

CHAPTER 1

Motivation for a Magnesium Battery

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1.1 Introduction

Batteries, as one of the most efficient and versatile energy storage technologies, play a central role in the ongoing global transition from fossil fuels to renewable energy. They are key enablers for the decarbonisation of both the transport sector (electric mobility) and the power sector (stationary storage of intermittent, and decentralized renewable energy sources), and are essential in a broad range of strategic industries (including automotive, power grids, aerospace, portable electronics, medical devices, and robotics).^{1,2}

The increasing demand for more and better batteries is currently starting to put pressure on established technologies such as the Li-ion battery and researchers worldwide have started to search for alternatives that have the potential to be “better” in terms of storage capacity, power, safety, and costs. For a few years, sustainable solutions have started to move into focus, as supply risks are foreseen in the mid- to long-term for certain elements that are used in current Li-ion batteries. Magnesium batteries have been regarded as one possible option and preliminary work already started

in the late 1980s on the study of the properties of such systems. Overall, the work on this new type of batteries has been motivated mostly by three factors:

1. the scientific curiosity of researchers who are entering a *new and less explored field* with numerous scientific and technical challenges – with the benefit that the gained knowledge will lead to a more comprehensive understanding of electrochemical energy storage
2. the ongoing *need for “better” batteries* in order to satisfy the demands of future applications, and
3. the need for *sustainable storage solutions*, based on globally abundant resources that are available in the long term, materials which are inherently safe, non-toxic, recyclable and less costly.

The first item offers a series of new opportunities for doing research on topics which have been less explored so far. As will be shown later, the bivalent nature of the magnesium ion not only offers the possibility of carrying and storing more charge per ion, it also poses serious scientific challenges when it comes to explaining and improving the mobility of the hard cation in liquids and, in particular, in solid host structures.

The second item deals with the expectation that the physical properties of the bivalent Mg should allow the building of batteries that can outperform current Li-ion batteries, in particular by offering higher energy densities. These assumptions have been triggered by the sheer materials data of the magnesium anode, which is highly promising, see also Table 1.2. In that respect, it is regarded as highly promising that the Mg anode can be used in a metallic, *i.e.* undiluted form, rather than the Li anode, which uses a graphite host to intercalate Li ions, in order to prevent the formation of metallic dendrites, see below. This safety measure dilutes the lithium concentration by a factor of ten.

The need for sustainable storage solutions, mentioned under item 3, moves more and more in the focus of battery development, in particular because more and more applications based on large batteries are considered in practice. Electrochemical storage in large batteries for stationary storage systems but also in sports utility vehicles (SUVs) and trucks will consume a large amount of raw materials. The materials demand to realize large applications exhaustively would by far exceed the demand of portable and mobile applications. As an example, the estimated global energy-storage demand of cell phones and tablets is in the order of 40–150 GWh, while the estimated demand of home storage is up to 3000 GWh; for trucks it would be up to 62 500 GWh.³ In the same study, the demand for Li and Co for the battery industry has been predicted based on various scenarios. In accordance with other studies in the field, the results conclude that, under realistic growth scenarios, there may be a shortage of cobalt in the next 10 years and lithium resources from salt lakes and mines might dwindle in the

2050s. Recycling of cobalt and other heavy metals in batteries is possible and is being done already. However, only a few percent of Li-ion batteries are recycled at the moment and strong efforts will be needed to ramp up the global recycling capacities, in order to deal with the enormous returns of spent batteries from battery vehicles that are expected from the 2030s onwards. The current industrial recycling processes depend on recovering cobalt and nickel metals or their alloys. Lithium is typically not recycled at the moment, mostly because there is limited or no economic benefit to recycle lithium in today's commercialized technologies. In effect, there are large energy costs and the chemical clean-up procedures needed for the variety of cathode chemistries and sortation based on chemistry is challenging and difficult.⁴ It is therefore expected that federal regulations will have to be established in order to initiate Li recycling. This may, however, have a negative impact on future battery costs, which are actually expected to drop.

In the following, an outline will be given on major research directions which are dealing with the aims for pushing research to new frontiers and developing technologically viable solutions. Moreover, the need for “better” batteries will be illustrated and the growing demand for sustainable storage solutions will be discussed.

1.2 Overview on Research Topics

At its still early stage of development, two major issues in the work on Mg batteries have been the *development of electrolytes* for transport and reversible stripping/plating of the doubly charged Mg ion and the *development of cathodes* which can either reversibly insert and de-insert Mg ions or convert the Mg into a certain compound by a chemical reaction, see also Chapters 5–10. In both fields it became apparent that the concepts that have been established in other battery types cannot just be transferred to Mg technology. Rather, it has turned out to be essential to considerably expand upon the existing knowledge on Mg chemistry and electrochemistry by doing in-depth research on the new systems in order to generate a knowledge base which may eventually help to enable viable technical solutions. Also *anodes* are a matter of research, in particular composite anodes or alloys with Mg. A new field is the use of new compounds that can insert Mg ions at low potentials.

1.2.1 Electrolytes

Electrolytes for secondary magnesium batteries have been a particular challenge from the beginning after it became clear that the classical approach for making electrolytes, which is for example pursued in Li-ion, NiMH or NiCd technology, may not work: dissolving an electrolyte salt in a solvent

and using the solution as an electrolyte was simply not successful for the Mg battery in the first phase of development. There, the anions of the tested salts either reacted with the magnesium anode, or the anode was covered by a passivation layer. In both cases, the electrochemical reaction stops. A similar passivation layer also forms at the anode of Li-ion battery cells (the so-called SEI, solid electrolyte interface), but there, the singly charged and softer Li ion can easily penetrate the layer, while the hard and doubly charged Mg ion can obviously not pass the rigid interphase layers on the Mg surfaces.⁵

Preliminary work in the context of the later magnesium battery dates back to more than 100 years ago when Grignard developed Mg organo-metallic reagents,⁶ which were later tested as electrolytes as they are capable of reversibly stripping and plating magnesium.⁷ In this work by Gregory *et al.*, Mg electrolytes were synthesized in ethereal solvents *via* the reaction of an organomagnesium compound with aluminium chloride (AlCl₃) or trialkylborane as a Lewis acid. This publication inspired numerous follow-up studies because they not only demonstrated the first feasible electrolyte (even if the performance was not yet convincing), they also published the first table with suggestions for potential insertion materials, investigated some of them and published the first data, see Table 1.1.

With a similar synthetic concept, Aurbach *et al.* prepared a second generation of electrolytes through the reaction between Bu₂Mg and EtAlCl₂ in tetrahydrofuran (THF) and demonstrated the first prototype of a good

Table 1.1 Mg²⁺ intercalation materials. Adapted from ref. 1 with permission from the Royal Society of Chemistry.

Material	$E_{\text{Mg-cathode}}$, V	Capacity	
		Moles Mg/mole host	Ah g ⁻¹
Co ₃ O ₄	2.28	0.80	0.222
Mn ₂ O ₃	2.40	0.66	0.224
Mn ₃ O ₄	2.40	0.66	0.154
MoO ₃	2.28	0.50	0.143
PbO ₂	3.10	0.25	0.056
Pb ₃ O ₄	3.10	0.25	0.020
RuO ₂	2.55	0.66	0.266
V ₃ O ₅	2.66	0.66	0.194
WO ₃	2.16	0.50	0.116
TiS ₂	1.63	0.15	0.157
VS ₂	1.71	0.34	0.154
ZrS ₂	2.60	0.66	0.228
MoB ₂	1.15	0.66	0.301
TiB ₂	1.25	0.42	0.324
ZrB ₂	1.20	0.66	0.313

rechargeable Mg battery.⁸ Unlike the former chemically very aggressive and dangerous Grignard reagents the electrolyte was made *via* a Lewis acid–base reaction of an organometal compound as a base and AlCl_3 as an acid. The active component in this electrolyte is a binuclear Mg complex where two Mg atoms are bridged by three Cl atoms. The residual six coordination sites are occupied by coordinated solvent molecules. With a Chevrel phase as the cathode, several thousand cycles were demonstrated. Later studies had the goal of further simplifying the synthesis, to reduce the strongly reducing character of the organometallic components in the electrolyte, and, recently, to develop electrolytes that no longer contain corrosive constituents.

A first approach in that direction was realized by Mohtadi *et al.*, who demonstrated reversible stripping and plating of Mg from solutions of $\text{Mg}(\text{BH}_4)_2$ in THF.⁹ The electrolyte did not contain corrosive Cl but had a narrow stability window and only a low salt concentration was possible, leading to low ionic conductivity. A few years later, the same group presented an electrolyte based on Mg closoborate. This anion is much more stable due to the aromatic system of the boron cage. It also offers a higher ionic conductivity. However, the synthesis of such compounds is expensive and time-consuming.¹⁰ Further progress was made when an electrolyte based on a similar rationale, namely a Mg salt with a big and weakly coordinating, very stable anion was presented by Zhao-Karger *et al.*¹¹ The salt can be synthesized by a simple and straightforward one-step reaction from $\text{Mg}(\text{BH}_4)_2$ and hexafluoro-isopropanol, rendering $\text{Mg}[\text{B}(\text{OR}^{\text{F}})_4]_2$ in a quantitative yield, with H_2 gas as the only by-product. The electrolyte can then be made from solutions of the salt in a variety of solvents. The ionic conductivity of such systems is in the order of 10 mS cm^{-1} , which is in the range of current electrolytes for Li-ion batteries. The electrochemical stability window is 4.3 V *vs.* Mg, the electrolyte is stable in air and is non-nucleophilic, making it compatible with a sulfur cathode so that Mg–S cells can also be built. In effect, this work and the pioneering studies before have paved the way back to realizing the “classical” electrolyte concept which was mentioned above.

In spite of the technical advances, there are a lot of issues which need to be understood and overcome. As an example, the control of the interaction of the electrolyte and potential side products with the battery electrodes will be crucial for the development of viable systems with high energy efficiencies. Most publications so far have reported extensive overpotentials which hint at serious kinetic barriers in the transition of the Mg ion from the electrolyte to the surface of the metal anode. In this process, the Mg ion needs to strip off its solvent shell, migrate to the interface, potentially penetrate surface layers and receive electrons so that it becomes metallic and plates at the anode when charging the battery.^{12–14} It is the aim of an increasing number of studies to understand these limitations and to find ways how these barriers can be removed or mitigated. It is obvious

that further studies at the electrolyte–electrode interface will reveal more details of the structure and composition of the adlayers, their origin and their interference with the plating process. This will be essential for achieving further progress in the field.

1.2.2 Cathodes

The development of viable insertion cathodes is one of the most challenging endeavours in research and development. So far, only a few effective Mg cathode materials have been reported. Gregory *et al.* started to evaluate the ability of transition metal oxides, sulphides, and borides to reversibly insert Mg^{2+} ions, see Table 1.1. Some of these hosts were investigated by Novak *et al.* in the 1990s, with $\text{Mg}(\text{ClO}_4)$ in tetrahydrofuran (THF) as an electrolyte. The conclusion was that only V_2O_5 showed a reasonable capacity.¹⁵ Later, Aurbach *et al.* achieved the first breakthrough by introducing a new electrolyte using Mo_6S_8 (*i.e.* the Chevrel phase) as a cathode and Mg metal as an anode. This cell is still a good working reference for Mg-ion batteries, with a volumetric energy density comparable to that of a Li-ion battery. In recent years, the experimental work on Mg insertion hosts was still concerned with synthesizing and testing structures that were suggested in Gregory's early work. In addition, conceptually new approaches to identifying suitable materials have been explored, *e.g.* the development of metastable materials.¹⁶ This approach offers new opportunities in identifying a new functional multivalent cathode material. It may also be of general interest as a general concept because metastable compounds can obviously offer sufficiently low migration energies to support reversible cycling with multivalent ions.

In addition to this more conceptual and experimental work, computer-aided design and *ab initio* calculations have been used to reveal suitable atomic configurations and structures for the diffusion of Mg in host materials such as spinels or layered compounds.¹⁷ Recent work has also shown that co-intercalation of solvent or shielding of the hard Mg^{2+} ion by coordinated solvent can lead to a softening of the ion so that faster insertion and de-insertion is enabled in certain matrices.¹⁸

Moreover, it was found by Matsubara *et al.* (see Chapter 11) that the motion of Mg ions in oxidic hosts can be greatly facilitated by the presence and interaction of other inserted and mobile ions, such as Li^+ .

An alternative to cathode insertion materials are conversion electrodes, sulfur electrodes in particular, which offer high capacities at reasonable voltages. As shown in Table 1.2, an effective and efficient Mg–S battery would have quite interesting features when compared to a Li–S battery. The first work on a Mg–S system^{19,20} already indicated that Mg–S batteries are feasible, but besides the already mentioned issue of overpotential, there is a capacity loss upon cycling. So far, the origin has mostly been attributed to polysulfide intermediates that form in both Li–S and Mg–S batteries²¹ and are partly soluble in organic electrolyte.

Table 1.2 Comparison of theoretical properties of the Mg–S system with Li–S (metal anode) and Li–S (graphite anode), based on materials values.

	Mg/S	Li/S
Theor. grav. cap. anode [mAh g ⁻¹]	2205	3861 (LiC ₆ : 372)
Theor. vol. cap. anode [mAh cm ⁻³]	3832	2062 (LiC ₆ : 833)
Theor. energy density [Wh L ⁻¹]	3200	2800 (LiC ₆ : 1100)
volumetric change S → M _x S (molar volume S ~16 cm ³ mol ⁻¹)	molar volume MgS: 19.9 → 24% expansion	molar volume Li ₂ S: 27.7 → 72% expansion

1.2.3 Anodes

Four types of anodes have been investigated for Mg batteries so far:

- sheets of pure Mg metal
- finely dispersed Mg particles in carbon composites
- sheets of Mg-based alloys
- Insertion compounds for Mg at low potential

Using plain Mg metal appears to be the most simple and straightforward approach. Mg metal is not expensive and can be machined by various techniques – although the mechanical properties of Mg are not favourable. A practical advantage is, that the metal sheet can be used both as an electrode and a collector. This has been demonstrated in a collaborative project²² where the first pouch cells with sulphur cathode and Mg metal anode were fabricated and tested. However, although the concept appears simple and convincing, the power density of such systems is limited and the abovementioned adlayers on the Mg surface obviously provide kinetic barriers for Mg transfer which lead to considerable overpotentials during charging. Therefore, the formation mechanism, the composition, and the prevention or removal of such layers is an important topic of research. This is closely associated with the work on electrolytes, as such layers typically form when impurities are present in the electrolyte and/or decomposition products of the electrolyte salt or the solvent can chemically interact and form a solid film.

Finely dispersed Mg particles in carbon have already been used in early studies on Mg–S batteries²¹ as they offer the advantage of a larger surface for the electrochemical reaction.²³ This enhances the rate capability of the system and reduces the overpotentials. However, there are also trade-offs due to the reduced capacity of the electrode due to the addition of carbon. Moreover, finely dispersed magnesium may strongly react with oxygen in air so that passivation may occur when handling the material in an uncontrolled atmosphere.

Compared to the pure metal, magnesium alloys can improve the ductility of the metal anode so that fabrication is easier and more safe. In addition, as Mg metal may not be compatible with electrolytes that are not made from ethereal solvents, a suitable alloy may mitigate or prevent such effect due to its altered electrochemical properties compared to those of the pure element. Alloying elements dissolve and redeposit during galvanostatic cycling without having a negative effect on the electrochemical properties of Mg.

Recently, the search for other anode materials has started and there will be a review on alternative anodes in Chapter 5. Various types of compounds have been tested as hosts for the insertion of Mg ions, including candidates that are known from Li ion technology, such as graphite or titanates. There, it may be beneficial to co-intercalate either solvent molecules (graphite) or other ions such as Li^+ or Na^+ (titanates) in order to achieve reversible behaviour. Other compounds such as phosphorenes and borophenes have been proposed as new candidates and mostly studied by theoretical modelling, but little is known about the behaviour of various structural configurations when Mg ions are inserted and de-inserted.

1.2.4 Mg Deposition and the Lack of Dendrite Formation

The formation of dendrites in batteries with metal anodes and liquid electrodes poses a major safety risk as the fine metallic needles can grow through the separator and cause short-circuits inside the battery, which may trigger the release of hazardous substances, fire, and explosions.

As was confirmed in many studies, the use of Mg metal as an anode does obviously not pose the risk of the formation of dangerous dendrites. This is a particular feature and advantage of the Mg metal anode as most other metals such as Li, Na, and Zn, do form dendritic structures in liquid electrolytes. There are several models in the literature to explain the formation of dendrites in Li-ion batteries, but only recently was a first attempt made towards an explanation of the different trends for dendrite formation of the different metals. Jäckle *et al.*²⁴ investigated different scenarios for self-diffusion of Li, Na, Mg, Al, and Zn using density functional theory calculations. They studied self-diffusion barriers including diffusion barriers that are relevant for three-dimensional growth such as barriers for diffusion across steps in order to find out whether there are “simple” relationships which would explain the trends of dendrite formation. Their results suggest that Li dendrite growth is an inherent property of the metal, which is also in agreement with experimental observations.

Overall, the following challenges are key and need to be addressed for the development of next generation electrode materials for Mg:

- *Increasing the ionic mobility of the bivalent Mg ion* within host matrices through a better understanding of structure–property relationships. Multivalent ions pose a particular challenge for intercalation electrodes,

as their mobility is usually low in host materials. Therefore, strategies need to be developed for designing an “ideal” geometrical and chemical environment of the mobile ion in order to optimize both ion packing density and mobility.

- *Improving the stability of electrode materials:* Current insertion hosts often suffer from structural instability. The challenge here is to design and synthesize tailored positive and negative electrode materials for Mg batteries with excellent cycle life at a high rate.
- Identification of principles governing the storage of magnesium ions in host materials: the structures of the materials need to be clarified to reveal and comprehend *the magnesium storage mechanisms*.
- Synthesizing highly reactive nanocomposites for multivalent conversion electrodes with *high reversibility on the microscale in the solid*. The understanding of the materials' conversion reactions and a quantification of the energy barriers for the fundamental steps is key for faster kinetics and improved reversibility.

1.3 Need for Better Batteries

The term “better batteries” is often used in the literature, mostly to express the fact that higher energy densities are desirable of batteries. In that respect, Mg technology offers a – so far only theoretical – perspective to be better or at least similar to the current Li-ion technology. The term “magnesium battery” rather than “magnesium-ion battery” (similar to “lithium-ion battery”) already displays one of the major differences between the lithium and the magnesium technology: in the current Li-ion battery, Li is stored as an ion at the anode of the battery cell, in an insertion material such as graphite, for example. This is done as a safety measure because dendrites may form at a Li metal anode, as already mentioned above. However, they are not formed when magnesium metal or alloy is used as an anode. Therefore, it is possible to utilize an “undiluted” magnesium metal anode, thus offering very high gravimetric and volumetric capacity. This striking advantage is currently compromised by the lack of suitable cathode materials that show good capacity.

Another feature of a “better battery” is a higher rate capability. This is particularly important for applications where fast charging is needed, such as in automotive applications. However, from the current state of knowledge, the data from Mg metal anodes together with the studied cathode materials does show a moderate to slow charging and discharging behaviour so that a battery would have to be optimized in terms of its components in order to allow fast charging.

A key feature of a battery is its lifetime, particularly if it is to be used in large stationary applications for thousands of charge and discharge cycles. Lifetime has a critical impact because big batteries are expensive and both calendar and cycle life have a direct impact on the cost of the stored kWh, and on the cost of the storage itself. The longer the depreciation period of

a battery, the lower the cost per charge and discharge cycle. It is difficult to foresee the potential of Mg technology at the moment as it is still in an early stage of development. The numbers that are currently elaborated for one or the other battery configurations are most likely prone to change in the next few years, when progress will be made in the different components of the battery.

Fabrication cost is another important factor and also here it is not clear at the moment what the cost of a Mg battery will be. The low price of Mg metal is often used as an argument when the technology is compared with Li-ion technology, for example. In fact, a sheet of Mg metal as both collector and active material of an anode would be simpler and probably less costly in the case that the currently high price for Mg sheets from laboratory suppliers would be lowered by mass production. What is still unclear however, is the price of the electrolyte, because there is as of yet no standard electrolyte. There is a wide span in the costs of currently published systems, depending on how many synthesis steps are required, in which yield the electrolyte is obtained and whether costly or cheap reagents and solvents are involved.

Also the cathode side remains open. Current configurations do not seem to be competitive and there are as of yet no viable technical solutions. In the case in which the current concepts can be further developed, insertion cathode materials will most likely be based on transition metals as in Li-ion technology. If no viable insertion materials can be identified, conversion electrodes may be an alternative, in particular the magnesium–sulphur battery, where carbon–sulphur composites would be employed as a cathode.

An inherent disadvantage which may lead to higher costs is certainly the low discharge voltage of Mg batteries. Compared to cells that deliver a higher voltage, more cells are necessary in order to store the same amount of energy, which has an impact on the fabrication cost and size and volume of a battery pack.

1.4 Need for Sustainable Solutions

As indicated above, future battery generations will have to take sustainability aspects into account. In that respect there are issues with the current Li-ion technology.²⁵ One reason is that many of the materials used in Li-ion batteries are on the Critical Raw Materials (CRM) lists, see the EU list,²⁶ for example. In particular, lithium, graphite, cobalt, nickel and copper are among a list of 33 materials that are used in significant amounts in low carbon technologies, including battery technology. Interestingly, magnesium has been a member of such lists, not because of its abundance but rather due to the fact that most Mg is currently produced in China, which is regarded as a rather political risk. If Mg could also be produced in significant amounts in other regions of the world, the material could be removed from this list. More information on the resource situation of magnesium will be given in the next Chapter.

1.4.1 Cathode

There are strong efforts being undertaken worldwide to reducing the amount of cobalt in NCM materials ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$), which are used in power tools, e-bikes and electric drivetrains. The increase in the relative amount of nickel is possible and commercial batteries with NCM compositions of 8,1,1 have been announced for 2019. Further reduction seems possible, but the structural stability of the material decreases with increasing Ni content and thermal runaway starts at lower temperatures compared to the NCM 1,1,1 composition. The high reactivity of Ni^{4+} at the end of charge leads to low thermal stabilities and side reactions with the electrolyte. Thus, decomposition already starts below 150 °C and Ni oxide decomposes under the release of pure oxygen, which is a major safety concern in a battery with an organic electrolyte.²⁷ In the case that all of these issues can be resolved, Ni is still a critical raw material and the approach may be viable only if substantial amounts of Ni are recycled from used batteries in the mid- to long-term. Hence, large automotive companies such as Volkswagen have recently pointed out that they have the goal to not use Co and Ni in future battery generations. As alternatives to NCM materials, other compositions have been considered, such as manganese spinel ($\text{Li}_2\text{Mn}_2\text{O}_4$) or olivine (LiFePO_4), which offer high power but lower capacities. The Li-S battery has been announced as an alternative several times already, but it is still under development. This is mostly because there are fundamental issues that have not yet been solved, for example, the capacity decay due to the formation of soluble polysulfides and side reactions of certain electrolyte solvents with polysulfide intermediates.

It is difficult to make a statement about the sustainability of cathode materials for magnesium batteries at present. As already mentioned, the work is in progress and so far, the materials investigated have been made from elements other than those in the cathodes of Li-ion batteries. Vanadium-based materials have been proposed, but it is too early to regard them as a viable and commercially attractive option. If yes, it may be interesting to know that the abundance of vanadium is similar to that of lithium in the Earth's crust.

1.4.2 Anode

The anode of current Li-ion batteries is made from graphite, which is again rated as a critical raw material. Here, it seems that there are alternatives with long-term options such as synthetic graphite, which can eventually be made from processed biomass. At the moment this is not a commercially attractive option because the synthetic route is more expensive than the mining and clean-up of natural graphite. There is a perspective that graphite may not be needed any more when solid state batteries have overcome their technical and economic obstacles because Li metal is the anode of choice in combination with a solid electrolyte.

In comparison, a magnesium battery would not need natural graphite as the anode may be made directly from a metal sheet or from a composite with carbon. The carbon, however, can be porous or have other particular properties, which may need dedicated synthesis efforts.

1.4.3 Electrolyte

The current electrolyte in Li-ion batteries is typically based on LiPF_6 as a conducting salt which poses a potential risk in case the housing of the battery is damaged. When released in humid air, the hexafluorophosphate reacts with H_2O to form HF, which is highly toxic and can cause severe injuries and even death in persons that come into contact with it.

The current electrolytes of magnesium batteries are quite different from their Li counterparts due to their completely different chemical compositions. The early electrolytes based on Lewis acid–base complexes contain the binuclear Mg_2Cl_3^+ complex, which is co-ordinated by solvent molecules. Depending on the synthesis method and on the so-called Schlenk equilibrium of the system, there may be different anions, including organometallic compounds, which can be aggressive and toxic. Recently published electrolytes based on salts with large and weakly co-ordinating anions provide a softer chemistry with a more viable perspective. They are not aggressive or very toxic and are even stable in air.

1.5 Magnesium as a Resource

Magnesium is one of the most abundant elements in the Earth's crust. As dolomite, a mixed carbonate of magnesium and calcium, it forms entire mountain chains with a content of 13 mass% Mg. The mineral magnesite, which is found as a white sand in stone pits, is pure MgCO_3 , with a Mg content of 28.5 mass%. In addition, sea water contains 1270 ppm of Mg (Li: 0.1 ppm) and the Mg content in the brine of salt lakes is also high. According to the assessments of the US Geological Survey (USGS) the current economically viable reserves amount to 8.5 Mio tons, which corresponds to a lifetime of 306 years, given the global annual production of 27 700 tons remains constant. The resources are much larger, however, and amount to 12 billion tons, which would last for 433 000 years, sea water and salt lakes not included. While most of the global resources are found in Russia (27%) and China (25%) and two thirds of the currently produced Mg comes from China, followed by Turkey (10%), Russia (5%) and Austria (3%). Although there seems to be no issue with the abundance of Mg worldwide, it has nevertheless been regarded as a critical raw material, due to the current dominating market power of China. It is certainly an advantage that magnesium is easily recyclable without experiencing any loss in quality. Worldwide, the market share of recycled Mg is in the order of 15 to 20%. An overview of the features of magnesium as a resource is given in Table 1.3.

Table 1.3 Factsheet of magnesium as a resource. (Data: US Geological Survey²⁸).

Properties:	<ul style="list-style-type: none"> • Chemical element “Mg”, with atomic number 12 • Silvery light metal with a density of only 1.7 g cm^{-3} • The lightest metallic material • Mg is corrosion resistant, resistant against acids, tough and ductile • The metal burns at $650 \text{ }^\circ\text{C}$ with a white, very light flame. It also burns under water
Use:	<ul style="list-style-type: none"> • Aluminium–magnesium alloys (43%) • Die casts (37%) • Desulfurization- and deoxidation-additive in steel- and cast iron production (10%) • Production of fire resistant materials (10%)
Largest producers of magnesium:	<ul style="list-style-type: none"> • China (68.6%) • Turkey (10.1%) • Russia (4.9%) • Austria (2.7%) • Slovakia (2.2%) • Spain (2.2%)
Available reserves:	8.5 Mio. Tons
Available resources:	>12 Bio. Tons
Statistical lifetime of reserves:	306 years
Statistical lifetime of resources:	433 212 years
Recycling rate:	In Germany 50% of the magnesium is recycled, worldwide 15–20%.
Annual global production of magnesium:	27 700 Mio. Tons

1.6 Conclusion

Mg batteries are one of the few options to complement or even replace Li ion batteries in the future. Although the basic properties of the Mg anode are promising, such as the bivalency of the Mg ion, the high volumetric storage capacity of the anode, the non-toxicity of Mg, and the lack of dendrite formation which allows the building of batteries with a metal anode, battery cells with competitive properties have not yet been reported. This is mostly due to the lack of suitable cathodes allowing high capacities and voltages and the presence of overpotentials, especially during plating and capacity fading due to unstable electrolytes and/or unstable electrodes. The research to address all of these issues in order to realize viable solutions is exciting and so far, no dead-ends are in sight, so the success of this technology will largely depend on the skills and effort that are put into this fascinating field of energy research and technology.

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