CuSbS₂ as a negative electrode material for sodium ion batteries

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ABSTRACT

CuSbS₂ was tested as a negative electrode material for sodium-ion batteries. The material synthesized by ball milling offers a specific charge of 730 mAh.g⁻¹, close to the theoretical value (751 mAh.g⁻¹), over a few cycles. The reaction mechanism was investigated by means of operando X-ray diffraction, ¹²¹Sb Mössbauer spectroscopy, and Cu K-edge X-ray absorption spectroscopy. These studies reveal a sodiation mechanism that involves an original conversion reaction in two steps, through the formation of a ternary phase, CuSb_(1-x)S_(2-y), as well as a Na_xS alloy and Sb, followed by an alloying reaction involving the previously formed Sb. The desodiation process ends with the reformation of the ternary phase, CuSb_(1-x')S_(2-y'), deficient in Sb and S; this phase is responsible for the good reversibility observed upon cycling.

KEYWORDS

Negative electrode, Na-ion battery, ternary phase, conversion material

1. INTRODUCTION

With the advancement of developing countries, energy needs are constantly growing. According to estimates, during the day, solar energy can provide 4000 trillion kWh [1] and, thanks to photovoltaic (PV) technology, part of this energy (~24%) can be converted into electricity [1]. Unfortunately, this energy source is intermittent and, therefore, it needs to be coupled to an energy storage system [2]. Due to the low abundance of lithium in the Earth's crust, and its price, the more crust-abundant sodium could provide a solution to this storage application problem, while reducing the overall price of batteries [3,4,5]. Recently, French researchers developed a Na-ion battery (NaB) prototype that was able to deliver a specific energy of 90 Wh.kg⁻¹ with 99% coulombic efficiency over 4000 cycles [6], at a lower cost compared to similar Li-ion batteries (LiB). This NaB prototype outperforms the LiB first

commercialized by Sony in 1991, clearly demonstrating the enormous potential of NaBs. However, the knowhow acquired from LiB technology cannot simply be transferred to NaBs, as was demonstrated by the degradation of polyvinylidene fluoride (PVDF) binder for conversion based materials in NaBs [7]. From an energy density point of view, both systems (LiBs and NaBs) suffer from similar problems in terms of low specific charge for the negative electrode materials due to limitations imparted by single electron exchange in carbonaceous materials. Conversion-based materials, first introduced by Tarascon et al. [8], show very high specific charges due to multiple electron reactions; however, this is unfortunately accompanied by large changes in volume. This work opened up new pathways for the discovery of high-energy-density anodes based on conversion reactions. For example, Klein et al. [9] obtained promising results through the inclusion of CuS, CuO, and CuCl₂ in Na-based systems. They demonstrated that these materials need to be considered for NaBs, despite the additional effort required for the engineering of suitable electrodes [10]. Recently, binary or ternary materials such as Sb₂S₃, that combine Sb or Sn with sulfur, have been attracting interest [11, 12]. The optimization of these materials by carbon coating led to specific charge that reached 699 mAh.g⁻¹ after 100 cycles in Na-ion batteries and it was shown that the good reversibility depends on the efficiency in the reformation of the Sb₂S₃ phase at the end of charge. In order to buffer the Sb₂S₃ volume change, estimated to be about 266%, we decided to investigate CuSbS₂ as the ternary compound; the volume change should be reduced to approximately 212% due to the addition of inert Cu. Moreover, the presence of Cu is expected to enhance the electronic conductivity of the electrode following discharge [13] and then probably to help in the reformation of the pristine phase at the end of charge. CuSbS₂, also considered as a promising solar absorber [14], has already been tested in an LiB anode in which it achieved a specific charge of 450 mAh.g⁻¹ after 10 cycles [15]. To combine the conversion and alloying processes, Zhang et al. [15] suggested the following reaction mechanism:

In the present work, the material was synthesized by ball milling and high temperatures, leading to particle sizes that differed depending on the technique used. X-ray diffraction (XRD), scanning electron microscopy (SEM), and electrochemical performance were used to characterize the synthesized CuSbS₂. Finally, reaction mechanisms were investigated by means of operando XRD, X-ray absorption spectroscopy at the Cu-K edge (XANES), and ¹²¹Sb Mössbauer spectroscopy.

2. EXPERIMENTAL SECTION

2.1 Synthesis

CuSbS₂ was prepared by mechano-synthesis (ball milling, BM), and at high temperature, in a sealed tube (ST). For the BM synthesis, a stoichiometric amount of antimony (99.5%, 325 mesh, ABCR), sulfur (99.5%, Aldrich) and copper flakes (99%, 1-5 μm, Alfa Aesar) were introduced in a 45 mL stainless steel vessel with 30 stainless steel balls of 5 mm diameter (weight ratio of balls to powder was 13:1) and placed in a ball mill (PULVERISETTE 7,

Fritsch), and milled at 800 rpm for 33 hours in total (10 min active, 10 min inactive for 99 cycles). For the ST synthesis, the precursor powders were inserted, in stoichiometric amounts (1 g in total), into a silica tube, which was then sealed under vacuum. The tube was placed into a muffle oven where the temperature was risen to 500°C for 1 day and sustained at this temperature for 5 days. The sample was cooled to room temperature over 10 h.

2.2 Electrochemistry

Electrodes were prepared by ball milling a mixture of 70 wt.% active material, 9 wt.% carbon black (CB, SuperC65, Imerys), 9 wt.% vapor-grown carbon fibers (VGCF, Showa Denko), and 12 wt.% carboxymethylcellulose sodium salt (CMC, Alfa Aesar) in deionized water. The slurries were cast onto the copper foil to be used as the current collector, and dried under air at room temperature. The 13 mm electrodes were punched and dried under dynamic vacuum at 120°C for 2 h. Active material loadings were between 3 mg.cm⁻² and 4 mg.cm⁻². The thickness was measured with a Mitutoyo tool at ca. 40 μm and the electrode porosity was estimated to 70% [16]. Electrochemical cells were assembled in an Ar-filled glove box using glass fiber separators and metallic sodium as the counter electrode. A mixture of 1M NaClO₄ dissolved in propylene carbonate (PC) was used as the electrolyte. The performance of each cell was measured in galvanostatic mode at 25°C between 5 mV and 2.5 V or 1.05 V (versus Na⁺/Na), at a C/3 rate (1 Na per unit formula reacts in 3 h), and monitored by an ASTROL cycling device. The cyclic voltammetry (CV) was measured in a similar electrochemical cell at a scan rate of 0.05 mV.s⁻¹.

2.3 X-ray diffraction (XRD)

XRD measurements were performed in reflection mode at room temperature with a PANalytical Empyrean diffractometer using copper Kα-radiation. The operando measurements were performed using a homemade, in situ cell described elsewhere [17], with a powder electrode made by mixing 70 wt.% of active material with 30 wt.% carbon additives "CB" (superC65 and VGCF). A current corresponding to a C/4 rate was applied.

2.4 Scanning Electron Microscopy (SEM)

SEM measurements were performed in a Carl Zeiss Ultra55 scanning electron microscope using the secondary electron mode.

2.5 ¹²¹Sb Mössbauer

In order to reach loadings of around 50 mg suitable for ¹²¹Sb Mössbauer analysis, samples were prepared as a compressed electrode composed of 70 wt.% CuSbS₂ and 30 wt.% Super C65. For ex situ samples, the batteries were cycled at C/10. A Ba^{121m}SnO₃ source was used for the ¹²¹Sb Mössbauer spectroscopic investigations. The samples were placed within thin-walled PMMA

containers with at a loading of about 10 mg Sb.cm⁻². Measurements were conducted in the usual transmission geometry at 5 K (Continuous Flow Cryostat System of Janis Research Co LLC). The source was kept at room temperature. Spectral fitting was performed using Normos software [18].

2.6 X-ray absorption spectroscopy (XAS)

For the ex situ samples, the electrodes were cycled as described in section 2.2 (above), with a potentiostatic step of 8 h, to ensure proper sodiation/lithiation. After cycling, the electrodes were washed with dimethyl carbonate (DMC). The remaining powder was mixed with carbon in order to fill a capillary (d = 1 mm). A similar preparation of the capillaries was used for the reference samples CuO (Aldrich) and Cu₂O (Aldrich). XAS measurements were carried out at the Cu K-edge (8979 eV) on the SuperXAS beamline of the Swiss Light Source (SLS, PSI, Switzerland). A Si(111) channel-cut monochromator, in transmission mode, was used [19], allowing spectra to be acquired in 50 ms. The spectra presented are the results of the summation of 2400 spectra (total acquisition time of 2 min. per sample). For each measurement, the reference spectrum consisting of Cu foil, placed after the sample toward the beam penetration, was also recorded. Data were treated using the ATHENA software and the calibration was done using the Cu foil reference spectrum [20].

3. RESULTS

The XRD pattern of the BM sample (Figure 1a) reveals broad Bragg peaks, indicative of low crystallinity, typical of materials produced using this type of synthesis route. All peaks could be indexed in an orthorhombic system (space group *Pnma* – ICSD card85133). The ST sample presented a pattern where the peaks are fine and intense, attributed to the same orthorhombic system. However, a minor impurity, assigned to CuS (hexagonal system, space group *P6₃/mmc* – ICSD card n°855269), was detected.

For the BM sample, the SEM image reveals particle morphologies with aggregates of the order of tens of μm in size (Figure 1b). Smaller particles (below 1 μm in diameter) are also distinguishable, indicative of broad particle size distribution in the sample, owing to the synthesis conditions. As expected, for the high temperature, sealed-tube synthesis, the SEM image (Figure 1c) reveals larger particles that range from 10 to 50 μm.

Figure 1 → a) XRD patterns of the materials synthesized by ball milling (BM) and high temperature (ST); SEM images of the b) BM and c) ST materials.

The galvanostatic curves for the CuSbS_2 electrodes are shown in Figure 2. For the BM material (Figure 2a), the first sodiation curve can be decomposed into three main potential plateaus, at 1.25 V, 0.95 V and 0.5 V. Zhang et al. [15] reported that the lithiation curve for CuSbS_2 is also described by three plateaus: the first plateau at 1.5 V (vs. Li^+/Li) is related to the conversion of CuSbS_2 in Li_2S , Cu and Sb, and the two last plateaus at 0.75 V (vs. Li^+/Li) and 0.6 V (vs. Li^+/Li) are linked to the alloying reaction of Sb and "solid electrolyte interphase" (SEI) formation, respectively. By comparison with the Li system, the potential plateaus should be 300 mV lower versus Na^+/Na , without considering polarization, due to differences in particle size. In the first sodiation curve, the first potential plateau, at 1.25 V, is assumed to be related to the conversion of CuSbS_2 , involving sodiation of the sulfur species, which known to be sodiated above 1.2 V. Consequently, the final potential plateau, at 0.5 V, is probably linked to the alloying reaction of Sb into Na_3Sb , whereas the origin of the second plateau, at 0.95 V, is unclear, but cannot be due to SEI formation. Komaba et al. [5] identified electrolyte decomposition on a hard carbon electrode at between 0.5 V and 0.2 V. During the first charge (or desodiation), two main potential plateaus are clearly shown at 0.7 V and 1.4 V. A third electrochemical process can be seen in the cyclic voltammetry curve (Figure S1), with a peak at 1.9 V, but a corresponding potential plateau is hardly distinguishable in the galvanostatic curve.

During the second sodiation, an additional potential plateau appears at 1.5 V, followed by the two additional potential plateaus already visible during the first sodiation process, at 0.95 V and 0.5 V. The potential plateau described in the first sodiation, at 1.25 V, is no longer present during the second cycle. The phase formed at the end of the first desodiation process is different to that of the pristine CuSbS_2 phase, as only the first plateau was observed to change.

Interestingly, the second desodiation curve exhibits a clear potential plateau at 1.9 V, unlike the first sodiation curve.

In Figure 2b, galvanostatic curves for the 2nd, 5th and 10th cycles are compared against the normalized specific charge. The 2nd and the 5th sodiation curves show three similar potential plateaus, but higher polarizations (100 mV) are noticed at the 5th cycle for the potential plateaus at 0.95 V and 0.5 V. Similar polarizations are observed for the potential plateaus at 0.7 V and 1.4 V during desodiation. These observations confirm the two reversible redox processes (sodiation/desodiation) at 0.95 V / 1.4 V and 0.5 V / 0.7 V. Interestingly, the final potential plateau for the second desodiation sits at 1.9 V, whereas a 2.25 V plateau is observed for the 5th desodiation, resulting in an increase in polarization of 350 mV. The last desodiation step in the mechanism might be the origin of this fading since an increase of polarization translates a building-up resistance [16].

During the 10th cycle, the first potential plateau of the sodiation curve, that was observed at 1.5 V in the 2nd and 5th cycles, vanishes during desodiation at 1.9 V, along with the final potential plateau.

The galvanostatic curves for the ST material (Figure 2c) show the same potential plateaus as were observed for the BM samples; however, higher polarizations are expected since the diffusion of Na in large particles is slower than in small particles.

Figure 2 → Galvanostatic curves for the first and second cycles (cycled between 2.5 V – 5 mV) for a) BM and c) ST; and b) galvanostatic curves for the 2nd, 5th and 10th cycles plotted against normalized specific charge.

The electrochemical performance of the BM and ST electrodes, cycled in the 2.5 V – 5 mV potential window, are presented in Figure 3. For both compounds, during the first discharge, a

specific charge of 1005 mAh.g^{-1} is obtained, whereas the theoretical specific charge was calculated to be 751 mAh.g^{-1} . For the second discharge, the specific charges drop to 730 mAh.g^{-1} and around 475 mAh.g^{-1} for BM and ST, respectively. The high irreversible charge observed is most likely due to the conversion and alloying reactions that generate high volume changes, particle fractures [15], and consequently higher electrolyte decomposition. It is not surprising to have higher irreversible charge for the larger particles produced during the ST synthesis, compared to the smaller particles obtained from the BM method. We suspect a core-shell reaction process preventing a proper sodiation/desodiation at such rate. The coulombic efficiency further confirms the irreversible contribution of the first cycle, since it starts at 65% and rises to 90% for BM, with similar rises (55% to 78%) observed for the ST sample.

Until the 6th cycle is reached, the specific charge is maintained at around 730 mAh.g^{-1} (close to the theoretical value) for the BM electrode, after which the specific charge stabilizes at around 470 mAh.g^{-1} up to the 20th cycle. Interestingly, the specific charge of the ST electrode reaches 450 mAh.g^{-1} after the third cycle, and this value is sustained until the 20th cycle. The conversion and alloying reactions are more reversible with small particles as opposed to big agglomerates, as demonstrated in other papers [21].

After 20 cycles, the specific charge of both materials decreases to 200 mAh.g^{-1} for ST and 70 mAh.g^{-1} for BM. The faster fading observed for the BM electrode originates from its high surface area that is responsible for the increased rate of electrolyte decomposition. This is further illustrated by the lower coulombic efficiency of BM, which is below 90%, compared to that of ST, which is higher than 90%, after six cycles. In previous work [21], we noticed similar differences in behavior between Sn nanoparticles and Sn micrometer particles in a NaB cathode. In order to investigate the correlation between the different potential plateaus, the BM electrode was cycled within a $1.05 \text{ V} - 5 \text{ mV}$ potential window, which should result in an electrochemical reaction without any plateaus at potentials higher than 1 V (see Figure 2). A reversible, but limited, specific charge of 270 mAh.g^{-1} , with coulombic efficiency values greater than 96%, is demonstrated. This result confirms that the electrochemical reactions that occur in this potential window are not responsible for the observed specific charge fading, even if the effects of lower volume changes cannot be excluded.

Figure 3 → Evolution of the specific charge and the coulombic efficiency for different CuSbS_2 electrodes.

Operando XRD patterns collected during the first sodiation of the ST electrode are shown in Figure 4 in the form of a contour plot. During the first few cycling hours, the CuSbS_2 Bragg peaks diminish and fully disappear by the end of the 1st potential plateau. Over the same period of time, a new intermediate phase is formed. This phase is referred to as X1, and is characterized by two broad peaks centered at 19.0° and 31.2° . This phase has not been reported previously, and no match could be found in the ICSD database. The Na_2S pattern is observed as a distinct peak at around 31° with no peak at lower angle, whereas the Na_2S_4 pattern has four main peaks at 20° , 22° , 30.5° and 32° . Following sodiation, this intermediate phase disappears by the end of the first potential plateau, whereas the peak at 28.8° remains. The latter peak reveals the formation of Sb during the second potential plateau. Consequently, during the two first potential plateaus, CuSbS_2 is converted into amorphous Na_2S , and potentially into Na_2S_2 and Sb, in a similar fashion to the chemistry observed for the Li-ion system. The formation of a phase containing Cu, Na and S cannot be excluded and will be discussed later. During the last potential plateau, the Sb peak, formed during the second step of the mechanism, decreases in intensity, consistent with the alloying reactions of Sb into Na_xSb and Na_3Sb [22]. However, in the patterns presented in Figure 4, no trace of Na_3Sb is visible, which could indicate that this phase is amorphous, or well dispersed with small particles. Only at the end of the discharge is a broad, unassigned peak (X2), centered at 35.2° , observed. Moreover, the CuS impurity peak disappears.

Figure 4 → Operando XRD measurements for the first sodiation.

To gain further insight into the reaction mechanism, the pristine CuSbS_2 (BM) electrode and the BM electrode cycled at 750 mV and 5 mV, were examined by ^{121}Sb Mössbauer spectroscopy. The experimental spectra taken at 5 K are presented in Figure 5 along with transmission integral fits. The spectrum of pristine CuSbS_2 was well reproduced with a single signal at an isomer shift of $\delta = -13.6(1) \text{ mm.s}^{-1}$, and an experimental line width of $\Gamma = 3.4(1) \text{ mm.s}^{-1}$. As a consequence of the lone-pair on the antimony atoms, this signal is subject to a quadrupole splitting of $6.7(2) \text{ mm.s}^{-1}$. These experimental data are in good agreement with those tabulated [23]. The spectrum of the sample cycled at 750 mV (Figure 5, middle) shows a symmetrical signal which could be simulated by one signal at $\delta = -10.1(1) \text{ mm.s}^{-1}$, and an experimental line width of $\Gamma = 5.0(1) \text{ mm.s}^{-1}$. The significantly increased line width is indicative of superposition. The domains of differing composition of the $\text{CuSb}_{(1-y)}\text{S}_{(2-x)}$ solid solution result in a distribution of signals (i.e. a distribution of slightly different isomer shifts) that lead to the observed envelope. Due to the broadness of this signal, we cannot exclude the presence of small quantities of antimony ($\delta = -11.6(1) \text{ mm.s}^{-1}$) [24]. The less negative isomer shift observed for the $\text{CuSb}_{(1-y)}\text{S}_{(2-x)}$ solid solution indicates lower electron density at the antimony nuclei as compared to pristine CuSbS_2 . This result is in full agreement with the general trend in observed for a diverse range of antimony chalcogenides, as reviewed by Lippens [24]. Apart from a small amount of antimony (19(2) %), the main phase detected in the

spectrum of the sample cycled at 5 mV (Figure 5, bottom) is Na_3Sb (81(2) %). The isomer shifts of -11.3 mm.s^{-1} for antimony and -8.7 mm.s^{-1} for Na_3Sb are in close agreement with the literature data [24-25]. These values were fixed in the final spectral fitting. Independent refinement of all parameters shows too large correlations. Small deviations in isomer shift values are also the consequence of the shapes of the samples (nanoscale material after cycling). The presence of residual antimony can be explained by the limited performance of the highly loaded electrode required for the Mössbauer analysis.

Figure 5 → ^{121}Sb Mössbauer spectra of pristine CuSbS_2 (top), CuSbS_2 cycled @ 750 mV (middle) and CuSbS_2 cycled @ 5 mV (bottom).

Finally, the role of Cu was investigated by XANES (Figure 6). The spectrum of pristine CuSbS_2 was compared to the spectra of an intermediate phase taken during the first sodiation process (0.75 V), at the end of the first sodiation, and at the end of the first desodiation. The intermediate state corresponds to the material obtained at the end of the second potential plateau. In Figure 6a, we focused on the Cu K-edge of these spectra in order to determine the evolution of the degree of oxidation of the material upon cycling, using Cu metal, Cu (I) and Cu (II) as references. The edge of the pristine CuSbS_2 lies between the edges of the metallic

Cu and Cu (I), whereas the edge of the fully sodiated sample lies before that of metallic Cu. This confirms that reduction of CuSbS₂ has occurred during sodiation. After desodiation, the edge of the spectrum shifts to an energy value close to that of the pristine material, symbolizing the oxidation of the sodiated state. However, the degree of oxidation is probably slightly lower than that of the pristine CuSbS₂, since a shoulder appears at 8982 eV. The phase obtained following desodiation differs from that of pristine CuSbS₂. The analyses of the full XANES spectra are presented in Figure 6b. The spectrum of the intermediate phase (0.75 V) is different to the one obtained at the end of the sodiation, and to that of the pristine material. It would appear that at the end of the second potential plateau we do not yet have extrusion of Cu onto Cu metal, which could indicate that an intermediate phase has been created, consistent with the X1 phase observed by XRD. Following sodiation (Figure 6c), the pre-edge feature observed at the end of sodiation, as well as remaining signal, provides evidence of the presence of Cu metal [26]. Its presence increases the electrical conductivity of the electrode and, therefore, would be beneficial for electrochemical performance [13]. Finally, the spectrum at the end of desodiation and the one at 0.75 V show similar features. Hence, the end of the desodiation process provides a compound close in nature to the one obtained at the second step of sodiation.

Figure 6 → a) Close-up of the Cu K-edge of the various XANES spectra, and b) full XANES spectra at the Cu K-edge of BM for the first cycle at OCV (pristine), after 0.75 V sodiation, at the end of sodiation (5 mV), and the end of desodiation (2.5 V). c) Comparison of the XANES spectra at the Cu K-edge for the Cu metal foil and BM at the end of sodiation.

4. DISCUSSION

XRD, XAS, and ^{121}Sb Mössbauer spectroscopic analyses indicate that the first step of the reaction mechanism is linked to the “decomposition” of the pristine material. Normally, only S should react at potentials higher than 1 V and be observable by the techniques applied in this study. By analogy with the reactions in LiBs [15], the conversion reaction was expected to lead to the formation of Na_2S , Cu and Sb. Here, the extruded metallic Cu was only detected at the end of the sodiation process, after the conversion of Sb into Na_3Sb . Even if sample relaxation before the XAS measurement is not excluded, the formation of binary or ternary phases is possible, especially when the ability of Cu to assume the 1+ oxidation state is taken into account. The reverse reaction probably begins with the decomposition of Na_3Sb into Sb; however, the reformation of a ternary phase cannot be fully excluded at this stage. Moreover, this reaction mechanism does not account for the observed fading, due to its good reversibility within the limited potential window. The second and third potential plateaus observed during desodiation are related to recombination processes that lead to a new ternary phase that is close in nature to the one obtained at 0.75 V during sodiation. At this stage, as both Sb and S are active toward Na, a phase deficient in Sb and S, compared to the pristine phase, can be expected. We propose the following overall mechanism (equations (2,3)):

However, this ternary phase is also “hard” to obtain since a dramatic increase in the polarization of the last potential plateau, corresponding to the formation of this phase, is observed. It could be due to the degradation of the interphases (growing of the SEI, particles agglomeration and/or electrode decomposition) preventing the reformation of the ternary phase.

5. CONCLUSIONS

CuSbS_2 was successfully synthesized by ball-milling and high-temperature routes, giving materials of different crystallinity. The small particles obtained by BM display the best electrochemical performance, with a specific charge of 730 mAh.g^{-1} sustained for a few cycles. The electrochemical mechanism of the first cycle was investigated by mean of XRD and ^{121}Sb Mössbauer and XAS spectroscopies. Sodiation begins with the formation of Sb through a partial conversion reaction that involves a novel $\text{CuSb}_{(1-x)}\text{S}_{(2-y)}$ ternary phase. We assumed that polysulfides such as Na_2S are simultaneously formed during this process, but no direct evidence was found. Sodiation continues by the alloying reaction of Sb into Na_3Sb followed by the rest of the conversion reaction. The first step of the desodiation process involves the decomposition of Na_3Sb into Sb followed by the back conversion reaction to CuSbS_2 . However, the final compound is different in composition to pristine CuSbS_2 . We propose that a $\text{CuSb}_{(1-x')}\text{S}_{(2-y')}$ phase, deficient in Sb and S is obtained. Due to the involvement of $\text{CuSb}_{(1-x)}\text{S}_{(2-y)}$, the mechanism for sodiation is different to that for lithiation, where Cu metal has been detected as an intermediate phase [15].

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