Rechargeable Magnesium–Sulfur Battery Technology: State of the Art and Key Challenges

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Inspired by the first rechargeable Mg battery about 20 years ago, based on a Chevrel phase cathode, a Mg foil anode, and a magnesium organo-aluminate electrolyte, research on rechargeable batteries using sulfur as the cathode together with Mg as the anode has gained substantial and increasing interest. In particular, the safety characteristics of magnesium–sulfur (Mg–S) batteries, the high abundance of both magnesium and sulfur, and the high theoretical volumetric energy density of magnesium render this system specifically interesting for mobile applications that require high volumetric energy densities, i.e., the automotive and aviation sector. While the development of Mg–S batteries is still at a nascent stage, some breakthroughs have already been accomplished. Consequently, it appears necessary to provide a comprehensive up-to-date review about the current achievements to facilitate further improvements in this field.

In this review, the state of the art in Mg–S batteries is summarized, focusing on sulfur conversion cathodes, magnesium anode materials, currently employed electrolyte systems, as well as on current collectors and separator design. In addition, the challenges and some possible future work to realize a practically applicable and technically viable Mg–S battery are highlighted.

1. Introduction

Since Volta’s invention, energy storage technology has shown a great potential in the field of portable and mobile electrical power applications, especially in the automotive industry.[1,4] In the field of rechargeable batteries, lithium-ion batteries (LIBs) currently represent the dominating cell technology; nonetheless, lithium–sulfur (Li–S) batteries clearly have the potential and a level of readiness to replace LIBs in the near future.[3,4] In the 1960s, Herbert et al. published a US Patent in the field of Li–S batteries.[5] However, the research on Li–S batteries was paused due to the emerging of LIBs in 1991.[6] The main advantages of LIBs, including stable electrochemistry and long cycle life, has made LIBs one of the leading technologies of electric energy storage during that time.[7] They have been commercialized in the areas of portable applications, electric vehicles and mobile robotics.[7] After the year 2000, the need for high energy density in applications, such as military power supply, led to the resurgent of Li–S batteries, because of their high theoretical energy density (2600 Wh kg−1), which is about four to five times higher than that of LIBs.[5,8]

Despite its favorable electrochemical characteristics, Li–S batteries suffer from several drawbacks. On the one hand, the formation of a passivation film generated from dissolved corrosive polysulfides as well as continuous lithium erosion is critically limiting the performance of Li–S cells.[9,10] On the other hand, lithium-based batteries display some safety issues, such as the uncontrolled formation of lithium dendrites, which bear the potential to pierce the separators and to lead to short microcircuits.[9,11,12] At the same time, lithium dendrites tend to dissolve in the local region and detach from lithium anodes, resulting in delithiation and formation of “dead” lithium. This can further decrease cycle stability and specific capacities.[9,13–15]

As an alternative to Li–S batteries, rechargeable Mg–S batteries (Figure 1c), first reported by a research group of Toyota Motor Corp. in 2011,[12] show some attractive advantages and research in this field has recently accelerated (Figure 1a).[16] The mechanism of Mg–S batteries is based on the redox reactions between Mg and sulfur. During discharge, the Mg anode is oxidized to form Mg2+ ions and two electrons. Mg2+ migrates to the sulfur cathode through the electrolyte and separators, whereas the electron transfer from the anode to the cathode proceeds via an external electrical circuit. On the cathode side, sulfur is stepwise converted into long chain polysulfides, short chain polysulfides and, finally, MgS. During charging, Mg2+ ions are reduced and deposited (plated) onto the anode. The magnesium (poly)sulfides are ideally reoxidized to their original state, i.e., to sulfur.

Mg–S batteries show the following advantages. Magnesium generally does not plate in a dendritic manner, which translates into better safety characteristics of Mg anodes.[17] Moreover, Mg–S cells possess a higher theoretical volumetric capacity than Li–S batteries (2062 vs 3832 mAh cm−3) due to the divalent nature of Mg2+ and the higher physical density of magnesium (0.53 vs 1.74 g cm−3).[18] In addition, Mg is the fifth-most...
abundant metal on earth.\textsuperscript{19} In view of these merits and the high abundance of sulfur, increasing interest has been raised on post Li–S battery systems, including magnesium-selenium batteries, Mg–S batteries, which display higher energy density, low costs and improved safety in comparison to Li–S batteries.\textsuperscript{11,20–23}

Despite the advantages of Mg–S batteries, major issues in this field are related to the severe overcharge behavior and low sulfur utilization of the cathode during charging and discharging in general, the formation of magnesium polysulfides and the slow diffusion of Mg\textsuperscript{2+}, which all result in poor electrochemical behavior.\textsuperscript{17,22,24,25} Substantial efforts have been made to improve cell performance so far, including the modification of cathode materials, anodes and separators,\textsuperscript{25} the synthesis of novel electrolyte systems,\textsuperscript{24,26} which all to some extent can improve the cell behavior. Figure 1d gives a timeline of all the novel findings in the area of Mg–S batteries in each year. Figure 1b demonstrates an overview of the topics addressed in the published research articles in Mg–S batteries. According to this survey, the research community developed a strong preference for investigating novel electrolyte systems, modifying sulfur cathode materials and carrying out mechanistic studies. By contrast, only few research groups devoted their work to the other components of a Mg–S battery, such as the anode and the separator. Major improvements related to the latter two will also be thoroughly discussed in the following sections.

Several reviews already discussed the developments in Mg batteries based on intercalation cathode materials.\textsuperscript{1,15,27–30} By contrast, accounts on Mg batteries containing a sulfur-based conversion cathode, which benefits from high theoretical energy density, a reasonable potential difference with Mg, nontoxicity and high earth abundance\textsuperscript{11,31,32} are rare. This review solely refers to Mg–S batteries that use sulfur-based conversion cathodes.

The purposes of this review are to summarize and highlight the most up-to-date and novel findings for Mg–S batteries, addressing sulfur-based conversion cathodes and Mg anode materials, separator modifications as well as various electrolyte systems. Furthermore, since the research on Mg–S batteries is still at an initial stage, some challenges, including the capacity decay mechanism, a lack of suitable electrolyte systems and the passivation of the Mg anode, which so far impedes any superior electrochemical performance in Mg–S batteries, will also be addressed. In addition, we also listed and discussed some possible future prospects for high energy Mg–S batteries. Finally, the currently reported Mg–S systems have been summarized in a table for easy comparison.

This review on rechargeable Mg–S batteries is arranged in the following sequences. In the first section, currently applied anode materials (various forms of Mg anodes) and prospective anodes are discussed. Next, various sulfur-based conversion cathodes, which mainly focus on sulfur accommodated in micro/meso/nanoporous carbon materials are introduced. This section is followed by the discussion about the performance of different current collectors, especially of concomitantly used Cu current collectors together with a nucleophilic electrolyte. Further on, electrolyte systems are thoroughly explained, in the sequence of nucleophilic electrolytes and nonnucleophilic electrolytes. Specifically, nonnucleophilic electrolytes are outlined in a detailed manner, including hexamethyldisilazide (HMDS)-, bis[(trifluoromethanesulfonfonyl)imide (TFSI)-, and boron-based electrolytes. Also, various additives that are beneficial for cell performance, such as Li salts, are explained. Furthermore, recent progress in separator design, which can to some extent solve the problem of the reoxidation of Mg\textsuperscript{2+}, is discussed. Finally, full device design and interface issues of the electrodes are briefly introduced. Conclusions, current challenges and an outlook to future investigation in the area of high-energy Mg–S batteries are provided.

2. Anode Materials

In the field of Mg–S batteries, the Mg anode plays a crucial role in electrochemical performance since the interactions between the Mg metal and electrolyte have a direct influence on the electrochemical performance.\textsuperscript{1,15,19,27–30,33,34} It is well known that the blocking layers on the Mg anode formed via electrolyte decomposition or reaction with traces of water and oxygen prevent the diffusion of Mg\textsuperscript{2+} ions; consequently, the reversible Mg deposition and dissolution are impeded.\textsuperscript{19,33,34} For instance, polar aprotic solvents including carbonates and nitriles, tend to form an impermeable layer on the metal surface, which limits the variety of the electrolyte.\textsuperscript{34–38} Surprisingly, compared to the
number of studies carried out on different electrolyte systems and cathode materials, comparably few research groups dedicated their work to the anode material.

### 2.1. Forms of Mg Metal Currently Used as Anode Material

Among all reported Mg–S batteries, currently used anode materials are mainly composed of metallic magnesium in form of magnesium discs, \(^{[37,38]}\) plates, \(^{[24]}\) ribbons, \(^{[39]}\) or foils. \(^{[18,24,25,37,40–43]}\) These types of anodes generally have a low surface area. As already outlined, Mg does not form dendrites during charge. While this substantially improves safety and longevity of the anode, it prevents the formation of new and reactive anode surface, which in terms negatively influences cycle behavior.

Friedrich and co-workers\(^{[44]}\) addressed this issue and reported on pressed magnesium powder anodes with an increased surface area. They compared the electrochemical performance of anodes based on pressed and conventional magnesium foil, respectively. For the preparation of powder-based magnesium anodes, they ball-milled a mixture of magnesium powder and graphite powder in a weight ratio of 4:1 and compressed the ground powder with a hydraulic press at 75 and 350 MPa, respectively. The resulting anodes were termed pressed anode at low pressure (PALP) and pressed anode at high pressure (PAHP).\(^{[44]}\) The authors stated that the PALP anode showed a dull surface and could soak more electrolyte than the PAHP anode and Mg foil, which both had a shiny surface. In order to compare the electrochemical behavior of cells based on these different anode materials, the authors conducted cycle tests with a cathode material containing 50 wt% elemental sulfur (50S) using an [HMDS]_2Mg-based electrolyte system at 0.1 C (Figure 2).

Clearly, cells containing a pressed anode (Figure 2a,b) showed better Coulombic efficiencies than those based on a
Figure 2. Electrochemical behavior of cells using a) a pressed anode prepared at low pressure with diglyme and an ionic liquid (DEGIL) as electrolyte solvent; b) a pressed anode prepared at high pressure; c) magnesium foil, diglyme and tetroglyme (DEGTEG) as solvent and a cathode material containing 50 wt% elemental sulfur, 0.1 C; and d) Bode and e) Nyquist plots for symmetrical magnesium cells with Mg foil, a PAHP anode and a PALP anode.[44] Reproduced with permission.[44] Copyright 2017, ECS Transactions.
Mg foil (Figure 2c) due to a more efficient charging.[44] Furthermore, cells containing pressed anodes lasted for 100 cycles while those based on Mg foil were reported to fail after only 15 cycles.[46] Notably, the authors also found that cells containing pressed anodes prepared at low pressure showed better electrochemical behavior and better voltage plateau recovery than those based on PAHP.[44] According to Figure 2a, a PALP-based cell gave an initial discharge capacity of 600 mAh g\(^{-1}\) sulfur and clearly showed two voltage plateaus at 1.4 and 1.1 V,[44] respectively, indicating the formation of magnesium polysulfides. The recovered voltage plateaus were also observed in the second and third cycles. However, after ten cycles, the voltage plateau at 1.4 V vanished.[44] By comparison, a cell (Figure 2b) showed only one plateau at 0.7 V in the initial cycle. In the second and third cycles, the voltage plateau increased to 1.3 V. In the following cycles, the plateaus were hardly visible.[44] Figure 2d shows the Ohmic resistance, which is in general a result of the contact resistance of the current collector, the cell configuration, the inner electrode resistance and the electrolyte resistance.[44] These three symmetric Mg–Mg cell setups, for which the same electrolyte but three different forms of anodes were used (PALP, PAHP, and foil), clearly revealed the origin of the Ohmic resistance, which is related to the different physical forms of the anodes. According to Figure 2d, the Ohmic resistance of a cell based on Mg foil or PAHP was 8 Ω; whereas the Ohmic resistance of a PALP anode was 19 Ω. The much higher Ohmic resistance of the PALP anodes was attributed to the electrolyte soaked into the electrode. The Nyquist plots in Figure 2e also prove the higher porosity of the PALP anodes, since the phase angle with PALP anodes (−45°) is lower than that of anodes based on Mg foil or PAHP (−90°). In summary, pressed Mg anodes, PALP, at least to some extent, improve the whole cell performance.

2.2. Prospective Anodes

Carbonate-based solvents are known to be noncorrosive and more stable versus anodic oxidation compared to ether-based solvents.[35] However, the reaction between the Mg metal and carbonate solvents tends to form an impermeable layer on top of the Mg anode, which in turn prevents Mg deposition during charging.[31,46,47] Therefore, to compensate for that, the design of an appropriate conductive and protective artificial interphase on Mg anodes presents a potentially feasible approach.[46,48–50] Further on, a physically deposited atomic layer, which is thin and conductive, might also be an attractive approach to protect the metal surface from corrosion by traces of oxygen or water, sulfur and the electrolyte.[51] Due to the special application in battery technology, the traditional technologies such as chemical vapor deposition and physical vapor deposition were found unsuitable, since these methods did not deliver protective layers with the necessary appropriate thickness and high uniformity.[51] Thus, the protective layer should uniformly cover the surface and be a few nanometers thick to maintain high ionic conductivity without increasing cell impedance in the battery.[51] Therefore, the concept of atomic layer deposition which was first applied in Li batteries using a Al\(_2\)O\(_3\) layer, is currently considered more suitable for Mg anodes.[51–53]

3. Cathode Materials

A high energy density Mg battery should contain a well-performing cathode material, which is able to deliver reversibly high capacities, show low capacity fading upon charging/discharging, possess a high electrochemical potential against Mg/Mg\(^{2+}\) and which is earth abundant.[44] In the field of Mg batteries, intercalation cathodes,[55–59] e.g., transition metal sulfides such as TiS\(_2\) and MoS\(_2\),[23,38,60–62] as well as transition metal oxides such as V\(_2\)O\(_5\),[63,64] or MnO\(_2\),[65,66] MoO\(_3\),[67] conversion cathodes such as sulfur and oxygen, organic cathodes such as 2,5-dimethoxy-1,4-benzoquinone[68–72] and carbon-based cathodes such as fullerenes[73] have been studied and reported so far.[19,31,58,68,74,75] Here, we solely focus on sulfur-based conversion cathodes, since the other types of cathode materials have already been summarized in several reviews.[1,14,27,59,64,75,76]

3.1. Active Cathodes Materials

In sulfur-based conversion cathodes, unlike in intercalation cathodes, the discharge and charge processes reduce and oxidize elemental sulfur.[77] Table 1 lists some examples for conversion cathodes, including sulfur- and oxygen-based ones. The main drawback of oxygen as cathode material is the formation of the discharge product, MgO, which forms irreversibly and is electrochemically inactive.[54] Also, the disadvantages of metal halide as cathodes (e.g., CuF\(_2\) and AgCl) are the irreversibility and poor solubility of the discharge products.[54] In view of these drawbacks, a sulfur-based cathode is considered an attractive candidate for rechargeable Mg batteries. Sulfur is earth abundant, nontoxic and, most important, has a relatively high theoretical energy density (1675 mAh g\(^{-1}\)).[19] Therefore, in this section, Mg batteries containing sulfur-based conversion cathodes will be thoroughly discussed.

Similar to Li–S technology,[5,8,78–81] the reported cathode materials in Mg–S batteries so far mainly focus on carbonaceous materials containing elemental sulfur (α or β-S\(_8\)).[40] Different groups utilized various porous, conductive, high surface area carbon additives for the accommodation of S\(_8\) in the cathode to improve the utilization of active material and to reduce the diffusion of polysulfides, which should further improve cell performance. A carbon-based matrix material should possess high electrical conductivity and a good interaction with both the sulfur and the polysulfides.[82] At the same time, it should have a high mechanical stability to uphold the volume change caused by the sulfur during cycling.[82] Further...
on, the electrolyte should easily migrate into the cathode material.[85] The applied carbon materials include carbon black,[12,88] activated carbon clothes (ACC),[24,52] and metal organic frameworks (MOFs).[43]

Active carbon clothes were first applied in Li–S batteries by Aurbach and co-workers.[84] The binder-free monolithic cathode material was composed of an activated carbon fiber cloth and elemental sulfur. The ACC–S cathode was prepared by overlaying elemental sulfur with active carbon cloth discs in a stainless-steel vessel, maintaining the temperature at 155 °C for 10–15 h, which facilitated the impregnation of S into the ACC. The simple preparation methods and the promising electrochemical results in Li–S batteries allowed for the utilization of this cathode material in Mg–S batteries by Gao et al.[24,26,85] and Zhao-Karger et al.[43] In 2018, Gao et al.[85] studied the fundamental mechanism of Mg-ACC/S batteries using both experimental and computational approaches to verify the stepwise pathway of the formation of the individual magnesium polysulfides from elemental sulfur and the dissolution of long-chain polysulfides in the initial stage. The latter is followed by a solid-state transition from short chain polysulfides to magnesium sulfides.

Generally, the use of elemental sulfur may result to some extent in the so-called ‘shuttle effect.’[78,86] This phenomenon was observed by Gao et al.,[26] using an ACC–S cathode material and 0.25 m Mg(TFSI)₂-based electrolyte. The high-order magnesium polysulfides (MgSₓ, 3 < x < 8) which directly form via the reduction of elemental sulfur, can easily dissolve in ether-based solvents, which renders them electrochemically addressable. However, at the same time, they can migrate from the cathode to the anode, resulting in the loss of active material and in capacity fading.

One possible way to avoid the dissolution of polysulfides is the encapsulation of sulfur in carbon-based materials such as microporous,[87,88] mesoporous,[89] or hollow carbonaceous materials.[90–92] The currently applied porous carbon materials in Mg–S batteries include CMK-3,[37,41,93] nitrogen-doped graphene,[21] carbon nanotubes (CNTs),[40] carbon nanofibers,[25,94] and reduced graphene oxide (rGO).[82]

In 2009, Nazar and co-workers investigated CMK-3/S composite cathode materials for use as cathode materials in Li–S batteries.[95] Due to the good performance of the CMK-3/S composite cathode, it was further applied to Mg-S batteries by Ha et al.,[37] Zhao-Karger et al.,[17] and Gao et al.[85] The main advantages of applying CMK-3, the most famous mesoporous carbon framework formed from carbon nanotubes, is that it allows for the creation of highly ordered interwoven composites.[95] A highly ordered mesoporous carbon framework has a uniform pore diameter (3–4 nm), a very high pore volume, interconnected porous structures that can be filled with sulfur (Figure 3a), leading to an electrical contact between sulfur and carbon, a prerequisite for electrochemically addressing the sulfur.[95] The authors prepared a CMK-3/S composite following a melt-diffusion strategy (Figure 3b). After the impregnation of the sulfur into the channels of carbon at 160 °C by capillary forces, the Brunauer–Emmett–Teller (BET) surface area decreased from 1976 to 46 m² g⁻¹, indicating the partially filling of the channels. Moreover, the ionic conductivity remained at 0.2 S cm⁻¹, showing that the electrical current transport paths were not blocked.[95]

By using this type of cathode in a Mg–S battery, a specific discharge capacity of 250 mAh g⁻¹ sulfur at a charge and discharge rate of 20 mA g⁻¹ was reached for 20 cycles with a modified nonnucleophilic electrolyte, (HMDS)₂Mg–2AlCl₃–MgCl₂/tetraglyme.[17] The same group used a CMK-3/S cathode to examine the electroactivity of the conductive salt, Mg[B(hfip)]₂ in diglyme-tetraglyme. The cell delivered around 200 mAh g⁻¹ sulfur at 0.1 C. Based on these results, an electrochemical mechanism was proposed for the CMK-3/S cathode (Figure 3c).

The entire discharge process can be divided into three steps. In the first step, a solid liquid two-phase reduction takes place, i.e., the elemental sulfur in the cathode is transformed into MgSₓ, which dissolves in the electrolyte and which is subsequently converted into MgS. The discharge process reaches a first voltage plateau around 1.5 V, providing a specific discharge capacity around 370 mAh g⁻¹ sulfur, which is close to the theoretical specific discharge capacity for the conversion of S₈ into MgS₄. Accordingly, the reaction of the first step can be written as[17]

$$S₈ + 4e^- + 2Mg^{2+} → 2MgS₄$$  \hspace{1cm} (1)

The second step is assigned to a liquid–solid two-phase reduction from MgS₄ to MgS. The reaction is described in Equation (2)[17]

$$2MgS₄ + 4e^- + 2Mg^{2+} → 4MgS$$  \hspace{1cm} (2)

The final entails the reduction of MgS₂ into MgS[17]

$$2MgS₂ + 4e^- + 2Mg^{2+} → 4MgS$$  \hspace{1cm} (3)

Yu and co-workers[95] also investigated the capacity degradation mechanism of both the discharge and charge process in Mg–S batteries. A Mg–S₄ cell based on a Mg(HMDS)₂–AlCl₃ electrolyte was applied and a clear discharge plateau around 1.5 V and two slopes (1.5–1.0 and 1.0–0.3 V) were observed (Figure 3c), resulting in ~1080 mAh g⁻¹ sulfur discharge capacity; the charge profile showed undistinguishable plateaus. From the second cycle on, the discharge capacity first dropped to 400 and then to 200 mAh g⁻¹ sulfur, without showing any clear plateaus in the discharge profile. Spin-polarized DFT calculations were performed to shed light on the nature of the polysulfides species formed during charge and discharge. Figure 3d shows the stable structure with the lowest formation energies. The stable structures of MgₓS₈ (x = 1, 2, 3, 8) are amorphous, whereas the most stable structure MgS is crystalline. More importantly, in situ XAS measurement results suggest that MgₓS₈ is formed irreversibly; consequently, from the second cycle on the discharge capacity solely originates from the oxidation of low-order Mg₃S₈ to MgS. Notably, MgS was found to be electrochemically virtually inactive in the chosen electrolyte. Recently, Nakayama et al.[96] elucidated the nature of the phase of the formed MgS after discharge, which is metastable zinc blende MgS rather than the rock salt phase. The high stability of both MgₓS₈ and MgS was made responsible for the high polarization and the unclear charge plateaus.[95]
Overall, the opening circuit voltage in the Mg–S batteries lies around 1.8 V. During its entire discharge reaction, Mg–S batteries based on an S₈ cathode can be operated between 0.4 and 1.8 V, where the discharge plateaus are at 1.6 and 1.0 V, respectively, resulting in a specific discharge capacity of 800 mAh g⁻¹ sulfur. In comparison, the initial discharge process in rechargeable Li–S batteries can take place between 1.0 and 3.0 V, with two discharge plateaus at 2.4–2.1 and 2.1–1.5 V, respectively, resulting in a higher theoretical gravimetric energy density around 1000 mAh g⁻¹ sulfur, but a lower volumetric energy density of 2062 mAh cm⁻³ compared to the one of Mg–S batteries (3832 mAh cm⁻³, vide supra). In addition, unlike in the Li–S system, where the lithium polysulfides have similar stability and are all redox-active, the discharge products from Mg–S batteries, Mg₃S₈ and MgS, were found to be highly stable, which significantly impedes and often stops recharging of the batteries.

Apart from the mesoporous CMK-3/S cathode, another porous cathode material, e.g., graphdiyne, was utilized. In 2017, Du et al. successfully synthesized a sulfur-containing cathode based on sulfur graphdiyne (SGDY) via a thermal reaction. The authors stated that the SGYD cathode was compatible with the nucleophilic APC electrolyte in the presence of LiCl, which was attributed to the reduced electrophilicity of the SGYD cathode. Graphdiyne (GDY), a conductive carbon allotrope, has a layered structure, which is formed by benzene rings, linked by butadiyne linkages (Figure 4a). Due to the unique structure, GDY has uniformly distributed pores with a diameter of 5.42 Å and large interlayer distances of 0.365 nm. The synthesis of SGYD is accomplished by the thermally induced cleavage of elemental sulfur into shorter sulfur chains (Sₙ, 1 ≤ x ≤ 4) at 350 °C, which further react with the available carbon–carbon triple bonds in GDY and anchor in the triangle pores of GDY. XPS, XRD, and FTIR results all indicated the presence of C=S bonds and S=S bonds instead of S₈ in the SGYD structure. Together with the size of the carbon skeleton GDY, only short-sulfide units (Sₙ, 1 < x < 5) are accommodated in the structure, which are electrochemically reactive sites. Also, the conjugated linkages in the carbon matrix provide high electrical conductivity of the cathode material. All these results are beneficial for the proposed structure of SGYD in Figure 4a.

Overall, sulfur is confined within the nanopores, which prevents its dissolution and consecutive shuttle effects. Using a SGYD cathode, they observed an initial discharge capacity of 1125 mAh g⁻¹ sulfur and a charge capacity of 540 mAh g⁻¹ sulfur for 35 cycles at a charge/discharge rate of C/30 (Figure 4b). Figure 4c shows the charge/discharge profiles for two cycles, the following cycles are overlapping, indicating the good...
reversibility of the cell. However, from the 36th cycle on, severe overcharging was observed, which was attributed to the reduction of the electrolytes or the corrosion of the cell.[86]

Wang et al.[88] used a similar setup, i.e., microporous carbon working as the carbon host for the adsorption of small $S_{2-4}$ inside its microporous structure and of $S_8$ molecules on the outside wall of the carbon and prepared a sulfur at microporous carbon composite (S@MC) as the electrochemical active material. This setup allowed for a fast transport of ions into the microporous carbon, a better adsorption of polysulfides and higher ionic conductivity. The composite material had a sulfur content of 64.7% and was coated onto a Cu current collector as the cathode. Apart from high conductivity, the major benefit of a Cu current collector is that it allows for the formation of copper sulfides via reaction with the free sulfur that exists outside the carbonaceous matrix during the cathode drying process at 50 °C. The strong interaction between Cu and S protects the sulfur from reacting with the nucleophilic electrolyte: This increases cycle stability and suppresses the dissolution of polysulfides.[88,99] This novel concept for the stabilization of the cathode material by copper has also been used by Zeng et al.[99] In a similar approach, Cui et al.[100] filed a patent about the cathode based on sulfur, a metal sulfide and a ternary copper composite. The metal sulfides comprised FeS$_2$, SnS$_2$, MoS$_2$, Co$_3$S$_4$, and Ni$_2$S$_3$. The authors claimed that these cathode materials could successfully suppress the shuttle effect on the cathode side when used in Mg–S batteries. For example, the dissolution of copper was made responsible for the formation of an intermediate Cu$_x$S phase, which was identified to promote the electrochemical conversion of MgS and consequently improve both cell capacity and cycle stability.

While mostly carbonaceous materials are used for the accommodation of sulfur, cathode materials for Mg–S batteries are not entirely limited to these materials. Until now, the majority of cathode materials applied in Mg–S batteries originally stem from Li–S battery technology and are mainly based on elemental sulfur or accommodation sulfur in microporous or mesoporous carbon material. However, the same issues observed with Li–S batteries still exist, particularly the shuttle effect. An alternative approach that can reduce the shuttle effect is by covalently binding sulfur to a conductive carbon matrix, which has successfully been applied in the field of Li–S batteries.[101–108] Moreover, a protective coating on the active material in the cathodes could also be an alternative approach to prevent the dissolution and loss of sulfur from the cathode material.[109]

3.2. Current Collectors

In Mg–S batteries, the choice of the current collector has also a great impact on the electrochemical behavior particularly in the case of halogen-containing corrosive electrolytes, the nature of the electroactive cathode materials and the dissolution of polysulfides during cycling.[110] The currently reported commercial metal-based current collectors include aluminum foil,[18,21,37,40] stainless-steel (SS) foil,[41,43,85,99,111] carbon-coated aluminum foil,[44] copper,[39,40,88,99,112] and the anticorrosion alloy Inconel 625.[17,82,99] While Cu is generally considered unstable against chloride-containing electrolytes,[111] Zeng et al.[99] recently reported that a sulfur cathode is compatible with the traditional APC electrolyte using copper as current collector below 1.7 V versus Mg/Mg$^{2+}$. The electrochemical behavior of the cell was even better than the one with a stainless-steel current collector. They also observed that the electric conductivity of the cathode using a Cu current collector was higher after drying at 50 °C (926 µS cm$^{-1}$) than without drying (769 µS cm$^{-1}$). Formation of copper sulfides at the interface between S and Cu, which could to some extent protect the free sulfur in the cathode from reacting with APC electrolytes (vide supra), was indeed confirmed by XRD measurements. In
comparison, the diffraction peaks of copper sulfides were not observed on cathodes based on stainless-steel current collectors dried at 50 °C. Also, the TGA results of the cathode with a stainless-steel current collector suggest a reaction of sulfur with the nucleophilic electrolyte as evidenced of the large weight loss of sulfur in the cathode after cycling. Due to the unique advantages of the Cu current collector, it was also applied in combination with other halogenated electrolytes including the organic magnesium boron-based (OMB) electrolyte, the boron-centered base magnesium (BCM) electrolyte, and a trifluoromethanesulfonate-based electrolyte. Apart from the commercial current collectors, Muthuraj et al. developed an effective current collector, which is stable against corrosive electrolytes and can also catch polysulfides. Very recently, they presented a N- S-dually doped carbon cloth (DCC) as current collector, which possesses a 3D interconnected porous structure that provides superior cycle stability and high conductivity. Notably, due to the hydrophobic property of the carbon cloth, the formed magnesium polysulfides can barely be trapped inside the porous structure, leading to the dissolution of polysulfides in the electrolyte. To overcome this issue, the authors N- and S-doped the carbon cloth to increase the hydrophilicity of the surface, which successfully suppressed the dissolution of polysulfides and improved cycle performance. Their results showed that using S@Gd as the electroactive material and an HMDS-based electrolyte, the cell with a DCC current collector was capable of delivering around 388 mAh g⁻¹ after 40 cycles at 0.01 C with Coulombic efficiencies ≈90%. By contrast, the cell with a undoped carbon cloth as current collector could only be cycled over 18 cycles, and severe overcharging was observed, underlining the advantages of the DCC current collector.

4. Electrolyte Systems

Mg–S batteries still suffer from limitations in terms of the electrolyte systems. The general requirements for a suitable electrolyte include high ionic conductivity, good electrochemical and chemical stability toward the electrodes, good thermal stability and sufficiently low toxicity and flammability. In addition, an appropriate electrolyte system should allow for a reversible Mg deposition and dissolution and also provide a wide voltage window. Therefore, the design of novel electrolyte systems that are fully compatible with Mg–S batteries and the underlying chemistry is of great importance. It is worth to mention that a large group of the traditional electrolytes in Mg batteries have nucleophilic properties, which are generally incompatible with sulfur cathodes. Therefore, the modification of the cathode for compatibility with the nucleophilic electrolytes is under investigation. At the same time, new non-nucleophilic electrolyte systems that are compatible with sulfur cathodes are intensely synthesized and investigated.

4.1. Nucleophilic Electrolytes

The Grignard-based nucleophilic all-phenyl complex (APC) electrolyte, which can be synthesized by the reaction between PhMgCl and AlCl₃, is generally considered incompatible with S-based conversion cathodes, due to the nucleophilicity of the organomagnesium compounds, although this electrolyte shows high oxidative stability against Mg (3.2 V) and high cycle efficiency (around 100%). Therefore, the APC electrolyte was initially not considered for application in Mg–S batteries. However, in 2017, the selection of an appropriate current collector and the development of new cathode materials have brought the APC electrolyte back for use in Mg–S batteries.

As has already been discussed in Section 3.2, the utilization of a Cu-based current collector rather than a stainless-steel current collector allows for the successful cycling of a cell based on an S₈ cathode and an APC electrolyte. The cell was able to cycle for 20 cycles, indicating the principle possibility of combining an APC electrolyte with a sulfur cathode. However, the cell could only deliver around 100 mAh g⁻¹ after the 20th cycle at 0.005 C. The authors explained this unsatisfactory cycle performance with the formation of irreversible discharge products. Addition of LiCl into the nucleophilic electrolyte successfully improved cycle performance, which was ≈300 mAh g⁻¹ after the 40th cycle at a discharge rate of 0.005 C. The same research group further improved the electrochemical behavior of the cell by developing a novel cathode active material, S@microporous carbon, in combination with a Cu current collector and a nucleophilic APC electrolyte containing LiCl as additive. Using this system, the Mg–S cell was capable of delivering 368 mAh g⁻¹ at 200th cycle at 0.1 C.

As mentioned in Section 3.1, the SGDY cathode was also reported to be compatible with the nucleophilic APC electrolyte. The reduced electrophilicity of short-chain sulfides in SGDY compared to the long-chain sulfides formed from S₈ was made responsible for the compatibility with the APC electrolyte, even though the current collector was Al instead of Cu.

4.2. Nonnucleophilic Electrolytes

Due to the electrophilic nature of the sulfur cathode, nonnucleophilic electrolytes are of great importance and have consequently been applied in the majority of Mg–S batteries. In this section, the less/nonnucleophilic electrolyte systems in Mg–S batteries are divided into chloride-containing and chloride-free, noncorrosive electrolytes.

4.2.1. Chloride-Containing, Non/Less Nucleophilic Electrolytes

A common approach to the synthesis of Mg salts for the electrolyte is the combination a Mg complex containing a nonnucleophilic base, such as [HMDSMgCl] [21,123] bis(diisopropyl)amide, with a boron- or aluminum-containing Lewis acid. Liebenow et al. reported that the Hauser base–derived magnesium hexamethyldisilazide chloride (HMDSMgCl) electrolyte supported magnesium stripping and plating in rechargeable Mg batteries. Muldoon and co-workers reported a performance improvement of the HMDSMgCl electrolyte by forming a molecular species possessing a [Mg₂(μ-Cl)₃][HMDSAlCl₄] species (Figure 5a) upon
addition of a Lewis acid (AlCl₃). While voltage stability was not improved using an in situ formed [Mg₂(µ-Cl)₃][HMDSAI₂Cl₃] species (Figure 5b), the use of purified stoichiometric [Mg₂(µ-Cl)₃][HMDSAlCl₃] increased stability to 3.3 V. This substantial increase in voltage stability was explained by the removal of unreacted HMDSMgCl in the electrolyte, which starts to decompose at 2.5 V. In addition, they stated that this electrolyte was also compatible with sulfur cathodes.[12] Using purified [Mg₂(µ-Cl)₃][HMDSAlCl₃] in THF as the electrolyte, Muldoon and co-workers prepared a cell using an elemental sulfur/carbon black composite as cathode material and Mg foil as the anode. The open-circuit voltage (OCV) was 0.55 V (Figure 5c), which was only about one half of the theoretical cell voltage (1.77 V). Also, the discharge voltage started from 0.89 V. Fracturing of the resistive surface layer on the Mg anode was considered one reason of the slightly increasing initial voltage.[12] Notably, the initial discharge capacity was 1200 mAh g⁻¹sulfur. However, substantial capacity fading was observed in the second cycle, with a specific discharge capacity of only 394 mAh g⁻¹sulfur, which was attributed to the polysulfide shuttle effect. In addition, the active compound [Mg₂(µ-Cl)₃.6THF][HMDSAlCl₃] could only be obtained from flammable and volatile THF.[11]

Since single crystals of the bisamide-based, nonnucleophilic electrolyte based on [Mg₂(µ-Cl)₃.6THF][HMDSAlCl₃] can only be obtained from THF, which limits the solvent selection, Fichtner and co-workers[17] successfully modified the electrolyte by a one-step reaction between magnesium bis(hexamethyldisilazide), [(HMDS)₂Mg], and AlCl₃ in different ethers (diglyme, tetraglyme). This simple reaction lead to an electrochemically active compound, [Mg₂Cl₃][HMDSAlCl₃], which dissolved in diglyme and tetraglyme. Importantly, according to the cyclic voltammograms of the electrolyte (Figure 6a), Mg plating and stripping was successful, and the stability of the electrolyte was maintained up to 3.2 V. Moreover, Mg plating and stripping was found to take place when the ionic liquid (IL) N-methyl-N-butyl-piperidinium TFSI (PP14TFSI) was added to the electrolyte (Figure 6b).

The authors also stated that the corresponding electrochemical behavior of Mg–S cells, shown in Figure 6b,c, was better than the previously described electrolytes prepared from THF investigated by Muldoon and co-workers[12] As can be seen from Figure 6c, a cell containing a tetraglyme (TEG)-based electrolyte had an OCV of about 2 V.[17] The discharge curve showed two voltage plateaus, indicating the formation of high- and low-order polysulfides.[17] It delivered an initial discharge capacity of 550 mAh g⁻¹sulfur at 0.01 C (C/100), dropping to 250 mAh g⁻¹sulfur after 20 cycles (Figure 6d). In addition, the authors also investigated the influence of the IL PP14TFSI as a cosolvent in the electrolyte.[17] It showed that after the addition of IL to the electrolyte the initial capacity and the capacity at the 20th cycle increased to 800 mAh g⁻¹sulfur and 280 mAh g⁻¹sulfur, respectively.[17] Due to the attractive electrochemical properties and the simplicity in synthesis, this type of electrolytes was also utilized by Vinayan et al.,[83] Yu and Arumugam,[25] Friedrich and co-workers,[14] and Muthuraj et al.,[15] though with combinations of different cathodes, anodes and current collectors.
Gao et al.\cite{24} reported improved electrochemical data using the previously published electrolyte, i.e., 0.1 M (HMDS)$_2$Mg–2AlCl$_3$–MgCl$_2$ in the presence of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). According to their cyclic voltammograms, Mg plating and stripping successfully took place in the LiTFSI-containing electrolyte and the voltage was stable up to 2.8 V (vs Mg). Also, increasing amounts of LiTFSI were found to increase both the plating and stripping current density, which was explained by an increasing ionic conductivity. In order to study the compatibility of the electrolyte with the sulfur cathode, they carried out galvanostatic tests using active carbon cloth/elemental sulfur as the cathode and Mg foil as the anode. The corresponding cycle behavior is illustrated in Figure 7. The discharge curves (Figure 7a) clearly show two voltage plateaus at 1.75 and 1.0. Also, an increase in discharge capacity during cycling was observed and attributed to a slow infiltration of the cathode material with electrolyte. Notably, the discharge capacity of the cells containing LiTFSI remained at 1000 mAh g$^{-1}$ sulfur at 0.03 C up to 30 cycles (Figure 7b); whereas cells without LiTFSI delivered only 10 mAh g$^{-1}$ sulfur. The higher discharge capacity was attributed to a lower kinetic barrier of reoxidation for MgS$_x$ (4 < x < 8), either by reacting Li$^+$ with MgS$_x$ (4 < x < 8), thereby forming soluble, higher-order MgLi polysulfides, as well as to an ion exchange reaction between Li$^+$ and MgS and MgS$_2$, forming electrochemically active Li$_2$S and Li$_2$S$_2$.

In terms of morphology of the deposits on Mg foil, SEM investigations revealed that after LiTFSI addition spherical Mg deposits about 2 μm in diameter formed without any observable dendrite formation (Figure 7c,d). In view of these findings, LiTFSI is considered a promising additive for Mg–S batteries as also outlined by Zhou et al.\cite{42}

In a similar approach, Li$^+$ was added to the electrolyte. Zuo et al.\cite{124} added an excess of metallic Li into an, e.g. [HMDS]$_2$Mg-based electrolyte to improve the electrochemical performance of a Mg–S battery at high current rates. They indeed observed that cell capacity did not decay even at high current rates. Stress test results showed that the cell capacity remained around 1100 mAh g$^{-1}$ at current rates of 0.3 C, 0.5 C, 1 C, and 2 C. Even at 5 C, the discharge capacity was still around 1000 mAh g$^{-1}$.

In 2019, Nuli et al.\cite{112,125} reported on a novel electrolyte for rechargeable Mg–S batteries consisting of MBA and AlCl$_3$ dissolved in THF. The authors pointed out that the electron-rich amide in MBA limits the anodic stability of the salt, since electrons can be easily withdrawn from it at high voltages. By contrast, introduction of the Lewis acid AlCl$_3$ stabilizes the Mg–N bond in MBA even at high potentials since the high electron affinity of AlCl$_3$ could suppress the withdrawal of electrons from the Mg–N bond.\cite{112} Consequently, the molar ratio of MBA and AlCl$_3$ was adjusted from 2:1 to 1:2. According to their Mg plating/stripping test results (Figure 8a), the higher the amount of AlCl$_3$ was, the higher both cycle efficiency and stability were. The authors also compared the oxidation stability of the 0.25 M MBA–AlCl$_3$/THF electrolyte with the traditional nucleophilic 0.4 M APC electrolyte, (PhMgCl)$_2$–AlCl$_3$/THF. Results suggest that the stability of the MBA–2AlCl$_3$/THF electrolyte (2.35 V/Al, 2.65 V/SS) was better than the one of the APC electrolyte.

Figure 6. Cyclic voltammograms of (HMDS)$_2$Mg–2AlCl$_3$ in a) diglyme (DEG), tetraglyme (TEG); b) diglyme and ionic liquid (DEGIL), tetraglyme and ionic liquid (TEGIL); electrochemical performance of Mg–S batteries (cathode: CMK3-S composite; anode: pressed Mg); c) initial charge–discharge curves using PVDF binders; d) cycle stability.\cite{17} Reproduced with permission.\cite{17} Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Figure 7. Electrochemical data of Mg–S batteries (cathode: ACC/S; anode: Mg foil) with 0.1 M (HMDS)_2Mg–2AlCl_3 and 1.0 M LiTFSI as additive at 0.03 C and room temperature; a) charge–discharge curves; b) cycle stability with and without LiTFSI; c) top view of Mg deposits on Mg foil; and d) cross-section of Mg deposits on Mg foil. [24] Reproduced with permission. [24] Copyright 2015, American Chemical Society.

Figure 8. a) Cycle efficiency with an MBA–AlCl_3/THF electrolyte at molar ratios of MBA:Al of 2:1, 1:1 and 1:2 (working electrode: stainless steel); b) cycle stability of a Mg–S@MC cell with 0.25 mol L\(^{-1}\) BMA/AlCl_3 (molar ratio = 1:2) and 1 mol L\(^{-1}\) LiCl in THF at 0.04 C; discharge and charge profiles of Mg–S@MC cell with c) 0.25 mol L\(^{-1}\) BMA/AlCl_3 (molar ratio = 1:2) in THF; and d) 0.25 mol L\(^{-1}\) BMA/AlCl_3 (molar ratio = 1:2) and 1 mol L\(^{-1}\) LiCl in THF. [112] Reproduced with permission. [112] Copyright 2019, Royal Society of Chemistry.
(1.3 V/Al, 2.2 V/SS) when using an Al or stainless-steel working electrode. Based on single-crystal X-ray analysis, the formula of the electroactive species is $[\text{Mg}_2(\mu-\text{Cl})_3(\text{THF})_6][\text{AlCl}_4]$. Using this electrolyte, the discharge capacity of the Mg–S@microporous carbon (MC) at a discharge capacity of 0.04 C was only around 100 mAh g$^{-1}$ in the third cycle (Figure 8c).

In order to further improve the electrochemical performance by introducing Li ions into the electrolyte, Nuli and co-workers[112] additionally dissolved 1 mol L$^{-1}$ of LiCl into 0.25 mol L$^{-1}$ MBA/0.5 mol L$^{-1}$ of AlCl$_3$ in THF. As illustrated in Figure 8c,d, a higher retentivity of the major capacity contribution at 1.1 V was successfully established by the addition of LiCl. The discharge capacity was retained at 537 mAh g$^{-1}$ after the 30th cycle with a Coulombic efficiency of 94%. Clearly, the addition of LiCl successfully reduced the amount of magnesium polysulfides in the electrolyte. The authors claimed that this electrolyte system outperformed other reported ones due to the simple preparation method and the commercial availability of the starting materials.

By using different combinations of the anion and cation in the magnesium salt, one can tailor its stability and conductivity. In 2017, Du et al. [40] reported on an OMBB electrolyte, which contained bulky tetranuclear Mg-containing species $[\text{Mg}_4\text{Cl}_6(\text{DME})_6]^{2+}$, and a bulky $[\text{B}(\text{hfip})_4]$ counter anion (Figure 9a) by a simple reaction between tris(hexafluoroisopropyl) borate $\text{B}[\text{HFP}]_3$, MgCl$_2$ and excessive Mg powder in DME. They optimized the MgCl$_2$/B[HFIP]$_3$ ratio to 1.2 in order to obtain the lowest plating overpotential ($-0.11$ V vs Mg/Mg$^{2+}$), the highest oxidative peak current (25.3 mA) and the highest Coulombic efficiency (98.67%). The obtained electroactive cation $[\text{Mg}_2(\mu-\text{Cl})_3(\text{THF})_6][\text{AlCl}_4]$ distinguished itself from the well-known $[\text{Mg}_2(\mu-\text{Cl})_3(\text{THF})_6][\text{AlCl}_4]$ by utilization of donor ligands of different ethereal solvents and the large and bulky $[\text{B}(\text{hfip})_4]$ counter anions. Furthermore, the use of tetranuclear $[\text{Mg}_4\text{Cl}_6(\text{DME})_6]^{2+}$ instead of mononuclear $[\text{Mg}(\text{DME})_3]^{2+}$ was reported to lower the energy needed for Mg deposition, which results in high Mg plating/striping reversibility.[126]

Examination of the oxidative stability of the 0.5 mol OMBB electrolyte (Figure 9b) indicated that the electrolyte was stable up to 3.3 V versus Mg/Mg$^{2+}$ on a Pt electrode, up to 3 V versus Mg/Mg$^{2+}$ on an Al electrode, up to 2.5 V versus Mg/Mg$^{2+}$ on a stainless-steel electrode, and up to 2 V versus Mg/Mg$^{2+}$ on a Cu electrode.[40] The comparably low stability against nonnoble metals was attributed to the chloride ions in the electrolyte. The OMBB electrolyte showed good cycle performance in combination with an S-CNT cathode (Figure 9c).

Another simple salt, Mg[TFSI]$_2$, was considered as an attractive alternative because of its high anodic stability, ionic conductivity and high solubility in ethers.[39] However, its use lead to poor electrochemical performance. Ha et al.[37] introduced 0.3 mol Mg[TFSI]$_2$ in glyme/diglyme and tested its compatibility.
with a sulfur-based cathode. They applied C/200 for the initial discharge to initiate Mg stripping. At this discharge rate the Mg–CMK/S cell delivered an initial discharge capacity of 500 mAh g\(^{-1}\). The current rate was then increased to C/100, which led to a fast deterioration over the next four cycles. Similarly, Itaoka et al.\(^{[111]}\) studied the electrochemical behavior of Mg–S batteries using elemental sulfur and a bis(alkenyl) compound with a crown ether unit and a linear ether unit as cathode material together with a Mg(TFSI)\(_2\)-based electrolyte. The cell showed an initial discharge capacity of 500 mAh g\(^{-1}\) sulfur; however, after ten cycles, the battery delivered no further capacity, suggesting an incompatibility between the Mg(TFSI)\(_2\) salt with Mg–S batteries. The incompatibility between glyme-based solvent and Mg(TFSI)\(_2\) was reported to result in dendrite growth on the Mg batteries. The high dielectric constant of tetraglyme (7.7) was expected to promote the dissolution of Mg(CF\(_3\)SO\(_3\))\(_2\). However, Mg deposition/ stripping was still not achieved, especially in the first few cycles. To overcome this, AlCl\(_3\) as Lewis acid was added to facilitate Mg(CF\(_3\)SO\(_3\))\(_2\) dissociation and to form the electroactive species, [Mg\(_2\)(μ-Cl)\(_3\)](THF)\(_3\)][(CF\(_3\)SO\(_3\))AlCl\(_3\)], which resulted in an efficient Mg plating and stripping performance, indicating the inherent oxide layer on the Mg anode had been removed upon cycling.\(^{[133,134]}\) Next, anthracene, a π-rich molecule, which can further decrease the large overpotentials by accelerating the reaction of Mg(CF\(_3\)SO\(_3\))\(_2\) with AlCl\(_3\), was added as a coordinating ligand. At last, a Mg–S@microporous carbon cell containing 0.125 M Mg(CF\(_3\)SO\(_3\))\(_2\) + 0.25 M AlCl\(_3\) + 0.25 M MgCl\(_2\) + 0.025 M anthracene/TFH and tetraglyme (1:1, v:v) electrolyte was cycled at 0.05 C (Figure 10a,b).\(^{[135]}\) Nearly 100% Coulombic efficiency was reached after few cycles; however, the discharge capacity dropped dramatically after two cycles to only 50 mAh g\(^{-1}\) sulfur after the 50th cycle, which was attributed to large amounts of unreacted sulfur in the cathode and a poor Mg-ion dissociation.\(^{[136]}\)

Finally, addition of Li\(^+\) ions into the electrolyte to promote the dissolution of Mg\(^{2+}\) was attempted in order to decrease the kinetic barrier and increase the solubility of the low-order polysulfides and consequently improve the electrochemical performance.\(^{[24]}\) The authors added LiCl (Figure 10c,d) and LiCF\(_3\)SO\(_3\) (Figure 10e,f), respectively, to a 0.125 M Mg(CF\(_3\)SO\(_3\))\(_2\) + 0.25 M AlCl\(_3\) + 0.25 M MgCl\(_2\) + 0.025 M anthracene/THF and tetraglyme (1:1, v:v) solution. Figure 10c,d shows that the plateau at 1.05 V of the discharge curve persists longer, leading to a higher discharge capacity and reversibility in the presence of LiCl, indicating that Li\(^+\) successfully promotes Mg dissolution. Interestingly, the use of 0.5 M LiCF\(_3\)SO\(_3\) as the additive improved the cell performance even more. The cell was able to deliver around 400 mAh g\(^{-1}\) sulfur at 0.05 C for 50 cycles, indicating that the addition of CF\(_3\)SO\(_3\)Li also reduces the destructive effect on Mg plating.\(^{[137]}\)

### 4.2.2. Non/Less Corrosive, Nonnucleophilic Electrolytes

Muldoon et al.\(^{[113]}\) stated that chlorides in the electroactive species [Mg\(_2\)(μ-Cl)\(_3\)]\(6\)THF\((1:1)\) are a main factor for corrosion. In addition, the bulky nature of the cation, i.e., the two octahedrally coordinated Mg atoms connected by three chlorides, is not beneficial for Mg ion transport. Consequently, research on the synthesis of novel, chloride-free salts for Mg–S batteries is of growing importance. Li et al.\(^{[21]}\) synthesized a chloride-free electroactive salt, [Mg(THF)\(_3\)][AlCl\(_3\)]\(_2\) (Figure 11a), by reacting MgCl\(_2\) with two equivalents of AlCl\(_3\) in THF and an IL, i.e., N-methyl-N-butyl pyrrolidinium bis(trifluoromethanesulfonyl) imide (PYR14TFSI) at 95 °C.\(^{[21]}\) At elevated temperature, AlCl\(_3\) completely replaced the chloride ions in MgCl\(_2\).\(^{[113]}\) The obtained salt was reported to have high ionic conductivity (8.5 mS cm\(^{-1}\)) and good ionic stability (2.5 V vs Mg). Furthermore, according to cyclic voltammetry (CV; Figure 11b), a stable and reversible Mg plating and stripping was demonstrated. To further understand the stability of the interface between the electrolyte and the Mg surface, electronic impedance spectroscopy (EIS) measurements on a symmetrical Mg–Mg cell
containing [Mg(THF)₆][AlCl₄] in PYR14TFSI/THF were conducted (Figure 11c). Results revealed that the bulk resistance of the electrolyte remained constant upon cycling while the semicircle, which represents the interfacial resistance, decreased after 60 cycles and stayed stable afterward, indicating the interface between Mg surface and electrolyte was not stable in the initial cycles, but slowly stabilizes within the first 60 cycles.[21] Li et al. also investigated the cycle performance of a Mg–S battery using the as-prepared electrolyte (Figure 11d). The cell delivered around 700 mAh g⁻¹ for the initial cycle; however, the discharge capacity dropped sharply in the following 19 cycles to only 130 mAh g⁻¹. They observed capacity fading was explained by the poor electric conductivity during cycling and a shuttle effect of the cathode material.[21]

Research on novel Lewis acid is also ongoing. Xu et al.[135] synthesized a Y-based electrolyte by substituting AlCl₃ by YCl₃. They reacted MgCl₂ and two equivalents of YCl₃ with the IL PYR14TFSI and diglyme at 120 °C. They stated that YCl₃ outperformed AlCl₃ for the following reasons. First, the higher standard electrode potential of the Y ion (−2.372 V vs SHE) compared to the Al ion (−1.66 V vs SHE) prevents the codeposition of Al on Mg. Second, YCl₃ is known to be a good water scavenger, which can remove traces of water in the electrolyte.[135] They compared the cell performance of the newly synthesized Y-based electrolyte with the one of a conventional Al-based electrolyte using a magnesium polysulfide cathode material. Figure 12a shows that the cell with the Y-based electrolyte was stably cycled for 50 cycles with a discharge capacity...
around 900 mAh g$^{-1}$. In contrast, the cell with the Al-based electrolyte cycled for only 20 cycles with a sharp capacity decay. Further, EIS data (Figure 12b) revealed a lower impedance of the Y-based electrolyte.[135]

Recently, Zuo et al.[136] filed a patent on a novel electrolyte for Mg–S batteries. They dissolved 0.2–0.8 mol L$^{-1}$ of AlCl$_3$ and 0.006–0.024 mol L$^{-1}$ of TiCl$_4$ in an ether-based solvent. Then, excess of Mg was added to the solution, and stirred for 3–5 h.

Figure 11. a) Single crystal X-ray structure of [Mg(THF)$_6$][AlCl$_4$]; b) cyclic voltammogram using the as-prepared electrolyte (Pt disc as working electrode; Mg plate as counterelectrode and reference electrode; scan rate: 25 mV s$^{-1}$); c) Nyquist plot of a symmetrical Mg–Mg cell using [Mg(THF)$_6$][AlCl$_4$] in PYR14TFSI/THF as electrolyte at different cycles; d) cycle performance of Mg/S cell at 0.01 C (cathode: N-doped graphene-S-carbon black; anode: Mg disc). Reproduced with permission.[21] Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 12. a) Cycle performance and b) EIS data of Mg–S battery containing a Y-based and an Al-based electrolyte, respectively (cathode: magnesium polysulfide cathode; anode: Mg foil; current rate: 0.04 C).[135] Reproduced with permission.[135] Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
The weight ratio between Mg and the solution was maintained between 3:10 and 12:10. Finally, the solution was filtered and ready for use in Mg–S batteries. They claimed that the electrolyte was cheaper than all reported ones while at the same time showing both high stability and Coulombic efficiency (99.6%).

One group of noncorrosive electrolytes are those on weakly coordinating anions (WCAs). WCAs are known to possess some unique properties, including a low nucleophilicity and high solubility of their salts in some low polarity solvents. [137] Owing to these superior properties, WCAs have been considered as attractive candidates for the synthesis of new salts for electrolytes used in Mg–S batteries. [138,139] Recently, Zhao-Karger et al. [41] have synthesized a fluorinated magnesium alkoxyborate–based electrolyte for Mg–S batteries. They prepared the conductive salts by the reaction of Mg[BH$_4$]$_2$ with fluorinated alcohols (R$_F$-OH) in ethereal solvents (such as DME), as shown in Equation (4). [41] By using hexafluoro-2-propanol (hfip), the conductive salt, Mg[B(hfip)$_4$]$_2$·3 DME was obtained after removal of the solvent. [41]

$$\text{Mg[BH}_4\text{]}_2 + 8\text{R}_F^-\text{OH} \rightarrow \text{Mg[B(OR)_2]_4} + 4\text{H}_2\text{↑}$$ (4)

Zhao-Karger et al. also studied the crystal structure of this compound by single-crystal X-ray crystallography (Figure 13a). [41] The crystal unit consists of Mg$^{2+}$ ions solvated by three dimethyl ether (DME) molecules, leading to a slightly distorted octahedral coordination geometry. [41] In the anion, the boron center is bound to four hexafluoroisopropoxy groups resulting in a tetrahedral structure. The authors also stated that the obtained magnesium salt turned out to be water and air insensitive as evidenced by NMR analysis. [41]

Zhao-Karger et al. examined a 0.6 mM Mg[B(hfip)$_4$]$_2$·3 DME/DME electrolyte by CV for its propensity to support reversible Mg deposition and dissolution (Figure 13b). [41] Based on the CV results, successful Mg plating and stripping was confirmed. Moreover, the current density gradually increased upon scanning, indicating enhanced Mg plating. This finding was explained by a facilitated nucleation of Mg crystals triggered by the Mg deposition during the first cycle. [41] The same authors applied 0.8 mM Mg[B(hfip)$_4$]$_2$ in diglyme/tetraglyme as electrolyte for Mg–S batteries (cathode: S-CMK-3; anode: Mg plate). [41] They charged and discharged the cell at 0.1 C at room temperature (Figure 13c,d). [41] Charge and discharge profiles of the initial to the 5th cycle as well as of the 10th and the 20th cycle are given in Figure 13c. The initial cycle possessed a discharge capacity around 400 mAh g$^{-1}$ sulfur, which increased to 500 mAh g$^{-1}$ sulfur in the second cycle, due to the activation of Mg anode during cycling. [41] After the second cycle, the discharge capacity decreased but remained around 200 mAh g$^{-1}$ sulfur up to the 100th cycle (Figure 13d). Based on these results, the authors...
stated that the fluorinated alkoxyborate-based electrolytes are promising candidates for Mg–S batteries.\[41\]

The same research group also investigated the influence of the concentration of the conductive salt in the electrolyte, Mg[B(hfip)\textsubscript{4}]\textsubscript{2} \cdot 3 DME on battery behavior by using ACC-based sulfur composites as cathode materials.\[43\] Since ionic conductivity is a key parameter in the quantification of ion mobility in the electrolyte, which also influences the rate capability of batteries, they evaluated the ionic conductivity of the electrolyte solutions at room temperature.\[43\] Measurements revealed (Figure 14d) that the ionic conductivity increased linearly when the concentration was increased from 0.1 to 0.3 m. At a higher concentration, the ionic conductivity decreased again (Figure 14d). The better performance of the cell containing the 0.3 m electrolyte was explained by the suppression of the solubility and the diffusion of magnesium polysulfides by increasing the concentration of the magnesium conductive salt, which could further avoid a fast capacity decay.\[43\]

Zhang et al.\[114\] also synthesized a so-called boron-centered base magnesium (BCM) electrolyte by reacting tris(2\textsubscript{H}-hexafluoroisopropyl)borate (THFPB) with MgF\textsubscript{2} in DME (Equation (5))

$$\text{MgF}_2 + n\text{DME} + 2\text{THFPB} \rightarrow [\text{Mg(DME)}]^{2+} + 2[\text{THFPB}]^- \quad (5)$$

In a freshly prepared BCM electrolyte, the fluoro-tris(hexafluoro-2-propoxy) borate (FTHPB\textsuperscript{−}) anion (Figure 15c) is formed due to the strong affinity between the boron center and the F\textsuperscript{−} in MgF\textsubscript{2}. After cycling, according to mass spectroscopy, the electroactive species in the electrolyte comprise [Mg(DME)]\textsuperscript{2+} (Figure 15d) and the tetra(hexafluoroisopropyl) borate anion ([TrHB]\textsuperscript{−}; Figure 15e).

For the formation, the authors proposed the following chemical reaction\[114\]

$$\text{Mg} + n\text{DME} + 2\text{THFPB} \rightarrow [\text{Mg(DME)}]^{2+} + 2[\text{TrHB}]^- \quad (6)$$

Notably, both the effective anion [TrHB]\textsuperscript{−} and the cation formed upon cycling had a similar, if not the same structure than Mg[B(hfip)\textsubscript{4}]\textsubscript{2} reported by Zhao-Karger et al.\[41,43\] Zhang et al.\[114\] also examined the electrochemical compatibility of the BCM electrolyte with a Mg anode by CV (Figure 15a). They noticed that current density increased upon cycling, indicating improved electrochemical properties. Their explanation was that MgF\textsubscript{2} has a low solubility and the electroactive species was only gradually generated over several cycles.\[114\] In addition, they investigated the cycle stability of the Mg–S cell using the BCM electrolyte (Figure 15b).

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Figure 14. Electrochemical behavior of a Mg–S cell (cathode: ACC-based sulfur composites; anode: Mg foil; electrolyte: Mg[B(hfip)\textsubscript{4}]\textsubscript{2} \cdot 3 DME in DME); a) charge–discharge profiles at 0.1 C (0.4 m Mg[B(hfip)\textsubscript{4}]\textsubscript{2} \cdot 3 DME in DME); b) cycle stability (0.4 m Mg[B(hfip)\textsubscript{4}]\textsubscript{2} \cdot 3 DME in DME); c) charge–discharge profiles at 0.1 C (0.3 m Mg[B(hfip)\textsubscript{4}]\textsubscript{2} \cdot 3 DME in DME); d) influence of electrolyte concentration (Mg[B(hfip)\textsubscript{4}]\textsubscript{2} in DME) on ionic conductivity at 23 °C.\[43\] Reproduced with permission.\[43\] Copyright 2018, American Chemical Society.
The cell delivered a discharge capacity around 1000 mAh g\(^{-1}\), indicating that the BCM electrolyte might be a promising model electrolyte for Mg–S batteries.\(^{[114]}\)

In addition, on the basis of this electrolyte, Hintennach filed a patent related to additives in an electrolyte.\(^{[140]}\) He pointed out that the addition of a mixture of two thiobarbituric acids derivatives such as thiobarbital and 2-thiobarbituric acid, at a concentration between 0.01 and 1.9 wt\%, respectively, was beneficial for both Mg–S and Mg ion batteries.

4.3. Summary and Prospective Electrolyte Systems for Mg–S Batteries

Research on electrolyte systems suitable for Mg–S batteries is still ongoing; nonetheless, some achievements have already been accomplished. Table 2 summarizes all clearly identified electroactive species in the electrolytes investigated so far. The development of novel electrolyte systems that are compatible with a sulfur cathode clearly depends on the successful realization of noncorrosive magnesium salts, utilization of various solvents and additives. Apart from that, an in-depth understanding of the underlying chemistry at the surface of the electrodes and in the electrolytes is of great importance for the future development too. For the prospective magnesium salts, boron- or aluminum-centered weakly coordinating anions are promising candidates. In addition, a polymer-based electrolyte may also be worth to be studied for the following reasons: i) no internal short circuits and ii) no leakage and easy fabrication.\(^{[62]}\) However, the problems in polymer electrolytes, such as the incompatibility with the Mg anode and a low Mg ion transfer number need to be solved for a successful application in cells.

5. Separator Design

Separators play a crucial role in liquid electrolyte batteries. They are placed between the cathode and anode to prevent any physical contact but allow for free ion transportation.\(^{[141,142]}\) Currently used separators in Mg–S batteries are mainly based on commercial glass fiber sheets\(^{[17,18,24,40–44,85,86,114]}\) and microporous polymer membranes;\(^{[21,39,82,88,99,111,112]}\) a brief comparison between these two types of separators is illustrated in Figure 16a. Generally, glass fiber separators outperform others in terms of thermal dimensional stability, porosity, permeability and ionic conductivity; but they are more costly and require more electrolyte.\(^{[141,142]}\)

Due to the low solubility and irreversibility of the low-order magnesium polysulfides (MgS, Mg\(_3\)S\(_8\)), the surface modification of separators is also feasible in the field of Mg–S batteries to enhance the cell performance.\(^{[25,95]}\) Yu and Arumugam\(^{[15]}\) recently presented an activated carbon nanofiber (CNF)-coated glass fiber separator, which was prepared by a vacuum-filtration process (Figure 16b). The purpose of the CNF coating was to
act as a current collector to increase sulfur utilization and at the same time to trap the polysulfides intermediates. The coating layer on the separator plays an important role to reactivate and reuse the sulfur species that diffuse out of the active material upon cycling. The cell with a coated separator delivered around 950 mAh g\(^{-1}\) for the first cycle; the capacity remained around 800 mAh g\(^{-1}\) at C/50 at the 20th cycle. By comparison, a cell with an uncoated separator was capable of delivering about 1000 mAh g\(^{-1}\) for the first cycle; however, the capacity dropped dramatically to only 200 mAh g\(^{-1}\) after the 20th cycle at C/50.

Table 2. Summary of available electrolyte systems in terms of cations, anions, solvents, and additives for use in Mg–S batteries.

| Type          | salt cation | salt anion       | additives | solvents            |
|---------------|-------------|------------------|-----------|---------------------|
| Nucleophilic  | ![Nucleophilic structure](image) | ![Nucleophilic structure](image) | ![Nucleophilic structure](image) | ![Nucleophilic structure](image) |
| Non-nucleophilic | ![Non-nucleophilic structure](image) | ![Non-nucleophilic structure](image) | ![Non-nucleophilic structure](image) | ![Non-nucleophilic structure](image) |

![Diagram of electrolyte systems](image)
clearly indicating the performance enhancement brought by the CNF-coated separator.

Finally, an approach that utilizes a catalyst to reactivate electrochemically inert MgS and Mg3S8 to reform high-order polysulfides or S is another approach to improve the discharge capacity and cycling life. It has been reported that TiS2 has a catalytic effect on the activation of low-order magnesium polysulfides. In 2019, Xu et al. presented a TiS2-coated separator prepared by a vacuum-filtration process. The Mg–S cell with the coated separator (for the configuration refer to Figure 16c) delivered around 800 mAh g\(^{-1}\) for 30 cycles at 0.05 C, while a cell without any TiS2 could only deliver around 200 mAh g\(^{-1}\) for 20 cycles. XPS measurements confirmed that both the S and the polysulfide peak showed up at the fully charged state, indicating that TiS2 successfully reoxidized both MgS and Mg3S8 back to higher-order polysulfides and S and that the Mg–S bond in MgS can be broken by TiS2 (Figure 16c).

6. Electrode–Electrolyte Interfaces and Full Device Design

Interface issues concerning the electrodes in Mg–S batteries and those in their analogous Li–S batteries are quite different. In Li–S batteries, the lithium polysulfides are formed and dissolved in the electrolyte solution and then further reduced to insoluble Li2S at the Li anode, where a so-called solid electrolyte interphase (SEI) forms, whose composition is crucial for cell performance. Ideally, the formed SEI allows for the permeation and transportation of Li\(^+\) ions; hence Li dissolution and deposition are still possible. By contrast, in Mg–S batteries, the SEI layer is more a blocking layer. The reduction of the sulfur at the cathode leads to a general formation of soluble MgS8. MgS8 is then further reduced to MgS, which leads to the blocking of the Mg anode and a high impedance of the cell. In addition to this blocking of the Mg surface from polysulfides, thereby preventing any further reduction of sulfur, the deposition of electrolytes also destroys the Mg surfaces. Ding et al. observed some dendrite growth on a Mg anode when using Mg(TFSI)\(_2\)/diglyme as electrolyte, leading to a so-called “soft short-circuit” phenomenon, since the cells were not purely resistive. Due to the native oxide layer on the Mg surface, only parts of the surface are electrochemically active if the electrolyte cannot remove the blocking layer on the Mg anode. Consequently, current density is not homogeneous over the entire surface, leading to the observed dendrite formation. Typical components on the surface of a cycled anode include Mg metal, MgF2, Mg(TFSI)\(_2\) and MgO, where magnesium fluoride and oxide originate from the decomposition of Mg(TFSI)\(_2\) dissolved in diglyme. Further on, using in situ AFM and optical microscopy, Hu et al. observed that the use of Mg(HMDS)\(_2\)-AlCl3 dissolved in different ethers (diglyme and tetraglyme) influences the Mg anode surface due to different dynamic processes. Due to the differences in the chemical structure between diglyme and tetraglyme, the dynamic stripping processes of the two solvents are different, too. Diglyme has three oxygen atoms, which allows, together with three chloride atoms, for the formation of anionic hexacoordinated Mg\(^{2+}\) complexes. By comparison, tetraglyme, having five oxygen atoms, can form cationic monochloride complexes, which benefit from the chelating effect of the oxygens and thus experience better solvation. Consequently, the stripping process with tetraglyme as solvent is slow and homogeneous. Therefore, the use of tetraglyme improves the reversibility of a cell.

When selecting the cathodes, anodes, electrolytes, etc., for the construction of a full Mg–S battery, it is necessary to consider the compatibility of the individual components. Table 3 summarizes published data of Mg-S batteries. To date, solvents for the electrolytes are limited to ethers, such as THF, DME,
Table 3. A summary of currently reported Mg–S batteries (in chronological order).

| Author/Year | Cell type | Cathode | Sulfur loading [wt%] | Anode | Separator | Electrolyte | Anodic stability [V vs Mg/Mg²⁺] | Coulombic efficiency [%] | Capacity [mAh g⁻¹, used / current rate / cycle number] |
|-------------|-----------|---------|----------------------|-------|-----------|-------------|-------------------------------|--------------------------|---------------------------------|
| Muldoon and co-workers 2011[12] | Coin cell | S@carbon black on porous carbon substrate | 61 | Mg foil | No data | [Mg(µ-Cl)₂·6THF] [HMD5AICl₆]·THF (nonnucleophilic) | 3.3/Pt | 95–100 | 394/no data/2nd |
| Ha et al. 2014[37] | Coin cell | 70% CMK3 / S–20% Super P–10% PVDF on Al | 69.3 | Mg disc | No data | 0.3 µ (TFSI) / DME-diglyme (nonnucleophilic) | 4.2/Al 4.8/SS | No data | 100 @C/30 /4th |
| Zhao-Karger et al. 2014[17] | Swagelok type cell | 75% S / CMK–15% Super P–10% PVDF in NMP or CMC in water on Inconel 625 | 55% | Pressed Mg powder and carbon black (4:1 wt) Pellet | Borosilicate glass fiber sheet | 1.2 µ (HMDS)₂Mg·2AlCl₃–MgCl₂ in diglyme or tetraglyme/PP14TFSI (nonnucleophilic) | No data | ≈ 100 | ≈ 150 @0.01 C/20th (PVDF, diglyme) ≈ 200 @0.01 C/20th (CMC, diglyme) ≈ 250 @0.01 C/20th (PVDF, diglyme) ≈ 260 @0.01 C/20th (CMC, diglyme) |
| Gao et al. 2015[24] | Swagelok type cell | ACC–S | 15 wt% 0.5 mg cm⁻² | Mg foil | Whatmann glass fiber | 0.1 µ (HMDS)₂Mg·2AlCl₃ + 1 µ LiTFSI (nonnucleophilic) | 2.7/Pt | =92 | 1000 @0.03 C/30th |
| Itoaka et al. 2015[111] | Coin cell | Sulfur/bis(undec-10-enoxy-methylbenzo-18-crown-6-ether (BUMB18C6); sulfur-oxybis(2,1-ethanediyl) ester (UOE2); on SS | No data | Mg plate | Celgard 2500 | 0.5 µ Mg(TFSI)₂ in triglyme or acetonitrile (nonnucleophilic) | No data | No data | 23 @0.01 C/10th (acetonitrile) 68.1 @0.01 C/10th (triglyme) |
| Li et al. 2016[21] | Coin cell | S–N-doped graphene–carbon black–PVDF in NMP; on Al foil | 50 wt% | Mg disc | Celgard 2400 | [Mg(THF)]₂[AlCl₃]₆/PYR14(TFSI) in THF (salt) (nonnucleophilic) | 2.4/AI–C 2.5/Al 2.1/Cu 2.3/ss | No data | 40 @0.01 C/20th |
| Vinayan et al. 2016[82] | Swagelok type cell | Reduced graphene oxide–S (rGo–S) 75% rGo–S–15% Super P–10% PVDF on Inconel 625 | 49 wt% | Pressed Mg powder and carbon black (4:1 wt) composite pellet | Celgard 2500 | (HMDS)₂Mg·2AlCl₃–MgCl₂ in diglyme (nonnucleophilic) | No data | =100 | 236 @0.01 C/50th |
| Yu and Arumugam 2016[25] | Coin cell | CNF–S | 50 wt% | Mg foil | Carbon nanofiber-coated glass fiber | 3.6 µ (HMDS)₂Mg·2AlCl₃–MgCl₂ in tetraglyme (nonnucleophilic) | No data | =85 | 800 @0.01 C/20th |
| Sievert et al. 2017[44] | Swagelok type cell | 70% elemental S–20% carbon black–10% PVDF; on Al/C | 1 mg cm⁻² | Pressed Mg/graphite anode | Glass fiber (Whatman GF/A) | HMDSMgCl (nonnucleophilic) | No data | =100 | 30 @0.1 C/100th |
| Du et al. 2017[40] | Coin cell | S–CNT 80% S–CNT–10% Super P–10% PVDF in NMP; on Cu | 1 | Mg foil | Glass fiber | OMBB 0.5 µ [MgCl₂(DME)]₆ / β[B(HFP)]₂ / 2 β[B(HFP)]₂–MgCl₂ (nonnucleophilic) | 3/AI 3.2/Al 2.0/Cu 2.5/ss | 100 @0.1 C/100th |
| Gao et al. 2017[26] | Swagelok type cell | ACC–S | 1 | Mg disc | Glass fiber | 1 µ (TFSI)₂–MgCl₂ in DME (nonnucleophilic) | No data | 93 | 600 @0.01 C /100th |
### Table 3. Continued.

| Author/Year | Cell type | Cathode | Sulfur loading [wt%] | Anode | Separator | Electrolyte | Anodic stability [V vs Mg/Mg^{2+}] | Coulombic efficiency [%] | Capacity [mAh g^{-1} sulfur] / current rate / cycle number |
|-------------|-----------|---------|----------------------|-------|-----------|------------|-----------------------------------|--------------------------|----------------------------------------------------------|
| Du et al. 2017[86] | Coin cell | 70% SGDY–20% Super P–10% PVDF; on Al | 1 | Mg disc | Glass fiber | All-phenyl complex (PhMgCl){_2}–AlCl_{3} + LiCl in THF (nucleophilic) | No data | 100 | 800 @0.1 C/100th |
| Zeng et al. 2017[99] | Coin cell | 70% S–20% Super P–10% PVDF in NMP; on SS/Cu | No data | Mg ribbon | Entek PE membrane | APC | 0.4 μ (PhMgCl){_2}–AlCl_{3} + LiCl in THF (nucleophilic) | 1.7/Cu | 100 | 300 @0.005 C/40th |
| Robba et al. 2017[84] | Pouch cell | Graphite/S–multwalled CNT; on Al | No data | Mg foil | Glass fiber (Whatman GF/A) | 0.4 μ (TFSI){_2}–MgCl_{2} (1:1) in tetraglyme:1,3-dioxolane (DOL) (1:1) (nonnucleophilic) | 2.5/Al | No data | 400 @C/60/4th |
| Zhang et al. 2017[114] | Coin cell | 80% S/C composite–10% acetylene black–10% PVDF in NMP; on Cu | 85 wt% | Mg foil | Glass fiber | BCM (0.5 μ THFPB + 0.05 μ MgF_{2} in DME) (nonnucleophilic) | 2/Cu | ≈100 | 900 @0.03 C/30th |
| Zhao-Karger et al. 2017[41] | Swagelok type cell | 75% S/CMK-3–15% carbon black–10% CMC on SS | 1 mg cm^{-2} | Mg foil | Borosilicate glass fiber sheet GF/C | 0.8 μ Mg(B(hfip)){_2} in diglyme:tetraglyme (1:1) (nonnucleophilic) | 3/Al | ≈100 | ≈200 @0.1 C/100th |
| Gao et al. 2018[85] | Swagelok type cell | S-ACC on SS; S/CMK-3 on SS | 1 mg cm^{-2} | Mg disc | Glass fiber | Mg(TFSI){_2} in DME (nonnucleophilic) | 3.0/SS | 100 | 668 @0.01 C/20th |
| Aurbach and co-workers 2018[147] | – | Carbon cloth/S | – | Mg foil | – | Mg(TFSI){_2}–MgCl_{2} in DME (nonnucleophilic) | – | – | – |
| Muthuraj et al. 2018[115] | Coin cell | 70% S/rGO–20% Super P–10% PVDF in NMP; on N, S dual doped carbon cloth current collector | 1 mg cm^{-2} | Mg disc | Activated CNF-coated glass fiber | (HMDS){_2}Mg–2AlCl_{3}–MgCl_{2} in tetraglyme (nonnucleophilic) | – | ≈93 | 388 @0.01 C/40th |
| Wang et al. 2018 | Coin cell | 70% S@MC–20% Super P–10% PVDF in NMP 20 μm; on Cu | 64.7 wt% | Mg | PE membrane | APC: 0.4 μ (PhMgCl){_2}–AlCl_{3} + 1 μ LiCl/THF (nucleophilic) | 1.7/Cu | ≈100 | 368.8 @0.1 C/200th |
| Zhou et al. 2018[22] | Coin cell | MOF-S | 1 mg cm^{-2} | Mg foil | Glass fiber (Whatman GF/A) | (HMDS){_2}Mg–2AlCl_{3} with LiTFSI additive (nonnucleophilic) | No data | No data | 400 @0.1 C/200th |
| Zhao-Karger et al. 2018[43] | Swagelok type cell | S-ACC on SS | 1.2 mg cm^{-2} | Mg foil | Glass fiber | MgB(hfip){_2} in DME (nonnucleophilic) | – | ≈93 | 200 @0.1 C/100th |
| Xu et al. 2019[33] | Coin cell | MgS_{8}@G-CNT | 0.7–1 mg cm^{-2} | Mg metal | No data | YCl_{3}–MgCl_{2} in N-methyl-(N-butyl)pyrrolidinium bis(trifluoromethanesulfonil) imide/diglyme (1/1, v/v) (nonnucleophilic) | 3.0/Pt | 98.7 | 900 @0.04 C/50th |
diglyme, triglyme, and tetraglyme. This is a result of the finding that carbonate-based solvents react with Mg anodes, resulting in blocked, carbonate-containing anode surfaces. In addition, due to the nucleophilic character of the polysulfides, the electrolyte may not be electrophilic, unless both the cathode and the separators are specifically modified.\footnote{\cite{347,448}}

7. Summary and Outlook

Over the last ten years, increasing attention has been devoted to novel rechargeable Mg–S batteries due to their safety characteristics, high energy density and earth abundance of both magnesium and sulfur. However, some major issues still exist in this field, which impede the development of reliable Mg–S batteries. One major challenge is related to the formation of magnesium polysulfides. The intermediary polysulfides dissolve in the electrolyte, leading to severe overcharging, loss of active material and low sulfur utilization of the cathode during charge and discharge. This results in a shuttle effect, capacity decay and irreversible reactions, which will in turn lead to short cycle life and capacity fading. The final products, MgS and MgS$_2$, are also electrophilically active, since they lack solubility and are hard to reoxidize during charging. With regards to these issues, novel cathode materials for Mg–S batteries, which are able to suppress the shuttle effect and which possess a high sulfur content need to be synthesized and further studied. To date, cathode systems are generally based on elemental sulfur or sulfur species confined in microporous carbon materials, which can to some extent immobilize sulfur and magnesium polysulfides, too. Since the design principles of cathode materials for Mg–S batteries are at least similar to those of Li–S batteries in terms of high sulfur loading, high conductivity and good surface chemisorptivity, polymers containing covalently bound sulfur as cathode material might present a future research direction. Also, it is important to study the fundamental electrochemistry behind the individual redox reactions in order to understand the capacity decay phenomenon and to further improve cell performance. In that regards, Cu-based current collectors as well as modified separators have been reported to be beneficial to increase reversibility and maintain capacity.

With regards to Mg anodes, research in this area is far less active as compared to electrolytes and cathode materials. Unlike Li metal, which deposits in a dendritic manner and creates high surface area upon cycling, Mg generally does not plate in a dendritic manner. This is beneficial for safety reasons; however, it reduces the active surface area, which in turn results in a poor electrochemical performance of the cell. In view of this challenge, pressed Mg anodes out of Mg powder or nanoparticles that possess a high surface area are under investigation. Another major challenge is related to the manipulation of the Mg anode surface with the electrolyte system. Thus, commonly used carbonate-based electrolytes in Li batteries are unsuitable for Mg batteries, due to the formation of an impermeable layer on the Mg surface, which hinders Mg deposition and dissolution. The generation of an artificial conductive layer on Mg anodes, which could protect the Mg anodes from reacting with the electrolytes, might be a new direction for novel anodes. Also, the utilization of magnesium ion insertion anodes, which can host Mg$^{2+}$ ions, is another possible solution for the use of magnesium salts in polar aprotic solvents used in the electrolytes. For example, Bi nanotubes, which can be formed in situ, can effectively accommodate the volume change of the anodes, decrease the diffusion length of Mg$^{2+}$ and retain the electronic contact. However, the compatibility of magnesium ion insertion anodes with sulfur-based cathode has not yet been addressed, but might also present a novel route to prevent reaction of the electrolyte and especially of the polar solvents with the Mg metal.

In terms of electrolyte development for Mg–S batteries, major challenges are related to the divalent nature of the Mg$^{2+}$ ions, which possess a higher energy barrier between electrolyte and Mg anodes than monovalent Li ions, resulting in sluggish Mg plating and stripping. Also, sufficient transport properties and anodic stability are crucial for the cycle performance. For example, a suitable viscosity of the electrolyte that can allow for the fast migration of Mg ions, and at the same time, reduce the Mg polysulfide shuttle effect, is important. In addition, corrosion-free electrolytes with a large potential window are desirable for practical Mg–S batteries. Up to now, nucleophilic electrolytes, which are known to react with the sulfur cathode,

| Author/Year | Cell type | Cathode | Sulfur loading [wt%] | Anode | Separator | Electrolyte | Anodic stability [V vs Mg/Mg$^{2+}$] | Coulombic efficiency [%] | Capacity [mAh g$^{-1}$ / current rate / cycle number] |
|-------------|-----------|---------|----------------------|-------|---------|------------|---------------------------------|------------------|-----------------------------------------------|
| Yang et al. 2019$^{[112]}$ | Coin cell | 80% S@ microporous carbon–10% super P–10% PVDF in NMP on Cu | 55 wt% | Mg Ribbon | PE separator | Mg(CF$_3$SO$_2$)$_2$–AlCl$_3$ in THF and tetryglyme (nonnucleophilic) | 2.35/Pl, 2.5/SS, 2.0/Cu, 1.85/Al | ≈90 | 400 @0.05 C/50th |
| Zhao et al. 2019$^{[112]}$ | Coin cell | 80% S@ microporous carbon–10% super P–10% PVDF in NMP on Cu | 55.8 wt% | Mg metal | PE separator | Magnesium bis(diisopropyl)amide MBA–AlCl$_3$–LiCl in THF (nonnucleophilic) | 1.85/Cu, 2.35/Al, 2.65/SS | ≈94 | 400 @0.04 C/100th |
were applied, together with modified cathode materials, but are increasingly replaced by nonnucleophilic electrolytes for which variations both in the Mg salt and the Lewis acid have been carried out to obtain new electroactive species. Specifically, cationic, chloride-containing electrolytes have been found to be corrosive to the cell body. Consequently, the development of chloride-free noncorrosive Mg compounds is an ongoing research. So far, nonnucleophilic fluorinated alkoxyborate-based magnesium electrolytes seem to be the most promising systems; both in terms of anodic stability, capability of Mg plating and stripping, alternative conductive salts containing boron- and aluminum-based weakly coordinating anions, together with the addition of lithium salts and ionic liquids might be another future research direction. Further on, polymer-based electrolytes that benefit from low leakage and practical use are also interesting.

In summary, rechargeable Mg–S batteries are currently still in a nascent stage. Fortunately, growing interest is devoted for obtaining a high energy-density system that outperforms Li batteries. A practical and reliable Mg–S cell might be soon realized.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

magnesium anode, magnesium battery electrolytes, magnesium–sulfur batteries, post lithium–sulfur batteries, sulfur-based cathodes

References

[1] P. Saha, M. K. Datta, O. I. Velikokhatnyi, A. Manivannan, D. Alman, P. N. Kumta, Prog. Mater. Sci. 2014, 66, 1.
[2] H. Budde-Meiwes, J. Drillkens, B. Lunz, J. Muenix, S. Rothgang, J. Kowal, D. Sauer, Proc. Inst. Mech. Eng., Part D 2013, 227, 761.
[3] L. Medenbach, P. Adelhelm, Top. Curr. Chem. 2017, 375, 81.
[4] C. Wadia, P. Albertus, V. Srinivasan, J. Power Sources 2011, 196, 1593.
[5] Y. X. Yin, S. Xin, Y. G. Guo, L. J. Wan, Angew. Chem. 2013, 1258, 13426; Angew. Chem., Int. Ed. 2013, 52, 13186.
[6] H. Tian, T. Gao, X. Li, X. Wang, C. Luo, X. Fan, C. Yang, L. Suo, Z. Ma, W. Han, C. Wang, Nat. Mater. 2016, 17, 19.
[7] J. Dewulf, K. Denturck, H. Van Langenhove, W. Ghysout, J. Tytgat, Resour., Conserv. Recycl. 2010, 54, 229.
[8] T. Cleaver, P. Kovacic, M. Marinescu, T. Zhang, G. Offer, J. Electrochem. Soc. 2018, 165, A6029.
[9] X. Xu, S. Wang, H. Wang, B. Xu, J. Energy Storage 2017, 13, 387.
[10] J. Zheng, M. Gu, H. Chen, P. Meduri, M. H. Engelhard, J. Zhang, J. Liu, J. Xiao, J. Mater. Chem. A 2013, 1, 8464.
[11] Z. Zhao-Karger, M. Fichtner, MRS Commun. 2017, 7, 770.
[12] H. Kim, T. S. Arthur, G. D. Allred, J. Zajicek, J. G. Newman, A. E. Rodnyansky, A. G. Oliver, W. C. Boggess, J. Muldoon, Nat. Commun. 2011, 427, 1.
[13] L. Wang, Y. Ye, N. Chen, Y. Huang, L. Li, F. Wu, R. Chen, Adv. Funct. Mater. 2018, 28, 1800919.
[14] M. Huang, M. Li, C. Niu, Q. Li, L. Mai, Adv. Funct. Mater. 2019, 29, 1807847.
[15] X. Hong, J. Mei, L. Wen, Y. Tong, A. J. Vasileff, L. Wang, J. Liang, Z. Sun, S. X. Dou, Adv. Mater. 2018, e1802822.
[16] J. Muldoon, (Toyota Motor Engineering & Manufacturing), US20110244338, 2011.
[17] Z. Zhao-Karger, X. Zhao, D. Wang, T. Diernant, R. J. Behm, M. Fichtner, Adv. Energy Mater. 2015, 5, 1401155.
[18] A. Robba, A. Vizintin, J. Bitenc, G. Mali, J. Arcon, M. Kavčič, M. Žitnik, K. Bučar, G. Aquilanti, C. Martineau-Corcos, A. Randon-Vitanova, R. Dominko, Chem. Mater. 2017, 29, 9555.
[19] H. D. Yoo, I. Shterenberg, Y. Cofe, G. Gershinski, N. Pour, D. Aurbach, Energy Environ. Sci. 2013, 6, 2265.
[20] H. Tian, T. Gao, X. Li, X. Wang, C. Luo, X. Fan, C. Yang, L. Suo, Z. Ma, W. Han, C. Wang, Nat. Commun. 2017, 8, 14083.
[21] W. Li, S. Cheng, J. Wang, Y. Qiu, Z. Zheng, H. Lin, S. Nanda, Q. Ma, Y. Xu, F. Ye, M. Liu, L. Zhou, Y. Zhang, Angew. Chem. 2016, 128, 6516; Angew. Chem., Int. Ed. 2016, 55, 6406.
[22] Z. Zhang, B. Chen, H. Xu, Z. Cui, S. Dong, A. Du, J. Ma, Q. Wang, X. Zhou, G. Cui, Adv. Funct. Mater. 2018, 28, 1701718.
[23] Z. Zhao-Karger, X. Zhao, O. Fuhr, M. Fichtner, RSC Adv. 2013, 3, 16330.
[24] T. Gao, M. Noked, A. J. Pearse, E. Gillette, X. Fan, Y. Zhu, C. Luo, L. Suo, M. A. Schroeder, K. Xu, S. B. Lee, G. W. Rubloff, C. Wang, J. Am. Chem. Soc. 2015, 137, 12388.
[25] X. Yu, M. Arumugam, ACS Energy Lett. 2016, 1, 431.
[26] T. Gao, S. Hou, F. Wang, Z. Ma, X. Li, K. Xu, C. Wang, Angew. Chem. 2017, 129, 13711; Angew. Chem., Int. Ed. 2017, 56, 13526.
[27] D. Aurbach, G. S. Suresh, E. Levi, A. Mitelman, O. Mizrahi, O. Chusid, M. Brunelli, Adv. Mater. 2007, 19, 4260.
[28] J. Muldoon, C. B. Bucur, A. G. Olifer, T. Sugimoto, M. Matsui, H. S. Kim, G. D. Allred, J. Zajicek, Y. Kotani, Energy Environ. Sci. 2012, 5, 5941.
[29] J. Song, E. Sahadeo, M. Noked, S. B. Lee, J. Phys. Chem. Lett. 2016, 7, 1736.
[30] C. B. Bucur, Challenges of a Rechargeable Magnesium Battery, Springer, Switzerland 2018.
[31] Z. Zhao-Karger, M. Fichtner, Front. Chem. 2018, 6, 656.
[32] L. Kong, C. Yan, J.-Q. Huang, M.-Q. Zhao, M.-M. Titirici, R. Xiang, Q. Zhang, Energy Environ. Mater. 2018, 1, 100.
[33] D. Aurbach, I. Weissman, Y. Cofe, E. Levi, Chem. Rec. 2003, 3, 61.
[34] Z. Lu, A. Schechter, M. Moshkovich, D. Aurbach, J. Electroanal. Chem. 1999, 466, 203.
[35] R. Mohtadi, F. Mizuno, Beilstein J. Nanotechnol. 2014, 5, 1291.
[36] L. C. Merrill, L. J. Schaefer, Front. Chem. 2019, 7, 194.
[37] S. Y. Ha, Y. W. Lee, S. W. Woo, B. Koo, J. S. Kim, J. Cho, K. T. Lee, N. S. Choi, ACS Appl. Mater. Interfaces 2014, 6, 4063.
[38] Y. Cheng, Y. Shao, J. G. Zhang, V. L. Sprengle, J. Liu, G. L. Chem. Commun. 2014, 50, 9644.
[39] Y. Yang, W. Wang, Y. Nuli, J. Yang, J. Wang, ACS Appl. Mater. Interfaces 2019, 11, 9062.
[40] A. Du, Z. Zhang, H. Qu, Z. Cui, L. Qiao, L. Wang, J. Chai, T. Lu, S. Dong, T. Dong, H. Xu, X. Zhou, G. Cui, Energy Environ. Sci. 2017, 10, 2616.
[41] Z. Zhao-Karger, M. E. Gil Bardaji, O. Fuhr, M. Fichtner, J. Mater. Chem. A 2017, 5, 10815.
