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Prospective Article

Magnesium–sulfur battery: its beginning and recent progress

Zhirong Zhao-Karger, Helmholtz Institute Ulm (HIU), Helmholtzstr. 11, D-89081 Ulm, Germany
Maximilian Fichtner, Helmholtz Institute Ulm (HIU), Helmholtzstr. 11, D-89081 Ulm, Germany; Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany
Address all correspondence to M. Fichtner at **m.fichtner@kit.edu**

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Abstract

Rechargeable magnesium (Mg) battery has been considered as a promising candidate for future battery generations because of its potential high-energy density, its safety features and low cost. The challenges lying ahead for the realization of Mg battery in general are to develop proper electrolytes fulfilling a multitude of requirements and to discover cathode materials enabling high-energy Mg batteries. The combination of Mg anode with a sulfur cathode is one of the promising electrochemical couples due to its advantages of safety, low costs, and a high theoretical energy density of over 3200 Wh/L. However, the research on magnesium–sulfur (Mg–S) battery is just at its beginning and the development of suitable electrolytes has been the key challenge for further improvement, and, thus, in the focus of recent research. In this review, we highlight the recent progress achieved in Mg electrolytes and Mg–S batteries and discuss the major technical issues, which must be resolved for the improvement of Mg–S batteries.

Introduction

Lithium-ion battery (LIB) is the dominant technology for electrical energy storage in various applications such as portable electronics and electric vehicles. While unrivaled in their performance, the current LIBs are approaching their capacity limits of the intercalation compounds and there are also concerns about safety and the resource situation.[1–3] For example, concerns have been raised that the world's cobalt (Co) resources and reserves may not be sufficient to enable a global electromobility even when Co-poor next generation NMC materials (i.e., NMC 622 and 811) will be used.[4] All these reasons have led to an increasing interest in batteries based on alternative chemistries, which are not based on Li anymore and an increasing attention is focusing on new battery systems beyond lithium that possess higher energy density, consist of low-cost materials, and are safer and long lasting.

Magnesium battery

Mg battery has been proposed as an attractive candidate for future rechargeable batteries, mostly due to the high volumetric capacity of 3837 mAh/cm^3 of the metal, which is significantly higher than that of lithium (2062 mAh/cm^3) and sodium (1136 mAh/cm^3).[5] It is worth noting that the volumetric energy density of a battery has to be considered particularly to control the size of battery packs for portable devices and vehicles. In contrast to Li or Na, Mg as a metallic anode has the nature of dendrite-free deposition.[6,7] Moreover, Mg has a reduction potential of −2.4 V versus SHE and can be safely handled in air. An important aspect of cost and sustainability is the high abundance of Mg element in the earth crust and its ready availability in various minerals all over the globe, e.g., as dolomite ($CaCO_3{\cdot}MgCO_3$) or as magnesite ($MgCO_3$).

Currently, the introduction of Mg batteries is impeded by several technical obstacles, such as the lack of an electrolyte, which is cost-effective, efficient, and chemically compatible with the electrode materials. In addition, the quest for practical cathodes offering high capacity and energy density is ongoing. So far, only a few types of conventional intercalation materials have been identified that are capable of storing Mg^{2+} ions reversibly.[8–15] Thus, the challenges to realize the rechargeable Mg battery technology are not only the improvement of the electrolyte toward high oxidative stability, but also the discovery of cathode materials enabling high performance of Mg batteries.

General aspects of lithium–sulfur and magnesium–sulfur

Sulfur (S) is an attractive candidate for cathodes of the next-generation batteries owing to its high theoretical capacity of 1673 mAh/g, its natural abundance, non-toxicity, and low cost. When paired with a Li metal anode, the lithium–sulfur (Li–S) battery provides a high theoretical energy density of 2800 Wh/L and 2600 Wh/kg. Li–S battery has therefore been suggested as a promising high-energy post-Li-ion battery and extensively investigated in the past decade.[16,17] However, material issues are still to be solved for the commercialization of Li–S batteries such as the problems associated with the chemistry of S. Li metal anodes would have to be employed

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to ultimately achieve Li–S batteries with high-energy densities, but this would enhance the risk of dendrite growth. With a graphite anode, the theoretical energy density of the Li–S system drops from 2800 to 1100 Wh/L.

In contrast, Mg can be used as a metallic anode in Mg batteries, and the combination of Mg with S is therefore regarded as a promising electrochemical couple, too. The two-electron conversion reaction of $Mg^{2+} + S + 2e^- \leftrightarrow MgS$ yields a theoretical cell voltage of 1.77 V, thus offering a theoretical energy density of over 3200 Wh/L. Another aspect is that the reaction of a single Mg with S results in a volume expansion of 24%, while the active material expands by 72% when Li_2S is formed.

Compared with the considerable technological advancements in Li–S batteries, the R&D of Mg–S battery is still in an early stage. The key challenge in the development of Mg batteries is to discover a suitable electrolyte, which is chemically compatible to the electrophilic S and capable of reversible Mg deposition/dissolution in a wide operating voltage range.

The research work on Mg batteries in general has been timely reviewed and thoroughly discussed,[8–15,18–20] so that we will focus on the properties of Mg electrolytes in view of the application to S cathodes. Thereafter, we will illustrate the progress that is being made on Mg–S battery and discuss future prospects for high-energy Mg and Mg–S batteries.

Challenges and advances in the development of magnesium electrolytes

Organomagnesium-based electrolytes and the nucleophilicity problem

The common magnesium (Mg) analogues of Li ion conducting salts such as $Mg(BF_4)_2$, $Mg(ClO_4)_2$, etc. are not suitable for reversible stripping an plating of Mg ions in aprotic solvents because they either react with the anode or passivate the Mg.[5,21] Gregory et al. initially synthesized Mg electrolytes through the reaction of an organomagnesium with aluminum chloride ($AlCl_3$) or trialkylborane (Lewis acid) in ethereal solvents.[5] Using the same synthetic concept, Aurbach et al. prepared the so-called DCC electrolytes through the reaction between Bu_2Mg and $EtAlCl_2$ in tetrahydrofuran (THF) and demonstrated the first prototype rechargeable Mg battery.[6] An optimized electrolyte APC was generated through reaction of PhMgCl and $AlCl_3$, which exhibits an oxidative stability of 3.2 V versus Mg in cyclic voltammetric (CV) measurements [Fig. 1(a)], a conductivity of 5 mS/cm (30 °C) and a cycling efficiency of almost 100%.[22] Spectroscopic analysis revealed that these solutions contain multiple species, including $MgCl^+$, $Mg_2Cl_3^+$ as electrochemical active species, $Ph_nAlCl_{4-n}^-$ (n = 1–3), $MgCl_2$, Ph_2Mg, and PhMgCl resulting from various transmetalations of the ligands and the Schlenk equilibrium [Fig. 1(b)].[23,24]

Other approaches have also been explored by replacing $AlCl_3$ with other Lewis acids such as tri(3,5-dimethylphenyl) borane (Mes_3B) and aluminum triphenoxide [$Al(OPh)_3$] to react with PhMgCl.[25,26]

Although these organomagnesium based electrolytes show good electrochemical performance, they are complex chemical mixtures of various species that coexist under dynamic equilibrium in the ethereal solvents. The presence of organomagnesium components (RMgX and MgR_2), which are highly nucleophilic and extremely air and moisture sensitive, precludes them from being used for the electrophilic cathodes such as S and air. These limitations have motivated research on non-nucleophilic electrolytes, which are both electrochemically and chemically suited for the incorporation S or air as cathode for potential high-energy Mg batteries.

Non-nucleophilic magnesium electrolytes

Hauser base-based electrolytes

The reversible Mg deposition of the non-nucleophilic Hauser-base hexamethyldisilazide magnesium chloride (HMDSMgCl) was first reported by Liebenow et al.,[27] and the electrolyte showed superior electrochemical properties compared with those of Grignard reagent-based electrolytes. Later, Muldoon and co-workers applied the previously established strategy from Aurbach by adding $AlCl_3$ to the solution of Liebenow's electrolyte HMDSMgCl and observed an increased current density for Mg plating/stripping. The electrolyte was purified by re-dissolving the recrystallized products in THF, achieving a voltage stability of 3.2 V. The compatibility of the system with a S cathode was verified.[28] From a practical point of view, the Grignard reagent $EtMgCl_2$, which is needed for the preparation of the precursor compound HMDSMgCl and the necessary purification step generate a great deal of synthetic expenses.

Zhao-Karger et al. established a convenient approach toward the non-nucleophilic electrolytes through a simple one-step reaction of magnesium-bis(hexamethyldisilazide) $(HMDS)_2Mg$ and $AlCl_3$ at the ratio of 1 : 2 in ethereal solvents.[29] The in situ generated electrolytes in THF show an oxidative voltage of about 3.3 V, which is as good as the solution prepared by re-dissolving crystals. As this reaction can be conducted also in other solvents, higher stabilities are possible [Fig. 2(a)]. Quantitative crystals were isolated from the THF solution and the structure was confirmed by single-crystal x-ray diffraction as $[Mg_2(\mu\text{-}Cl)_3{\cdot}6THF][HMDSAlCl_3]{\cdot}THF$ [Fig. 2(b)].

Nuclear-magnetic resonance spectroscopic (NMR) and mass spectrometric (MS) characterization confirm that the reaction (1), in which the $Mg_2Cl_3^+$ cation is in the known equilibrium (2):

$$(HMDS)_2Mg + 2AlCl_3 \rightarrow [Mg_2Cl_3][HMDSAlCl_3] + HMDSAlCl_2 \quad (1)$$

$$Mg_2Cl_3^+ \leftrightarrow MgCl^+ + MgCl_2 \quad (2)$$

This type of reactions has been used for the synthesis of organoaluminum compounds $RAlCl_2$,[30] in which one equivalent of organomagnesium R_2Mg reacts with two equivalents of $AlCl_3$, followed by the addition of a non-polar solvent to

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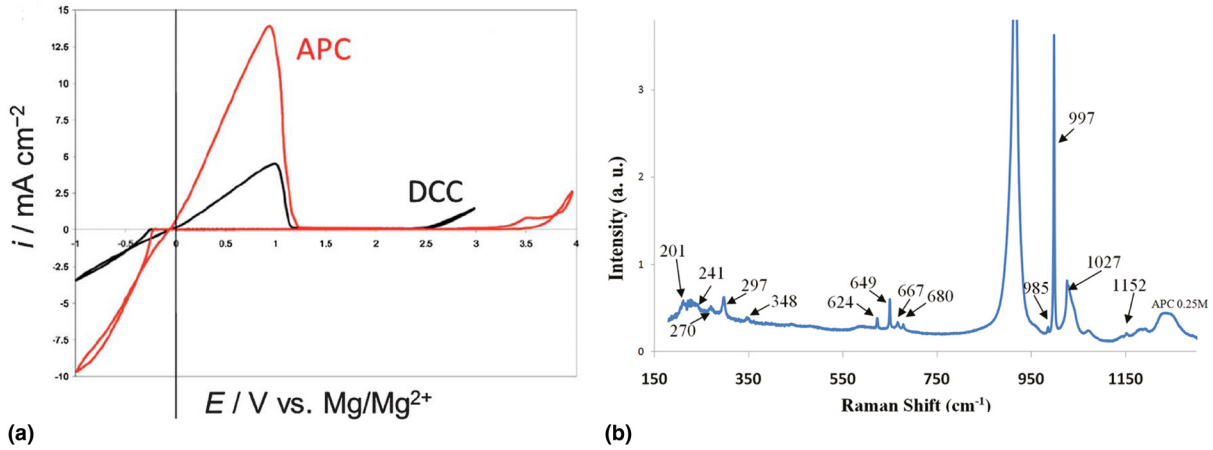


Figure 1. (a) Comparative cyclic voltammograms of APC and DCC electrolyte solutions on Pt electrodes. Reproduced with permission from Ref. 22. Copyright (2007) WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Raman spectrum of a 0.25 M APC solution. Reprinted with permission from Ref. 24. Copyright (2011) American Chemical Society.

shift the equilibrium (2) to the right direction, while the $RAlCl_3^-$ anion transfers one Cl^- to $MgCl^+$ ion forming the product $RAlCl_2$:

$$R_2Mg + 2AlCl_3 \rightarrow [Mg_2Cl_3][RAlCl_3] + RAlCl_2 \quad (3)$$

$$RAlCl_3^- + Mg_2Cl_3^+ \rightarrow MgCl_2 + RAlCl_2 \quad (4)$$

These results indicate that the combination of $(HMDS)_2Mg$ with $2AlCl_3$, in accordance with the reaction stoichiometry, leads to exclusive $HMDSAlCl_3^-$ anions in the solution. This is the obvious reason for the superior electrochemical performance when compared with the electrolyte generated from HMDSMgCl–$AlCl_3$ containing several anionic species in form $HMDS_nAlCl_{4-n}^-$ ($n = 1$–3).[28] Owing to the favorable electrochemical and chemical properties and its simplicity in preparation, this type of electrolyte has been employed in different Mg battery systems with both intercalation and conversion cathodes, including Mo_6S_8,[29] vanadium oxychloride (VOCl),[31] S,[32–35] Se,[36] and iodine.[37]

Fluorinated alkoxide-based electrolytes

Apart from amido groups, some research groups also explored the feasibility with alkoxide magnesium chlorides ROMgCl using the Lewis acid–base concept. Wang et al. employed the phenolate magnesium chlorides ^{R}PhOMgCl to react with $AlCl_3$ in THF and demonstrated highly reversible Mg deposition/dissolution.[38] Bartlett and co-workers studied the substituent effects on the electrochemical behaviors of the ^{R}PhOMgCl-type electrolytes.[39,40] When R is a strongly electron withdrawing group such as 4-CF_3, the electrolyte exhibits an anodic stability of 2.9 V and ionic conductivity

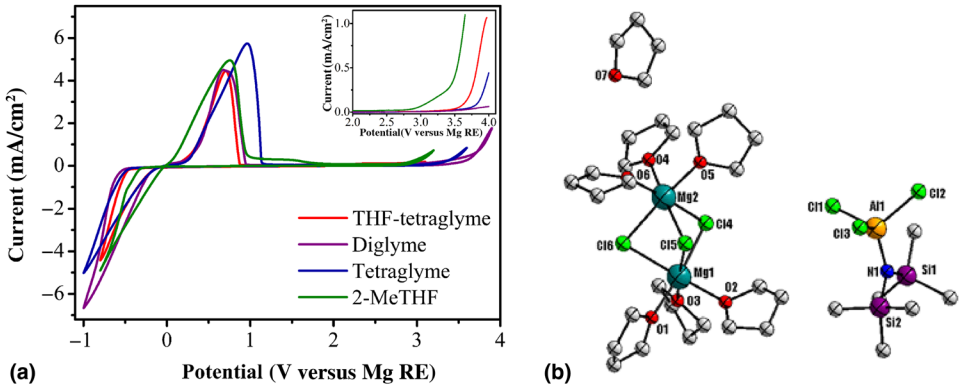


Figure 2. (a.) Cyclic voltammograms of the Mg deposition/dissolution of $(HMDS)_2Mg$–$2AlCl_3$ in different solvents on Pt electrode at a scan rate of 25 mV/s. (b) ORTEP plot (50% thermal probability ellipsoids) of $[Mg_2(\mu\text{-}Cl)_3{\cdot}6THF][HMDSAlCl_3]{\cdot}THF$. Hydrogen atoms are omitted for clarity. Reprinted from Ref. 29 with permission from the Royal Society of Chemistry.

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of 2.2 mS/cm. ^{27}Al NMR study revealed that several $(^{R}PhO)_xAlCl_{4-x}^-$ ($x = 1$–4) species are present in the solution, similarly to the reactions of organomagnesium chlorides with $AlCl_3$. The same group recently carried out the reaction of fluorinated alkoxy magnesium chlorides ^{F}ROMgCl with $AlCl_3$ and investigated the electrolyte performance.[41] According to their comparison studies, a solution composed of 1.2 M $[(CF_3)_2(CH_3)]$COMgCl and 0.20 M $AlCl_3$ in THF exhibits an anodic stability of 3.2 V and an ionic conductivity of 3.5 mS/cm, which is in accordance with the trends of the calculated HOMO energies.

To circumvent the need of the Grignard reagent for the synthesis of *R*OMgCl, Arnold and co-workers combined magnesium dialkoxides $Mg(OR)_2$ (R = alkyl, aryl) with $AlCl_3$ to form Mg electrolyte.[42] The solution obtained from the combination of fluorinated magnesium dialkoxide $Mg(HFIP)_2$ (HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol) and $AlCl_3$ in 1,2-dimethoxyethane (DME) exhibits promising electrochemical properties such as anodic voltage >3 V on Pt electrode, nearly 100% coulombic efficiency for Mg cycling and a conductivity of 4.77 mS/cm (26.3 °C).[43]

In comparison to the organomagnesium-based electrolytes, the combinations of less reactive reagents such as amides, alkoxides with $AlCl_3$ improve the electrolytes with respect to chemical compatibility and safety features without sacrificing their electrolytic properties. The fluorinated alkoxide-based electrolytes should be chemically compatible with S. However, they have not been investigated for Mg–S batteries so far.

Magnesium chloride-based electrolytes

In recent years, Mg electrolytes based on inexpensive and practically convenient $MgCl_2$ have been reported by several research groups. A short review about such electrolytes has been published in 2016.[44] Herein we will briefly summarize the versatile utilities of $MgCl_2$ in Mg electrolytes.

It is known in chemistry that $MgCl_2$ can interestingly act both as Lewis acid and base depending on the reaction counterparts. The reaction of $MgCl_2$ with a strong base results in a magnesiate anion with the formula $R_nMgCl_{3-n}^-$ ($n = 1$–3) by accepting a ligand from the base counterpart.[45] With an acid, $MgCl_2$ tends to form the binuclear cation $Mg_2Cl_3^+$ by transferring one chlorine atom to its acid counterpart. The organoaluminum Lewis acid acts as a Cl acceptor and converts into a tetrakis-ligated aluminate by taking a chloride from $MgCl_2$. This reaction has been often used to formulate new Mg electrolytes as shown in the following.

Combinations of magnesium chloride with aluminum-based Lewis acids

The first study on the $MgCl_2$–$AlCl_3$ electrolyte showed high overpotential and low efficiency for Mg cycling, and co-deposition of Al.[46] In 2014, Doe et al. resumed this combination and demonstrated that the DME solution of $MgCl_2$–$AlCl_3$, the so called "MACC" in a ratio of 3 : 2 offers an anodic stability of 3.1 V versus Mg, Coulombic efficiency of 99% and conductivity of 2 mS/cm (25 °C).[47] As a full inorganic electrolyte, the MACC electrolyte has drawn much attention in the community, and has been extensively studied in recent years.[48–52] Recently, Li et al. synthesized the MACC electrolyte in binary solvents of THF and N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide. Single-crystal x-ray diffraction reveals the solid structure with the ion pair $[Mg(THF)_6]^{2+}[AlCl_4]^-$.[53]

The oxidative stability of 2.5 V versus Mg on Pt electrode for this electrolyte is inferior to the reported MACC solution in a pure ethereal solvent and the ionic liquid possibly contributed to the high ionic conductivity of the electrolyte (8.5 mS/cm).[53] More recently, Luo et al. reported the beneficial effects of post-treatment with Mg powder on the electrochemical performance of $MgCl_2$/$AlCl_3$ electrolytes in ethereal solvents.[54] It should be noted that it is known that $AlCl_4^-$ anion is capable of Al deposition and has been used as active anion for Al batteries.[55] The Al co-deposition has been found in the work on MACC as well.[48]

Liu et al. and Zhao-Karger et al. simultaneously reported their studies on electrolytes based on $MgCl_2$–Al Lewis acid combinations.[56,57]

$$2MgCl_2 + R_nAlCl_{3-n} \rightarrow Mg_2Cl_3^+ + R_nAlCl_{4-n}^- \quad (5)$$

Liu et al. reacted $MgCl_2$ with a Lewis acid to yield the electrolyte.[56] The Lewis acid–base pairs $MgCl_2$–$AlEtCl_2$ and $MgCl_2$–$AlPh_3$ in THF exhibited an voltage stability of 3.1 and 2.9 V on glassy carbon or Pt electrode, respectively. In addition, experiments on sulfur compatibility indicated that these electrolytes, except the one generated from $MgCl_2$–$AlPh_3$, were chemically unchanged when S powder was added.

Zhao-Karger et al., with the intention to validate the transmetalation reaction (5), investigated the reactions of $MgCl_2$ with Et_nAlCl_{3-n} ($n = 1$–3) in ethereal solutions.[57] The crystal structure of the dimeric complex $[Mg_2(\mu\text{-}Cl)_3\cdot 6THF][Et_2AlCl_2]$ resulting from the mixture of $MgCl_2$–Et_2AlCl confirmed the supposed reaction (5) [Fig. 3(a)]. All the solutions are capable of reversible Mg deposition. Figure 3(b) illustrates representative cyclic voltammograms of the tetraglyme solutions, in which the electrolyte based on the combination of $MgCl_2$ and $EtAlCl_2$ exhibits the highest anodic stability up to 2.9 V. Zhao-Karger et al. additionally applied this straightforward synthesis to yield an air-stable phenolate electrolyte.[57] The 0.6 M diglyme solution resulting from reaction of $MgCl_2$ and dichloroaluminum phenolate $PhOAlCl_2$ demonstrates an anodic stability of 3.4 V [Fig. 3(c)], which is 0.7 V higher than that reported for a solution prepared by the reaction of PhOMgCl and $AlCl_3$ in THF.[38]

These results indicate that the reactions between $MgCl_2$ and organoaluminum compounds can lead almost purely to the electrochemically active binuclear Mg complexes, more efficiently and convenient compared to the alternative approaches with organomagnesium and alkoxide magnesium chlorides. This reaction

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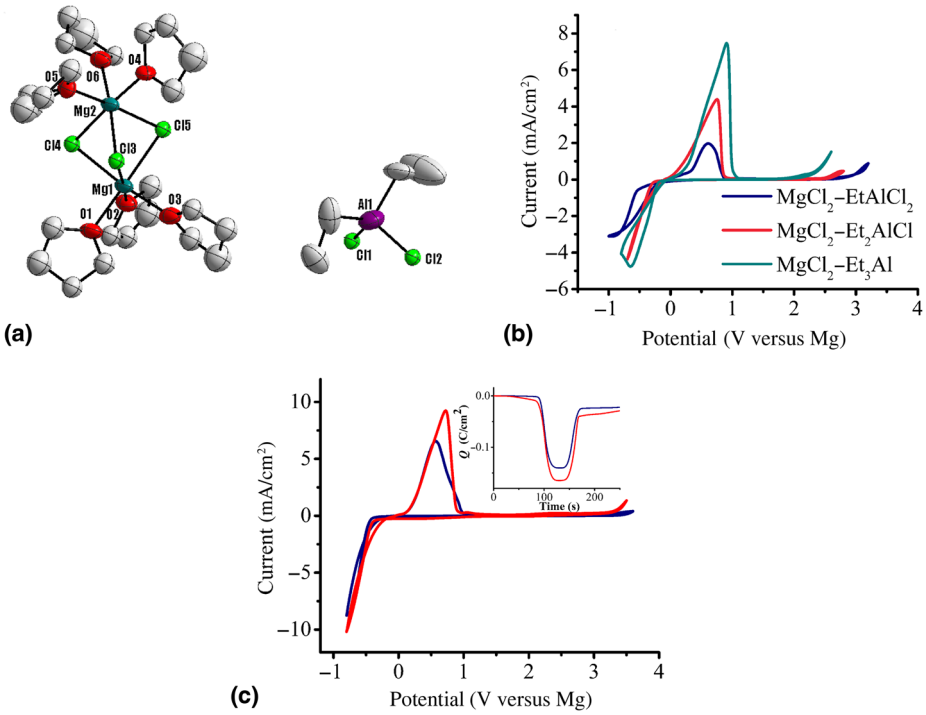


Figure 3. (a) ORTEP plot (50% thermal probability ellipsoids) of $[Mg_2(\mu\text{-}Cl)_3{\cdot}6THF][Et_2AlCl_2]$. Hydrogen atoms are omitted for clarity. Cyclic voltammograms: (b) $MgCl_2$–Et_nAlCl_{3-n} (n = 1–3) electrolytes; (c) $MgCl_2$–$PhOAlCl_2$ electrolytes under argon (blue) and after being stirred in dry air overnight (red); inset shows the charge balance of Mg deposition/dissolution, on Pt electrode at a scan rate of 25 mV/s. Reprinted from Ref. 57 with permission from the Royal Society of Chemistry.

was also used to modify the bisamide based electrolyte.[32] With addition of $MgCl_2$, the initial byproduct $(HMDS)AlCl_2$ in the Mg $(HMDS)_2$–$AlCl_3$ electrolyte is transformed to the active species $[Mg_2Cl_3]^+[HMDSAlCl_3]^-$. Thus, the concentration of HMDS electrolyte can be increased to 1.8 M.

Miscellaneous combinations

Pellion technologies patented the preparation of non-aqueous electrolyte through the reaction of $MgCl_2$ and magnesium bis (trifluoromethane sulfonyl)imide $[Mg(TFSI)_2]$ at varying molar ratios in ethereal solvents and ionic liquid N, N-propyl-methyl-pyrrolidinium-bis(trifuoromethylsulfonyl) imide. The electrolyte solution in DME exhibits an voltage stability of ~3.5 V on Pt and ionic conductivity >5 mS/cm (28 °C).[58] Aurbach and co-workers studied the role of the chloride anions for the enhancement of the reversible Mg deposition of $Mg(TFSI)_2$.[59] Recently, Sa et al. also reported the enhancement of the electrochemical activity of $Mg(TFSI)_2$ in THF and diglyme through addition of $MgCl_2$.[60] Single-crystal x-ray diffraction unveils the solid structure with the ion pair $[Mg_2Cl_3(THF)_6]^+[TFSI]^-$.

Liao et al. reported the reaction of $Mg(HMDS)_2$ with $MgCl_2$ in THF at 1 : 4 ratio, showing an anodic stability of 2.8 V and good reversibility.[61] The same group also made an extended study on the reactions of $MgCl_2$ with phenolate/alkoxide Mg chlorides.[62] The electrolytes prepared by reacting (tBuO)MgCl–$MgCl_2$ in THF exhibited anodic stability up to 3.3 V and close to 100% efficiency.

These results reflect the great diversity of the Mg coordination chemistry. In contrast to the well-known electrochemical activity of the $Mg_2Cl_3^+$ cation, the mechanism of reversible Mg deposition from anionic Mg species is still unexplored. One of a drawback of this type of electrolytes is that the phenolate/alkoxide $MgCl_2$ need to be synthesized from Grignard reagent EtMgCl in THF under stringent conditions.

More recently, Lee and co-workers[63] reported that: $MgCl_2$ in a mixture of dipropyl sulfone (DPSO) and THF yields crystals with an interesting solid structure where $[Mg(DPSO)_6]^{2+}$ cation pairs two $[MgCl_3(THF)]^-$ anions [Fig. 4(a)]. A DPSO/THF (1/1, v/v) solution with $MgCl_2$ salt shows a high reversibility of Mg deposition/dissolution, exhibiting an oxidative stability of about 3.0 V [Fig. 4(b)]. An Mg cycling efficiency of >90% and an ionic conductivity of 1.1 mS/cm (30 °C) were measured.

Electrolytes from chloride-free magnesium salts

Although great progress has been achieved in developing Mg electrolytes, the above-mentioned electrolytes are generally generated through Lewis base–acid or transmetalation reactions yielding the binuclear $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$ cation and anions in equilibria, which have great influences on the properties of

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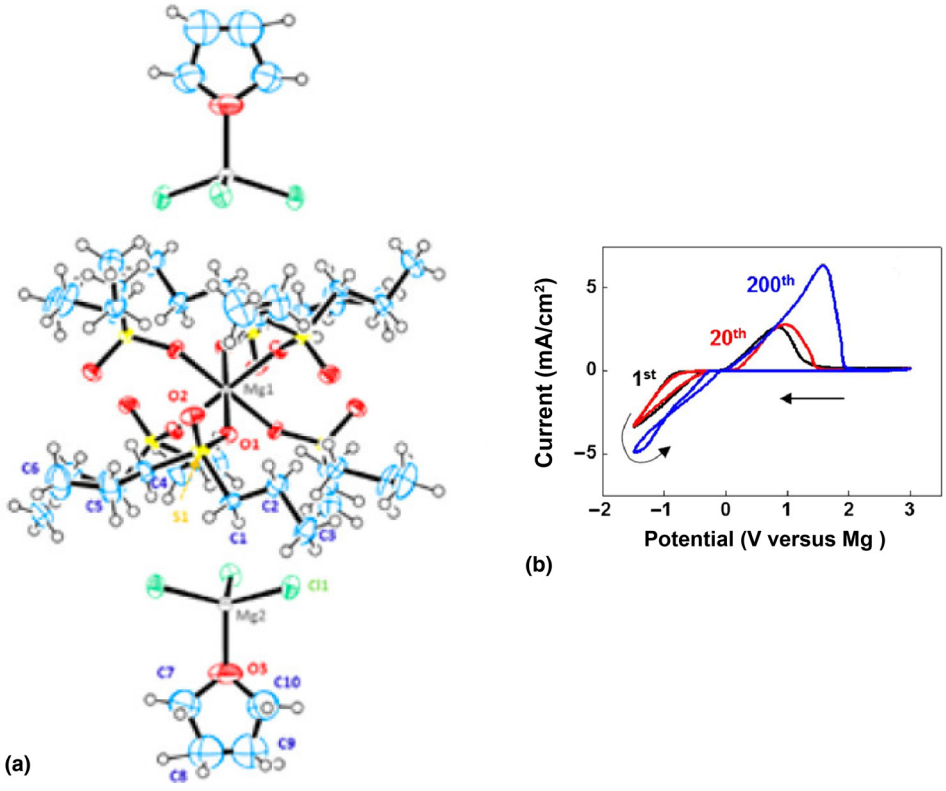


Figure 4. (a) X-ray crystal structure of Mg salt in DPSO/THF (Mg, gray; Cl, green; O, red; S, yellow; C, blue). (b) The 1st, 20th, and 200th cyclic voltammograms in DPSO/THF, Mo as the working electrode at 25 °C and a scan rate of 20 mV/s. Reproduced with permission from Ref. 63. Copyright (2017) American Chemical Society.

the electrolytes.[24,57] In addition, corrosion on metallic current collectors has been verified with such chloride ion containing electrolytes.[64,65] It has therefore been one of the goals to develop highly ion conductive Mg salts, which have favorable electrolytic characteristics, are chemically compatible with the electrode materials and non-corrosive against battery parts. In addition, they should be non-toxic, stable at ambient conditions, and be economically prepared from low-cost starting materials.

Mohtadi et al. reported the capability of reversible Mg deposition of magnesium borohydride [$Mg(BH_4)_2$] in glymes.[66] Kar et al. showed both experimentally and theoretically the reversible Mg redox behavior of $Mg(BH_4)_2$ in alkoxyammonium-based ionic liquids.[67] Watkins et al. have recently designed ionic liquids with a polyether chain attached to an organic pyrolidinium cation to chelate the Mg ion.[68] $Mg(BH_4)_2$ dissolved in this ionic liquid showed superior coulombic efficiency and higher current density compared with the THF solutions. However, the low anodic stability (1.7 V versus Mg) makes $Mg(BH_4)_2$ unsuitable for practical Mg batteries.

Expanding on the early work on $Mg(BBu_4)_2$ of Gregory et al.,[5] Muldoon et al. synthesized several magnesium organoborates such as $Mg(BPh_4)_2$ and $Mg(BAr_F)_2$, BAr_F = tetrakis [3,5-bis(trifluoromethyl)phenyl] borate.[69] However, the solutions of such complexes either have low-voltage stability or are incapable of Mg deposition.

Ha et al. demonstrated the reversible Mg deposition of commercially available salt $Mg(TFSI)_2$ when dissolved in glyme.[70] However, this electrolyte shows a high overpotential (about 2 V) and a low cycling efficiency. Recently, Ma et al. reported the enhancement of electrochemical properties of $Mg(TFSI)_2$ tetraglyme solution by adding some quantities of $Mg(BH_4)_2$ to scavenge water and suggested that removal of water from the electrolytes is vital to achieve reversible Mg cycling.[71] The overpotential between Mg reduction and oxidation was reduced to 0.35 V with this approach, but the high oxidative stability of $Mg(TFSI)_2$ was also sacrificed due to the presence of $Mg(BH_4)_2$.

In another attempt, the TOYOTA group tried to take advantage from the well-known stability of boron cages (closoboranes) and Tutusaus et al. reported magnesium monocarborane (MMC) $Mg(CB_{11}H_{12})_2$ in glyme, which exhibits favorable electrolytic properties with high anodic stability of 3.8 V and high Mg cycling efficiency.[72] Recently, they also studied the interfacial phenomena between Mg metal and the selected electrolytes including MMC an $Mg(TFSI)_2$ solutions.[73] McArthur et al. synthesized the same compound with an alternative method.[74] The same group also prepared Mg salt with smaller 10-vertex closo-carborane anions.[75] The tetraglyme solution of

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such salt enables the Mg electrolyte with an oxidative stability >3.5 V. However, the nontrivial multistep synthesis of the starting materials and the associated high costs are the major drawbacks of such compounds from an application point of view.

Magnesium hexafluorophosphate $Mg(PF_6)_2$ was investigated when dissolved in THF/CH_3CN (acetonitrile).[76] However, the CV data indicate that the electrolytes have a low efficiency for Mg plating/stripping. Magnesocene has also been proven to be capable of Mg plating/striping, but the extremely low conductivity and low-voltage stability hinders a practical application.[77]

Recently, Arnold and co-workers reported that magnesium hexafluoroisopropylaluminate $Mg[Al(hfip)_4]_2$ in ethereal solvents can reversibly deposit Mg with high oxidative stabilities (>3.5 V versus Mg/Mg^{2+}) and conductivities (>6 mS/cm).[78] This conductive salt solution was synthesized via a three-step reaction. Firstly, both educts of magnesium fluoroalkoxide $Mg(hfip)_2$ and aluminumfluoroalkoxide $Al(hfip)_3$ need to be synthesized, followed by mixing them in DME.

In 2017, Zhang et al. reported the Mg electrolytes containing boron-centered anions (BCM).[79] The authors initially carried out the reaction of MgF_2 with tris(2H-hexafluoroisopropyl) borate $B[OCH(CF_3)_2]_3$ (THFPB) and characterized the reaction as:

$$MgF_2 + n\mathrm{DME} + 2B[OCH(CF_3)_2]_3 \rightarrow [Mg(DME)_n]^{2+} + [FB[OCH(CF_3)_2]_3]^- \quad (6)$$

The electrolytic properties of the reaction mixture using only 0.05 M MgF_2 as Mg source were examined by CV measurements, showing reversible Mg deposition, but with large overpotential and low coulombic efficiency. Surprisingly, a new anion species tetra(hexafluoroisopropyl)borate anion (denoted as $[TrHB]^-$) was detected in the initial solution after some CV cycles, implying an unanticipated side reaction during Mg cycling. In fact, THFPB was mixed with MgF_2 in a molar ratio of 10 : 1, which is in excess of five times the supposed reaction stoichiometry of 2 : 1. Therefore, the BCM electrolytes prepared in this study contain the chemically reactive component, which are indeed incompatible with Mg anode.

As bulky and weakly coordinating anion (WCA) can be excellent candidates for the formulation of electrolyte salts in LIBs,[80] Zhao-Karger et al. considered to synthesize Mg salts containing fluorinated alkoxyborate and alkoxyaluminate anions used for electrolytes.[81] This class of compounds has the formula of $Mg[Z(OR^F)_4]_2$, Z = Al, B; R^F = fluorinated alkyl group. In general, one can expect that weaker cation–anion interactions result in higher ionic conductivities. In this study, very robust and versatile routes were presented for synthesis of Mg alkoxyborates and Mg alkoxyaluminates in pure solid form, which can then be conveniently dissolved in various solvents and additionally mixed with additives to meet electrolyte and battery requirements.

The fluorinated Mg alkoxyborates can be synthesized by a one-pot reaction of $Mg(BH_4)_2$ with a fluorinated alcohol or an exchange reaction between a sodium alkoxyborate and magnesium halide in an ethereal solvent as expressed in the general Eqs. (7) and (8), respectively.

$$Mg(BH_4)_2 + 8R^F{-}OH \rightarrow Mg[B(OR^F)_4]_2 + 4H_2 \uparrow \quad (7)$$

$$2Na[B(hfip)_4] + MgBr_2 \rightarrow Mg[B(hfip)_4]_2 + 2NaBr \downarrow \quad (8)$$

The fluorinated alkoxyaluminate-based Mg salts can also be prepared through a metathesis reaction between $Na[Al(hfip)_4]$ and magnesium bromide ($MgBr_2$) as Eq. (9)

$$2Na[Al(hfip)_4] + MgBr_2 \rightarrow Mg[Al(hfip)_4]_2 + 2NaBr \downarrow \quad (9)$$

Magnesium tetrakis(hexafluoroisopropyloxy) borate ($Mg[B(hfip)_4]_2$) can be straightforwardly synthesized by the dehydrogenation reaction of $Mg(BH_4)_2$ with hexafluoro-2-propanol (hfip) in DME. The solid structure was determined by x-ray crystallography as $Mg[B(hfip)_4]_2{\cdot}3$DME [Fig. 5(a)]. It consists of typical ionic pairs, in which the Mg^{2+} ion is coordinated by three DME molecules with a slightly distorted octahedral geometry. In the counter anion $B(hfip)_4^-$, the boron (B) atom is bonded with four hexafluoroisopropyloxy groups with a tetrahedral geometry.

The thermal stability of $Mg[B(hfip)_4]_2{\cdot}3$DME was examined to be stable up to 150 °C, where DME starts to release from the complex. Moreover, it has been proofed that $Mg[B(hfip)_4]_2{\cdot}3$DME is fairly stable with addition of water and in ambient air, which is in sharp contrast to the homologous anion $Al(hfip)_4^-$ based salts being highly water sensitive.

Owing to the high electronegativity of fluorine atom, the fluorinated Mg alkoxyborates have good solubility in aprotic solvents, which make them suited for use in electrolytes. The 0.6 M DME solution of $Mg[B(hfip)_4]_2$ exhibited reversible Mg plating/stripping and a very high anodic stability [4.3 V on stainless steel (SS) electrode] [Figs. 5(b) and 5(c)]. A high ionic conductivity (6.8 mS/cm, at 25 °C) and coulombic efficiency (>99%) have also been detected.

Magnesium–sulfur batteries

Intercalation cathode materials have drawn a great deal of attention to be used for Mg batteries due to their potentially promising electrochemical characteristics that can result in high discharge voltage, high-energy density, and cycling stability. However, the strong electrostatic forces between the doubly charged Mg^{2+} ions and surrounding anions in crystal matrix makes the Mg^{2+} insertion reaction kinetics intrinsically slow. The electrochemical performance, e.g., cycling ability, cell voltage, and achievable capacity of the common intercalation compounds in Mg batteries falls far behind from that of in Li-ion batteries.[15] So far, Mo_6S_8 is still the most successful cathode enabling effectively reversible Mg^{2+} ion insertion/extraction owing to its unique crystallographic structure.[6] However, the high molecular weight and the relatively low discharge voltage (<1.5 V versus Mg/Mg^{2+}) leads to the low gravimetric energy density of the Mg cell. An alternative way to improve the energy density of an Mg battery is to utilize a

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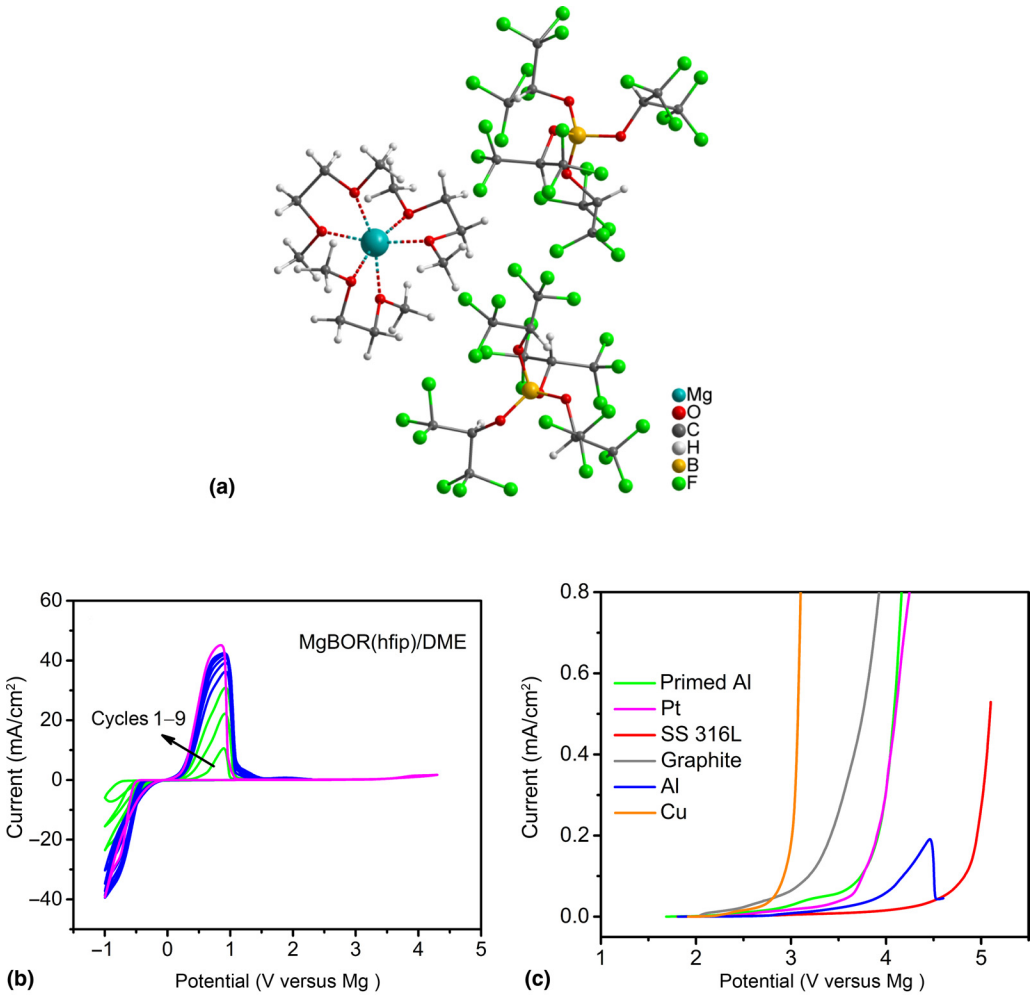


Figure 5. (a) Ball-and-stick representation of the $Mg[B(hfip)_4]_2{\cdot}3DME$ crystal. Electrochemical properties of $Mg[B(hfip)_4]_2$ in DME. (b) Cyclic voltammograms on Pt electrode at a scan rate of 25 mV/s. (c) Linear sweep voltammograms on various electrodes at a scan rate of 5 mV/s. Reprinted from Ref. 81 with permission from the Royal Society of Chemistry.

conversion cathode with high capacity. The conversion of S to sulfide in the Mg–S cell may circumvent the sluggish Mg^{2+} insertion kinetic in intercalation cathodes.

As already mentioned, Mg–S battery possesses higher energy density compared to the Li–S system when graphite anode is used for the safety reasons caused by Li metal anode. With Mg metal as a safe anode, the Mg–S full cell could reach a theoretical-specific energy of 1722 Wh/kg and 3200 Wh/L, respectively, which are much higher than those of a Li_2S/graphite cell (908 Wh/kg, 1100 Wh/L). In addition, the low cost of both Mg and S can make the Mg–S battery an attractive candidate for future battery generations. In the following, we summarize and discuss the recent progress on Mg–S batteries with different electrolytes.

Hexamethyldisilazide electrolytes

Muldoon et al. presented their non-nucleophilic HMDSMgCl–$AlCl_3$ electrolyte in THF solution and the proof-of-concept of a Mg–S battery.[28] In this study, the cell exhibited a low open-circuit voltage (OCV) of about 0.5 V and discharge voltage of 0.89 V (Fig. 6), which is only half of the theoretical cell voltage of 1.77 V. The initial discharge capacity reached 1200 mAh/g and the capacity declined to 394 mAh/g in the second cycle. The cell could be cycled for a few cycles with severe overcharging feature, which was attributed to the well-known polysulfide shuttle mechanism.

Moreover, the HMDSMgCl–$AlCl_3$ system restricts the opportunities to tune the physiochemical properties of the electrolyte by variation of the solvent because the crystalline product can be obtained in THF only.[28] However, THF is not a proper solvent for electrolyte because of its low boiling point of 68 °C and high flammability.

With the more convenient approach using $(HMDS)_2Mg$ and $AlCl_3$,[29] it was demonstrated that the Mg–S batteries with the bisamide-based electrolytes in glymes or binary glyme and ionic liquid considerably outperform those with previous

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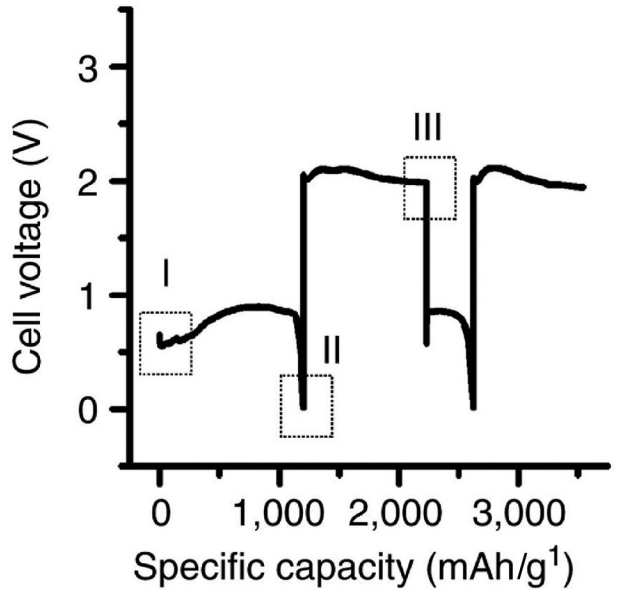


Figure 6. Discharge/charge behavior of the Mg–S cell in HMDSMgCl–$AlCl_3$ electrolytes in THF. Reprinted with permission from Ref. 28. Copyright (2011) Nature Publishing Group.

electrolytes solution in THF.[32] As shown in Fig. 7(a), the OCVs in the cells were about 2 V. The cell using the electrolyte in diglyme (DEG) exhibited a sloping voltage profile with an initial discharge capacity of 250 mAh/g. However, with additional N-methyl-N-butyl-piperidinium bis(trifluoro methanesulfonyl)imide (IL) in the electrolyte, the cell containing DEGIL showed two discharge plateaus, in which flat discharge voltage plateau at 1.65 V is close to the theoretical emf value of 1.77 V. Both cells containing the electrolyte solution in tetraglyme (TEG) and in mixtures of tetraglyme and ionic liquid (TEGIL) resembled a voltage profile similar to that of DEGIL but delivering higher capacity of 550 and 800 mAh/g, respectively. The cells comprised of S cathode with PVDF or CMC as binder and the electrolyte TEGIL remained a reversible capacity of about 260 mAh/g after more than 20 cycles [Fig. 7(b)]. Based on ex situ studies by means of UV–vis and XPS, a reaction mechanism was proposed for the Mg–S cell.[32] As shown in Fig. 7(c), S reduction reaction takes place in two steps: a fast solid–liquid two phase reduction forming high-order polysulfide (MgS_8, MgS_6, MgS_4), followed by a slow liquid–solid reduction forming insoluble MgS_2 and MgS. A fraction of the low-order Mg-PS produced during the first discharge is obviously not electrochemically active in the

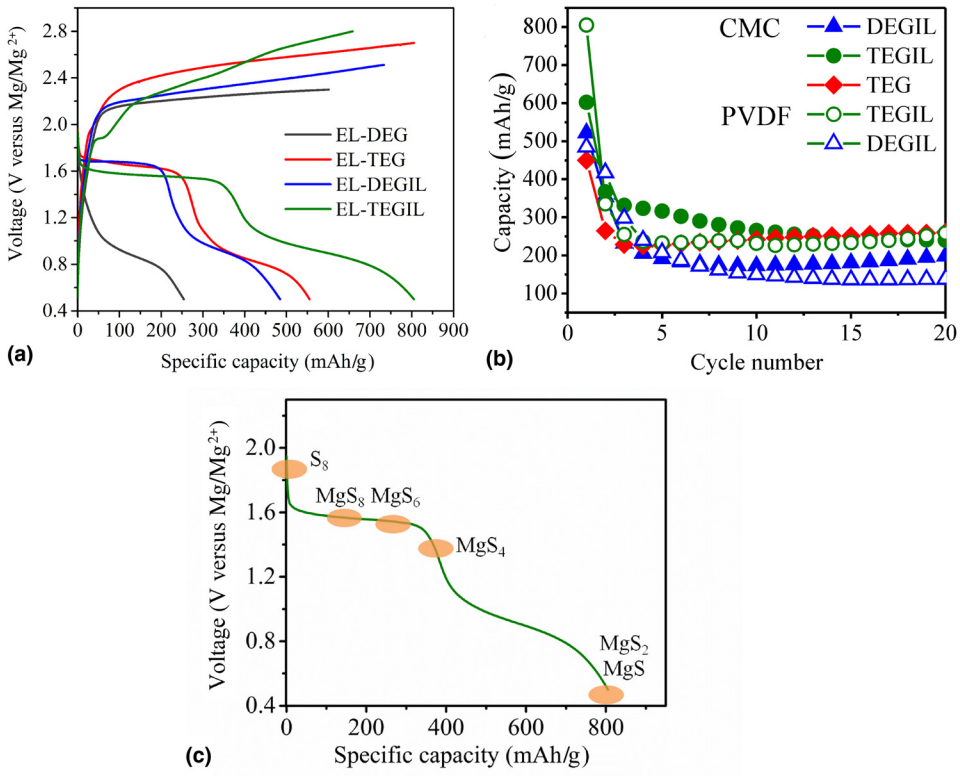


Figure 7. Results with $(HMDS)_2Mg + AlCl_3$ electrolyte: (a) Initial discharge–charge curves of sulfur cathodes with PVDF binder. (b) Cycling performance of sulfur cathode in the electrolyte in diglyme/IL (blue), in tetraglyme/IL (green), in tetraglyme (red). (c) The proposed discharge mechanism of Mg–S cell. Reprinted with permission from Ref. 32. Copyright (2015) WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim.

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subsequent recharge any more, possibly due to high kinetic barriers originating from its insulating nature and insolubility.

The study demonstrated the reversible cycling of Mg–S batteries at discharge voltage close to the theoretical voltage. However, it also indicated that the Mg–S system encounters critical problems such as the large overpotential during charge, polysulfide dissolution leading to loss of S in the cathode, capacity fading, and poor coulombic efficiency.

In a new attempt, Gao et al. introduced lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in the above-mentioned Mg bisamide-based electrolyte to enhance the reversibility of the Mg–S cell.[33] The authors assumed that Li^+ either undergoes an ion exchange reaction with MgS and MgS_2, transforming them to rechargeable Li_2S and Li_2S_2, or reacts with MgS and MgS_2 to form the long-chain polysulfide MgLi-PS, thereby decreasing the kinetic barrier for re-oxidation of MgS and MgS_2 (Fig. 8).

The cell demonstrated a capacity of 1000 mAh/g with two discharge plateaus at 1.75 and 1.0 V and stable capacity after 30 cycles. Considering the fact that electrolyte used in this work contains 1 M LiTFSI and 0.1 M Mg salt, this cell configuration can be also regarded as a dual ion battery.

In order to transfer successful concepts in the development of Li–S batteries, a sulfur nanocomposite was fabricated as cathode material by dispersing S on the highly functionalized rGO (reduced graphene oxide) and improved cycling stability and rate capability of the Mg–S batteries.[34] Yu and Manthiram recently demonstrated an advanced cell design with a cathode comprising activated carbon nanofibers (CNFs) filled with sulfur powder and a CNF-coated separator.[35] The thin layer of CNF on the separator serves as both a polysulfide captor and a current collector.as shown in Fig. 9(a). In this study, the Mg–S cells with the bisamide-based HMDS-electrolyte delivered a remarkable discharge capacity of ~1200 mAh/g at the first discharge and last for 20 cycles without suffering a fast capacity decline after the first cycle [Figs. 9(b) and 9(c)].

The bisamide electrolytes have also been employed for Mg batteries with Se and selenium–sulfur (SeS_2) cathode, respectively.[36] The Se cathode delivered a reversible capacity of 480 mAh/cm^3 for 50 cycles at a current rate of 2 C. The improved battery performance with a SeS_2 cathode could give a perspective of new sulfur based cathode materials combining the merits of both Se and S.

MACC electrolytes

MACC electrolyte is based on the reaction of $MgCl_2$ with two equivalents $AlCl_3$ in binary solvent of THF and an ionic liquid. It is fully inorganic, it was supposed to be chemically compatible with S and has recently been tested for Mg–S batteries.[53] With the nitrogen-doped graphene–sulfur (NG–S) cathode, the cell was cycled 20 times. However, the cells suffered from rapid capacity decline from 700 to 130 mAh/g in the first

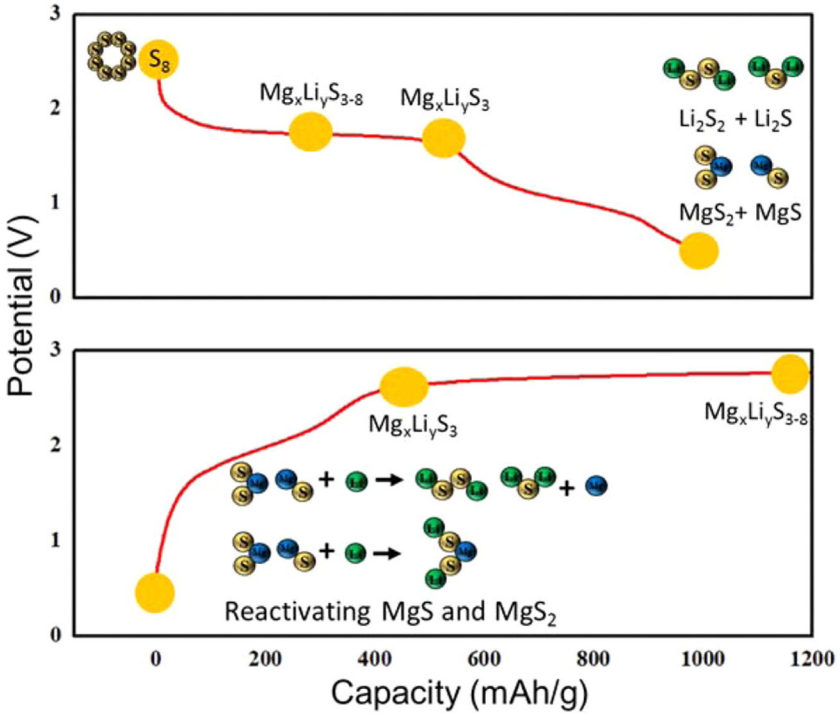


Figure 8. The proposed discharge mechanism of Mg/S Battery with LiTFSI Additive. Reprinted with permission from Ref. 33. Copyright (2015) American Chemical Society.

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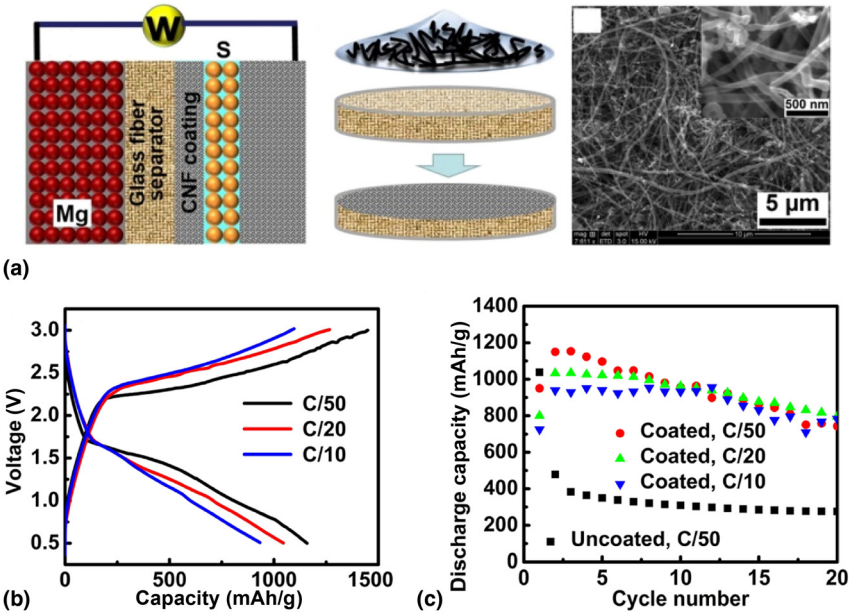


Figure 9. (a) Schematic representation of a Mg–S cell with activated-CNF-coated separator(left), preparation of the CNF-coated separator (middle), scanning electron microscopy image of the CNF(right). (b) Discharge/charge profiles of the Mg–S cells at various C-rates. (c) Discharge capacities. Reprinted with permission from Ref. 35. Copyright (2016) American Chemical Society.

cycles, a low discharge potential (<1 V) and large overpotential (>1.5 V).

Conductive salt-based electrolytes

Recent progress on new chloride-free electrolytes mitigates corrosion of cell components and has inspired researchers to develop better Mg–S batteries. However, the Cl-free metal borohydrides MBH$_4$ (M = Li, Na) can react with S forming sulfurated borohydrides, under evolution of hydrogen gas[82] making Mg(BH$_4$)$_2$ chemically incompatible with sulfur. The more inert and more stable carborane-based electrolytes from the same group are supposed to be non-nucleophilic, but have not been employed for Mg–S cells so far.

Ha et al. have evaluated the battery performance of Mg–S cells using Mg(TFSI)$_2$ in glyme as electrolyte.[70] The Mg/CMK3-S cell exhibited a very low-discharge plateau of 0.2 V with a capacity of 500 mAh/g in the first discharge and the cell could be cycled only for several cycles. Itaoka et al. prepared sulfur composites with S and bis(alkenyl) compound with a crown or linear ether unit.[83] With the electrolyte solution of Mg(TFSI)$_2$ in THF or CH$_3$CN, the cell delivered the first discharge capacity of ~600 mAh/g, but rapid capacity drop

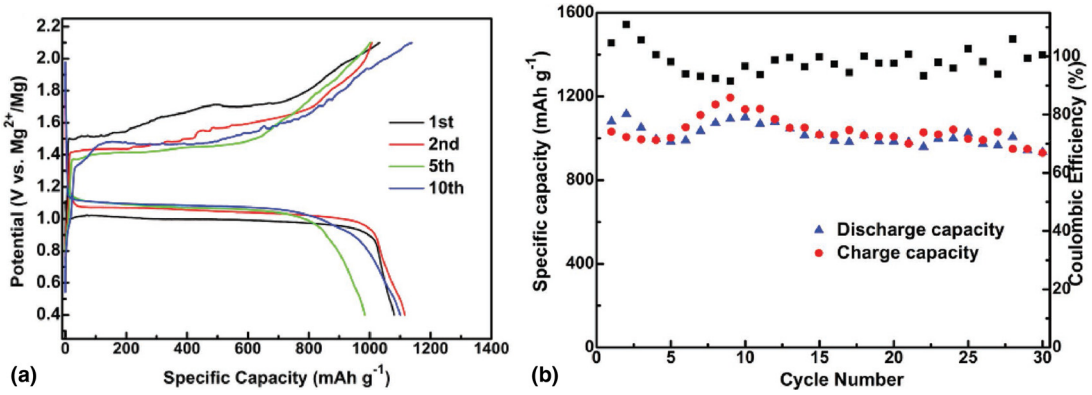


Figure 10. The electrochemical performance of S/C cathodes: (a) Discharge/charge profiles, (b) Cycling behavior. Reprinted with permission from Ref. 79. Copyright 2017 WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim.

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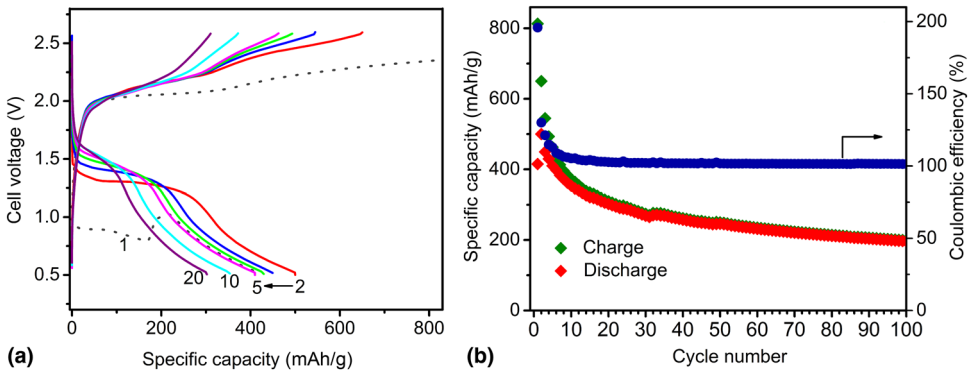


Figure 11. Battery performance of the Mg–S cell using $Mg[B(hfip)_4]_2$ in diglyme/tetraglyme as electrolytes: (a) Discharge/charge profiles, (b) Cycling behavior. Reproduced from Ref. 81 with permission from the Royal Society of Chemistry.

appeared in the second cycle. Additionally, a very low-discharge voltage (<1 V) and a large voltage hysteresis (>1.5 V) were observed. These results indicate that $Mg(TFSI)_2$ electrolytes are probably not suitable for the Mg–S cell.

Recently, Zhang et al. prepared the so-called boron-centered anion-based magnesium (BCM) electrolyte and examined its utility for Mg–Se and Mg–S batteries.[79] A first discharge capacity of 1081 mAh/g was measured for the S cathode using the electrolyte with a surprisingly low Mg concentration of 0.05 M. A relatively flat discharge voltage plateau at about 1.1 V was reported. [Fig. 10(a)]. Interestingly, the overcharging behavior is much less significant compared with the previous

Table I. A comparison of some electrolytes and their utilities in Mg–S batteries.

Electrolyte	Anodic stability on Pt (V)	Ionic conductivity at r.t. (mS/cm)	Coulombic efficiency (%)	Compatibility with sulfur	Mg-S batteries capacity (mAh/g_{sulfur}) @current rate (mA/g_{sulfur}) /cycle number
APC[22]	3.2	5 (30 °C)	~100	No	–
HMDSMgCl–$AlCl_3$[28]	2.5–3.3	No data	95–100	Yes	390@0.05/2
$(HMDS)_2Mg$–$AlCl_3$[29,32]	3.9	~2	~100	Yes	260@20/20[32] 1000@71/30[33] 236@20/50[34] 800@167/20[35]
$^{F}ROMgCl$–$AlCl_3$[41]	3.2	3.5	98	No data	–
$Mg(hfip)_2$–$2AlCl_3$[43]	>3	4.77	~100	No data	–
MACC[47,53]	3.1[47], 2.5[53]	2[47], 8.5[53]	99	Yes	70@17/20[53]
$Mg(TFSI)_2$–$MgCl_2$[59,60]	>3	5 (28 °C)	93	Yes	No data
$Mg(BH_4)_2$[66]	1.7	No data	94	No	–
$Mg(TFSI)_2$[70,71]	4/Al	5.2	No data	Yes	~200@33/4[70]
$Mg(CB_{11}H_{12})_2$[72]	3.8/Al	2.9	99	Yes	No data
$Mg(PF_6)_2$[76]	4/Al	28	99	Yes	No data
Magnesocene ($MgCp_2$)[77]	1.8/SS	0.012	98	No data	No data
$Mg[Al(hfip)_4]_2$[77]	3.5	>6	>99	Yes	No data
BCM [78]	3.5/SS	1.1	~80–99	Yes	933@50/30
$Mg[B(hfip)_4]_2$ (MgBOR-hfip)[80]	4.3/SS	6.8	~100	Yes	200@167/100

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reports and an overpotential during charge and discharge was <0.4 V. The Mg–S cells were cycled for 30 times with capacity retention >86% [Fig. 10(b)]. Se/C cathode reached a maximum specific capacity of 615 mAh/g in the 7th cycle and had capacity retention of 75% after 100 cycles.

In the study, the authors revealed that the chemical composition of electrolyte from the initial reaction mixture changed during the CV cycling, namely one of the component reacted with Mg anode, forming a new electrochemical active anion.[79] This reaction can contribute to the discharge current in the cells and contribute to the measured capacities, which can be the reason for the capacity increase in the initial cycles of both systems.

A recent study investigated the compatibility and electrochemical performance of new $Mg[B(hfip)_4]_2$ electrolytes in Mg–S cells.[81] The sulfur cathode S/CMK-3 was prepared as previously described.[32] The Mg–S cells were tested with the solution of $Mg[B(hfip)_4]_2$ in glymes. Figure 11(a) illustrates the discharge/charge curves for the extensive cycle at a current rate of 0.1 C (167 mA/cm^2). The discharge voltage remained at about 1.5 V after the first cycles. A discharge capacity of ~200 mAh/g was retained after over 100 cycles [Fig. 11(b)]. The data indicate that the overcharging behavior is a serious issue, which needs to be resolved before the Mg–S battery can be regarded as a viable system.

The properties of some electrolytes and their applications to Mg–S batteries are summarized in Table 1.

Summary and future prospects

In this review, we have summarized recent achievements in the development of Mg electrolytes, which exhibit both good electrochemical properties and chemical compatibility. The recent accomplishment in the novel highly efficient Mg ion-conductive salts provides an optimistic prospect for the realization of Mg battery technology. In particular, the new class of Mg ion conducting salts fluorinated alkoxyborates and alkoxyaluminates shows promising electrochemical characteristics compared with other state-of-the-art electrolytes. The non-corrosive nature and the robust, economic synthesis are additional advantages for practical use. These ionic Mg compounds can serve as universal electrolyte salts to be suitable to any type of cathode and anode materials, which could pave the way for high-energy Mg batteries.

The Mg–S batteries with the fluorinate alkoxyborate-based electrolytes exhibit a stable cyclability with a cell voltage close to the theoretical value and a good coulombic efficiency. To further improve the Mg–S system, efforts in cathode design and optimization of electrolyte solvent or solvent blend will be critical.

Still, fundamental understanding is lacking to a great extent and the chemistries taking place in the cells and the reactions at the electrode–electrolyte interface are not understood. It is not clear, yet, whether the formation of soluble polysulfides or the sluggish electrochemical reactivity of MgS_x species are responsible for the rapid capacity degradation in the first cycles. Expanding the knowledge basis in that field will be of paramount importance to developing strategies for enhancing the battery performance.

Acknowledgment

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