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SnO₂-carbon composites for lithium-ion battery anodes

J. Read*, D. Foster, J. Wolfenstine, W. Behl

Army Research Laboratory, AMSRL-SE-DC, 2800 Powder Mill Road, Adelphi, MD 20783-1197, USA

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Abstract

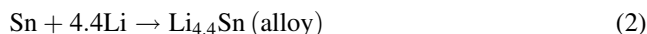
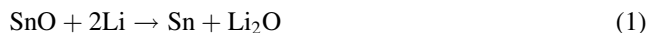
A SnO₂-carbon composite prepared by heat treating a mixture of colloidal SnO₂ and sucrose demonstrated a reversible lithium storage capacity of 680 mA h/g on the 1st cycle. The discharge curve of the composite did not exhibit the 1.0 V plateau characteristic of SnO₂. The high reversible capacity of the composite suggests that lithium is stored in both tin and carbon. The composite demonstrated reduced capacity fade over SnO₂ as well as SnO:graphite and Sn:graphite composites. Published by Elsevier Science B.V.

Keywords: Lithium-ion; Anodes; SnO₂; Composite; Carbon

1. Introduction

Since the introduction of commercial lithium-ion batteries for portable devices in the 1990's, the search for new anode materials to improve energy density has been ongoing. Tin oxide based materials such as SnO, SnO₂, and SnSiO₃ have been identified as possible candidates for next generation anode materials since they have demonstrated improved lithium storage capacity over carbon [1]. These materials can theoretically store lithium at capacities of up to 876 mA h/g (e.g. SnO), a significant improvement over the 372 mA h/g provided by graphite.

Tin oxide reacts with lithium in a two step process as follows [2]:



The first step in the reduction of SnO results in the formation of nanometer sized tin regions dispersed within a Li₂O matrix. The second step is a lithium alloying step that provides the reversible lithium storage capacity of these materials.

The lithium-alloying step causes a large volume change in the Sn regions. The Li₂O matrix prevents these tin regions from cracking. As this material is cycled, the tin regions aggregate into larger and larger regions. The Li₂O matrix slows the aggregation process but does not prevent it [3]. When the tin regions become too large they cannot

withstand the volume change and cracking occurs, resulting in a loss of capacity.

Courtney et al. [3] demonstrated that if the tin regions are small enough initially and if they are prevented from aggregating, capacity fade is reduced. Courtney used “spectator ions” (e.g. B₂O₃, P₂O₅) that do not undergo lithium alloying to create a dilution effect and keep the tin regions small. These spectator ions are similar to the Li₂O formed in reaction (1) above.

Several authors have combined tin or tin oxide with graphite in an attempt to reduce capacity fade [4,5]. The approach has been to prevent the tin from becoming electrically disconnected through the use of a conductive graphite matrix. The composites in these studies still show significant capacity fade that could be attributed to the tin component of the material.

Our approach is unique in that we use carbon as a diluent in place of the oxides to prevent tin agglomeration. We use a hard carbon that is less dense than either B₂O₃ or P₂O₅, meaning that less weight percent carbon is required to get the same dilution effect. The hard carbon has pores that can trap tin oxide particles. The hard carbon can also reversibly store lithium.

To use carbon as a diluent, we disperse 150 Å particles of SnO₂ in a hydrocarbon precursor, then carbonize the precursor to form a hard carbon. We mix the SnO₂ and hydrocarbon in a ratio that, upon carbonization, will give us a composite that is less than 25 vol.% SnO₂. A low volume percent of SnO₂ particles should mean that individual particles are isolated from each other and hence, agglomeration of Sn should be difficult. With the high density of SnO₂ (6.95 g/cm³) and the low density of the hard carbons

* Corresponding author. Tel.: +1-301-394-313; fax: +1-301-394-273.
E-mail address: jeffrey_read@mail.arl.mil (J. Read).

we are using (1.8 g/cm^3), we can produce composites that are greater than 50 wt.% SnO_2 yet <25 vol.% SnO_2 . Our approach is unique to that used by Lee et al. [4] and Dayal [5] in that we: (i) use a hard carbon as diluent, (ii) have a more uniform distribution of SnO_2 in carbon than could be obtained by mechanical milling, and (iii) can control the SnO_2 particle size in the composite precisely. The SnO_2 particles are trapped and separated by the carbon, not just mechanically mixed with or dispersed on carbon, as with previous studies [4,5].

2. Experimental

The composite was prepared by mixing a 15 wt.% aqueous colloidal suspension of SnO_2 (Alfa Aesar), average particle size 150 Å, with ACS grade sucrose powder (Fisher) in a weight ratio such that after carbonization of the sucrose a 52:48 wt.% SnO_2 -carbon composite should result. The sugar is added to the colloidal suspension and the mixture stirred until the sugar dissolves. The water is removed under vacuum at 70°C . The vacuum dried powder is ground and then heated in air at 185°C for 15 h to de-water the sugar. The material is ground again then heat treated in a quartz tube under flowing ultra high purity (UHP) grade argon (<5 ppm O_2) as follows: (1) $20 \rightarrow 225^\circ\text{C}$ at 30°C/min ; (2) $225 \rightarrow 450^\circ\text{C}$ at 1°C/min ; (3) $450 \rightarrow 600^\circ\text{C}$ at 30°C/min ; (4) hold at 600°C for 15 min and (5) rapid cooling to 20°C . This heat treatment procedure closely follows that used for preparing hard carbons from sugar precursors [6,7]. As discussed in the results section, X-ray powder diffraction and thermogravimetric analysis (TGA) established that heat treating the vacuum dried powder to 600°C produced a SnO_2 -carbon composite while heat treating to higher temperatures resulted in a reduction of the SnO_2 to Sn. The heat treatment was, therefore, limited to 600°C for this study.

Anode electrodes were prepared by coating acetone slurries of the SnO_2 -carbon composite (20 wt.%), Super P carbon black (5 wt.%), Kynar 2801 (37.5 wt.%), and dibutyl phthalate “DBP” (37.5 wt.%) on a glass plate. The electrodes were dried to an average thickness of 175 μm . Cathode electrodes were prepared in a similar fashion using Chemetals LiMn_2O_4 spinel (56 wt.%), Super P carbon black (6 wt.%), Kynar 2801 (18 wt.%), and DBP (20 wt.%). A low weight percent of the SnO_2 -carbon composite was used in the anode electrode because the capacity of the anode was expected to be 1200 mA h/g or greater and the anode was to be matched to a spinel cathode which provides only 120 mA h/g.

Cells for cycling studies were built by laminating SnO_2 -carbon anodes to copper grids and LiMn_2O_4 cathodes to aluminum grids. The anode was laminated to the cathode using a PVDF/DBP/Silica separator. A nickel tab was used for the anode collector and an aluminum tab for the cathode collector. The cells were designed to be anode limited based on an assumed 1st discharge capacity of 1200 mA h/g. The

cells were placed in a solvent to extract the DBP and dried under vacuum for 2 h at 105°C . Cells were taken into a <1 ppm moisture and <1 ppm O_2 dry box and soaked in 1 M LiPF_6 ethylene carbonate:dimethyl carbonate (2:1 by weight) electrolyte. A lithium reference electrode was mounted on the backside of the anode and the cells were then sealed in foil laminate bags for cycle testing.

For X-ray studies, SnO_2 -carbon electrodes were laminated to copper grids, placed in a solvent to extract the DBP, dried in air, then the powder diffraction pattern was recorded. The electrodes were then re-dried under vacuum for 2 h at 105°C . Two electrode cells with a lithium electrode, Celgard 2300 separator, and 1 M LiPF_6 EC:DMC (2:1 by weight) electrolyte were built and put on test. After 1 charge/discharge cycle, the SnO_2 -carbon electrode was removed from the cell, washed with DMC, and then the powder diffraction pattern collected.

Cycling studies were carried out on a MACCOR Series 4000 tester. X-ray spectra were collected on a Phillips PW1840 powder diffractometer with a Fe tube. The X-ray spectra were converted to $\text{Cu K}\alpha_1$ spectra for presentation. TGA was carried out on a Perkin-Elmer Series 7 Analyzer under UHP grade argon. Chemical analysis for Sn was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Scanning electron microscopy (SEM) was used to characterize the morphology of the heat treated powders.

3. Results and discussion

Fig. 1 shows the evolution of the X-ray powder pattern upon successive heating of the composite to a final temperature of 1050°C . The upper temperature was chosen because it gives the best hard carbon in terms of the compromise between reversible and irreversible lithium storage capacity [6,7]. Upon heating from room temperature to 600°C , the diffraction pattern remains that of SnO_2 , but with broad diffraction peaks. The particle size for the 600°C

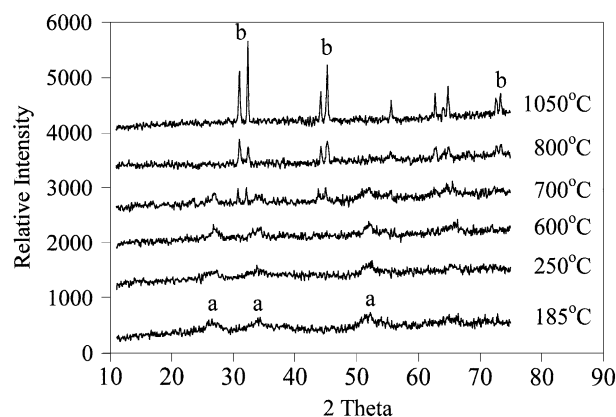


Fig. 1. X-ray powder patterns of the SnO_2 -carbon composite upon successive heating: (a) SnO_2 and (b) Sn.

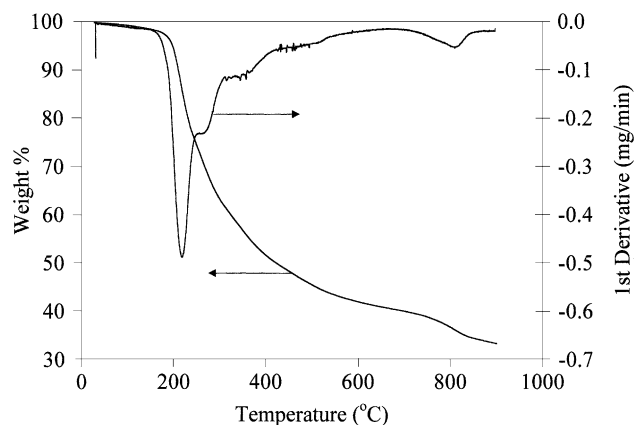


Fig. 2. TGA of the 32:68 SnO₂-sugar composite at a 10°C/min ramp rate.

heat treated composite calculated using the Scherrer formula is 45 Å and supports the assumption that the SnO₂ is in the form of small particles. Upon heating to 700°C, Sn is observed to form and is present in the sample along with SnO₂. At 800°C all of the SnO₂ has been converted to Sn. Subsequent heating to 1050°C sharpens the Sn diffraction lines indicating that small regions of Sn are coalescing into larger regions of Sn and giving more intense diffraction lines. SEM of both the 700 and 1050°C materials confirm the presence of Sn as spheres, 1–5 μm in diameter on the surface of the particles.

Fig. 2 shows the TGA at a ramp rate of 10°C/min on the vacuum dried powder before the de-watering step at 185°C. The vacuum dried powder is 32% SnO₂ and 68% sucrose. The TGA shows five peaks from 25 to 900°C. By correlating the X-ray data in Fig. 1 to the TGA, it was determined that the first four peaks at 225, 278, 364, and 502°C are associated with sugar decomposition and carbonization while the 5th peak at 830°C is the result of SnO₂ reduction to Sn by carbon. The TGA and X-ray data indicates that heating the vacuum dried powder at 600°C should produce a SnO₂-carbon composite where the sugar has been converted to carbon and no reduction of SnO₂ has occurred.

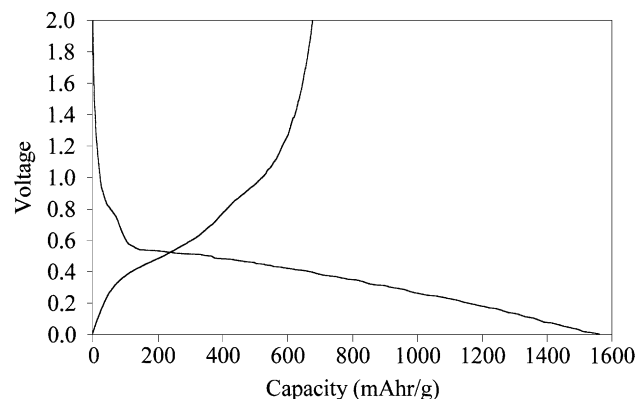


Fig. 3. 1st discharge and 1st charge curves of the SnO₂-carbon composite at 0.02 mA/cm².

Chemical analysis using ICP-OES determined that the 600°C heat-treated composite was 44 wt.% Sn. This corresponds to a composite containing 56% SnO₂, in close agreement with the 52% calculated from the initial mix. Assuming a density for the carbon component of 1.8 g/cm³, the volume percent SnO₂ is calculated to be 24.7%.

Fig. 3 shows the 1st discharge and charge of the SnO₂-carbon composite versus Li at 0.02 mA/cm² between 0 and 2.0 V. The discharge shows a small plateau at 0.8 V with a sloping discharge between 0.5 and 0 V. The discharge curve does not show the large 1.0 V plateau characteristically seen for SnO₂. The 1.0 V plateau has been identified with the formation of Li₂O and Sn upon initial discharge [2]. The 1st discharge capacity of 1560 mA h/g and 2nd discharge capacity of 680 mA h/g are in excellent agreement with values calculated by adding the individual capacities of SnO₂ and sugar carbon. Table 1 shows the capacity of our composite compared to other tin based materials as well as the sugar based carbon. From Table 1 it is observed that the 2nd discharge capacity for the SnO₂-carbon composite is between that of SnO₂ and the sugar carbon and twice that of graphite. The discharge capacity is also significantly higher than that of the Sn:graphite or SnO:graphite composites.

Table 1
Observed and calculated capacities of Sn based anode materials

Material	Observed capacity (mA h/g)		Calculated capacity (mA h/g)		Notes ^a	Reference
	1st discharge	2nd discharge	1st discharge	2nd discharge		
Sn	800	–	994	994	1	[2]
SnO	1200	825	1274	876	2	[2]
SnO ₂	1450	650	1494	783	3	[2]
Graphite	403	300	372	372	4	[4]
Sn:graphite (44:56)	590	510	644	644	5	[5]
SnO:graphite (30:70)	1020	570	642	458	6	[4]
Sugar carbon	1148	764	–	–	7	[6]
SnO ₂ -carbon	1560	680	1317	700	8	This work

^a (1) Calculated capacities based on alloying 4.4 Li per Sn; (2) calculated capacities based on Li₂O formation and alloying 4.4 Li per Sn; (3) calculated capacities based on Li₂O formation and alloying 4.4 Li per Sn; (4) calculated capacities based on the formation of LiC₆ intercalate; (5) calculated capacities based on alloying 4.4 Li per Sn and the formation of LiC₆ intercalate; (6) calculated capacities based on observed SnO and KS-6 capacities; (7) sugar carbon heat treated at 600°C under argon; (8) 56:44 wt.% SnO₂-carbon composite. Calculated capacities based on observed SnO₂ and sugar carbon capacities.

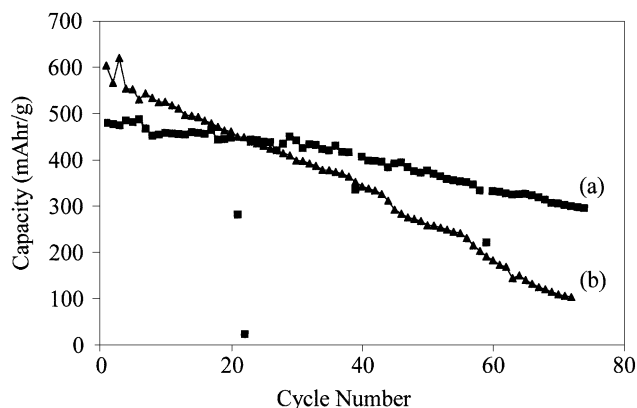


Fig. 4. Cycling of the SnO₂-carbon composite between (a) 0 and 1 V and (b) 0 and 2 V.

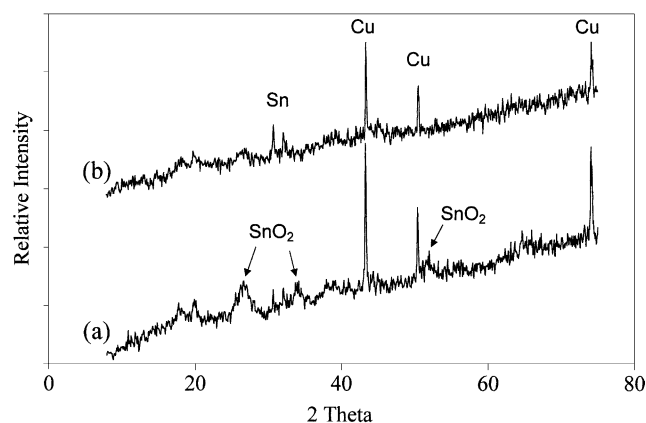


Fig. 5. X-ray powder pattern of the SnO₂-carbon composite electrode (a) before cycling and (b) after cycling.

Table 2
Cycling of Sn based anode materials

Material	Cycling range (V)	Initial capacity (mA h/g)	Capacity retained at cycle (%)				Reference
			10	20	30	40	
SnO	0.8–0.1	550	78	55	42	32	[3]
SnO	2.0–0.0	875	71	57	46	–	[4]
SnO ₂	1.3–0.2	525	88	79	70	63	[8]
SnO ₂	1.0–0.0	570	90	84	75	68	[9]
Sn:graphite (28:72)	1.0–0.0	455	82	76	75	69	[5]
Sn:graphite (44:56)	1.0–0.0	510	84	63	54	–	[5]
SnO:graphite (14:86)	2.0–0.0	480	90	–	83	–	[4]
SnO:graphite (30:70)	2.0–0.0	570	80	–	–	–	[4]
SnO ₂ -carbon	2.0–0.0	604	87	76	66	57	This work
SnO ₂ -carbon	1.0–0.0	480	95	93	90	83	This work

Fig. 4 shows the cycling characteristics of the SnO₂-carbon composite over 70 cycles at 0.06 mA/cm². Two different cycling voltages are used to evaluate the composite material and its ability to cycle over a wide voltage range. Courtney et al. [2] has shown that capacity fade is not only a function of the dilution effect but also cycling voltage. From Fig. 4, it is obvious that higher charge voltage results in increased capacity fade. The sensitivity of this material to cycling voltage is similar to that seen for SnO₂ [8].

Table 2 compares the cycling behavior of our composite to other Sn based materials [9]. The capacity fade of our composite evaluated at 40 cycles shows a clear improvement over SnO and SnO₂. Our composite retains 83% of its initial capacity at 40 cycles when the voltage is limited between 0.0 and 1.0 V. When compared to other Sn:graphite or SnO:graphite composites of similar Sn content over the same cycling voltage range, our composite shows superior capacity fade characteristics. This improvement is most likely a result of the ability of hard carbon to act as a diluent.

Fig. 5 shows the change in the X-ray powder pattern of a SnO₂-carbon electrode upon cycling. Before cycling (a) only peaks from SnO₂ are seen. After cycling between 5 mV and 2.0 V (b) the intensity of the SnO₂ peaks are greatly dimin-

ished and Sn peaks are exhibited. This supports the theory that SnO₂ is reduced to Sn and Li₂O [2]. Diffraction from the copper current collector can be seen at 43, 50, and 74° 2θ.

4. Conclusions

Heat treating a mixture of colloidal SnO₂ and sucrose at 600°C produces a composite that can reversibly store lithium. The shape of the discharge curve on the 1st cycle is significantly different than that seen for SnO₂ alone, suggesting that the carbon material affects the potential at which the SnO₂ reacts. The X-ray data on cycled electrodes confirms that the SnO₂ in the composite is being reduced to Sn. A reversible capacity of 680 mA h/g was observed for a 56 wt.% composite of SnO₂ and sugar carbon. This is between that of SnO₂ and a sugar carbon and twice that of graphite. The hard carbon material is providing a significant portion of the lithium storage capacity seen in the composite.

The fade behavior of the SnO₂-carbon composite is improved over SnO₂ alone and better than other Sn:graphite or SnO:graphite composites as a result of incorporating

SnO₂ in a hard carbon network. The voltage dependence of the fade is still present. Further work is needed to minimize capacity fade in this composite material with variations in SnO₂ to carbon ratio, carbon precursors, SnO₂ particle size, and heat treatment procedures.

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