Investigation of the Effects of Copper Nanoparticles on Magnesium-Sulfur Battery Performance: How Practical Is Metallic Copper Addition?

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Rechargeable magnesium sulfur (Mg/S) batteries suffer from fast capacity fading due to difficulty of reoxidation of MgS and the polysulfide shuttle. Other works have reported that use of Cu current collectors or CuS at the cathode improves cycleability. Here we investigate Cu nanoparticles grown on carbon nanofibers (Cu@CNF) as an additive for the Mg/S battery cathode to test the effects of Cu metal on capacity and rate performance at controlled Cu loading. The Mg/S battery with Cu additives can run at 1 C with a capacity of 452 mAh/g after 100 cycles. It was confirmed via X-ray photoelectron spectroscopy that Cu$_2$S forms during cathode formation and contributes to the high initial capacity, but then converts back to metallic Cu. Upon extending cycling, the Cu additives promote the formation of smaller, more dispersed discharge product particles, thereby enhancing reversibility. Finally, it is found that the loading of S and Cu at the cathode must be low to achieve substantial and sustained benefits of the Cu additives.
Investigation of the effects of copper nanoparticles on magnesium-sulfur battery performance: How practical is metallic copper addition?

Peng He, Hunter O. Ford, Laura C. Merrill, and Jennifer L. Schaefer*

Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN

*Jennifer.L.Schaefer.43@nd.edu

Abstract: Rechargeable magnesium sulfur (Mg/S) batteries suffer from fast capacity fading due to difficulty of reoxidation of MgS and the polysulfide shuttle. Other works have reported that use of Cu current collectors or CuS at the cathode improves cycleability. Here we investigate Cu nanoparticles grown on carbon nanofibers (Cu@CNF) as an additive for the Mg/S battery cathode to test the effects of Cu metal on capacity and rate performance at controlled Cu loading. The Mg/S battery with Cu additives can run at 1 C with a capacity of 452 mAh/g after 100 cycles. It was confirmed via X-ray photoelectron spectroscopy that Cu2S forms during cathode formation and contributes to the high initial capacity, but then converts back to metallic Cu. Upon extending cycling, the Cu additives promote the formation of smaller, more dispersed discharge product particles, thereby enhancing reversibility. Finally, it is found that the loading of S and Cu at the cathode must be low to achieve substantial and sustained benefits of the Cu additives.
Introduction

Lithium ion (Li-ion) batteries are the most widely used electrochemical energy storage devices today. The Mg battery is a promising alternative to Li-ion, and worldwide attention regarding this technology has increased in recent years due to the high abundance, low cost, and high volumetric charge storage capacity of magnesium metal. However, to create a high energy density Mg battery, the magnesium metal anode must be paired with a high capacity cathode. Furthermore, it is desirable for the cathode to be cheap and safe.

Sulfur, with a high theoretical capacity of 1675 mAh/g and currently studied for use as the active cathode material in Li-based and Na-based batteries, may be paired with the Mg anode. However, the serious polysulfide shuttling effect, the reaction between sulfur and conventional nucleophilic Mg electrolytes, and poor rate performance pose significant challenges to the development of the practical magnesium/sulfur (Mg/S) battery. The shuttling effect is caused by the dissolution of polysulfides in electrolyte; both the lithium/sulfur (Li/S) and the Mg/S battery suffer from the shuttling effect. Approaches to address this challenge are numerous and include applying nanocarbons with high specific surface area as a host material for elemental sulfur, modification of the separator, use of new electrolyte and separator materials, coating a polymer film on the electrode surface as a physical barrier, and using inorganic compounds to trap polysulfide anions. The challenge of electrolyte reactivity is unique to Mg/S as many of the original Mg-based electrolytes that were demonstrated to support reversible Mg deposition and dissolution are nucleophilic and thus chemically reactive with sulfur. However, many non-nucleophilic electrolytes have since been developed to support Mg/S, such as those based on hexamethyldisilazide (i.e., HMDSMgCl, Mg(HMDS)2+AlCl3) and borate-based salts. Finally, it is found that the rate performance of Mg/S cells is poor compared to that of Li/S. This is presumably due to reduced electrochemical reaction (oxidation/reduction) kinetics for MgSx species.

Interestingly, Nuli and colleagues found that the Mg-S battery assembled with a copper current collector can reversibly cycle with nucleophilic electrolyte. The formation of CuS and Cu2S on the copper current collector surface is observed, and the copper sulfides are hypothesized to adsorb cyclic S8 and polysulfides, thus preventing their reaction with the nucleophilic electrolyte. The copper current collector enables high sulfur utilization and capacities at reasonable rates (300 mAh/g-S after 40 cycles at a rate of 10 mA/g-S), whereas the initial capacity with a stainless steel current collector is less than 30 mAh/g-S. The use of copper current collectors also results in stable cycling of Li-S and Na-S batteries. Oh and colleagues studied the interaction between the copper current collector and sulfur and found Cu2S contributed to the capacity of the Mg/S battery. In other works, CuS is directly used as a cathode material and paired with the Mg anode, resulting in reasonable discharge capacities at relatively high charge/discharge rates.

In all cases of copper use in the Mg/S system, it is an inactive material in terms of energy storage, adding mass, volume, and non-negligible cost. Commodity Cu metal pricing is 6.17 USD/kg (0.395 USD/mol), compared with 4.96 USD/kg (0.119 USD/mol) for Mg and only 0.14 USD/kg (0.045 USD/mol) for S at the time of this writing. With these metrics in mind, we have fabricated sulfur cathodes containing Cu nanoparticles with varying Cu:S molar ratios to enable further study of the copper-sulfur interaction, charge storage capacity, and rate capability in the Mg/S battery, in the scenario of controlled copper
loading. Due to the inherently high surface area to mass ratio, the use of Cu in nanoparticle form enables the best-case-scenario for performance enhancement with metallic copper to be investigated.

Experimental

Chemicals

Carbon nanofiber (CNF) was bought from Pyrograf Products Inc. Potassium permanganate, ethanol, sulfur powder, ammonium hydroxide solution (28%), 1-methyl-2-pyrrolidinone (NMP), 1,2-dimethoxyethane (DME), magnesium chloride, sulfuric acid, nitric acid, and copper standard (1000 mg/L in 2% nitric acid, TraceCERT) were all purchased from Sigma Aldrich. Copper acetate monohydrate and sodium hydrosulfide hydrate were bought from VWR. Poly(vinylidene fluoride) (Kynar HSU 900, PVDF) was donated by Arkema. Magnesium bis(trifluoromethanesulfonyl)imide (Mg(TFSI)2) was obtained from Solvionic.

Materials synthesis

Synthesis of Cu@CNF: Carbon nanofibers were oxidized by KMnO4 in concentrated sulfuric acid to prepare oxidized CNF. Then copper oxide nanoparticles were grown on the oxidized CNF. A solution consisting of 90 mg oxidized CNF, 120 mL ethanol, and 2.5 mL water was sonicated for 3 h. After that, the well dispersed oxidized CNF solution was mixed with 3 mL of 0.6 M aqueous copper acetate solution and 2.5 mL of aqueous ammonium hydroxide solution (30 wt%). The hydrolysis reaction was conducted at 80 °C for 20 h. The solution was then filtered to obtain the copper oxide and oxidized CNF composite (CuO@OCNF). CuO@OCNF powders were reduced under 5% H2 and 95% Ar at 550 °C to synthesize the copper nanoparticle and CNF composite (Cu@CNF). The high copper content Cu@CNF (h-Cu@CNF) was prepared in a similar manner, except that the carbon nanofibers were oxidized using 150% higher KMnO4/C mass ratio to prepare strongly oxidized CNF and the hydrolysis reaction was conducted at 85 °C for 40 h to increase the copper content.

Synthesis of CuS@CNF: CuO@OCNF was heated to 150 °C under argon in a tube furnace. Excess sodium hydrosulfide hydrate was placed at the end of the tube furnace with a stir bar before the heating step so that it wouldn’t decompose before the temperature reached the set point. Once the temperature stabilized at 150 °C, the small vial containing sodium hydrosulfide hydrate was pushed to the center of tube furnace and decomposed to produce hydrogen sulfide. CuO@OCNF reacted with hydrogen sulfide to form copper sulfide on the carbon nanofiber surface (CuS@CNF).

Electrode fabrication: Both Cu@CNF and h-Cu@CNF were used to prepare cathodes. Cu@CNF powder was mixed with sulfur powder in the amount required for the targeted Cu:S ratio (1:1, 1:2 and 1:4); the copper content of Cu@CNF was obtained from ICP-OES measurements. The mixture was then sealed in a glass tube and heated to 155 °C to make a uniform ternary composite. The Cu-S composite (90 wt%) and PVDF (10 wt%) were mixed with 1-methyl-2-pyrrolidinone (NMP) in a small vial and stirred for 24 h. The slurry was then coated on stainless steel foil and dried at 50 °C for 12 h. The sulfur loading of these cathodes are in the range of 0.05 - 0.10 mg/cm2. Three CNF and sulfur control cathodes were fabricated with different sulfur content since the Cu-S cathodes have different sulfur content. The CuS cathodes were fabricated in the same manner.
The cathodes with higher sulfur loading (0.35 - 0.5 mg/cm\(^2\)) were prepared in a similar way using h-Cu@CNF. Different from the low loading cathodes, to keep the sulfur content of the three Cu-S cathodes the same, extra CNF were added into the cathodes. The sulfur content for the three cathodes are 22.3 wt%, and a single CNF and sulfur control cathode was made for comparison.

**Electrolyte:** Magnesium bis(trifluoromethanesulfonyl)imide (Mg(TFSI)\(_2\)) was dried under vacuum at 200 °C for 24 h. The Mg(TFSI)\(_2\)/MgCl\(_2\)/DME electrolyte was prepared by adding 1.1693 g dry Mg(TFSI)\(_2\) and 0.3809 g magnesium chloride to 4 mL of 1,2-dimethoxyethane (DME) (0.5 M Mg(TFSI)\(_2\), 1 M MgCl\(_2\)) and stirring overnight.\(^{10}\) The electrolyte was stored on molecular sieves and filtered before use.

**Battery assembly:** The Mg/S 2032-type coin cells were assembled in an argon glovebox with a glass fiber separator, 160 uL electrolyte, a magnesium disk anode (scratched with a spatula to remove MgO from the surface), and an aforementioned cathode.

**Characterization**

The copper content of the Cu@CNF, h-Cu@CNF and CuS@CNF was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima 8000). The composites were digested in concentrated nitric acid by refluxing for 16 h before the ICP-OES measurement. X-Ray diffraction (XRD, D8 Advance Davinci, Bruker) using Cu-K\(\alpha\) radiation (\(V = 40\) kV, \(I = 40\) mA) was used to characterize Cu@CNF and CuS@CNF with a step size of 0.005° and a step time of 4 s in the range of 20° to 80°. The Scanning Electron Microscopy (SEM) Magellan 400 (FEI) was used to characterize the morphology of Cu@CNF and CuS@CNF and the cathodes. All of the electrochemical measurements were carried out on a Neware Battery Testing System. The Mg/S batteries with low sulfur loading were discharged to the potential cut-off of 0.5 V and charged to the capacity cut-off of 1500 mAh/g S while the high sulfur loading batteries were discharged to 0.5 V and charged to the capacity cut-off of 1200 mAh/g S. Batteries with CuS cathodes were discharged to 0.5 V and charged to 2.0 V. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI VersaProbe II. The C 1s line at 284.8 eV was used to calibrate all of the XPS data.

**Results and discussion**

Figures 1a – 1b display the SEM images of the synthesized Cu@CNF and h-Cu@CNF composites. In both cases, the carbon-supported nanoparticles have a similar morphology and particle size (50 – 200 nm). The small size of these particles provides significant surface area for Cu-S interaction. The XRD patterns of Cu@CNF, h-Cu@CNF, and CuS@CNF (Figure S1) confirm the successful synthesis of the targeted nanoparticles. The copper content of these composites as determined by ICP-OES are 14.1 wt%, 57.5 wt% and 12.5 wt%, respectively.

The Cu@CNF (14.1 wt% Cu) composite was then mixed with sulfur based on fixed Cu to S molar ratios to make the Cu-S cathodes as described in the Materials and Methods section. Different Cu:S ratios will result in different sulfur contents in the cathodes (Cu:S of 1:1 result in 6.6 wt% S, 1:2 is 12.4 wt% S, and 1:4 is 22.2 wt% S). Therefore, three copper-free CNF-S cathodes with various sulfur contents were fabricated for comparison.
The cycling data for the Mg/S batteries with different Cu:S ratios and corresponding CNF-S controls at the rate of 0.1 C (167.5 mA/g) are shown in Figure 2a. While all of batteries exhibited reasonably high initial discharge capacities, the discharge capacities for the copper-free control cells precipitously dropped off after cycle one while the copper-containing batteries maintained high capacities. Interestingly, the discharge capacities of the control cells then improved for several cycles, eventually achieving high capacity by 10 to 15 cycles. The cathodes with copper nanoparticles outperformed the control cells on the basis of sulfur utilization after extended cycling. The cathode composition Cu-S-1-1 delivered stable discharge capacities that exceeded that of the control (about 795 mAh/g S after 50 cycles compared with 521 mAh/g S for the copper-free case). The capacity difference between Cu-S-1-2 cathode and the corresponding control after 50 cycles is about 600 mAh/g. The Cu-S-1-4 cathode has the lowest sulfur utilization among the three Cu-S cathodes, but it shows a stable capacity.

As the addition of copper does add mass to the system, the modified discharge capacities (based on total mass of copper and sulfur in cathode) for the low rate testing are shown in Figure 2b. For the lowest sulfur loading case (CNF-S-1), the long-term capacity is relatively high (about 600 mAh/g) even without copper. It should be noted that the carbon to sulfur ratio within the cathode strongly affects the cycling behavior, and that low sulfur loadings will not ultimately yield a practical system. Although the system is not practical, it allows the fundamentals of the Cu-S interaction to be studied.

Figure 2c displays the corresponding voltages profile for low rate cycling of a CNF-S control cell with 6.6 wt% sulfur and a coin cell with a 1:1 Cu/S cathode. In the first discharge of the control cell, there is only a single discharge plateau at 0.7 V. In contrast, for the Cu-S cathode, the first discharge curve shows two plateaus, one at 1.25 V and the other one at 0.9 V. The plateau at 1.25 V corresponds to the reduction of long-chain polysulfides while the 0.9 V plateau is the reduction of short-chain polysulfides. The first cycle discharge curve is similar to the work of Wang and colleagues which employs the same electrolyte.10 However as the cell continued to cycle, the first plateau at 1.25 V shortened and finally disappeared. The potential of the second plateau gradually increased with continued cycling to 1.1 V. After the fifth cycle, the shape of the discharge curves remained consistent.

The charge curves in Figure 2c reveal the serious polysulfide shuttling effect which is consistent with other works.17,27 Therefore, a capacity cut-off is used instead of a potential cut-off. As observed in
Figure 2c, after the first cycle the charge potential consistently plateaus at 2.2 - 2.3 V. We hypothesize that the charge product in this case is primarily higher order polysulfides or dissolved neutral S₈ rather than solid-state S₈. This results in the following cycles in the lack of a discharge plateau at 1.25 V which corresponds to the reduction of solid-state elemental sulfur to high order polysulfides.

The rate performance of the Mg/S batteries with different Cu:S ratios is displayed in Figure 2d. Due to the low sulfur content, the Cu-S-1-1 cathode delivers a capacity comparable to the theoretical value for a few cycles at 0.1 C. It is found that the batteries continue to deliver significant capacity (>1000 mAh/g for Cu-S-1-1) upon increasing in the charge/discharge rate from 0.1 C to 2 C, with the amount of sulfur utilization tracking with the amount of copper.

![Figure 2](image-url)
As higher sulfur loadings are presumably necessary for practical systems, h-Cu@CNF powder (57.5 wt% Cu) was synthesized and mixed with sulfur powder to prepare anodes with higher weight percentage and areal loading of sulfur. Extra CNFs were added into the Cu-S-1-2 and Cu-S-1-4 cathodes to keep the sulfur content (22.3 wt% S) consistent. Only one CNF-S control (CNF-S-4) is needed in this case. The sulfur loading of the four cathodes are higher at 0.35 - 0.5 mg/cm².

The cycling data for the Mg/S batteries with higher sulfur loading at the low rate of 0.1 C (167.5 mA/g) are shown in Figure 3a. The cathodes show the same behavior as the low sulfur loading cathodes, but with an overall lower capacity on the basis of sulfur utilization at similar sulfur content. Thus, we can say that the copper additives are less effective at higher concentration. It is shown in Figure 3b that the addition of copper improves the capacity retention for continued cycling at the elevated rate of 1 C. The cycling data appears “noisy” in terms of capacity stability; this phenomenon was consistent for all cells tested at these higher sulfur loadings, and we attribute it to the irregular deposition of solids within the cathode and/or the glass fiber separator. Full exploration of this behavior is outside the scope of work here, but will be the subject of future investigations.

Both the copper-containing and copper-free cathodes achieved higher sulfur utilization when cycling at 1 C compared with cycling at 0.1 C. There are two explanations for this result. The first explanation relates to localization of dissolved sulfur species. At high discharge rates, there is reduced time for solubilized polysulfides (MgS₄₋₈) to diffuse away from the cathode before undergoing further reduction. The second explanation relates to the distribution of the MgS discharge product. It could be that slow discharge allows for the formation of larger MgS deposits. MgS is known to be difficult to oxidize, likely due to the insulating nature and low solubility of MgS. Mg²⁺ diffusion is extremely slow in MgS since it tends to crystalize. If the discharge product is only partially reoxidized during charge, then capacity is lost.

The capacities of the Cu/S cathodes at 0.1 C and 1 C based on total Cu and S mass are shown in Figure 3c and 3d. In both cases, the cathode composition Cu-S-1-2 outperformed the other cathodes in terms of capacity and cycling stability. Although copper can improve the capacity based on sulfur mass, the mass of copper will decrease the total energy density.

Table 1 compares the results of this work with other works utilizing copper in some form at the magnesium-sulfur battery cathode. The cathode with Cu nanoparticles reported here achieves the highest capacity and at the highest current density (600 mA/cm²) but has relatively low sulfur loading. The Super-P-S cathode with Cu current collector is reported operating at very low current density (6-7 mA/cm²). The sulfur@microporous carbon cathode has a higher surface area and therefore delivers a better capacity than Super-P-S cathode and at a higher current density (up to 117.4 mA/cm²). When taking the Cu mass into consideration, the Cu nanoparticle based S cathode still shows a higher capacity than many CuS cathodes, for which testing was reported at rates up to 300 mA/cm².
Figure 3. Discharge capacities for Mg/S batteries with Cu+S cathodes (high copper content) with varying Cu:S ratio and the CNF-S control a) at 0.1 C and on the basis of S mass, b) at 1 C and on the basis of S mass, c) at 0.1 C and on the basis of the total Cu and S mass and d) at 1 C and on the basis of the total Cu and S mass.

Table 1. Performance of other reported magnesium-sulfur batteries with copper-containing cathodes with current collector type, sulfur content and loading, discharge capacity, and current density specified for comparison

| Cathode          | Current Collector | Sulfur Content (wt %) | Sulfur Loading (mg S/cm²) | Discharge capacity at cycle 30 | Current Density (mA/g S) | Areal Current Density (mA/cm²) | Refs |
|------------------|-------------------|-----------------------|---------------------------|--------------------------------|--------------------------|---------------------------------|------|
| Cu-S-1-1         | SS                | 22.3                  | 0.36                      | 700                            | 233                      | 1675                            | 600  | This work |
| Super-P/S        | Cu                | 70                    | 0.6 - 0.7                 | 350                            | –                        | 10                              | 6 - 7 | 18        |
| Sulfur@microporous Carbon | Cu        | 70                    | 0.6 – 0.7                 | 320                            | –                        | 167.5                           | 100.5 – 117.2 | 19 |
| CuS-I            | –                 | 20                    | 1 - 1.4                   | 100                            | 150                      | 50 - 70                          | 4    |
| CuS-II           | Carbon paper      | 23.3                  | 0.82                      | –                              | 200                      | 150                             | 41   | 5         |
| CuS-III          | Carbon paper      | 23.3                  | 0.82                      | –                              | 120                      | 150                             | 41   | 10        |
| CuS-IV           | W                 | 21.3                  | –                         | –                              | 300                      | 300                             | –    | 24        |
| Cu₅S₅            | Carbon paper      | 15.2                  | 0.43                      | –                              | 180                      | 92                              | 40   | 30        |
XPS was used to further interrogate the interaction between Cu and S in the cathodes. Figure 4a displays the XPS spectra in the region of interest for copper of the as-prepared Cu nanoparticle containing composite, the composite after S melt infusion, and the cast Cu-S cathode (Cu:S ratio = 1:4). The spectra for the Cu nanoparticle-CNF composite only shows a Cu0 peak at 933 eV.31 However, after mixing with sulfur and melting at 155 °C, a Cu+ peak at 932.3 eV also appears which indicates the formation of Cu2S.32 No Cu2+ secondary peak is observed here.33 The XPS spectra of the cast Cu-S cathode is similar to that of the Cu-S mixture with both Cu0 and Cu+ peaks present. We obtained similar results for the 1:1 and 1:2 case which were shown in Figure S4. NuLi and colleagues reported the formation of CuS on a Cu current collector which differs from our result.18

After discharge, the peak for metallic copper Cu0 is recovered and maintained upon charging. This result agrees with the cycling profiles; sulfur is charged to higher order polysulfides rather than elemental sulfur or CuS. Hence, these are actually Mg-polysulfide batteries. As shown in Figure 4b, it is found that a similar result in obtained by starting with the CuS@CNF cathode. The CuSO4 at 934.7 eV is caused by surface oxidation of CuS.34 Here, the presence of CuS in the starting cathode in additionally confirmed by the satellite peaks. After cycling, however, only Cu0 is detected.

Figure 4. (a) XPS spectra of Cu nanoparticle, Cu/S mixture and Cu/S cathode; (b) XPS spectra of CuS cathode (* satellite peak).

Figures 5a – 5d display the SEM images of the CNF-S cathode and Cu-S-1-1 cathode in the charged state after 30 cycles. In the CNF-S cathode, dense micron scale discharge products are observable following charge. In comparison, aggregates are seen in the Cu-S-1-1 cathode that presumably contain the remaining discharge products and copper. It is observable that the aggregates are composed of smaller
primary particles. We hypothesize that due to the interaction between copper and sulfur, that the copper nanoparticles provide nucleation sites for MgS growth. More uniform distribution of the discharge product as smaller particles aids in the reoxidation of MgS.

The inclusion of Cu nanoparticles in the cathodes has two major effects: stabilization of the cycling behavior in the first few cycles and higher sulfur utilization in the long term. The stabilization in the initial cycles is due to the formation of Cu(I)-Sx species during the melt-infusion, which mitigates the dissolution of elemental sulfur out of the cathode and into the electrolyte during the rest period after cell fabrication and prior to the first discharge. This conclusion is confirmed through the use of UV-Vis absorbance measurements of electrolyte solutions after sitting with Cu@CNF+S powders and CNF+S powders (see Figure S5). The uniform distribution of Cu(I)-Sx species throughout the cathode is hypothesized to result in a more uniform distribution of the MgS discharge product, whereas in the absence of Cu, larger MgS deposits may form on the first cycle that are slow to reoxidize in subsequent cycles. The higher sulfur utilization in the longer term with the inclusion of Cu nanoparticles is hypothesized to be due to the continued interaction between Cu and polysulfides that results in diminished loss of active sulfur species due to dissolution and subsequent reaction at the anode. Eventual loss of capacity is due to the aggregation of the Cu nanoparticles over time that instigates the formation of larger MgS deposits.

Figure 5. SEM images of the CNF-S-4 cathode after 30 cycles (a, b) and the Cu-S-1-1 cathode after 30 cycles (c, d).
Conclusions

In summary, Cu nanoparticle additives in Mg/S battery cathodes were investigated. The formation of Cu₂S during the melt infusion process leads to high discharge capacity in initial cycles. After several charge/discharge cycles, the Cu⁺ peak was not observed via XPS, indicating that the long-term improvement in cycling stability results from the interaction between the Cu metal and magnesium polysulfides. SEM images post-cycling show that large discharge product particles do not remain following charge in the Cu containing cathodes. The Cu nanoparticles nucleate growth of distributed discharge products that are more easily oxidized. However, the positive effects of the Cu nanoparticle additives are diminished in the case of lower Cu:S ratios and also in cathodes with higher overall sulfur loading. Finally, we note that the polysulfide shuttling effect in these batteries is serious even with the addition of Cu nanoparticles. We caution that the addition of Cu nanoparticles into the cathode may have limited practicality for Mg/S batteries due to the required amount and relative cost of Cu metal. We suggest exploration of other avenues that also lead to formation of dispersed solid MgSₓ discharge products to enable long term cycleability of the Mg/S battery.

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