Copper sulfides for rechargeable lithium batteries: Linking cycling stability to electrolyte composition

CrossMark

Birte Jache, Boris Mogwitz, Franziska Klein, Philipp Adelhelm*

Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 58, 35392 Giessen, Germany

HIGHLIGHTS

- The reversibility of copper sulfides strongly depends on the electrolyte composition.
- Cycling stability is poor in carbonate-based electrolytes.
- Ether-based electrolytes improve the cycling stability.
- Specific conductivities of CuS and Cu_2S are determined.

ARTICLE INFO

ABSTRACT

Copper sulfides are attractive electrode materials as their reaction with lithium offers high capacity and energy density. However, the reversibility is poor and (nano)structuring is considered necessary to achieve moderate improvements. In contrast, we show in this study that the electrolyte is a major factor that governs the reversibility of the cell reaction. All our experiments were done with commercially available copper sulfides (CuS and Cu_2S) without any special nanostructure. Different electrolyte compositions were tested among $LiPF_6$ in EC/DMC and LiTFSI in DOL/DME. While rapid capacity fading is found in cells containing carbonate-based electrolytes, cells with ether-based electrolytes show a much better electrochemical performance. For a mixture of 1 M LiTFSI in DOL/DME, Cu_2S can be cycled with capacities of around 200 mAh g^{-1} for more than 150 cycles with coulombic efficiencies >98.4%, for example. The improved stability in the ether-based electrolyte further allowed us to study how the discharge and charge voltage change during prolonged cycling. Our study underlines that improvements in the Li/CuS and Li/Cu_2S system are still possible by very simple measures, but further studies on the complex Li–Cu–S phase behavior are necessary to understand the discharging and especially the charging mechanisms.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Copper sulfides have been investigated as battery active materials for lithium-ion batteries for several decades. The general characteristics of the cell reactions can be briefly summarized as follows. Reaction of CuS or Cu_2S with lithium to form Cu and Li_2S comes along with an energy release of 961 Wh kg^{-1} or 552 Wh kg^{-1}, respectively. For comparison, commercially applied $Li_{0.5}CoO_2$ theoretically provides 548 Wh kg^{-1}. Besides, copper sulfides are highly conductive which intrinsically should ease the cell reaction compared to many other electrode materials. As the main disadvantage, copper sulfides are known to suffer from poor

capacity retention and hence short life time [1,2]. Therefore, they were often considered and used as primary battery materials [3–5]. Several studies were carried out to determine reasons for the poor reversibility [6–8], but precise determination of the reaction mechanisms for the different copper sulfide species has been proven difficult due to the limited cycle life and the existence of several intermediate phases with complex stoichiometries [7,9].

Overall, various factors are thought to be responsible for the poor electrochemical performance of the Li/Cu/S system: (1) loss in structural stability due to volume changes during cycling, (2) decomposition of the electrolyte at the cathode and/or the metallic lithium anode, and (3) loss of active material due to dissolution of sulfide species [4,6–8]. On the other hand, it was reported that the cycling stability of CuS can be improved to some extent by nanostructuring [9–17]. For example, Wang et al. described lately the *in situ* preparation of a nanostructured copper sulfide cathode with an

* Corresponding author. Tel.: +49(0)641 9934501; fax: +49(0)641 9934509.
  E-mail address: Philipp.Adelhelm@phys.chemie.uni-giessen.de (P. Adelhelm).

excellent stability for more than 100 cycles at different C-rates (up to 2C) with specific capacities between 376 mAh g^{-1} and 447 mAh g^{-1} in a electrolyte composed out of 1 mol L^{-1} LiClO$_4$ and a solvent mixture of DME/DOL (2:1, *v/v*) [13]. They concluded that the special nanostructure, which consisted of 3D connected nano-flakes on copper, was the main reason for the improved cycling stability. On the other hand, Han et al. synthesized a CuS material with a hierarchical structure consisting of nano-spheres which only showed a poor cycle life [11]. In an electrolyte composed of 1 M LiPF$_6$ dissolved in EC/DMC (1:1, *v/v*), 582 mAh g^{-1} were achieved in the first cycle followed by a rapid decrease of the specific capacity and an overall capacity retention of around 13.8% after the first ten cycles. Débart et al. studied commercial CuS-powders and found nearly the theoretical capacity value during first discharge (1 M LiPF$_6$ in EC/DMC (1:1, *w/w*)). However, the capacity rapidly dropped to approx. 50 mAh g^{-1} after five cycles which was related to loss of active mass as a result of Li$_2$S dissolution in the electrolyte [9]. Altogether it remains unclear whether nanostructuring alone can be linked to an improved cycling stability. And even though also using alternative electrolytes has been suggested in literature as potential method to improve the cycling stability, no correlation could be established either.

In this work, we show that the composition of the electrolyte solution is a major factor that governs the cycle life of copper sulfide in lithium-ion cells, especially when discharged to low potentials. As only commercially available powders are used in our study, we conclude that nanostructuring is probably less important for achieving a stable cycle life. In order to study the reversibility of the cell reaction in more detail, the two copper sulfides CuS and Cu$_2$S are studied separately. Also the impact of the current collector on the cycling stability is discussed.

2. Experimental

Electrode slurries were made from as received CuS (>99%, *Sigma Aldrich*) or Cu$_2$S (>99.5%, *Sigma Aldrich*), a conductive carbon (SuperPLi, *TIMCAL Graphite*), polyvinylidene fluoride (PVDF Solef 1310, *Solvay*) and *N*-methyl-2-pyrrolidone (NMP, *Sigma Aldrich*). The content of copper sulfide, conductive carbon and binder was 75 wt%, 15 wt% and 10 wt%, respectively. The electrodes were prepared by doctor blading the slurry onto aluminum foil ($d = 20$ μm). The thicknesses of the electrodes were approximately 200 μm in wet condition and around 40–50 μm in the dried state. Circular electrodes ($d = 1.2$ cm) were punched out and contained between 2 mg and 3 mg of active mass each. The electrodes were further dried at $\vartheta = 80$ °C for 3 h under vacuum to evaporate residual NMP and then transferred to an argon filled glove box (MBraun Labmaster sp) where three-electrode Swagelok type cells were assembled. Metallic lithium foil (*Rockwood Lithium*) was used as counter and reference electrode. Whatman glass microfiber filters (GF/A) were used as separator. As electrolyte three different mixtures of conductive salts and solvents were used. A commercially available 1 M solution of LiPF$_6$ in 1:1 *w/w* EC/DMC (LP30, SelectiLyte from *Merck*), a 1 M solution of LiTFSI in 1:1 *w/w* DOL/DME (*Sigma Aldrich*) and a 1 M solution of LiTFSI in 1:1 *w/w* EC/DMC. Electrochemical measurements were conducted at room temperature using a Maccor (Model 4300) battery cycler. Cells were cycled galvanostatically (constant current, CC) at different C-rates between 0.8 V and 3.0 V. The C-rate was calculated based on the theoretical capacity of CuS ($Q = 560$ mAh g^{-1}) or Cu$_2$S ($Q = 337$ mAh g^{-1}), i.e. 1C corresponds to a current of $i_{CC} = 560$ mA g^{-1} (CuS) or $i_{CC} = 337$ mA g^{-1} (Cu$_2$S). Capacities are given in mAh per gram of copper sulfide species (mAh g^{-1} (CuS) or mAh g^{-1} (Cu$_2$S)). Additionally, cyclic voltammetry was conducted (Biologic VMP3) with a voltage sweep rate of 0.05 mV s^{-1} for 20

cycles. WAXS diffraction patterns were taken with a PANanalytical X'Pert Pro in a 2θ angular range between 20° and 60°.

All samples for conductivity measurement were prepared by pressing the powders into small rods (approx. 3 mm in diameter and 6 mm in length) at 5 kN in a uniaxial press. These rods were used without further treatment. Standard 4-probe measurements were carried out by pressing 4 Pt-wires (0.1 mm) to the pellet within a PTFE sample holder (Fig. 1). The DC conductivities were measured using a Keithley 2420 Sourcemeter. Additional AC measurements were performed with a Novocontrol Alpha-AK/ZG4 system. All experiments were done at room temperature, light exposure was excluded.

3. Results and discussion

3.1. Cell reaction

The basic electrochemical reaction of copper sulfides with lithium is a unique kind of conversion reaction that includes a macroscopic phase separation (a so-called displacement reaction). During discharge, lithium ions diffuse into the copper sulfide lattice leading to the formation of lithium sulfide. At the same time the copper ions diffuse out of the lattice and form macroscopic metallic copper dendrites upon reduction [9]. This behavior is different from the conventional conversion reaction for which a nanocomposite structure is observed that consists of transition metal nanoparticles that are finely dispersed in a Li$_a$X-matrix ($a = 1,2$ or 3 and X = anions) [1,2]. For the conversion reaction of CuO with lithium one finds Cu nanoparticles dispersed in a Li$_2$O matrix after discharge, for example. The difference between both mechanisms is illustrated in Fig. 2.

The general discharge profile of the Li/CuS system is characterized by two well defined plateaus and the formation of Li$_2$S and Cu as the final discharge products. The appearance of a second plateau is indicative for an intermediary phase that has been differently explained literature. Both formation of Cu$_{2-x}$S phases [3,8,16] and
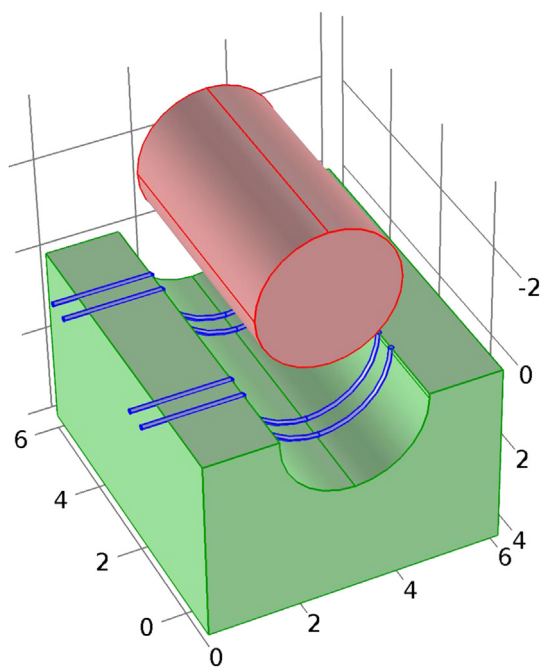

Fig. 1. Sample holder for 4-probe conductivity measurements. Green: PTFE-block; blue: Pt-wires; red: sample rod. All scales in mm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)