Novel tin oxide spinel-based anodes for Li-ion batteries

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Abstract

In this study, a series of inverse spinel M_2SnO_4 (M = Mg, Mn, Co) oxides were produced and tested to probe the effect the oxide matrix has on the electrochemical performance of tin oxides. Generally, these new oxides show similar behaviour to SnO_2 with the formation of a more complicated mixed metal oxide matrix affecting the potentials of tin reduction and lithium insertion. A reasonable correlation is observed between the potential of the initial reduction of the spinel oxide to metallic tin and the enthalpy of formation of the metal oxide (MO). Amongst the spinels, Mn_2SnO_4 exhibits the best reversibility and Mg_2SnO_4 the worst. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The need for smaller and more powerful rechargeable Li-ion batteries is driving research into improved battery materials. A set of promising anode (negative electrode) materials are those based on tin oxides [1], due to their large lithium ion capacities at low potentials, as well as their availability and safety.

Tin oxides are thought [2] to have a two step reaction with lithium, e.g. for SnO_2

$$SnO_2 + 4Li^+ + 4e^- \Rightarrow 2Li_2O + Sn \tag{1}$$

$$Sn + xLi^+ + xe^- \Leftrightarrow Li_xSn \qquad (0 < x < 4.4) \tag{2}$$
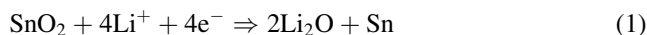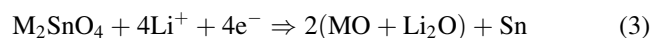
The initial step involves the irreversible reduction of the tin oxide to tin metal particles in a lithium oxide matrix. The second step is the reversible alloying of the Li^+ into the tin metal. For tin metal, this alloying causes a large volume expansion, causing disruption of the material and eventual loss of capacity. In these oxide materials, the volumetric change seems to be avoided or at least buffered and the oxide matrix is thought to play an important role in this stabilisation.

The initial oxide material has two effects on the electrochemical insertion of lithium. Firstly, it is broken down to form the supporting matrix for the tin particles. The oxide matrix then has to provide a lithium-ion conducting medium that transports the Li^+ to the metal. Unfortunately, the lithium inserted oxides are quite amorphous and hard to observe by typical X-ray methods, so it is difficult to relate their structures to their electrochemical behaviour. One possibility to alleviate this difficulty is to add spectator ions to modify the properties of the matrix, without changing the fundamental electrochemistry, as we have attempted in this study.

The M_2SnO_4 inverse spinels, where M = Mg, Mn, Co or Zn, form an iso-structural series of materials to probe the effect of different atoms in the oxide. Mn and Co have no known alloys with lithium, unlike Zn and Mg. MgO would not be expected to be reduced at these potentials, and so no Mg metal would be formed to alloy with the lithium. The Zn_2SnO_4 spinel is excluded from this work as it is covered in an earlier paper [3], and does have quite different properties, as Li readily reduces and alloys with the zinc. The Mg, Mn and Co spinels should behave electrochemically as the SnO_2, with slightly different products.

$$M_2SnO_4 + 4Li^+ + 4e^- \Rightarrow 2(MO + Li_2O) + Sn \tag{3}$$

$$M_2SnO_4 + 8Li^+ + 8e^- \Rightarrow 2Li_2O + Sn + 2M \tag{3a}$$

$$Sn + xLi^+ + xe^- \Leftrightarrow Li_xSn \qquad (0 < x < 4.4) \tag{4}$$

The above reactions (3) and (4) should transfer the same number of Li^+ as reactions (1) and (2). The ($MO + Li_2O$) could be mixed or a separate oxide phase. If M is also reduced, as shown in Eq. (3a), 12.4 Li^+ would be required for full reduction.

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Table 1
Method of preparation and selected physical properties of prepared materials

Material	Starting materials	Firing temperature (°C)	Molecular mass	Structure	a_0 (Å)
SnO_2	Cassiterite	–	150.69	Rutile	–
Mg_2SnO_4	$MgCO_3$, SnO_2	1400	231.30	Spinel	8.637
Mn_2SnO_4	MnO, SnO	900 (under Ar)	292.56	Spinel	8.880
Co_2SnO_4	Co_3O_4, SnO_2	1200	300.55	Spinel	8.637
Zn_2SnO_4	ZnO, SnO_2	1200	313.45	Spinel	8.657

These various spinels were prepared and studied electrochemically as possible lithium battery materials.

2. Experimental

The spinel materials were produced by standard solid state synthesis from SnO_2 and $(MgCO_3)_4MgOH·5H_2O$, Mn_2O_3 or Co_3O_4 at temperatures from 900 to 1440°C. The Mn_2SnO_4 was produced under Ar atmosphere. The materials were checked by powder XRD to be all spinel (S.G. Fd$\bar{3}$ ms). The Mn_2SnO_4 and Co_2SnO_4 materials still contained a small (<5%) amount of SnO_2 impurity that could not be eliminated. See Table 1 for details of synthesis and structure. Note Mn_2SnO_4 has a slightly larger cell size, presumably due to magnetic interactions.

Electrochemical testing was performed using porous "Bellcore"-type plastic electrodes [4], to facilitate X-ray-based studies. The electrodes were formed by doctor-blading a slurry of 11.6% of the active oxide material, 1.4% Super S carbon, 5.5% PVDF, 9.5% propylene carbonate and 72% acetone onto a glass plate to form a self-supporting sheet, typically 50–70 μm thick. The propylene carbonate was extracted using ether before transfer into an Ar-filled glovebox. The electrodes were assembled into 2325 coin cells (NRC, Canada) with 1 M $LiPF_6$ 2EC:DMC (Merck), one or two 0.025 μm polypropylene separators and a 11 mm diameter Li foil disk counter/reference electrode.

The cells were cycled between 1.5 and 0.02 V at a constant current between 0.02 and 0.10 mA, depending on the cell, on a Macpile system. See figure captions for details. For clarity only the first one and a half cycles are shown and the potentials are plotted with respect to the $Li^+/Li(m)$ reference.

3. Results and discussion

Fig. 1 shows the first one and a half cycles of a galvanostatic charge for each of the spinels. The equivalent profile of SnO_2 is included for comparison.

The initial sweep (reduction half cycle) for each material, which includes the irreversible tin oxide reduction (reactions (3) or (3a)), as well as the initial Li^+ insertion into the tin (reaction (4)), exhibits significant variations. Two important features are the overall number of lithium ions inserted during the half cycle and the voltage plateau corresponding to the reduction of the oxide (reaction (3)). In all, the materials there was significantly less than 12.4 Li^+ per Sn atom inserted, and so it would seem only reaction (3) is going to completion and the secondary metals are not being completely reduced. SnO_2 has an initial plateau at about 0.9 V_{Li}, and has an initial insertion of 8.4 Li^+ per Sn atom.

The magnesium spinel exhibits a large plateau at 0.15 V_{Li}, which is at a significantly lower potential than is observed for the other oxides. The capacity of the initial half cycle is about 6 Li per Sn atom, lower than the expected 8.4. The low capacity of this material is possibly due to the lithium magnesium oxide matrix formed not being as good an electronic or ionic conductor as the other matrices and so hindering the formation of the lithium–tin alloy. This is
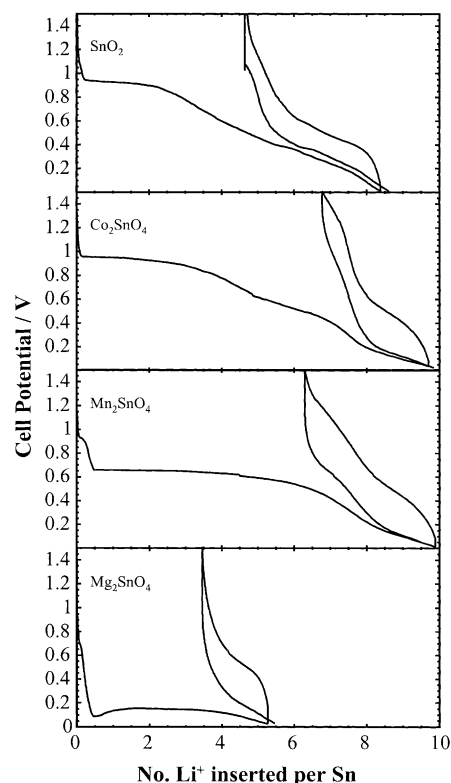

Fig. 1. Voltage profile of first 1.5 cycles for galvanostatic cycling of various cells between 1.5 and 0.02 V. Cells charged at: Mg_2SnO_4 0.1 mA; Co_2SnO_4 0.02 mA; Mn_2SnO_4 0.05 mA; SnO_2 0.05 mA.

supported by the lower reversible capacity observed for this material.

The manganese spinel has a plateau at about $0.7 V_{Li}$, again lower than the $0.9 V_{Li}$ plateau of the SnO_2. The initial shoulder at $0.9 V_{Li}$ is probably due to the small amount of SnO_2 impurity. The initial capacity is 9.6 Li inserted per Sn, which is larger than the expected 8.4 for Sn(IV), but not large enough to include the reduction of both of the Mn(II) to Mn(0). The voltage profile of the initial discharge for the cobalt spinel is similar to that of the manganese spinel, with much the same initial capacity but with a higher plateau potential of $0.9 V_{Li}$, similar to that of SnO_2. The slightly larger than expected capacity observed for these materials may reflect partial reduction of Co or Mn.

The changes in the plateau potential can be partially explained by consideration of the effect of the lattice on the tin reduction. The reduction of a tin oxide to tin metal involves the break up of the oxide lattice which requires extra energy, and so stabilises the Sn(IV) compared to the free species, making it harder to reduce. This is obvious in the shift of the SnO_2 reduction potential down to about $0.9 V_{Li}$ from the $\sim 3 V_{Li}$ expected for solution Sn^{4+}. Stronger lattices would, therefore, be expected to stabilise the tin further, lowering the reduction potential more. A gauge of the strength of the oxide lattice can be obtained from the enthalpy of formation of the M(II)O species. MgO is very stable, with a large negative ΔH_f^{θ}, with Mn, Sn and Co with increasing ΔH_f^{θ} (see Fig. 2, plot of ΔH_f^{θ} vs. plateau potential).

The presence of the strong Mg–O bond would be expected to make Mg_2SnO_4 lattice significantly stronger than the other oxides, giving the most stable Sn(IV). The Mn–O bond in the Mn_2SnO_4 will also stabilise the Sn(IV) compared to SnO_2. The Co–O bond is about the same strength as the Sn–O bond and so should have about the same stability as SnO_2. This corresponds to the relative level of the voltage
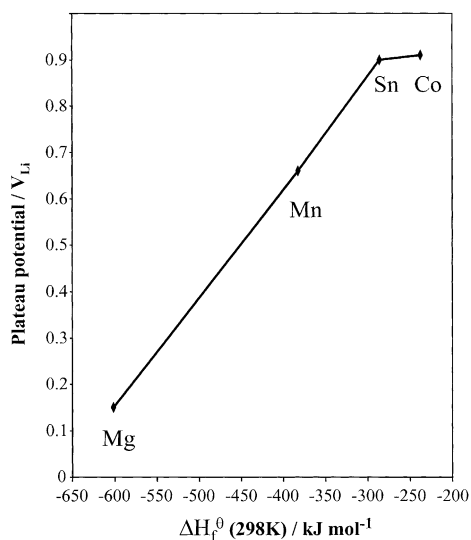
plateaux. This can be clearly seen when the plateau potential is plotted versus ΔH_f^{θ} (MO) as shown in Fig. 2, however, further data are required to fully confirm this relationship.

It is intriguing that it is only the tin that is reduced and not the cobalt when their reduction potentials and enthalpies of formation are similar [5]. The formation of a lithium cobalt oxide on the tin reduction may help to stabilise the cobalt. Mg(II) has a similar reduction potential to Li(I) with Mn(II) at slightly higher potentials [5] and so neither oxide would be expected to be reduced.

As the other metals do not seem to react with the lithium, the model suggests the Li insertion should be the same for all of the materials, as the tin metal formed should be similar in all. From the plots, however, it can be seen that the voltage profiles are slightly different. The Mg spinel profile rises to a sharp peak indicating little lithium capacity above $1 V_{Li}$, but this is probably due to the poor conduction in the magnesium lithium oxide. Both the Mn and Co spinels show extra capacity above $1 V_{Li}$ compared to the SnO_2 although the reversible capacity is lower than that of the SnO_2.

The changes in the reversible insertion of the Li are hard to explain without detailed knowledge of the structure of the oxide matrix. It is perhaps related to the distribution of particle sizes and accessibility of lithium ions to the metal particles.

4. Conclusion

Several iso-structural M_2SnO_4 spinels have been prepared and exhibit significant reversible lithium capacity on electrochemical testing. The electrochemical behaviour of the three spinels is dependent on the metal in the structure, both during the initial discharge, as well as in the subsequent cycling. This shows that the initial oxide framework has an effect on the electrochemistry of the lithium insertion and deinsertion, as well as the expected tin reduction. Further work is still needed in order to fully understand the important role of the oxide matrix in these interesting, and potentially useful, tin oxide-based electrodes.

Fig. 2. Relationship between plateau potential of various M_2SnO_4 (and SnO_2) and enthalpy of formation of M–O. Potential measured at two Li^+ inserted per Sn atom.

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