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In situ XAS of the reaction mechanism of lithium with tin-based composite oxide glass

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We have measured the XAFS spectra of tin-based composite oxide (TCO) glass with nominal composition of $Sn_{1.0}B_{0.56}P_{0.40}Al_{0.42}O_{3.47}$ during the discharge and charge cycles in an in a non-aqueous cell. Our results confirm the amorphous nature of TCO material and show that Sn in TCO is coordinated with 3 oxygen atoms at a distance of 2.12 Å. Upon discharge (i.e., Li insertion), initially, Li interacts with the electrochemically active Sn-O center forming metallic Sn, most likely in the form of highly dispersed clusters, and Li_2O. Upon further discharge, our results are consistent with a model in which additional Li alloys with Sn forming various alloys with composition dependent on the amount of Li inserted. The formed alloys appear to be in the form of highly dispersed clusters and/or amorphous in nature. Their local structure differs somewhat from the crystalline structure of the known Li-Sn alloys such as LiSn, Li_7Sn_3, or Li_7Sn_2. Upon charging (i.e., Li removal), metallic Sn is reversibly produced with a Sn-Sn distance intermediate to those of gray and white Sn.

Key words: in situ XAFS, tin-based composite oxide, structure.

1. Introduction

Currently, Li-ion rechargeable batteries employ $LiCoO_2$ as a cathode material and a carbon-based intercalation compound such as LiC_6 as an anode material. The LiC_6 material, however, has a capacity limited to the theoretical value of 370 mAh/g and suffers from a significant irreversible loss in capacity after only one cycle. Due to these issues, safety concerns, and requirements for higher capacities, a new class of anode material based on a tin-based composite oxide (TCO) glass has been proposed as an alternative (Idota, 1997). TCO material has significantly higher gravimetric and volumetric capacities than those of carbon-based material. The Sn-based composite oxide consists of Sn, B, P, Al, and O in varying proportions. To date, the reaction mechanism of Li with this type of Sn-based composite oxide is not yet understood and needs clarification. X-ray diffraction analysis provides minimal structural information due to the amorphous nature of this material (Idota, 1997) However, x-ray absorption spectroscopy, is uniquely suited for the elucidation of the structure and composition of amorphous materials.

2. Experimental

The TCO material used in this investigation has a nominal composition of $Sn_{1.0}B_{0.56}P_{0.40}Al_{0.42}O_{3.47}$ and its XRD pattern shows an amorphous band similar to that published elsewhere (Idota, 1997). The electrochemical cell consists of a rolled bonded cathode of TCO, a Celgard separator, a Li foil anode, and 1 M $LiPF_6$ electrolyte dissolved in 1:1:3 (v/o) propylene carbonate: ethylene carbonate: dimethyl carbonate (McBreen, 1997). The total mass of TCO in the electrode is 0.0985 g. The cell was first discharged and then charged at a rate of 35.6 mA/g of TCO over the voltage range 2.5-0.14 V vs. Li/Li^+ using a computer-controlled cycler. The capacity passed during the discharge cycle is 708 mAh/g, which corresponds to a Li/Sn mole ratio of 5.4. At the end of the charge cycle, only 424 (60%) mAh/g was passed.

The XAS measurements were continuously collected during both the discharge and charge cycles. The XAS experiments were performed on beamline X-11A of the National Synchrotron Light Source with the electron storage ring operating at an electron energy of 2.8 GeV and stored current in the range of 110 to 350 mA. Data were collected with a variable exit double-crystal monochromator using two flat Si (311) crystals. The x-ray absorption edge jump for this electrode was near 0.9 at the Sn K-edge. The change in the Li/Sn ratio between successive scans was kept near 0.07. Quantitative analysis of EXFAS spectra were made using theoretical standards generated with version 6.01 of the FEFF code (Zabinsky, 1995) employing structural data for crystalline SnO and metallic white Sn. The many body amplitude reduction factor, S_o^2, was determined from XAFS data of metallic white Sn to be equal to 1.0. Fits were made in r-space using the curve fitting FEFFIT code of the UWXAFS package (Stern, 1995). Other details are published elsewhere (Mansour, 1998).

3. Results

A comparison of the XANES for control TCO electrode and after being discharged to states, where the amount of Li inserted corresponds to a Li/Sn ratio of 1.9 and 5.35 are shown in Figure 1. Reference spectra of SnO and metallic Sn (white) are shown for comparison purposes.

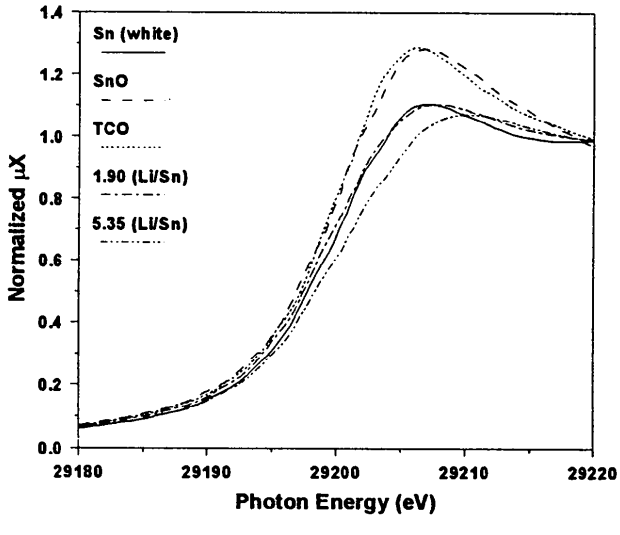

Figure 1

XANES for control TCO electrode, after being discharged to states corresponding to a Li/Sn ratio of 1.9 and 5.35, along with reference spectra for SnO and metallic Sn (white).

The spectra clearly show that the oxidation-state of Sn in TCO is +2, similar to that of Sn in SnO. Upon discharging to a state where the amount of Li inserted corresponds to a Li/Sn ratio near 1.9, the XANES is similar to that of metallic Sn. Thus, indicating the formation of metallic Sn. Accordingly, Li reacts with the electrochemically active Sn-O center forming metallic Sn and presumably Li_2O, as proposed earlier on the basis of an in situ XRD study of crystalline phases (Courtney & Dahn, 1997). At this state of discharge, the amount of Li inserted (2 moles of Li for every mole of Sn) is consistent with this mechanism. Upon further discharge, the edge energy slightly shifts to a higher energy but with no significant change in overall shape of the data indicating that the data is dominated by contributions for Sn-Sn type of bonding.

In Figure 2, we show Fourier transforms of the Sn K-edge EXAFS of a few spectra selected from a set taken during the discharge cycle as a function of the Li/Sn ratio, along with that for control TCO material.

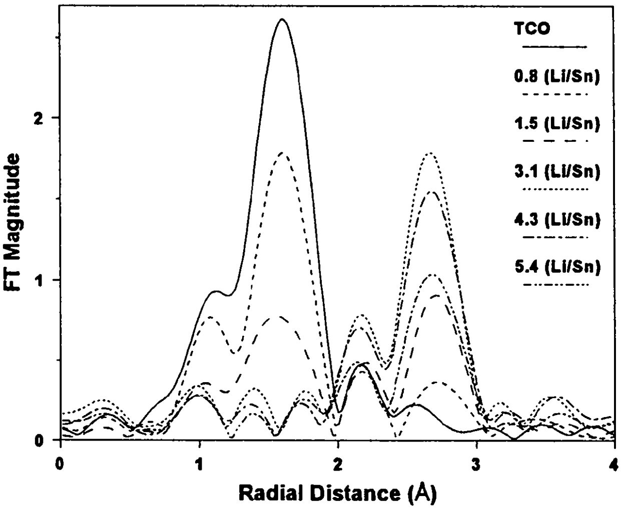

Figure 2

Fourier transforms of Sn K-edge k^3-weighted EXAFS of a few spectra selected from a set taken during the discharge cycle at various Li/Sn ratios, along with that of control TCO.

The FT of the control TCO material displays a single peak, which corresponds to a Sn-O interaction, with no contributions from higher coordination spheres confirming the amorphous nature of TCO material. As TCO is discharged, the amplitude of this peak decreases with increase in the Li/Sn ratio and diminishes when the Li/Sn ratio approaches 2.2. A second peak, which corresponds to Sn-Sn bonding, emerges near a Li/Sn ratio of 1.2. The amplitude of this Sn-Sn contribution increases reaching a maximum near a Li/Sn ratio of 2.9 and levels of up to a Li/Sn ratio of 4.2. On further discharging, the amplitude of the Sn-Sn peak decreases with increase in the Li/Sn ratio up to 5.4.

The FT data of EXAFS spectra taken during the charge cycle are shown in Figure 3. The data show that the Sn-Sn distance does not vary much during the charge cycle (i.e., Li removal). In addition, the data show that the Sn-Sn distance for charged TCO is slightly shorter than that of metallic Sn (white). Furthermore, the data show the absence of any Sn-O contribution upon Li removal down to a Li/Sn ratio of 2.6.

A summary of local structure parameters for Sn as a function of the Li/Sn ratio for XAFS spectra taken during the discharge cycle is listed in Table 1. Only data for every fourth scan were listed here due to lack of space. Analysis of model compounds with FEFF shows that the backscattering amplitude from Li atoms is significantly less that that of oxygen or tin and hence, the Li contribution to the EXAFS spectra is small and can be ignored.

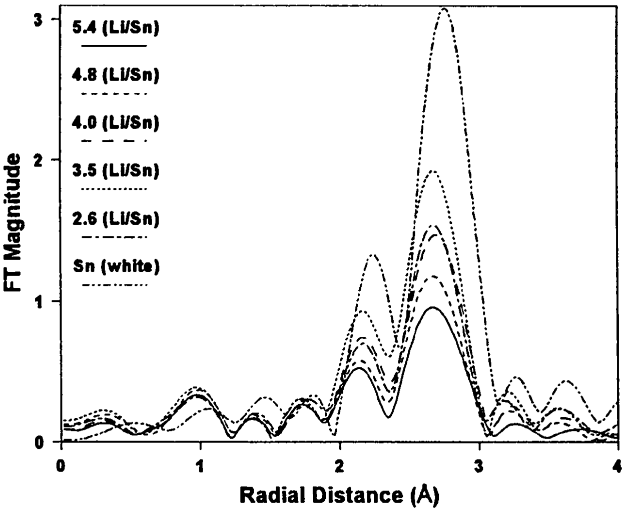

Figure 3

Fourier transforms of Sn K-edge k^3-weighted EXAFS of a few spectra selected from a set taken during the charge cycle at various Li/Sn ratios, along with that for metallic Sn (white).

Table 1

Summary of local atomic structure parameters for TCO material as a function of the Li/Sn ratio during the discharge cycle. Uncertainties in the data are included in parenthesis.

Li/Sn ratio	X-Y Pair	N	R (Å)	$\Delta\sigma^2$ (10^{-3}Å^2)
0	Sn-O	3.2(0.3)	2.115(0.006)	8.1(0.9)
0.34	Sn-O	2.7(0.3)	2.120(0.010)	8.7(1.4)
0.64	Sn-O	2.3(0.3)	2.114(0.011)	8.6(1.6)
0.94	Sn-O	2.1(0.3)	2.121(0.012)	9.2(1.8)
	Sn-Sn	0.7(0.5)	2.932(0.038)	12.0(5.4)
1.34	Sn-O	1.5(0.3)	2.130(0.017)	10.7(2.5)
	Sn-Sn	1.5(0.5)	2.945(0.020)	14.6(2.8)
1.71	Sn-O	0.9(0.3)	2.126(0.025)	10.2(3.6)
	Sn-Sn	1.9(0.4)	2.932(0.012)	13.2(1.7)
2.19	Sn-Sn	2.0(0.4)	2.920(0.010)	10.7(1.4)
2.72	Sn-Sn	2.0(0.3)	2.897(0.006)	9.3(0.9)
3.06	Sn-Sn	2.4(0.2)	2.894(0.004)	10.2(0.6)
3.37	Sn-Sn	2.2(0.2)	2.893(0.005)	9.1(0.7)
3.67	Sn-Sn	2.2(0.2)	2.901(0.003)	9.3(0.5)
3.99	Sn-Sn	2.1(0.2)	2.905(0.003)	9.2(0.5)
4.31	Sn-Sn	2.1(0.1)	2.911(0.003)	10.1(0.4)
4.76	Sn-Sn	1.9(0.2)	2.918(0.005)	10.4(0.7)
5.06	Sn-Sn	1.9(0.2)	2.918(0.005)	11.2(0.7)
5.35	Sn-Sn	1.7(0.2)	2.924(0.005)	11.3(0.8)

The data show that Sn in TCO is coordinated with 3 oxygen atoms at a distance of 2.12 Å compared to 4 at 2.22 Å in crystalline SnO. Upon discharge, the Sn-O distance remained constant while the coordination number decreased with increase in the Li/Sn ratio. The decrease in the coordination number is consistent with the reaction of Li with the electrochemically active Sn-O center forming metallic Sn. The Sn-Sn contribution could only be detected at a Li/Sn ratio greater than 0.64 indicating that below this ratio Sn is present either atomically dispersed in the TCO matrix or in a highly disordered form. For Li/Sn ratios in the range 1-2, the Sn-Sn distances are in the range 2.92-2.94 Å and are intermediate to those of white and gray Sn. The Sn-Sn distance decreases with increase in the Li/Sn ratio reaching a minimum near 2.89 Å at a Li/Sn ratio near 3. Note that the initial 2 moles of Li inserted for every mole of Sn in TCO are consumed by the reaction of Li with the electrochemically active Sn-O center producing metallic Sn and presumably Li_2O. At a Li/Sn ratio of 3, only 1 mole of Li is available for every mole of metallic Sn in TCO and thus, the formation of LiSn is expected. However, the Sn-Sn distance is about 0.1 Å shorter than that of LiSn. This could be due to the formation of highly dispersed clusters with just a few atoms and/or an amorphous phase of Li-Sn. The Sn-Sn distance then smoothly increases from 2.89 to 2.92 Å for Li/Sn ratios in the range 3.0-5.4. At a Li/Sn ratio of 5.4, only 3.4 moles of Li are available to react with metallic Sn in TCO. Thus, the formation of at least one of the following phases, namely, Li_7Sn_3, Li_5Sn_2, $Li_{13}Sn_5$ or Li_7Sn_2 is expected. The Sn-Sn distance of 2.92 Å observed at a Li/Sn ratio of 5.4 is slightly smaller than that for Li_7Sn_3 (2.94 Å) (Muller, 1974) or Li_7Sn_2 (3.00 Å) (Frank, 1975a) and only slightly larger that those of Li_5Sn_2 (2.88 Å) (Frank, 1975b) and $Li_{13}Sn_5$ (2.86 Å) (Frank & Muller, 1975c). The observed coordination number of 1.7 ± 0.2 at a Li/Sn ratio of 5.4 is closer to that characteristic of Li_7Sn_3 ($N = 1.3$) than those characteristic of Li_5Sn_2 ($N = 1.0$), $Li_{13}Sn_5$ ($N = 0.8$), and Li_7Sn_2 ($N = 0.5$) suggesting that the formation of Li_7Sn_3 is most likely to occur. However, the formation of Li_7Sn_3 does not account for the amount of Li inserted during the discharge process. Thus, the possibility of forming a number of phases can not be excluded. Furthermore, the true nature of Li-Sn phases being formed during the discharge process may differ somewhat from that of the known crystalline phases of Li-Sn alloys. The formation of highly dispersed clusters with just a few atoms and/or amorphous phases could lead to significant differences in local structure and chemistry relative to crystalline phases. Our results are in general agreement with results obtained on the basis of an in situ x-ray diffraction study on crystalline Sn oxide materials (Courtney & Dahn, 1997). In the XRD study, however, crystalline phases of Li-Sn alloys were identified.

Upon charging (i.e., Li removal), local structure parameters (not shown here) are quite similar to those observed during the discharge cycle for the same Li/Sn ratio. In the fully charged state where only metallic Sn is expected to form, the Sn-Sn distance is 2.90 Å, which is close to that observed during the initial stages of the discharge process. A coordination number of 2.5 ± 0.3 was observed in contrast to 6 (4 at 3.02 Å and 2 at 3.18 Å) for white Sn and 4 (at 2.81 Å) for gray Sn. The low coordination number for metallic Sn, formed as a result of Li removal, is probably due to the highly dispersed nature of the Sn particles.

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