Electrical Energy Storage by a Mg/CuS Battery

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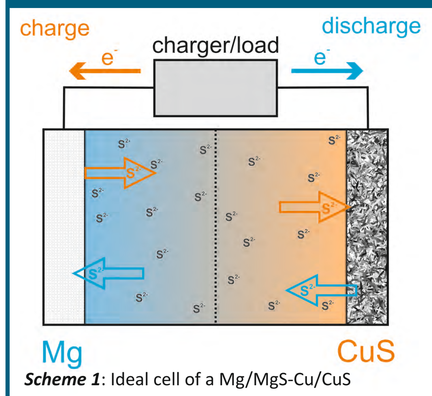
Indroduction to the Mg/CuS Battery



Scheme 1: Ideal cell of a Mg/MgS-Cu/CuS

discharge:

$Mg \rightarrow MgS + 2e^-$ $\quad CuS + 2e^- \rightarrow Cu + S^{2-}$

charge:

$MgS + 2e^- \rightarrow Mg + S^{2-}$ $\quad Cu \rightarrow CuS + 2e^-$

Alternatively, the Mg/MgS-Cu/CuS accumulator can generally also be built in the discharged state, i.e. MgS vs. Cu instead of Mg vs. CuS.

Here we want to report on our investigations of the Mg/CuS battery.

Alkalisulfide based Electrolytes

For the Mg/MgS-Cu/CuS accumulator we investigate different electrolytes. The alkalisulfide based electrolytes are solvent-salt systems. The used solvents were dried and distilled for high purity.

Li_2S-DEC/Sulfolan/DMSO

For this electrolyte system we used anhydrous lithium sulfide dissolved in a mixture of carbonic ether, sulfolane and dimethyl sulfoxide.

K_2S-Ionic Liquids

Another approach is to use ionic liquids as electrolyte systems. The solubility tests for K_2S in various ionic liquids are summarized in ***Table 1***. For the solubility test we used 50 mg anhydrous K_2S in 1 mL ionic liquid.

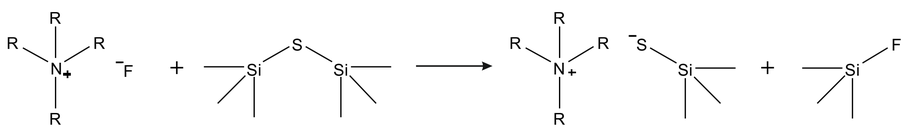
Table 1: Solubility test for K_2S in different ionic liquids

	(BMIm)Cl	(BMIm)(PF$_6$)	(OMIm)(OTf)	(BMIm)(NTf$_2$)	(BMIm)(BF$_4$)	(BMPyrr)(NTf$_2$)	(Oct$_4$P)(PF$_6$)	(Oct$_4$P)(NTf$_2$)	(Bu$_3$PhP)(NTf$_2$)
K_2S (50 mg/1mL)	-	+	+	+	-	o	o	-	-

solubility: soluble - moderate - slightly

Synthesis of sulfur based Electrolyte Materials

Synthesis of tetraalkyammonium trimethylsilylsulfides [1]:



R = Me, Et, Bu

Synthesis of Disodiumpolysulfides (Na_2S_x; X = 2, 3) [2]:

$$2\,Na + x\,S \xrightarrow{NH_3} Na_2S_x \quad x = 2, 3$$

For the synthesis of disodiumpolysulfide we used stoichiometric amounts of sodium and sulfur in liquid ammonia.

After 4 h reaction time we obtained a mixture of different polysulfides (Na_2S, Na_2S_2 and Na_2S_3). The reaction product was washed with CH_3CN to remove the Na_2S_3.

The Rietveld refinement of the X-ray powder diffraction analysis shows two phases (***Figure 1***):

- Na_2S_2 (major phase)
- Na_2S (traces).

Synthesis of Ditetrabutylammoniumhexaasulfide [3]:

$$Na_2S \cdot 9\,H_2O + 5\,S \longrightarrow [Na_2S_6]^* \xrightarrow{+2\,TBABr} (TBA)_2(S)_6 + 2\,NaBr$$

The mixture of $Na_2S \cdot 9\,H_2O$ and S was heated in water to dissolved the starting materials. This dark red solution was cooled to ambient temperature. Then a solution of TBABr in water was added rapidly to the cooled solution. This mixture was sealed and stored at 4 °C for 24 h. The solid was filtrated and washed with cold water.

EA(calc.): C 56.16 (56.74); H 10.76 (10.71); N 3.99 (4.14); S 28.94 (28.40). UV/Vis (λ_{max} in CH_3CN, 25 °C): 610 nm.

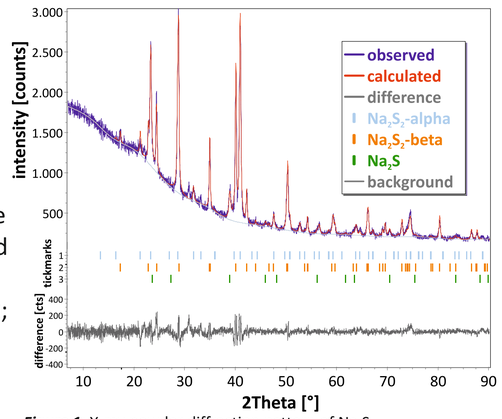
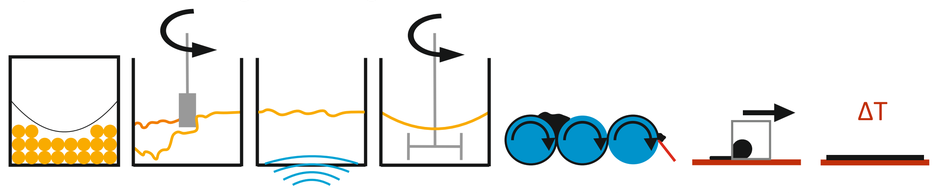


Figure 1: X-ray powder diffraction pattern of Na_2S_2

Electrode Preparation

When producing the electrodes, the paste preparation is crucial. Many parameters have to be considered in each individual step of the process (***Scheme 2***). The properties to be achieved are high adhesion and high homogeneity as well as no cracking or blistering.



Scheme 2: Paste preparation, coating and drying on laboratory scale - from left to right: ball milling, mixing, ultra-sonication, dispermat, 3-roller, coating knife and air drying

In this project two types of electrodes are designed: active carbon and Cu/CuS electrodes. In a second step, the active carbon electrodes are loaded with Mg/MgS for the use as positive magnesium electrode. For this purpose, particles with different surface areas are processed into the pastes and coated onto the current collectors. The active carbon substrate for the Mg/MgS loading consists of water-based pastes (carbon black + CMC on Al). The Cu/CuS electrodes are based on NEP (Cu/CuS + carbon black + PVDF on Cu).

Investigated factors are:

- particle sizes and properties
- solvent properties
- pretreatment processes
- dispersing
- coating method
- drying parameters

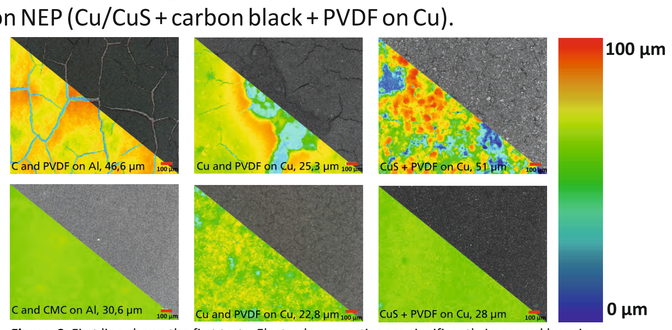
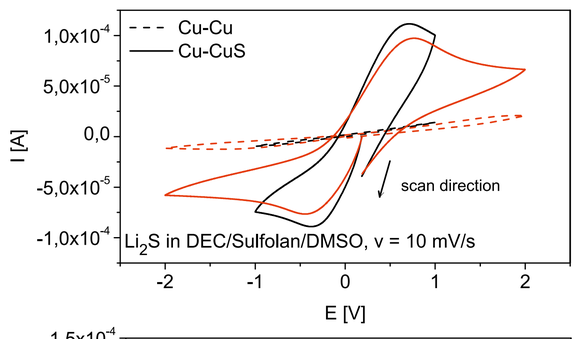
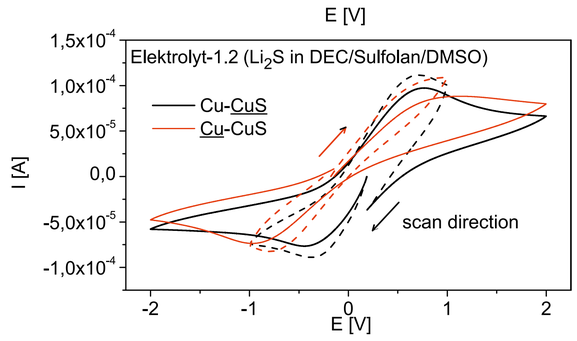
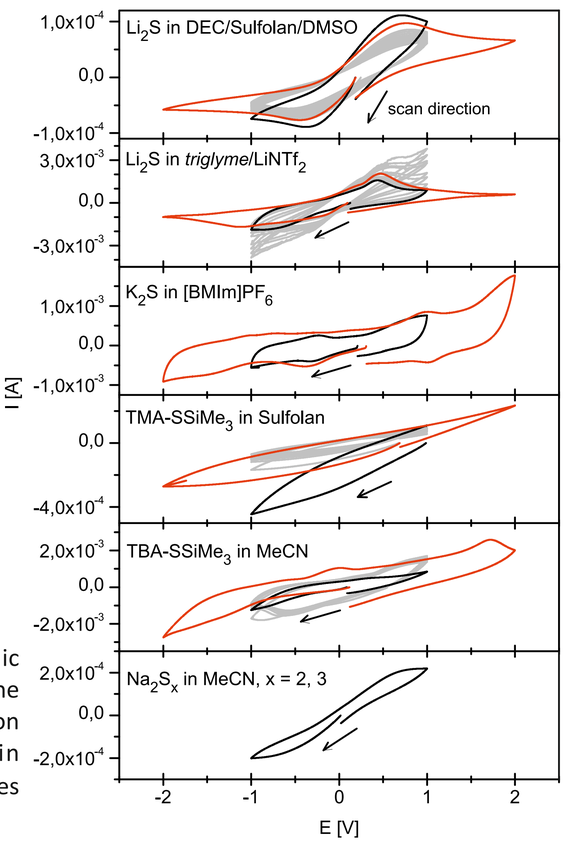


Figure 2: First line shows the first tests. Electrode properties are significantly improved by using another binder, 3-roller and ball milling processing steps (second line).

Electrochemical Characterization







Different electrolytes were characterized by cyclic voltammetry in a half-cell setup of Cu vs. CuS. The reversible electrode reactions (reduction and reoxidation of CuS) are observed in the case of Li_2S in DEC/Sulfolan/DMSO, while for some other candidates additional redox peaks are detected.

Summary

Cu- and CuS-electrodes have been prepared by coating Cu- and CuS pastes onto a copper foil. Processing steps for the paste preparation (Cu/CuS + Carbon Black + PVDF dispersed in NEP) have been optimized.

We also were able to synthesize different types of sulfur salts for the development of sulfur based electrolytes. For the electrochemical tests these salts were dissolved in organic solvents and characterized by cyclic voltammetry in a half-cell setup of Cu vs. CuS. In addition, sulfide containing ionic liquids also were tested.

With a combination of molecular dynamics simulations in combination with different experiments, the behavior of electrolytes can be well understood at molecular level. Tests of sulfide containing electrolytes are very promising as the solubility of alkali sulfides can be increased by adding additives to the solvent.

References

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