A Review of Advanced Energy Materials for Magnesium– Sulfur Batteries

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Magnesium-sulfur batteries promise high volumetric energy density, enhanced safety, and low cost for electrochemical energy storage. The current obstacles to practical applications of reliable magnesium-sulfur batteries are finding electrolytes that can meet a multitude of rigorous requirements along with efficient sulfur cathodes and magnesium anodes. This review highlights recent advances in designing better electrolytes, cathodes, and anodes. A suitable electrolyte for magnesium-sulfur batteries should allow to reversibly electroplate/strip divalent magnesium ions and should be compatible with the sulfur cathode and the other cell's components. Another challenge to be addressed is the careful engineering of the interface and microstructure in the sulfur scaffold to effectively mitigate the soluble magnesium polysulfide shuttle and to enhance the reaction kinetics. We highlight that the ongoing research in this field encourages the fundamental understanding of the reaction mechanisms and the interplay among the different components by diverse characterization techniques.

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1. Introduction

Energy density, materials sustainability, safety, and overall efficiency are primary considerations in current battery technologies.^[1-5] Lithium-ion batteries (LIBs) based on intercalation chemistry have dominated portable electronics and electric vehicles.^[6,7] However, LIBs fail in catching up with the ever-growing safety and energy density demand of emerging mobile applications, such as electric vehicles and unmanned aerial vehicles, owning to their energy density limitations.^[8–11] The advent of lithium-sulfur (Li-S) and lithium-oxygen (Li-O2) batteries has offered prospects to significantly enhanced energy density in a cost-effective manner.^[12–20] Nevertheless, the practical applications of such battery systems are strongly plagued by these grand challenges, including low active material loading,^[21-23] severe inter-

mediate shuttle, $^{[24]}$ sluggish end-product kinetics, $^{[25,26]}$ and dangerous lithium dendrite growth. $^{[27-31]}$

The exploration of earth-abundant electrode materials with high capacity and enhanced safety brings the magnesium (Mg) and aluminum (Al) ion batteries to researcher's eyes. For example, the recent demonstration of Al-S batteries is very inspiring, encouraging the research of more sustainable battery technologies.[32-34] Magnesium (Mg) ion batteries are alternatives choices comparing with Al-ion battery counterpart due to less polarity of Mg²⁺, which is beneficial to Mg²⁺ transport in electrodes.^[35–38] Although the Mg metal has a relatively higher reduction potential of -2.37 V versus SHE in comparison with lithium (Li) metal (-3.04 V),^[39] the divalent Mg²⁺ enables two electrons transfer per Mg atom resulting thus in a theoretical specific capacity of 2205 mAh g^{-1} . Considering the heavier density of magnesium than that of lithium, the volumetric capacity of magnesium anode could reach to 3833 mAh mL^{-1} , almost double value of lithium (2062 mAh mL⁻¹). The detailed electrochemical characteristics of magnesium and lithium when used as anode materials are summarized in Figure 1a. Furthermore, metallic magnesium can be safely processed under air and does not form dendrites, thus fulfilling important aspects of easy fabrication and safety operation in battery devices.^[37,40] On the other hand, the intrinsic lithium dendrite growth continuously consumes electrolytes and has the potential of causing catastrophic explosion, which presents pressing challenges for the lithium metal batteries.^[41-44]

Despite the attractive attributes, the development of Mg-ion batteries is impeded by limited choices in cathode materials which

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can offer high capacity and reversibility.^[39,45,46] The first Mg-ion battery prototype was successfully assembled using a suitable electrolyte that is neither proton donor nor acceptor in conjunction with a favorable Mo₆O₈ host that can reversibly intercalate Mg²⁺ with relatively fast kinetics.^[47] Thereafter, vanadium oxide,^[48,49] Prussian blue analogs,^[50,51] molybdenum sulfide/oxide,^[52–54] titanium sulfide,^[55] manganese oxides,^[56,57] and transition metal silicates^[58] have been explored as cathodes to pair the Mg anode. However, all these choices as cathode hosts possess low chargestore capability per molecular unit, compromising thus the key advantage of high energy density Mg-ion batteries.

The redox couple S/Mg where sulfur is the cathode and magnesium the anode is energy-dense, safety, and cost-effective.^[35,59] Sulfur and magnesium are abundant elements in the earth crust and they are readily available in various mineral byproducts. The twoelectron transfer between sulfur cathode and magnesium anode yields a theoretical voltage of 1.77 V,^[60] endowing the Mg–batteries with an impressive theoretical energy density of 3221 Wh L⁻¹, surpassing Li–S batteries (2856 Wh L⁻¹). The intrinsic dendrite-free plating of Mg²⁺ on the Mg anode surface eliminates safety concerns, unlike in Li–S batteries where due to the lithium dendrite growth their broad commercialization has been limited, unless a breakthrough achieved in solid-state electrolyte.^[61–63] If the lithium metal anode is replaced by the conversional graphite anode and Li₂S is used as cathode to guarantee safe operation, the energy density of this electrochemical combination is not competitive to even current Li–ion batteries (Figure 1b).

In this contribution, recent advances in Mg–S batteries are reviewed through specifying the achievements in sulfur cathode, non-nucleophilic electrolyte, and Mg metal anode, respectively. Conclusions and current challenges are included, in order to inspire further exploration of Mg–S and other rechargeable batteries.

2. Principles of Mg-S Batteries

A schematic illustration of the components in a Mg-S cell is shown in Figure 2a. A commonly performed Mg-S cell is comprised of a magnesium metal anode, an organic electrolyte, and a sulfur-based composite cathode. The magnesium metal is oxidized to produce Mg²⁺ which mitigates to the sulfur cathode through the organic electrolyte and separator, while electrons arrive in the active sulfur materials via an external electrical circuit to keep the sulfur cathode electric neutrality during the discharge reaction. The successive reduction in sulfur during discharge process generates magnesium polysulfides (Mg-PSs) with various chain lengths, analogous to lithium polysulfides. Specifically, elemental sulfur is firstly converted to long-chain polysulfide during the reduction, and then the long-chain polysulfide cleaves to short-chain polysulfide, followed by solid-state transition from short-chain polysulfide to MgS (Figure 2b).^[64,65] The intermediate Mg-PSs readily dissolved in electrolyte causes shuttle effect, rendering low Coulombic efficiency and active loss from cathode. The end-products (S, MgS₂, and MgS) are insoluble in electrolyte and re-distributed on the conductive scaffolds.^[66] The charge reaction is generally reversed from MgS_2/MgS to S, but accurate pathways have not been clearly identified yet. The redox reactions can be expressed as following.



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Li–S batteries, Li metal anodes, etc.



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Researcher at the Department of Physics and Astronomy at the University of Pennsylvania. He received his Ph.D. in Chemical Engineering from Tsinghua University, China in 2014, followed by a 3-year postdoc training at A. J. Drexel Nanomaterials Institute and the Department of Material Science and Engineering at Drexel University. His research

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Magdalena Titirici obtained her PhD at the University of Dortmund, Germany. Between 2006– 2012 she led the group "Sustainable Carbon Materials" at the Max Planck Institute of Colloids and Interfaces, Potsdam, Germany where she also did her "Habilitation. In 2013 Dr Titirici became an Associate Professor in Materials Science Queen Mary University of London. She was

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Qiang Zhang received his bachelor and Ph.D. degree from Tsinghua University, China in 2004 and 2009, respectively. After a stay in Case Western Reserve University, USA, and Fritz Haber Institute of the Max Planck Society, Germany, he joined in Tsinghua University, China at 2011, and promoted to be a full professor at 2017. His current research interests are advanced

energy materials, including lithium metal anode, lithium sulfur batteries, and electrocatalysis. He is editor of Journal of Energy Chemistry, Guest Editor of Advanced Functional Materials (Li-S batteries) and Energy Storage Materials (Li metal anode). He has been awarded NSF for Outstanding Young Scholars, Young Top-Notch Talent from China, and Newton Advanced Fellowship from Royal Society, UK. He is selected as 2017 Highly Cited Researchers by Web of Science, Clarivate Analytics. More details can be found in his Research ID (B-1799-2012 http://www.resea rcherid.com/rid/B-1799-2012), ORCID (0000-0002-3929-1541) or GoogleScholar http://scholar.google.com/citations?user= qkcc0OYAAAAJ&hl=en. Mg anode: anodic reaction

$$Mg \to Mg^{2+} + 2e^{-} \tag{1}$$

Sulfur cathode: cathodic reaction

$$S + Mg^{2+} + 2e^- \rightarrow MgS$$
 (2)

Overall cell operation

$$Mg + S \rightarrow MgS$$
 (3)

The development of efficient Mg–S batteries is currently hindered by the choice of electrolyte that can effectively transfer Mg^{2+} and are chemically and electrochemically compatible with sulfur cathodes, Mg anodes, and other battery parts.^[38,67] Because of this, it is difficult to evaluate the influence of rationally designed sulfur cathodes and Mg anodes on the battery performance. Commonly used electrolytes (carbonates) in Li–ion battery systems form a passivating solid electrolyte interface (SEI) that is impermeable for Mg^{2+} transfer.^[68,69] The sulfur cathode with electrophilic features prevents the use of nucleophilic electrolytes and non-nucleophilic electrolyte was firstly proposed by Muldoon and coworkers to enable the proof-of-concept of a Mg–S cell.^[70]

Another significant challenge is to improve kinetics in order to host reversibly divalent Mg^{2+} .^[71,72] Sulfur and MgS/MgS_2 are electronically and ionically insulating. This requires a rational design of the host architecture to establish kinetically favorable redox reactions. The dissolution of Mg-PS intermediates into organic electrolyte requires tailored porosity and the manipulation of interfacial properties to mitigate Mg-PS diffusion. Therefore, discovering sulfur hosts that can suppress Mg-PS migration and facilitate electron/ion transportation will be highly beneficial to an electrochemical performance of Mg–S batteries.

Metallic Mg anodes have been rarely investigated in Mg–S batteries. The commercial Mg sheets need to be intensively polished under Ar to remove the magnesium oxides, since they are electrochemically inactive and block Mg²⁺ deposition.^[20,73] The manipulation of the interfacial properties between the Mg anode and the electrolyte to allow efficient/ reversible Mg²⁺ deposition/dissolution dominate the research on Mg anode, as failing to do so would offset the feasibility of structure design in Mg anodes.^[74]

Progress and step-changes in Mg–S battery performance depend on advances in sulfur host design, organic electrolyte development, and Mg anode construction.^[75] In the following sections, we present recent development in the three core components of Mg–S batteries.

3. Non-Nucleophilic Electrolytes

The electrolyte is one of the most important components in Mg–S batteries.^[67,76] An ideal electrolyte must be ionically conductive for Mg^{2+} ion, electronically insulative, and chemically compatible with all the other cell parts in redox reactions that neither react with sulfur nor passivate with Mg anode. Electrophilic sulfur is prone to obtain/share electrons from molecules/ions, while the nucleophilic electrolyte has the capability to donate electrons. The Mg-ion batteries with intercalation hosts can use nucleophilic electrolyte to allow reversible Mg^{2+}



Figure 1. Comparison of electrochemistry of lithium/magnesium anode and related battery systems. a) Capacities and reductive potentials for lithium and magnesium metal anodes. b) Energy densities and thermodynamic equilibrium voltage of Li–S and Mg–S batteries.

lithiation. However, the conventional nucleophilic electrolyte would irreversibly react with electrophilic sulfur, causing cell death immediately.

The first demonstration of a Mg–S battery prototype was done by Muldoon in 2011 through the reaction of AlCl₃ with hexamethyldisilazide magnesium chloride (HMDSMgCl) in tetrahydrofuran (THF) solvent, forming a non-nucleophilic $[Mg_2(\mu-Cl)_3\cdot 6THF][HMDSAlCl_3]$ complex with a voltage stability up to 3.2 V.^[70] The obtained products were further purified by re-dissolving them in THF in order to remove any unreacted HMDSMgCl, as it could narrow the working potential window of electrolyte. The crystal structure of this complex was determined by single-crystal X-ray diffraction (**Figure 3a**). The cation consisting of two octahedrally coordinated Mg centers bridged by three chlorine atoms. The anion was an aluminum atom tetrahedrally coordinated by one HMDS group and three chlorine atoms. The voltage stability of as-obtained electrolyte was 0.8 V higher than that of HMDSMgCl electrolyte and the Coulombic efficiency reached to 100% (Figure 3b). This non-nucleophilic electrolyte allowed the Mg/S coin cell to deliver a high discharge capacity of 1200 mAh g^{-1} (Figure 3c). However, it is found that the cell exhibited a large overpotential $(\geq 1.0 \text{ V})$ and the capacity rapidly dropped discharge to 394 mAh g^{-1} in the subsequent cycle. These drawbacks were mainly attributed to the significant shuttle of Mg-PS between electrodes and Cl⁻ corrosion to cell parts, which indicated the exploration of Mg-PS shuttle-retarded hosts and corrosion-free electrolytes. This pioneering research was followed by the preparation of other Mg complexes, such as [(HMDS)₂Mg],^[66] ROMgCl,^[77] RSMgCl,^[78] and MgCl₂.^[79] These were all investigated as non-nucleophilic Mg electrolytes, for now with limited potential for the practical operation of Mg-S batteries.

One important drawback of the chloride-based cations is their corrosive nature to all cell parts.

Therefore, research to discover noncorrosion electrolytes is critical.^[80] In this respect, Li et al.^[81] synthesized a $[Mg(THF)_6][AlCl_4]_2$ complex in ionic liquid/THF cosolvents. The chloride-free cation significantly alleviated corrosion activity. The molecular structure of [Mg(THF)₆] [AlCl₄]₂ complex is shown in Figure 3d. The cation consists of only one Mg atom octahedrally coordinated by THF, avoiding a bulky binuclear cation (e.g., $[Mg_2(\mu-Cl)_3.6THF]$) that is detrimental for the transport of Mg²⁺ in the electrolyte and electrolyte–electrode interface. The evaluation of the symmetric Mg Electrolyte |Mg cells showed an excellent Coulombic efficiency close to 100% below a current density of 300 μ A cm⁻², despite the fact that remarkable polarization and voltage fluctuation were identified at relatively higher current densities (Figure 3e). The application of this electrolyte allows an initial discharge capacity of 700 mAh g^{-1} . However, this drops rapidly to 130 mAh g^{-1} in the first five cycles (Figure 3f). The proposed capacity fading mechanism was shuttling of polysulfides from the cathode, resulting in a dense and resistive film on the Mg anode. To increase the



Figure 2. a) Schematic illustration of challenges of Mg–S batteries. b) Working mechanism and speciation evolution of sulfur cathode in discharge process (reproduced with permission from ref. [66], © Wiley-VCH 2014).



Figure 3. Non-nucleophilic electrolyte in Mg–S batteries. a) Crystal structure of $[Mg_2(\mu-Cl)_3 \cdot 6THF][HMDSAlCl_3]$ determined by single-crystal X-ray diffraction. b) CV profiles of various Mg salts in THF solvent (Green: HMDSMgCl; Blue: in situ formation of $[Mg_2(\mu-Cl)_3 \cdot 6THF][HMDSAlCl_3]$; Red: crystal $[Mg_2(\mu-Cl)_3 \cdot 6THF][HMDSAlCl_3]$. Inset in (b) is the charge balance between deposition and dissolution of Mg. c) Discharge and charge profiles of a Mg–S cell (reproduced with permission from ref. [70], © Nature Publishing Group 2012). d) X-ray crystal structure of $[Mg(THF)_6][AlCl_4]_2$ complex. e) Cycling behavior of a symmetrical cell with $[Mg(THF)_6][AlCl_4]_2$ at different current densities. Inset is the Coulombic efficiency of cells. f) Cycling performance with 20 cycles (reproduced with permission from ref. [81], © Wiley-VCH 2016).

operation current density, oxidative stability and Mg salt concentration, the same group recently prepared another mono-magnesium ion electrolyte by adding Mg salt and AlCl₃ in dimethyl ether (DG) solvent, forming a $[Mg(DG)_2][HMDSAlCl_3]_2$ with a high concentration of 1.5 m.^[40] The operation current density in symmetric cells could be enhanced to 5.0 mA cm⁻² and the anodic stability could be extended to 3.5 V. However, the attempts to apply electrolytes in Mg–S batteries failed to narrow the cell overpotential and the capacity based on sulfur was not impressive, which implied enough space to optimize the electrolyte recipes to promote the sulfur interconversions.

Boron (B)-based electrolytes are another important electrolyte family for Mg–S batteries. B-centered anions are generally compatible with the Mg anodes and are chloride-free electrolytes.^[82,83] Mohtadi et al.^[84] were the first to report magnesium borohydride ([Mg(BH₄)₂]) electrolytes in THF and DME solvent. However, the anodic voltage was less than 1.7 V, which affected the suitable function of the sulfur cathode.

Very recently, Zhang et al.^[82] proposed a well-defined boroncentered anion-based magnesium electrolyte (BCM electrolyte). This possesses advantages of easy synthesis, high ionic conductivity, wide potential window (3.5 V vs Mg), compatibility with electrophilic sulfur, and non-corrosivity to cell assemblies. They summarized the chemical and electrochemical properties of various anion regimes in a non-nucleophilic electrolyte, and their specific problems encountered practical applications as depicted in colored boxes in **Figure 4a**. In their strategy, the properties of BCM electrolyte, such as electrochemical window, salt concentration, and compatibility with Mg anode, could be easily tuned through a precise selection of anions groups. Especially, the tris(2H- hexafluoroisopropyl) borate (THFPB)/MgF₂ salts in DME solvent resulted in [Mg(DME)_n][FTHB]₂ complex (Figure 4b), which exhibited a wide operation window of 3.5 V. Coupling of Mg anode and sulfur cathode with 85 wt.% sulfur contents and 1.5 mg cm⁻² sulfur loading, the cell delivered a discharge capacity of 1081 mAh g⁻¹ with a flat voltage plateau of 1.1 V while no overcharge was observed in the following cycles (Figure 4c). The superb capacity retention (30 cycles with 86.4% vs first discharge capacity) indicated the great success of the electrolytes enabled by novel design concept. The same group simplified even further the synthetic procedure of the magnesium salts and enhanced the Mg stripping/plating efficiency through a one-step in-situ formation of tetranuclear [Mg₄Cl₆(DME)₆]²⁺ cation. The larger tetranuclear complex needs less additional energy to desolvate during the Mg plating, which benefits the formation kinetically.^[85]

Tuning anion–cation interactions is versatile to manipulate the ion association and conduction. Zhao-Karger et al.^[86] presented a series of Mg salts containing weakly coordinating fluorinated alkoxyaluminate and alkoxyborate anions. High electronegativity of fluorine atoms leads to a good solubility in aprotic solvents. The crystal structure of the targeted magnesium tetrakis(hexafluoroisopropyloxy)borate (Mg[B (hfip)₄]₂) consists of Mg²⁺ cation solvated in DME and [B(hfip)₄]⁻ anions where the boron atom is bonded with four hexafluoroisopropyloxy groups with a tetrahedral geometry. CV tests suggested a gradual increase in the current density during the in initial cycles, most probably due to the Mg deposition in the first cycle facilitating the nucleation of crystalline phases during the subsequent cycles. The anodic current density was as high as 45 mA cm⁻² and oxidative voltage stability with



Figure 4. Boron (B)-based electrolyte in Mg–S batteries. a) Decorated periodic table for directing efficient Mg-ion electrolytes. b) BCM electrolyte containing THFPB and MgF₂ salts with a scan rate of 5 mV s⁻¹. c) Charge/discharge profile of the cell with BCM electrolyte at a current density of 0.05 A g⁻¹, showing excellent reversibility and stable plateaus (reproduced with permission from ref. [82], Wiley-VCH 2017).

other electrode ingredients, linear sweep was performed with various substrates such as stainless steel (SS), Al, primed Al, and Cu, indicating the feasibility of the developed electrolyte for the sulfur cathode.

Previous research in Li–ion and Li–S batteries has suggested that electrolyte additives could significantly enhance the physicochemical properties of the electrolytes and could have a positive impact on the electrochemical performance of the battery system.^[87–89] The current state of the art on the function of the electrolyte additives in Mg–S batteries aims at activating Mg reversibility and suppressing the Mg–PS shuttle.^[66,90–92] LiTFSI was an efficient Mg electrolyte additive to mediate the chemical reactivation of MgS_x as demonstrated with a very high capacity of 1000 mAh g⁻¹ after 30 cycles (**Figure 5a**).^[90] It was suggested that

the higher order Mg-PS solubility was mediated by Li⁺ and that this had a direct influence on the rechargeability of low-order Mg-PS. The surface interaction between magnesium and sulfur with the assist of lithium increased the high-order Mg-PS solubility during the discharge process, which accelerated the reaction kinetics of insoluble low-order Mg-PS. In the charge process, MgS was firstly lithiated by Li⁺ due to the natural negative potential of the Mg metal and then the formed MgLi-PS. This enabled further reaction with the dissolved elemental sulfur to form soluble higher order MgLi-PS (Figure 5b). The introduction of LiTFSI could increase the solubility of Mg-PS species thereby promoting their migration toward Mg anode, which then deposited on the surface of the Mg anode. The buildup of Mg impermeable layer on the Mg anode may

account for large charge/discharge hysteresis and shot cycle life of cells. The combination of the Li mediator and the cell configurations that acquired from Li–S batteries is an option to simultaneously increase sulfur utilization and impede active species moving.

Opposite to increase the solubility of Mg-PS, low donor number (DN) solvents have an inferior solvation power toward Mg compounds. This leads to a reduced tendency for the Mg-PS shuttle.^[66] Ionic liquids (ILs) have also been demonstrated to be another efficient electrolyte additive for Mg-S batteries. ILs possess superb chemical and thermal stability, nonflammability and low vapor pressure, and thus have the prospect of enhancing the electrolyte stability as co-solvents. Zhao-Karger et al. proposed a new electrolyte system that contained a (HMDS)₂Mg in diglyme solvents plus a TFSI-based IL as a weakly coordinating co-solvent to alter the thermodynamic and kinetic properties of sulfur and magnesium interconversion. The addition of IL in diglyme (DEG) and tetraglyme (TEG) results in oxidation stabilities up to about 3.0 V (Figure 5c). The cell containing DEGIL and TEGIL exhibited a drastic capacity increase (490 and 800 mAh g^{-1} , respectively) comparing with the cells that contain only DEG or TEG (250 and 550 mAh g^{-1} , respectively). In addition, the introduction of IL in DEG exhibited quite remarkable changes in the discharge behavior, where two plateaus are presented instead of only one plateau in DEG cells (Figure 5d). This work also investigated the influence of binder on the Mg–S battery performance. Incorporation of carboxymethylcellulose (CMC) binder displayed enhanced discharge capacity mainly ascribed to the presence of oxygen atoms in CMC that provided better anchoring sites to bind the mobile sulfur species (Figure 5d,e). As expected, the limited solubility of long-chain Mg-PS inevitably increased the resistivity of Mg²⁺ transport, which manifested as large charge/discharge gap. The rational design of the interface of cathode/IL to allow high sulfur utilization was expected to surmount this challenge.

Ongoing research on searching for suitable electrolytes in terms of cell compatibility, ionic conductivity, viscosity, and chemical/electrochemical stability yielded significant advancements in battery performance improvement along with fundamental insights into the mechanism of Mg–S batteries. The development of non-nucleophilic electrolyte capable of coupling electrophilic sulfur relies on the exploration of magnesium salts, solvents, and additives to stepwise fulfill the rigorous requirements of Mg–S systems.



Figure 5. The functions of electrolyte additives on electrochemical behavior of Mg–S batteries. a) Schematic presentation of sulfur species with LiTFSI additive, and comparison of 30 cycles stability with/without LiTFSI. b) The mechanism of discharge/charge processes regulated by LiTFSI reactivation (reproduced with permission from ref. [90], \bigcirc American Chemical Society 2015). c) CV profiles of the electrolyte IL in DEG and TEG solvent at a scan rate of 25 mV s⁻¹. d) Initial discharge–charge curves of sulfur cathode using (d) PVDF binder and (e) CMC binder with different electrolyte compositions (reproduced with permission from ref. [66], \bigcirc Wiley-VCH 2014).

4. Sulfur Cathodes

Due to the development of Mg-based electrolytes with non-nucleophilic features to match the electrophilic sulfur cathode, ^[70,93] a great deal of research has been done on the rational design of efficient sulfur hosts and cell configurations in order to build express electronic and ionic pathways and restrain the Mg-PS shuttle.^[94,95] The same design principles of sulfur cathode in Li–S batteries are also applicable to Mg–S batteries. These include tuning hierarchical porosity to store sulfur and developing sulphifilic interfaces to anchor Mg-PS intermediates.^[96] However, the divalent Mg²⁺ ions exhibit much higher diffusion barrier compared with the monovalent Li⁺, resulting in large overpotentials and sluggish reaction kinetics.

Initial attempts to investigate sulfur cathodes coupled with nonnucleophilic electrolytes were based on the simple physical mixture of sulfur powders with carbon black or acetylene black.^[70] Nevertheless, Mg-PS diffusion and insoluble redox products deposition inevitably block the Mg²⁺ transportation and impact the reversibility of sulfur conversion.^[97]

Two-dimensional (2D) graphene-based materials possess unique characteristics such as high conductivity, large specific surface area, excellent chemical stability, and tunable heterogeneous surface capability. Vinayan et al. reported a graphene–sulfur cathode to improve cyclability and rate capability of Mg–S cells (**Figure 6a**). This method delivered an initial discharge capacity of 1024 mA h g⁻¹ and a capacity of 236 mA h g⁻¹ remained after 50 cycles (Figure 6b).^[98] This improved battery performance was attributed to the fact that graphene can act as a buffer to accommodate the volume changes upon

electrochemical cycling between sulfur and MgS. In addition, the large surface area of graphene was beneficial to disperse active sulfur and oxygen groups over the surface of graphene and improve the interaction with sulfur. However, the quick capacity fading was identified in the initial cycles and the obtained S-rGO composites could not bear with enough current density, implying the lack of regulating the sulfur re-deposition to obtain enough contact areas between active materials and conductive substrates. Graphdiyne is an analogue of graphene, with butadiyne linkages $(-C \equiv C - C \equiv C)$ to benzene rings, which leads to lower atom density^[99,100]. The opening of acetylenic bond ($-C \equiv C-$) has the possibility to bind polysulfides by forming sulfur-rich organic compound cathode to immobilize Mg-PS (Figure 6c).^[101] Du et al.^[101] designed sulfide graphdiyne that can help in forming lower molecular weight sulfides (S₂₋₄). The proposed sulfide graphdiyne cathode was compatible with Grignard reagent-based electrolytes (all phenyl complex [APC] type electrolytes) and demonstrated an attractive discharge capacity of 1124.9 mA h g^{-1} which is maintained to 458.9 mA h g^{-1} after the 36th cycle. However, a large overpotential was identified and the discharge plateau dropped to 0.8 V (Figure 6d), which is way below the theoretical one (1.77 V). This was potentially attributed to the low Mg²⁺ mobility in the incapsulated smaller sulfur molecular species within the graphdiyne. It is noteworthy that the binding active sulfur to the graphdiyne scaffold through opening acetylenic bonds resulted in the low discharge plateau, which may compromise the energy density of Mg-S batteries. This distinct lithiation behavior is analogous to sulfur/polymer cathode in Li-S batteries.

Recently, metal-organic framework (MOF)-derived carbons have gained popularity in the field of energy storage due to their



Figure 6. Application of 2D materials in sulfur cathode for Mg–S batteries. a) SEM image of S-rGO composite. b) Cycling performance of S-rGO cathode at 20 mA g^{-1} and charge/discharge curves at various current densities (reproduced with permission from ref. [98], \bigcirc The Royal Society of Chemistry 2016). c) Preparing sulfide graphdiyne cathode. d) Initial charge/discharge profiles of sulfide graphdiyne cathode (reproduced with permission from ref. [101], \bigcirc Wiley-VCH 2017).

ultrahigh surface area and tuneable structural topology.^[102,103] Zhou et al.^[94] used ZIF-67 as a precursor to produce functional carbon scaffolds with nitrogen (N) and cobalt (Co) co-doping that can effectively trap soluble polysulfides through strong chemical interactions between sulfur species and carbon scaffolds (**Figure 7a, b**). The as-obtained sulfur cathode in combination with a lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt mediator exhibited a high initial capacity of 600 mA h g⁻¹ at 1 °C during the first cycle. The capacity was preserved at 400 mA h g⁻¹ after 200 cycles, and this was maintained even at a ultrahigh rate of 5 °C (Figure 7c). The impressive cyclability and rate capability of the MOF-derived carbon sulfur cathode implied that the sulfur host can effectively accelerate the kinetics of sulfur reaction with Mg²⁺ guest ions, providing a viable solution to the future development of high power S–Mg batteries.

Modifying the cell's configuration also represents a feasible route to improve the battery performance and safety.^[104] Manthiram's group has pioneered a new concept where a carbon interlayer introduced between the separator and cathode in Li–S batteries resulted in a clearly improved electrochemical performance.^[105,106] Similarly, they

demonstrated a sulfur cathode with a preactivated carbon nanofiber (CNF) matrix filled and a CNF-coated separator (Figure 7d).^[95] The modified CNF separator simultaneously traped polysulfide intermediates and acted as an upper current collectors to facilitate higher sulfur utilization. This sandwiched structure delivered a remarkable discharge capacity of 1200 mA h g⁻¹ during the first cycle. This capacity was maintained for at least 20 cycles which were not observed for the unmodified cells (Figure 7e). One of the critical factors to dictate cycling performance is to re-activate the "dead" sulfur during the subsequent cycling. The coating layer on separator acted as an activator to reuse the sulfur species that diffuse out of conductive substrates. This could explain the high discharge capacity of uncoated cells whereas exhibited rapid capacity decay upon cycling.

Clear advances in Mg-S batteries require a combination of better cathode configurations; however, this alone is not sufficient and efficient electrolytes that can transport ${\rm Mg}^{2+}$ while being compatible with other cell components are needed. Here, the case of Li-S batteries represents a good inspiration for developments in the Mg-S counterparts.^[107], and great achievements are foreseeable if further breakthroughs in electrolyte are realized.



Figure 7. Functional sulfur cathode for Mg–S batteries. a) Schematic illustration of ZIF-C-S composite preparation. b) SEM image and corresponding elemental distribution of ZIF-C-S composite. c) Cyclability and rate capability of ZIF-C-S cathode with LiTFSI mediator (reproduced with permission from ref. [94], \bigcirc Wiley-VCH 2018.) d) Cell configuration of Mg–S cell with an activated CNF-coated separator. e) SEM image of the CNF-coating layer (reproduced with permission from ref. [95], \bigcirc American Chemical Society 2016).



Figure 8. Schematic illustration of morphology evolution of Mg deposition/stripping in DEG system (a1–a7) and TEG system (b1–b7) (reproduced with permission from ref. [108], \bigcirc Elsevier 2018).

5. Magnesium Anodes

The attractive feature of Mg-S batteries is their high energy density. This can be achieved only when magnesium anodes are employed, otherwise their energy density cannot surpass current Li-ion batteries.^[35] Research in Mg-S batteries being concentrated on searching for efficient electrolytes resulted in less publications on the Mg anode. A reversible electroplating/striping of Mg^{2+} on the anode surface is the prerequisite to a good performance. Hu et al.^[108] directly observed the morphology evolution of Mg plating/stripping in DEG- and TEG-based electrolyte with the assistance of in situ atomic force microscopy (AFM) and optical imaging (Figure 8). It was revealed that the Mg plating behavior strongly depends on the nature of the solvents used. The DEG system with weak solvation of Mg²⁺ induces rapid dynamic processes and nonuniform nucleation and stripping. On the other hand, TEG molecule with five oxygen atoms exhibits a strong solvation toward Mg^{2+} , which reduces the desolvation process, thus resulting in uniform nucleation, crystallization, and stripping. Therefore, the TEG system exhibits a higher specific capacity and better reversibility than the DEG system.

Porous electrodes are known to render better charge transport properties due to the interconnected channels and scaffolds for a rapid diffusion of ions and electrons in a working cell. A powder Mg anode was proposed and demonstrated the effectiveness of structure design on the improvement of Mg–S batteries.^[109] However, the electrochemical behavior of sulfur conversion is quite complex, depending on process pressure, electrolyte recipes, and concentration, leading to puzzling conclusions. The interface and structure design in Mg anodes still leave enough space to explore, while the breakthrough of electrolyte might boost the research of this field.

Design of alloy or intercalation anodes to host Mg²⁺ ions is another trend to develop high efficiency Mg-based batteries, since these hosts process the capability to buffer volume variation due to pre-formed skeleton.^[110–113] The successful application of Bi nanotubes as an alternative anode material for rechargeable Mg-ion batteries has demonstrated the feasibility of nanostructured alloy anode in view of accommodating the large volume change and reducing Mg²⁺ diffusion length.^[111] However, the alloy or intercalation anodes have not yet been reported in the Mg–S system.

In the current stage, Mg–S batteries are far less competitive to Li–ion technologies in terms of energy/power densities and cycle life. The research of specific electrodes and electrolyte components is still in the

proof-of-concept step. For example, most of the reported sulfur content in cathodes only accounts for 20~40%, and flooded the electrolyte dosage (electrolyte/sulfur ratior \geq 20). Even in such test conditions, the cycle life is hardly more than 100 cycles. Besides, stable and longterm electrochemical plating/stripping of magnesium ions on magnesium anode is urgently required, which is the prerequisite to design matched amount of magnesium to sulfur cathode. Accordingly, the scientific and engineering challenges result in difficulties to assess real energy/power densities and cycling life in pouch cells, which is a critical step to design a practical battery. Despite such a pessimistic scenario, the recent achievements in electrolyte and electrodes, both in mechanistic understanding and in performance enhancement, present a tiny light to go ahead for Mg–S batteries, aiming at push battery technology beyond Li-ion chemistry.

6. Conclusions and Prospects

The exploration of Mg-S batteries is ongoing, targeting an energy density that outperforms the current Li-ion and ongoing Li-S/O2 systems. Particular research interests are given to non-nucleophilic electrolytes for Mg-S batteries where three preliminary attempts have been done. The first one aims at achieving a periodical deposition/dissolution of Mg²⁺ to generate a Mg-conducting SEI, analogous to the case in the anode of Li-ion batteries. This expectation was inherently limited by the fact that the strong polar magnesium ions with divalency exhibit a much higher energy barriers to crossover between electrolyte and anode than that of monovalent Li⁺. The second attempt relates to compatible Mg salts and organic solvent to electrophilic sulfur cathodes and other cell components. Specifically, the applied electrolyte should exhibit enough oxidative stability to allow complete extraction of Mg from the sulfur cathode during the charge process. Due to this, magnesium chloride-based electrolytes are not favorable choices considering the chloride corrosion to cell parts, although some chloride-based electrolytes have been identified as a wide working potential. Instead, boron-based electrolytes with the assistance of efficient additives (e.g., Li salts and ionic liquid) present good opportunities to meet the specific requirements for practical Mg-S batteries. Finally, the electrolyte has to exert efficient transport properties, such as ionic conductivity/diffusivity, viscosity, transference number, and dielectric constants. For instance, a low viscosity of electrolyte is beneficial to Mg²⁺ transport,

while a too low viscosity will aid Mg-PS shuttle, resulting in rapid capacity decay during cycling. Sufficient dielectric constant helps the disassociation of the magnesium salt in solution and thus increases its concentration, which mitigates the Mg-PS crossover.

Rapid redox kinetics of sulfur cathode and magnesium anode calls for rational design of the interface properties and the scaffold structure, wherein electron and working ions transfer/transport take place. However, the development of sulfur cathode and Mg anode is far less active comparing with the electrolyte. In sulfur cathode, the conversion reaction involves the formation of soluble and insoluble sulfur species, leading to the dissolution and re-distribution of active materials on the conductive matrix, respectively. The design principles of sulfur cathode in Li–S batteries are also applicable to Mg–S batteries, among which surface chemisorptivity, charge conductivity, and electrode porosity are anticipated to play vital roles in regulating the kinetic features and the transport of active species. In magnesium anodes, the electroplating of divalent Mg²⁺ in aprotic solvents is not straightforward and their interfacial mechanism has not been elucidated and this severe hinders the development of efficient magnesium anodes.

Rechargeable Mg–S batteries are still in their early stage. Mg–S batteries feasible for practical applications require significant breakthroughs in sulfur cathode, electrolyte, and magnesium anode. Besides the innovations from material perspectives to build better Mg–S batteries, critical mechanistic understandings of working Mg–S cells should also deserve special attentions.

- (1) Why is the discharge plateau obtained from experiments far below theoretical one? Most of Mg–S cells displayed the discharge plateau at around 1.0 V or below, whereas the theoretical one is 1.77 V. It is not reasonable to ascribe such large gap to the solely sluggish kinetics of Mg/S reactions. Some other mechanisms are highly requested to determine discharge plateaus, such as electrolyte solvation capability, and passivation of sulfur cathode or anode immediately after assembling cells.
- (2) What are the final products of redox reactions? In principle, MgS and S are the final discharge and charge products to store and release theoretical energy. However, there are not sufficient evidences to confirm the surmise. The chemical bond between magnesium and sulfur is too strong to break for the following charge. For instance, there has never been a report on the MgS as a cathode material for Mg–S batteries. Therefore, the final redox products are more probably a mixture of sulfur species or amorphous MgS.
- (3) What is the critical role of soluble Mg-PS in the redox reactions? It is generally believed that lithium polysulfides serve as a catalyst to propel the sluggish kinetics of Li₂S₂/Li₂S deposition and dissolution. If the solid products cover the conductive matrix in the Mg–S chemistry, solution-mediated charge transport/transfer would be a dominant routine to guarantee successive redox reactions. Therefore, it is supposed that soluble Mg-PS also act as promotor to regulate deposition–dissolution behavior of Mg-PS species.

To answer these questions, different characterization techniques are needed to gain a deeper understanding of the chemistries of sulfur species and the electrolyte recipes, as well as transport properties of the working ions to facilitate the development of this technology. Fortunately, booming researches in this field are on the road toward reliable Mg–S batteries, and the proof-of-concept Mg–S cell with high energy density might be soon foreseeable.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrolyte, energy materials, magnesium anode, magnesium-sulfur batteries, sulfur cathode

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