ANL/CMT/CP-100487

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November 1999

To be presented at the 13th International Battery Association Materials Symposium, November 7-11, 1999, Marrakesh, Morocco

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Introduction

Binary intermetallic compounds containing lithium, or lithium "alloys", such as Li_xAl, Li_xSi and Li_xSn have been investigated in detail in the past as negative electrode materials for rechargeable lithium batteries [1]. It is generally acknowledged that the major limitation of these systems is the large volumetric expansion that occurs when lithium reacts with the host metal, either by insertion or by a series of displacement reactions. For example, as x increases in the lithium-tin system, Li_xSn, several discrete compounds form [2]. A maximum value is reached at $x \approx 4.4$ (or $Li_{22}Sn_5$), resulting in a massive volume change of 358% (per tin atom). Such large increases in volume limit the practical use of lithium-tin electrodes in electrochemical cells, particularly when they are cycled over a wide compositional range. Over the past decade, considerable progress has been made to improve the cycling properties of these intermetallic electrodes by embedding them in an inert composite matrix [3-5]; nevertheless, these electrodes still do not yet meet the stringent performance requirements that will allow them to compete with the conventional negative electrodes of lithium-ion batteries, namely, carbon-based materials such as graphite.

It is generally recognized that metal oxide electrodes, MO_y, in lithium-ion cells operate during charge and discharge by means of a reversible lithium insertion/extraction process, and that the cells offer excellent cycling behavior when the crystallographic changes to the unit cell parameters and unit cell volume of the Li_xMO_y electrode are kept to a minimum [6]. An excellent example of such an electrode is the spinel $Li_4Ti_5O_{12}$, which maintains its cubic symmetry without any significant change to the lattice parameter (and hence unit cell volume) during lithium insertion to the rock-salt composition $Li_7Ti_5O_{12}$ [7, 8]. This spinel electrode is an example of a ternary Li_xMO_y system in which a binary MO_y framework provides a stable host structure for lithium. With this approach, we have turned our attention to exploring ternary intermetallic systems Li_xMM' in the hope of finding a system that is not subject to the high volumetric expansion that typifies many binary systems.

In this paper, we present recent data of our investigations of lithium-copper-tin and lithium-indium-antimonide electrodes in lithium cells. Our data show that lithium can be inserted reversibly into selected intermetallic compounds such as Cu_6Sn_5 and InSb with NiAs- and zinc-blende-type structures, respectively, between 1.2 and 0.2 V vs. Li with relatively small expansion of the lithiated intermetallic structures.

Experimental

The preparation of Cu_6Sn_5 and InSb materials, and the configuration and evaluation of electrochemical cells, Li/1M $LiPF_6$ in ethylene carbonate/diethyl carbonate (50:50

mixture)/intermetallic electrode, have been described elsewhere [9, 10]. Structural characteristics of the initial and cycled electrodes were obtained by profile refinement of powder X-ray diffraction patterns collected on a D5000 Siemens diffractometer with CuKα radiation.

Results and Discussion

The room-temperature structure of Cu_6Sn_5 (alternatively, $Cu_{1.2}Sn$) is related to that of NiAs; it is referred to as η'-Cu_6Sn_5 [11]. The η'-Cu_6Sn_5 phase has a complex structure in which 0.2 Cu atoms occupy one-fifth of the available trigonal bipyramidal interstitial sites of a CuSn (NiAs) framework. Lithium insertion into η'-Cu_6Sn_5 occurs at approximately 400 mV vs. Li; lithium insertion is accompanied by the simultaneous diffusion of one-half of the Sn atoms within the crystal lattice to yield a structure resembling that of Li_2CuSn [9, 12]; the Cu and Sn atoms in the resulting "Li_2CuSn" product adopt the positions of Zn and S in a zinc-blende-type configuration. In order to simplify the figures and the discussion, the η'-Cu_6Sn_5 structure is regarded to have the ideal NiAs stoichiometry, CuSn. The ideal lithiated zinc-blende structure, Li_2CuSn, is shown in Fig. 1 (top); the lithium atoms reside in Cu_3Sn_3 hexagonal channels, the direction of which runs perpendicular to the plane of the paper. In reaction (a) of Fig. 1, lithium extraction from the hexagonal channels of Li_2CuSn occurs with the simultaneous diffusion of 50% of the Sn atoms from their columns into the channels to generate an ideal NiAs structure. The topotactic CuSn (zinc-blende) to CuSn (NiAs) transformation is sluggish; it results in considerable hysteresis in the electrochemical discharge/charge profile [9]. Moreover, this transformation is accompanied by a 59% expansion in the unit cell volume on lithium insertion, which is probably too high for this copper-tin electrode to be considered attractive as an intermetallic insertion (negative) electrode for lithium cells.

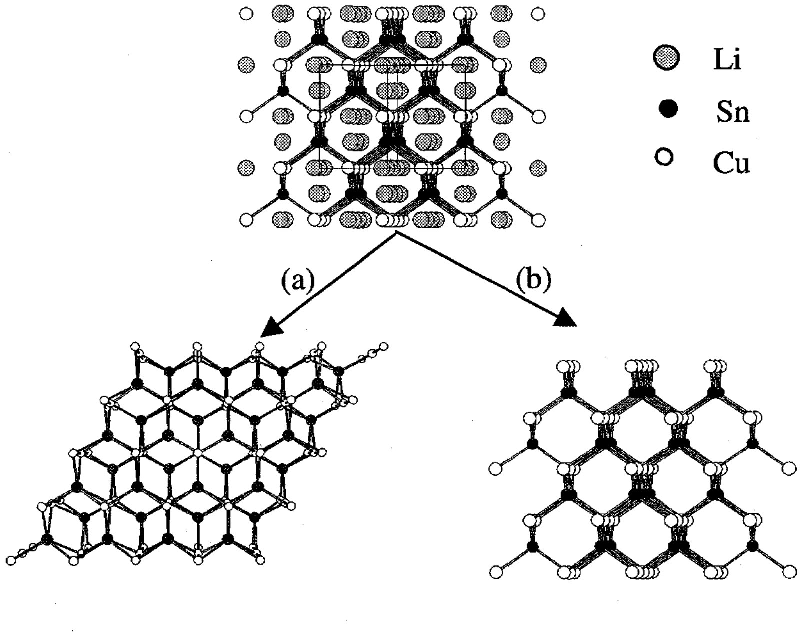

Figure 1. **A schematic illustration of the transformation of Li_2CuSn (top) to (a) "CuSn" with the ideal NiAs type structure and (b) "CuSn" with the ideal zinc-blende-type (ZnS) structure.**

The zinc-blende framework has a favorable three-dimensional interstitial space for lithium diffusion [10, 12]; thus, it would appear that instead of using materials like η′-Cu_6Sn_5 with a NiAs-type structure as a host structure for lithium, a better approach would be to select a stable zinc-blende type structure as the host electrode that would remain stable on lithiation as shown in Fig. 1, reaction (b) [12]. In the ideal reaction, no displacement of the host atoms within the framework would occur. We selected the semiconducting phase InSb for our initial studies of materials with the zinc-blende structure because a) the atoms of the InSb host structure are relatively large, thus providing an interstitial space that might be able to accommodate lithium, and b) because InSb has good electrical properties; it is an excellent semiconductor with a narrow band gap (0.23 eV) and a high electron mobility at 77 K [13].

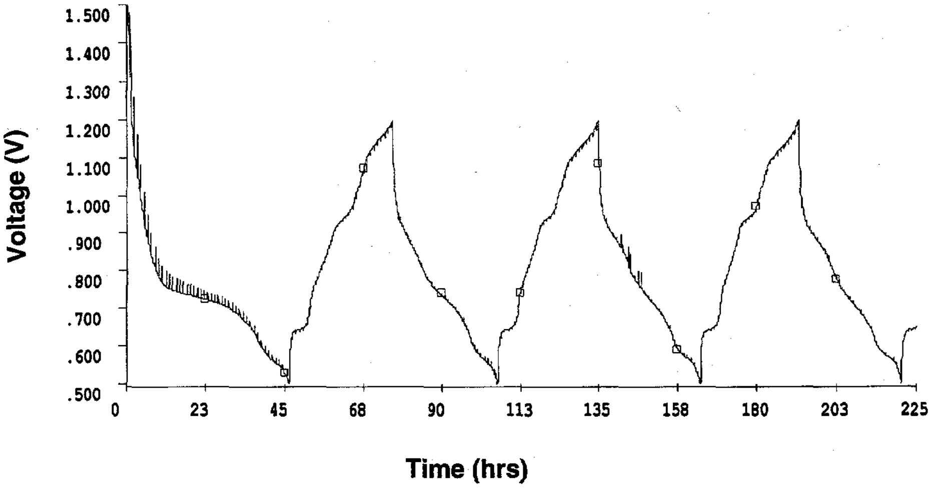

Figure 2. The first four cycles of a Li/Li_xInSb cell (C/12 rate)

The electrochemical profile of a Li/Li_xInSb cell for the first four cycles is shown in Fig. 2 [10]. It is apparent from the shape of the initial voltage profile and subsequent cycles that one "break-in" cycle is required. During the initial reaction of lithium, most of the capacity is delivered with a steadily decreasing voltage between 800 and 600 mV vs. metallic lithium. The voltage profile is altered significantly on the subsequent extraction of lithium from the electrode, but thereafter remains constant on discharge and charge. The abrupt change in profile is not yet understood; it is believed that it may involve slight structural changes to the InSb framework [10]. An expanded view of the third charge and discharge cycle of a Li/Li_xInSb cell is shown in Fig. 3. It is apparent that lithium reacts with the InSb electrode in three discrete steps D(1), D(2) and D(3). X-ray diffraction patterns of the Li_xInSb electrode at $x \approx 2.5$ and at the top of charge $x \approx 0$ showed characteristic peaks that could be attributed to structures with zinc-blende-type character [10]. These findings immediately suggest that the reaction of lithium with InSb occurs by an insertion reaction whereby lithium is introduced into the interstitial sites of a zinc-blende framework. Although further structural characterization of Li_xInSb electrodes is necessary, it is proposed that the reaction sequence occurs as follows:

D(1): $Li + \square_1\square_2InSb \rightarrow Li\square_2InSb$
D(2): $Li + Li\square_2InSb \rightarrow Li_2InSb$
D(3): $Li + Li_2InSb \rightarrow Li_{2+x}In_{1-x}Sb + x\,In\ (x \leq 1)$

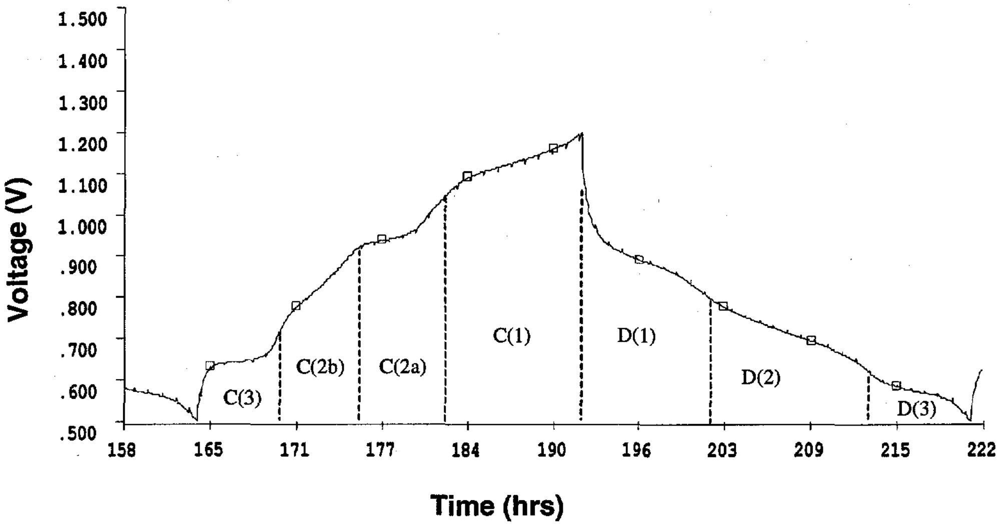

Figure 3. The voltage profile of a Li/Li_xInSb cell (C/12 rate)

Each step corresponds to the reaction of one lithium per formula unit or, alternatively, to 113 mAh/g InSb. The cubic zinc-blende structure contains two crystallographically independent interstitial sites, $\square_1$ and $\square_2$, for lithium. Thus, from the voltage profile in Fig. 3 it seems reasonable to propose that the first two reaction processes correspond to the filling of these two sites. At a composition of Li_2InSb, all the interstitial sites are full, and the lithiated zinc-blende structure cannot accommodate any more lithium. Thus, step D(3) is interpreted as a lithium insertion process that occurs with the simultaneous extrusion of In; note that the voltage plateau associated with D(3) is short, indicating that this step does not go to completion. At x=1, the final product would be Li_3Sb; this interpretation is fully consistent with the X-ray diffraction pattern of "$Li_{2.5}InSb$", which shows a Li_3Sb-type structure. Note also that Li_3Sb has a cubic lithiated zinc-blende structure, $Li_2(LiSb)$, in which the (LiSb) component has the zinc-blende framework derived from the parent InSb. Analysis of Li_xInSb electrodes by high-resolution electron microscopy after extensive lithiation to 200 mV vs. Li has provided evidence of In extrusion from a residual $Li_{2+x}In_{1-x}Sb$ matrix [14]. What is remarkable about this reaction is that the volume expansion throughout the whole process is isotropic and is limited to approximately 5.6% [10].

Figure 4 shows that Li_xInSb electrodes are tolerant to lithiation at high rates. For example, at a relatively low C/12 rate, it was possible in some cells to obtain the theoretical capacity (340 mAh/g) from the electrode. At a high C/1 rate after nine cycles, a capacity of 200 mAh/g was obtained; after reducing the rate to C/12, almost all the original capacity (320 mAh/g) could be recovered. Note that because of the relatively high density of InSb (5.8 g/ml), a practical gravimetric capacity of 320 mAh/g translates to a volumetric capacity of 1856 mAh/ml, which is more than twice that of the theoretical value of graphite (approximately 800 mAh/g).

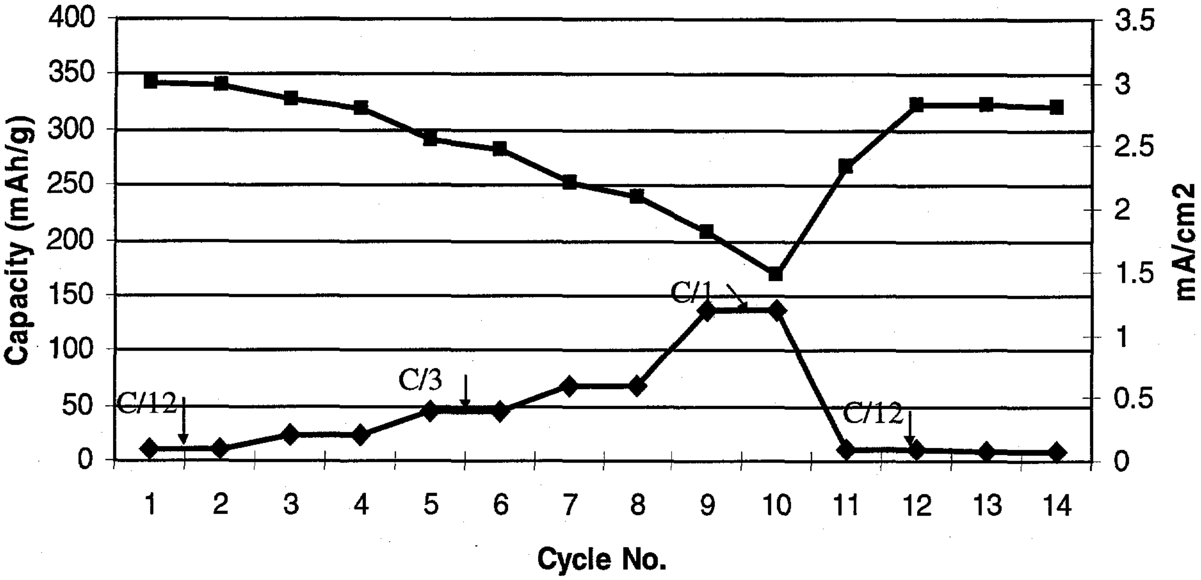

Figure 4. **The capacity derived from a Li_xInSb electrode as a function of discharge rate (measured over 14 cycles)**

Conclusions

The studies on Cu_6Sn_5 and InSb have demonstrated that intermetallic compounds with NiAs and zinc-blende-type structures can be used as host structures for lithium at potentials <1V vs. metallic lithium. The compound Cu_6Sn_5 is unstable to lithiation and transforms to a Li_2CuSn zinc-blende-type structure with a volume expansion near 60%. By contrast, the InSb host structure appears to remain stable to lithiation; it expands isotropically by less than 6% to a composition "Li_2InSb". Further lithiation is possible. In this instance, metallic indium is extruded from the structure; complete lithiation results in Li_3Sb, which is the end-member of the system $Li_{2+x}In_{1-x}Sb$ at x=1. The excellent rate capability of the Li_xInSb electrode is attributed to the energetically favorable interstitial space for lithium in the InSb host framework and to the good electrical conductivity of the electrode at all states of discharge and charge. These findings auger well for the further development of intermetallic insertion compounds as negative electrodes for lithium-ion batteries.

Acknowledgments

Support for this work from the Chemical Sciences Division of the Office of Basic Energy Sciences and from the Office of Advanced Automotive Technologies, U.S. Department of Energy, under Contract No. W31-109-Eng-38 is gratefully acknowledged.

References

1. M. Winter, J. O. Besenhard, M. E. Spahr and P. Novak, *Adv. Mater.*, **10**, 725 (1998).
2. I. A. Courtney, J. S. Tse, O. Mao, J. Hafner, and J. R. Dahn, *Phys. Rev. B*, **58**, 15583 (1998).

3. J. Yang, M. Winter and J. O. Besenhard, *Solid State Ionics*, **90**, 281 (1996).
4. J. O. Besenhard, J. Yang, and M. Winter, *J. Power Sources*, **68**, 87 (1997).
5. O. Mao, R. A. Dunlap, I. A. Courtney and J.R. Dahn, *J. Electrochem. Soc.* **145**, 4195 (1998).
6. M. M. Thackeray, *J. Electrochem. Soc.*, **142**, 2558 (1995).
7. K. M. Colbow, J. R. Dahn and R. R. Haering, *J. Power Sources*, **26**, 397 (1989).
8. E. Ferg, R. J. Gummow, A. de Kock and M. M. Thackeray, *J. Electrochem. Soc.*, **141**, L147 (1994).
9. K. D. Kepler, J. T. Vaughey, and M. M. Thackeray, *Electrochem. and Solid-State Lett.*, **2**, 307 (1999).
10. J. T. Vaughey, J. O. O'Hara and M. M. Thackeray, *Electrochem. and Solid-State Lett.*, (1999). In press.
11. A.-K. Larsson, L. Stenberg and S. Lidin, *Acta Crystallogr. Sect. B*, **50**, 636 (1994).
12. J. T. Vaughey, K. D. Kepler, R. Benedek and M. M. Thackeray, *Electrochem. Comm.*, **1**(11), 517 (1999).
13. O. Madelung and R. Poerschke, Semiconductors, eds. J. W. Corbett and G. D. Watkins (Gordon and Breach, New York, 1971) p. 273.
14. T. Sarakonsri and S. A Hackney, Unpublished data.