

# Copper–tin anodes for rechargeable lithium batteries: an example of the matrix effect in an intermetallic system

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## Abstract

Lithium batteries are typically constructed from a lithium cobalt oxide cathode and a carbon anode. We have investigated intermetallic anode materials based on tin, which can provide a high theoretical capacity at a slightly higher voltage (0–400 mV) than metallic lithium and thus reduce the safety concerns associated with the carbon anode. In particular, we have investigated the copper–tin system at around the composition  $\text{Cu}_6\text{Sn}_5$  and have determined the effect on cycling and capacity of electrodes with various ratios of copper to tin. Anode compositions that are slightly copper rich ( $\text{Cu}_6\text{Sn}_4$ ) were found to exhibit greater utilization of the tin than those with the stoichiometric bronze ratio ( $\text{Cu}_6\text{Sn}_5$ ) or those having a slight excess of tin ( $\text{Cu}_6\text{Sn}_6$ ). The differences in electrochemical behavior are explained in terms of an inert matrix model. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Lithium battery; Anode; Intermetallic; Tin alloy

## 1. Introduction

Lithium batteries represent an important area of study and a developing market for commercial battery companies. Conventional lithium-ion cells are constructed from a lithium cobalt oxide cathode and a carbon anode. When graphite is used, this electrochemical couple provides a cell voltage of approximately 4 V. There is some concern about the cost of the cathode, irreversible capacity losses with cycling and safety of the anode [1]. We have been searching for alternative anode materials to carbon and have been investigating intermetallic materials based on tin which provide a high capacity at a slightly higher voltage (0–400 mV) than metallic lithium, thus reducing safety concerns.

It is known that although the capacity of pure tin is high (990 mAh/g), it has a limited cycle life. This has been attributed to a number of causes, including electronic isolation of the lithiated product and poor electrical contact with the current collector caused by the frequent expansion/contraction cycles associated with the lithiation [2]. It has been suggested that isolating the tin within a host matrix would solve many of these problems [2]. One of the

more recently publicized methods was reported by Fujifilm Celltec. They successfully loaded tin oxide ( $\text{SnO}$ ) into a porous borophosphate glass, and were able to demonstrate high capacity and low fade with cycling [3]. Later reports by Courtney and Dahn [4] indicated that the reaction mechanism involved the decomposition of the tin oxide to tin metal and a subsequent alloying reaction with lithium. Although under certain conditions the tin oxide was shown to be a stable anode system, problems with an initial large irreversible capacity have limited its usefulness. An alternative to the oxide precursor is to use a tin intermetallic compound that offers the possibility of reducing the irreversible capacity loss effects. We have chosen to investigate intermetallic compounds in the copper–tin system because they are easy to synthesize, stable in an air environment, and because structural decomposition would encase the lithium/tin alloy in a conductive copper matrix. Here, we report preliminary results on alloy compositions at and around the  $\epsilon$ -bronze,  $\text{Cu}_6\text{Sn}_5$ .

## 2. Experimental

Three compositions were synthesized in the copper–tin system:  $\text{Cu}_6\text{Sn}_5$ ,  $\text{Cu}_6\text{Sn}_4$  and  $\text{Cu}_6\text{Sn}_6$ . The copper–tin intermetallics were synthesized by direct reaction of the

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elements. Elemental copper (Johnson Mathey 99.9%) and tin (Aldrich, 99.8%) powder were mixed in a stoichiometric ratio to yield the desired product. The mixed powders were then pressed into a pellet, placed into an alumina crucible, and heated under an argon atmosphere at 400°C for 12 h. The gray brittle product was then ground and sifted to approximately 400 mesh. X-ray diffraction analysis of the product gave the expected product distribution in each case. The stoichiometric bronze  $\text{Cu}_6\text{Sn}_5$  was a single phase compound, the composition  $\text{Cu}_6\text{Sn}_4$  gave a mixture of copper and  $\text{Cu}_6\text{Sn}_5$ , while the composition  $\text{Cu}_6\text{Sn}_6$  yielded  $\text{Cu}_6\text{Sn}_5$  and tin.

Additionally, we synthesized the lithium–copper–tin Zintl phase,  $\text{Li}_2\text{CuSn}$  with a  $\text{MnCu}_2\text{Al}$ -type structure. Elemental lithium, copper, and tin were weighed out in stoichiometric amounts and placed in a tantalum tube, one end of which had been crimped shut to form a metal test tube. The sample was heated to 900°C under an argon atmosphere, held for 3 h, and cooled radiatively to room temperature. The violet-purple sample was then isolated from the tube as a powder. X-ray analysis of the sample confirmed the isolation of the desired phase [5].

Laminates of the intermetallic materials and pure tin were evaluated in 1225 coin cells vs. Li metal. The electrolyte used was 1 M  $\text{LiPF}_6$  in ethylene carbonate/diethyl carbonate (50:50). The positive electrode laminates were made by doctor-blading slurries containing approximately 6 mg of active copper–tin material (81% by mass), mixed with carbon (XC-72, 9% by mass) and binder (Kynar 2801, 10 mass%) in tetrahydrofuran (THF). The air-sensitive  $\text{Li}_2\text{CuSn}$  laminates were made in a glove box. Cell construction is described elsewhere [6]. Cells were discharged and charged at constant current (0.1 mA) between either 1.2 and 0.0 V, or 1.2 and 0.2 V.

### 3. Results and discussion

The concept of using an inert matrix to shield a battery anode was proposed by Huggins a number of years ago [2]; this concept has been exploited extensively by Besenhard et al. [7,8,10] and Yang et al. [9], for example in their studies of Sn–Sb and Sn–Ag intermetallic electrodes. We have investigated the use of intermetallic compounds as anodes, termed  $M'M$ , where  $M'$  is an inactive metal and  $M$  is a component that alloys with lithium. We chose to concentrate specifically on the  $\epsilon$ -bronze,  $\text{Cu}_6\text{Sn}_5$ . The structure of  $\text{Cu}_6\text{Sn}_5$  is shown in Fig. 1. It was anticipated that extensive lithiation of  $\text{Cu}_6\text{Sn}_5$  would initially result in a breakdown of the parent compound to form copper (the inactive component) and tin (the active component). Thereafter, further lithiation of the system forms a series of lithium–tin alloys ( $\text{Li}_x\text{Sn}$ ,  $x \leq 4.4$ ), the sequence of which follows the known phase diagram. The tin provides the anode capacity, while the displaced copper, dispersed into the solid, acts as an electronically conducting matrix. It is

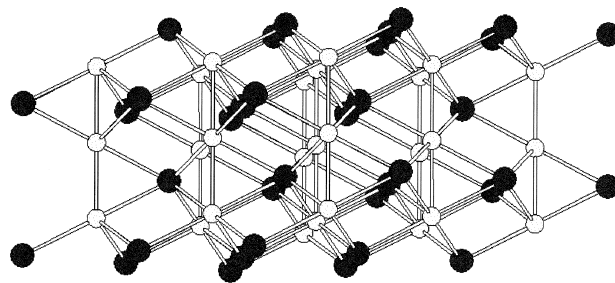


Fig. 1. The structure of  $\text{Cu}_6\text{Sn}_5$ . The black spheres represent the trigonal prismatic coordination of the tin site, while the gray spheres represent the copper, which has octahedral coordination.

envisioned that this matrix will mitigate some of the unwanted expansion and contraction observed in lithium alloy systems.

In our experiments, the three samples synthesized had the composition  $\text{Cu}_6\text{Sn}_{5+\delta}$  ( $\delta = 0, \pm 1$ ). The sample with  $\delta = 0$  is the single-phase bronze, the sample with  $\delta = 1$  has excess tin in the starting material, and the sample with  $\delta = -1$  has an excess of copper. When lithiated to a ' $\text{Li}_{4.4}\text{Sn}$ ' composition,  $\text{Cu}_6\text{Sn}_{5+\delta}$  materials have theoretical capacities of 647, 605 and 551 mAh/g, corresponding to  $\delta = +1, 0$ , and  $-1$ , respectively. Fig. 2(a and b) shows the voltage profile for Li/Sn and Li/ $\text{Cu}_6\text{Sn}_5$  cells. All cells with Cu–Sn electrodes had profiles similar to pure tin and exhibited a distinct voltage plateau around 400 mV vs. lithium. In a Li/Sn cell, it is known, according to the phase diagram, that this plateau corresponds to the formation of  $\text{Li}_7\text{Sn}_3$ . The Li/Cu–Sn cells cycled better than the pure tin cells, all of which had been prepared in the same manner (Fig. 3). Interestingly, we found that the greater the amount of copper in the alloy, the better the utilization of the tin. Thus,  $\text{Cu}_6\text{Sn}_4$  exhibited the highest capacity per mass of tin present (Fig. 4). We believe that this effect is related to the microstructure produced during the structural decomposition of the alloy, which should lead to finely divided tin in an inactive copper matrix. It is believed that the additional copper might lead to more finely divided tin, and that the high surface area of the tin particles could be accessible to lithium through grain boundary diffusion. The capacity fade of the Cu–Sn materials was slightly less than that of pure tin, suggesting that the presence of a copper matrix only partially reduces the problems associated with expansion/contraction of  $\text{Li}_x\text{Sn}$  alloys on cycling. It is speculated that the addition of even more copper might improve the cycle life, but it would do so at the expense of cell capacity. The capacity retention was improved by raising the lower cutoff voltage from 0 V to 200 mV, but with a loss of cell capacity (Fig. 5). The copper-rich  $\text{Cu}_6\text{Sn}_6$  electrode provided the highest, and most stable rechargeable capacity of all the materials tested; it provided a steady capacity of approximately 200 mAh/g for 20 cycles (Fig. 5).

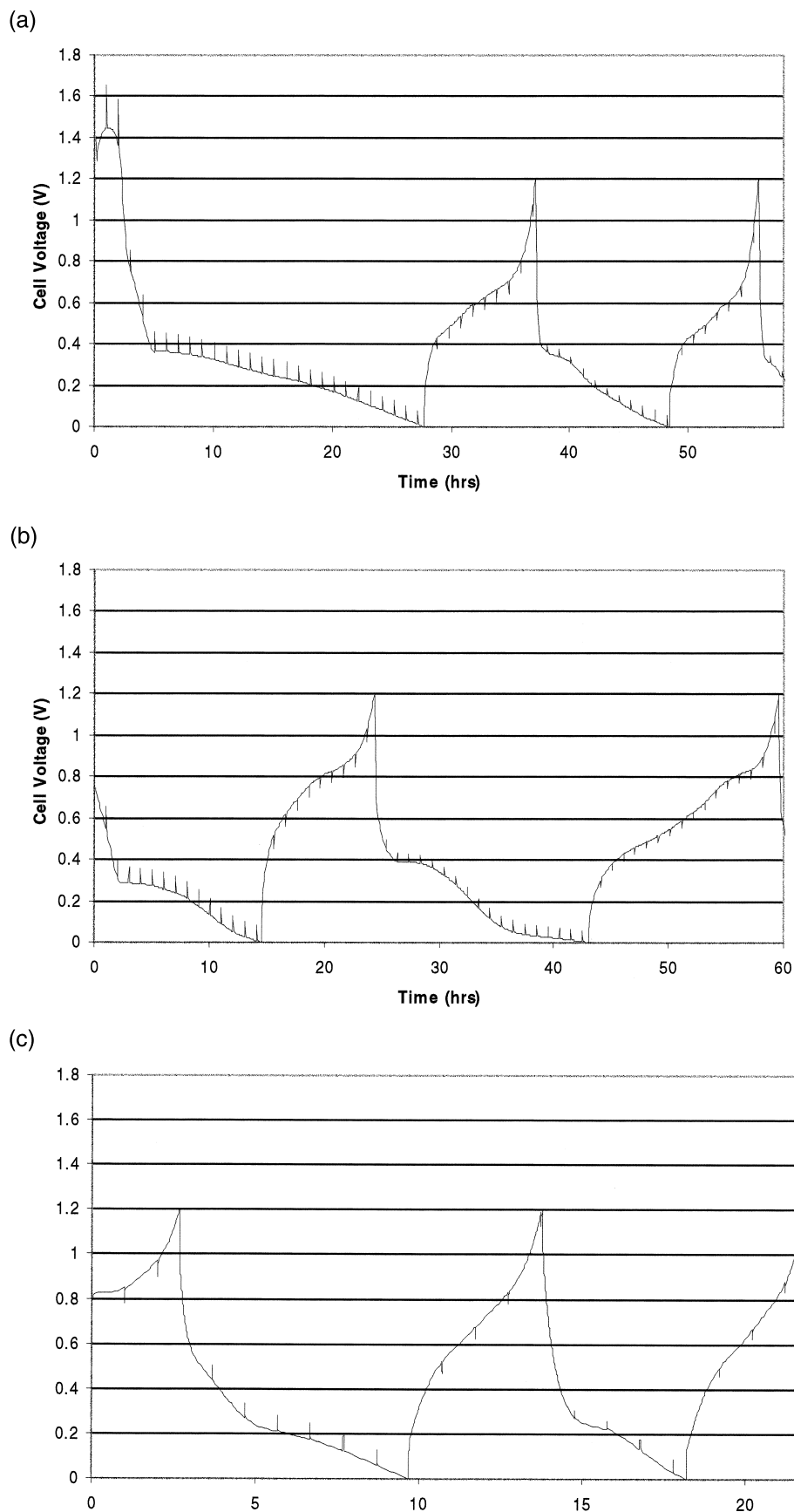


Fig. 2. The electrochemical profiles of the first discharge and subsequent charge of a typical (a) Li/Sn cell, and (b) Li/Cu<sub>6</sub>Sn<sub>5</sub> cell, and (c) the charge and subsequent discharge of a typical Li/Li<sub>2</sub>CuSn cell.

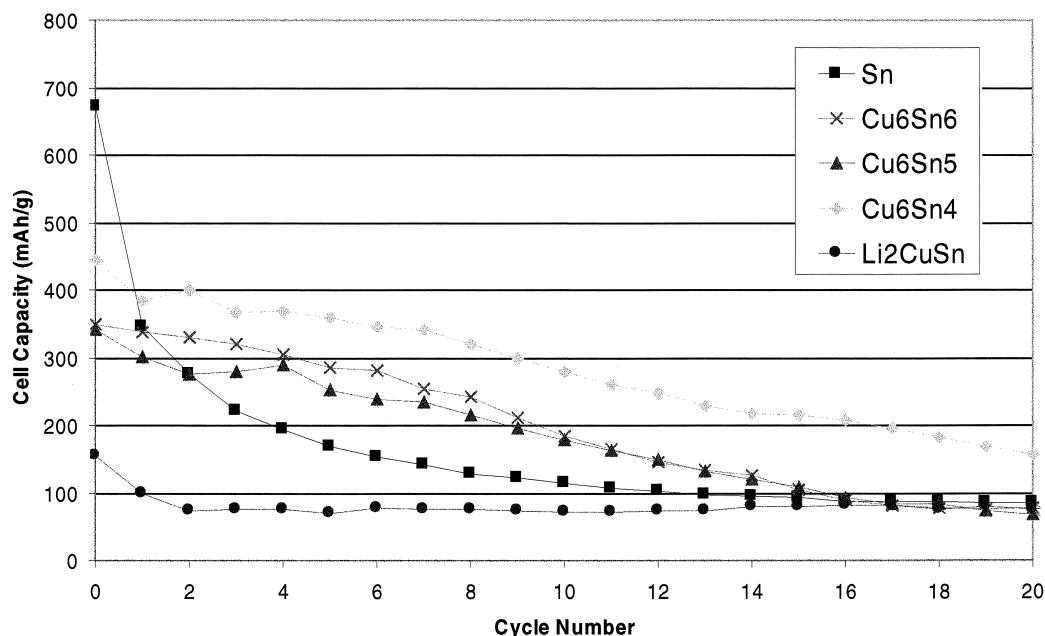


Fig. 3. Capacity vs. cycle number for Li/Sn, Li/Li<sub>2</sub>CuSn, and Li/Cu<sub>6</sub>Sn<sub>5+ $\delta$</sub>  ( $\delta = 0, \pm 1$ ) cells over the range 1.2–0.0 V (20 cycles).

We also investigated the lithium–copper–tin Zintl phase, Li<sub>2</sub>CuSn, shown schematically in Fig. 6. For this compound, apart from the initial delithiation, the cycling profile is similar to that observed for Cu<sub>6</sub>Sn<sub>5</sub> (Fig. 2c). Interestingly, delithiation of Li<sub>2</sub>CuSn occurs at  $\sim 800$  mV, which is 400 mV greater than the potential for the delithiation of Li<sub>7</sub>Sn<sub>3</sub>, i.e., the Li–Sn phase with a similar

lithium to tin ratio. In the Li/Li<sub>2</sub>CuSn cells (Fig. 3), the reversible electrode capacity ( $\sim 80$  mAh/g) was significantly below the theoretical capacity of 647 mAh/g (for ‘Li<sub>4.4</sub>Sn · Cu’); we partly ascribe this low capacity to the electrical isolation of some of the material due to some oxidation of the highly reactive Li<sub>2</sub>CuSn particles during processing. Overpotential problems caused by this effect

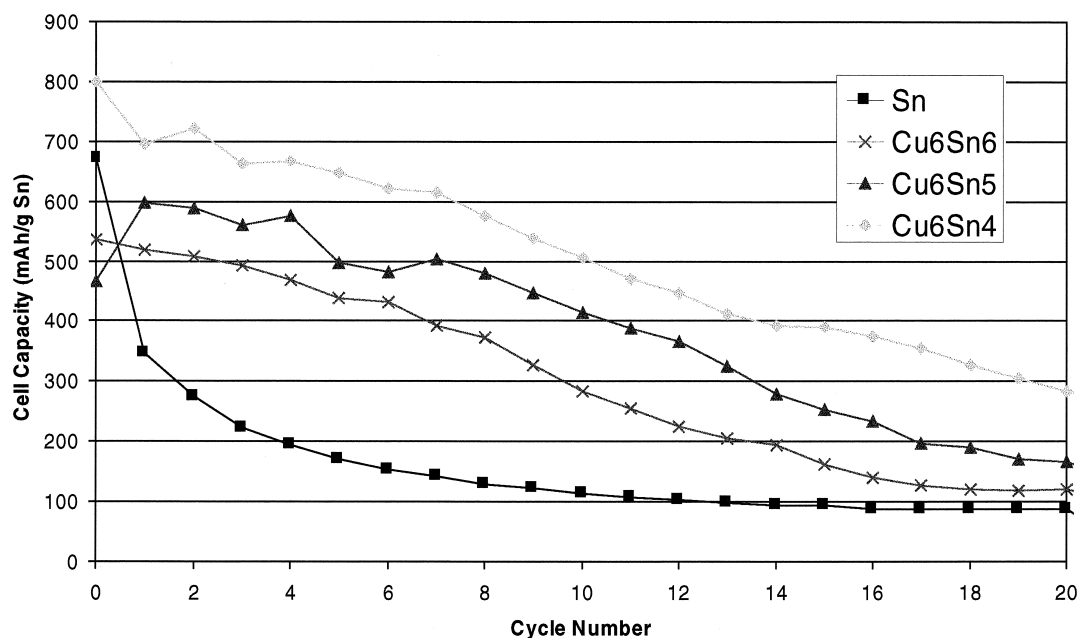


Fig. 4. Cell capacity in mAh/g Sn vs. cycle number for Li/Sn and Li/Cu<sub>6</sub>Sn<sub>5+ $\delta$</sub>  ( $\delta = 0, \pm 1$ ) cells cycled over the range 1.2 to 0.0 V (20 cycles).

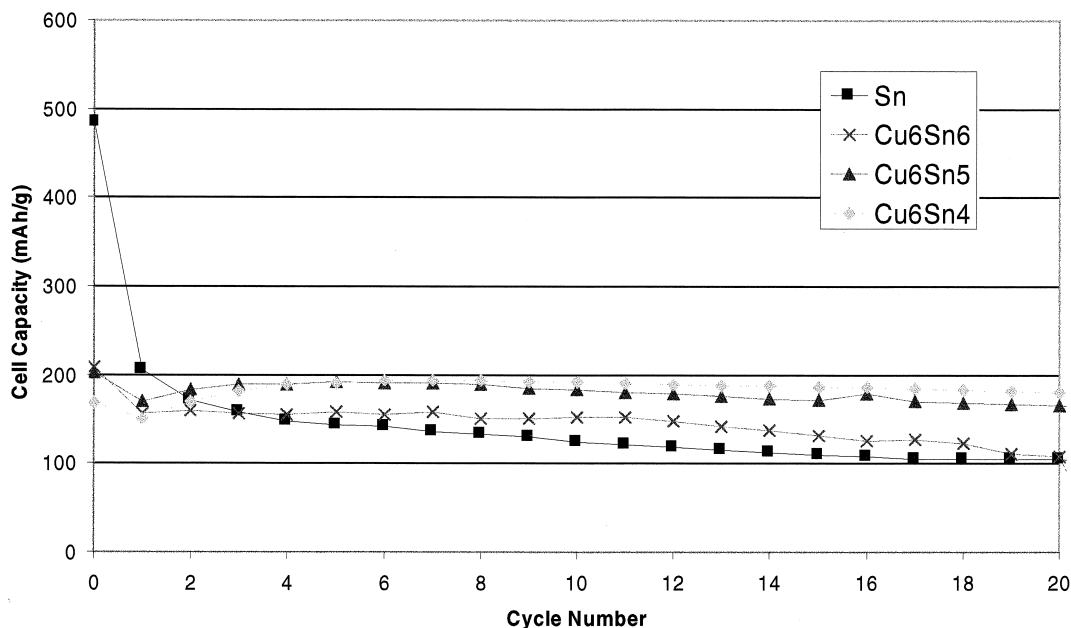


Fig. 5. Cell capacity vs. cycle number for Li/Sn and Li/Cu<sub>6</sub>Sn<sub>5+ $\delta$</sub>  ( $\delta = 0, \pm 1$ ) cells cycled over the range 1.2 to 0.2 V (20 cycles).

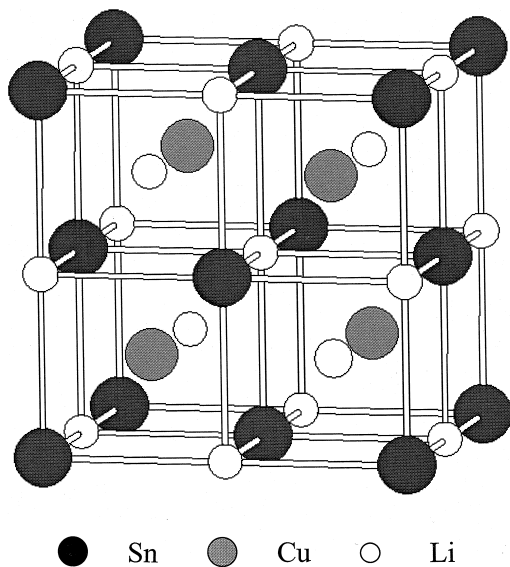


Fig. 6. The structure of Li<sub>2</sub>CuSn. Lithium atoms occupy the interstitial sites created within a copper (gray spheres) and tin (black spheres) metal array.

would contribute to the low capacity. Extensive lithiation of Li<sub>2</sub>CuSn electrodes results, like Cu<sub>6</sub>Sn<sub>5</sub>, in the decomposition of the structure to form active Li<sub>x</sub>Sn domains in an inactive copper matrix.

#### 4. Conclusions

Copper–tin intermetallic materials have been investigated as anode materials to replace carbon in lithium-ion cells. This preliminary study has demonstrated the strong effect that an inactive matrix element can have on the

utilization of an active Sn component. It is anticipated that with improved processing techniques, further enhancement of practical capacities and cycling behavior of these copper–tin intermetallic materials will be achieved.

#### Acknowledgements

Support from the Advanced Battery Program, Chemical Sciences Division, Office of Basic Energy Sciences, US Department of Energy under contract no. W-31-109-Eng-38 is gratefully acknowledged.

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