Role of Cu current collector on electrochemical mechanism of Mg-S battery

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Abstract

Development of magnesium sulfur battery is accompanied with all known difficulties present in Li-S batteries, however with even more limited choice of electrolytes. In the present work, the influence of current collector on electrochemical mechanism was investigated in light of different reports where improved behavior was ascribed to electrolyte. Notable differences in cycling behavior are reported when Al current collector is replaced by Cu current collector independent of electrolyte. The initial reduction of sulfur follows similar reaction path no matter of current collector but formation of MgS can be in competition with formation of CuS in the presence of Cu cations. With the subsequent cycling cells prepared from cathodes deposited on Cu current collector show decrease in the voltage and formation of single plateau during cycling. The change corresponds to the involvement of Cu into the reaction and formation of redox couple Mg/CuS as determined by Cu K-edge XANES measurements. Corrosion of Cu foil is identified by SEM and serves as a source of Cu cations for the chemical reaction between Cu and polysulfides. Mg/CuS redox couple shows improved cycling stability, but theoretical energy density is severely reduced due to substitution of S with CuS as cathode active material.

Keywords: Magnesium, sulfur, rechargeable batteries, current collector, copper, corrosion

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1. Introduction

Rechargeable magnesium batteries are considered as one of the most promising technologies for energy storage, mainly due to the high volumetric capacity (3833 mAh cm^{-3}), low cost and natural abundance of magnesium, but finding suitable cathode materials remains a challenge. Majority of materials that can reversibly insert magnesium exhibit high transport energy barriers and consequently sluggish magnesium ion mobility.[1] As an alternative, use of conversion materials is being actively utilized to avoid transport limitations. The highest interest has been focused on the combination of magnesium anode and sulfur cathode extensively studied in the past years.[2–5]

Few studies showed, that the mechanism of sulfur reduction follows similar reactions as that of Li-S system.[5,6] Therefore it is understandable that the long term cycling in the practical Mg-S batteries is hindered by similar difficulties such as fast capacity fade, self-discharge and high polarization due to polysulfide solubility and kinetic barriers for precipitation of MgS.[5] To tackle these challenges different approaches are proposed. While some work went into structuring the cathode,[7] most of the groups focused on discovery of suitable electrolytes that would improve reversibility and stability of the system.[3,5,8,9] From the first electrolyte, $\text{Mg}_2\text{Cl}_3\text{-HMDSAICl}_3$ in THF,[10] and subsequent improvement with magnesium bis(hexamethyldisilazide) $[(\text{HMDS})_2\text{Mg}]$, AlCl_3 and MgCl_2 in glymes and addition of ionic liquid,[5] the research has been expanded to simpler TFSI-anion based salts in different ethers.[3,6] Recent reports show use of the mixtures involving different types of boron-centered hexafluoroisopropyl (HFIP) salts.[2,4,11] Furthermore use of very concentrated electrolyte for Mg-S batteries[3], based on TFSI anion which is beneficial for lowering polysulfide solubility,[12] exhibited some improvement in terms of stability and efficiency.

Some intriguing results were also published by Cui's group, [4,9,11] who reported combinations of tris(2H-hexafluoroisopropyl) borate (THFPB) with either MgF_2 , MgO or MgCl_2 salts in 1,2-dimethoxyethane (DME). Their results show initial capacity of up to 1081 mAh g^{-1} at 0.05 A g^{-1} and capacity retention of more than 85% in 30th cycle. High rate capability was also displayed.[9] Results in all cases exhibit very distinctive electrochemical behavior, when comparing charge-discharge curves. Plateaus are visible at somewhat lower voltages (around 1.1 V in case of $\text{Mg}(\text{B}(\text{HFIP})_4)_2$) with MgF_2) and are extremely flat, with fast voltage drop at the end of discharge, while other groups usually report more gradual decline at the end of the discharge, observed also in our recent work.[6] While observed differences were explained with use of different electrolytes, authors discarded use of non-convenient current collector (CC) in the combination with sulfur cathode, although change from Cu-CC to Al-CC significantly influence the electrochemical behavior of the cells.[11] This can also be observed in another report by NuLi and coworkers,[13] who identified the formation of CuS and Cu_2S for sulfur electrodes on copper current collectors. It is worth nothing that their

electrochemical measurements were performed in 0.4 M (PhMgCl)₂-AlCl₃³⁺ 1.0 M LiCl in THF, which is considered nucleophilic and as such considered incompatible with electrophilic sulfur cathode. Therefore, one could argue that difference in electrochemical behavior can arise from this specific electrolyte.[13] However, the shape of discharge-charge curves in MgS batteries with Cu-CC resembles on the behavior of CuS cathodes coupled with Li metal, where single discharge plateau at 1.7 V vs. Li/Li⁺ exhibits. [14] This value is in good correlation with reported plateau at 1.1 V [10], considering difference in redox potentials between Li/Li⁺ and Mg/Mg²⁺ couples.

Here we compare electrochemical performances of sulfur based cathodes deposited on Al and Cu current collector in selected electrolytes (TFSI and HFIP - based). A distinct difference in the electrochemical behavior of two cathodes is reported in three different electrolytes and degradation of current collectors was evaluated by using scanning electron microscopy (SEM). Cu involvement in the Mg-S electrochemical mechanism was determined by *ex situ* Cu K-edge XANES measurements. Although Cu dissolution during formation cycles leads to improved electrochemical stability, cells cycled in the presence of Cu cations cannot be considered anymore as Mg-S cells since presence of Cu considerable decreases energy density of the newly formed redox couple.

2. Experimental part

Cathode preparation:

Carbon/sulfur (C/S) composite was prepared by ball-milling Ensaco 350G carbon (Imerys) and sulfur (Sigma Aldrich) for 30 min at 300 rpm in a mass ratio of 75:25, followed by impregnation process. The mixture was heated to 155 °C in argon atmosphere at a rate of 0.2 °C min⁻¹ and kept at that temperature for 5 h. The obtained composite was cooled down with 0.5 °C min⁻¹ rate. Cathodes were prepared by mixing C/S composite, multiwalled carbon nanotubes (MWCNT – Sigma Aldrich) and polytetrafluoroethylene (PTFE) as binder in the mass ratio of 80:10:10 with 2-propanol. Self-standing electrodes with a diameter of 12 mm (average sulfur loading 0.90 mg/cm²) were pressed onto different current collectors and dried for 1 h at 50 °C.

Electrochemical characterization

Laboratory Swagelok cells were assembled inside an argon-filled glovebox. The sulfur cathode was separated from the magnesium foil (Gallium Source, 99.95%, 0.05 mm) anode with two glass fiber separators (Whatmann GF/A). Different types of electrolyte have been used: (a) **TFSI based** – 0.4 M Mg(TFSI)₂, 0.4 M MgCl₂ in tetraglyme:1,3-dioxolane (TEGDME:DOL) (1:1 vol%), (b) **HFIP-Cl based**– 0.45 M Mg(B(HFIP)₄)₂, 0.45 M MgCl₂ in TEGDME:DOL (1:1 vol%) and (c) **HFIP based** without chlorides – 0.6 M Mg(B(HFIP)₄)₂ in DME. The electrolyte quantity was normalized

to 80 μL per cell. Cells were cycled with a current density of C/10 or C/50 in a potential window depending on the type of current collector. All experiments were performed using a Bio-Logic VMP3 potentiostat/galvanostat. Linear sweep voltammetry (LSV) was performed in the range between OCV and 4.5 V vs Mg^{2+} , at 5 mV s^{-1} . Cyclic voltammetry measurements (CV) were performed with sweep rate of 5 mV s^{-1} in the voltage range between 0.1 V and upper cut off voltages defined for Al and Cu current collector for each electrolyte separately.

SEM measurements

A field-emission scanning electron microscope (FE SEM Supra 35 VP Carl Zeiss) equipped with an energy dispersive X-ray spectrometer INCA Energy 400 (Oxford, UK) was used to obtain SEM images. Air and moisture sensitive samples were transferred from the glovebox in a custom-made vacuum transfer holder to avoid degradation of samples.

Cu K-edge XANES measurement

Cu K-edge XANES spectra were measured ex-situ on samples charged or discharged to the different cut-off voltages. Samples were prepared in the form of homogeneous pellets in glovebox and vacuum-sealed in pouch cells, adapted for the XAS measurements in transmission mode. CuS reference compound was measured on a homogeneous pellet pressed from micronized CuS powder mixed with boron nitride (BN). The total absorption thickness of the samples was about 2 above the Cu K-edge. The XAS spectra were recorded at the beamline P65 of PETRAIII at DESY, Hamburg. A Si(111) double crystal monochromator was used with energy resolution of about 1 eV at 9 keV. The beam size on the sample was 1.2 mm horizontal and 0.2 mm vertical. The intensity of the monochromatic X-ray beam was measured by three consecutive 5 cm long ionization detectors filled with following gas mixtures: 1000 mbar N_2 (first), 1000 mbar Ar (second), 1000 mbar Kr (third). Samples were placed between the first and second ionization cell. The absorption spectra were measured in the energy region from -150 eV to $+1000 \text{ eV}$ relative to the Cu K-edge (8979.0 eV) in a continuous scan mode. The scan duration was 180 s. The signal from detectors during scan was integrated in the time domain to obtain energy steps of 0.2 eV in the XANES region. We measured absorption scans on two different spots of the battery to reduce potential effects of radiation damage and to check for eventual sample inhomogeneity. The exact energy calibration was established with simultaneous absorption measurement on a $5 \mu\text{m}$ thick Cu metal foil placed between the second and the third ionization chamber. Absolute energy reproducibility was $\pm 0.02 \text{ eV}$. The analysis of XANES spectra was performed with Demeter (IFEFFIT) program package.[15]

3. Results and discussion

Electrochemical characterization

Stability of current collectors in batteries depends on the voltage window needed for redox chemistry on the negative or positive electrode. We performed linear sweep voltammetry (LSV) measurements to test the stability region for Cu-CC and Al-CC (Figure 1). The instability of Cu-CC is clearly visible already at approximately 2.0 V vs. Mg/Mg^{2+} and barely depends on electrolyte. Even though the exchange current is very low, cathodes with redox activity above 2V are not compatible with Cu-CC. Interestingly the TFSI-Cl based electrolyte that contains MgCl_2 exhibits higher stability than HFIP based electrolyte without MgCl_2 additive. The reason for this difference is probably due to different passivation layers on Mg electrode. Stability window of Al-CC is higher and first increase of exchange current starts above 2.5 V vs. Mg/Mg^{2+} .

Figure 1: Linear sweep voltammograms for Al and Cu current collectors, in TFSI- and HFIP-based electrolyte (without MgCl_2). Sweep rate used was 5 mV s^{-1} .

Similar conclusion can be brought from cyclic voltammograms, presented in the Figure 2. The best stability has been obtained with Al-CC in TFSI-Cl based electrolyte, while use of Cu-CC in both electrolytes show high currents at low potentials. Note that voltage range for tests was adjusted to results obtained by LSV (Figure 1). Similarly, measurements of both CC in HFIP based electrolyte show instability at relative low potentials (already around 2.0 V vs. Mg/Mg^{2+}) i.e. this anodic instability can be a competitive electrochemical process to the oxidation of MgS back to sulfur.

Figure 2: Typical cyclic voltammograms of Al (a,b) and Cu (c,d) current collectors in TFSI-Cl based electrolyte (0.4 M $\text{Mg}(\text{TFSI})_2$, 0.4 M MgCl_2 in TEGDME:DOL 1:1)(a,c) and HFIP-based electrolyte (0.6 M $\text{Mg}(\text{B}(\text{HFIP})_4)_2 \times 3\text{DME}$ in DME) (b,d).

Use of Cu-CC instead of Al-CC for C/S cathode is compared in Figures 3 and 4. Although difference is only in the current collectors used, a distinctively different voltage profiles can be observed during reduction and oxidation process for sulfur based cathode. In the classical set up where carbon sulfur composite is pressed on Al-CC, a typical two voltage plateau is observed during reduction with high polarization (Figure 3a) and followed by rapid capacity fading in the subsequent cycles (Figure 3b). Although measurements with sulfur composite pressed on Cu-CC were performed almost at identical conditions; the only difference is in the change of oxidation cut-off voltage to avoid additional side reactions, we observed completely different electrochemical properties (Figure 3c,d). Note that specific capacities in Figures 3 and 4, where Cu-CC is used, are calculated based on CuS (right y-axis) and S (left y-axis) molecular weight. Four differences can be observed: a) polarization of the cell with Cu-CC is significantly lower compared to the cell with Al-CC; b) specific capacity increases with Cu-CC and decreased with Al-CC; c) capacity during reduction (sulfur conversion into sulfide) is higher than oxidation capacity in the case of Cu-CC, while in the cell with Al-CC difference is in the agreement with behavior observed in Li-S batteries; and d) voltage curve with Al-CC resembles classical sulfur reduction in glyme solvents while in the case of using Cu-CC voltage profile is altered to lower value suggesting different electrochemical equilibria. One can argue that differences in the stability, voltage profile and polarization are in the function of electrolyte, however electrochemical results obtained with HFIP based electrolytes show that electrochemistry is

similar no matter of salt selection as long as Cu-CC is used (Figure 4).

Figure 3: Electrochemical behavior of Mg-S batteries with TFSI-Cl based electrolyte (0.4 M $\text{Mg}(\text{TFSI})_2$, 0.4 M MgCl_2 in TEGDME:DOL 1:1) at C/10 current rate. Charge-discharge curves of sulfur cathodes pressed on Al current collector (a) and corresponding capacity stability (b), compared with cycling behavior of S-cathodes pressed on Cu current collector (c,d).

In all measurements with C/S composite pressed on Cu-CC (Figures 4 e-h) we always observe different electrochemical characteristics compared to cells where C/S composite was pressed on Al-CC current collector (Figures 4 a-d). Cell containing HFIB-Cl based electrolyte and Cu-CC (Figure 4e,f) showed similar electrochemical properties as cell cycled in TFSI based electrolyte (Figure 3c,d). Similar electrochemical behavior was observed in the cell with Cu-CC cycled in HFIB based electrolyte without chlorides, but the change of potential occurred in higher cycles (Figure 4g). With added chlorides in the electrolyte and C/S composite pressed on Cu-CC, changes are very similar no matter if TFSI or HFIP based electrolytes are used, while changes without chlorides are substantially slower, but even without chlorides in electrolyte, new equilibrium is established after several initial cycles.

Figure 4: 1st and 10th cycles with charge and discharge capacities for batteries assembled with Al-CC in HFIP-Cl based electrolyte (0.45 M Mg(B(HFIP)₄)₂×3DME and 0.45 M MgCl₂ in TEGDME:DOL 1:1) (a,b) and HFIP based electrolyte (0.6 M Mg(B(HFIP)₄)₂×3DME in DME) (c,d). Their copper counterparts are depicted in bottom half: HFIP-Cl based electrolyte (e,f) and HFIP based electrolyte (g,h). All batteries were cycled at C/10 rate.

With those set of experiments, we have identified environment with different electrochemical characteristics of sulfur cathode. Cells cycled in the presence of Al-CC have classical electrochemical signature of sulfur based batteries where sulfur reduction proceeds through two steps process consisting of solid-liquid and liquid-solid equilibria.[6] Oppositely, cells with Cu-CC cycled always show a single plateau at 1.1V. Similar cycling behavior was shown by Wu [16] when studying CuS nanoparticles as cathode material for Mg batteries. In their work, an elemental Cu was detected as a final discharge product. However, they observed that MgS failed to participate in the reversible charge reactions, resulting in loss of active sulfur content and predominant cycling of intermediate Cu₂S.

Reaction of Cu with sulfide species can reduce the amount of polysulfides in electrolyte [13] since polysulfides react with Cu ions before they dissolve into the (bulk) electrolyte. Cu mitigates polysulfide diffusion to metallic magnesium and precipitation of MgS on the negative electrode. Such mechanism explains improved electrochemical stability. The source of Cu ions in the electrolyte is corrosion of Cu-CC in the electrolyte due to presence of chlorides or even polysulfides. Cu cations compete with magnesium cations and since equilibrium voltage in cells with Cu-CC is for 0.3V lower compared to cells with Al-CC, we can conclude that CuS phase is preferable formed instead of MgS.

The proposed redox reaction mechanism on the positive electrode accompanied with Cu corrosion is shown in the Scheme 1. During the first discharge, conversion of sulfur is accompanied with the formation of MgS and corrosion of Cu-CC where Cu cations react with sulfur/polysulfides and form CuS. Latter is formed as well during first charge where sulfur from MgS is oxidized. Rate of corrosion of Cu-CC is rate determine step for chemical formation of CuS. If Cu dissolution is lower compared to formation of polysulfides, mixed electrochemical signature is obtained as observed in HFIB-based electrolytes without chlorine (Figure 4g). In such a case part of active materials (sulfur) is lost as we still observe capacity fading but less pronounced as in the case of Al-CC cells. As soon as rate of Cu dissolution is higher than rate of polysulfide chemical formation of CuS is favored and at higher cycles sulfide anion formed from conversion of CuS reacts with magnesium cation during discharge, while during charging MgS is converted into CuS.

Scheme 1: The proposed redox reaction mechanism in the presence of Cu-CC

SEM images of current collectors

Evidences of Cu involvement in electrochemical reactions during cycling can be observed with naked eye during disassembly of the battery. Cu foil is thinned and becomes porous, after more cycles it is practically impossible to remove it from the cathode material, whilst Al CC can be easily peeled away. The difference is even more evident under SEM (Figure 5), where we observe severe degradation of Cu CC (Figure 5b), especially when comparing with Al CC (Figure 5a), where only some of the cathode residue is visible. The same trend can be observed in other electrolyte, based on HFIP salt without chlorine (Figures 5c,d). Although electrolyte was chlorine free, we observed significant changes in the morphology of Cu CC that is consistent with the change of electrochemical signature of C/S composite (Figures 4g,h).

Figure 5: SEM images of the morphology of Al (a) and Cu (b) current collectors in TFSI based electrolyte and Al (c) and Cu (d) CC in HFIP-based electrolyte without MgCl_2 after cycling at C/10 for 10 cycles. Cathode composite was peeled away from the current collectors.

Cu K-edge XANES

Cu K-edge XANES analysis was used to evaluate involvement of Cu species in electrochemical reactions. We prepared several samples of magnesiated sulfur cathodes pressed on Cu CC at selected points of discharge and charge. The Cu K-edge XANES spectra measured on the samples and on reference Cu samples (Cu metal with fcc crystal structure and CuS) are shown on Figure 6. The linear combination fit (LCF) analysis [15] was applied to the Cu K-edge XANES spectra of the MgS battery

samples (Figure 7). The spectra can be completely described by a linear combination of the XANES profiles of Cu fcc metal and CuS reference compound. In this way the relative amounts of each Cu compound in the sample was determined (Table 1). The XANES results confirm formation of CuS during battery operation and reveal its relative amount at different states during cycling (batteries were stopped at the end of discharge and charge during different cycles). Uncertainty of the relative amounts of CuS is about $\pm 2\%$, mainly due to the inhomogeneity of cathode material.

Figure 6: Cu K-edge XANES measured on the *ex situ* samples of MgS batteries with Cu current collector, and on reference Cu samples (Cu metal with fcc crystal structure and CuS). Spectra are shifted vertically for clarity.

Figure 7: LCF analysis of XANES spectra measured on *ex situ* samples of sulfur cathodes on Cu current collector at the end of second discharge (a) and second charge (b), cycled at C/10 current rate in 0.45 M Mg(B(HFIP)₄)₂*3DME and 0.45 M MgCl₂ in TEGDME:DOL 1:1 electrolyte. Black dots: experiment; orange line: best-fit linear combination of XANES profiles of Cu fcc metal foil, and CuS reference compound. Fit components are shown below.

Table 1: Relative amount of Cu fcc metal and CuS in the precycled Cu-MgS battery with Cu current collector samples, stopped at each precycled state (end of discharge and charge during different cycles), as determined by LCF analysis of Cu XANES spectra with reference XANES profiles of Cu fcc metal, and CuS reference compound. Uncertainty of

relative amounts of each component is $\pm 2\%$.

Sample	Cu metal (fcc)	CuS
2 nd discharge	89%	11%
5 th discharge	89%	11%
1 st charge	68%	32%
2 nd charge	64%	36%

Considering the first reduction of the sulfur cathode pressed on the Cu CC shows different voltage profile from higher cycles (Figure 3), this reduction mainly consists of reaction between Mg and S, forming predominantly MgS. However, this reaction is already accompanied with formation of some CuS (Scheme 1). This can be explained with the fact that corrosion of Cu CC was observed even at the bare contact with electrolyte or in the experiment where we used cathode without sulfur. Corroded Cu^{2+} cations react with polysulfides soluble in the glyme-based solvents. During the first charge, oxidation process of MgS occur and soluble polysulfides are formed, which can further react with Cu^{2+} cations, forming additional CuS phase, available for cycling in subsequent cycles. The presence of CuS was confirmed with Cu k-edge XANES measurements of the samples, collected at the end of first and second charge and at the end of second and fifth discharge (Figure 6). After second discharge and charge, considerable amount of CuS was detected along with Cu metal. Amount of detected CuS is higher after charge (oxidation process on the cathode) which is consistent with the proposed mechanism in previous reports,[16,17] and amount of metallic Cu is higher after discharge (reduction process on the cathode) (Table 1). Thus, formation of Cu metal nanoparticles can be explained by conversion reaction of CuS during reduction process on the cathode. With principal component analysis of the Cu K-edge XANES spectra we were able to confirm, that no other Cu species were present in our samples. Similar degradation process of the current collector has been observed recently in the study of sodium sulfur batteries. [18] Part of Cu signal may also be contributed to small parts of Cu CC that remained attached on the electrode. Comparison of samples collected after two and five discharges shows just a slight difference in CuS content, which can be explained with small capacity increase in the formation cycles.

Although we cannot completely exclude a competitive reaction between magnesium and sulfur, the change of voltage profile clearly points out different electrochemical equilibria since electrochemistry is very sensitive to any changes in the coordination or composition. While Mg/CuS redox pair displays improved electrochemical cycling over contemporary Mg/S batteries, application of CuS cathode severely decreases the energy density of the system. Theoretical energy density for such

system drops from 1712 Wh/kg for Mg/S to only 526 Wh/kg for Mg/CuS. Such big drop in energy density is a consequence of theoretical capacity of CuS cathode (478 mAh/g) being only a third of a S cathode capacity (1672 mAh/g) and additional reduction due to decreased operating voltage of 1.1 V versus 1.77 V for Mg/CuS and Mg/S, respectively.

4. Conclusion

Influence of current collectors on the electrochemical behavior and mechanism of Mg-S batteries is carefully studied in this work. Even by visual inspection, degradation of Cu CC can be observed during cycling in Mg-S batteries. Significant differences between cycling of cathodes with Al or Cu current collectors suggest different mechanism of reduction/oxidation reactions. Through electrochemical tests in several different electrolytes we demonstrate that changes of electrochemical mechanism do not depend on Mg electrolyte, but solely choice of current collector. With the use of Cu K-edge XANES measurements we were able to confirm the formation of CuS and changes in its relative content during cycling. This explains severe degradation of Cu CC observed by SEM even in electrolytes without chlorine. Finally, cells compromising Cu-CC with sulfur composite cannot be considered as Mg-S batteries due to formation of CuS//Mg redox pair that significantly decreases energy density on the cell level.

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