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（博士課程）
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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Copper sulfides are gaining significant attention as alternative cathode materials with high theoretical capacities (337 mAh g^{-1} for Cu_2S and 560 mAh g^{-1} for CuS) and high electronic conductivities (10^{-3} S cm^{-1} for Cu_2S and 10^{-4} S cm^{-1} for CuS). Despite their attractive features, copper sulfides suffer from the rapid capacity fading with the increase of the cycle number due to the dissolution of lithium polysulfides in the electrolyte. To implement the approaches to improve the electrochemical properties of copper sulfides the requirements for the understanding of their reaction mechanisms, the effect of chemical composition and the current collector are essential. The present study introduces main results as follows:

(1) Stoichiometric Cu_2S 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 Cu_2S electrode coated on an Al foil current collector exhibited a first discharge capacity of 335 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 Cu_2S structure with the space group $P2_1/c$ to the tetragonal $Cu_{1.96}S$ structure with space group $P4_32_12$ gradually progressed during the initial five cycles. The Cu_2S electrode coated on the Al foil showed large scattering in the charge process, which were caused by the corrosion of Al foil by Cu in the cycling.

(2)The corrosion issues occurred between the stoichiometric Cu_2S and an Al foil current collector during cycling were avoided through changing the current collector.

Stoichiometric Cu_2S with monoclinic crystal structure coated on a CFP current collector exhibited high capacity, excellent cycling stability, and good rate capability. Effective electron path and corrosion prevention on a CFP current collector enhanced active mass utilization, and near theoretical capacity of 330 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 1st cycle, the cell still exhibited relatively high capacity of 280 mAh g^{-1} at 0.1 C and 250 mAh g^{-1} at 1 C. Stoichiometric Cu_2S 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 Cu_2S was further tested coated on a Cu foil current collector. 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 Cu/S ≈ 3.2 molar ratio electrode coated on a Cu foil current collector showed excellent rate capability of 350 mAh g^{-1} at 5 C due to the fast charge transfer and efficient electrode utilization facilitated by the excess of Cu.

(3) Stoichiometric CuS prepared by SP and followed annealing and sulfur excess CuS_{1+x} by one-step SP. Firstly, stoichiometric CuS was successfully prepared by SP at 400 °C with $[Cu/S]_0$ = 0.4 molar ratio precursor solution and further low temperature annealing at 150 °C for 1 h. The 1st discharge and charge reactions revealed coated on a CFP current collector that the 1st cycle is not reversible due to the formation of low crystallinity CuS during the charging process. Whereas, the different reaction mechanism of stoichiometric CuS when coated on a Cu foil current collector occurred with the formation of $Cu_{1.96}S$ as the final product after charging instead of CuS due to the additionally introduced Cu cations from the current collector. However, due to the gradual accumulation and dissolution of unreacted Li_2S_x in the electrolyte, eventually, it suffered from a low Coulombic efficiency. Therefore,

to trap the dissolved Li_2S_x 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. The cell showed extremely stable cycling stability at 0.1 C at 460 mAh g^{-1} for 30 cycles and 1 C at 440 mAh g^{-1} for 200 cycles.

The further galvanostatic testing of sulfur excess CuS_{1+x} allowed achieving extremely high cycling performance of copper sulfides. The extra improvements were obtained through addition of a carbon by WBM method to increase the reaction activity between Cu and Li_2S, which gave a capacity of 1200 mAh g^{-1} at 0.1 C in the case of $CuS_{1.58}$ electrode with 5 wt.% carbon content.

In summary, the study sheds a light into complex electrochemical properties of copper sulfide cathodes. Different approaches to improve electrochemical properties were investigated and showed the attractiveness of copper sulfides as promising cathode materials.