

論文 / 著書情報  
Article / Book Information

題目(和文)	
Title(English)	Study of rechargeable lithium batteries with copper sulfides used as cathode materials
著者(和文)	Kalimuldina Gulnur
Author(English)	Gulnur Kalimuldina
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第10626号, 授与年月日:2017年9月20日, 学位の種別:課程博士, 審査員:谷口 泉,伊東 章,森 伸介,菅野 了次,西方 篤
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第10626号, Conferred date:2017/9/20, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

## Thesis outline

The thesis investigated physical and electrochemical properties of copper sulfides used as cathode materials for rechargeable lithium batteries. The main conclusions summarized as follows:

**Chapter 1** represents the background of the environmental problems and ways of the solutions, as well as the importance of the development of renewable energy sources have been demonstrated. The focus was made on rechargeable batteries as a promising renewable energy storage system with a great potential. The brief history of the lithium battery technology, views on conventional cathode materials have been presented. Then metal sulfides, particularly copper sulfides, have been induced as alternative cathode materials with promising high capacities, high conductivities, and abundance. The examples of the recent publications on the copper sulfides ( $\text{Cu}_2\text{S}$ ,  $\text{CuS}$ ) were provided, and then the challenges of the reported approaches were pointed out. Finally, the objectives of this study were presented.

**Chapter 2** reported stoichiometric  $\text{Cu}_2\text{S}$  prepared by SP and annealing process. Firstly, copper sulfides were prepared by SP with annealing over a wide range of Cu/S molar ratios in the precursor solutions and different synthesis and annealing temperatures. Stoichiometric  $\text{Cu}_2\text{S}$  with the monoclinic structure of space group  $P2_1/c$  could be prepared via SP at 400 °C followed by annealing at 460 °C for 2 h, which was verified by XRD and ICP-OES analyses. The lattice constants of the stoichiometric  $\text{Cu}_2\text{S}$  obtained from the XRD patterns by Rietveld refinement were  $a = 15.237 \text{ \AA}$ ,  $b = 11.884 \text{ \AA}$ , and  $c = 13.492 \text{ \AA}$ , which were in good agreement with those reported in the literature. The  $\text{Cu}_2\text{S}$  sample comprised spherical particles with a geometric mean diameter of 0.45  $\mu\text{m}$ , a geometric

standard deviation of 1.55, and a BET specific surface area of  $4.7 \text{ m}^2 \text{ g}^{-1}$ . The stoichiometric  $\text{Cu}_2\text{S}$  was used as a cathode active material, and its electrochemical properties were investigated using  $\text{Li} \mid 1 \text{ M LiTFSI in DOL:DME} = 1:1 \mid \text{Cu}_2\text{S}$  cells in the potential range from 1.0 to 3.0 V versus  $\text{Li/Li}^+$ . The  $\text{Cu}_2\text{S}$  electrode coated on an Al foil current collector exhibited a first discharge capacity of  $335 \text{ mAh g}^{-1}$  at a charge-discharge rate of 0.1 C, which corresponds to 99.4% of its theoretical capacity. *Ex situ* XRD analysis of the fully charged and discharged electrodes showed that the phase transformation from the monoclinic  $\text{Cu}_2\text{S}$  structure with the space group  $P2_1/c$  to the tetragonal  $\text{Cu}_{1.96}\text{S}$  structure with space group  $P4_32_12$  gradually progressed during the initial five cycles. The  $\text{Cu}_2\text{S}$  electrode coated on the Al foil showed gradual capacity fading in the discharge process and large scattering in the charge process, which were caused by the corrosion of Al foil by Cu in the cycling. The chapter identifies from the investigation of the actual electrochemical properties of copper sulfides coated on an Al foil current collector that alternative current collectors should be used to avoid undesirable surface reactions between the electrode and the current collector.

**Chapter 3** reported the continuous of the chapter 2 with the electrochemical characterizations of stoichiometric  $\text{Cu}_2\text{S}$  coated on different current collectors of carbon fiber paper and Cu foil. The corrosion issues occurred between the stoichiometric  $\text{Cu}_2\text{S}$  and an Al foil current collector during cycling were avoided through changing the current collector. Stoichiometric  $\text{Cu}_2\text{S}$  with monoclinic crystal structure coated on a CFP current collector exhibited high capacity, excellent cycling stability, and good rate capability. The minor capacity drop and plateau flattening from 2.25 to 1.85 V during the initial cycles could be linked to the phase change from monoclinic  $\text{Cu}_2\text{S}$  to tetragonal  $\text{Cu}_{1.96}\text{S}$ , which was detected by *ex situ* XRD analysis. Effective electron path and corrosion prevention

on a CFP current collector enhanced active mass utilization, and near theoretical capacity of  $330 \text{ mAh g}^{-1}$  was stable for 50 cycles at 0.1 C and 1.0-3.0 V cut-off voltage. When the cut-off voltage was increased to 1.2-3.0 V to avoid SEI formation and irreversible discharge capacity at the 1<sup>st</sup> cycle, the cell still exhibited relatively high capacity of  $280 \text{ mAh g}^{-1}$  at 0.1 C and  $250 \text{ mAh g}^{-1}$  at 1 C. *Ex situ* XRD analysis showed that the phase transformation during charge, from monoclinic  $\text{Cu}_2\text{S}$  to tetragonal  $\text{Cu}_{1.96}\text{S}$ , progresses slower at 1.2-3.0 V than that of at 1.0-3.0 V. The reason could come from the incomplete electrochemical reactions, which caused higher charge transfer resistance and lowered kinetics. At higher charge-discharge rates, stoichiometric  $\text{Cu}_2\text{S}$  coated on a CFP current collector showed excellent capacity retention without severe decay between 0.1 and 5 C at various cut-off voltage. However, further increase of C-rate up to 10 C showed the decrease of Coulombic efficiency due to the lower conductivity of CFP.

Therefore, stoichiometric  $\text{Cu}_2\text{S}$  was further tested coated on a Cu foil current collector. The evidence of the cycling failure of stoichiometric  $\text{Cu}_2\text{S}$  coated on an Al foil current collector due to the corrosion by Cu confirmed further by the change of the current collector, where the electrode's electrochemical properties have been significantly improved. Cu foil has a higher electronic conductivity than CFP, and thus much higher rate capability up to 30 C has been achieved without severe capacity fading. Moreover, during the chemical composition studies, the  $\text{Cu/S} \approx 3.2$  molar ratio electrode coated on a Cu foil current collector showed excellent rate capability of  $350 \text{ mAh g}^{-1}$  at 5 C due to the fast charge transfer and efficient electrode utilization facilitated by the excess of Cu. The results confirm that the different chemical compositions of  $\text{Cu}_2\text{S}_x$  are demonstrating different electrochemical performances affected by Cu amounts in the electrodes.

**Chapter 4** reported stoichiometric CuS prepared by SP and followed annealing and sulfur excess CuS<sub>1+x</sub> by one-step SP. Firstly, stoichiometric CuS with a hexagonal crystal structure and space group *P6<sub>3</sub>/mmc* was successfully prepared by SP at 400 °C with [Cu/S]<sub>0</sub> = 0.4 molar ratio precursor solution and further low temperature annealing at 150 °C for 1 h. The cathode electrode of stoichiometric CuS was coated on a CFP current collector to study its electrochemical reaction mechanism by *ex situ* XRD analysis without effects of the reaction between electrode and current collector. The 1<sup>st</sup> discharge and charge reactions revealed that the 1<sup>st</sup> cycle is not reversible due to the formation of low crystallinity CuS during the charging process. This affected to the lower charge capacity on the 1<sup>st</sup> cycle and rapid capacity fading on the following cycles to less than 50 mAh g<sup>-1</sup> after 20 cycles at 0.1 C owing to the low reaction activity between Li<sub>2</sub>S and Cu leading to the dissolution of unused Li<sub>2</sub>S<sub>x</sub> in the electrolyte. Whereas, the different reaction mechanism of stoichiometric CuS when coated on a Cu foil current collector occurred with the formation of Cu<sub>1.96</sub>S as the final product after charging instead of CuS due to the additionally introduced Cu cations from the current collector. Stoichiometric CuS coated on a Cu current collector had a stable cyclability up to 15 cycles at 450 mAh g<sup>-1</sup> at 0.1 C. However, due to the gradual accumulation and dissolution of unreacted Li<sub>2</sub>S<sub>x</sub> in the electrolyte, eventually, it suffered from a low Coulombic efficiency. Therefore, to trap the dissolved Li<sub>2</sub>S<sub>x</sub> and reduce their migration to the lithium metal side, the cell preparation was modified through the insertion of a CFP interlayer between stoichiometric CuS electrode and separator in both current collectors. In the case of stoichiometric CuS coated on a Cu foil current collector with a CFP interlayer, the cell showed extremely stable cycling stability at 0.1 C at 460 mAh g<sup>-1</sup> for 30 cycles and 1 C at 440 mAh g<sup>-1</sup> for 200 cycles.

The further galvanostatic testing of sulfur excess  $\text{CuS}_{1+x}$  allowed achieving extremely high cycling performance of copper sulfides. The electrode of  $\text{CuS}_{1.58}$  coated on a Cu foil current collector showed capacities of  $900 \text{ mAh g}^{-1}$  at  $0.1 \text{ C}$  and  $720 \text{ mAh g}^{-1}$  at  $1 \text{ C}$ , respectively. The extra improvements were obtained through addition of a carbon by WBM method to increase the reaction activity between Cu and  $\text{Li}_2\text{S}$ , which gave a capacity of  $1200 \text{ mAh g}^{-1}$  at  $0.1 \text{ C}$  in the case of  $\text{CuS}_{1.58}$  electrode with 5 wt.% carbon content.

**Chapter 5** represents main conclusion from this study.