Electrochemical Comparison Between SnO_2 and Li_2SnO_3 Synthesized at High and Low Temperatures

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Abstract. Li_2SnO_3 has been synthesized at 1000 °C from Li_2CO_3 and SnO_2 (high temperature form - HT) and it has also been prepared from ball-milled SnO_2 and Li_2CO_3 at 650 °C (low temperature form - LT). The Li_2SnO_3 materials have been tested as a negative electrode for possible use in a Li-ion cell and their electrochemical behaviour has been compared with that of SnO_2. In theory, Li_2SnO_3 and SnO_2 should be able to cycle the same number of lithium atoms per tin atom but on the initial discharge SnO_2 has inserted more lithium than Li_2SnO_3. During the initial discharge of SnO_2 and Li_2SnO_3, a side electrochemical reaction seems to be occurring. The resultant compound apparently inserts lithium reversibly for potentials around 1 V; however, cycling from 0.02-2 V significantly degrades performance compared to 0.02-1 V. Li_2SnO_3 (HT) allows the de-insertion of more lithium than Li_2SnO_3(LT) and SnO_2 in the first charge.

1. Introduction

Research interest in tin-based oxide compounds as a Li-ion battery anode has risen in recent years following Fujifilm's publication in 1997 [1]. They reported a reversible capacity over 600 mAh/g for an amorphous tin (II) composite oxide, which is much higher than that for graphite [2]. Theoretically graphite offers capacities of 372 mAh/g, however, the optimum practical reversible capacity is only 90% of this value. It is thought that tin-based oxide composites may replace graphite negative electrode materials commercially in the future. In order to understand the phenomenon occurring whilst cycling, in-situ XRD measurements have been performed on a variety of tin-based oxide compounds from which the following mechanism has been suggested [3]. Tin oxide is reduced to produce tin metal and Li_2O irreversibly, and then the reduced tin forms a reversible range of alloys with lithium. $Li_{4.4}Sn$ is the highest lithium-tin alloy formed during the electrochemical process, thus the whole cell irreversibly loses half of its initial capacity. Despite this irreversible loss caused by the Li_2O formation, it is believed that the Li_2O matrix minimizes the volume expansion resulting from the lithium-tin alloying/de-alloying process. The role of the Li_2O in the electrode performance is far from being well understood.

Winter et al. reported a reduction in the expected volume expansion during the formation of lithium-tin alloys whilst using small tin particle sizes [4]. Therefore, it is thought that the combination of small particle size and the presence of the Li_2O matrix would enhance the cycle life of the battery. Several tin-based intermetallic phases such as Sn/SnSb [5], Sn/SnAg [5] and Cu_6Sn_x [6-7] have been tested and they confirm that the volume expansion resulting from the lithium insertion causes much less cracking with fine particle sizes and, therefore increases the cyclability. Decreasing particle size increases the surface area of the metal. As a result, the lithium irreversibly consumed for SEI formation should rise, diminishing the amount of lithium available for cycling. We have tested Li_2SnO_3 materials prepared at two different temperatures as a possible Li-ion battery negative electrode wherein the Li_2O matrix should promote volume

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stability. In theory, Li_2SnO_3 should form more Li_2O than SnO_2 on initial insertion - as per Courtney and Dahn's equations [3]. Moreover, the number of lithium atoms inserted/de-inserted per tin atom for both oxides should be equal. The aim of this paper is to analyse the behaviour of Li_2SnO_3 prepared at two different temperatures and compare it to that of SnO_2.

Li_2SnO_3 crystallises into a monoclinic structure - space group C2/c. This crystal structure was first investigated by Lang et al. [8-9] and finally solved by Hoppe et al. [10] using single crystal X-ray diffraction data. The lattice parameters (a = 5.2889(2) Å, b = 9.1872(3) Å, c = 10.0260(3) Å and β = 100.348(2)°) were confirmed by Rietveld refinement of neutron diffraction data [11]. The oxygen atoms form a distorted cubic close-packed network with the cations occupying all of octahedral sites present. There are two types of metal layers perpendicular to the c axis, one composed of lithium only, the other composed of lithium and tin in a 1:2 ratio. The cations in the mixed metal layers form hexagonal close-packed planes in which the tin atoms occupy the vertices of the hexagons and the lithium atoms the centre of the hexagons. Low temperature 'intermediate structures' of Li_2SnO_3 were reported where changes in the ordering of lithium and tin on the mixed layers lead to a loss of translational order in the c direction [12]. These low temperature 'intermediate structures' are probably metastable [10].

Courtney et al. have previously studied Li_2SnO_3 synthesised at 1000 °C [3]. They emphasised the importance of the electrochemical behaviour of atoms which are not involved in the alloying/de-alloying process. The derivative profile shows no emergence of bulk lithium-tin phases during the first discharge but clusters begin to appear in subsequent cycles. Tin aggregation is presumably hindered by the presence of "spectator atoms". In-situ XRD showed no presence of tin peaks at the end of the initial charge. This could be the result of the formation of three moles of Li_2O per mole of Li_2SnO_3 compared to two moles per mole of SnO_2, which should slow down the aggregation of tin metal.

2. Experimental Details

SnO_2 (cassiterite) was milled for 12 hours under acetone using zirconia balls prior to grinding with Li_2CO_3 in stoichiometric amounts. The resultant mixture was fired at 650 °C to form LT Li_2SnO_3. HT Li_2SnO_3 was prepared at 1000 °C from non-milled cassiterite. Analysis of both the LT and HT materials were performed using X-ray scattering ($CuK_{\alpha 1}$ radiation). The XRD patterns allowed the calculation of SnO_2 particle size using the Sherrer formula and the determination of the structural phases present. Before milling, the SnO_2 had a crystallite size in the range 1-5 μm and after milling 220 ± 10 nm.

In order to prepare the electrodes, active material (11.6 %), carbon S (1.4 %), PVDF (5.5%) and PC (9.5 %) were mixed in acetone to form a slurry [3]. The slurry was stirred for 4 hours at 50 °C and then the PC was removed from the negative electrodes by immersion into ether.

Cells were assembled in an argon filled glove box using lithium as the counter reference electrode for electrochemical tests. The electrolyte employed is $LiClO_4$ in ethylene carbonate - dimethylene carbonate (1:1). All galvanostatic tests were performed using a Macpile II or a Maccor at constant current (0.05 mA).

3. Results

The galvanostatic plots for Li_2SnO_3 (LT), Li_2SnO_3 (HT) and SnO_2 are shown in Fig. 1a. During the initial discharge a large plateau is observed for all the oxides, which corresponds to their reduction to tin metal. The profile of SnO_2 is in accordance with previous work, SnO_2 is reduced to tin metal at approximately 0.9 V and below 0.9 V lithium-tin alloys are formed [3, 13-14]. Li_2SnO_3 displays a very short plateau at about 0.36 V and a long plateau around 0.18 V. The latter corresponds to the reduction of the oxide and to the formation of the lithium-tin alloys. On the first charge, a plateau is observed near 0.4 V for both oxides, which represents the dealloying of tin metal. A similar plateau to the initial charge plateau is observed during the second discharge around 0.3 V, it corresponds to lithium-tin alloy formation.

In order to clarify all the phenomena occurring upon cycling, the galvanostatic data of Li_2SnO_3 and SnO_2 have been differentiated with respect to potential and plotted in Fig. 1b. A derivative plot gives useful indications, which do not appear clearly in a galvanostatic plot, in order to fully understand the processes that occur on cycling. A peak in a derivative plot is the sign of an electrochemical process.

Overall, the derivatives of the galvanostatic profiles of Li_2SnO_3 (LT), Li_2SnO_3 (HT) and SnO_2 are quite similar. In the case of Li_2SnO_3 during the first discharge two cathodic peaks are observed at about 0.36 and 0.18 V. The peak at 0.18 V corresponds to the reduction of Li_2SnO_3 to

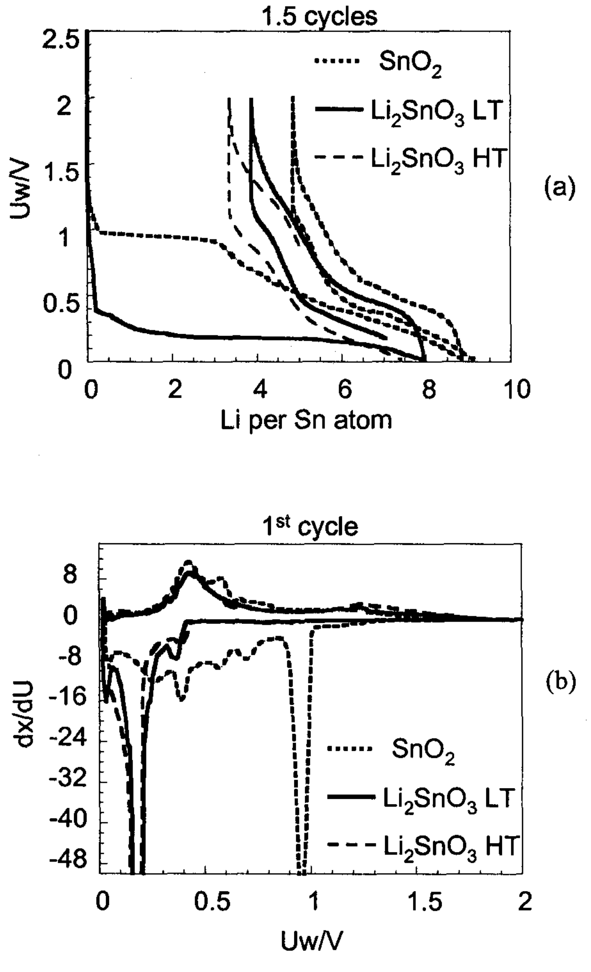

Fig. 1. SnO_2, Li_2SnO_3 (LT) and Li_2SnO_3 (HT), (a) galvanostatic plot - first 1.5 cycles, (b) derivative plot - 1st cycle.

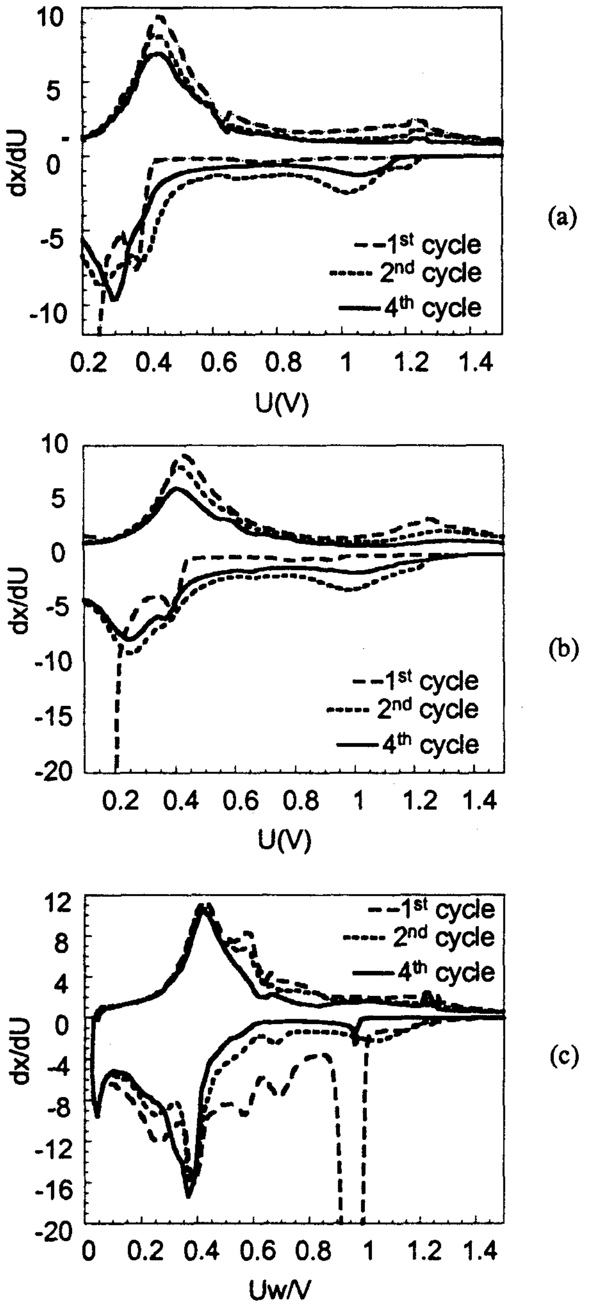

Fig. 2. Derivative plot of (a) Li_2SnO_3 (LT), (b) Li_2SnO_3 (HT) and (c) SnO_2.

tin metal and the formation of lithium-tin alloys and the matrix Li_2O as described earlier. The reduction of SnO_2 occurs at approximately 0.92 V. During the rest of the discharge of SnO_2, four peaks appear at about 0.68, 0.58, 0.38 and 0.26 V, they correspond to the formation of various lithium-tin alloys [15]. The cathodic peak observed around 0.36 V for Li_2SnO_3 during initial discharge resembles a lithium-tin alloy peak observed for SnO_2 (see Fig. 1b). It is quite unlikely that these are related however, because this latter peak appears before and not after the reduction of Li_2SnO_3.

On charging, Li_2SnO_3 exhibits two anodic peaks near 0.4 and 1.25 V (see Fig. 1b). The anodic peak at about 0.4 V corresponds to the dealloying of tin metal. During the charge process for SnO_2, the de-alloying of tin metal is associated with peaks around 0.42, 0.59, 0.68 and 0.76 V. It can also be seen that a very similar anodic peak to Li_2SnO_3 around 1.25 V is observed for SnO_2.

Figure 2 shows the derivative plot of cycle 1, 2 and 4 for the Li_2SnO_3 and SnO_2 samples. The anodic peak around 1.25 V observed during the initial charge, decreases during subsequent cycles (see Fig. 2). The cathodic peak during the following cycles around 0.36 V for Li_2SnO_3 (LT) has slightly shifted to more positive potential (see Fig. 2a). In the meantime the same peak for

Table 1. Capacities and number of lithium inserted/de-inserted of Li_2SnO_3 and SnO_2.

	1st irrev. capacity [mAh/g] Lithium inserted		1st rev. capacity [mAh/g] Lithium de-inserted	
	Theory	Experiment	Theory	Experiment
Li_2SnO_3 (1000 °C)	1233 8.4	1177 8.02	643 4.4	685 4.67
Li_2SnO_3 (650 °C)	1233 8.4	1167 7.93	643 4.4	596 4.06
SnO_2	1501 8.4	1580 8.84	750 4.4	712 3.98

Li_2SnO_3 (HT) has slightly shifted to more negative potential (see Fig. 2b). The derivative plots of Li_2SnO_3 (HT) and (LT) are very smooth for the first two cycles (see Fig. 2), which means that large tin grains have not been formed [16]. Li_2SnO_3 (LT) fourth cycle (see Fig. 2a), however, shows some evidence of a sharp cathodic peak around 0.3 V, which perhaps indicates the onset of a bulk lithium-tin alloy formation. The intensity of the Li_2SnO_3 (HT) cathodic peak around 0.25 V has decreased in the fourth cycle (see Fig. 2b). The SnO_2 derivative plot is relatively smooth but the cathodic peak around 0.38 V is quite sharp which is a sign of tin aggregation (see Fig. 2c).

According to the suggested mechanism [3], Li_2SnO_3 and SnO_2 should insert and de-insert the same amount of lithium per tin, although SnO_2 theoretical gravimetric or volumetric capacities are greater than for Li_2SnO_3. As shown in Table 1, Li_2SnO_3 has inserted less lithium than SnO_2 during the initial discharge but Li_2SnO_3 (HT) has inserted more than Li_2SnO_3 (LT). During the first charge Li_2SnO_3(HT) has de-inserted more lithium than Li_2SnO_3 (LT) and SnO_2. In the Li_2SnO_3 (HT) case, more lithium has been de-inserted on the discharge than the theoretical 4.4 lithium (see Table 1), this must imply that a process in addition to dealloying is occurring.

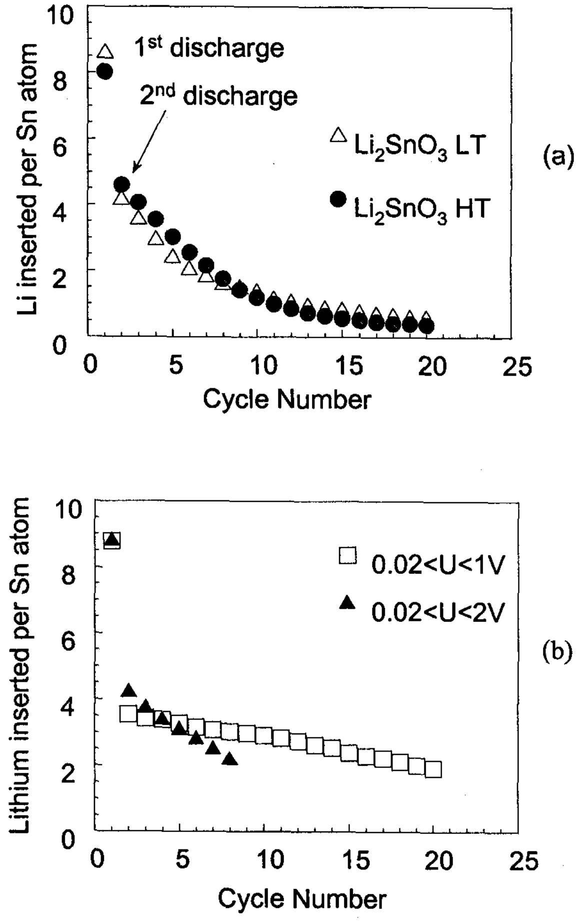

Fig. 3. Electrochemical performance of (a) Li_2SnO_3 (LT), Li_2SnO_3 (HT) and (b) SnO_2.

The cycling performances of Li_2SnO_3 (LT) and (HT) are shown in Fig. 3a and the cycling performance of SnO_2 is shown in Fig. 3b. The number of lithium inserted per tin atom is plotted versus the cycle number. Li_2SnO_3 was tested galvanostatically between 0.01 and 2 V with a current of 0.05 mA. SnO_2 was tested with the same current in two regimes, up to 1 and 2 V respectively (see Fig. 3b), 0.02 to 1 V is one of the best and most widely used voltage windows for testing tin oxide compounds [17]; although it obviously misses any events between 1 and 2 V. Li_2SnO_3 LT and HT display similar cyclability (see Fig. 3a). Until the tenth cycle, Li_2SnO_3 HT seems to retain capacity slightly better than Li_2SnO_3 LT however, the capacity fade of Li_2SnO_3 LT and HT are very similar and Li_2SnO_3 cycles poorly. In the initial cycle SnO_2 tested to 1 V and to 2 V, have inserted similar number of lithium atoms (see Fig. 3b). At the fifth cycle the irreversible loss of SnO_2 tested to 2 V increases dramatically, in comparison the capacity loss of SnO_2 tested to 1 V decreases much more slowly.

4. Discussion

The SnO_2 initial discharge plateau around 0.92 V corresponds to about 3 lithium per tin (see Fig. 1a). This plateau gradually decreases from three lithiums per tin atom to four lithiums per tin atom and beyond. Four lithium atoms are required to reduce the tin oxide to tin metal and form the matrix Li_2O in relation to the equation proposed by Courtney [3]. The Li_2SnO_3 initial discharge peak near 0.18 V corresponds to around 6.5 lithium per

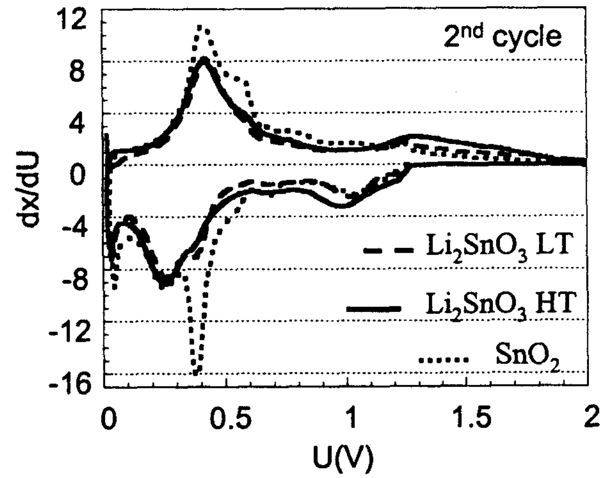

Fig. 4. 2nd cycle derivative plot of Li_2SnO_3 (LT), Li_2SnO_3 (HT) and SnO_2.

tin atom; this latter amount of lithium reduces Li_2SnO_3 to tin metal and forms the matrix Li_2O and lithium-tin alloys. The Li_2SnO_3 reduction peak is at much more negative potentials than tin oxide and close to lithium metal because of the large lattice energy of Li_2SnO_3.

In Fig. 1b, the Li_2SnO_3 cathodic peak around 0.36 V is at the same potential as that reported for the formation of a lithium-tin alloy by C.J. Wen et al. [15]. As the reduction of Li_2SnO_3 (see Fig. 1) occurs below 0.36 V i.e. 0.18 V, this may mean an early and partial reduction in this region. This peak at 0.36 V corresponds to approximately 0.5 lithium per tin. The Li_2SnO_3 (LT) form exhibits broader X-ray diffraction peaks than the HT form, indicating a smaller particle size and a certain amount of disorder due to non-attainment of equilibrium at the low reaction temperature. In tandem with this, the LT form may also exhibit some short-range order parallel to c, as such ordering might be anticipated at this temperature even in samples that had not attained compositional homogeneity. The peak near 0.36 V is less accentuated for Li_2SnO_3 synthesised at 1000 °C, therefore this peak could relate to the reduction of the low temperature "ordered form" of Li_2SnO_3; however it is more likely that this is related to the larger surface area of the LT form.

To clarify the electrochemical behaviour of Li_2SnO_3, the second derivative cycle of Li_2SnO_3 has been compared to the second derivative cycle of SnO_2 in Fig. 4. The cathodic peak around 1 V seems to be very close to the initial SnO_2 reduction peak, and would suggest a re-oxidation of tin metal. So far no attention has been drawn to this phenomenon although similar features are seen in earlier data [3]. This peak emerges only during the second reduction as shown in Figs. 2 and 4. The anodic peak at 1.25 V on the other hand, was already present on the initial charge for both oxides (see Fig. 1). This latter peak and the cathodic peak approximately at 1 V appear to be connected because their magnitude decreases in a related manner (see Fig. 2). The only conviction is that the same process occurs whilst cycling Li_2SnO_3 and SnO_2.

Obviously an unexpected electrochemical reaction is taking place during the initial reduction and forms a compound or species, which is able to insert lithium reversibly. On oxidation this compound de-inserts at 1.25 V and inserts lithium at the second discharge near 1 V. The cathodic and anodic peaks respectively around 1 and 1.25 V have no relation with the initial cathodic peak near 0.36 V that appears during the first discharge (see Fig. 1b). The only atoms present are tin, lithium and oxygen; therefore this new species or compound is certainly the result of a combination between these. One possibility is that this compound forms a framework, which has the ability to insert or intercalate a small amount of lithium.

In theory Li_2SnO_3 and SnO_2 should have the same number of lithium per tin inserted/de-inserted during cycling thus, the cycling performance should be very similar for both oxides with perhaps a better a higher performance for Li_2SnO_3 because of the higher concentration of Li_2O. The cycling performance (see Fig. 4) shows that SnO_2 and Li_2SnO_3 still have similar cyclability for identical electrochemical conditions (tested up to 2 V) even if the Li_2SnO_3 derivative plot is smoother than SnO_2 (see Fig. 2). The smoothness of the derivative curve for Li_2SnO_3 (see Figs. 2a and 2b) could be due to the formation of 3 moles of Li_2O per mole of Li_2SnO_3 compared to 2 moles per mole of SnO_2. This should slow down the aggregation of tin metal and restrain volume expansion that occurs while cycling. Previous work [3] showed that tin produced from Li_2SnO_3 is less crystalline than tin produced from SnO_2. One would therefore expect [4] that tin produced from Li_2SnO_3 would be less likely to crumble on lithium insertion; however, the cyclability of Li_2SnO_3 from 0.02-2.00 V is not better than that from SnO_2 (see Fig. 3). The extra Li_2O produced from the reduction of Li_2SnO_3 presumably forms a more intimate composite with tin, which can explain the smoothness of the differential capacity of Li_2SnO_3. It can also be envisaged that the tin regions formed from Li_2SnO_3 during the discharge process will exhibit different mechanical properties to those formed from SnO_2.

Li_2O is known to be a good cation conductor, which allows the alloying and dealloying of tin metal, therefore the poor cycling behaviour of Li_2SnO_3 is surprising. Presumably, the properties of Li_2O generated by Li_2SnO_3 do not fulfil the requirement needed for Li-ion batteries in comparison to SnO_2. In addition cycling Li_2SnO_3 up to 2 V allows the compound synthesised during the initial discharge to insert reversibly lithium. As a result the cycling behaviour of Li_2SnO_3 is affected by the presence of this unidentified compound. SnO_2 cycles better when the electrochemical test has been performed up to 1 V (see Fig. 3b) so the effect of this unidentified compound is erased.

5. Conclusion

We have revealed evidence of an additional electrochemical process occurring during the initial lithium insertion process in tin-based oxide composites that has not been discussed previously. This reaction occurs at potentials just above 1 V. The result of this electrochemical reaction is the formation of a framework, which inserts reversibly lithium above 1 V only after the first reduction. Until now no evidence of a re-oxidation of tin metal in this region has been reported. The same phenomenon is observed for Li_2SnO_3 and SnO_2. Allowing this framework to reversibly insert lithium perhaps damages the electrode and as a result the cycling performance of the active material is poor. More investigations on these systems are in progress in our group especially in-situ and ex-situ XRD measurements.

6. References

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Paper presented at the 7th Euroconference on Ionics, Calcatoggio, Corsica, France, Oct. 1-7, 2000.

Manuscript rec. Dec. 18, 2000; acc. Mar. 9, 2001.