An *In Situ* X-ray Absorption Spectroscopy Study of InSb Electrodes in Lithium Batteries

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Introduction

Recently we have reported on several intermetallic compounds, such as η'-Cu_6Sn_5 and InSb, that exhibit promising electrochemical properties as negative insertion electrodes for lithium batteries.[1-3] We have performed detailed studies of the electrochemical reaction of lithium with InSb using *in situ* EXAFS. In these materials, the reaction progresses by a mechanism of lithium insertion/metal displacement from a Sn or Sb array of atoms.[2-4]

Previous electrochemical studies indicated that the zinc-blende structure of InSb is "conditioned" during the initial electrochemical reaction with lithium;[2-3] thereafter, the InSb electrode cycles reversibly over several distinct plateaus between 1.2 and 0.5 V. During lithium insertion, the face-centered cubic (fcc) Sb array in InSb (a = 6.478 Å) remains intact and yields Li_3Sb (a = 6.572 Å).[5-6] On extrusion of metallic In, only a 4.4% volume expansion results, neglecting the volume of the extruded In. Data from *in situ* x-ray diffraction and cyclic voltammetry strongly suggest that the stability of the fcc Sb array plays an important role in the reversibility of the electrochemical reaction.

Methods and Materials

For the *in situ* EXAFS cells, small holes (3/16") were punched in either side of the coin cell before assembly and then covered with a polyimide film. The film had been coated with a 100 Å copper film to aid current collection. After assembly, the x-ray window was covered with an epoxy resin to provide additional strength, yet allow the beam to pass through the cell. The initial cell configuration was thus Li/electrolyte/InSb. Greater details of the electrode fabrication are given elsewhere.[2,3]

To achieve time resolution suitable to following the electrochemical reaction, the EXAFS scans were taken in continuous mode (i.e., with a constantly moving monochromator). This reduced the time per scan from 15 minutes to about 6 minutes by eliminating the time overhead required to step the monochromator between data points. By increasing the measurement speed, we could maintain a constant current in the battery cell for the duration of the experiment, and we did not have to interrupt the current to take long EXAFS measurements.

Results and Discussion

During the conditioning discharge performed with the coin cell, the structural changes are minor as Li is first inserted: a slight increase in the In–Sb distance, $R_{\text{In–Sb}}$, is detected. The first evidence of In extrusion during the conditioning cycle becomes visible around 0.70 ± 0.02 V as a slight decrease in the amplitude of the first-shell In–Sb peak in the Fourier transform. During the conditioning cycle, about 1.4 Li atoms per Sb atom intercalate into the framework of the electrode before the magnitude of the In–Sb path in the Fourier transform decreases noticeably. Subsequently, the In–Sb coordination number, $N_{\text{In–Sb}}$, decreases as In is extruded from the lattice, although the characteristic In metal scattering paths cannot be fit reliably until the potential decreases below 0.62 V. At this point the EXAFS signal has nearly disappeared above 8 Å^{-1}. Throughout the reaction the Sb provides a stable framework. Antimony-edge EXAFS spectra confirm that during Li insertion and In extrusion, the fcc Sb array remains in place.

Figure 1 shows the In-containing phase distribution over the subsequent charge cycle. At the start of the charge, the distribution of the indium in the electrode was approximately 70% as LiIn (lithiated In metal), 20% as In metal, and up to 10% as Li_xIn_ySb. Upon charging, LiIn first reverts to metallic In during the initial plateau in the potential at 0.62 V. The In distribution at the end of the first plateau is approximately 90% as In metal. Near the peak of the charge, the amplitude of the nearest-neighbor In–Sb path is smaller than in the initial electrode material, indicating that the displaced In has not been entirely reincorporated into the Li_xIn_ySb phase. In fact, quantitative evaluation shows that as much as 40% of the In remains in the metallic phase.

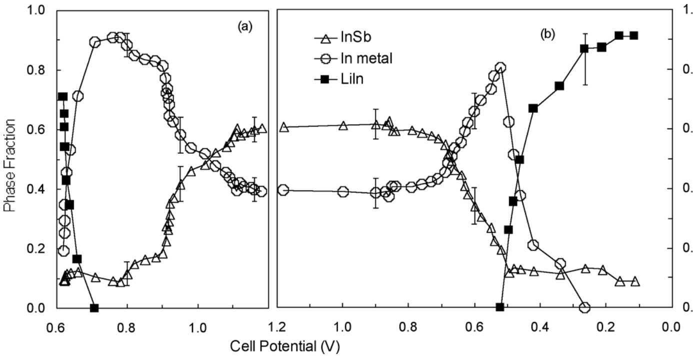

FIG. 1. Distribution of indium in its various phases—Li_xIn_ySb (triangles), metallic In (circles), and LiIn (squares)—as a function of cell potential upon charging (panel a) and discharging (panel b). Error bars are shown for representative points.[4]

In a final cycle, the lithium coin cell was discharged from 1.2 V to 0 V. In a reversal of the processes that have been described for the charge, In is extruded from the Sb (fcc) array and replaced by Li. At about 0.5 V, where 80% of the In is present as a metal, Li starts to react with the In metal, forming LiIn.

After one "conditioning" cycle, the cell cycles extremely well when limited to the range where the primary mechanisms are Li insertion and In extrusion (above 0.5 V), although a significant fraction of the In (as much as 40%) is not reincorporated into the Sb framework. This explains the loss of capacity observed between the conditioning cycle and the following cycles. On the other hand, the cell has a reduced reversible capacity when discharged below 0.5 V.

Acknowledgments

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References

[1] K.D. Kepler, J.T. Vaughey, and M.M. Thackeray, Electrochem. Solid State. Lett. **2**, 307 (1999).

[2] J.T. Vaughey, J.O. O'Hara, and M.M. Thackeray, Electrochem. Solid State Lett. **3**, 13 (2000).

[3] C.S. Johnson, J.T. Vaughey, M.M. Thackeray, T. Sarakonsri, S.A. Hackney, L. Fransson, K. Edström, and J.O. Thomas, Electrochem. Comm. **2**, 595 (2000).

[4] A.J. Kropf, H. Tostmann, C.S. Johnson, J.T. Vaughey, and M.M. Thackeray, in press.

[5] NBS Circular 539, **4**, 73 (1955).

[6] G. Brauer and E. Zintl, Z. für Physikalische Chemie **37B**, 323 (1937).