Mesoporous tin oxides as lithium intercalation anode materials

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Abstract

Mesoporous tin oxides have been prepared by a surfactant templating method. Characterization with transmission electron microscopy techniques showed that the compounds formed as hexagonal mesoporous phases, retaining their mesostructural nature with a pore size of about 4 nm after calcination at 350 °C. These materials showed good electrochemical performance as anode materials for lithium ion batteries, with over 400 mAh/g charge capacity and good reversibility. © 2002 Published by Elsevier Science B.V.

1. Introduction

The discovery of ordered mesoporous silica by scientists at Mobil Corporation [1] was followed by attempts to synthesize mesoporous metal oxides. Much of the initial work was motivated by the potential use of these materials as catalysts because of their three-dimensional, framework structures consisting of a regular, well-defined pore or channel system with pore sizes between 2 and 20 nm. Early examples of mesoporous metal oxides include the oxides of antimony [2], tungsten [2], tin [3], titanium [3], and lead [4], all of which were prepared as biphasic composites with the templating surfactant. However, removal of the organic template led to the collapse of the mesoporous structure.

The tin oxide materials are of particular interest because of their applications in gas sensors, optical electronic devices and lithium ion batteries, in addition to their possible catalytic properties. The utilization of mesoporous tin oxide for such applications requires a stable mesoporous structure with no surfactant present. Ulaggappan and Rao [3] used an anionic surfactant as a templating agent to obtain mesoporous tin oxide with an average pore size of 3.2 nm which was stable to 400 °C. Chen and Liu [5] have explored both neutral and electrostatic templating approaches to prepare mesoporous SnO_2. After calcination at 500 °C, the mesoporous structure was still retained with an average *d* spacing of 3.4 nm.

2. Experimental

In this work we used an anionic surfactant, sodium dioctylsulfosuccinate, AOT, as a templating surfactant. Tin acetate Sn(II) and $SnCl_4$ were selected as starting tin sources in an attempt to prepare mesoporous Sn(II) and Sn(IV) oxides, respectively. Because Sn(II) and Sn(IV) occur as cationic species in solution and polymerize to a tin–oxygen network between pH = 4 and 8.5, HCl was added to bring the solution to pH = 8. The molar ratio of $Sn:AOT:H_2O$ was 1:1:500. The gel obtained using these procedures was then stirred for 72 h at room temperature to promote crystallization. After aging for 2 days, the water was decanted. The solid product was filtered, washed with distilled water and air-dried at 100 °C. The surfactant was removed by calcination at 350 °C for 6 h in a flowing N_2 atmosphere or air atmosphere.

For electrochemical investigation, the samples were ground and composites were formed by mixing each sample with 10% each of acetylene black as a conducting agent and polyvinylidene fluoride (PVDF) powder as a binder. After *N*-methyl-2-pyrrolidone (NMP, Aldrich) was added to the powder and further ground to form a slurry, the mixture was spread on a copper foil. The electrode was then dried under vacuum at 100 °C for 12 h. Typical loading of the active material in the electrode was about 10 mg/cm². The anode performance of the material was studied in a two-electrode test cell using lithium metal as the counter electrode. A microporous film (Celgard 2400, Hoechst Celanese) was used as a separator and the electrolyte was 1 M $LiPF_6$ in EC/DEC (Merck). Cell assembly was carried out in a dry box under an argon atmosphere. The cell was cycled at a

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constant current density from 0.1 to 1 mA/cm^2 on a battery testing system (Arbin Instruments, model 2043). The cut-off voltage was typically from 0 to 1.4 V versus Li/Li$^+$.

Raman scattering spectra were recorded on an I.S.A. Jobin-Yvon T64000 in the triple subtractive mode with a scan time of 16 s and 10 accumulations using a 180° scattering geometry. The 514 nm line of an argon laser operating at 300 mW was used for excitation. However, evidence of some thermal damage to the mesoporous SnO$_2$ sample under this power level was observed. Therefore, the Raman spectrum of a fresh sample was measured at an excitation power of 50 mW, with no damage apparent.

3. Results and discussion

The mesoporous morphology of the compounds was confirmed by transmission electron microscopy (TEM) using a JEOL JEM-2000FX system. Samples prepared from both Sn(II) and Sn(IV) starting materials yielded mesoporous phases as indicated by TEM measurements. Although, we will continue to refer to the mesoporous SnO samples, it is clear that a significant fraction of the Sn(II) has been transformed into Sn(IV) in these samples. A typical TEM picture of SnO$_2$ is shown in Fig. 1. The mesoporous structure apparent in the TEM observations showed an average pore spacing of about 4.6 nm. After calcination, the mesoporous structure was retained but the pore spacing decreased to about 3.3 nm.

Fig. 2 shows the initial charge–discharge curve of the sample prepared as SnO (and calcined in air) cycled at a constant current of 0.2 mA/cm^2 over the voltage range of 0–2.0 V. The charge–discharge profiles were similar to those of SnO$_2$ as reported in the literature [6]. The discharge curve can be divided into three parts: a plateau at 1.4 V, another
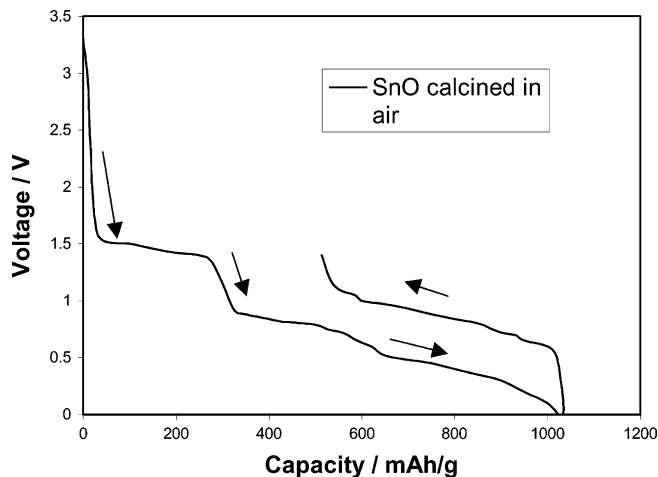
Fig. 2. Initial charge–discharge profile of an electrode prepared with mesoporous SnO calcined in air.

plateau at 0.9 V, and a monotonous decrease to 0 V. However, the charge process appears to result from a two-phase reaction. Therefore, the reaction mechanism(s) for lithium intercalation and de-intercalation in the tin oxide mesoporous hosts appear to follow the equations given by Coutney and Dahn [6]. In that mechanism, discharge is described as a reduction of the tin oxide and lithium ion to lithium oxide and metallic tin, accompanied by an alloying of the tin with lithium. The formation of the lithium oxide and metallic tin is an irreversible reaction responsible for the irreversible capacity in these systems. The charge process is an oxidation of lithium in the lithium–tin alloy to form lithium ion.

The initial charge–discharge behavior of several tin oxide samples is summarized in Table 1. The capacity loss for the first cycle of SnO$_2$ was 520 mAh/g (48%), for SnO calcined in air the corresponding value was 414 mAh/g (40%) and for
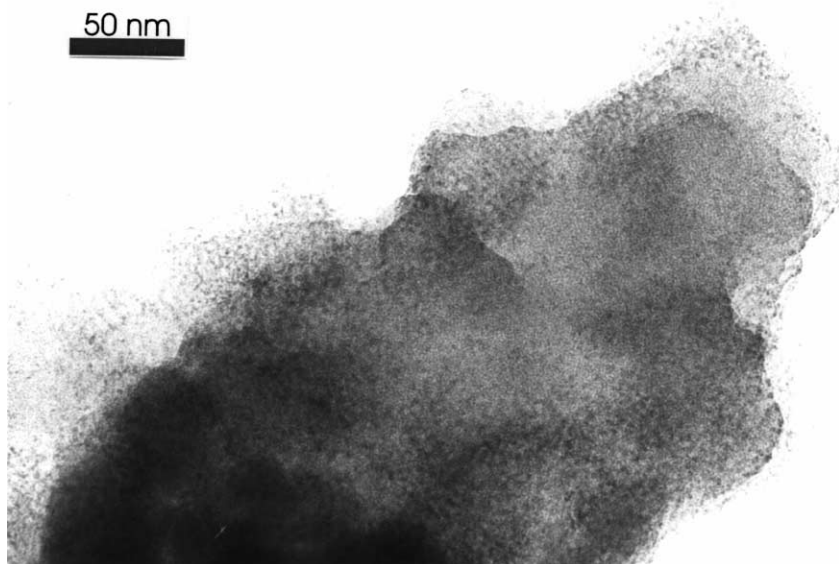
Fig. 1. TEM image of a typical mesoporous SnO$_2$ sample with a pore spacing of about 3.3 nm.

Table 1
Initial charge–discharge data for several Sn–O mesoporous compounds

Sample	First discharge (mAh/g)	First charge (mAh/g)	Irreversibility (irreversible capacity/discharge capacity) (%)
SnO_2	1080	560	48
SnO (calcined in air)	1034	620	40
SnO (calcined in N_2)	890	535	39

SnO calcined in an N_2 atmosphere the loss was 355 mAh/g (39%). The discharge behavior of the SnO_2 and SnO samples calcined in air was quite similar, which may well be due to the formation of SnO_2 when SnO was calcined at 500 °C in air. However, the discharge behavior of the SnO calcined in N_2 was somewhat different, in that the first discharge capacity was lower than those of SnO_2 and SnO calcined in air. Although, the discharge mechanism may slightly depend on differences in the initial materials produced in the two kinds of calcination atmospheres, the final reaction product may well be the same when discharged to 0 V versus Li/Li$^+$. These data suggest that some of the Sn(II) is transformed into Sn(IV) during the matrix preparation process, probably the calcination step.

To examine the possibility that some of the Sn(II) transformed into Sn(IV) during the calcination of the mesoporous material prepared as SnO, Raman vibrational spectra of the tin oxide materials were measured. Fig. 3 compares the Raman spectra of the SnO and SnO_2 mesoporous matrices, and pure microcrystalline SnO_2. The dominant feature in the spectrum of all three samples is the band at about 630 cm^{-1}, which has been assigned to the A_{1g} symmetric Sn–O stretching mode in pure crystalline SnO_2 [7]. This relatively sharp band is superimposed on a very broad feature extending from about 700 cm^{-1} down to about 400 cm^{-1} and is evident
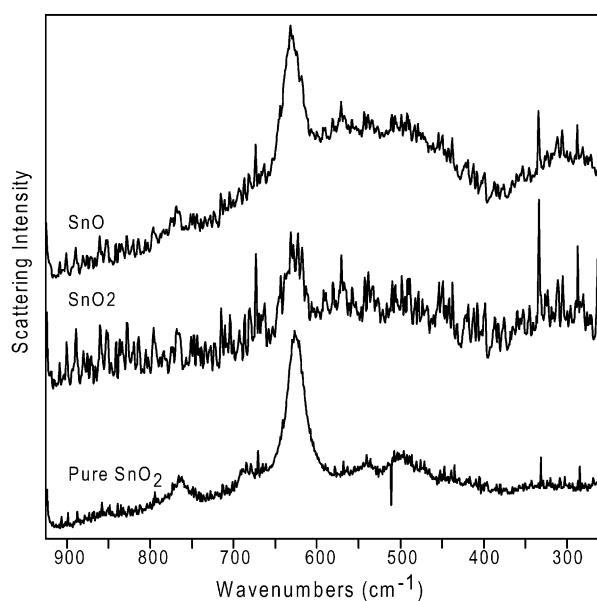
in both mesoporous samples. Also apparent in the spectra of the matrices is another broad feature beginning at about 350 cm^{-1} and extending down to about 250 cm^{-1}. There have been a number of spectroscopic studies of nanocrystalline SnO_2 that have interpreted the spectra in terms of volume or bulk modes, and surface modes [7–11]. Although, these studies refer specifically to SnO_2 in the cassiterite structure, space group D_{4h}^{14}, there are several conclusions to be drawn from these studies that can be applied to our spectra of the mesoporous tin oxide materials. Ocana et al. [10] have pointed out that all of their spectra of nanocrystalline SnO_2 consist of bands that correspond to the cassiterite structure and "a variable number of broad features with variable intensity in the region 600–300 cm^{-1}". In another Raman study, Abello et al. [11] found that new bands appear as the crystallite size decreases, rather than the band-width of existing bands increasing with decreasing size. Applying the observations of these papers and the conclusions therein to our spectra of the mesoporous materials, we suggest the following interpretation. The spectra shown in Fig. 3 contain a contribution from the Sn–O stretching vibrations of Sn–O units in the interior of the wall framework in which the local oxygen environment of the Sn atoms defines a distorted octahedron, similar to that of the bulk cassiterite structure. This vibrational motion is responsible for the relatively sharp band at 630 cm^{-1}. There is a second contribution from Sn–O units in the walls of the framework leading to the broad bands.

As can be seen in Fig. 4 and Table 1, the cycling behavior of these materials showed good reversibility. Several trends
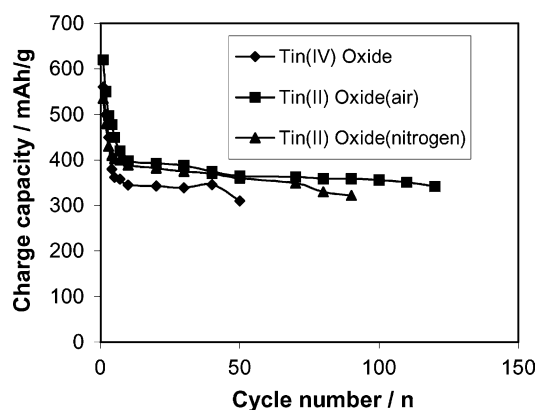

Fig. 3. Raman scattering spectra of microcrystalline SnO_2 and mesoporous tin oxide prepared as SnO and SnO_2.

Fig. 4. Cycling behavior of three mesoporous tin oxide samples at a current density of 0.2 mA/cm^2 and a cut-off voltage range of 0–1.4 V vs. Li/Li$^+$.
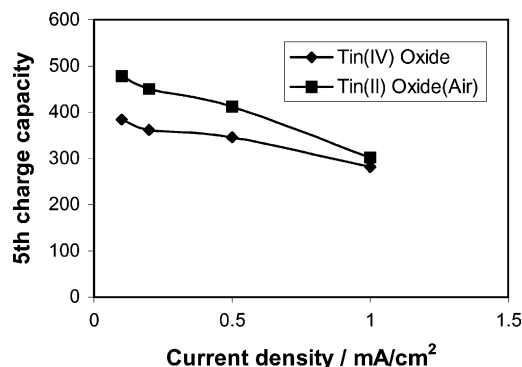
Fig. 5. Rate capacity of two mesoporous tin oxide samples at a cut-off voltage range of 0–1.4 V vs. Li/Li$^+$.

can be recognized in these samples. The sample prepared as mesoporous SnO calcined in an N$_2$ atmosphere exhibited the least capacity loss, while mesoporous SnO$_2$ and SnO calcined in air showed better reversibility. When the capacity reached 350 mAh/g, the SnO calcined in air showed a very good cyclability. Even at the 110th cycle, the charge capacity was over 300 mAh/g which is a good specific capacity and cyclability compared with the existing carbon materials [12] and crystalline SnO$_2$ powders [6].

The rate capacity behavior of two mesoporous tin oxides is illustrated in Fig. 5. The electrodes were cycled at a constant current density from 0.1 to 1 mA/cm^2 over a voltage range of 0–1.4 V. In general, the materials showed good capacity retention. At a current density of 1 mA/cm^2 (approximately C/2 rate), both of the materials had a capacity of 280 mAh/g.

4. Conclusions

Pure mesoporous tin oxides were prepared by a surfactant templating method following literature procedures. Although samples were prepared both as Sn(II)O and Sn(IV)O$_2$, electrochemical measurements and Raman spectroscopic studies argue that a significant amount of Sn(II) was converted to Sn(IV), presumably in the calcination step. Electrochemical characterization showed that the initial discharge and charge capacity, capacity loss and reversibility of the mesoporous samples depended somewhat on the calcination atmosphere used to remove the template. This probably reflects subtle differences in the structure or

composition of the host matrix after calcination. It is interesting to note from the data in Table 1 that the two samples prepared as SnO yielded a somewhat lower irreversibility loss than the sample prepared as SnO$_2$.

The Raman spectra of the samples are interpreted in terms of "bulk" modes similar to those of the cassiterite phase of SnO$_2$ and vibrations of Sn–O units in the surfaces of the mesoporous framework. The electrochemical performance of these materials is comparable to carbon-based intercalation anode materials. These data indicate that the mesoporous tin oxide host framework provides good intercalation pathways for lithium ions and is robust with respect to lithium intercalation and de-intercalation reactions. Consequently, there may be potential applications for mesoporous tin oxides as anode materials in lithium ion batteries.

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