# *In Situ* X-Ray Study of the Electrochemical Reaction of Li with η'-Cu<sub>6</sub>Sn<sub>5</sub>

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The electrochemical reaction of lithium with crystalline intermetallic  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub> has been studied by means of *in situ* X-ray diffraction. The reaction of Li with Cu<sub>6</sub>Sn<sub>5</sub> proceeds in two distinct steps. A first discharge plateau at approximately 0.4 V vs. Li is attributed to the coexistence of Cu<sub>6</sub>Sn<sub>5</sub> and a ternary Li<sub>2</sub>CuSn-type phase. Upon further reaction Li<sub>2</sub>CuSn coexists with a Li-rich tin phase (Li<sub>4,4</sub>Sn) and metallic Cu at a potential below 0.1 V. During the charge, the initial intermetallic is reformed in a multistep reaction. First, some Li can be removed from Li<sub>4,4</sub>Sn making Li<sub>4,4-x</sub>Sn with the same structure. As Li is removed from Li<sub>4,4-x</sub>Sn it reacts with the available Cu to make Li<sub>2</sub>CuSn. Then, lithium can be removed from Li<sub>2</sub>CuSn, making vacancies in the structure to form Li<sub>2-x</sub>CuSn. When x in Li<sub>2-x</sub>CuSn reaches about 1, the removal of further lithium results in the formation of a second phase, Cu<sub>6</sub>Sn<sub>5</sub>. The 0.8 V plateau during the charge of Li/Cu<sub>6</sub>Sn<sub>5</sub> cells is associated with this coexistence of Li<sub>2-x</sub>CuSn and Cu<sub>6</sub>Sn<sub>5</sub>. The *in situ* experiments show that both the Li<sub>4,4</sub>Sn and the Li<sub>2</sub>CuSn phases can exhibit a range of Li stoichiometries, especially as Li is removed from their structures. When Li/Cu<sub>6</sub>Sn<sub>5</sub> cells are charged and discharged above the lower plateau, to prevent the continual expulsion and reincorporation of Cu from the cathode grains, better cycling is obtained than when cycling includes the lower plateau where metallic copper is formed.

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Lithium-ion cells normally use graphite negative electrodes and lithium transition metal oxide positive electrodes. In order to increase the energy density and specific energy of such cells, new electrode materials must be found. Lithium alloys offer larger specific and volumetric capacities than graphite, and these have been the subject of recent research. In particular, Mao *et al.* have shown that intermetallic compounds like FeSn<sub>2</sub><sup>-1</sup> and active/inactive nanocomposites like FeSn<sub>2</sub>/SnFe<sub>3</sub>C<sup>-2</sup> function well as anodes although their cycle life is limited. The limited cycle life of such alloys is probably caused by relatively large volume changes associated with the reversible reaction of Li.

In recent papers Kepler *et al.* and Thackeray *et al.*<sup>3,4</sup> have reported electrochemical data on Li/Cu<sub>6</sub>Sn<sub>5</sub> cells. It was found that Cu<sub>6</sub>Sn<sub>5</sub> reacts reversibly with lithium to deliver an initial discharge capacity of approximately 350 mAh/g. Based on structural similarity, it was proposed that this reaction could be described as an insertion of lithium in the Cu<sub>6</sub>Sn<sub>5</sub> structure to reversibly form Li<sub>2.17</sub>CuSn<sub>0.83</sub> (or Li<sub>13</sub>Cu<sub>6</sub>Sn<sub>5</sub>) that has the same structure as Li<sub>2</sub>CuSn. In this paper we do not distinguish between Li<sub>2.17</sub>CuSn<sub>0.83</sub> and Li<sub>2</sub>CuSn. In Ref. 3 and 4, it is suspected that further reaction of Li with Li<sub>2</sub>CuSn could result in the formation of Li-Sn alloys and the simultaneous expulsion of Cu. Surprisingly, even when discharged to 0 V, this reaction does not occur under the conditions used in Ref. 3 and 4. It is also shown that better cycling life is achieved when the discharge cut-off voltage is raised to 200 mV from 0 V.

In other work, Thackeray's group studied the material discharged to zero volts and the reaction below 400 mV was attributed to the extrusion of Cu and the formation of Li-Sn alloy.<sup>5</sup> The extraction of lithium from Li<sub>2</sub>CuSn was studied in Ref. 6. However the results in Ref. 3-6 are not self-consistent, nor are they of the highest possible quality. Thus, we decided to undertake a careful study of the reaction of lithium with  $Cu_6Sn_5$ .

Here, we show that the reaction of Li with  $Cu_6Sn_5$  results first in the formation of  $Li_2CuSn$  as an intermediate phase through a twophase reaction, and finally leads to a disordered  $Li_{4.4}Sn$  alloy and nanoscopic grains of Cu. These reactions are found to be basically reversible although some aspects of the mechanism are different during discharge and charge. The changes we observe in the charge-discharge cycle life depending on the selected voltage window are easily explained by the structural changes involved in these two reactions.

#### Experimental

Samples of  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub> powder were prepared by heating stoichiometric mixtures of elemental Cu and Sn powders (purity >99.9%) under argon flow at 400°C for a 10 h period.<sup>3</sup> The heating rate was 1°C/min. To ensure good homogeneity and contact of the reactants, the Cu/Sn mixture was intensively ground in a mortar and pressed into a pellet at a pressure of 200 bar.

The HT-Li<sub>2</sub>CuSn reference phase was prepared from powdered Sn and Cu, and Li foil in stoichiometric proportions. Reagents were poured in a stainless steel tube under purified argon in a glove box. The glove box was equipped with a welder. The ends of the stainless steel tube were TIG welded closed within the glove box. The sealed tube was heated at 700°C under argon flow for a 10 h period.<sup>7</sup> The tube was opened in a He-filled glove box, and the recovered purple-colored powder was finely ground in an agate mortar. A weight comparison showed that no leakage occurred during the annealing treatment.

X-ray diffraction was performed using a Siemens D5000 diffractometer equipped with a Cu target and diffracted-beam monochromator. Air-sensitive samples were characterized in a specially designed airtight X-ray holder as described in Ref. 8. In situ X-ray experiments were conducted using an in situ cell as reported in Ref. 9. For all *in situ* measurements the counting time was set to be 15 s for a step of 0.05°. The ranges between 20 and 58° (experiment no. 1) and between 36 and  $42^{\circ}$  (experiment no. 2) in scattering angle were measured repeatedly while the cell was discharged and charged once. The cell was cycled using a constant current corresponding to C/100 (experiment no. 1) or C/30 (experiment no. 2), at room temperature. To improve counting statistics, two electrode disks were stacked in the cell to effectively make an electrode having twice the thickness. The C-rate is calculated assuming a full reaction of Sn in Cu<sub>6</sub>Sn<sub>5</sub> with Li (*i.e.*, formation of Li<sub>4 4</sub>Sn). (The C-rate is the current needed to discharge the battery in 1 h.)

Electrochemical tests were made in 2325 coin cell hardware constructed as detailed in Ref. 10. The electrolyte used was 1 M LiPF<sub>6</sub> dissolved in a 33/67 v/v mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) solvents (Mitsubishi Chemical). The negative electrode was a 250  $\mu$ m thick Li foil. For the preparation of the positive electrode, the powder was dispersed in a plastic matrix according to Bellcore technology.<sup>11</sup> The plastic layer was made by mixing 56 wt % active material and 6 wt % Super-S carbon black, and by intimately dispersing this mixture in 15 wt % copolymer (Kynar 2801, 88:12 VDF:hexafluoro-propylene copolymer, Elf-Atochem)

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**Figure 1.** (a) Solid dots show the XRD of  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub> along with the fit as determined by Rietveld refinement shown by the solid line. (b) Difference plot between the experimental data and the refinement.

binder matrix plasticized with 23 wt % dibutylphthalate (DBP). After addition of anhydrous acetone and stirring for 24 h, the slurry was coated on a glass substrate, the acetone evaporated and the resulting dried plastic layer was cut into disks. Before use in coin cells, the DBP was extracted by three successive rinses in anhydrous ether.

Electrochemical experiments were carried out using a current corresponding to C/30, at  $30 \pm 0.1$ °C. Different cutoff potentials were used as indicated later.

## **Results and Discussion**

Figure 1 shows the X-ray diffraction (XRD) pattern of the starting material along with a calculated pattern determined by Rietveld refinement. The pattern was fitted successfully to a hexagonal structure with cell parameters  $a = 4.2012 \pm 0.0002$  Å and  $c = 5.0928 \pm 0.0003$  Å in excellent agreement with earlier reported data.<sup>12</sup> The refined site occupation in space group  $P6_3/mmc$  (no. 194) leads to the formula Cu<sub>0.545</sub>Sn<sub>0.455</sub> that perfectly matches the expected Cu<sub>6</sub>Sn<sub>5</sub> suggest that it has monoclinic symmetry,<sup>13</sup> but we found better agreement when refining to the hexagonal structure.



Figure 3. Voltage as a function of X-ray scan number and capacity measured for the first cycle of the  $Li/Cu_6Sn_5$  *in situ* X-ray cell. (C/100, 0.0-2.0 V.)

The first discharge of a Li/Cu<sub>6</sub>Sn<sub>5</sub> cell at C/100 (Fig. 2a) revealed two plateaus on discharge, one at about 0.4 V and another below 0.1 V. Figure 2a shows that the calculated capacity for the formation of Li<sub>2</sub>CuSn (330 mAh/g) is much less than the length of the first discharge (630 mAh/g). The lengths of the two plateaus match the theoretical capacity for the consecutive formation of Li<sub>2</sub>CuSn and Li<sub>4.4</sub>Sn + Cu, respectively. Based on these preliminary observations, we believe that the end product of the full lithiation of Cu<sub>6</sub>Sn<sub>5</sub> is not Li<sub>2</sub>CuSn, but instead is Li<sub>4.4</sub>Sn + Cu. The differential capacity *vs.* voltage (Fig. 2b) clearly shows these two discharge plateaus. Figure 2b shows a broad and symmetric peak at 0.45 V followed by a sharp one at 0.8 V during the charge. Note that the anisotropy and shape of this latter peak is characteristic of a two-phase reaction.

In order to shed some light on these reactions, we performed an *in situ* X-ray experiment. The voltage *vs.* scan number plot is shown in Figure 3. The evolution of the X-ray patterns during scans 0-20 (Fig. 4) clearly indicates that the first discharge plateau corresponds to the formation of Li<sub>2</sub>CuSn phase. In this region, the Cu<sub>6</sub>Sn<sub>5</sub> peaks (strongest peak at 30.4°) vanish progressively while broader peaks of the ternary phase grow. Figure 5 compares *in situ* scan no. 20 (end of first plateau) to the XRD pattern of HT-Li<sub>2</sub>CuSn prepared by solid-state reaction. Only a small difference in peak positions can be observed, and that could probably be attributed to the difference in Cu and Sn stoichiometries.



**Figure 2.** (a) Voltage *vs.* capacity of the first discharge/charge cycle of a  $\text{Li/Cu}_6\text{Sn}_5$  cell cycled between 2.0 and 0.0 V at C/100. (b) Differential capacity *vs.* voltage of the cell shown in (a).



Figure 4. First *in situ* X-ray experiment for the  $\text{Li}/\text{Cu}_6\text{Sn}_5$  cell. Scans collected along the first discharge plateau.



Figure 5. Comparison of the X-ray patterns of HT-Li<sub>2</sub>CuSn and *in situ* scan no. 20. This scan corresponds to the end of the first discharge plateau. Asterisks indicate Li-Sn and Cu-Sn impurities.

Figure 6 shows the appearance of another series of peaks located at scattering angles of 23, 38.5, and  $43.5^{\circ}$  while the Li<sub>2</sub>CuSn peaks disappear during the discharge on the second plateau. These new peaks have been previously attributed to a disordered Li-rich Sn alloy.<sup>14</sup> Once the cell reaches 0.0 V, the pattern shows mainly the Li<sub>4.4</sub>Sn phase. The complete transformation into Li<sub>4.4</sub>Sn confirms the observed value of the first discharge capacity (630 mAh/g) compared to the calculation for the full reaction of tin (600 mAh/g). The strongest diffraction peak of copper (the 111 peak) is found at a scattering angle of about 43.3°. The top panel of Fig. 6 shows a peak consistent with the presence of copper, but this peak is also present in the



**Figure 6.** First *in situ* X-ray experiment for the  $\text{Li}/\text{Cu}_6\text{Sn}_5$  cell. Scans collected along the second discharge plateau until 0 V. The end product is identified as disordered Li<sub>4.4</sub>Sn.

disordered Li<sub>4.4</sub>Sn phase. At the end of the reaction of Li with FeSn<sub>2</sub>, <sup>15</sup> Li<sub>4.4</sub>Sn was found to coexist with nanoscopic grains of Fe. This Fe could not be detected by XRD after the first discharge, but it could be observed by Mössbauer spectroscopy. We suspect the copper formed here is similarly small, and hence difficult to observe by XRD.

Figure 7 shows the *in situ* X-ray results during part of the subsequent charge. First there is a transformation of  $Li_{4.4}$ Sn into the  $Li_2$ CuSn phase. However, this transformation appears quite unusual. There is a progressive shift of the  $Li_{4.4}$ Sn peak located at about 38.5° toward the  $Li_2$ CuSn peak located at about 40.5° (Fig. 7 and 8). At the same time, the  $Li_2$ CuSn(111) peak (24.5°) grows continuously without any noticeable shift in position, and only a small shift is observed for the (113) reflection (48°). It is our opinion that the transition proceeds as follows

$$Li_{4,4}Sn \rightarrow Li_{4,4-x}Sn + xLi$$

and simultaneously

$$\text{Li}_{44-x}\text{Sn} + \text{Cu} \rightarrow \text{Li}_2\text{CuSn} + (2.4 - x) \text{Li}_2$$



**Figure 7.** First *in situ* X-ray experiment for the  $\text{Li}/\text{Cu}_6\text{Sn}_5$  cell. Scans collected during the first part of the recharge and showing the transformation of  $\text{Li}_{4,4}$ -Sn into  $\text{Li}_{4,4-x}$ Sn and  $\text{Li}_2$ CuSn.



**Figure 8.** Evolution of the position of the  $Li_{4,4}Sn$  (110 of bcc substructure) and  $Li_2CuSn$  (022) peaks observed along the first cycle (*in situ* experiment no. 1). A smooth evolution of the peak position is observed during the first stage of the recharge. The peak positions for  $Li_2CuSn$  (homemade) and  $Li_{4,4}Sn$  (JCPDS 18-753) are given as guidelines.

During such a process, the Bragg peaks of  $Li_{4,4-x}Sn$  would shift in position as *x* changes and the  $Li_2CuSn$  phase would appear. Such a reaction scenario occurs apparently because of the slow diffusion of Cu to be reincorporated into the  $Li_2CuSn$  phase.

The top two panels of Fig. 7 and all of Fig. 9 show the *in situ* results collected during the second charge plateau. The voltage varies during the region of scans 65-73 (see Fig. 2), and this corresponds to a region where the (022) peak of Li<sub>2</sub>CuSn shifts appreciably in angle. Most likely this is caused by a region where Li<sub>2-x</sub>CuSn can have a variable stoichiometry. During scans 73-80, the Bragg peaks of Cu<sub>6</sub>Sn<sub>5</sub> reappear in a two-phase region during a corresponding plateau in Fig. 3. The reaction during charge above 0.5 V is best described by

$$\text{Li}_2\text{CuSn} \rightarrow \text{Li}_{2-x}\text{CuSn} + x\text{Li}$$
, for about  $0 < x < 1$ 

followed by

$$\text{Li}_{2-x}\text{CuSn} \rightarrow \frac{1}{6}\text{Cu}_6\text{Sn}_5 + (2-x)\text{Li}_6$$



Figure 9. First *in situ* X-ray experiment for the  $\text{Li}/\text{Cu}_6\text{Sn}_5$  cell. Scans collected during the final part of the recharge.

(Notice that we have not balanced the second reaction with respect to tin content. This is because we do not know the exact stoichiometry of the phase we are calling Li<sub>2</sub>CuSn, which could be Li<sub>2</sub>CuSn<sub>0.83</sub>, as discussed in the introduction.) The small amount of nontransformed Li<sub>2-x</sub>CuSn contributes to the irreversible capacity evaluated to about 120 mAh/g on the first cycle.



**Figure 10.** Second *in situ* experiment for the Li/Cu<sub>6</sub>Sn<sub>5</sub> cell. The scans are collected along a charge-discharge sweep (C/30) over the Li<sub>2</sub>CuSn  $\leftrightarrow$  Li<sub>4,4</sub>Sn plateau.



Figure 11. Capacity vs. cycle number for Li/Cu<sub>6</sub>Sn<sub>5</sub> cells measured at C/30. The different voltage ranges and the corresponding reactions are indicated.

Figure 10 shows *in situ* X-ray diffraction results recorded near the composition  $Li_{4,4}Sn$ . The first 15 scans correspond to the removal of Li, making  $Li_{4,4-x}Sn$  (probably with some parallel back reaction to  $Li_2CuSn$ ) and scans 16-30 to the reverse reaction with the removed lithium. The Bragg peak near 38° (corresponding to the 110 peak of the body-centered cubic (bcc) substructure of  $Li_{4,4}Sn$ <sup>14</sup>) shifts reversibly during this experiment, suggesting a single-phase reaction. The peak does broaden near scan 15, suggesting the formation of the  $Li_2CuSn$  phase. In addition, the voltage profile shows significant hysteresis, not expected for a single-phase process. Thus, it is possible that some formation of  $Li_2CuSn$  has occurred during charge to 0.5 V.

If no Li<sub>2</sub>CuSn forms during charge to 0.5 V, then the hysteresis in the voltage profile must have another origin. The equilibrium Li-Sn phase diagram does not show single-phase regions, and this hysteresis may therefore result from a tendency of the small (several nanometers) Li<sub>4.4-x</sub>Sn grains to attempt to phase separate into regions of significantly different Li concentration, as the bulk phase diagram would predict.

Figure 11 compares the charge-discharge cycling of Li/Cu<sub>6</sub>Sn<sub>5</sub> cells constrained to different upper and lower voltage cutoffs. Three ranges were tested, 0.0 - 2.0 V, 0.0 - 0.6 V (restricted to the range Li<sub>2</sub>CuSn  $\leftrightarrow$  Li<sub>4.4</sub>Sn + Cu), and 0.2 - 2.0 V (restricted to Cu<sub>6</sub>Sn<sub>5</sub>  $\leftrightarrow$  Li<sub>2</sub>CuSn). The capacity *vs.* cycle number declines rapidly when the entire voltage range is accessed. There is an improvement when restricted ranges are used. In the low-voltage range, Cu is repeatedly expelled and reincorporated, and we feel that this is the cause for the relatively poor reversibility observed here. If the back reaction of copper could be hindered, as it was for Fe in Li/FeSn<sub>2</sub> cells charged only to 0.55 V, <sup>16</sup> then we expect good cycling would ensue.

Figure 11 shows that the best cycling results are obtained for cells that are never discharged below 0.2 V. This was also observed by

Thackeray's group.<sup>3,4</sup> Unlike<sup>3,4</sup> we attribute the improved cycling to the fact that the Cu atoms are not expelled into a second distinct phase in this voltage region. That is, the Cu atoms are always found next to tin atoms in both Cu<sub>6</sub>Sn<sub>5</sub> and in Li<sub>2</sub>CuSn. They are not expelled to form copper. Kepler<sup>3</sup> and Thackeray<sup>4</sup> argue that a topotactic reaction is responsible for the improved cycling in this region. We do not agree. The volume change associated with the Cu<sub>6</sub>Sn<sub>5</sub> to Li<sub>2</sub>CuSn transition is about 45%, and structural integrity most likely will not be maintained. It is interesting to note that the same group invokes much smaller lattice changes in two-phase regions as the cause of capacity loss in the LiMn<sub>2</sub>O<sub>4</sub> – Li<sub>2</sub>Mn<sub>2</sub>O<sub>4</sub> reaction.<sup>17</sup> Finally, the cycling performance in the high-voltage region, although best, is still poor compared to that obtained for topotactic reactions, such as Li insertion in graphite, where hundreds of fully reversible cycles can be obtained.

## Conclusion

A careful survey of the structural modifications occurring during the electrochemical reaction of Li with crystallized intermetallic  $\eta'$ -Cu<sub>6</sub>Sn<sub>5</sub> has been performed. During discharge, this reaction proceeds in two distinct single first-order transitions, namely, Cu<sub>6</sub>Sn<sub>5</sub>  $\leftrightarrow$ Li<sub>2</sub>CuSn and Li<sub>2</sub>CuSn  $\leftrightarrow$  Li<sub>4.4</sub>Sn + Cu. The reverse reactions occur during charge, but both Li<sub>4.4-x</sub>Sn and Li<sub>2-x</sub>CuSn appear to show some range of variable Li stoichiometry during charge. Although the full understanding of all of the mechanisms is not yet totally achieved, we found that large volume expansion and copper expulsion leads to poor capacity retention for extended cycling tests. Finally, this study clearly shows that situations where alloys have similar structure (but very different volumes!) do not ensure long cycle life for the electrochemical insertion/alloying reaction.

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#### References

- 1. O. Mao, R. A. Dunlap, and J. R. Dahn, J. Electrochem. Soc., 146, 405 (1999).
- O. Mao, B. L. Turner, D. W. McClure, I. A. Courtney, L. J. Krause, and J. R. Dahn, Electrochem. Solid-State Lett., 2, 3 (1999).
- K. D. Kepler, J. T. Vaughey, and M. M. Thackeray, *Electrochem. Solid-State Lett.*, 2, 307 (1999).
- M. M. Thackeray, J. T. Vaughey, A. J. Kahaian, K. D. Kepler, and R. Benedek, *Electrochem. Commun.*, 1, 111 (1999).
- M. M. Thackeray, C. S. Johnson, A. J. Kahaian, K. D. Kepler, and J. T. Vaughey, *ITE Battery Lett.*, 1, 26 (1999).
- J. T. Vaughey, K. D. Kepler, R. Benedek, and M. M. Thackeray, *Electrochem. Com*mun., 1, 517 (1999).
- 7. H. Pauly, A. Weiss, and H. Witte, Z. Metallkde, 59, 47 (1969).
- 8. R. A. Dunlap, D. A. Small, D. D. McNeil, M. N. Obrovac, and J. R. Dahn, J. Alloys
- Compd., 289, 135 (1999).
- 9. M. N. Richard, I. Koetschau, and J. R. Dahn, J. Electrochem. Soc., 144, 554 (1997).
- 10. A. M. Wilson and J. R. Dahn, J. Electrochem. Soc., 142, 326 (1995).
- 11. D. Guyomard and J-M. Tarascon, U.S. Pat. 5,192,629 (1993).
- 12. A. Westgren and G. Phragmen, Z. Anorg. Chem., 175, 80 (1928).
- 13. A. K. Larsson, Acta Crystallogr., B50, 636 (1994).
- 14. J. R. Dahn, I. A. Courtney, and O. Mao, Solid State Ionics, 111, 289 (1998).
- 15. O. Mao, R. A. Dunlap, and J. R. Dahn, J. Electrochem. Soc., 145, 4195 (1998).
- 16. O. Mao, R. A. Dunlap, and J. R. Dahn, J. Electrochem. Soc., 146, 405 (1999).
- 17. M. M. Thackeray, J. Electrochem. Soc., 142, 2558 (1995).