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

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S Supporting Information

ABSTRACT: Rechargeable magnesium sulfur (Mg/S) batteries suffer from fast capacity fading, because of the difficulty with reoxidation of MgS and the polysulfide shuttle. Other works have reported that use of Cu current collectors at the cathode improves cyclability. 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 operate 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.



KEYWORDS: magnesium battery, copper nanoparticles, polysulfides, sulfur cathodes, carbon nanofiber

1. INTRODUCTION

Lithium ion (Li-ion) batteries are the most widely used electrochemical energy storage devices today. The Mg battery is a promising alternative to the Li-ion battery, and worldwide attention regarding this technology has increased in recent years, because of the high abundance, low cost, and high volumetric charge storage capacity of magnesium metal.¹ 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 inexpensive and safe.

Sulfur, with a high theoretical capacity of 1675 mAh/g and currently studied for use as the active cathode material in Libased and Na-based batteries, may be paired with the Mg anode.² However, the serious polysulfide shuttling effect,³ the reaction between sulfur and conventional nucleophilic Mg electrolytes,⁴ 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,^{5,6} modification of the separator,^{7,8} use of new electrolyte and separator materials,^{9,10} coating a polymer film on the electrode surface as a physical barrier, and using inorganic compounds to trap polysulfide anions.¹² 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 + $AlCl_3$)¹³⁻¹⁵ and borate-based salts.¹⁶ 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 MgS_x species.¹⁷

Interestingly, Nuli and colleagues found that the Mg/S battery assembled with a copper current collector can reversibly cycle with nucleophilic electrolyte.¹⁸ The formation of CuS and Cu₂S on the copper current collector surface was observed, and the copper sulfides are hypothesized to adsorb cyclic S₈ and polysulfides, thus preventing their reaction with the nucleophilic electrolyte.^{18,19} The copper current collector enabled high sulfur utilization and capacities at reasonable rates (300 mAh/g after 40 cycles at a rate of 10 mA/g), whereas the initial capacity with a stainless steel current collector was <30 mAĥ/g.18 Oh and colleagues studied the interaction between the copper current collector and sulfur and found that Cu₂S contributed to the capacity of the Mg/S battery.²⁰ We have seen similar positive effects of use of a copper current collector in the Mg/S battery in our laboratory (see Figure S1 in the Supporting Information). In other works,

 Received:
 June 21, 2019

 Accepted:
 August 26, 2019

 Published:
 August 26, 2019



Figure 1. SEM images of (a) low copper content Cu@CNF and (b) high copper content h-Cu@CNF.

copper sulfide was directly used as a cathode material and paired with the Mg anode, resulting in reasonable discharge capacities at relatively high charge/discharge rates.^{21–24}

The use of copper current collectors, copper powder, and copper nanoparticles also result in stable cycling of Li/S and Na/S batteries.^{25–29} These works found that the chemical bonding between sulfur and copper helps to improve the specific capacity and capacity retention. The addition of copper metal, combined with use of a highly porous carbon as a host material for sulfur, can provide an effective chemical confinement of polysulfides and benefit the transfer of electrons and ions.^{25–29}

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.³⁰ With these metrics in mind, we have fabricated sulfur cathodes containing copper 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. Because of 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.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Carbon nanofiber (CNF) was purchased from Pyrograf Products, Inc. Potassium permanganate, ethanol, sulfur powder, ammonium hydroxide solution (28 wt %), 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 purchased from VWR. Poly(vinylidene fluoride) (PVDF) (Kynar HSU 900) was donated by Arkema. Magnesium bis(trifluoromethanesulfonyl)imide (Mg(TFSI)₂) was obtained from Solvionic.

2.2. Materials Synthesis. 2.2.1. Synthesis of Cu@CNF. Carbon nanofibers were oxidized by $KMnO_4$ in concentrated sulfuric acid to prepare oxidized CNF.³¹ Copper oxide nanoparticles then were grown on the oxidized CNF. A solution consisting of 90 mg of oxidized CNF, 120 mL of ethanol, and 2.5 mL of 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 (28 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 (Cu0@OCNF).³¹ Cu0@OCNF powders were reduced under 5% H₂ and 95% Ar at 550 °C to synthesize the copper nanoparticles 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 a 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.

2.2.2. 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 would not 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).

2.2.3. 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 inductively coupled plasma–optical emission spectroscopy (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 0.06–0.12 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 $(0.35-0.42 \text{ mg/cm}^2)$ 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.

2.2.4. Electrolyte. $Mg(TFSI)_2$ 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 of dry $Mg(TFSI)_2$ and 0.3809 g of 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.

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



Figure 2. Discharge capacities for Mg/S batteries with Cu+S cathodes (low copper content) with varying Cu:S ratios and corresponding CNF-S controls (a) at 0.1 C and on the basis of S mass and (b) at 0.1 C and on the basis of the total Cu and S mass. (c) Representative voltage profiles for select cycles in the cases of the 1:1 Cu:S cathode and corresponding copper-free CNF-S-1 cathode when operated at a rate of 0.1 C. (d) Charge–discharge rate capability for Mg/S batteries with Cu+S cathodes with varying Cu:S ratio.

2.3. Characterization. The copper content of the Cu@CNF, h-Cu@CNF and CuS@CNF was determined via ICP-OES (PerkinElmer, Model Optima 8000). The composites were digested in concentrated nitric acid by refluxing for 16 h before the ICP-OES measurement. X-ray diffraction (XRD) (Bruker, Model D8 Avance Davinci) using Cu K α radiation (V = 40 kV, I = 40 mA) was used to characterize Cu@CNF, h-Cu@CNF, and CuS@CNF with a step size of 0.005° and a step time of 4 s in the range of $20^{\circ}-80^{\circ}$. Scanning electron microscopy (SEM) (Model Magellan 400, FEI) was used to characterize the morphology of Cu@CNF, h-Cu@CNF, CuS@CNF, and the cathodes. All of the electrochemical measurements were performed on a Neware Battery Testing System. The Mg/S batteries with low sulfur loading were discharged to the potential cutoff of 0.5 V and charged to the capacity cutoff of 1500 mAh/g, while the high sulfur loading batteries were discharged to 0.5 V and charged to the capacity cutoff of 1200 mAh/g. 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.

3. RESULTS AND DISCUSSION

Figures 1a and 1b display the SEM images of the synthesized Cu@CNF and h-Cu@CNF composites, respectively. In both cases, the carbon-supported nanoparticles have a similar morphology and particle size (most in the range of 20-50 nm and average size of 42 nm; see Figure S2 in the Supporting Information). The small size of these particles provides significant surface area for Cu–S interaction; the copper nanoparticle surface area is estimated at ~ $20 \text{ m}^2/\text{g}$, as

calculated from the particle size distribution. The XRD patterns of Cu@CNF, h-Cu@CNF, and CuS@CNF (see Figure S2) confirm the successful synthesis of the targeted nanoparticles. The copper content of these composites, as determined by ICP-OES, are 14.1, 57.5, and 12.5 wt %, respectively.

The Cu@CNF (14.1 wt % Cu) composite was then mixed with sulfur, based on fixed Cu:S molar ratios, to make the Cu–S cathodes, as described in the Experimental Section. Different Cu:S ratios will result in different sulfur contents in the cathodes (Cu:S of 1:1 results 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 the 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 10–15 cycles. This response is possible if short-chain sulfur, contained in the pores of the CNF-S control cathodes, as apparent by the low discharge plateau voltage, $^{32-34}$ converts to magnesium sulfide that is not fully reoxidizable, which results in the



Figure 3. Discharge capacities for Mg/S batteries with Cu+S cathodes (high copper content) with varying Cu:S ratios 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.

capacity fade from cycle 1 to cycle 2. Meanwhile, neutral elemental sulfur dissolved out of the cathode after cell assembly (as described later and interrogated with UV-vis measurements) may not be electrochemically accessible in the first cycle but later diffuse back to the cathode, allowing the regain of capacity. 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 (~795 mAh/g after 50 cycles, compared with 521 mAh/g for the copper-free case). The capacity difference between the Cu-S-1-2 cathode and the corresponding control after 50 cycles is ~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.

Since 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. On this basis, the Cu-S-1-4 cathode shows the highest total capacity of 400 mAh/g-[Cu+S] after 50 cycles. For the lowest sulfur loading case (CNF-S-1), the longterm capacity is relatively high (~600 mAh/g), even without copper. Note that (i) the C:S ratio within the cathode strongly affects the cycling behavior, and (ii) 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 Cu-S-1-1 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-1-1 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 longchain polysulfides, while the 0.9 V plateau is the reduction of short-chain polysulfides. 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. Similar results are found when cycling the CuS@CNF cathode as shown in Figure S3 in the Supporting Information. Interestingly, a similar first cycle discharge voltage profile also is present with the Cu-S-1-2 cathode, while, for the Cu-S-1-4 cathode, the result looks more like that of the CNF-S control (see Figures S3b and S3c). Cyclic voltammagrams of the cells prior to charge-discharge cycling are displayed in Figure S4 in the Supporting Information; an obvious difference in reduction peak is observed between the CNF-S control and the Cu-S cathodes, whereas the oxidation peaks are at more similar potentials.

The charge curves in Figure 2c reveal a serious polysulfide shuttling effect, which is consistent with other works.^{17,35} Therefore, a capacity cutoff is used instead of a potential cutoff. 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.

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

				Dischar (ge Capacity at Cycle 30			
cathode	current collector	sulfur content (wt %)	sulfur loading (mg S/cm ²)	mAh/g-S	mAh/g-[Cu+S]	current density (mA/g S)	areal current density (mA/cm ²)	ref
h-Cu-S-1-1	stainless steel	22.3	0.36	700	233	1675	600	this work
Super-P-S	Cu	70	0.6-0.7	350	-	10	6-7	18
S@MP Carbon	Cu	70	0.6-0.7	320	-	167.5	101-117	19
CuS-I	-	20	1-1.4	-	100	150	50-70	22
CuS-II	Carbon	23.3	0.82	-	200	150	41	21
CuS-III	Carbon	23.3	0.82	-	120	150	41	21
CuS-IV	W	21.3	-	-	300	300	-	23
Cu ₉ S ₅	Carbon	15.2	0.43	-	180	92	40	24



Figure 4. (a) XPS spectra of the Cu nanoparticles grown on CNFs, the Cu/S mixture after melting, and the Cu/S cathodes as prepared, after discharge (Cu-S-1-1-D), and after charge (Cu-S-1-1-C); (b) XPS spectra of the CuS cathodes as prepared, after discharge, and after charge (the asterisk symbol (*) denotes a satellite peak).

The rate performance of the Mg/S batteries with different Cu:S ratios is displayed in Figure 2d. Because of 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.

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 cathodes with higher weight percentage and areal loading of sulfur. Extra CNFs were added into the h-Cu-S-1-2 and h-Cu-S-1-4 cathodes to keep the sulfur content consistent (22.3 wt % S). Only one CNF-S control (CNF-S-4) is needed in this case. The sulfur loading of the four cathodes are higher at 0.35–0.42 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 contents. 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.³⁶ 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.³⁷ MgS is known to be difficult to oxidize, likely due to the insulating nature and low



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

solubility of MgS.² The Mg²⁺ diffusion is extremely slow in MgS since it has a tendency to crystallize.³⁸ If the discharge product is only partially reoxidized during charge, then capacity is lost.

The capacities of the Cu/S cathodes at 0.1 and 1 C based on total Cu and S mass are shown in Figures 3c and 3d. In both cases, the cathode composition h-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/cm^2) but has relatively low sulfur loading. The Super-P-S cathode with Cu current collector is reported operating at very low current density ($6-7 \text{ mA/cm}^2$). The sulfur@microporous (S@MP) carbon cathode has a higher surface area and therefore delivers a better capacity than the 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.

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 Cu–S cathode (Cu:S ratio = 1:1) as prepared and before electrochemical cell assembly. The spectra for the

Cu nanoparticle-CNF composite only shows a Cu⁰ peak at 933 eV.³⁹ 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.⁴⁰ No Cu²⁺ secondary peak is observed here.⁴¹ The XPS spectra of the 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 1:2 and 1:4 cases, which are shown in Figure S5 in the Supporting Information. NuLi et al. reported the formation of CuS on a Cu current collector, which differs from our result.¹⁸

After discharge, the peak for metallic copper Cu^0 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 is obtained by starting with the CuS@CNF cathode. The peak for CuSO₄ at 934.7 eV is caused by surface oxidation of CuS.⁴² Here, the presence of CuS in the starting cathode in additionally confirmed by the satellite peaks. After cycling, however, only Cu⁰ is detected.

Figures 5a-d display the SEM images of the CNF-S-4 cathode and the h-Cu-S-1-1 cathode in the charged state after 30 cycles. In the CNF-S-4 cathode, dense micrometer-scale discharge products are observable following charge. In comparison, aggregates are seen in the h-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, because of the interaction between copper and sulfur, the copper nanoparticles provide nucleation sites for MgS growth. More

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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 $Cu(I)-S_x$ 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 S6 in the Supporting Information). The uniform distribution of $Cu(I)-S_r$ species throughout the cathode is hypothesized to result in a more uniform distribution of the MgS discharge product. In the absence of Cu, larger MgS deposits may form on the first cycle, which 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. The eventual loss of capacity is due to the aggregation of the Cu nanoparticles over time, which instigates the formation of larger MgS deposits.

4. CONCLUSIONS

In summary, Cu nanoparticle additives in Mg/S battery cathodes have been 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 of the cathodes 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 at 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, because of the required amount and relative cost of Cu metal. We suggest exploration of other avenues that also lead to the formation of dispersed solid MgS_r discharge products to enable long-term cyclability of the Mg/S battery.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.9b01236.

XRD patterns, SEM images, voltage profiles, cyclic voltammetry, XPS, and UV-vis data (PDF)

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Author Contributions

J.L.S. conceived and guided the study; P.H. conducted most of the experiments, analyzed data, and wrote the first draft of the manuscript; H.O.F. and L.C.M. helped prepare samples and analyze data. All authors contributed to revising the manuscript, and then reading and approving the submitted version. Funding

We gratefully acknowledge financial support from the National Science Foundation, through Grant No. CBET-1706370 and Amazon Catalyst at ECS.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Notre Dame Materials Characterization Facility for XRD and UV-vis instrumentation, the Notre Dame Center for Environmental Science and Technology for ICP-OES instrumentation, and the University of Notre Dame Integrated Imaging Facilities for SEM instrumentation.

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