Application of a Sulfur Cathode in Nucleophilic Electrolytes for Magnesium/Sulfur Batteries

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We report the potential feasibility of a high-capacity and low-cost sulfur cathode that is compatible with nucleophilic electrolytes for Mg/S batteries. The electrochemical performance of sulfur in an easily prepared (PhMgCl)2·AlCl3/THF nucleophilic electrolyte depends on cathode current collectors. A sulfur cathode that uses Cu as a current collector, which is electrochemically stable in the range of operating voltage, exhibits an initial discharge capacity approximately corresponding to 659 mAh g−1, and maintains a reversible capacity of 113 mAh g−1 after 20 cycles at a current density of 10 mA g−1. It is different from the sulfur cathode with few capacities that uses stainless-steel as a current collector. Copper sulfides formed when sulfur is coated on a Cu current collector at 50 °C provide a strong chemical interaction between Cu and sulfur, which protects sulfur and increases its compatibility with the electrolyte. A metal-stabilized sulfur cathode provides an effective approach to improve the electrochemical performance of Mg/S batteries in nucleophilic electrolytes.

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Manuscript submitted February 21, 2017; revised manuscript received July 17, 2017. Published August 24, 2017.

There is a constant increase in the demand for low-cost, high-energy-density rechargeable batteries that utilize environmentally friendly elements for applications, such as market-competitive electric vehicles and large-scale power storage systems due to fossil energy shortage and environmental issues. Following the rapid development of electric vehicles with space available to mount battery packs, it is now necessary for batteries to possess good safety characteristics1 and high volumetric energy density, which is more important than gravimetric energy density.2 Rechargeable magnesium batteries with magnesium as the anode may correspond to superior candidates compatible with post Li-ion batteries that contain a lithium metal anode, (Li/S) batteries yield a theoretical volumetric energy density exceeding 4000 Wh L−1 as compared to 2800 Wh L−1 for lithium/sulfur batteries.5,9 Moreover, N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonylethyl) imide (PF6-TFSI) was used to improve the discharge performance of Mg/S battery to a maximum corresponding to 1.65 V, which is close to the thermodynamic value of voltage (~1.7 V). Furthermore, MgCl2 was used as an inorganic and cheap Mg2+ ion source in combination with either Lewis acids (AlCl3, AlPh3, or AlCl3) or Mg salts (such as magnesium(II) bis(trifluoromethane sulfonylethyl)imide, Mg(TFSI)) to form high-performance electrolytes for Mg/S batteries.9,10 A simple chloride-free [Mg(THF)3]+ cation salt with AlCl4− as a counteranion was synthesized in an ionic liquid solvent to develop non-chlorinated electrolytes to overcome the issue of corrosion of magnesium electrolytes that contain a [Mg2(μ-Cl)2(THF)6][HMDSAlCl3] as an additive was proposed to improve the reversibility of Mg/S batteries by activating inactive MgS and MgS2 through deposition-dissolution, by simply using Cu as the cathode current collector. Moreover, Mg/S batteries that use the mononuclear Mg electrolyte composed of [Mg(THF)3][AlCl4] salt and ionic liquid/THF co-solvents exhibited good cycling performance. Specifically, Mg(TFSI)2 dissolved in glyme-based solvents with a highly reduced corrosive nature toward the current collector was proposed as a potential electrolyte for Mg/S batteries, although it suffered from the shuttle phenomenon due to the high solubility of polysulfides.11 Furthermore, a non-nucleophilic Mg electrolyte based on (HMDS)2Mg that uses lithium bis(trifluoromethanesulfonylethyl)imide (LiTFSI) as an additive was proposed to improve the reversibility of Mg/S batteries by activating inactive MgS and Mg2 through Li+.12 On the other hand, some efforts have also been made to add the dissolution of magnesium polysulfide (MgSx, x ≥ 4) by using a sulfur-carbon composite8,11,14 or fabricating new elemental selenium (Se) and selenium-sulfur solid solution (SeS2) cathodes to physically restrain polysulfides, facilitate electron transport, and provide free-space to accommodate the volume change in S/polysulfides.15

This study reported on the feasibility of a sulfur cathode in a typical nucleophilic electrolyte, (PhMgCl)2·AlCl3/THF,16 which is easily prepared and possesses high anodic stability and reversibility of Mg deposition-dissolution, by simply using Cu as the cathode current collector. Reversible discharge-charge of the Mg/S cell was demonstrated for over 20 cycles with specific capacities. The dissolution of polysulfides led to a rapid capacity fade in the Mg/S system. However, the study proved the concept of rechargeable Mg/S batteries with nucleophilic electrolytes by rationally designing a metal-stabilized sulfur electrode.

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Experimental

Cyclic voltammograms (CVs) were conducted in a three-electrode glass cell inside an argon-filled glove box (Mbraun, Unilab, Germany) or a two-electrode coin cell by using an electrochemical instrument of a CHI660A Electrochemical Workstation (Shanghai, China). Chronoamperometry was performed in a two-electrode coin cell by using an Autolab PGSTAT 302N (Metrohm Autolab, Switzerland). With respect to the three-electrode cells, the working electrode was a copper foil (15 μm, Sigma-Aldrich), which was polished by metallographic abrasive paper (800C0), and subsequently, cleaned using tissues, as counter and reference electrodes. With respect to the two-electrode cells, the working electrode was a copper foil (15 μm, Shanghai Xiaoyuan Energy Technology Co., Ltd., China) or stainless steel (SS, type 316, 25 μm thickness, Shenda Metals Co., Ltd., China), and magnesium ribbon acted as the counter electrode.

Additionally, 70 wt% sulfur (99.95%, Aladdin reagent), 20 wt% Super-P carbon powder (Timcal), and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidinone were mixed with a magnetic stirrer under an air atmosphere for 6 h at room temperature, coated on Cu or SS current collectors using a scraper, and dried by heating under vacuum at 50°C for 12 h. This was followed by the fabrication of CuS (99.99%, Aladdin reagent), Cu2S (99.5%, Alfa Aesar), and Mo6S8 synthesized by following procedures in extant study17 electrodes on a Cu current collector by using the same fabrication procedure as that used for the sulfur electrode. The electrode possessed 12 mm diameter and 100 μm layer thickness and contained approximately 0.6–0.7 mg active material. The electrochemical performance was examined via CR2016 coin cells with a Mg counter electrode, an Entek PE membrane separator (ET 20–60, 37% porosity, 20 μm thickness), and 0.4 mol L−1 (PhMgCl2)-AlCl3/THF electrolyte. The cells were assembled in an argon-filled glove box. Galvano-static discharge-charge (magnesiumation-demagnesiumation) measurements were conducted at an ambient temperature on a Land battery measurement system (Wuhan, China) with a cutoff voltage corresponding to 0.5–1.7 V vs. Mg.

Furthermore, X-ray powder diffraction (XRD) analysis was performed on a Rigaku diffraction meter D/MAX-2200/PC equipped with a Cu Kα radiation. An electronic conductivity measurement was performed using a four-point probe tester (ST2263, Suzhou Jingge Electronic Co., Ltd.), and thermogravimetric analysis (TGA) was performed using a Thermo Gravimetric Analyzer (TGA/Pyris 1 TGA) under Ar atmosphere. X-ray Photoelectron Spectroscopy (XPS) analysis was performed on an AXIS UltraDLD. The spectra were acquired using monochromatic Al Kα (1486.6 eV) radiation. The C 1s line with a binding energy of 284.8 eV was used as a reference. Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were conducted on a JEOL field-emission microscope (JSM-7401F). Moreover, UV-Vis spectra were recorded on a UV-Vis-NIR spectrophotometer (Cary 500 Scan).

Results and Discussion

It is widely accepted that Cu is not stable and is subject to pitting or corrosion in electrolytes based on magnesium organohalolamines because it contains chlorides in either the anions or cations of the salts.18 Fig. 1a shows the CVs on a Cu electrode in 0.4 mol L−1 (PhMgCl2)-AlCl3/THF electrolyte by using a three-electrode glass cell (Mg ribbon as both reference and counter electrodes). The increase in the cathodic current from approximately −0.2 V vs. Mg corresponds to Mg deposition, and the anodic peak at approximately 0.7 V vs. Mg is derived from the electrochemical dissolution of deposited Mg. In the forward scan, a small anodic oxidation current (approximately corresponding to 0.3 μA cm−2) is observed until a potential of 1.88 V vs. Mg. The operating voltage of a two-electrode battery may be lower than the voltage stability of the electrolyte observed in a three-electrode cell.19 The cyclic voltammetry measurement is further conducted using a two-electrode coin cell with a Cu foil as the working electrode and a Mg ribbon as the counter electrode. The Cu electrode in the coin cell is stable below 1.7 V vs. Mg, and an increase in anodic current (about 0.3 mA cm−2) is observed above 1.78 V vs. Mg, as shown in the inset of Fig. 1a. The corrosion resistance of Cu at 1.7 V is further investigated using chronoamperometry. The corrosion resistance of stainless steel (SS) is also measured to perform a comparison. As shown in Fig. 1b, a significantly lower current density corresponding to 0.2 μA cm−2 for a two-electrode coin cell with a Cu working electrode that is similar to that of an SS working electrode, is observed during 48 h in chronoamperometry. This confirms 1.7 V stability of the Cu current collector in the electrolyte. A discharge-charge measurement is conducted using conventional Mo6S8 as the cathode material to further ensure the operating voltage range of a two-electrode coin cell system. Fig. 1c shows the 2nd discharge-charge curve of the Mg/Mo6S8 coin cell with Cu as the cathode current collector and 0.4 mol L−1 (PhMgCl2)-AlCl3/THF electrolyte at 0.5 C rate (based on a theoretical specific capacity corresponding to 128.8 mAh g−1 for Mo6S8). The cutoff voltage range is set at 0.5–1.7 V vs. Mg. The curve exhibits two obvious discharge plateaus at 1.15 V and 1.08 V, which are related to the Mg2+ intercalation for the occupation of the inner and the outer sites, respectively, and a charge plateau at 1.2 V in addition to a sloping curve between 1.6 V and 1.7 V, which are associated with the de-intercalation of Mg2+ from the outer and inner ones, respectively.1 The discharge capacity and charge capacity approximately correspond to 74 and 71 mAh g−1, respectively. Capacities lower than those reported in extant study18 are mainly related to a few impurities in synthesized Mo6S8. Rietveld refinement of XRD in Fig. 1d demonstrates the presence of 18.15 wt% MoS2 and 4.66 wt% MoO3 in synthesized Mo6S8. As shown in the inset of Fig. 1c, the capacity retention rate at the 20th cycle approximately corresponds to 84% of the 2nd cycle. The good electrochemical performance of Mo6S8 indicates that Cu can be used as the cathode current collector when the upper limit of the charge voltage for the coin cell is lower than 1.7 V.

Figs. 2a and 2b show the initial three galvanostatic discharge-charge profiles of Mg/S coin cells in a voltage range corresponding to 0.5–1.7 V at a current density of 10 mA g−1 (approximately 0.006 C, based on the theoretical capacity of 1671 mAh g−1 for sulfur) by using Cu and SS as the cathode current collectors, respectively. The cell with a Cu current collector delivers an initial discharge capacity approximately corresponding to 659 mAh g−1 and a charge capacity approximately corresponding to 405 mAh g−1 based on the sulfur material. The first discharge curve exhibits a sloping voltage profile from 1.5 V to 1.4 V and a stable voltage plateau at 1.1 V, which is followed by a slowly decaying tail. The fore-mentioned processes correspond to the reduction of the solid cyclo-Ss to dissolved polysulfide MgSx (which is subsequently reduced to MgS2), MgS2 to solid MgS2, and then MgS2 to MgS.4 The first discharge curve exhibits a voltage plateau at 1.3 V and a sloping voltage profile from 1.6 V to 1.7 V, which correspond to the conversion of MgS/MgS2 to low-order polysulfides and further to high-order polysulfides or sulfur. In the following discharge curves, the stable voltage plateau at 1.1 V for main capacity contribution shortens obviously. This seems some sulfur and/or polysulfides dissolve into the electrolyte. Additionally, MgS/MgS2 formed after the first discharge may also not be completely converted back into elemental sulfur in the first charge.14 The capacity quickly decreases to 392 mAh g−1 in the second discharge and further to 315 mAh g−1 in the third cycle corresponding to approximately 91% and 93% discharge-charge coulometric efficiencies, respectively. When SS is used as the cathode current collector, Mg/S cell delivers an initial discharge capacity of 9 mAh g−1 (as shown in the discharge-charge curve in Fig. 2b), which is considerably lower than that of the cell with a Cu current collector. The extra initial charge capacity of 228 mAh g−1 is potentially due to the interaction of soluble sulfur with the Mg anode. The capacities exhibit a significant decrease to less than 5 mAh g−1 in subsequent cycles. The low capacity is not surprising because of the loss of active

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electrophilic sulfur, which dissolves and/or reacts with the nucleophilic electrolyte. This fully proves that the Cu current collector is responsible for the exceptional electrochemical performance of the sulfur cathode in (PhMgCl)$_2$-AlCl$_3$/THF nucleophilic electrolyte.

The reaction of (PhMgCl)$_2$-AlCl$_3$/THF electrolyte with sulfur, as reported by Muldoon, is considered. The components of sulfur electrodes that use Cu and SS as the current collectors are confirmed by XRD measurements. As shown in Fig. 3a, the pattern exhibits main peaks centered at $2\theta = 23.07^\circ$, 25.83$^\circ$, 26.71$^\circ$, and 27.70$^\circ$, which match well with the (222), (026), (311), and (206) reflections of the Fddd orthorhombic phase of sublimed sulfur (JCPDS no. 78-1889). In addition to S, a few weak peaks are related to CuS (JCPDS no. 06-0464) and Cu$_2$S (JCPDS no. 83-1462) for the sulfur electrode with Cu current collector after heat-treatment at 50$^\circ$C. They are produced in the drying process of the electrode at 50$^\circ$C under vacuum. Electronic conductivity measurements are performed on S electrodes with the Cu current collector following natural drying at room temperature and heated drying at 50$^\circ$C under vacuum. Electronic conductivity measurements are performed on S electrodes with the Cu current collector following natural drying at room temperature and heated drying at 50$^\circ$C under vacuum. The sulfur electrode on Cu after heat-treatment at 50$^\circ$C exhibits an electronic conductivity (926 $\mu$S cm$^{-1}$) exceeding that without the heat-treatment (769 $\mu$S cm$^{-1}$), which indicates that the copper sulfides formed in the interface of the S/Cu current collector improve the electronic conductivity of the sulfur electrode with the Cu current collector. However, diffraction peaks corresponding to copper sulfides are absent in the sulfur electrode with SS as the current collector after heat-treatment at 50$^\circ$C. Unless mentioned otherwise, all electrodes are fabricated by heat-treatment at 50$^\circ$C under vacuum. The state and content of sulfur in the electrodes are further measured using TGA. As shown in Fig. 3b, there are approximately 20 wt% residues in both electrodes that correspond to the conductive carbon black Super-P contained in the electrodes. The 10 wt% PVDF binder decomposed at a temperature exceeding 390$^\circ$C is removed, and the sulfur contents in the two electrodes are approximated correspond to 70 wt%, which is the same as the amount of active material in the electrode slurry. This is different from a one-step weight loss for the sulfur electrode on SS since the TGA curve of the sulfur electrode on Cu consists of three steps. The first weight loss releases approximately 25% of S in a temperature range (90$^\circ$C to 250$^\circ$C) similar to that of sulfur electrode on SS, which is mainly attributed to the evaporation of elemental S. The second and third steps range from approximately 340$^\circ$C to 415$^\circ$C and 415$^\circ$C to 455$^\circ$C with 35% and 10% weight losses, respectively. The third step is related to the decomposition of Cu$_2$S and CuS in the electrode, and is demonstrated by the TGA curves of commercial Cu$_2$S and CuS powders. The second step is similar to those reported in C-Cu-S composites synthesized by a chemical reaction between Cu and S, which are attributed to strong chemical bonding between S and Cu. The delay in extracting S from the electrode confirms the occurrence of chemical bonds between sulfur and Cu current collector through copper sulfides. Additionally, the temperature ranges of weight loss for the sulfur electrode on Cu are evidently different from those of the
mixtures of Cu and S powders with 2:1 and 1:1 molar ratios, which suggests that Cu$_2$S and CuS are already formed at 50°C heat-treatment in the electrode and not due to further heating in TGA.

To further examine the interaction between Cu and S, XPS measurements are conducted to determine the oxidation state of sulfur and copper in the pristine electrode. Fig. 4a presents the S 2p binding energy spectra of the electrodes with Cu and SS current collectors. With respect to the electrode on SS, the dual peaks positioned at 164.1 and 165.3 eV are assigned to characteristic peaks of 2p$_{3/2}$ and 2p$_{1/2}$ of elemental S. The spectrum for the electrode on Cu exhibits two peaks of 2p$_{3/2}$ and 2p$_{1/2}$ at 162.4 and 163.4 eV, respectively, with a peak splitting corresponding to 1.0 eV. This is consistent with the 160–164 eV range expected for S in sulfide phases. It is reported that the monolayer of S enhances surface self-diffusion on Cu (111) by several orders of magnitude. Additionally, the “shake-up” satellites at approximately 945 eV and 965 eV for the Cu 2p$_{3/2}$ and 2p$_{1/2}$ core levels, respectively, are associated with the existence of Cu$^{2+}$. The XRD, TGA, and XPS results demonstrate the occurrence of chemical bonds between Cu and S in the electrode with Cu as the current collector, which indicates that the S is not only physically loaded on the Cu current collector but also chemically interacts with the Cu substrate by forming of copper sulfides with the mixed valence states of Cu$^{1+}$ and Cu$^{2+}$ ions.

As is widely known, S and polysulfide intermediates are non-conductive and their electrochemical reactions only occur when the S loading thickness on the conductive matrix is within an electron tunneling range. Therefore, a key challenge in Li/S batteries involves increasing S utilization at a high S loading with low “shuttle reaction”. An attempt for increasing the S loading involves uniformly distributing a thin-layer S in conductive materials through a strong interaction between S and a conductive host. For example, a polymer-S composite cathode synthesized by a chemical reaction between polyacrylonitrile and S exhibits good cycle life and rate capability. On the other hand, transition metal sulfides formed by reacting transition metals (Co, Ni, ...
Ti, and Cu) with S are investigated as cathode materials for lithium-ion batteries and exhibit a fairly stable cycle life. The strong bonds between metal and S allow the S in metal sulfides to directly form Li$_2$S and metal without forming soluble high-order polysulfide during lithiation. Among the transition metals, Cu is a highly conductive, naturally abundant, and low-cost element. The CuS cathode is easily formed when S is coated onto a Cu foil at 60°C. A copper-stabilized sulfur-microporous carbon (MC-Cu-S) composite with a high S loading of 50% is synthesized by uniformly dispersing 10% highly electronically conductive Cu nanoparticles into microporous carbon (MC) followed by wet-impregnating S, and is reported as a cathode for carbonate electrolyte Li-S batteries. In the composite of MC-Cu-S, the microporous structure of the MC physical confines the S, while the Cu nanoparticles anchored in the MC further chemically interact with S/polysulfides CuS$_x$, thereby resulting in a more effective reduction in the active material loss on prolonged cycling. It is demonstrated that CuS and Cu$_2$S exhibit some reversible electrochemical activity in Mg(AlCl$_2$BuEt)$_2$/THF nucleophilic electrolyte via the displacement of transition metal that occurs in the magnesiation process. With respect to Cu$_2$S, the initial process exhibits a discharge capacity of less than 4 mAh g$^{-1}$ with a 1.3 V discharge voltage plateau. After the first cycle, the discharge capacity quickly decreases to less than 1 mAh g$^{-1}$ and declines with progressive cycling. The discharge plateaus indicate that CuS and Cu$_2$S are involved in the electrochemical reaction. However, the contribution of CuS and Cu$_2$S to the electrochemical properties of the sulfur electrode is negligible, and this demonstrates that S in the electrode is responsible for the high reversible capacity of the cell. The strong interaction between Cu and S results in adhering and loading additional S on the current collector during the fabrication process of the electrode. Furthermore, the Cu-S bonds from copper sulfides, which form at the interface of sulfur active material and Cu current collector and diffuse easily to the surface of the electrode, absorb and stabilize S and polysulfides formed during magnesiation/demagnesiation to restrain the reaction of sulfur with the nucleophilic electrolyte and improve the electrochemical performance of the Mg/S cell.

To further examine the redox reactions that occur during the discharge and charge processes in the Mg/S cell with the Cu current collector, the electrochemical measurements were performed. Figs. 5a and 5b show discharge and charge curves, respectively, for the initial three cycles of Mg/CuS and Mg/Cu$_2$S cells at 10 mA g$^{-1}$. With respect to CuS, the initial discharge and charge capacities approximately correspond to 26 and 3 mAh g$^{-1}$, respectively, and the discharge capacities significantly decrease to approximately 4 mAh g$^{-1}$ and 2 mAh g$^{-1}$ in two subsequent cycles. During the first discharge process, two voltage plateaus are observed at approximately 1.4 and 1.1 V, which disappear in subsequent discharge curves, indicating the displacement of the transition metal that occurs in the magnesiation process.

![Figure 4](image-url)  
**Figure 4.** XPS spectra of S 2p for the sulfur electrodes with Cu and SS current collectors (a), and Cu 2p for the sulfur electrode with Cu current collector (b).

![Figure 5](image-url)  
**Figure 5.** Initial three discharge-charge curves of Mg/CuS (a) and Mg/Cu$_2$S (b) coin cells with Cu as the cathode current collector at 10 mA g$^{-1}$. 

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The cells are disassembled at different discharge and charge stages and the sulfur electrodes are analyzed through XPS. The cells are disassembled in an argon-filled glove box. The electrodes are separated, rinsed with anhydrous THF to remove the electrolyte residues, dried in the glove box, and subsequently, maintained without exposure to air prior to the measurements. Fig. 6a shows the S 2p spectra of the sulfur electrodes after cycling. The spectrum of the as-prepared sulfur electrode is enclosed as a reference. The as-prepared sulfur electrode exhibits two characteristic peaks at 162.4 and 163.4 eV, which correspond to S 2p\(^{3/2}\) and S 2p\(^{1/2}\) doublets, respectively, of S in the sulfide phases. After discharging the Mg/S cell to 1.2 V, the main S 2p\(^{3/2}\) and S 2p\(^{1/2}\) peaks shift to 161.9 and 162.9 eV. These peaks at lower binding energy are related to Mg-S bonds in high-order magnesium polysulfides (MgS\(^x\), 4 ≤ x ≤ 8). After discharging the Mg/S cell to 0.8 V, the peaks broaden over a span from 163.5 to 161.0 eV and shift to a much lower binding, and are most reasonably assigned to the Mg-S bonds in low-order magnesium polysulfides. After discharging to 0.5 V, the 2p\(^{3/2}\) peak positioned at 160.9 eV is assigned to the Mg-S bond in MgS\(_2\) and MgS. The existence of the peak for polysulfides implies the partial utilization of sulfur and explains the relatively low discharge capacity. After re-charging the cell to 1.7 V, the MgS returns to MgS\(_x\) (1 ≤ x ≤ 8), and this confirms the successful transition between S and MgS via polysulfide intermediates to indicate the reversibility of the cell. Fig. 6b shows the corresponding Mg 2p spectra of the sulfur electrodes after cycling. The peak exhibited at approximately 50.5 eV is mainly due to the formation of MgS\(_x\).  

Fig. 7a illustrates the CV curves of the Mg/S coin cell with Cu as the cathode current collector at 0.05 mV s\(^{-1}\). During the first cathodic scan, two main reduction peaks are observed at approximately 1.35 V and 1.0 V along with a shoulder peak at 0.9 V, which corresponds to the formation of higher-order magnesium polysulfides (MgS\(^x\), 4 ≤ x ≤ 8) from elemental sulfur, the reduction of these higher-order magnesium polysulfides to lower-order magnesium polysulfides, and the further formation of MgS\(_2\) and MgS. During the first anodic scan, a strong oxidation peak is observed at approximately 1.43 V, which is attributed to the oxidation of MgS and MgS\(_2\) back to polysulfide MgS\(^x\) (x > 2). The current increase above 1.6 V is relative to further oxidation to higher-order polysulfides or elemental sulfur. During the second cathodic scan, the peak currents exhibit an obvious decrease, suggesting that a little sulfur and/or polysulfides dissolve into the electrolyte, leading to capacity fading of the cell. The peak voltages shift toward a more positive direction. The same CV behavior with a large overpotential in the first reduction process is also reported in a Li/S cell with a high S loading, which results from the large strain/stress due to large volume change. The relatively stable cathodic and anodic current peaks in the following scans demonstrate the cycling stability of the S cathode in the nucleophilic electrolyte.
The discharge-charge cycling performance and corresponding coulombic efficiency of Mg/S coin cell with Cu as the cathode current collector at 10 mA g⁻¹ are presented in Fig. 7b. The data indicate an obvious capacity fading for the initial cycles, which is similar to that observed in the Mg/S battery system by using the carbon-sulfur nanocomposite.2,8,11,14 This is mainly due to the presence of some elemental sulfur without bonding with Cu within the cathode. Subsequently, relatively stable cyclic stability is observed for further cycles. At the end of the 5th cycle, the discharge and charge capacity values approximately correspond to 250 and 244 mA h g⁻¹, respectively. The capacity continuously decreases and stabilizes at approximately 113 mA h g⁻¹ at the 20th cycle. After a few initial cycles, the charge capacity contribution gradually increases when compared to the corresponding discharge capacity. As shown in the inset of Fig. 7b, coulombic efficiencies exceeding 100% are potentially due to the polysulfide shuttle effect, which acts as a parasitic side reaction.14 Furthermore, an increase in the current density to 20 mA g⁻¹ maintains the discharge capacity at approximately 99 mA h g⁻¹ after 20 cycles. This reveals that the dissolution and shuttle effects are prevented to a certain extent and indicates that the strong interaction between Cu and S and higher electronic conductivity of copper sulfides increase the S utilization and enhance the cycling stability of the S cathode in the nucleophilic electrolyte. The cycle performance considerably improves when compared to that in previous studies involving Mg/S cells where S, N-doped graphene-S nanocomposite cathodes and non-nucleophilic Mg electrolytes were used2,11 and are lower than those observed in very recent studies that employed S-graphene nanocomposite, S-mesoporous carbon composite and non-nucleophilic Mg electrolytes8,13. The effort to support S by using a carbon matrix significantly improves S utilization and restrains the solubility of polysulfides. Specifically, the C-S composite cathodes exhibit an outstanding cycling life by infusing S into the pores of carbon materials. However, the S loading is limited to approximately 50% in the C-S composite due to the insulating nature of S/polysulfides and the side reaction between high-order polysulfides and electrolytes, which leads to a low overall capacity.

The morphology and structural changes in S electrodes with Cu and SS current collectors after cycling are explored to further understand the reason for the feasible discharge-charge cycling of S cathode in the nucleophilic electrolyte. The cells after 20 cycles at 10 mA g⁻¹ are disassembled and characterized via SEM. The results are shown in Fig. 8. Prior to cycling, the S cathode surfaces on Cu (Fig. 8a) and SS (Fig. 8b) exhibit a typical electrode morphology, namely rough without cracks. After 20 cycles, sulfur particles embedded in Super-P carbon are still visible from the electrode with a Cu current collector (Fig. 8c). With respect to the S electrode on SS (Fig. 8d), several cracks and holes along with the appearance of the substrate that are labeled with hollow boxes are observed when compared to the relatively smooth and dense surface of the S electrode on Cu (Fig. 8c). The corresponding EDX results in Table I show that the sulfur component in the S electrode with the SS current collector exhibits a significant decrease. However, the loss amount for the electrode with a Cu current collector is significantly lower. The loss of sulfur in the electrode with the SS current collector suggests the existence of the reaction of electrophilic sulfur with the nucleophilic electrolyte and/or the dissolution of sulfur in the electrolyte. However, the strong interaction between the S active material and Cu current collector through copper sulfides restrains the reaction. The capacity fading of the cell with a Cu current collector is most likely caused by the dissolution of S and/or polysulfides in the electrolyte. The electrolytes of the Mg/S cells with Cu and SS as the cathode current collectors and Li/S cell with Cu as the cathode current collector and 1 mol L⁻¹ LiPF₆/EC+DMC (1:1 by volume) electrolyte are extracted by immersing the separators in THF. The dissolution of species into the electrolytes is inspected through UV-Vis spectroscopy. As shown in Fig. 9, strong absorbance peaks appear at 240 nm and 265 nm for the S electrodes on Cu and SS, respectively, to indicate the dissolution of elemental sulfur based on the analysis of Mg/S and Li/S batteries.8,36 The peaks for the S electrode on Cu (especially at 265 nm) are weaker than those on SS, which suggests that the concentration of dissolved S in the electrolyte is lower. Additionally, a weak peak appears at approximately 300 nm for the S electrode on Cu in Mg/S and Li/S cells, which is attributed to the $S_6^{2-}$ anion.36,37 The peak is not obvious for

![Figure 8](image_url)

**Figure 8.** The morphologies of S cathodes with Cu (a, c) and SS (b, d) current collectors before (a, b) and after (c, d) 20 cycles of discharge and charge at 10 mA g⁻¹.

![Figure 9](image_url)

**Figure 9.** UV-Vis spectra of the electrolytes in the Mg/S cells with Cu and SS as the cathode current collectors and Li/S cell with Cu as the cathode current collector and 1 mol L⁻¹ LiPF₆/EC+DMC (1:1 by volume) electrolyte after 20 cycles of discharge and charge at 10 mA g⁻¹.
the S electrode on SS in the Mg/S cell, which indicates the presence of polysulfides in the cell containing the S electrode with the Cu current collector and demonstrates that the electrochemical conversion of sulfur to polysulfides occurs in the cell. However, it appears that the dissolution of elemental sulfur in the electrolyte is more dominant than that of polysulfides during the cycling, which can result in the capacity fading of the cell.

Although the Mg/S cell exhibits unsatisfactory cycling stability and rate performance, which mainly results from the high solubility of the discharge products and the insulating nature of sulfur, the preliminary research confirms a new configuration that makes sulfur cathode compatible with nucleophilic electrolytes. A further work is needed to improve the electric/ionic conductivity of the sulfur material, effectively prevent the dissolution of intermediate polysulfides, and ensure the integrity of the electrode structure on cycling. A rechargeable Mg/S battery with significantly improved reversibility is also demonstrated using LiTFSI as an additive of non-nucleophilic electrolyte.13

The presence of Li+ enables the reactivation of the short-chain Mg-PS (MgS and MgS2) either through an ion-exchange reaction and their transformation into rechargeable Li2S and Li2S2 or through a strong coordination between Li+ and the surface S2− and S22− of MgS and MgS2, which increases their solubility and reduces the re-oxidation kinetic barrier by forming MgLi-PS. The cycling stability and rate performance are also improved by the addition of LiCl in the (PhMgCl)2-AlCl3/THF electrolyte. Fig. 10a shows the initial three galvanostatic discharge-charge profiles of the Mg/S coin cell with the Cu cathode current collector at 10 mA g−1. The first discharge curve shows two voltage plateaus at 1.4 V and 1.1 V, followed by a slowly decaying tail. The first charge curve exhibits a voltage plateau at 1.3 V and a sloping voltage profile from 1.6 V to 1.7 V. In the following discharge curves, the voltage plateau at 1.4 V shortens and increases, while the voltage plateau at 1.1 V for the main capacity contribution dose not evidently shorten. This indicates that the presence of Li+ reactivates the short-chain Mg-PS species.13 The initial discharge capacity corresponds to approximately 512 mAh g−1, the capacity decreases to 388 mAh g−1 in the second discharge, and is subsequently maintains at 384 mAh g−1 in the third discharge. Fig. 10b shows the cell cycles for more than 40 cycles with a comparatively stabilized capacity corresponding to approximately 290 mAh g−1. An increase in the current density to 20 mA g−1 maintains the capacities at approximately 150 mAh g−1 at the 40th cycle.

In summary, the strategy in the present study, which is based on Cu as the current collector of sulfur electrode, provides a new direction such that the sulfur cathode is compatible with nucleophilic electrolytes by forming a bonding interaction between S and Cu. Although further studies are necessary to fundamentally understand the details of the interaction and role of the Cu current collector, the current study conceptually provides a new opportunity to prevent sulfur from reacting with nucleophilic electrolytes and to reach the potential application of a sulfur cathode in nucleophilic electrolytes for rechargeable magnesium batteries.

Conclusions

This study reported on the potential feasibility of a high-capacity and low-cost sulfur cathode that is compatible with the (PhMgCl)2-AlCl3/THF nucleophilic electrolyte for Mg/S batteries. The Cu current collector plays a key role with respect to the exceptional electrochemical performance of the S cathode. Specifically, Cu chemically stabilizes S to form copper sulfides while loading sulfur on a Cu foil at 50 °C. The strong interaction between Cu and S through copper sulfides protects sulfur from the electrolyte and increases the compatibility of sulfur with the electrolyte. The electrochemical conversion of the chemical bonding sulfur to magnesium polysulfides successfully occurs in the nucleophilic electrolyte. The strategy based on metal-stabilized sulfur through chemical bonds provides a new direction to make sulfur compatible with nucleophilic electrolytes.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (project no. 21273147, 21573146) and the Shanghai Municipal Science and Technology Commission (project no. 11JC1405700).

References

1. D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gitzbar, R. Turgeman, Y. Cohen, M. Moshkovitch, and E. Levi, Nature, 274, 724 (2000).
2. H. S. Kim, T. S. Arthur, G. D. Alfred, J. Zajicek, J. G. Newman, A. E. Rodnyansky, A. G. Oliver, W. C. Boggess, and J. Muldoon, Nature Commun., 2, 427 (2011).
3. D. P. Lv, T. Xu, P. Saha, M. K. Datta, M. L. Gordin, A. Manivannan, P. N. Kumta, and D. H. Wang, J. Electrochem. Soc., 160, A351 (2013).
4. J. Muldoon, C. B. Bacur, A. G. Oliver, T. Sugimoto, M. Matsui, and H. S. Kim, Energy Environ. Sci., 5, 5941 (2012).
5. X. L, K. T. Lee Ji, and L. F. Nazar, Nat. Mater., 8, 500 (2009).
6. Z. Zhao-Karger, X. Y. Zhao, O. Fuhr, and M. Fichtner, RSC Adv., 3, 16330 (2013).
7. C. Wall, Z. Zhao-Karger, and M. Fichtner, ECS Electroin., 4, C8, (2015).
8. Z. Zhao-Karger, X. Y. Zhao, D. Wang, T. Diemant, R. J. Behm, and M. Fichtner, Adv. Energy Mater., 5, 1401155 (2014).
9. T. B. Liu, Y. Y. Shao, G. S. Li, M. Gu, J. Z. Hu, S. C. Xu, Z. M. N.; L. Chen X, C. M. Wang, and J. Liu, J. Mater. Chem. A, 2, 3430 (2014).
10. Y. W. Cheng, R. M. Stolzy, K. S. Han, Y. Y. Shao, B. W. Arej, N. M. Washton, K. T. Mueller, M. L. Helm, V. L. Sprengle, J. Liu, and G. S. Li, Phys. Chem. Chem. Phys., 17, 13307 (2015).

Figure 10. Initial three discharge-charge curves of Mg/S cell with Cu as the cathode current collector in 0.4 mol L−1 (PhMgCl)2-AlCl3+1.0 mol L−1 LiCl/THF electrolyte at 10 mA g−1 (a). The cycling performance of the Mg/S cells at 10 mA g−1 and 20 mA g−1 (b); the inset shows the corresponding coulombic efficiency.
11. W. F. Li, S. Cheng, J. Wang, Y. C. Qiu, Z. Z. Zheng, H. Z. Lin, S. Nanda, Q. Ma, Y. Xu, F. M. Ye, M. N. Liu, L. S. Zhou, and Y. G. Zhang, *Angew. Chem. Int. Ed.*, **55**, 6406 (2016).

12. S.-Y. Ha, Y.-W. Lee, S. W. Woo, B. Koo, J.-S. Kim, J. Cho, K. T. Lee, and N.-S. Choi, *ACS Appl. Mater. Interfaces*, **6**, 4063 (2014).

13. T. Gao, M. Noked, A. J Pearse, E. Gillette, X. L. Fan, Y. J. Zhu, C. Luo, L. M. Suo, M. A Schroeder, K. Xu, S. B. Lee, G. W. Rubloff, and C. S. Wang, *J. Am. Chem. Soc.*, **137**, 12388 (2015).

14. B. P. Vinayan, Z. Zhao-Karger, T. Diemant, V. S. K. Chakravadhanula, N. I. Schwarzburger, M. A. Cambaz, R. J. Behm, C. Kübel, and M. Fichtner, *Nanoscale*, **8**, 3296 (2016).

15. Z. Zhao-Karger, X.-M. Lin, C. B. Minella, D. Wang, T. Diemant, R. J. Behm, and M. Fichtner, *J. Power Sources*, **323**, 213 (2016).

16. O. Mizrahi, N. Amir, E. Pollak, O. Chusid, V. Marks, H. Gottlieb, L. Larush, E. Zinigrad, and D. Aurbach, *J. Electrochem. Soc.*, **155**, A103 (2008).

17. E. Lancry, E. Levi, A. Mitelman, S. Malovany, and D. Aurbach, *J. Solid State Chem.*, **179**, 1879 (2006).

18. J. Muldoon, C. B. Bucur, A. G. Oliver, J. Zajicek, G. D. Allred, and W. C. Boggess, *Energy Environ. Sci.*, **6**, 482 (2013).

19. S. Y. Zheng, P. Han, Z. Han, P. Li, H. J. Zhang, J. H. Yang, and C. S. Wang, *Adv. Energy Mater.*, **1400226** (2014).

20. S. Y. Zheng, F. Yi, Z. P. Li, Y. J. Zhu, Y. H. Xu, C. Luo, and J. H. Yang, *Adv. Funct. Mater.*, **24**, 4156 (2014).

21. P. C. Dai, X. N. Shen, Z. J. Lin, Z. Y. Feng, H. Xu, and J. H. Zhan, *Chem. Commun.*, **46**, 5749 (2010).

22. J. Xu, X. Yang, Q. D. Yang, T. L. Wong, and C. S. Lee, *J. Phys. Chem. C*, **116**, 19718 (2012).

23. G. Gordillo, C. Calderón, and P. Bartolo-Pérez, *Appl. Surf. Sci.*, **305**, 506 (2014).

24. W. L. Ling, N. C. Bartelt, K. Pohl, J. de la Figuera, R. Q. Hwang, and K. F. McCarty, *Phys. Rev. Lett.*, **93**, 166101 (2004).

25. P. J. Feibelman, *Phys. Rev. Lett.*, **85**, 606 (2000).

26. G. B. D. Rousseau, A. Mulligan, N. Bovet, M. Adams, V. Dhanak, and M. Kadodwala, *Surf. Sci.*, **600**, 897 (2006).

27. C. C. Chusuei, M. A. Brookshier, and D. W. Goodman, *Langmuir*, **15**, 2806 (1999).

28. J. L. Wang, J. Yang, J. Y. Xie, and N. X. Xu, *Adv. Mater.*, **14**, 963 (2002).

29. Y. J. Wang, J. Wu, Y. Tang, X. Lu, C. Yang, M. Qin, F. Huang, X. Li, and X. Zhang, *ACS Appl. Mater. Interfaces*, **4**, 4246 (2012).

30. S. Han, H. Kim, M. Song, P. S. Lee, J. Lee, and H. Ahn, *J. Alloys Compd.*, **349**, 290 (2003).

31. A. Sakuda, N. Taguchi, T. Takeuchi, H. Koyayashi, H. Sakurae, K. Tatsumi, and Z. Ogumi, *Electrochem. Commun.*, **31**, 71 (2013).

32. R. Cai, J. Chen, J. Zhu, C. Xu, W. Zhang, C. Zhang, W. Shi, H. Tan, D. Yang, H. H. Hng, T. M. Lim, and Q. Yan, *J. Phys. Chem. C*, **116**, 12468 (2012).

33. Y. Du, Z. Yin, J. Zhu, X. Huang, X.-J. Wu, Z. Zeng, Q. Yan, and H. Zhang, *Nat. Commun.*, **3**, 1177 (2012).

34. Y. Wang, X. Zhang, P. Chen, H. Liao, and S. Cheng, *Electrochim. Acta*, **80**, 264 (2012).

35. N. Amir, Y. Vestfrid, O. Chusid, Y. Gofer, and D. Aurbach, *J Power Sources*, **174**, 1234 (2007).

36. N. A. Cañas, D. N. Fronczek, N. Wagner, A. Latz, and K. A. Friedrich, *J. Phys. Chem. C*, **118**, 12106 (2014).

37. G. Bieker, J. L. Wellmann, M. Kolek, K. Jalkanen, M. Winter, and P. Bieker, *Phys. Chem. Chem. Phys.*, **19**, 11152 (2017).