

Influence of the synthesis surfactants on the electrochemical and physicochemical properties of copper zinc tin sulfide

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Received: January 23, 2024; Revised: March 18, 2024

Cu₂ZnSnS₄ (CZTS) materials were obtained using two synthesis protocols. Ascorbic acid (ASC sample) and polyvinylpyrrolidone (PVP sample) were used as surfactants. X-ray diffraction data reveal a single phase CZTS (kesterite) material for the PVP sample, while the ASC sample is a mixture of Cu₂ZnSnS₄, ZnS, ascorbic acid and possibly Cu₂SnS₃. UV-vis spectroscopy was used in complementary manner in order to determine the presence of ascorbic acid in ASC final product. The morphology shows particles of 2-5 nm "fused" in larger agglomerates. The delivered initial capacities are 1148 mAh g⁻¹ (ASC) and 1141 mAh g⁻¹ (PVP). The capacity loss is more than 90% for ~12 cycles for both samples. The conversion of Cu₂ZnSnS₄ to Li₂S and alloys seems to be partially reversible, most likely due to Li₂S dissolution in the electrolyte.

Keywords: solution-processed materials, eco-friendly surfactants, ascorbic acid, polyvinylpyrrolidone, Cu₂ZnSnS₄, Li-ion battery

INTRODUCTION

Sustainable energy sources hold the key for the future economic, secure and ecology-oriented worldwide progress [1-5]. The major challenges that need to be overcome concerning the "green" energy sources are increased efficiency, conversion and storage. This trend is valid at full strength for lithium-ion batteries. Being devices capable of storing energy and releasing it on demand, their usage extends from commercial electronics and transportation, to industrial and power-storage applications [6-8]. Extensively studied during 1980s and commercialized in early 1990s, graphite (and its variations) is a dominant anode material for commercial lithium-ion batteries (LIB) with aprotic electrolytes [8, 9]. As a matter of fact, anodes have a vital role in improving the electrochemical LIBs performance. However, graphite and its derivatives confine the delivered power and energy density [9]. Therefore, approaches for further development pass by searching of alternative anode materials. Materials that exhibit higher energies and power densities include metal oxides (Fe₂O₃, SnO₂, Li₄Ti₅O₁₂), metals, and metalloids (Si, Sn, and Ge), as the Sn-based compounds (already mentioned SnO₂ and also SnS₂, SnSb, FeSn₂) being among the most widely investigated [8, 9]. Yet, these materials suffer from high volume expansion issues during lithiation and delithiation processes leading to severe structure degradation, which in turn results in short cycle life and low rate capability [9].

Lately, another family has drawn significant attention as potential candidates for LIB anodes, namely the multicomponent copper-containing semiconductor chalcogenides, Cu₂ZnSnS₄ (CZTS) in particular. An important advantage of these semiconductors is their tolerability to solution-processing synthesis, which is an economically viable alternative of vacuum-based methods due to lower electricity consumption and consequently, lower environmental impact [10].

Therefore, the aim of the present work is the comparative study of solution-processed Cu₂ZnSnS₄ materials obtained *via* two different eco-friendly synthesis protocols using different surfactants: ascorbic acid and polyvinylpyrrolidone.

EXPERIMENTAL

Synthesis of CZTS material

Copper zinc tin sulfides were obtained through a sol-gel method followed by solvothermal conditions. Two different synthesis protocols were employed to prepare the materials.

Synthesis 1 (ASC sample)

In separate beakers 4.55 mmol Cu(CH₃COO)₂·H₂O (98+% Alfa Aesar), 2.275 mmol Zn(CH₃COO)₂·2H₂O (98%, VWR), 2.275 mmol SnCl₂·2H₂O (98%, Merck), 2.5 mmol L-(+)-ascorbic acid (99% Alfa Aesar) and 9.1 mmol thiourea (Sigma Aldrich, 99%) were dissolved in 50 ml of C₂H₅OH (96%, Valerus, Bulgaria) each, at 50 °C and constantly stirred. Ascorbic acid was used as

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a capping agent to suppress the single crystal growth of CZTS during the solvothermal synthesis. The solutions of copper and zinc acetates (sol 1) were mixed followed by the ones of ascorbic acid and thiourea (sol 2). Thereafter, sol 1 and sol 2 were slowly mixed. The $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solution was added to the newly formed main solution. The final solution was evaporated at $80\text{ }^\circ\text{C}$ and constantly stirred upon reaching 40 ml, then left to cool down to room temperature. To this solution was added 40 ml ethylene glycol (99%, Valerus) then the mixture was transferred into a 100 ml Teflon-lined autoclave at $200\text{ }^\circ\text{C}$ for 24 h. After cooling to room temperature, the suspension was filtered and washed with deionized water several times. This sample was denoted as ASC.

Synthesis 2 (PVP sample)

1.02 mmol SnCl_4 (98% Alfa Aesar), 0.51 mmol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99% Alfa Aesar) and 0.51 mmol ZnCl_2 (98% Alfa Aesar) were added to 20 ml ethylene glycol (99%, Valerus) at room temperature and constant stirring. After complete dissolution of the precursors, 5.1 mmol thiourea was added to the solution and stirred for *ca.* 10 min until completely dissolved. Finally, 0.0026 mmol polyvinylpyrrolidone MW 40000 (PVP, Alfa Aesar) was employed as a capping agent. The volume of the solution was supplemented to 50 ml with ethylene glycol and transferred into a 100 ml Teflon-lined autoclave at $200\text{ }^\circ\text{C}$ for 24 h. After cooling to room temperature, the suspension was filtered and washed with deionized water several times. This sample was denoted as PVP.

CZTS characterization

X-ray powder diffraction (XRD) data of the samples were collected on a Philips APD 15 diffractometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). UV-visible spectra were recorded of two drops of the CZTS colloidal solutions ($\sim 4.5\text{ mg cm}^{-3}$) diluted in 2 ml of deionized water using Metash UV-5800 spectrophotometer. The morphology of the material was observed by transmission electron microscopy (TEM) on JEOL JEM 2100, 80-200 kV.

Electrochemical testing in a lithium system

The active materials (AM) were tested electrochemically in a two-electrode laboratory cell. The working electrodes were prepared by mixing the active material, PVDF (Alfa Aesar) and carbon

black (CB) in N-methyl-2-pyrrolidone (NMP). The ratio of the slurry in wt.% was 70:10:20 (AM:PVDF:CB). The slurry was stirred for $\sim 24\text{ h}$ and then cast onto copper foil. The electrodes were dried in an oven at $60\text{ }^\circ\text{C}$ for 24 h under air. Cells were assembled in an argon filled glove box ($< 0.1\text{ ppm H}_2\text{O}$ and $< 0.1\text{ ppm O}_2$) using lithium foil as the counter electrode, Whatman (GF/C) separator soaked in 1M LiPF_6 in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as an electrolyte. The assembled cells were left for six hours at rest mode before the electrochemical measurements in order to ensure good electrolyte penetration in the pores of the AMs. Constant Current Constant Voltage (CCCV mode) tests were performed on Neware BTS (model: CT-4008-5V10mA-164) in the voltage ranges 0.05 - 3.0 V vs. Li/Li^+ at 15 mA g^{-1} . The end condition for the constant voltage in CCCV mode was decrease of the current to 20% of initial current used during galvanostatic charge. Cyclic voltammetry (CV) was performed on a Multi PalmSens4 (PalmSens BV) multi-channel potentiostat/galvanostat, in the voltage range 0.05 - 3.0 V vs. Li/Li^+ , with a sweep rate of 0.05 mV s^{-1} , where the counter Li electrode was also used as a reference, as its polarization is negligible.

RESULTS AND DISCUSSION

The XRD data of the samples fitted well to the tetragonal structure of $\text{Cu}_2\text{ZnSnS}_4$ (Figures 1a and 1b) with space group I-42m (ICSD 171983). Additional peaks are observed in the ASC sample (Figure 1a), which correspond to ZnS with hexagonal symmetry and space group P63mc (ICSD 31076). The presence of Cu_2SnS_3 (ICSD 50965) is very probable as a compensatory phase considering that the stoichiometric calculations were performed for $\text{Cu}_2\text{ZnSnS}_4$ product and the appearance of ZnS. However, closer look in the patterns disclosed that it is hard to determine whether Cu_2SnS_3 is present due to the reflection positions overlapping with $\text{Cu}_2\text{ZnSnS}_4$ phase (Figure 1a). Moreover, there is a peak at $\sim 20^\circ 2\theta$ (asterisk in Figure 1a) implying presence of ascorbic acid [11] although the ASC sample was filtered and washed several times. A peak at $\sim 255\text{ nm}$ in the UV-vis spectra (Figure 1c) shows further evidence for ascorbic acid residue in the final material [12]. The extracted band gap from Tauc plot (Figure 1c inset) was found to be 5.8 eV and 5.5 eV for ASC and PVP, respectively.

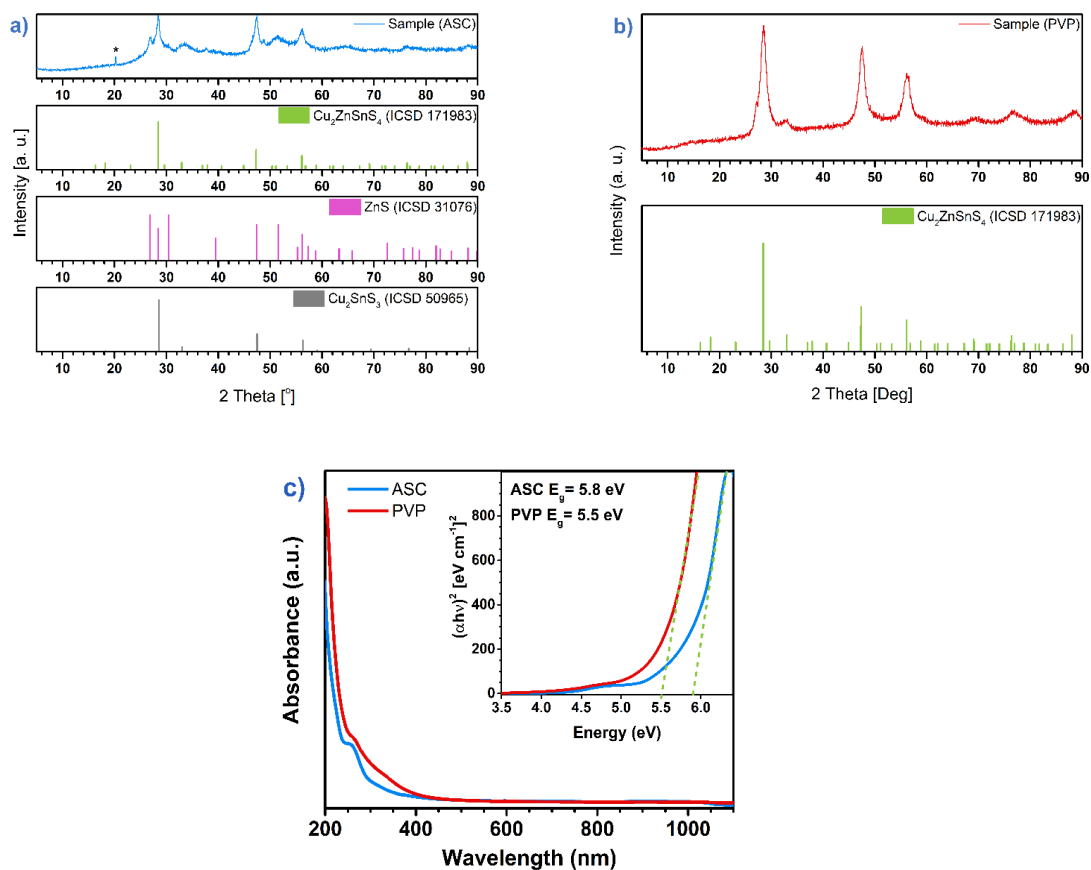


Figure 1. XRD patterns of (a) ASC and (b) PVP samples; c) UV-vis absorption spectrum and Tauc plots to determine the optical band gap (inset graph)

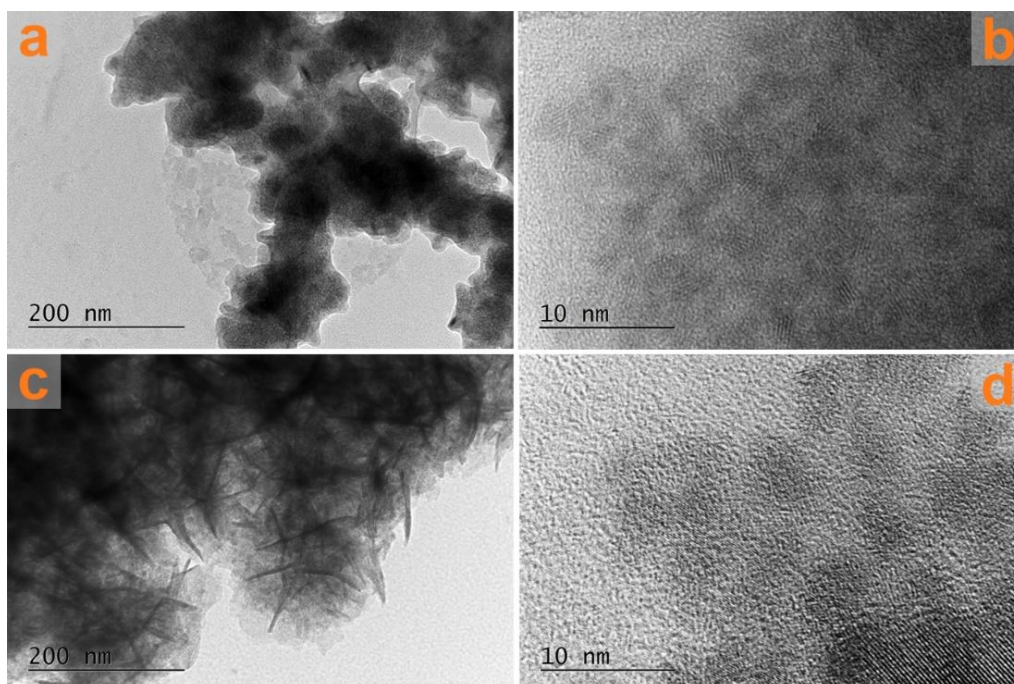


Figure 2. TEM micrographs of (a-b) ASC and (c-d) PVP

The TEM images of the two samples reveal presence of bulk agglomerates (Figures 2a and 2c). It is an evident flower-like morphology of the PVP agglomerates (Figure 2c). Both samples show agglomerates composed of nanoparticles with size of 2-5 nm (Figures 2 b and 2d).

Cyclic voltammetry (CV) was carried out at a scan rate of $0.05 \text{ mV}\cdot\text{s}^{-1}$ in the potential range 0.05–3.00 V vs. Li/Li in order to verify the electrochemical activity of the synthesized material (Figure 3).

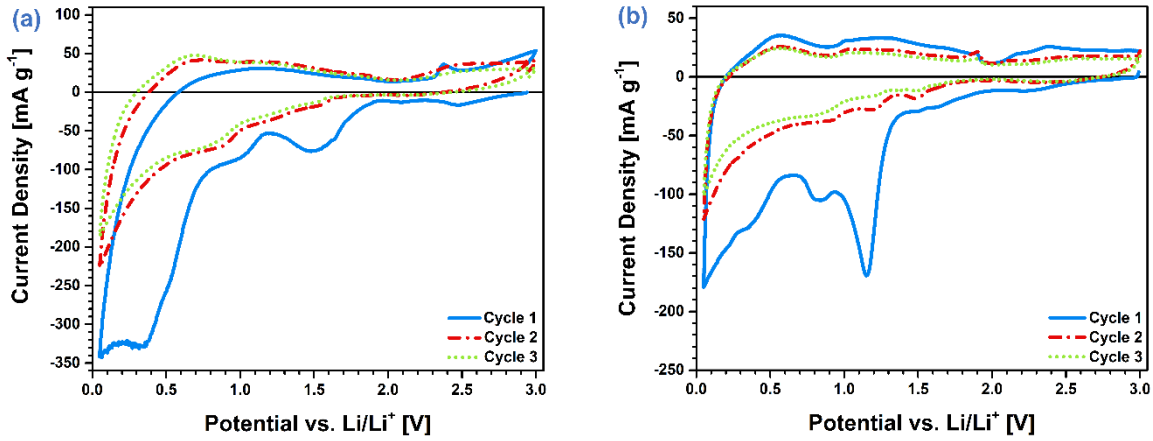


Figure 3. Cyclic voltammetry of (a) ASC and (b) PVP in the voltage range 0.05–3.00 V vs. Li/Li⁺ at a scan rate of 0.05 mV s^{-1} .

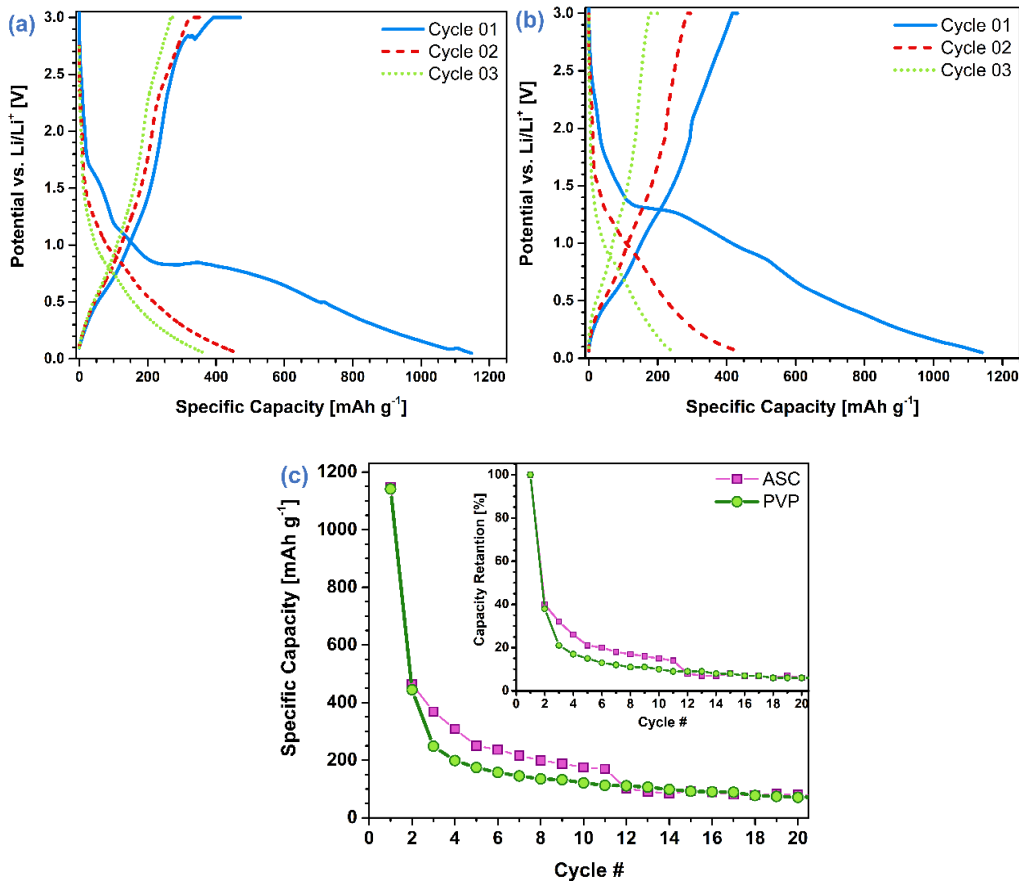


Figure 4. Galvanostatic tests: charge-discharge profiles in the voltage range 0.05–3.00 V vs. Li/Li⁺ (a) ASC and (b) PVP; (c) specific discharge capacity and capacity retention (inset) as a function of the cycles.

The electrochemical mechanism of these chalcogenide compounds is *via* conversion instead

of intercalation, which leads to formation of Li_2S and Cu-Zn/Cu-Sn alloys during the reduction process

[13]. The tested materials show different reduction curves. ASC first peak appears at 1.5 V vs. Li/Li⁺ followed by one at ~1 V vs. Li/Li⁺ and two strongly pronounced at 0.35 V and 0.05 V vs. Li/Li⁺ (Figure 3a). In contrast, PVP shows two strongly (at 1.15 V and 0.05 V) and two slightly pronounced (at 0.82 V and 0.35 V vs. Li/Li⁺) peaks (Figure 3b). The reduction curve of PVP sample seems to have closer resemblance to the reported in literature [9, 14-16] in comparison to the material synthesized with ascorbic acid. The reduction curve shape of ASC is most likely caused by ascorbic acid ligands on the surface of the active material particles, which prevent lithiation at higher potentials. Another contributor to the electrochemical behavior might be the ZnS phase, which main reduction electrochemical activity is within the 0.5-0.0 V vs. Li/Li⁺ range with peak maximum at 0.15 V vs. Li/Li⁺ [17]. Indirect proof for the presence of Cu₂SnS₃ phase in the ASC sample comes from the broad reduction peak at ~1.5 V vs. Li/Li⁺. The main electrochemical activity of Cu₂SnS₃ occurs in the ranges 1.5-1.0 and 0.5-0.05 V vs. Li/Li⁺ [6, 7, 18]. The oxidation curves of both materials are similar showing much lesser current density, which indicates poor reversibility. Peaks disappearance and current density decrease after the first cycle are evident. However, the materials performance stabilizes in the next cycles.

The performance of ASC and PVP materials was evaluated by employing galvanostatic tests at 15 mA g⁻¹ in the 0.05–3.00 V vs. Li/Li⁺ range (Figure 4). The first discharge curve plateaus are observed at different potentials: ~0.8 V (Figure 4a) and ~1.3 V (Figure 4b) for ASC and PVP, respectively. Both samples exhibit similar initial discharge specific capacities of 1148 mAh g⁻¹ (ASC) and 1141 mAh g⁻¹ (PVP) while the following charge capacities are less than a half (472 mAh g⁻¹ for ASC and 431 mAh g⁻¹ for PVP) indicating poor reversibility. The ASC shows slightly better performance in the first 10 cycles, thereafter both materials have similar outputs (Figure 4c). The capacity loss is more than 90% for ~12 cycles for the two CZTS samples (Figure 4c inset). Apparently, the conversion of Cu₂ZnSnS₄ to Li₂S and alloys seems to be partially reversible most likely due to the Li₂S dissolution in the electrolyte [19].

CONCLUSIONS

The present work is a comparative study of solution-processed Cu₂ZnSnS₄ materials obtained via two different eco-friendly synthesis protocols and surfactants: ascorbic acid (ASC) and polyvinylpyrrolidone (PVP). The X-ray diffractograms of both materials were indexed as Cu₂ZnSnS₄ phase with tetragonal structure.

However, additional peaks were observed in the ASC sample corresponding to ZnS, ascorbic acid and possibly Cu₂SnS₃. Further proof for the presence of ascorbic acid came from UV-vis spectroscopy. The morphology of the two samples consists of agglomerates composed of nanoparticles with size of 2-5 nm. The CV shows two different reduction curves for the studied samples. The PVP reduction curve shape is closer to that reported in literature, while the ASC behavior is most likely affected by the presence of ascorbic acid and ZnS. The galvanostatic tests displayed high initial capacities of 1148 mAh g⁻¹ (ASC) and 1141 mAh g⁻¹ (PVP). However, the capacity loss over the cycles is significant for both materials.

Acknowledgement: This study is funded by the Bulgarian National Science Fund (BNSF) under the scope of the “Competition for financial support of basic research projects on societal challenges 2018” program within the research project “Multifunctional Applications of Composite Graphene-Quantum Dots Systems (MULTIGRAPH)” contract No KII-06-OIIP04/2 14.12.2018.

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