

Electrochemistry

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Reversible S⁰/MgS_x Redox Chemistry in a MgTFSI₂/MgCl₂/DME Electrolyte for Rechargeable Mg/S Batteries

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Abstract: The redox chemistry of magnesium and its application in rechargeable Mg batteries has received increasing attention owing to the unique benefits of Mg metal electrodes, namely high reversibility without dendrite formation, low reduction potentials, and high specific capacities. The Mg/S couple is of particular interest owing to its high energy density and low cost. Previous reports have confirmed the feasibility of a rechargeable Mg/S battery; however, only limited cycling stability was achieved, and the complicated procedure for the preparation of the electrolytes has significantly compromised the benefits of Mg/S chemistry and hindered the development of Mg/S batteries. Herein, we report the development of the first rechargeable Mg/S battery with a MgTFSI₂/MgCl₂/DME electrolyte (DME = 1,2-dimethoxyethane, TFSI = bis(trifluoromethanesulfonyl)imide) and realize the best cycling stability among all reported Mg/S batteries by suppressing polysulfide dissolution. Mechanistic studies show that the battery works via S⁰/MgS_x redox processes and that the large voltage hysteresis is mainly due to the Mg anode overpotential.

Rechargeable Mg batteries, which combine Mg metal anodes with intercalation or conversion cathodes in a Mg²⁺-conducting electrolyte, are of particular interest owing to the high capacity, low redox potential, and high abundance of Mg metal.^[1] Most importantly, Mg deposition/stripping can be realized with 100% coulombic efficiency with no dendrite formation,^[2] which renders the Mg metal anode stable during prolonged cycling,^[1] avoids battery failure due to electrode/electrolyte consumption,^[3] and eliminates any safety concerns associated with dendrite formation. Since the development of the first rechargeable Mg battery prototype,^[4] tremendous efforts have been devoted to improving its energy density and reversibility. Many intercalation compounds (e.g., oxides,^[5–8] sulfides,^[9–11] and Prussian blue^[12]) have been investigated as possible cathodes, and conversion materials have been considered owing to their high capacity.^[13–16] Hybrid battery designs have also been proposed to take advantage of the properties of Mg metal anodes.^[17,18]

On the other hand, owing to their high capacity, sulfur cathodes have been extensively employed in various battery chemistries, such as Li/S,^[19] Na/S,^[20,21] and Al/S.^[22,23] Theoretically, combining Mg with S would provide one of the highest energy densities among all battery chemistries (1700 Wh kg⁻¹ and 3200 Wh L⁻¹).^[24] Moreover, the abundance of Mg and S renders Mg/S chemistry competitive for low-cost applications. To realize rechargeable Mg/S batteries, the electrolyte must be chosen carefully. A major group of Mg electrolytes uses Lewis acid–base complexes synthesized by the transmetalation reaction between Mg-centered Lewis bases and Al- or B-centered Lewis acids.^[25] The usage of nucleophilic Lewis bases (e.g., PhMgCl) has precluded these complex electrolytes from being used in Mg/S batteries owing to their incompatibility with sulfur. This problem was not solved until a non-nucleophilic electrolyte based on a silylamide Lewis base (MgHMDSCI) was used.^[26] This electrolyte enabled the early exploration of Mg/S chemistry,^[26,27] and later on, Mg/S batteries with inorganic electrolytes (MACC) were also reported.^[28] Several new complex electrolytes have been developed recently,^[29,30] but their compatibility with sulfur remains unknown. Another category of Mg electrolytes uses simple Mg ionic compounds, such as the commercially available Mg salts Mg(ClO₄)₂, Mg(BF₄)₂, and MgTFSI₂ (TFSI = bis(trifluoromethanesulfonyl)imide). Most of these salts are insoluble in ethereal solvents (the only viable solvents inert to Mg) owing to their strong ionic bonds (e.g., Mg(ClO₄)₂, Mg(BF₄)₂, and MgCl₂),^[31] and the only soluble one, MgTFSI₂, shows inferior coulombic efficiency and a large overpotential^[31,32] owing to the inevitable presence of traces of moisture and for other reasons.^[33–36] To address these issues, new Mg ionic compounds with bulky and weakly coordinating anions that are soluble in ethereal solvents and able to reversibly deposit/strip Mg have been developed.^[37–40] Their compatibility with sulfur was confirmed in several Mg/S batteries.^[38,39] All of these electrolytes have enriched our electrolyte options for studying Mg batteries. However, most of them are based on expensive precursors and have to be made through complicated synthesis procedures (see the Supporting Information, Table S1), which not only limits their accessibility to researchers, necessary for addressing many practical issues of this infant technology, but also compromises the practicality of Mg/S chemistry. Herein, we report the first rechargeable Mg/S battery based on MgTFSI₂/MgCl₂/DME electrolyte (DME = 1,2-dimethoxyethane).^[31] This electrolyte can be made by simply dissolving commercial Mg salts in DME, which renders it a readily available platform for the community to study Mg/S batteries either in fundamental investigations on S electrochemistry in Mg systems or for adapting the valuable experience of Li/S

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systems for addressing similar issues in Mg/S batteries. As we shall demonstrate below, the dissolution of polysulfide, a major cause for the capacity fading in previously reported Mg/S batteries with Mg-HMDS electrolytes,^[27,42] has, for the first time, been effectively suppressed by increasing the concentration of the MgTFSI₂/MgCl₂/DME electrolyte. As a result, we have developed a Mg/S battery with the best cycling stability thus far.

The sulfur/carbon composite cathode was made by impregnating sulfur into active carbon cloth by a melt-diffusion method. Morphological and crystallographic studies showed that the sulfur was distributed uniformly in the pores of the active carbon cloth (Figure S1). The obtained composite cathode shows typical two-stage behavior in a Li/S battery (Figure S2).^[41] The Mg electrolyte was simply made by blending dried MgTFSI₂ and MgCl₂ salts with DME and stirring overnight.^[31] Its electrochemical performance (Figure S3 and Figure 1 a) shows typical Mg deposition/stripping peaks. With an inert Pt electrode, the electrolyte is stable up to 3.0 V. However, the electrolyte is only stable up to approximately 2.5 V on the current collector in this study (Inconel alloy; Figure S4). The cumulative capacity during the Mg deposition/stripping (Figure 1 b) showed a coulombic efficiency of about 93%.^[31]

We then measured the electrochemical performance of Mg/S batteries. In 0.25 M electrolyte, both the discharge/charge curves feature three stages (Figure 2 a), namely a slope, a plateau, and another slope, indicating a stepwise reaction pathway. A discharge capacity of about 800 mAh g⁻¹ was delivered while the charge capacity far exceeds the

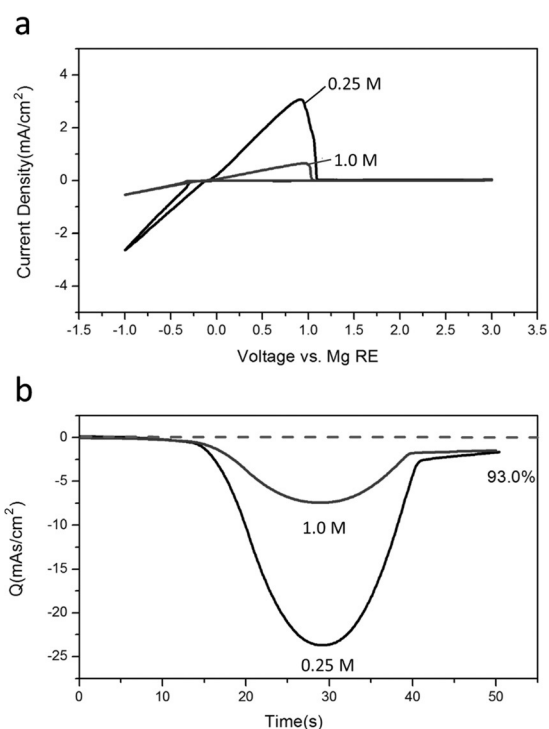


Figure 1. Electrochemical Performance of the MgTFSI₂/MgCl₂/DME electrolyte. a) Mg deposition/stripping and anodic stability on Pt. Scan rate: 100 mVs⁻¹. Reference electrode (RE): Mg disk; counter electrode (CE): Mg disk. b) Integrated Mg capacity over time.

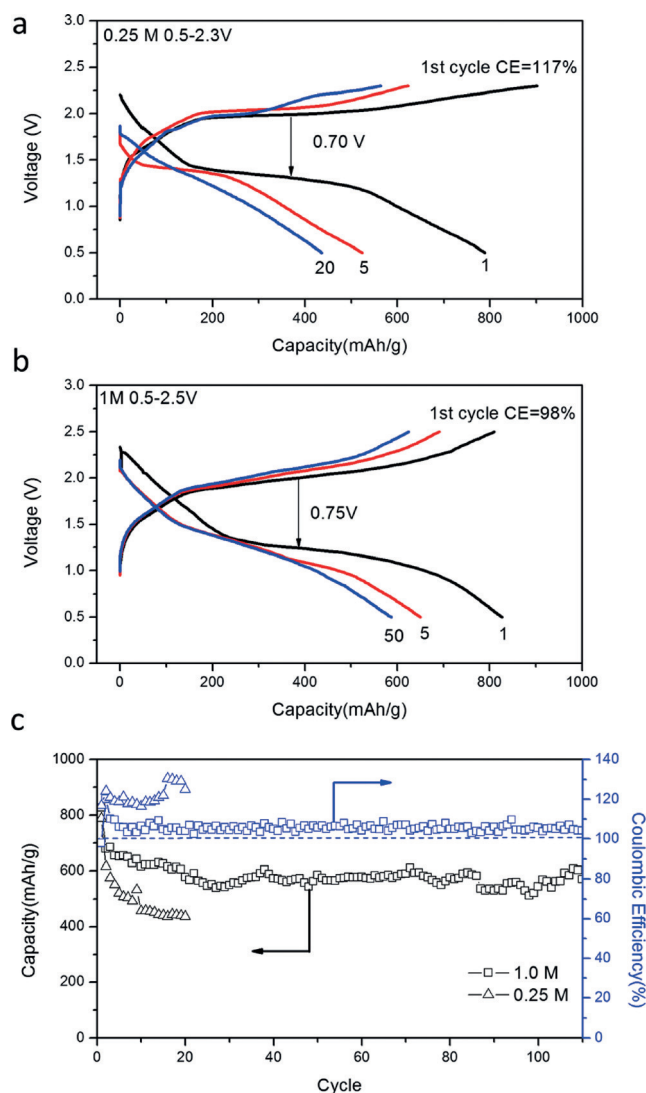


Figure 2. Electrochemical performance of the Mg/S battery with MgTFSI₂/MgCl₂/DME electrolyte. a) Voltage profiles in 0.25 M electrolyte. Current density: 200 mA g⁻¹. b) Voltage profiles in 1.0 M electrolyte. Current density: 100 mA g⁻¹. c) Cycling stability and coulombic efficiency. Sulfur loading: 1 mg cm⁻².

discharge capacity (coulombic efficiency of the first cycle: 117%), indicating serious polysulfide shuttling. The formation of polysulfides was confirmed by UV/Vis analysis of the discharged electrolyte (Figure S5 a), in which a new peak emerged at 350 nm. Mass spectrometry showed that the dissolved polysulfide species include S₆²⁻, S₅²⁻, and S₃⁻ (Figure S5 b and Table S2). The dissolution of polysulfides leads to the continuous loss of active material, which restricts the cycling performance of the Mg/S battery (Figure 2 c). This issue has been widely observed in other studies on Mg/S systems with Mg/HMDS electrolytes,^[27,42] and still lacks an effective solution. Below, we will demonstrate that this problem can be mitigated by simply increasing the concentration of the electrolyte.

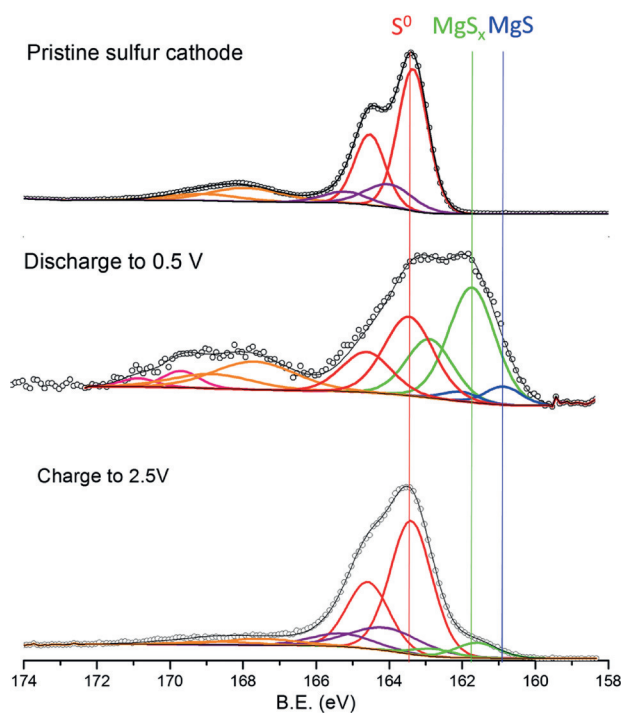
The solubilities of sulfur and polysulfide in both dilute (0.25 M) and concentrated (1.0 M) electrolyte were determined (Table 1). The solubilities of both sulfur and polysulfide are

Table 1: Solubility of sulfur and polysulfide in the MgTFSI₂/MgCl₂/DME electrolyte (mM of atomic sulfur).

	0.25 M	1.0 M
Sulfur	71.1	9.6
Polysulfide	> 254.8	13.3

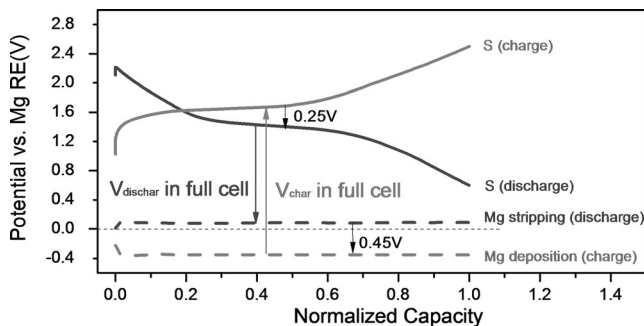
one order of magnitude lower in the concentrated electrolyte. This finding implies that in the concentrated electrolyte, fewer sulfur molecules (either in the form of elemental sulfur and polysulfide) are dissolved into the electrolyte during cycling, which is beneficial for suppressing the associated loss of active material. We then measured the electrochemical performance of a Mg/S battery with the concentrated electrolyte (Figure 2b). The charge capacity was close to the discharge capacity in the first cycle (CE = 98%). In subsequent cycles, the coulombic efficiency was around 106%, which is much closer to 100% than in the dilute electrolyte (Figure 2c). This reduced coulombic efficiency (from 117% in the dilute electrolyte to 106% in the concentrated electrolyte) suggests effective mitigation of shuttling effects, which is a result of the inhibited dissolution of polysulfide. Therefore, the battery shows much better cycling stability (Figure 2c). A capacity retention of 69% in the 110th cycle was achieved, which is by far the best cycling stability ever reported for rechargeable Mg/S batteries.^[26–28,39,42,43] This simple approach may not work for other electrolytes as concentrated electrolytes may become very viscous and nonconductive as we have shown for the Mg-HMDS electrolyte (Figure S6), which again manifests the benefit of the MgTFSI₂/MgCl₂/DME electrolyte.

To probe the reaction mechanism, we examined the oxidation states of sulfur by X-ray photoelectron spectroscopy (XPS). With a binding energy separation of 1.16 eV, the same full width at half maximum (FWHM), and an area ratio of 0.511, the S 2p spectra were fitted to spin-orbit-split doublets representing 2p_{1/2} and 2p_{3/2}, respectively (Figure 3). The pristine active carbon cloth/sulfur cathode gives rise to peaks at 163.3 eV (red) and 164.1 eV (purple), typical for elemental sulfur in an active carbon/sulfur composite.^[22] The peak at a higher binding energy of 166.0 eV (orange and pink) in the pristine sample (before electrolyte addition) originates from the oxidation of surface sulfur during sample preparation, which can be removed by Ar sputtering (Figure S7). The same peak in the cycled sample also results from SO_x and is due to the sulfonyl species in the TFSI anions.^[27] When discharged to 0.5 V, the peak for elemental sulfur (red) is greatly reduced in intensity, indicating the consumption of sulfur during battery discharge. Meanwhile, two sets of peaks appear (green and blue). The peak at 160.7 eV (blue) corresponds to MgS.^[26] The peak at 161.7 eV (green) has a binding energy between that of elemental sulfur (S⁰) and sulfide (S²⁻), which corresponds to MgS_x (x = 2–8). After charging to 2.5 V, the S⁰ peak is recovered at the expense of MgS and MgS_x (x = 2–8). The peak at 161.7 eV does not completely disappear, implying that not all MgS_x has been converted into elemental S. The XPS result reveals that the discharge product is mainly MgS_x (x = 2–8), suggesting that the battery functions by S⁰/MgS_x redox chemistry. Some

**Figure 3.** High-resolution XPS analysis. S 2p spectra of the carbon/sulfur cathode a) before discharge, b) after discharging to 0.5 V, and c) after charging to 2.5 V.

formed MgS_x remains inactive during cycling, which provides another reason for the capacity fading.

Large voltage hystereses were observed during discharge/charge in these Mg/S batteries (Figure 2). To reveal their origin, we measured the overpotentials of the S cathode and Mg anode by using a three-electrode cell (Figure 4). During discharge, the potential of S shows a plateau at 1.4 V, while the Mg anode shows a potential of 0.1 V. Their difference (1.3 V) agrees well with the discharge voltage in the full cell (Figure 2b). During charging, the potential of S demonstrates a plateau at 1.65 V while the Mg anode shows a potential of –0.35 V. Their difference (2.0 V) also agrees with the charge voltage in the full cell. Overall, the potential hysteresis of the S cathode is only 0.25 V whereas the potential hysteresis of the Mg anode is 0.45 V.

**Figure 4.** Potentials of the S cathode and Mg anode in a three-electrode set-up. Electrolyte: 1 M MgTFSI₂/MgCl₂/DME. Working electrode (WE): S; CE: Mg; RE: Mg. Current density: 100 mA g⁻¹.

Therefore, the large voltage hysteresis of the Mg/S battery during discharge/charge is mainly due to Mg anode polarization. Indeed, the larger overpotential for the anode is consistent with previous observations by Aurbach and co-workers.^[31] Nevertheless, the 0.25 V overpotential for the S cathode is much lower than previously reported values for cathode materials based on intercalation^[5,8,44] and conversion materials,^[14,45,46] as well as oxygen.^[15] These good kinetics greatly benefit from the dissolution of polysulfide, which triggers a non-topotactic, liquid–solid reaction at the interface that is much faster than Mg intercalation.^[16] As the dissolved polysulfide is thermodynamically unstable to Mg, the Mg metal anode is prone to undergoing a side reaction with the polysulfides, which form a surface layer covering Mg anode; however, we did not observe the failure of the Mg anode during cycling (Figure S8).

In conclusion, we have developed the first rechargeable Mg/S battery with a MgTFSI₂/MgCl₂ electrolyte, which could be a good system for studying the electrochemistry of sulfur in magnesium batteries owing to the compatibility of this electrolyte with sulfur and its simple synthesis from commercially available salts. The dissolution of polysulfide was found to cause the shuttling effect and loss of active material, and a significantly improved capacity retention, that is, stable cycling for up to 110 cycles, was achieved by suppressing the dissolution of polysulfide by increasing the electrolyte concentration. The battery functions via S⁰/MgS_x ($x=2-8$) redox chemistry and delivers an initial capacity of about 800 mAhg⁻¹. The chemical reversibility of the S⁰/MgS_x ($x=2-8$) redox couple confirms the possibility of constructing a Mg/S battery with long cycling stability. The large voltage hysteresis was identified to mainly originate from the Mg anode overpotential, which may potentially be addressed by optimizing this electrolyte,^[34] while the sulfur cathode shows better kinetics than intercalation or conversion cathodes. We have thus developed the first Mg/S battery that can be cycled for more than 100 times. More importantly, this study confirms the chemical reversibility of the redox-active couple in the Mg/S battery and the suitability of the MgTFSI₂/MgCl₂ electrolyte for fundamental studies and performance improvement for future Mg/S batteries. It also proposes a simple approach to address the polysulfide dissolution problem in Mg/S batteries. Additional work is necessary to further improve the cycling stability and to increase the sulfur loading (both the S/C and S/E ratio) to develop practical Mg/S technology.

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Conflict of interest

The authors declare no conflict of interest.

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