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Electrochemical performance of ball-milled ZnO–SnO₂ systems as anodes in lithium-ion battery

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Abstract

ZnO displays similar redox and alloying chemistry to the tin oxides on Li insertion. It might, therefore, be expected to be an interesting network modifier for tin oxides. ZnO/SnO₂ composites show degradation in cycling performance, however, for low ZnO levels, cyclability is improved by some milling, however, for high ZnO levels milling degrades performance, probably due to the increase of ZnO activity. On testing ZnO, it is found that it cycles very poorly. Both electrochemical and X-ray studies indicate that highly crystalline Li_xZn alloys are formed. It seems that the high degree of crystallisation on insertion is the determinant factor leading to the poor performance of ZnO and ZnO/SnO₂ composites compared to SnO₂. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: SnO₂; ZnO; Li_xZn alloys; Ball-milling

1. Introduction

Recently, the investigation of tin oxide-based negative electrodes has received considerable attention [1–4]. All these studies have confirmed that tin oxide compounds exhibit higher capacity than the commercially used carbon. The insertion of lithium into tin oxides has been investigated and a mechanism has been suggested [1]. Overall, tin oxide is reduced to tin metal and Li₂O, and then lithium–tin alloys are formed. The alloying (charge)/dealloying (discharge) of tin supplies the reversible capacity of the material. The irreversible loss during the first cycle is associated with the formation of amorphous Li₂O. By employing oxides, the idea is to use Li₂O as a matrix in order to constrain the host volume expansion [5] of the alloys occurring during cycling in order to extend the cell cycle life. The cycling performance is enhanced if the active material is finely dispersed in the matrix [6].

Focusing on the concept of fine particles, we have decided to ball-mill SnO₂ and ZnO together to produce fine powders for use as starting materials. Milling is a useful technique, which makes it possible to perform some syntheses and alloying mechanically [7]. It is difficult to envisage a mechanosynthesis from both oxides due to the hardness

of SnO₂ (6.5 on a scale of 10). According to Li et al. [6] milling can also produce particle sizes down to the nanoscale, smaller than by hand-grinding. Small initial particle size should facilitate the formation of finely dispersed alloys on lithium insertion and, in addition should ease the diffusion of lithium into the material.

As previously reported, lithium–zinc alloys [8,9] can be formed electrochemically and indeed ZnO follows a similar mechanism to that proposed above for tin oxides [10,11]. We have already reported [10,12], that mixing both oxides together induces an extra initial capacity. ZnO and SnO₂ when co-milled together have shown slight improvements in the reversible capacity when milling times increase [10]. In this work we are interested in the cycling behaviour of these oxides for various times of milling. In order to clarify the behaviour of the different milled mixtures, the cycling behaviour of ZnO has been studied in more detail.

2. Experimental

The oxides have a crystallite size in the range 1–5 μm before milling. Both oxides were ball-milled together with acetone as previously reported [10] using zirconia balls. ZnO (zincite) and SnO₂ (cassiterite) were mixed in molar ratios of 1:1 and 1:2. After a certain milling time, a fragment was removed for testing and the remainder is returned for further milling. XRD (using a Philips diffractometer with Cu

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$K\alpha$) was performed on all batches in order to determine the crystallite size of the ZnO and SnO₂ using the Scherrer formula. No new phases appear during milling, although the X-ray peaks become broader as the mixture becomes more amorphous.

Electrochemical testing was performed using porous “Bellcore”-type plastic electrodes [13], to allow future in situ X-ray and EXAFS studies. Electrodes were prepared by combining the active material (11.6%), the Super S carbon (1.4%), the PVDF (5.5%) and the propylene carbonate (9.5%) in acetone (72%) to form slurry.

It is essential to pre-grind the carbon and the active material together to obtain a uniform electrode and a better response of the electrode [14]. The propylene carbonate was removed from the electrode by immersion into ether, after stirring the slurry for 4 h at 50°C and drying on a glass substrate.

Batteries were assembled in an argon filled glove box. Lithium foil with a diameter slightly larger than the anode disc was used as a counter electrode. LiPF₆ in ethylene carbonate–dimethylene carbonate was used as electrolyte. The electrochemical tests were performed on a Macpile II and a Maccor battery testing systems at constant current (0.11 mA/cm²).

3. Results and discussion

After trying various voltage windows for the mixture of ZnO and SnO₂, the range 0.02–1.0 V was chosen to optimise cyclability. This result is in accord with previous studies of SnO₂ [15]. As predicted the irreversible capacity loss for both mixtures is about 60% as shown in Table 1 for various milling times. The first initial irreversible and reversible capacities are summarised in Table 1 as well as the initial crystallite size of the mixture calculated from the Scherrer

Table 1

Crystallite size of ZnO and SnO₂ for various milling times, initial capacity and first reversible capacity

Milling time	Crystallite size ± 10 nm		Initial capacity (mAh/g)	First reversible capacity (mAh/g)
	ZnO	SnO ₂		
ZnO	1–5 μm	–	1194	359
ZnO 4 h	69	–	1000	412
SnO ₂	–	1–5 μm	1491	667
SnO ₂ 4 h	–	65	1458	722
ZnO:SnO₂ (1:1)				
Non-milled	1–5 μm	1–5 μm	1207	480
10 h	53	56	1365	521
20 h	52	55	1525	548
30 h	42	43	1184	428
40 h	35	34	1366	436
ZnO:SnO₂ (1:2)				
Non-milled	1–5 μm	1–5 μm	1401	495
22 h	56	50	1532	613
40 h	34	33	1484	577
50 h	36	41	1294	449

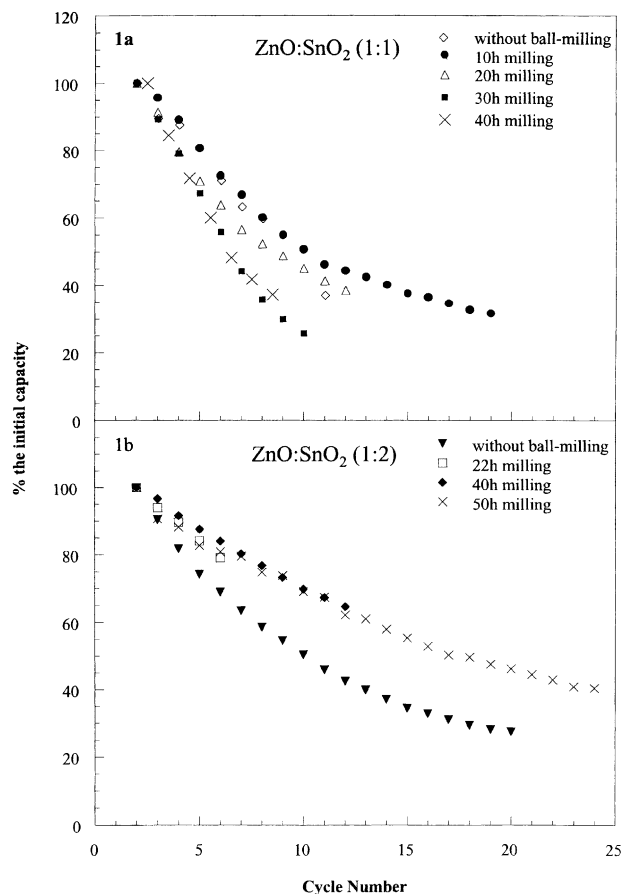


Fig. 1. Percentage of the initial capacity vs. cycle number of the (a) ZnO:SnO₂ (1:1), and (b) ZnO:SnO₂ (1:2) mixtures.

formula using silicon as standard. Although, long milling time reduces crystallite size, this reduction of particle size does not correlate with initial capacities. The normalised capacities versus cycle number of ZnO:SnO₂ (1:1) and ZnO:SnO₂ (1:2) with different milling times are presented in Fig. 1.

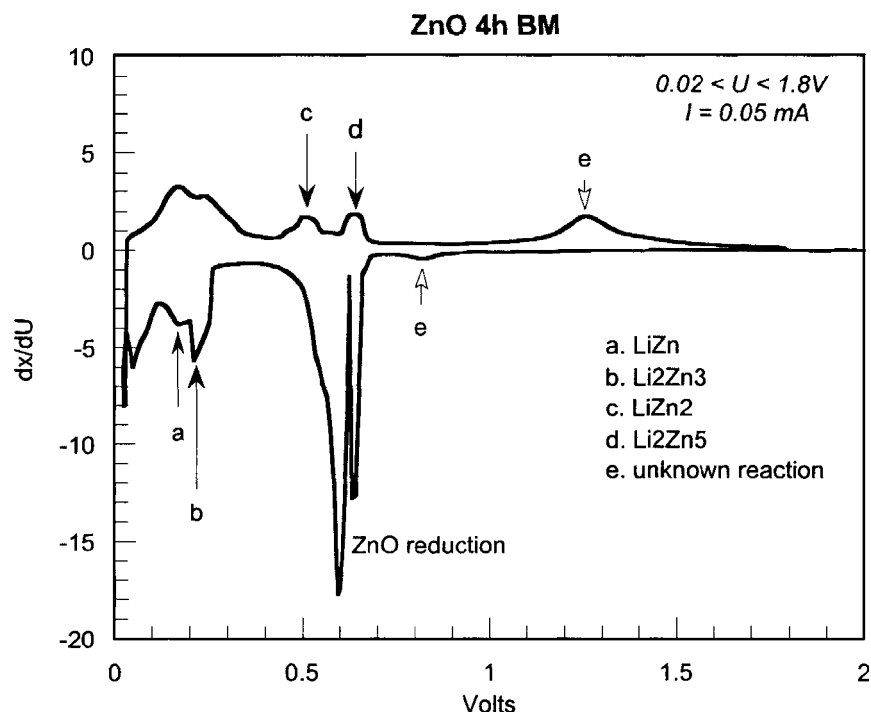


Fig. 2. Derivative of the galvanostatic test of ZnO.

The mixture ZnO:SnO₂ (1:1) in Fig. 1a exhibits an increase in capacity loss during cycling with long milling times. All mixtures show rapid capacity fade with samples milled 30 and 40 h displaying the fastest capacity drop. The non-milled mixture shows a similar capacity fade to 10 and 20 h milling. The rate of capacity drop seems to correlate with the crystallite size (see Table 1). Milling seems to impair cyclability despite improved particle size.

ZnO:SnO₂ (1:2) presents a different behaviour (see Fig. 1b) unlike ZnO:SnO₂ (1:1), milling improves cyclability. There is a significant difference between milled samples and the non-milled sample. The mixture tested without milling gives the worst profile. In this case milling improves the cycle life of the battery as expected. The crystallite size decreases up to 22 h milling and from 22 h the crystallite sizes are stabilised (see Table 1). This observation is in perfect agreement with the behaviour of the capacity decline of the mixture ZnO:SnO₂ (1:2). The capacity drops for 30 and 40 h are identical and higher than 22 h milling. There is no need to ball-mill the oxides for more than 22 h because the particles have reached an optimum point where it is impossible to reduce the particle size further (see Table 1).

Milling improves cyclability of the ZnO:SnO₂ (1:2) mixture but not for the ZnO:SnO₂ (1:1) mixture. The crystallite sizes are similar for both mixtures, therefore, the better cycling behaviour of the milled samples of the ZnO:SnO₂ (1:2) mixture is not connected to crystallite sizes and so must be related to the mixture composition. It seems that decreasing the particle size of SnO₂ by milling enhances cyclability,

however, milling ZnO in the presence of the harder SnO₂ results in a continual decrease in performance.

In order to understand better this phenomenon, we have investigated ZnO more deeply. ZnO seemed to be a good candidate for lithium ion batteries but according to our study, this appears incorrect. Non-milled and milled ZnO cycle very badly with an initial reversible capacity of 359 and 412 mAh/g, respectively, which faded rapidly over the first few cycles. ZnO was charged until 1.8 V to have a complete oxidation and the derivative of the galvanostatic test is shown in Fig. 2. Four different lithium–zinc alloys appear on the graph, LiZn (0.18 V), Li₂Zn₃ (0.24 V), LiZn₂ (0.5 V) and Li₂Zn₅ (0.64 V), which is in agreement with an earlier work done by Fujieda et al. [16] on a zinc alloy electrode. They demonstrated that discharging from Li₂Zn₅ generates possibly irreversible chemical reactions. Morphological changes during the formation of the Li_xZn alloys are quite significant and cause deterioration of the electrode. In Fig. 2 another phenomenon occurs between 0.75 and 1.8 V. The reaction occurs during the first few cycles and then quickly disappears on a similar time scale of the electrode degradation. Possibly this reaction produces a phase, which slows down considerably the lithium transport into the alloys. In order to clarify further the phenomena observed for ZnO, further studies such as in situ XRD and EXAFS are in progress. Initial X-ray analysis of Li inserted samples does indicate a high degree of crystallinity in the zinc alloys and again this may be an important factor resulting in poor performance of the ZnO.

4. Conclusion

ZnO is not a promising material to be used in a lithium-ion cell due to its poor cyclability. For ZnO/SnO₂ composites the presence of ZnO dilutes the SnO₂ and degrades its cyclability. For high SnO₂ contents, milling improves performance due to the reduction in size of the SnO₂ particles, as there is insufficient ZnO to have a major influence on cyclability. Lower SnO₂ contents, allows ZnO to play a more active role in the electrochemistry and so degrades cyclability. This is in contrast to investigations of the inverse spinel compound Zn₂SnO₄ [17] which exhibits considerably better long-term cycling efficiency than the mixed oxides. Clearly when ZnO is mixed with SnO₂ on an atomic scale it degrades cyclability much less.

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