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CuFe$_2$S$_3$ as electrode material for Li-ion batteries

Emmanuel Anger, Antoine Maignan, Tristan Barbier and Valerie Pralong*

Electrochemical performances of the isocubanite CuFe$_2$S$_3$ tested as electrode material for Li-ion batteries have been investigated. A first discharge capacity of 860 mA h g$^{-1}$ shows a conversion process leading to Li$_2$S, copper and iron nanoparticles. Interestingly, a reversible capacity of 560 mA h g$^{-1}$ at 1.5 V is observed with good cyclability up to 30 cycles. Ex situ X-ray diffraction (XRD) measurements allow a better understanding of the electrochemical mechanism.

The cubanite CuFe$_2$S$_3$ phase crystallizes within an orthorhombic structure (space group: Pcmn), with $a = 6.467$ Å, $b = 11.110$ Å and $c = 6.230$ Å. When the orthorhombic CuFe$_2$S$_3$ is heated above 473 K, an irreversible structural transition occurs and CuFe$_2$S$_3$ adopts a cubic structural type (space group: Fd3m, $a = 5.296$ Å). It should be noticed that cubanite and its cubic polymorph isocubanite are usually found in their natural states intimately intergrown with other sulfides such as chalcoprite and pyrrhotite. Synthesis of isocubanite CuFe$_2$S$_3$ has been first reported by S. Pareek et al. In this paper, we chose a synthetic protocol recently described by Barbier et al. Following precursors: Cu (99.0%), Fe (99.5%), and S (99.5%) from Alfa Aesar, were mixed in the appropriate ratio. After sealing the cold pressed powder in a silica tube, the latter was heated at 873 K for 48 h. The room temperature powder X-ray diffraction pattern of CuFe$_2$S$_3$ (depicted in Fig. 1) shows that CuFe$_2$S$_3$ crystallizes within the cubic form. Rietveld refinements were therefore carried out using Fd3m space group. However, extra peaks and peak shoulders which may be attributed to the chalcoprite phase can be observed (inset Fig. 1). Thus, from the refinements, the CuFe$_2$S$_3$ isocubanite (around 72 wt% – 63 at%) is the majority phase, while the minority one is the chalcoprite (around 28 wt% – 37 at%). The structural refinement leads to

$\dagger$ This product was characterized by XRD using a Philips X’Pert diffractometer with Bragg–Brentano geometry (CuK$_{α1,2}$ radiation). Note that due to their instability in air, the reduced phases XRD patterns were registered under vacuum using a chamber attached to a Bruker D8 diffractometer. Electrochemical characterizations of CuFe$_2$S$_3$ have been performed in Swagelok cells. Metallic lithium (Aldrich, 99.9%) has been used as negative electrode, LP30 from Merck [1 M LiPF$_6$ in an ethylene carbonate/dimethyl carbonate 1 : 1 (w/w) solvent] was used as the electrolyte, and the positive electrode was constituted of approximately 10 mg of a mixture of the active material with 50% weight of carbon (acetylene black). The electrochemical cells were cycled at constant current between 1.2 and 3.0 V at different galvanostatic rates on a VMP II potentiostat/galvanostat (Biologic SA, Clais, France) at room temperature. Potentiostatic intermittent titration technique (PITT) measurements were conducted using a potential step of 10 mV limited by a minimum current equivalent to a C/10 galvanostatic rate.
unit cell parameters $a = 5.3018(1)$ Å and $a = 5.2927(3)$ Å, $c = 10.4340$ Å for the isocubanite and chalcopyrite phases, respectively. The aforementioned unit cell parameters are close to those reported in the literature and then confirms their good crystallinity.

The isocubanite structure can be described as a tetragonal close-packed stacking of $S^{2-}$ anions, which occupy the 4$a$ (0, 0, 0) crystallographic site while Cu and Fe cations are randomly distributed over the two structurally equivalent tetrahedral sites 4$c$ (1/4, 1/4, 1/4) and 4$d$ (3/4, 3/4, 3/4). Different Rietveld refinements were therefore performed with both 4$c$ and 4$d$ crystallographic sites, and best result through low isotropic displacement parameters and reliability factors ($\chi^2 = 2.303$ and $R_{\text{Bragg}}$ factor = 6.98%) was obtained with all Cu and Fe atoms on the 4$d$ crystallographic site. Although the obtained sample is intergrown with chalcopyrite; as previously studied, the chalcopyrite phase forms submicronic domains, this isocubanite sample is well crystallized.

Note that the average particle size is about 1–2 μm without any particular shape.

The charge–discharge profiles of Li/CuFe$_2$S$_3$ (Fig. 2a) have been performed by a galvanostatic cycling at C/20/Li per formula unit (f.u.) in the potential window 0.5–3.0 V versus Li$^+$/Li. Starting from our material, the first discharge is fragmented in a series of two main processes happening between 1.80 and 0.50 V. The first one is a slope (A) from 1.80 to 1.50 V, it is attributed to the insertion of one lithium into CuFe$_2$S$_3$ through a solid solution, accordingly to literature. This insertion follows the eqn (1):

$$\text{CuFe}_2\text{S}_3 + \text{Li}^+ + e^- \rightarrow \text{LiCuFe}_2\text{S}_3$$

Note that the phase LiFeCuS$_2$ has been reported and our sample is an intergrowth between chalcopyrite CuFe$_2$S$_3$ and isocubanite CuFe$_2$S$_3$, a complete structural resolution of the lithiated phase is not possible. During the second process, we observe 5 plateaus at 1.50 (B), 1.46 V (C), 1.39 (D), 1.32 (E) and 0.82 (F) volt, respectively as shown on the derivative curve (inset Fig. 2a). These processes correspond to the reaction with 5 lithium and could then be assigned to copper and iron reduction to the metallic level as related in the case of Li/CuFeS$_2$ system following the eqn (2):

$$\text{LiCuFe}_2\text{S}_3 + 5\text{Li} \rightarrow \text{Cu}^0 + 2\text{Fe}^0 + 3\text{Li}_2\text{S}$$

Because of the nature of our material (intergrowth of isocubanite and chalcopyrite), it is interesting to point out that only two domains are observed in the course of the first discharge of pure CuFe$_2$S$_3$ phase (at 1.7 and 1.5 V, respectively). Charging process occurs mainly through one plateau at 1.80 V.
(G) as shown on the derivative curve (Red curve, Fig. 2b). This plateau could be attributed to copper and iron oxidation leading to a mixture of copper iron sulfides CuFeS2 [ref. 15, 23 and 24] and free sulfur formation. Consequently, this system becomes a hybrid between lithium ion and lithium sulfur battery. As observed on Fig. 2, the first discharge process is different than the second one where only one large plateau at 1.50 V (H) is observed. This can be due to SEI formation occurring at the same time than metal reduction in the first discharge. SEI formation has already been mentioned in similar conversion cathode study to be responsible for extra capacity like CuFeS2,15 Co3SiO4 (ref. 25) and CuCo2S4.26 In our case, an extra capacity of 260 mA h g⁻¹ is observed. We particularly have to consider the presence of CuFeS2 in our material. CuFeS2 has been previously investigated and possesses similar electrochemical properties compare to CuFeS2. Even if our material contains a large amount of CuFeS2, the electrochemical capacity cannot only be due to CuFeS2 activity. Therefore, this indicates that CuFe2S3 is an electroactive material.

A reversible capacity of 560 mA h g⁻¹ (C/20/Li) is observed in the potential window of 1.52 V to 1.80 V. Please, note that an additional phenomenon appears below 1.50 V. This latter could correspond to different phenomena like electrolyte degradation or lithium insertion in the surface electrolyte interface as mentioned in previous report.27,28 We believe that the irreversible capacity is mainly ascribed to this slope and the SEI formation.

Study at a rate of C/2/Li and a cut off at 1.0 V are displayed Fig. 2b. The curve of C/2/Li shows a reversible and stable capacity of 400 mA h g⁻¹ upon 9 cycles. Using this rate, a polarization of 340 mV is observed between formation and conversion of CuFeS2. This polarization is quite in accordance with previous electrochemical performance obtained for CuFeS2.27 We can notice that cutting off at 1.0 V improves the reversibility of the system. Note that the conversion process is not complete as last discharge plateau at 0.82 V is also cut off. Consequently, first reduction plateaus appeared at lower voltage and then stabilized at 1.47 V after few cycles (Fig. 2b).

The intermittent galvanostatic titration (GITT) reported in Fig. 3a shows a biphase process and allows us to access to the equilibrium potential in the course of the reduction with a thermodynamic potential of 1.65 V vs. Li+/Li. A polarization of 300 mV is observed. The potentiodynamic titration curve (PITT, Fig. 3b) reveals a bell-shape-type response on the reversible phenomenon, and confirms together with the sharpness of the peaks in the derivative curve (Fig. 2) that the irreversible process is biphase.

To confirm the structural conversion occurring in the course of the electrochemical process, ex situ X-ray diffraction patterns have been recorded at the end of the first discharge and charge (Fig. 4). We can see on the discharge pattern that CuFeS2 reflections disappeared (green middle curve, Fig. 4). Reflections on discharge pattern are attributed to copper (○), iron (Δ) and Li2S (+). After recharge (orange upper curve, Fig. 4), reflection close to CuFeS2 and attributed to CuFeS2 (+) are observed among undefined products (□). This validates the conversion mechanism.

The specific capacity decreases with the increase in current density (Fig. 5a). The reversible capacity is about 425 mA h g⁻¹ at the current density of C/5/Li and decreases down to 30 mA h g⁻¹ at 10C/Li. When the current density is tuned back at C/5/Li, the specific capacity rebounds to 350 mA h g⁻¹. This
Reduction that can form free sulfur.

Temperature (measured between 20 and 200 mohm cm).

Concerning resistivity, our isocubanite sample (containing compounds. Furthermore, they are both semi-conductors. However, extra electrochemical capacity are observed for both around 1.8 V and similar phenomena (conversion process, SEI formation, extra electrochemical capacity) are observed for both rates. The cut off at 1.2 V was necessary to avoid side reactions to occur as observed on the potential slope observed at the end of the first discharge. The capacity is rising in the first 10 cycles from 100 to 245 mA h g⁻¹ and stabilizes around 250 mA h g⁻¹. We believe this is due to the incomplete reaction together with side reaction despite the high voltage cut off.

The electrochemical behaviour of CuFe₂S₃ and CuFeS₂ are relatively close to each other's. Their working potential is around 1.8 V and similar phenomena (conversion process, SEI formation, extra electrochemical capacity) are observed for both compounds. Furthermore, they are both semi-conductors. Concerning resistivity, our isocubanite sample (containing chalcopryite) owns a resistivity of 0.7 mohm cm at 300 K while pure chalcopryite possesses a higher resistivity at room temperature (measured between 20 and 200 mohm cm).

Conclusions

In this work, we demonstrate the conversion of the intergrowth between the two phases CuFe₂S₃ and CuFeS₂ into Li₂S and native copper and iron particles. Moreover, ex situ XRD at the end of the charge showed that a new phase Cu₄Fe₃S₅ is formed. This new phase showed common diffraction peaks with the starting intergrowth but a complete structural resolution is not possible due to the low crystallinity of the material. More importantly, a reversible capacity of 425 mA h g⁻¹ at a C/5/Li rate upon 10 cycles and with a cut off at 1.0 V is obtained. The redox potential of 1.65 V vs. Li⁺/Li gives an energy density of 600 Wh kg⁻¹. This result points out that despite the intergrowth nature of the material between isocubanite and chalcopyrite, we obtain comparable performance for this family of materials.

Conflicts of interest

There are no conflicts to declare.

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