two technologies is a good starting point for the implementation of advanced production technology of Na-ion batteries, substantially lowering their cost.

Another great advantage is the abundance of resources, i.e., relative low cost, and the possibility of employing bio-waste materials from the production of the active electrode materials. This might compensate for the intrinsic low energy density of Na-ion batteries, enabling their penetration in the marks as a cost-effective, more sustainable technology. However, to establish these performances, researchers in the Na-ion battery field must solve the following challenges: 1) High energy (i.e., high capacity and voltage) cathode materials. The Na cathode materials still hold lower capacities than their Li counterparts. Thus, it is a must to identify high energy Na cathode materials with excellent cycling stability. 2) High capacity anode materials. While, hard carbon may be a possible solution, its potential is too close to the Na plating potential raising safety concerns. Some other materials are also currently under investigation, e.g., Sn/graphite composite, $Na_2Ti_3O_7$, etc. However, these materials are far from practical application because of high cost and/or low performance. 3) New electrolytes enabling lower costs and higher safety.

Upon looking at the whole system, it is recommended to systematically work and explore, new and advanced materials, enabling the introduction of viable, durable and less expensive Na-ion batteries. Nonetheless, the establishment of Na-ion batteries in the market seems to be more probable than other alternative electrochemical energy storage systems based on multivalent metal ions as well as halides.

3. Multivalent Metal Anodes (Mg, Zn, and Al) Based Batteries

3.1. Introduction

3.1.1. The Mg-Based Battery System

The main purpose of an Mg-based battery is simply the use of a metallic Mg as the anode. In combination with a suitable cathode, which can be based on an insertion- or conversion-type material, and a Mg-containing electrolyte, the reversible electrochemical deposition and dissolution of Mg during charge/discharge is desired. Since the rechargeable Mg batteries are still at a research and development stage, one of the main challenge has been to find appropriate electrolytes, which support efficient reversible Mg reduction and oxidation.[53] Various electrolyte compositions are studied in state-of-the-art cells; however, since no suitable solid electrolyte interphase (SEI) which would allow only Mg-ion transport with a transfer number close to unity was found thus far, all studied electrolytes are usually ether- or ionic liquid-based (both with low reactivity toward Mg metal). Such composition would ensure and enable the formation of a passivation-free Mg metal surface. Even though a focus on Mg-Cl-based complexes is noticeable, other complexes, as well as bare (solvated) Mg ions in ethereal solutions are studied. A stepwise reduction of the complex Mg-containing positive species, while electrodeposition during charge of the cell is expected and this may enable lower overpotentials compared to bare (solvated) Mg ions.[54] The cathode reaction in the state-of-the-art Mg-based battery (Mg–Mo_6S_8) is characterized by intercalation process of Mg-ions during discharge.[55] A schematic depiction of a Mg-based battery is shown in **Figure 4**.

Mg metal-based batteries gained high interest in the field of batteries when Aurbach and co-workers developed the

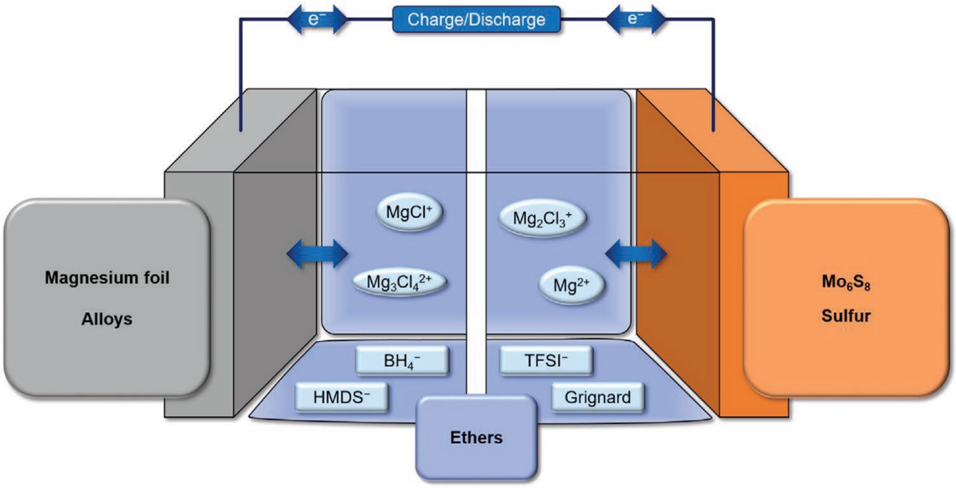

Figure 4. Schematic depiction of an Mg-based battery with common state-of-the-art materials. Gray: anode; blue: electrolyte including ions; orange: cathode.

first reversibly rechargeable Mg-Battery with a Chevrel phase cathode.[56] Since then, efforts have been made to develop new approaches to better understand the fundamentals of this bivalent battery chemistry. Besides the advantages in volumetric energy density and abundancy (discussed later on), additional important selling points of the technology are a presumed dendrite-free nature of Mg electrodeposition and lower toxicity, as well as potentially increased safety characteristics.[57] Mg electrodeposition and -dissolution occur homogeneously, while the overvoltage for the processes in most electrolyte formulations are high. The development of cationic Mg complexes by the combination of simple Mg-salts with $AlCl_3$ as a Lewis acid, reduces the overvoltage drastically, even though the operating voltages of such electrolytes are limited to a range below 3.5 V versus Mg/Mg^{2+}.[57] The major challenge in Mg-based battery systems are the cathode materials which are restricted to a few structures with certain properties.[58] The high charge density of the Mg ions substantially narrows and limits possible pathways for a good design of intercalation cathodes.

As mentioned, the most common cathode enabling Mg intercalation is the Chevrel phase of Mo_6S_8 ($x\ Mg^{2+} + 2x\ e^- + Mo_6S_8 \rightleftharpoons Mg_xMo_6S_8$; $0 \leq x \leq 2$).[56] Even though a high reversibility can be achieved, the cell voltage is quite low (1.2 V) and molybdenum is expensive. An alternative cathode is the conversion-type material based on elemental sulfur.[59] The volumetric energy density of Mg–S cells (3219 Wh L^{-1}) is comparable and even slightly higher to the one of Li-based systems (Li–S: 2946 Wh L^{-1}).[60] Even though a lower solubility of polysulfides was proposed in Mg-based compared to Li-based systems,[61] it is evident that reactions of migrated polysulfides lead to detrimental passivation and cell failure on the Mg metal anode.[62]

Further alternative cathode systems are organic electrode materials, such as poly(anthraquinone)s.[63] The main advantages of organic materials are their sustainability, flexibility, the absence of heavy metals, and their facile processing.[64] Even though the volumetric energy density of quinone-based cathodes is found to be approximately 650 Wh L^{-1},[65] the density ($\approx$ 1.1 kg L^{-1})[66] needs to be at least twice higher, in order to achieve comparable practical energy densities to LIBs.

3.1.2. The Zn-Based Battery System

Metallic zinc has been regarded as another promising anode material for various primary and secondary batteries, due to its high specific volumetric capacity (5855 mAh cm^{-3}), high abundance, and intrinsic benignity.[67] The alkaline Zn–MnO_2 and Zn–air batteries have already been commercialized, utilizing metallic Zn as an anode and conversion-type cathode or an air membrane, respectively. However, challenges remain in the rechargeability of zinc anode in alkaline electrolyte and the development of electrode materials.[68]

Unlike the Mg-based batteries, Zn-based battery can be fully recharged in aqueous electrolytes, benefiting from the fairly good stability of Zn metal and reversible stripping/plating reaction of Zn^{2+}/Zn in aqueous solutions. In this respect, aqueous rechargeable zinc-ion batteries (ZIBs) are considered as the most promising systems for large-scale energy storage, as alternatives to currently used lead-acid batteries. By using mild aqueous solution, Yamamoto and Shoji introduced an aqueous Zn–MnO_2 battery technology in $ZnSO_4$ electrolyte.[69] Following that, efforts have been devoted to develop Zn^{2+} as charge carrier for high-capacity and long-life aqueous rechargeable Zn battery.[70]

Besides the primary Zn–Mn, Ni–Zn, and Zn–air batteries, various cathode materials have been reported for rechargeable aqueous Zn batteries, e.g., manganese oxides, Prussian blue analogs, vanadium oxides, sustainable quinone analogs, etc.[68] MnO_2, with rich structural flexibility (α, β, γ, δ, λ, ε, and amorphous), has been widely investigated both in primary and secondary Zn batteries, due to the low cost of Mn resources and low toxicity. The Zn storage chemistries of Mn-based materials indeed depend on the electrolytes and materials structures. It has been proposed that the capacity of ε-MnO_2 in neutral or mild acidic aqueous electrolytes is induced by the reversible Zn^{2+} insertion/extraction.[71] However, when the α-MnO_2 is used as cathode in optimal mild aqueous $ZnSO_4$ with $MnSO_4$ additive, a highly reversible conversion reaction of $MnO_2 + H^+ + e^- \rightleftharpoons MnOOH$ is observed.[72]

On the other hand, the reversibility and efficiency of Zn stripping/plating reaction play a critical role in the development

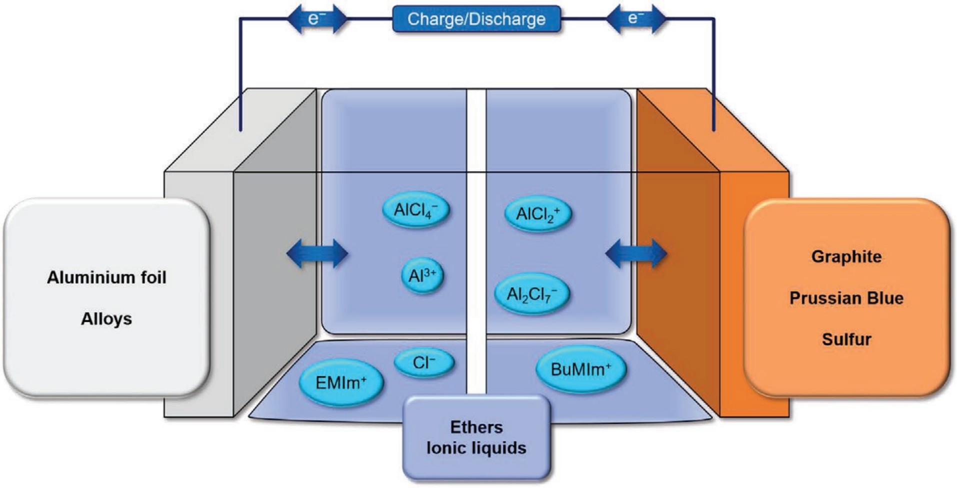

Figure 5. Schematic depiction of an Al-based battery with common state-of-the-art materials. Gray: anode; blue: electrolyte including ions; orange: cathode.

of high performance aqueous zinc batteries. By optimization of the electrolyte component, the effective suppression of hydrolysis of Zn^{2+} can be obtained, which is proved to be responsible for the high reversibility and dendrite-free Zn metal anode.[73] Although the theoretical energy density of MnO_2 in single electron reaction pathway is 308 Wh kg^{-1}, and specifically, the $Zn–MnO_2$ alkaline battery has a capital cost of \$ 10–65 per kWh,[74] zinc batteries are not a natural choice when high energy density is needed. Future work aiming at the development of high performance Zn battery technology for grid-scale application should be devoted to the sustainable and low-cost electrolyte design and affordable materials recycling processes, as well.

3.1.3. The Al-Based Battery System

Similar to Mg-based batteries, metallic Al anode as well as alloyed materials is in the research focus for high energy batteries. Generally, the electrolyte comprises complex ions in ethereal solution but mostly ionic liquids; Al–Cl complexes are formed possessing both positive and negative charge. Depending on the electrolyte formulation, the anionic (in ionic liquids) or cationic (in ethereal solution) species role is to facilitate electrodeposition of Al or alloying reactions at the metallic anode during charge. Simultaneously, negatively charged complexes are utilized at the cathode side to insert anions, when graphite is used as the hosting cathode. In another configuration, smaller anionic species (e.g., $AlCl_4^-$) are oxidized at the anode during discharge to form larger complexes (e.g., $Al_2Cl_7^-$), while Al-ions can react at the cathode (e.g., Al–S battery → formation of Al_2S_3). In ionic liquid-based electrolytes containing Al–Cl complexes, negatively charged species are active at both electrodes during charge/discharge.[75] A schematic depiction of an Al-based battery is shown in **Figure 5**.

Aluminum, as a trivalent atom shows superior volumetric energy densities, abundancy, and costs (see below). Nevertheless, similar to Mg systems, the electrolytes need to be inert toward the metallic anode, since Al possesses a robust passivation film. Nowadays, the only working battery setups in a lab with an Al anode are based on ionic liquids. The combination of 1-ethyl-3-methylimidazolium chloride (EMImCl) and $AlCl_3$, forms Cl-based complexes (e.g., $AlCl_2^+$, $AlCl_4^-$, $Al_2Cl_7^-$) and generates quite harsh conditions for the cell housing.[54,75] These complex-based electrolytes have an additional drawback, which is the limitation of only one charge from the cationic species $AlCl_2^+$, as well as the anionic species $AlCl_4^-$ and $Al_2Cl_7^-$, within the electrolyte.[76,77] This point is critical, since the trivalency of the Al cannot be used, and thus the strategy of the battery developer to use a complexed ionic material significantly reduces the energy density values drastically.

In addition, the complexing agents containing the Al ion are constituting the electrolyte itself, and thus, the capacity is mostly depending on the volume of the electrolyte being utilized in the cell. The use of high volume of electrolyte in the cell would promote an overall higher capacity, but yet dictate a lower energy density. Moreover, the electrolyte also might deplete during cycling.[54] Similarly to Mg systems, the identification of a proper cathode is of a great challenge. Intercalation of $AlCl_4^-$ into graphitic intercalation compounds was shown and reported in literature, but also here, only one charge could be used for energy storage and this charge would be distributed across a high number of carbon atoms, reducing the capacity to around 60 mAh g^{-1} of graphite, at the best.[77] Thus, these so-called dual-ion approaches show very low energy densities considering, that the electrolytes are part of the active materials as well. Besides the electrochemically rechargeable batteries, approaches for mechanically rechargeable Al systems are discussed and might have an impact on certain applications. Especially, in the case of Al–air batteries where the Al anode and electrolyte can be renewed after discharge (electrodissolution of the Al: $Al + 3OH^- \rightleftharpoons Al(OH)_3 + 3e^-$) and the most expensive part of the battery, the gas diffusion cathode with the catalyst, is conserved.[78] The discussion on such system is well elaborated in Section 5 of this Extended Review.

3.2. Sustainability and Cost

In the quest for supplementary battery systems besides Li ion batteries (LIB), the multivalent nature of earth alkaline metals,

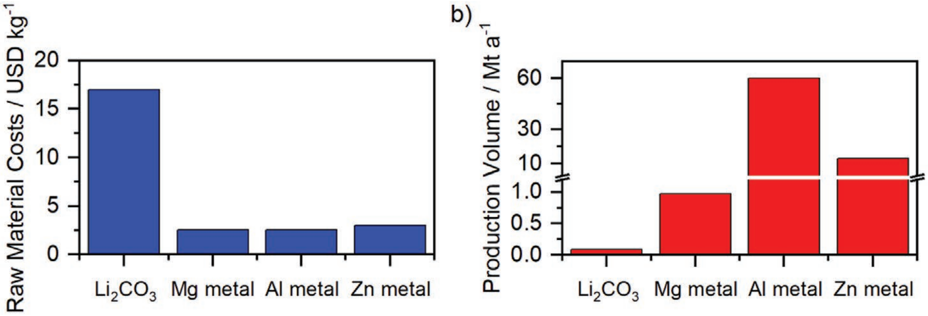

Figure 6. Comparison of a) raw material costs and b) production volume for Li_2CO_3, Mg, Al, and Zn metal. Data obtained from ref. [80].

Mg, Zn, as well as Al, is one of the great hopes in battery research. The abundancy of these metals is partially superior compared to Li. Al is the third most abundant element in the earth crust with about 8 wt%, followed by Ca with 3.8 wt%. Also the resources of Mg (2.2 wt%) and Zn (0.007 wt%) are higher compared to 0.002 wt% for Li.[79] Moreover, the price of the metallic products of Al (2.5 \$ kg^{-1}), and Mg (2.5 \$ kg^{-1}) is significantly lower compared to Li (17.0 \$ kg^{-1} for Li_2CO_3) (see **Figure 6**a).[80] The prices are not only influenced by the abundancy, but also by the huge production volume of Al, and Mg (see Figure 6b). Notably, Al is produced in a 60 Mt scale per year. The low prices of Mg and Al metal combined with high theoretical capacity values result in a much lower cost per kWh, compared to Li metal or lithiated graphite (LiC_6), this aspect is intensified especially if these anode metals are combined with a low-cost cathode active material such as sulfur (see **Table 2**; S: 0.07 \$ kg^{-1}; LiC_6–S: 11.4 \$ kWh^{-1}; Li–S: 9.8 \$ kWh^{-1}; Mg–S: 0.7 \$ kWh^{-1}; Al–S: 0.9 \$ kWh^{-1}).[80]

A possible large-scale battery application of the multivalent metals (Mg, Al, and Zn) is strongly motivated by their abundancy and costs. Nevertheless, Li resources are still sufficient for at least 25 years of battery production,[82] which gives enough time (hopefully) to intensify the research on the more abundant and potentially easier recyclable multivalent battery systems (especially when rechargeable aqueous and air batteries can be developed to an application level, as outlined in Section 5 of this Extended Review).

3.3. Safety and Durability

Batteries with multivalent metals are expected to have higher safety than nonaqueous LIBs. One reason is the higher melting point (Li: 180 °C, Mg: 650 °C, Al: 659 °C),[81] which reduces the risk of fast evolution of exothermic reactions, if the battery is damaged. Another one is the rapid metal passivation occurring on the surface of multivalent metals upon contact with moisture and air, substantially different from the exposure of metallic Li to air and moisture. In addition, the application of aqueous electrolytes would increase the safety due to the absence of volatile and highly flammable organic solvents. Also, the toxicity might be strongly reduced if highly fluorinated solvents and conducting salts, which are used in Li-based batteries, are to be replaced in the new cell design. The durability of multivalent metal-based batteries is hard to predict, since multivalent metal-based battery prototypes are very rare and yet lack of applicability, and thus research and industry approaches are needed to prove the durability of such Mg- and Al-based systems. It can be expected that the employment of conversion-type cathodes might limit the durability to a few hundred cycles, like for Li–S batteries. The combination with intercalation-type cathodes or organic cathodes may have higher success rates. For example, 1,4-poly(anthraquinone) did show a stable performance in Mg based cell design and a remaining discharge capacity of 78.7 mAh g^{-1} after 1000 cycles at 1C (10th cycle: 87.1 mAh g^{-1}).[83] A pouch battery cell using the Al || graphite system could be shown to achieve over 7500 charging and discharging cycles at a current density of 4000 mA g^{-1}.[77] For an Al–PQ-Δ (PQ-Δ = triangular phenanthrenequinone) battery a long-term cycling performance of more than 5000 cycles at 2000 mA g^{-1} was presented.[76]

3.4. Performance

Many cell chemistries are known and already commercialized for primary and aqueous batteries. Among them, the Zn–air

Table 2. Overview of electrochemical characteristics, specific energies and energy densities, as well as cost for various combinations of metal anodes and a conversion cathode type for nonaqueous battery systems.

Anode	Cathode	Cell voltage[b)] [V]	Th. specific energy [Wh kg^{-1}]	Th. energy density [Wh L^{-1}]	Cost[c)] [\$ kWh^{-1}]
LiC_6	Conversion[a)]	2.4	677	1518	11.4
Li	Conversion[a)]	2.4	2800	3061	9.8
Mg	Conversion[a)]	1.7	1647	3093	0.7
Al	Conversion[a)]	1.0	1094	2413	0.9

[a)] Conversion: S, 1672 Ah kg^{-1}, 3343 Ah L^{-1}; [b)] Cell voltage calculated using theoretic redox potentials[81]; [c)] Costs were calculated according to prices of the active materials. Cost for Li was calculated from the amount of Li in $LiCO_3$, cost for LiC_6 were calculated from the price of natural graphite and Li in $LiCO_3$.[80]

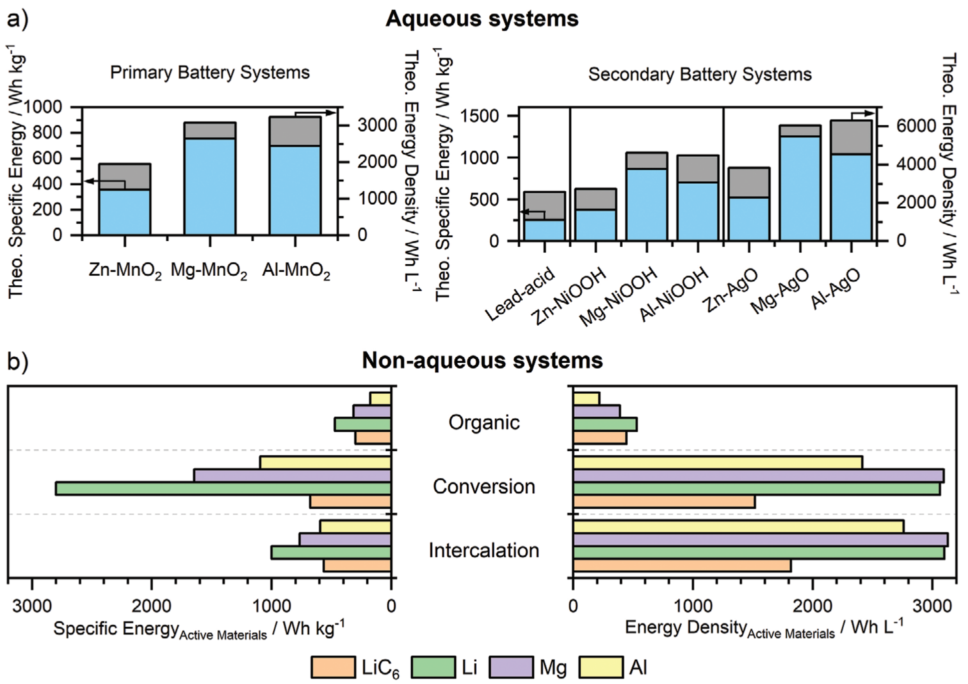

Figure 7. a) Specific energy and energy density plots for aqueous primary (left) and secondary (right) battery cells based on theoretical values. The energy values are calculated based on the electrode materials with theoretical specific capacities. b) Comparison of specific energy (left) and energy density (right) values of different cathode material types (intercalation:, e.g., MnO_2; conversion:, e.g., S; organic:, e.g., PAQS) in combination with various anode materials. Data can be found in Tables 3 and 4.

primary batteries (see also Section 5) are used for hearing aid and alkaline Zn–MnO_2 primary, as well as Zn–$Ni(OH)_3$ ("Ni–Zn") secondary batteries are established and are considered as commercially successful chemistries. Lead-acid batteries are being brought to the discussion table as they have the largest market share for secondary batteries both in terms of sales value and MWh of production.[84] In **Figure 7**a (corresponding data can be found in **Table 3**), the comparison of the specific energy and energy densities of these battery systems is presented. The opportunities of the multivalent elements Mg and Al for primary batteries are immense, since the theoretic values for the specific energy could be doubled (Mg–MnO_2: 757 Wh kg^{-1}; Al–MnO_2: 699 Wh kg^{-1}) and the energy density could be increased by more than 30% (Mg–MnO_2: 3079 Wh L^{-1}; Al–MnO_2: 3235 Wh L^{-1}), especially driven by the more negative redox potential of Mg (−2.37 V vs SHE) and Al (−1.76 V vs SHE), compared to Zn (Zn–MnO_2: 358 Wh kg^{-1}, 1952 Wh L^{-1}; −0.76 V vs SHE). For aqueous secondary (rechargeable) batteries, the theoretical energy density and specific energy of the established cell types (lead-acid: 252 Wh kg^{-1}, 2575 Wh L^{-1}; Zn–NiOOH: 373 Wh kg^{-1}, 2732 Wh L^{-1}; Zn–AgO: 524 Wh kg^{-1}, 3829 Wh L^{-1}) could be improved by the use of Mg and Al (e.g., Mg–NiOOH: 862 Wh kg^{-1}, 4623 Wh L^{-1}; Al–NiOOH: 701 Wh kg^{-1}, 4483 Wh L^{-1}; see Figure 7a and Table 3). Nevertheless, as simple comparison between the theoretical values does not necessarily display realism since suitable electrolyte systems and composition, cell setup and housing, control of deposition growth, side reactions, safety issues, are not being considered and need to be optimized. Thus, the implementation of Mg and Al in aqueous primary cells as well as secondary batteries is not trivial. Limitations of the electrolytes characteristics and passivation of the metals are severe and most challenging parameters prostrating aqueous multivalent batteries as promising but yet complex research systems.

Table 3. Overview of electrochemical characteristics and calculated values for anode, cathode, and cell capacities, as well as specific energies and energy densities, for various combinations of metal anodes and different cathode types in aqueous media. The energy values are calculated based on the electrode materials with theoretical specific capacities.

	Anode	Cathode	Cell voltage[a)] [V]	Th. specific energy [Wh kg^{-1}]	Th. energy density [Wh L^{-1}]
Primary	Zn	MnO_2	1.6	358	1952
	Mg	MnO_2	2.8	757	3079
	Al	MnO_2	2.5	699	3235
Secondary	Pb	PbO_2	2.1	252	2575
	Zn	NiOOH	1.7	373	2732
	Mg	NiOOH	3.3	862	4623
	Al	NiOOH	2.6	701	4483
	Zn	AgO	1.9	524	3829
	Mg	AgO	3.5	1252	6043
	Al	AgO	2.8	1040	6297

[a)] Cell voltage calculated using theoretic redox potentials.[81]

Among the secondary nonaqueous battery systems, Mg and Al have the highest volumetric capacities for metallic anodes, but cannot compete with Li in terms of gravimetric capacity (Mg: 2205 Ah kg^{-1}, 3833 Ah L^{-1}; Al: 2980 Ah kg^{-1}, 8043 Ah L^{-1}; Li: 3862 Ah kg^{-1}, 2062 Ah L^{-1}). However, to exploit the capability of multivalent metal systems in battery applications, the

Table 4. Overview of electrochemical characteristics and calculated values for anode, cathode, and cell capacities, as well as specific energies and energy densities, for various combinations of metal anodes and different cathode types for non-aqueous battery systems. The energy values are calculated based on the electrode materials with theoretical specific capacities.

Anode	Cathode[b)]	Cell voltage[a)] [V]	Th. specific energy [Wh kg^{-1}]	Th. energy density[Wh L^{-1}]
LiC_6	Intercalation	3.5	565	1817
	Conversion	2.4	677	1518
	Organic	2.2	300	445
Li	Intercalation	3.5	999	3098
	Conversion	2.4	2800	3061
	Organic	2.2	472	530
Mg	Intercalation	2.8	766	3127
	Conversion	1.7	1647	3093
	Organic	1.6	317	391
Al	Intercalation	2.1	593	2759
	Conversion	1.0	1094	2413
	Organic	0.8	176	220

[a)]Cell voltage calculated using theoretic redox potentials[81]; [b)]Intercalation: MnO_2, 308 Ah kg^{-1}, 1551 Ah L^{-1}; Conversion: S, 1672 Ah kg^{-1}, 3343 Ah L^{-1}; Organic: poly(anthraquinoyl sulfide), PAQS, 225 Ah kg^{-1}, 270 Ah L^{-1}.[63,81]

combination with suitable cathodes is necessary. Herein, we chose to discuss three cathode types: intercalation, conversion, and organic systems. The exemplary cathode materials for these cathode categories are MnO_2,[58,85–87] (308 Ah kg^{-1}, 1551 Ah L^{-1}), sulfur[59,75,88] (1672 Ah kg^{-1}, 3343 Ah L^{-1}), and poly(anthraquinoyl sulfide), (PAQS,[63] 225 Ah kg^{-1}, 270 Ah L^{-1}).

Al- and Mg-based cells in combination with the abovementioned cathode materials were listed and the theoretic specific energy as well as the energy density of the systems were estimated and calculated using the theoretical redox potentials (see Figure 7b and **Table 4**). For better comparison, the obtained values are compared with Li metal and lithiated graphite (LiC_6). Here, only the active materials are taken into consideration. More detailed calculations of state-of-the-art systems which also consider inactive materials and include Mg-based systems are described elsewhere.[60]

Mg- and Al-based systems are incapable of competing with Li-based systems in terms of specific energy (Figure 7b), when the metallic anode is combined with the cathodes described above (e.g., LiC_6–MnO_2: 565 Wh kg^{-1}, 1817 Wh L^{-1}; Li–MnO_2: 999 Wh kg^{-1}, 3098 Wh L^{-1}; Mg–MnO_2: 766 Wh kg^{-1}, 3127 Wh L^{-1}; Al–MnO_2: 593 Wh kg^{-1}, 2759 Wh L^{-1}). Nevertheless, Mg and Al are indeed able to outperform LiC_6. The volumetric values, however, indicate a slight benefit for Mg metal if combined with intercalation- and conversion-type cathodes (e.g., Li–MnO_2: 999 Wh kg^{-1}, 3098 Wh L^{-1}; Mg–MnO_2: 766 Wh kg^{-1}, 3127 Wh L^{-1} and Li–S: 2800 Wh kg^{-1}, 3061 Wh L^{-1}; Mg–S: 1647 Wh kg^{-1}, 3093 Wh L^{-1}). Aluminum metal cannot compete with metallic Li, since the 1.3 V redox potential difference plays a critical role in these observations. Only for organic cathodes, Li and LiC_6 show the highest energy density values because of the low density of the organic molecules, the lower voltage, and the corresponding amount of active material. Further calculations on the theoretical energy densities are also found elsewhere.[89]

These results might be surprising, since multivalent metal systems are prone to outperform state-of-the-art batteries in terms of capacity. This point is valid, albeit taking into a consideration the achievable cell voltages (which are herein still nonrealistic since overvoltage is not taken in the consideration and mostly not known until now), the high capacity and, especially, the very low redox potential of Li is strongly influencing the energy values. Despite this, multivalent systems for sure have an important characteristic for large-scale application (see later) and will strongly compete in the costs and price point of view. The more homogeneous electrodeposition of Mg and Al do allow the use of a real metal anode different from Li metal anodes, which still cause major safety problems and reduce the Coulombic efficiencies. Surface film formation increases the need of active materials in LIBs and Li metal batteries and with this, the overall cell energy. Furthermore, thin Li metal electrodes need a substrate (e.g., Cu) to be mechanically stable, which increases the price further on, side by side with the production costs. Aluminum, for example, can be obtained as thin foils with high purities and therefore, displays a major advantage.

3.5. Applications

The former subchapters described the beneficial sustainability, costs, and safety of Mg- and Al-based battery cells, while showing moderate theoretic energy values compared to Li-based batteries. With these characteristics, the multivalent metal systems may be considered as a perfect match for large-scale, moderate energy density applications like stationary energy storage. The price and safety, as well as the possibility of a large production volume of the materials will be key factors for this application field. Since Mg and Al are already produced in large quantities with well-established productions schemes (Figure 6b), this might be a compelling and most important advantage. The implementation of Mg- or Al-based batteries in mobile applications, especially electric vehicles, is unlikely but not excluded. The use of batteries based on multivalent metal anodes as supplementary battery devices in electromobility applications might be relevant, for example as an extender mileage battery system. Here, these systems can be used side-by-side with LIBs. Overall, Mg- and Al-based batteries are, within this perspective, expected to play a role in cost-driven battery applications.

3.6. Perspectives—Critical Opinion

In summary, both Mg and Al-based battery systems are still in early stages of development with only few fully rechargeable cells available (also see **Figure 8**, showing the state of development for Mg and Al compared to Li-based systems). Especially for Al, the improvements which can be achieved are still enormous and fundamental research is needed. However, these multivalent metal systems still need to prove that the full range

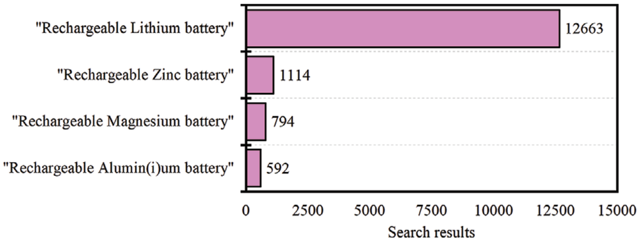

Figure 8. Search results for various keywords of Li, Zn, Mg, and Al systems. Obtained at 28th of February 2020, via Web of Science.

of charge can be used. Mg-based battery systems are actually, in this point, already more developed than Al-based batteries, where the situation with the Cl-complexes is critical in terms of energy density of the full cells. The metallic anodes, under certain conditions, could be used without surface layers, and therefore, can be envisioned to allow high Coulombic efficiencies and no need for (significant) overbalancing, (which would be attractive characteristics). Zn-based battery systems are recently revisited as promising (aqueous) battery technologies for grid-scale energy storage applications. Even if the sustainable Mn-based cathode materials can be applied and utilized in rechargeable Zn batteries, the energy density is still low, resulting from the reduced cell voltage. A thorough research in the field of cathode materials is needed for both systems and organic materials, because of their broad range of molecule design, are a suitable candidate to be combined with the multivalent anode materials. Nevertheless, it is assumed that Mg and Al anodes need to be paired with cathode-active materials which bear low cost to be more attractive compared to the state-of-the-art systems, since the benefits of the multivalent metals (charge, price, weight) can only be commercially competitive if the cathode (and electrolyte) materials price will be kept moderate.

Compared with the Li-ion and Na-ion batteries, these multivalent battery systems are still at the very early stage of research and development and are yet far from commercialization. As a very limited electrode materials are reported thus far (except the metallic anodes of Mg, Zn, and Al) more attention is needed to develop cathode materials that can host or alloy these multivalent metals. Further exploration and understanding of mild electrolytes are very crucial for these system developments. Interestingly, green and sustainable organic compounds could be designed and tailored as universal host materials to accommodate multivalent metal ions. Considering these advantages, effective approaches toward achieving organic multivalent metal ion rechargeable batteries are expected.[90] Moreover, the high volumetric energy density is the most important advantage to multivalent metal batteries, especially for Al and Mg-based systems.

4. Redox Flow Batteries

4.1. Introduction

The main advantage of RFBs consists in the separation of energy and power combining some aspect of batteries (energy storage mechanism) and fuel cells (external reservoir of reactants)—a combination of properties unique to this technology. The main benefits are the scalability of storage capacity (from several kW/kWh up to tens of MW/MWh),[91] the ability to operate in most environmental temperatures (–35 to 50 °C)[92] and long-term storage capability. However, besides the all-liquid RFB, where the chemical energy is stored in the anolyte and catholyte (which are stored in external reservoirs) two more kind of cell exist, which do not fulfill the above-mentioned energy and power splitting. These are all-solid phase, where the electrodes are covered by active materials and the flow species is a solvent or acid that allows the reaction to occur; and hybrid RFB, which has one solid active material on an electrode that is reacting with an anolyte or a catholyte.[93]

The general structure of the RFBs consists of components such as electrodes (or current collectors), external tanks, separators, pumps. In case of a stack configuration, bipolar plates and flow fields are also employed.[94] The external tanks store the redox active species, which are pumped into the anode and cathode compartments. These compartments are separated by a separator (porous separator or ion-exchange membrane) to prevent mixing of the two electrolytes, while allowing the ion transport. The electrochemical reactions take place at the electrodes with large surface areas upon discharge or charge, while the electrolytes continuously flow. The volume of the external tanks determines the energy output, since the active species are stored in these tanks as liquids, suspensions, or gases. The separators also play a crucial role on the performance of RFBs.[95–98] Generally, four different type of separators are reported: a) ion-exchange membrane, b) porous separator, c) hybrid membranes, and d) solid ionic conductors.[99] Depending on the cell chemistry, one of these separators can be utilized in the RFB.

Among the all-liquid RFB, the most common and commercially available type is the one using vanadium-based solutions (all-liquid) as anolyte and catholyte.[92] This approach will be discussed in detail later on. The less close to commercial application, instead, makes use of uranium or neptunium solutions,[92,100,101] both depicted in **Figure 9**. With respect to the costly metal salts, organic all-liquid RFBs promise advantages in terms of cost, abundancy, and tunability. This latter advantage comes from the possible incorporation of various chemical

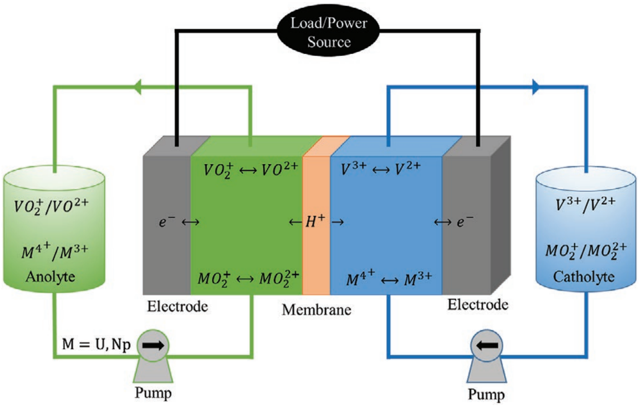

Figure 9. Working principle of an all-liquid RFB. All reactants and products are in solution for vanadium RFB and uranium/neptunium RFB.

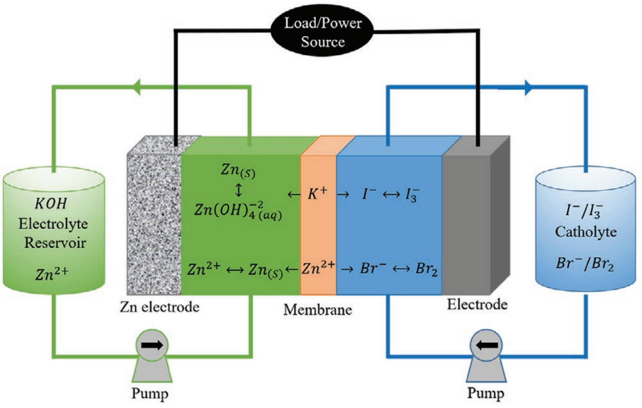

Figure 10. Working principle of a hybrid RFB for zinc iodine and zinc bromine cells.

modifications allowing the organic materials to have a wide potential range.[102]

For hybrid RFB, the most promising approaches are the zinc bromine and the zinc iodine cells, which operating principles are portrayed in **Figure 10**.[81,103–105] Currently, the zinc iodine system being evaluated only up to 70 cycles, remaining practically unviable, in terms of cyclic stability.[106] On the other hand, the bromine system is tested for more than 2000 cycles. Furthermore, hybrid RFBs include cells employing gaseous hydrogen as an anolyte.[92,99,107,108] Such systems are similar to hydrogen–oxygen regenerative fuel cells. Among several types, hydrogen-chloride,[109] hydrogen-bromide,[110] hydrogen-iron,[111] and hydrogen-vanadium[112] RFBs have attracted some attention, due to their ability of providing higher power and energy densities in comparison to traditional RFBs. In both hybrid and all liquid RFB there is use of a highly ionic conductive membrane which is also chemically and thermally stable.[95] Presently, Nafion is being proposed for this application, however, leading to high costs. Polymer microporous membranes are also in use as cheaper alternative but yield reduced performance.[95] Moreover, the all liquid and hybrid electrodes can contain noble metals for long-term reliability[113] which dramatically increase the battery price.

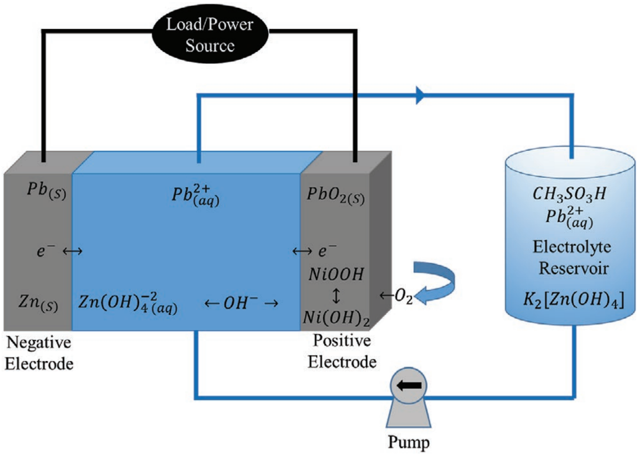

Figure 11. Working principle of a membrane-free all solid RFB for all-lead and Zn–Ni cells.

Finally, the all-solid RFB, described in **Figure 11**, do not contain any membrane since it makes use of only one electrolyte containing both the electrodes' species in the discharged state. Those batteries are reportedly containing all-lead[114,115] and Zn–Ni.[116] A very similar approach to Zn–Ni RFBs has also been reported consisting in the Zn–air flow battery,[117–119] which employs a carbon-based gas diffusion air cathode instead of the $Ni(OH)_2$–O_2 composite cathode. Such gas diffusion air electrodes consist of bifunctional catalysts[120] for oxygen reduction and evolution reactions. Besides Zn anode, other type of metals, such as lithium,[121] aluminum,[122] vanadium,[123–125] can also be utilized in a metal–air flow battery design.[126] In the vanadium-air flow battery, substitution of the VO^{2+}/VO^{2+} redox couple in the catholyte with H_2O/O_2 and a gas diffusion air cathode is required; hence, using only a single electrolyte tank. This leads to enhanced energy densities and reduced cell sizes, in comparison to the conventional all-liquid Vanadium RFBs.

4.2. Sustainability and Cost

The energy storage capacity of commercial vanadium RFBs ranges from 4 to 40 MWh. The overall cost is 550 \$ kWh^{-1}[127] in comparison to <200 \$ kWh^{-1} for Li-ion (the anticipation that by 2025 this value will be less than 90 \$ kWh^{-1}).[6,128,129] These values are still far from meeting the current cost target of the US Department of Energy.[119,130] While the uranium/neptunium RFB approach increases the system efficiency, the use of actinides is not sustainable. More promising from the cost point of view appears to be organic RFBs. For example, the bulk price of an organic quinone for RFB can be as low as 5–10 \$ kg^{-1}[131] versus the actual 10–12 \$ kg^{-1}[132] for vanadium oxide (V_2O_5). Furthermore, the content of noble metals and Nafion can be averted with the introduction of membrane-free, all-solid RFBs.

4.3. Safety and Durability

The safety issues, associated with this technology, are mainly environmental hazards in case of hazardous material spillage. In fact, the commercially available anolyte and catholyte are vanadium solutions which pose environmental issues.[133] The uranium/neptunium approach also poses the same environmental threat with an added radiation danger. A breakdown of possible environmental impacts for manufacturing vanadium-RFBs can be found elsewhere.[133] In certain hybrid cells hydrogen storage may cause an explosion if not handled correctly. In certain RFB chemistries, toxic gas (e.g., bromine, chlorine) evolution poses serious health and environmental concerns. One of the major issues with the conventional RFBs is the crossover (or cross-contamination) of the active species between catholyte and anolyte. Therefore, both the electrolyte compositions and, more importantly, the membranes must be optimized to minimize the capacity losses due to crossover. Most common way to minimize the crossover is using ion-selective membranes. Additionally, the membranes should provide good selectivity, chemical stability, low resistivity, and sufficient permeability. Furthermore, there are other factors that may limit the performance of RFBs. For example, nonhomogenous deposition of metal ions may lead to shape change and dendrite growth, high polarization losses due to sluggish kinetics of the reactions, corrosion of the electrodes, solubility and stability of the active species, inefficient electrocatalysts, conductivity of the electrodes, and influence of the flow frames. Noteworthy, most of the research on RFBs is mainly conducted on small scale laboratory cells with very limited cyclability. Thus, it is also of high importance to investigate the scale-up concepts to reach a practical applicability.

Among various types of RFBs, vanadium-RFBs provide an excellent durability by achieving cyclic performance of more than 10 000 cycles with efficiencies of above 65%.[93,130,134–136] A project on vanadium-RFBs by Sumitomo Electric Industries (Japan) was demonstrated a 4 MW/6 MWh system with more than 270 000 cycles.[136,137] Zinc–bromine RFBs show also good durability performance with a cyclability of more than 2000 cycles.[81,93]

4.4. Performance

Table 5 compares the performance of RFBs versus Li-ion batteries. From the cycle life expectancy of the above-mentioned cells, it is clear as only the vanadium RFB technology provides better cycle life expectancy, i.e., twice, than Li-ion batteries. In the case of power density, the zinc iodine RFB provides the most promising value, up to 100 mW cm^{-2}, allowing smaller form factors. On the other hand, the energy density directly translates to the device's ability to store energy. The highest energy density value is reported for the zinc iodine cell followed by organic and lead-acid RFBs.

4.5. Applications

Redox flow batteries are expected to outperform Li-ion only for stationary applications where their key feature of storing the energetic chemicals in external reservoir enables large-scale, energy storage from renewable sources during peak-production times and supplying when production falls. Furthermore, RFBs are very well suited for emergency power delivery, which has to remain off for long periods of time as reserve for grid power. Several demonstration/commercial RFB units exist in the market. Such systems were developed for local grid-load leveling mainly and other storage applications in Japan and Australia.[93,130,136]

4.6. Perspectives—Critical Opinion

For the further development of RFB moving away from heavy elements, which are highly dangerous in case of spillage and unsustainable for long term, is mandatory. Second, refrain from incorporating complex hydrogen storage into the RFB system, which reduces the RFB's ability to serve as a long-term energy storage device. The most promising RFB approach appears to be the all-solid RFB, which requires no membrane and only one flowing electrolyte. However, only the use of nontoxic and inexpensive multivalent metals would make this technology a competitive one with respect to Li-ion batteries. Further research should be directed towards fundamental studies to improve the understanding of the system. At the same time, developments of advanced materials and chemistries are also required to overcome the limitations of the current concepts and improve the system performances. It is also important to increase the low energy densities of RFBs and scaling-up capabilities in order to be competitive for large-scale grid storage applications.

5. Metal–Air Batteries

5.1. Introduction

Metal–air batteries (technically described as "metal–oxygen" batteries), broadly include those running on oxygen or air feedstock, are among several potential candidates as alternatives to current battery systems and they have attracted great interest in recent years.[5,139] The metal–air battery is composed of a metal anode, an air electrode, an ion conducting electrolyte, and a separator. Unlike the conventional lithium-ion batteries, metal–air batteries function through the redox reaction between the metal anode and oxygen at the air cathode, with a theoretical specific energies and energy densities (based on

Table 5. Comparison of the discussed RFBs to lithium-ion batteries. The parameters discussed are the cycle life, cell voltage, power and energy density. The energy densities of RFBs are mainly calculated by the amount of the active materials in the reservoir. Therefore, a fair comparison to the conventional battery chemistries is not straightforward.

Cell	Cycles	Cell voltage [V]	Power density [mW cm^{-2}]	Energy density[Wh L^{-1}]	Refs.
Li-ion	5000	3.60–3.85	–	250–693	[138]
Vanadium	10 000	1.15–1.55	75	15–25	[135]
Uranium/neptunium	20	0.68	70	–[a)]	[92,100]
Zinc iodine	70	2.0–2.2	10–100	330	[106]
Zinc bromine	>2000	1.6	40–80	60	[81]
Organic	100	0.5–5.0	10	80–140	[132]
Lead acid	2000	1.35	60	60–100	[92]
Zink nickel	1500	1.3–1.6	20	25–40	[116]

[a)] Untested parameter.

Table 6. A summary of the various metal–air batteries which represents the theoretical voltage, specific capacity, specific energy, and energy density values.

System	Primary product	Cell voltage [V]	Specific capacity [mAh g_{metal}^{-1}]	Specific energy [Wh kg_{metal}^{-1}]	Energy density [Wh L_{metal}^{-1}]	Specific energy [Wh kg^{-1}]	Energy density [Wh L^{-1}]	Refs.
			** Excluding O_2 uptake **			** Including O_2 uptake **		
Al–air	$Al(OH)_3$	2.7	2996	8091	21837	2784	6737	[142]
	Al_2O_3	2.1		6258	16897	3311	13145	[143]
Fe–air	$Fe(OH)_2$	1.28	960	1229	9677	764	2598	[144]
Li–O_2	Li_2O_2	2.96	3861	11 430	6104	3458	7988	[145]
	Li_2O	2.91		11 238	6001	5220	10 492	[146]
Mg–air	$Mg(OH)_2$	3.1	2201	6800	11 610	2848	6750	[147]
Mg–O_2	MgO	2.95		6493	11 299	3919	14 108	[148]
Na–O_2	Na_2O_2	2.33	1165	2716	2634	1601	4409	[149]
	NaO_2	2.27		2646	2567	1106	2433	[150]
Si–air	$Si(OH)_4$	2.09	3828	8001	18 644	2334	4201	[151]
	SiO_2	2.21		8461	19 748	3947	8643	[152]
Zn–air	ZnO	1.65	820	1352	9653	1086	6092	[153]

The essential difference between metal–air and metal–oxygen is whether pure O_2 or ambient O_2 (from air) was applied.

the metal anode) exceeding Li-ion batteries (up to 1000 Wh kg^{-1} and 5000 Wh L^{-1} at a material level[60,140]) (see **Table 6**).[141]

Because the electrochemistry differs considerably, the room temperature metal–air batteries with liquid electrolytes can be typically divided into two categories: i) aqueous or ii) nonaqueous. **Figure 12** represents the basic chemistries of aqueous and nonaqueous systems of a metal–air battery. The major difference between these two systems is the solubility of the oxygen reduction products and the specific reaction zone for the end products. In aqueous electrolytes, the oxygen diffuses into the cathode, and is reduced to hydroxyl ions (OH$^-$) when the cell is discharged. At the same time, the metal anode is oxidized and releases electrons to the external circuit. The hydroxyl ions generated at the air cathode would migrate across the electrolyte and combine with metal ions to form metal hydroxides or oxides in the vicinity of the metal anode surface. In case of nonaqueous electrolyte, the oxidized metal ions would migrate across the electrolyte and react with reduced (originated from the dissolved in the electrolyte) oxygen at the air cathode to form the metal oxides. When the cell is charged (for rechargeable metal–air batteries), these processes are reversed, with metal plating at the anode and oxygen evolving at the cathode. Because the solubility of oxygen is generally low in liquid electrolyte and a catalyst is required to facilitate its reduction, the cathode electrochemical reactions mainly take place at the liquid–gas–solid interface (i.e., the so-called three-phase zone in aqueous system and two-phase zone in nonaqueous system) in the air electrode.

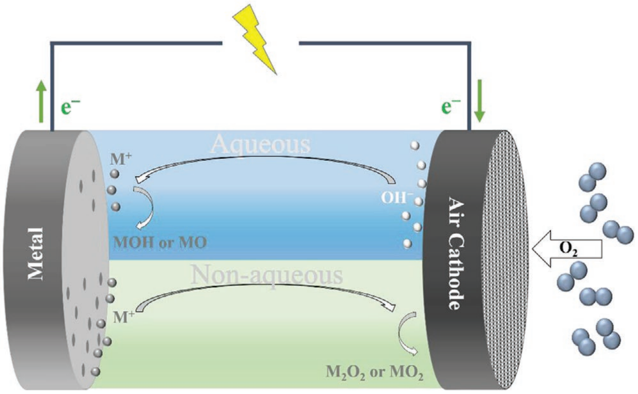

Figure 12. Schematic representation of metal–air batteries with aqueous (upper, blue) and nonaqueous (below, green) electrolytes. Discharge products are represented as MOH (metal hydroxide), MO, MO_2, M_2O_2 (metal oxides).

Each component of a metal–air battery holds a crucial impact on the overall system performance. While the metal anode is the sole active cell component, the air cathode membrane (which reduces oxygen from ambient atmosphere or from an O_2 gas supply) and the separator (when used) in conjunction with an ionic conductive electrolyte have also an impact on battery parameters.[106,139,153,154] The separator should provide low ionic resistance with sufficient chemical stabilities in the electrolytes. Moreover, in case of rechargeable batteries, the separator should be robust against any possible perforations due to metallic dendrite growth. The electrocatalyst materials embedded within the air cathodes are the key materials for oxygen reduction and evolution reactions. The design parameters and architecture of an air cathode (in terms of the identity of the active carbon type and surface area, the binder used, the location of the metal mesh current collector within the membrane, the pressure applied to form the membrane) are very important enabling sufficient gas diffusion channels, active sites, bifunctional electrocatalysts, good electrical conductivity, and fast kinetics, while mitigating any possible flooding concerns of the air cathode membrane.[120,155–157] Thus, each individual component of a metal–air battery should be heavily considered, since the battery performance would be limited if one of the component does not function properly.

5.2. Sustainability and Costs

The utilization of abundant active elements position the metal–air systems as very promising for applications in next-generation

Table 7. Values of crustal abundance, world resources, production volumes and costs of Al-, Fe-, Li-, Mg-, Si-, and Zn compounds.[80]

Metal	Crustal abundance [%]	World resources/ million tons	Production of metals in 2018/million tons	Cost [$ kg^{-1}]
Al	7.96	75 000$^{a)}$	60	2.53
Fe	4.32	110 000$^{b)}$	1 500	0.09$^{b)}$
Li	0.0018	62$^{c)}$	0.085$^{c)}$	17$^{c)}$
Mg	2.20	12 000$^{d)}$	0.97	2.53
Si	28.8	n.a.	6.7	3.04
Zn	0.0065	1900	13	3.02

$^{a)}$Bauxite; $^{b)}$Iron ore; $^{c)}$Lithium carbonate; $^{d)}$Magnesium oxide.

portable electronics, and energy storage of smart grids.[5,158] Besides the intrinsic theoretical energy, the renewed research interest can be further traced by the sustainability. In comparison to lithium, by using more abundant elements such as Mg, Al, Si, Fe, and Zn (e.g., Al is the most abundant metal in the earth's crust), these battery systems could reach drastically low cost and environmental compatibility, which would be more feasible for large-scale energy storage applications.[159] According to U.S. Geological Survey from 2019, the world resources and the production volumes of these metals are adequate enough to supply world demands for many decades (see **Table 7**).[80] The industrial sector also requires these metals to be used in various other applications; thus, the production volumes are very high, and the production costs are significantly lower in comparison to lithium. Such a significantly different production costs at the material level can be diminished once the energy storage costs at a system level is being considered. For example, the energy storage cost at a system level for Li-ion batteries varies between 70 and 250 $ kWh^{-1} while for Zn–air batteries it is between 70 and 160 $ kWh^{-1}.[128]

5.3. Safety and Durability

The metal–air battery is an innovative technology that combines safety and performance with an environmentally friendly low-cost solution.[155] A notable characteristic of metal–air batteries is their open cell structure, since these batteries use oxygen gas accessed from the ambient air as their cathode material, which prevents the pressure build-up within the cells. On the safety consideration, the toxicity of the metals (including their discharge products) and electrolytes are the general concerns; however, most of the intensively investigated systems are using abundant and environmentally friendly elements as the anodes, i.e., Al, Zn, Fe, and Si etc. In the nonaqueous metal–air battery systems, the most use of organic (aprotic) solvent raise the flammability and volatility issues, while the alkaline aqueous metal–air systems use a corrosive alkaline-based solution.[160] Both may lead to leaking concerns upon practical operation modes. Moreover, the stability of the metal anode in contact with the electrolyte is of a great concern due to a corrosion problem, which can produce internal pressure that potentially may lead to air cathode flooding as well as generation of an explosive hydrogen gas.[139] Especially, the exposure of an active lithium metal surface to humid air or to an aqueous electrolyte would lead to an induced explosion of the lithium–air system. Although the inactive metals of Zn and Al or even semiconductor, such as Si can strongly reduce the possibility of a direct reaction, the corrosion is still inevitable. For example, Al can be more easily corroded than Zn in alkaline solution (inducing to the H_2 gas evolution) although Al–air cells have a much greater energy density than zinc–air cells.[161]

All these critical points, as well as the degradation of the metal anodes and electrolyte evaporation will lead to a poor durability and performance decay. For open systems like zinc–air batteries, water loss from the liquid electrolytes is an important cause for performance degradation.[153] Thus, water retention in the aqueous electrolyte is crucial for improving the lifetime of such cells. Moreover, the dendritic metal deposition upon charging prevalent in alkaline electrolytes, for instance, zinc presents the irreversibility concern of the metal anode,[162] promoting the inferior surface passivation and a propensity to form macroscopically long, electrical-short-inducing dendrites.[163] On the cathode side, the development of highly active and durable bifunctional electrocatalysts is also another important parameter, which is in the locus of heavy research efforts, as it determines the efficient use of air cathode to maintain the cycle life of metal–air batteries.[164] Besides, the performance of an oxygen electrocatalyst could limit the properties of the electrochemical system, such as energy efficiency, rate capability, and cost, which makes it a key component of efficient metal–air batteries.[157]

5.4. Performance

The room temperature metal–air batteries with liquid electrolytes can be typically divided into two categories: i) aqueous or ii) nonaqueous. Therefore, the individual systems will be discussed separately based on electrochemical performance, rechargeability, and applications.

5.4.1. Aqueous Metal–Air Batteries

Aqueous electrolytes have the edge over other systems, especially when availability, cost effectiveness, and safety are considered. Many attempts have already been made to utilize various metal anodes, e.g., Fe, Zn, Na, Mg, Si (highly doped), Al, Li in aqueous alkaline electrolytes. Among these metal–air battery technologies, Zn–air and Fe–air possess the most promising electrochemical performance due to possibility to offer a better electrical rechargeability. Electrical rechargeability is the key parameter for discussing individual systems; hence, only Fe–air and Zn–air batteries will be considered as possible complementary systems to Li-based batteries.

A practical cyclic performance of iron electrodes in Fe–air batteries has been achieved up to 3500 cycles (in half-cells) with an average faradaic efficiency of 97%.[165] The first electrically rechargeable full-cell Fe–air battery was produced already in 1970 by a Swedish company.[166,167] It could be operated up to 1000 cycles with a very limited specific energy of 80 Wh kg^{-1}. More recent developed Fe–air batteries provide much higher specific energies of 453 Wh kg_{Fe}^{-1}, however only for

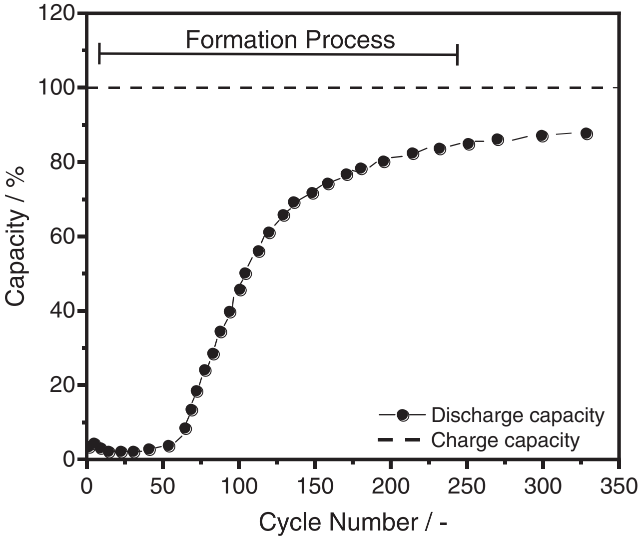

Figure 13. Critical formation process of carbonyl iron electrodes in aqueous 6 M KOH electrolyte. The data for the figure were obtained and Reproduced with permission.[170] Copyright 2018, Springer Nature.

20 cycles.[168] Rechargeable Fe–air batteries differ from other metal–air systems by requiring a critical formation process (for carbonyl iron electrodes) after which the electrodes could provide a stable discharge capacity, as shown in **Figure 13**.[169,170] Main challenge related to Fe–air technologies is mostly related to the bifunctional catalysts at the cathode. Anode originated problems such as corrosion and loss of active particles are of minor concerns.

Despite the early commercialization of primary aqueous Zn–air batteries in 1930s, the electrically rechargeable Zn–air systems could not take of beyond the research level until now. The primary batteries could provide specific energies more than 700 Wh $\mathrm{kg_{Zn}}^{-1}$ while only up to 300–500 Wh $\mathrm{kg_{Zn}}^{-1}$ have been achieved with the secondary batteries.[153,164] In a cell level, practical specific energies up to 500 Wh $\mathrm{kg_{cell}}^{-1}$ and volumetric energy densities up to 1400 Wh $\mathrm{L_{cell}}^{-1}$ may also be possible for coin cell type primary Zn–air batteries, while Li-ion batteries could provide up to 350 Wh $\mathrm{kg_{cell}}^{-1}$ and 810 Wh $\mathrm{L_{cell}}^{-1}$.[128] In terms of specific power and cycle life, however, Li-ion batteries are significantly better than both Fe– and Zn–air batteries.[128] The cycle life of rechargeable Zn–air batteries is highly dependent on the experimental conditions and is usually limited to several hundreds of cycles (<1000).[106,153,171,172] The main challenges originate from the inefficiency of bifunctional catalysts and cyclability of zinc anode. Differing from the Fe, reversibility of Zn is in general more challenging due to dendrite formation, shape changing and the fact that high surface area deposited Zn is more active in the aqueous media, resulting in a severe corrosion.[153,173,174] Despite this, the rate capability and more importantly, the cyclability of Zn–air batteries are mostly controlled by the performance of air electrode. Degradation of catalysts or poor activity toward both oxygen reduction and evolution reactions (ORR and OER) generally limits the energy efficiencies and power densities.

Other aqueous metal–air batteries, such as aluminum, silicon, and magnesium, are not electrically rechargeable as the reversibility of these elements are not thermodynamically feasible in aqueous solutions. Note that these elements are also highly prone to corrosion, which limits these batteries only to primary applications with low utilization efficiencies.[147,151,175]

In general, the challenges for aqueous systems are i) humidity dependency, ii) drying out, iii) flooding of air cathode, iv) parasitic corrosion reactions, v) CO_2 uptake, vi) bifunctional catalysts, and vii) rechargeability. Some of these challenges can be overcome by additional features to the individual battery systems, e.g., filtration, electrolyte management, mechanical recharging etc.; however, these features increase the complexity of the system and the advantage of high specific energies and cost effectiveness would be lost.

5.4.2. Nonaqueous Metal–Air Batteries

Nonaqueous electrolytes can be employed as alternatives to aqueous media due to the ability to provide higher electrochemical window stability with much less corrosivity. One of the key issues is that some of the metals tend to form a passive surface layer and the nonaqueous electrolyte must be capable of activating the passive surfaces. When operated under ambient conditions, the stability of nonaqueous electrolytes could be a compromised because of the presence of moisture and other impurities in the air. Also, the capacity of nonaqueous metal–air batteries is mainly defined by the availability of pores at the air electrode. In general, there are several metal–air systems based on non-aqueous electrolytes;[141,142,176] however, the operation is limited only to primary applications with low power capabilities. Hence, for nonaqueous systems, rechargeability and poor rate capability remain as great challenges. Recently, in 2016, a company called fluidic energy installed an ionic liquid based Zn–air system as backup to solar panels in Indonesia.[177] The performance and details of the system, however, remain unknown. In general, in order to utilize the cost efficiency of metal–air batteries, aqueous electrolytes may be better options in comparison to nonaqueous systems.

5.5. Applications

Considerable work was carried out on metal–air batteries in the sixties and early seventies of the previous century for a variety of applications ranging from communications transmitters for space applications to systems aimed at electric vehicle propulsion. The initial emphasis in the latter application was directed at developing a conventional electrically rechargeable Zn–air battery, but this soon became directed toward mechanically rechargeable systems because of materials corrosion problems at the air electrode, and negative electrode change.[178] Nevertheless, at least in the primary battery market, the Zn–air batteries have been successfully commercialized for hearing aid, navigation lights, or signal devices.

Of different types of primary metal–air batteries, although not fully electrically rechargeable at present, Zn–air, Al–air, Si–air, and Mg–air batteries may be recharged mechanically by quickly and simply replacing the discharged anode and spent electrolyte slurry with fresh metal electrode and electrolyte, making them "refuellable." But these will lose the user simplicity.[179] In this respect, the development of electrically rechargeable metal–air batteries is highly needed, among which the Zn–air so far has received the most favorable consideration.[177,179,180] However, the practical energy and particularly the cycling life are far from satisfactory, being hampered by problems associated with metal anodes, air catalysts and electrolytes. From the cyclability and resource efficiency point of view, rechargeable Fe–air batteries are positioned at the forefront with a price of lower energy densities than Zn–air.[166,181] Rechargeable alkaline Fe–air batteries can only be considered for a stationary applications due to long cycle life (>1000), low cost (<100 $ kWh^{-1}) and limited specific energy (<100 Wh kg^{-1}).[144] According to analysis of Cano et al., energy storage cost of Zn–air batteries can be 70 $ kWh$_{\text{system}}{}^{-1}$ on a system level while for Li-ion the cost can be up to 250 $ kWh$_{\text{system}}{}^{-1}$.[128] Therefore, Zn–air batteries can also be considered for stationary applications, as well as for low-power mobile applications.

At present, however, none of them are at a stage for a large-scale industrial deployment, and their viability to replace lithium-ion batteries for future EV applications also remains foggy and unclear.[141] Especially, due to the unique electrochemistry, the air breathing cathode often has an open porous architecture that permits continuous oxygen supply from surrounding air, which admits the dependency on environment. Solutions to these problems lie in the rational design and engineering of both cathode and anode materials.

5.6. Perspectives—Critical Opinion

In summary, the overall performances of metal–air batteries are not satisfactory, so far. Therefore, it would be quite optimistic to state that metal–air batteries could be the major energy storage devices in the future. Among the possible configurations, until now, aqueous metal–air batteries possess better chances with higher conductivities, easy handling, and cost effectiveness in comparison to nonaqueous systems. The research on metal–air batteries must continue, since they offer outstanding benefits if harnessing their maximum potential would be possible. Implementation of these batteries in a broader range requires overcoming the scientific and technical challenges—mostly air cathode is the bottleneck with inefficient catalysts, degradation, flooding etc. Further fundamental studies and research, especially on advanced bifunctional electrocatalyst are needed to develop a relatively low-cost and high performance materials. In the future, metal–air batteries can provide some advantages, depending on the applications especially for stationary or low-power mobile applications. Thus, metal–air battery systems can only partially conquer the energy storage market.

6. Summary and Perspective

We have explored and reported the most important technologies that can function side by side with Li-based battery technologies. The ability to be accurate in pointing on the most successful battery technology or technologies that would "inherent" the Li-based battery technologies would be incorrect.

The outcome of this Review is that depending on the application and the system needs, one may foresee a room to most of the technologies discussed in this Review. For example, in the case of mobile applications, Na-ion is considered for light-duty vehicles with a short-range, while multivalent metal anode-based batteries can be an option as range extender technologies. Zn–air system might also be employed for low-power mobile applications. These concepts are suited to be used "side-by-side" with LIBs, which are still the most suitable and affordable technology for mobile applications. In the case of stationary applications, although most of the "side-by-side" technologies hold a promising future, redox flow batteries with the current state of development seem to be the choice for large-scale applications. However, the forecast is rather more complicated due to the wide range of applications spanning from a few kWh (house storage utility) to several tens of MWh (for a grid storage application).

The need to address nowadays, which technology will be the next one in the evolution of power sources, may not be correct. The discussion brings to the reader's attention the "supermarket of power sources" technologies and as such, the end user/consumer will need to do the shopping between the technologies, to better fit the needs of the specific application. It is the authors' view that Li-based battery technology is here for a long time (many years to come) and the quest for the post lithium technology may be conceptually incorrect, while the quest should be for multi-technologies for different applications, as well as hybridization of technologies.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

metal–air batteries, multivalent batteries, redox flow batteries, sodium ion batteries, side-by-side technologies

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