

Letter to the Editors

## Tin oxide–tin composite anodes for use in Li-ion batteries

J. Wolfenstine <sup>a,\*</sup>, J. Sakamoto <sup>b</sup>, C.-K. Huang <sup>b</sup><sup>a</sup> *Geo-Centers, Army Research Laboratory, AMSRL-SE-C / Shady Grove, 2800 Powder Mill Road, Adelphi, MD 20783-1197, USA*<sup>b</sup> *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA*

Received 24 February 1998; revised 24 February 1998

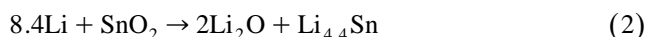
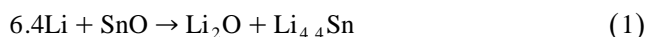
---

*Keywords:* Tin oxides; Composite; Irreversible loss; Li-ion batteries; Phase diagram

---

Currently, SnO and SnO<sub>2</sub> are under evaluation as replacement anodes for coke/graphite in Li-ion batteries [1–7]. They offer the advantages of: (i) higher specific reversible capacity compared to coke/graphite, leading to higher specific energy batteries and (ii) improved safety on repeated cycling, since their potential vs. Li<sup>+</sup>/Li is higher than that for coke/graphite.

It has been observed that as Li is titrated into SnO or SnO<sub>2</sub> the initial reaction involves the decomposition of SnO or SnO<sub>2</sub> into amorphous Li<sub>2</sub>O and metallic Sn [2–6]. With further Li titration a series of Li–Sn binary alloys form, until a final Li–Sn alloy composition of Li<sub>4.4</sub>Sn is reached, as shown by the following reactions:



It has been suggested that the irreversible Li loss is associated with the formation of amorphous Li<sub>2</sub>O during the first charging cycle [3,5–7]. The reversible Li capacity is associated with the alloying/dealloying of Sn. The experimental irreversible Li loss and the reversible Li capacity results for SnO and SnO<sub>2</sub> are in excellent agreement with the predictions of Eqs. (1) and (2), confirming that the irreversible Li loss in SnO and SnO<sub>2</sub> is due to the formation of Li<sub>2</sub>O and the reversible capacity is associated with alloying/dealloying of Sn [5,6].

In addition, it has also been suggested that Li<sub>2</sub>O acts as a binder to insure that the Li–Sn alloys do not suffer mechanical deterioration during repeated charging/discharging [3,5–7]. For example, it has been observed that metallic Sn alone cannot be cycled [3,6]. This is likely a

result that the Li–Sn alloys experience severe volume changes on alloying/dealloying (charging/discharging), which causes the unconstrained alloys to crack apart. Thus, a certain amount of Li<sub>2</sub>O must be present to prevent the Li–Sn alloys from suffering mechanical deterioration during repeated discharging/charging. The problem is; how to reduce the amount of Li<sub>2</sub>O formed during the decomposition of SnO and SnO<sub>2</sub>, yet insure that some is present to provide structural stability during repeated discharging/charging. This letter suggests one possible solution based on the Li–Sn–O ternary phase diagram.

From Eqs. (1) and (2), it is predicted that the irreversible Li loss (Li<sub>2</sub>O formation) for 1 mole of SnO<sub>2</sub> is twice that for 1 mole of SnO for the same reversible capacity (1 mole Li<sub>4.4</sub>Sn). This is in agreement with the experimental results of Courtney and Dahn [6] (1.8) and Huang et. al [5] (2.1). Hence, SnO is preferred over SnO<sub>2</sub> as an anode material. Thus, the remaining discussion will focus on SnO rather than SnO<sub>2</sub>.

An isothermal slice of the pseudo Li–Sn–O ternary phase diagram constructed using thermodynamic data [8–13] at room temperature is shown in Fig. 1. It is a pseudo ternary phase diagram because SnO is a metastable phase at room temperature [12,13]. SnO<sub>2</sub> is not shown on the diagram for clarity. However, the following discussion is applicable to SnO<sub>2</sub> as well. The dotted line connecting Li and SnO represents the titration of Li into SnO. From Fig. 1 it is observed that as Li is initially titrated into SnO, it decomposes to Li<sub>2</sub>O and Sn. Upon further Li addition a series of Li–Sn alloys form with increasing Li content until a final alloy composition of Li<sub>4.4</sub>Sn is reached (Point B). At this point, the SnO starting material is completely decomposed into Li<sub>4.4</sub>Sn and Li<sub>2</sub>O, in agreement with the prediction of Eq. (1). The relative amount of Li<sub>2</sub>O at point B is given by the ratio of DB/DA. As stated earlier, the

---

\* Corresponding author. Tel.: +1-301-721-3428; fax: +1-301-721-3402; e-mail: jeff\_wolfenstine@stinger.arl.mil.

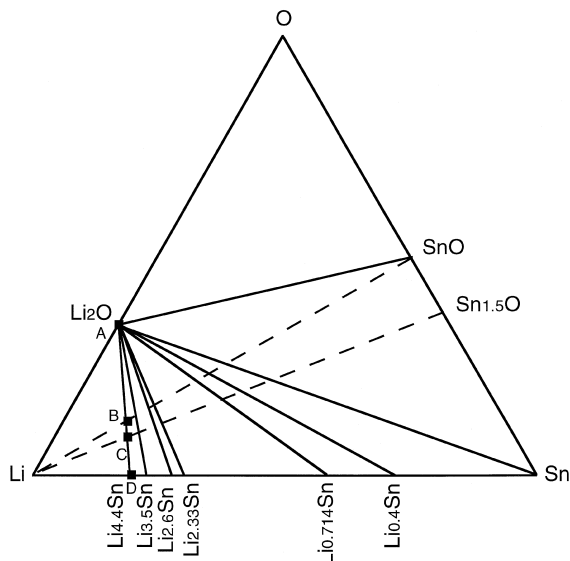
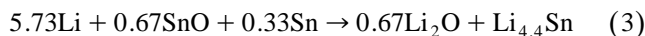


Fig. 1.

problem is how to reduce the amount of  $\text{Li}_2\text{O}$  and still insure that some is present to provide structural stability.

A possible solution based on the Li-Sn-O ternary phase diagram to reduce the amount of  $\text{Li}_2\text{O}$  formed during SnO decomposition is to use a composite composed of SnO and Sn. For example, select a SnO-Sn composite composed of 2/3 SnO and 1/3 Sn (mol%). The overall composition of the composite is  $\text{Sn}_{1.5}\text{O}$  and is shown on the phase diagram between SnO and Sn. The dotted line between Li and  $\text{Sn}_{1.5}\text{O}$  represents the titration of Li into the SnO-Sn (33 mol%) composite. From Fig. 1 it is observed that the same reactions happen for the SnO-Sn (33 mol%) composite as for SnO as Li is titrated into the composite. If enough Li is added to the SnO-Sn (33 mol%) composite it will also decompose entirely into  $\text{Li}_{4.4}\text{Sn}$  and  $\text{Li}_2\text{O}$  (Point C) according to the following reaction, based on one mole of  $\text{Li}_{4.4}\text{Sn}$  formed.



The relative amount of  $\text{Li}_2\text{O}$  in the SnO-Sn (33 mol%) composite given by the ratio of DC/DA is smaller than

that for 100 vol.% SnO (DB/DA). Thus, the SnO-Sn (33 mol%) (Eq. (3)) composite should exhibit a smaller irreversible Li loss compared to SnO (Eq. (1)). Since, the SnO-Sn composites can readily be prepared by simply mixing together fine SnO and Sn powders, it is quite easy to vary the SnO to Sn ratio and determine the ratio that optimizes the irreversible Li loss and also insures structural stability. Current work is underway to determine this optimum ratio.

A potential solution to reduce the irreversible Li loss ( $\text{Li}_2\text{O}$  formation) during the first charging of SnO based on the Li-Sn-O ternary phase diagram is to start with SnO-Sn composites instead of 100 vol.% SnO. This same procedure is applicable to other transition metal oxides that exhibit decomposition reactions with Li, which are under consideration for use as anodes in Li-ion batteries.

## References

- [1] J.S. Sakamoto, C.-K. Huang, S. Surampudi, M. Smart, J. Wolfenstine, *Mater. Lett.* 33 (1998) 327.
- [2] T. Brousse, R. Retoux, U. Herterich, D.M. Schleich, *J. Electrochem. Soc.* 145 (1998) 1.
- [3] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1997) 1395.
- [4] W. Liu, X. Huang, Z. Wang, H. Li, L. Chen, *J. Electrochem. Soc.* 145 (1998) 59.
- [5] C.-K. Huang, J.S. Sakamoto, M.C. Smart, S. Surampudi, J. Wolfenstine, in: D.S. Ginley, D.H. Doughty, T. Takamura, Z. Zhang, B. Scrosati (Eds.), *Materials for Electrochemical Energy Storage and Conversion II—Batteries, Capacitors and Fuel Cells*, Mater. Res. Soc., in press.
- [6] I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 2045.
- [7] I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 2943.
- [8] W.G. Moffat, *The Handbook of Binary Phase Diagrams*, Genium Pub., Schenectady, NY, 1990.
- [9] .
- [10] J. Wang, I.D. Raistrick, R.A. Huggins, *J. Electrochem. Soc.* 133 (1986) 457.
- [11] R.A. Huggins, *J. Power Sources* 22 (1988) 341.
- [12] O. Kubaschewski, C.B. Alcock, *Metallurgical Thermochemistry*, Pergamon, New York, 1979.
- [13] R.A. Swalin, *Thermodynamics of Solids*, Wiley, New York, 1972.