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PERSPECTIVE

The Key Role of Magnesium Polysulfides in the Development of Mg-S Batteries

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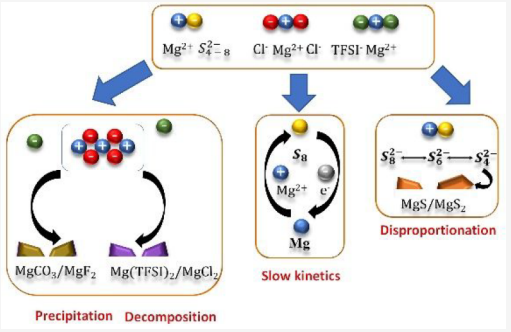
ABSTRACT: The magnesium−sulfur (Mg-S) battery has been investigated in the past decade due to its high theoretical capacity and low active material cost. However, there are still several key issues that have not been overcome to enable practical Mg-S batteries. In this Perspective, the reasons for the poor performance of the Mg-S battery compared to its Li counterpart are discussed. The unique properties of magnesium polysulfides and the resulting passivation problem of the Mg anode are emphasized in this Perspective to facilitate progress in Mg-S battery research.



Climate change instigated by the burning of fossil fuels and increasing carbon dioxide emissions have gained global attention in the past few decades. Rechargeable Li-ion batteries are now widely used in electric vehicles, which reduce lifecycle carbon dioxide emissions for transportation when cleanly generated electricity is used for charging. Batteries with increased charge storage capacity and based on more widely available elements are sought as further electrification of the transportation sector continues. The high abundance of magnesium and high volumetric charge storage capacity (3832 mAh/cm^3) of Mg metal make the concept of magnesium batteries attractive.

When the Mg metal anode is paired with a sulfur cathode, as sulfur also possesses a high charge storage capacity of 1675 mAh/g,[1] the Mg-S battery system has a theoretically high energy density based on the active material components alone. However, examination of the literature reveals that Mg-S batteries are researched with impractical designs such as very low areal loadings of sulfur and high carbon-to-sulfur ratios and electrolyte-to-sulfur ratios, that result in low system energy density compared with Li-S.[2−4] They are also typically tested at much lower charge/discharge rates.

Magnesium polysulfides, $MgS_x(d)$ (where d stands for *dissolved*, and generally x = 4−8), will form at the cathode and dissolve into the bulk electrolyte during the discharge of Mg-S batteries; $MgS_x(d)$ also forms at the anode from reduction of dissolved elemental sulfur during self-discharge. The shuttling effect which is well-known for Li-S batteries also happens in Mg-S batteries with many different electrolytes.[5−8] Therefore, the cycling stability, rate capability, and reversibility of Mg-S batteries are largely influenced by the properties of MgS_x.

Although polysulfides and sulfides are the discharge products formed within both Li-S and Mg-S batteries, there are big differences between the two systems. The Mg metal anode often suffers from passivation (that limits magnesium cation transport at the anode/electrolyte interface), caused by side reactions between Mg and the electrolyte at rest and/or during Mg plating or stripping.[1,9−11] Unlike in Li-ion batteries, the decomposition layer formed on the Mg surface may not conduct magnesium ions at a sufficient rate, which therefore limits rechargeability of the Mg anode. This is a common problem for magnesium batteries which use Mg metal anodes, including Mg-S batteries, and therefore Mg batteries employ unique electrolytes. Additionally, the solubility of $MgS_x(d)$ in liquid electrolyte is much lower than that of Li_2S_x.[2,12,13] Solution stability of $MgS_x(d)$, anode passivation by sulfur species, cathode reaction kinetics, and reversibility are more substantial concerns for Mg-S systems than Li-S.[12,14] The charge/discharge reaction pathways and polysulfide speciation vary between these systems.[15−17] Therefore, it is crucial to understand the unique properties of MgS_x for the development of highly reversible and stable Mg-S batteries.

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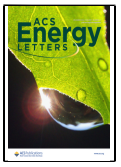

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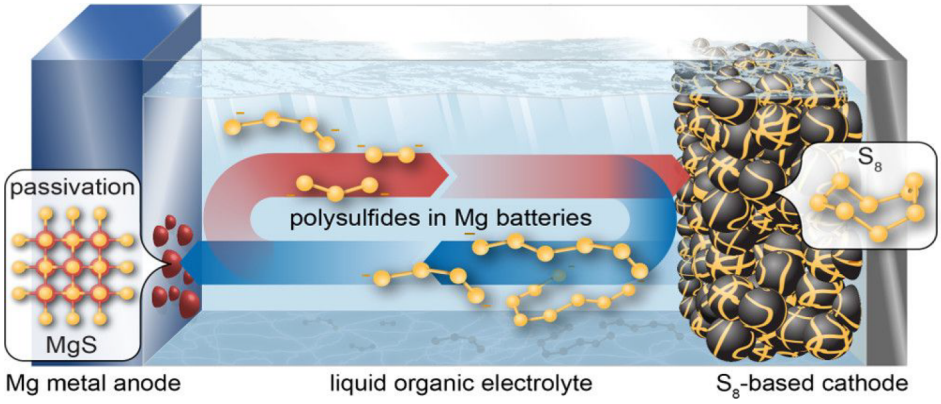

Figure 1. Illustration of self-discharge and shuttling effect in Mg-S batteries. Reprinted with permission from ref 14. Copyright 2021 American Chemical Society.

SELF-DISCHARGE AND SHUTTLING EFFECT

The elemental sulfur in cathodes is soluble to some degree in most liquid electrolytes. As depicted in Figure 1, the dissolved elemental sulfur can diffuse through the electrolyte and react with the metal anode directly, which is called self-discharge.[5,6,15] The products from the self-discharge reaction are metal sulfide (i.e., MgS, Li_2S) and polysulfides.[6,14,18,19] Soluble polysulfides formed at the metal anode surface can diffuse back to the cathode side and be oxidized to longer-chain polysulfides. The polysulfides shuttle between the two electrodes and result in a low Coulombic efficiency.

To study the self-discharge problem of Mg-S batteries, Vinayan et al. collected the Raman spectra of the sulfur cathode during the resting period of a Mg-S cell with 0.4 M $Mg[B(hfib)_4]_2$/DME electrolyte.[15] As shown in Figure 2a, the operando Raman spectra show a decrease in the intensity of the bulk sulfur peaks (150, 218, and 470 cm^{-1}) and an increase in the intensity of the peak (125 cm^{-1}) related to long-chain polysulfides (S_8^{n-}). This is a direct observation of self-discharge in Mg-S batteries. Another evidence of self-discharge in Mg-S batteries is the increase of impedance. Häcker et al. investigated impedance in great detail, using three different electrode couplings (symmetric S-S and Mg-Mg, and Mg-S) with similar cell configuration in order to conclusively identify the various elements. They found an increase in impedance for a cell at open-circuit potential (OCV) for 50 h with a $Mg[B(hfib)_4]_2$/DME electrolyte, as shown in Figure 2b.[6] The charge-transfer resistance on the Mg surface (semicircle in the left inset) is also found to be larger and more prominent in the Mg-S full cell, which might be attributed to dissolved S_8 diffusing to the anode surface to be reduced to polysulfides. It was confirmed that sulfur species diffuse into the electrolyte, causing the initial self-discharge and contributing to the solid electrolyte interphase (SEI) formation.

After that, a systematic study about the self-discharge in Mg-S batteries was conducted by Ford and co-workers.[5] They assembled a series of cells with magnesium bis(trifluoromethanesulfonimide) ($MgTFSI_2$) + magnesium chloride ($MgCl_2$)-based electrolytes. The cells were discharged to 200 mAh/g or rested at OCV and then aged for different periods of time. Then the cells were opened and submerged in tetrahydrofuran to extract soluble components, and ultraviolet−visible spectroscopy (UV−vis) was used to detect the presence of neutral sulfur and $MgS_x(d)$. In both cases, the concentration of polysulfides increases, peaks, and then decreases, which is shown in Figure 2c. Surprisingly, the concentration of polysulfides over time in cells purposefully discharged to 200 mAh/g is strikingly similar to that of the self-discharged cells (rested at OCV). The self-discharge problem in other Mg electrolytes like magnesium bis(hexamethyldisilazide) ($MgHMDS_2$) and aluminum chloride ($AlCl_3$)-based electrolyte and magnesium fluorinated pinacolatoborate (MgFPB)-based electrolytes is also verified.[5] The significant capacity decay (up to 90%) caused by self-discharge makes it difficult to achieve stable and reversible Mg-S batteries.

The dissolution of $MgS_x(d)$ also causes the shuttling effect which is well-known for metal−sulfur batteries. One major difference in the charge process between Li-S and Mg-S batteries is that a potential rise is usually seen at the end of the recharge plateau in Li-S cells, such that cells may be reliably charged to a cutoff potential.[20,21] However, in many Mg-S batteries the increase in potential at the end of charge is slow or a flat plateau is observed.[20] The low slope or flat plateau of charge passed versus potential indicates a serious shuttling problem in Mg-S batteries.[7,20,22,23] The difference in moisture level between typical Li-S and Mg-S electrolytes likely impacts charge-transfer kinetics for polysulfide reactions at the anode surfaces. Wu et al. studied the effect of water additives in Li-S batteries.[24] They found that the addition of 250 ppm water to the electrolyte led to stable charge/discharge behavior with high Coulombic efficiency, in contrast to use of a dry electrolyte. X-ray photoelectron spectroscopy (XPS) results show that H_2O addition results in the formation of an electronically resistive and lithium ion conductive SEI film with more LiOH on the Li anode, which protects the Li anode from the polysulfides while allowing rechargeability. However, water in Mg electrolytes will cause passivation of the Mg anode since the Mg metal is sensitive to water.[25] Most Mg electrolyte solvents are dried under molecular sieves, and the moisture level in typical Mg electrolytes is extremely low (<10 ppm water) by necessity to enable Mg plating and stripping. Multiscale continuum modeling by Richter et al. predicted that Mg-S batteries have a faster self-discharge than Li-S batteries with a similar cell design.[8] The extremely fast kinetics of the side reactions on the Mg surface are likely responsible for the rapid self-discharge. The serious shuttling effect and rapid self-discharge could result from the lack of an electronically insulating SEI on the Mg metal anode.

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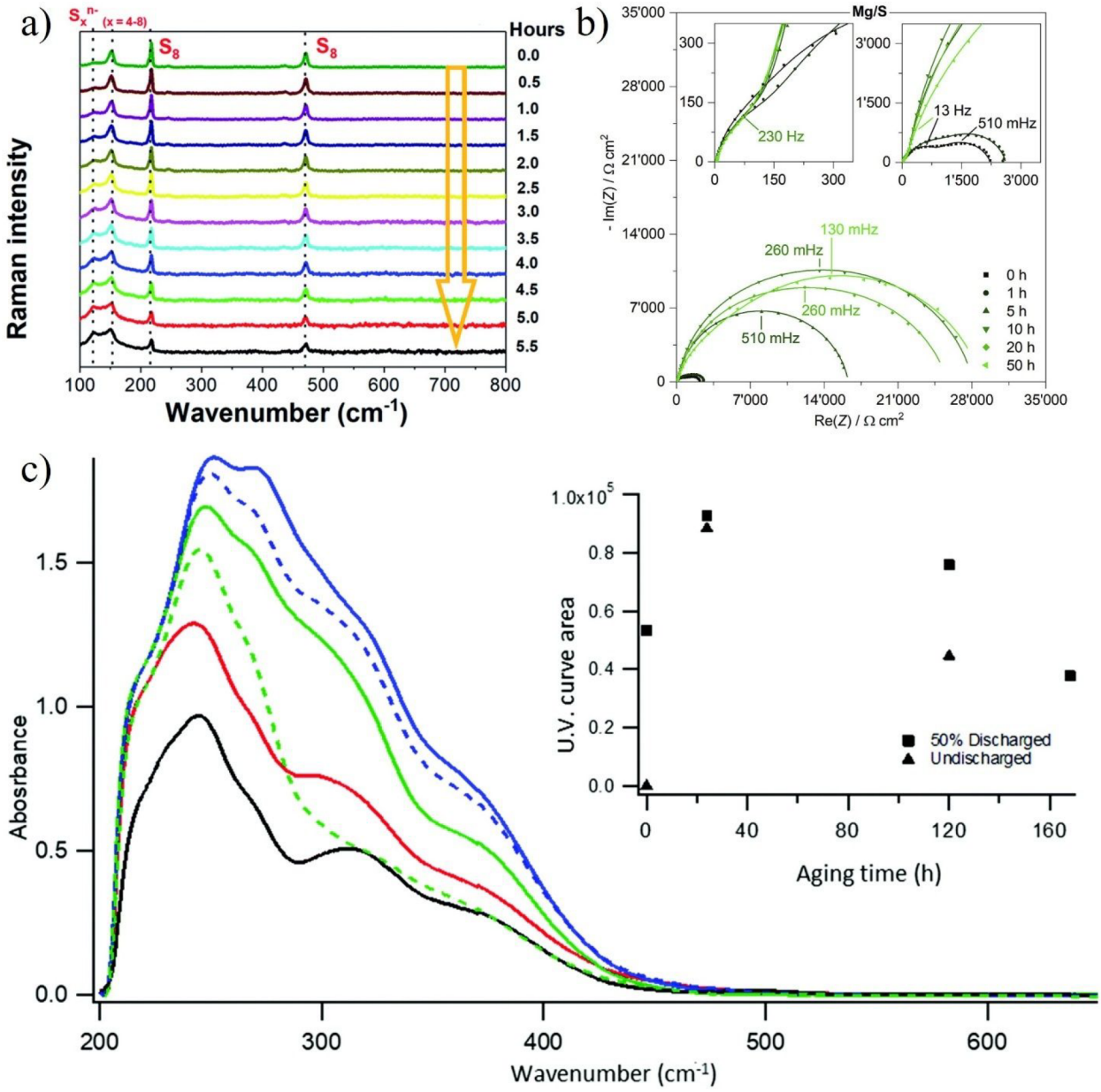

Figure 2. (a) Operando Raman spectra of the cathode in a Mg-S cell with 0.4 M $Mg[B(hfib)_4]_2$/DME electrolyte over a resting period under OCV. Reprinted with permission from ref 15. Copyright 2019 The Royal Society of Chemistry. (b) Nyquist plot for a Mg-S full cell with the same $Mg[B(hfib)_4]_2$/DME electrolyte during a 50 h OCV hold (the insets are impedance plots in the high-frequency region). Reprinted with permission from ref 6. Copyright 2020 Elsevier. (c) Background-subtracted UV−vis absorbance spectra for extracted solutions from Mg-S cells using the 0.25 M $Mg(TFSI)_2/MgCl_2$/DME electrolyte. The UV−vis absorbance spectra for 200 mAh/g discharged cells are plotted as solid lines and the UV−vis absorbance spectra for undischarged cells are plotted as dashed lines: solid red, 200 mAh/g discharged cell aged 0 h; solid blue, 200 mAh/g discharged cell aged 24 h; solid green, 200 mAh/g discharged cell aged 120 h; solid black, 200 mAh/g discharged cell aged 168 h; dashed blue, undischarged cell aged 24 h; and dashed green, undischarged cell aged 120 h. Inset shows total area under the spectra curves. Reprinted with permission from ref 5. Copyright 2021 The Royal Society of Chemistry.

Mg POLYSULFIDES' INSOLUBILITY AND INSTABILITY

It is found that MgS_x have very different properties compared to Li_2S_x. Bieker et al. characterized dilute Li_2S_8 and MgS_8 solutions (0.1−1 mM) in a variety of solvents with UV−vis spectroscopy. The relative quantities of polysulfide species and the absorption peak positions of S_4^{2-} and $S_3^{\bullet-}$ were found to differ between the Li and Mg polysulfide solutions in most of the investigated solvents.[13]

Meanwhile, the solubility of Li_2S_8 (expressed in the form of atomic sulfur) in DOL/DME is 6.6 M,[26] while the maximum reported concentration of $MgS_x(d)$ solution is 0.25 M (based on atomic sulfur).[2,5,12−14,27−30] Considering the self-discharge and the shuttling effect in sulfur batteries, one could hypothesize that the low solubility of $MgS_x(d)$ would be good for the battery performance if reaching the solubility limit prevented further dissolution of S_8 and loss of active material from the cathode. However, as discussed above, the self-discharge problem of Mg-S causes significant capacity decay

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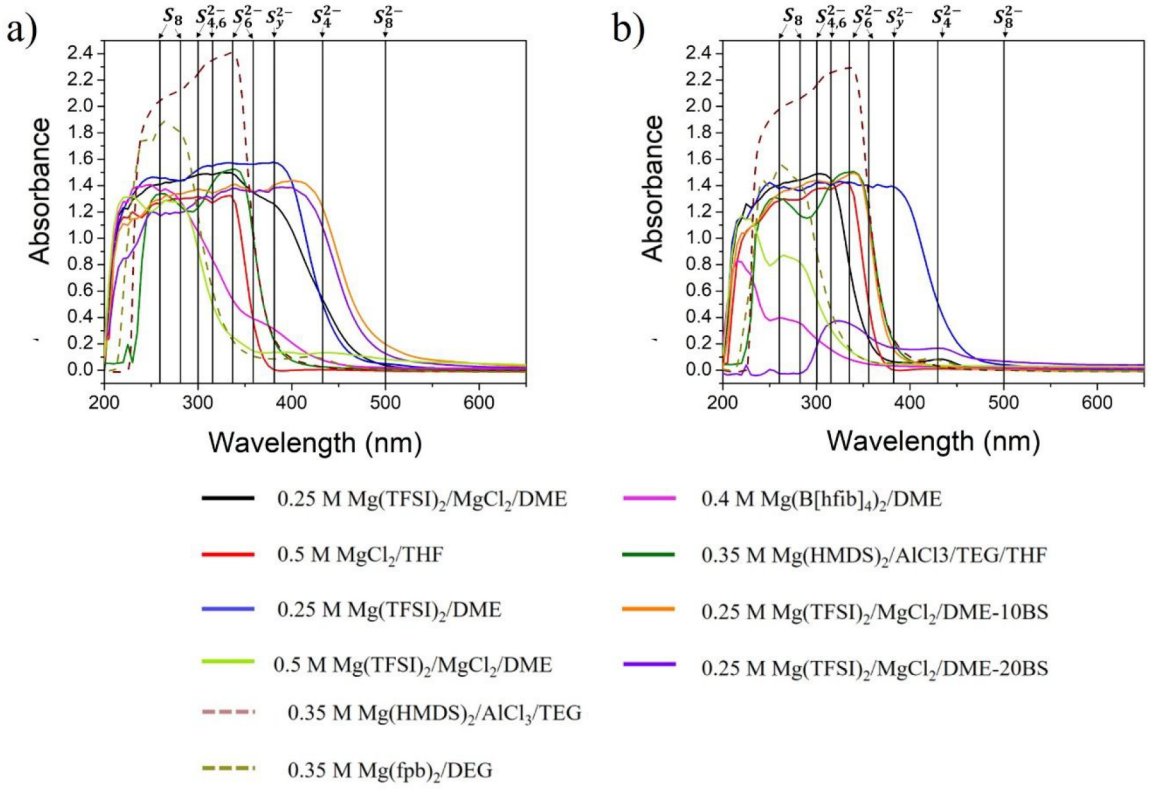

Figure 3. UV−vis spectra of MgS_x solutions in different electrolytes (a) after synthesis and (b) aged for 72 h, following subtraction of the corresponding UV−vis spectrum for the base electrolyte solution. Reprinted with permission from ref 12. Copyright 2021 IOP Publishing.

even under static conditions due to fast sulfur reduction kinetics on the Mg anode surface.[8]

Another factor for capacity decay with low polysulfide solubility is the solution instability of $MgS_x(d)$, due to disproportionation reactions and subsequent precipitation. He et al. chemically synthesized a series of 0.25 M MgS_x solutions in different Mg electrolytes and found that these MgS_x solutions are not shelf-stable on the time scale of just tens of hours.[12] Over time, the solution speciation evolved, as shown in Figure 3a,b, and sulfur crystals precipitated. The solution stability of $MgS_x(d)$ is found to be influenced by the electrolyte composition. The slow polysulfide disproportionation observed in this ex situ study may mimic part of the situation for the full cell, as electrochemically generated polysulfides may later disproportionate and result in elemental sulfur precipitation.

> The solution stability of the electrolyte in the presence of $MgS_x(d)$ generation should be considered to develop a suitable electrolyte for Mg-S batteries.

In the self-discharge study conducted by Ford et al., they observed the precipitation of $MgS_x(s)$ (where *s* stands for *solid*) on the surface of the Mg anode and within the separator.[5] In the electrolyte with a relatively high $MgS_x(d)$ solubility such as 0.25 M $Mg(TFSI)_2/MgCl_2$ in DME, $MgS_{6-8}(s)$ precipitates are observed across the entire cell, predominately where the electrolyte volume is stored (i.e., in the separator), while in the electrolyte with a low $MgS_x(d)$ solubility, sulfur-rich species are observed on the surface of the Mg anode. Notably, this study reports a method for the quantification of solid (and total) ionic sulfur via post-mortem derivatization and mass spectrometry.

Another problem related to the low solubility of $MgS_x(d)$ is precipitation of the electrolyte salts. Drvarič Talian et al. synthesized $MgS_x(s)$ and dissolved the solids in $Mg(TFSI)_2/MgCl_2$/TEGDME/DOL electrolyte.[29] When the $MgS_x(d)$ concentration reached 0.1 M, a white precipitate was observed (shown in Figure 4a). The precipitate was isolated and analyzed with IR and XRD, which confirmed that the precipitate has no characteristic peaks/bands of polysulfides,

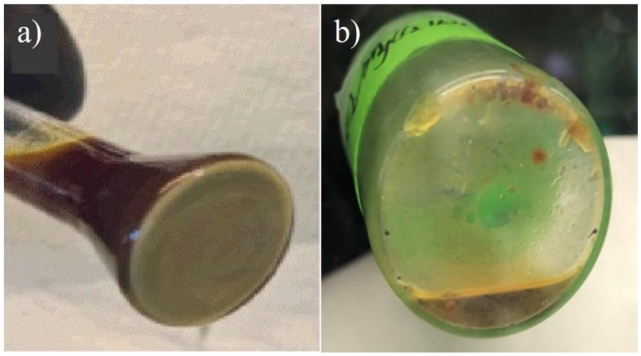

Figure 4. (a) White precipitate formed in 0.1 M MgS_x in $Mg(TFSI)_2/MgCl_2$/TEGDME/DOL electrolyte. Adapted from ref 29 (cropped from Figure 5). Copyright 2021 Wiley-VCH: https://creativecommons.org/licenses/by/4.0/. (b) The Li/Mg salt complex from mixed Li_2S_x solution and 0.25 M $Mg(TFSI)_2/MgCl_2$/DME electrolyte. Reprinted with permission from ref 12. Copyright 2021 IOP Publishing.

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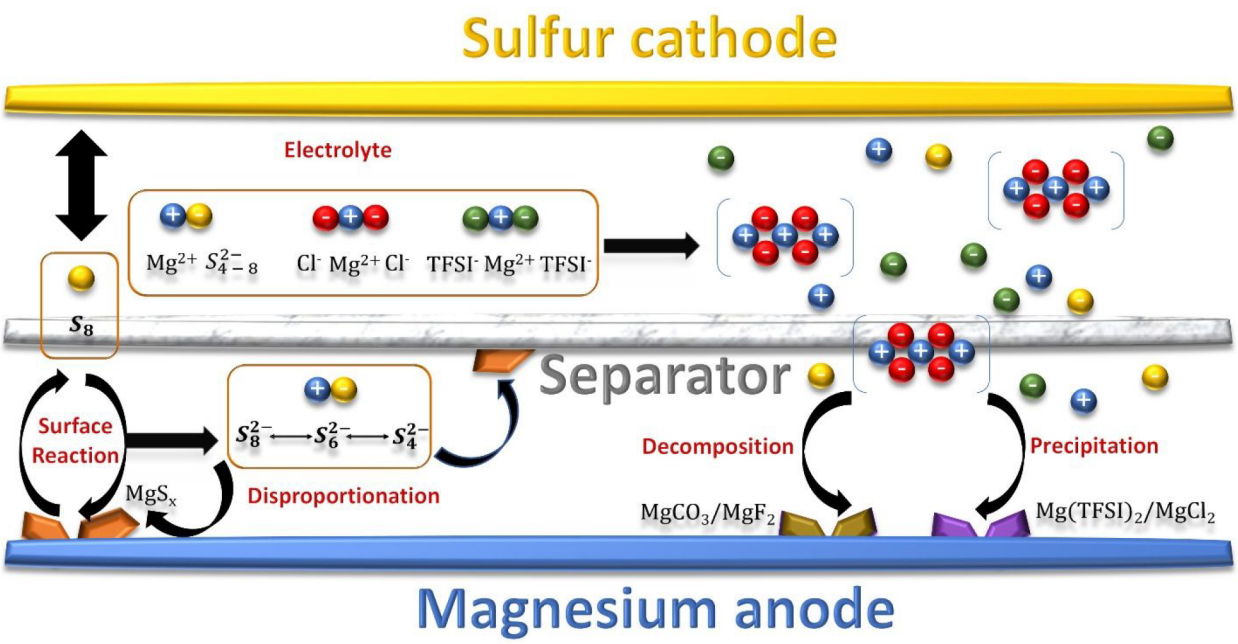

Figure 5. Schematic illustration of Mg passivation in a Mg-S cell containing the $Mg(TFSI)_2/MgCl_2$/DME electrolyte. ($[Mg_3Cl_4]^{2+}$ was chosen as the exemplary salt complex in the electrolyte.[42] Other complexes could also exist in this system.)

although it was also proven that it was neither pure $Mg(TFSI)_2$ or pure $MgCl_2$. The researchers assumed the solids were a $Mg(TFSI)_2/MgCl_2$ complex. In another work, a mixture of 0.25 M Li_2S_x (based on atomic sulfur) and 0.25 M $Mg(TFSI)_2/MgCl_2$/DME electrolyte was prepared by He et al.[12] Solids that precipitated from this solution after 12 h were found to be a Li/Mg salt complex (Figure 4b). It is known that $MgCl_2$ has low solubility in DME, but it can form a salt complex with $Mg(TFSI)_2$ and then dissolve in DME at substantially higher concentrations.[31] As 1 M $Mg(TFSI)_2/MgCl_2$/DME electrolyte can be easily prepared at room temperature, the salt precipitates observed in the $MgS_x(d)$ solutions indicate that the existence of $MgS_x(d)$ in the electrolyte could decrease the solubility of Mg salt or alter the structure of the ionic complex(es) in the electrolyte. The solution stability of the electrolyte in the presence of $MgS_x(d)$ generation should be considered to develop a suitable electrolyte for Mg-S batteries.

■ Mg ANODE PASSIVATION

The passivation of the Mg anode is a serious issue for all Mg batteries, but the low solubility and instability of MgS_x and the slow diffusion of magnesium in MgS make this problem even more severe in Mg-S batteries. The passivation of the Mg anode in sulfur-free cells is commonly caused by the chemical and electrochemical instability of coordinated anions/solvents in the presence of Mg metal and/or during Mg electrodeposition.[32] Mg^{2+} coordinates to solvents and anions in magnesium electrolytes, raising the reductive stability limits of solvents and anions to >0 V versus Mg/Mg^{2+}.[33,34] Different approaches, like fabricating artificial SEI layers (metal−organic frameworks, polymer, $BiCl_3$, $SnCl_2$, $SiCl_4$, and Li salt) on the Mg surface,[32] applying additives (iodine, $Bi(OTf)_3$, $GeCl_4$)[30,35−37] in Mg electrolytes to stabilize the Mg surface, and using a Mg alloy (Li, Ga, Sn, and Bi) as an alternative anode,[38] have been tried to solve the passivation problem. These approaches are somewhat effective at improving Mg anode reversibility in the absence of sulfur.

As illustrated in Figure 5, in a Mg-S cell the passivation of the Mg anode can also result from precipitation of salts, polysulfide, or elemental sulfur particulates due to disproportionation and solution solubility limitations, or via the formation of films, including insoluble magnesium sulfur species $MgS_x(s)$ such as MgS due to reaction of the unprotected Mg anode with dissolved S_8 and $MgS_x(d)$ formed during the discharge or self-discharge processes. The sulfur-induced passivation phenomena have been observed and studied in various ways. Current literature indicates the universality of the general phenomena regardless of electrolyte type, while the completeness and time scale of passivation are influenced by electrolyte composition and cell design, and the specifics of the reaction pathways to passivation are still under investigation.

Several groups have reported on the increase of overpotential for Mg stripping/plating due to the passivation of the Mg anode with the existence of sulfur in the electrolyte.[6,14,15,39] Gao et al. observed a small increase in the plating overpotential upon the addition of 50 mM S_8 to $Mg(TFSI)_2/MgCl_2$/DME electrolyte when cycling flooded three-electrode Mg-Mg-Mg cells and a substantial decrease in Coulombic efficiency for Mg plating and stripping with flooded three-electrode Pt-Mg-Mg cells.[40] Salama et al. studied the electrochemical performance of the Mg anode in flooded three-electrode glass cells with the addition of Li_2S_8.[41] They found that the well-conditioned $Mg(TFSI)_2/MgCl_2$/DME electrolyte showed fairly stable low overpotentials, 0.1 V for stripping and 0.15 V for plating of Mg, while the stripping overpotentials for the same electrolyte with 10 ppm Li_2S_8 addition increased to 0.2 V by the end of the test. A very large, spike-like overpotential also developed at the initiation of the first oxidation cycle, providing clear evidence of self-discharge and passivation occurring before the commencement of cycling. When the Li_2S_8 additive concentration increased to 50 ppm, the electrochemical performance

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of the cell showed a more dramatic decrease. The capacity retention of the cell is 0% after 7 cycles, which means the Mg anode can be fully passivated in a short time with just 50 ppm Li_2S_8 in this electrolyte under flooded conditions. XPS results indicate that a significant fraction of sulfur species on the Mg anode surface are in the form of MgS. Vinayan et al. also investigated the overpotential at Mg electrodes in symmetrical Mg/Mg cells with the addition of MgS_x in the $Mg[B(hfib)_4]_2$/DME electrolyte.[15] They found that the overpotential at the Mg electrode increased from 0.1 V for pure electrolyte to 0.34 V for low sulfur-containing electrolyte (14 mM S). It further increased to 1.4 V when the same electrolyte containing high amounts of sulfur species (51 mM S) was used.

More recent work by Laskowski et al. which uses elemental sulfur also investigated the relationship between the polysulfides' concentration and overpotential on the Mg anode.[14] They used a flooded three-electrode cell with Mg working and counter electrodes and Ag_2S quasi-reference electrodes to probe the electrochemical performance of the Mg anode. With the addition of 2 mg/mL S_8 in the electrolyte, the plating overpotential of the Mg anode significantly increased from <0.1 V to about 1.5 V; the passivation of the Mg anode was obvious. However, when they increased the concentration of S_8 to 5 mg/mL (156 mM) and 10 mg/mL (312 mM), they found the overpotential decreased with the increased S_8 concentration. These results indicate that varying S_8 concentrations result in varying polysulfide speciation that influences passivation. Their conclusions are that the rate of MgS formation at Mg/electrolyte interfaces is dependent on the dissolved polysulfides' chain lengths and that longer-chain polysulfides suppress passivation. There are two possibilities to explain these results. One possibility is that reduction of shorter-chain polysulfides to MgS is kinetically facile relative to the equivalent process for longer-chain polysulfides. The second possibility is that the reduction kinetics are similar for all chain lengths, but longer-chain sulfur species have more facile alternative pathways. It is not possible to distinguish these two possibilities based on the results obtained. It is generally believed that the reaction between Mg and $MgS_x(d)$ results in MgS formation on Mg anode surface. Since MgS is an electronic insulator and has a low Mg^{2+} diffusion rate, it at least partially passivates the Mg surface.

Since MgS is an electronic insulator and has a low Mg^{2+} diffusion rate, it at least partially passivates the Mg surface.

The solution instability of $MgS_x(d)$ should also be fully studied in the context of anode passivation. The sulfur and Mg salt precipitates observed in concentrated MgS_x solutions provide another possible passivation mechanism. For the $Mg(TFSI)_2/MgCl_2$/DME electrolyte as an example, the Mg salts complex could precipitate out from the electrolyte and passivate the Mg anode, too (Figure 5). Even if the Mg anode is protected by an artificial SEI layer that inhibits electron transfer but allows magnesium transport, the unstable $MgS_x(d)$ and the Mg salts in electrolytes could still precipitate out of the electrolyte continuously. The Mg anode could be passivated by these precipitates if they are insulating to magnesium transport.

SULFUR CATHODE MASS-TRANSFER LIMITATIONS AND REACTION KINETICS

Another reason for the poor performance of Mg-S batteries compared to Li-S batteries is the reaction kinetics. It is well-known that the diffusion rate of Mg^{2+} in solids is slow due to its high charge density (120 C mm^{-3} vs 52 C mm^{-3} for Li^+).[43−46] This difference results in much lower charge/discharge rates commonly employed for Mg-S (0.01 to 0.1 C-rate vs >1 C-rate).[3] Gao et al. studied the kinetics of the sulfur cathode during discharge in the $Mg(TFSI)_2$/DME electrolyte.[45] They demonstrated that sulfur reduction occurs through three consecutive steps: Stage (I) elemental sulfur to long-chain polysulfide (potential slope in 2.4−1.5 V), Stage (II) chain-shortening of polysulfide (potential plateau at 1.5 V), and Stage (III) solid-state transition from short-chain polysulfide to MgS (potential slope in 1.5−0.5 V). The kinetics for stage III is very sluggish due to the slow Mg^{2+} diffusion in $MgS_x(s)$. The researchers hypothesized that the low solubility of MgS_x in the electrolyte causes low sulfur utilization, due to blocking of unreacted sulfur. It is also well-known that dissolved polysulfides function as redox mediators in sulfur batteries. The low sulfur utilization and poor reversibility could also result from diminished polysulfide redox mediation.[4]

Xu et al. systematically studied the reaction pathways of the Mg-S batteries in $Mg(HMDS)_2/AlCl_3$ electrolyte.[16] They confirmed the formation of solid discharge products MgS and Mg_3S_8 during the discharge process by employing the synchrotron X-ray absorption spectroscopy (XAS) and found that the capacity degradation is mainly due to the formation of these irreversible discharge products. Vinayan et al. showed, with a combination of Raman spectroscopy, X-ray diffraction (XRD), and density functional theory (DFT) calculations, that MgS_2 dominates as the discharge product in the nitrogen-doped carbon matrix cathode unless a low potential hold at 0.2 V is maintained for an extended time, upon which a nanocrystalline MgS product was obtained, likely a zinc blende phase.[15] The nanocrystalline MgS was found to be reversibly oxidized upon charging, highlighting the importance of the cathode structure in reversible cycling. Zou et al. performed operando UV−vis measurements during galvanostatic discharge and charge of the two-electrode Li-S and Mg-S batteries to determine the types of polysulfides involved in each redox step.[4] They found that the Mg-S battery exhibited a lower concentration of all detected polysulfides compared with the Li-S battery during operation. Similar to other works, they identified MgS_2 precipitation and the slow solid-to-solid transformation of MgS_2 to MgS as limiting steps. The earlier formation of solid discharge products and the lack of polysulfide mediation in the Mg-S batteries resulted in low sulfur utilization and poor reversibility.

Achieving higher rates and reversibility without the use of more expensive inactive materials, especially as normalized on the basis of amounts of Mg or S used or charge capacity, is a notable goal.

A few strategies have been used to enhance reversibility and rate performance of Mg-S batteries. Gao et al. demonstrated

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that addition of a lithium salt into the magnesium electrolyte results in Li^+ mediation that enhances oxidation of the discharge products.[7] Zhou et al. demonstrated a ZIF-67 derivative carbon framework co-doped by N and Co atoms as an effective sulfur host for highly reversible Mg-S batteries even under high rates.[20] The discharge capacity is as high as ∼600 mAh/g at 1 C during the first cycle and is maintained at ∼400 mAh/g after 200 cycles, while strikingly, a capacity >300 mAh/g was achieved at a rate of 5 C, all with an electrolyte containing lithium salt. Of course, a primary objective for the research on magnesium batteries is to reduce the necessity for lithium. He et al. also applied Cu nanoparticles as an additive for the Mg-S battery cathode.[22] They found that the Cu additives promote the formation of smaller, more dispersed discharge product particles, thereby enhancing reversibility and rate capability, but too much Cu was required to get the desired effect. More recently, Wang et al. showed that a functional Mo_6S_8-coated separator mitigates polysulfide diffusion to the anode and has a catalytic effect on the polysulfide reaction, promoting cyclability, sulfur utilization, and Coulombic efficiency.[47] Achieving higher rates and reversibility without the use of more expensive inactive materials, especially as normalized on the basis of amounts of Mg or S used or charge capacity, is a notable goal.

FUTURE OPPORTUNITIES

The common issues for Mg-S batteries, as well as the impracticality of research on Mg-S cells with ultrahigh electrolyte/S ratios and low S/C ratios, are almost all related to the nature of MgS_x. Therefore, there are three potential directions to address these challenges by controlling the sulfur species solubility or location: prohibiting dissolution of sulfur/polysulfides, applying an artificial SEI that protects the anode and enables use of electrolytes with high polysulfide solubility, or using a coating at the cathode/electrolyte interface to keep solubilized sulfur and polysulfides inside the cathode.

One direction is to avoid dissolution of both S_8 and $MgS_x(d)$. All-solid-state Mg-S batteries are a possible solution since the diffusion and migration of sulfur and polysulfides is intrinsically slow in solid electrolytes. However, lack of polysulfide redox mediation results in slow sulfur reduction and oxidation kinetics at the cathode. Liquid electrolytes with reduced $MgS_x(d)$ solubility have shown some advantages, yet a solution that is compatible at the anode side in the long term is not yet established.[2,48] Additionally, sluggish solid-state Mg transport in solid electrolytes and solid discharge products will hamper rates, except in the instance of exceptional nanostructuring. More fundamental understanding and engineering of Mg transport in solids as well as solid-state Mg-S reactions could advance this area.

The second direction is to apply an artificial SEI layer on the Mg anode surface to protect the Mg anode from reaction with S_8 and $MgS_x(d)$ and enable the use of a wider range of electrolyte solutions. Increased solubility of $MgS_x(d)$ is likely to enhance polysulfide reaction kinetics and sulfur utilization. Zou et al. applied dimethyl sulfoxide (DMSO) as the solvent in Mg-S batteries and successfully increased the initial discharge capacity from 650 to about 1500 mAh/g.[4] The use of DMSO was enabled by simultaneous use of a solid inorganic electrolyte that protected the Mg anode. Whereas concentrated $MgS_x(d)$ in the electrolyte would cause serious polysulfide shuttling and passivation of the unprotected Mg anode, employing a stable SEI layer on the Mg anode with an electrolyte with increased solution stability of $MgS_x(d)$ is a practical way to address this issue. There are many recent reports of artificial SEI layers on Mg anodes that enhance Mg reversibility in Mg-Mg symmetrical cells and full cells with intercalation cathodes.[11,49−51] The effectiveness of these artificial SEIs in Mg-S batteries is yet to be proven. To develop a suitable SEI layer for Mg-S batteries, it is important to understand the evolution of the SEI layer during the self-discharge and $MgS_x(d)$ shuttling. Since the ionic conductivity and durability of the SEI are crucial for the battery performance, compositional changes of the SEI layer could cause dramatic differences in cycle life of Mg-S batteries. Systematic studies about compatibility between the SEI layers, various liquid electrolytes, and $MgS_x(d)$ are necessary. Characterization and computational modeling of SEIs in the presence of sulfur species and in battery operation would advance this area.

However, although the SEI layer could protect the Mg anode from reaction with unstable magnesium salts and organic solvents, the unique properties of $MgS_x(d)$ could still cause unexpected failure of the cell. The solution stability of $MgS_x(d)$ in electrolytes is key for the long-term stability of Mg-S batteries with liquid electrolytes. Solubilized polysulfides in the bulk electrolyte that cause precipitation of insoluble sulfur species and salts will lead to anode passivation and cell failure.

The third direction is the use of a coating or interlayer at the cathode/electrolyte interface to prohibit the transport of both sulfur and polysulfides into the bulk electrolyte, thus eliminating any reaction or precipitation of the sulfur species with the anode or within the separator.[52] Such an approach allows for solubilized polysulfides to act as redox mediators within the cathode and mitigates both loss of active material and anode passivation. A significant technical challenge with this approach is the development of an interlayer or coating that blocks the transport of both ionic polysulfides and neutral sulfur. A thin, defect-free coating of a framework material that selectively conducts magnesium species such as Mg^{2+} or $MgCl^+$ may be able to achieve the desired result.[10]

In all of the aforementioned cases, a high-surface-area, nanostructured cathode that promotes uniform distribution of solid discharge products is a necessary system component. The slow diffusion of magnesium in solid discharge products necessitates that those products be thin and/or confined to small dimensions with sufficient electron and magnesium transport to them in order to achieve a high degree of reversibility and improved rates. Li-S battery cathodes are much more advanced in this respect, but we note that the slower diffusion of magnesium cations through coatings and capsule layers significantly limits the design space for confinement of sulfur and discharge products in the Mg-S system.

> Efforts to characterize and quantify sulfur in real Mg-S cells should continue to be prioritized, especially in conjunction with efforts to use novel materials and cell designs.

Additionally, competitive system energy densities require that less electrolyte is used in concert with the high surface area cathode. While grid-scale storage applications require low

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cost, rather than explicitly high energy density, we note that capital costs scale with material amounts and system size.[53] Therefore, efforts to reduce electrolyte-to-sulfur ratios in Mg-S systems may benefit large-scale storage applications as well, as long as cycling stability and system lifetime are optimized. Cycle life (high Coulombic efficiency at the anode and high reversibility of the cathode) is the primary consideration for grid-scale storage applications of Mg-S due to non-negligible material cost. It is noted that varying electrolyte chemistry and concentration along with varying cell configurations (electrolyte volume, electrolyte-to-sulfur ratios, and cathode and anode designs) will influence the exact polysulfide speciation and solubility, along with reactions at both the anode and cathode; hence, researchers should be aware of these details when designing new studies and comparing results.

Finally, Mg-S battery research could benefit from researchers striving for a full accounting of sulfur amount and sulfur speciation within the cell as a function of cycling. Since capacity fade and failure of Mg-S batteries are typically due to the state of sulfur (i.e., anode passivation by sulfur species, precipitation of sulfur or polysulfides in the separator, solubilized polysulfides, non-rechargeable discharge product islands in the cathode, or unutilized elemental sulfur in the cathode), knowing exactly how much sulfur is in the form of which species and where it is in the cell as a function of time would be transformative. Efforts to characterize and quantify sulfur in real Mg-S cells should continue to be prioritized, especially in conjunction with efforts to use novel materials and cell designs.

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