

Nanostructured tin for use as a negative electrode material in Li-ion batteries

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Abstract

A series of mesoporous tin samples have been prepared by means of a liquid crystal templating method. TEM images and X-ray diffraction data show the mesoporosity and the scale of the repeat structure. The lithium insertion and extraction behaviour of liquid crystal templated films were compared with those obtained from non-templating electrolytes. It was found that the templated films showed higher extraction capacities, which were attributed to the ability of mesoporous tin to expand and contract with less structural degradation than nonporous tin. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The use of lithium metal in rechargeable lithium batteries has been questioned on grounds of safety and cycle efficiency. Binary [1–3] and ternary [4,5] lithium alloys have been considered as replacements for metallic lithium in rechargeable lithium cells as they are expected to be inherently safer. In addition, binary alloys may offer a higher gravimetric charge density than the other common alternatives to lithium metal; graphite and coke [6]. Various ‘high-capacity’ carbons have been demonstrated [7–10] but these tend to exhibit a large hysteresis in the charge/discharge behaviour, and hence low energy efficiency, under practical cycling conditions [11,12].

Lithium alloys extensively with tin, to a limiting stoichiometry of $\text{Li}_{22}\text{Sn}_5$ [19], which corresponds to a specific capacity of 991 mAh g^{-1} . This is considerably higher than those of graphite and coke, which are 372 mAh g^{-1} and $\sim 200 \text{ mAh g}^{-1}$, respectively [13,14].

There have been several recent studies on the lithium–tin system [1,15–19]. From these it has been observed that tin with particles of $0.2\text{--}0.4 \mu\text{m}$ exhibited a greater retention of extraction capacity over many cycles than particles of $2.0\text{--}4.0 \mu\text{m}$ or compact specularly reflective deposits

[18,20]. Finely dispersed tin formed in situ by the reaction of lithium with SnO_2 or SnO [21–26] has also been found to retain a high extraction capacity over many cycles. However, during the first half-cycle a relatively large amount of charge is passed irreversibly in the reduction of the tin oxides to tin and Li_2O .

The observation that electrodes composed of larger tin particles lose capacity relatively rapidly has been explained in terms of a ‘pulverisation’ process. Tin expands by as much as 259% on insertion of lithium [24]. This expansion and subsequent contraction, on removal of lithium, causes disintegration of the structure, with corresponding capacity loss. The ‘pulverisation’ is less extensive in smaller particles or if the degree of expansion is limited by reducing the extent of intercalation [24]. Therefore it was postulated that a nanostructured, porous tin electrode may reduce the extent of pulverisation. Hence, mesoporous (pores with diameters in the range $2\text{--}50 \text{ nm}$) tin may offer the benefits of high cycle life observed for finely dispersed tin in Li_2O , without the high first cycle irreversible capacities associated with reduction of the tin oxide to tin.

Silica may be produced by hydrolysis of silicon alkoxides in a sol–gel reaction. It has been demonstrated that by performing reactions of this type in a lyotropic liquid crystal (based on polyoxyethylene ethers) the resulting silica could be formed with a variety of nanostructures [27,28]. The structure of the silica formed was found to

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resemble the initial structure of the aqueous component of the liquid crystal. More recently nanostructured platinum has been produced by electrodeposition from a polyoxyethylene ether liquid crystal electrolyte [29]. However, the formation of mesoporous tin has not previously been documented in the literature. The object of this work was to synthesise mesoporous tin and to compare the lithium cyclability with other forms of tin.

2. Experimental

2.1. Templating electrolytes

Two polyoxyethylene ether surfactants were used in this study, octaethylene glycol monohexadecyl ether ($C_{16}EO_8$, > 98% Fluka) and Brij 76 (which is a mixture of polyoxyethylene ethers with an average composition of $C_{18}EO_{10}$, Aldrich). The surfactants were mixed with acidic aqueous solutions of $SnSO_4$ to form lyotropic liquid crystal phases. Further lyotropic templating electrolytes, containing *n*-heptane in addition to the components listed previously, were used. It was expected that the *n*-heptane would be incorporated into the oleophilic interiors of the polyoxyethylene ether liquid crystalline phase, increasing the radii of the liquid crystalline phase and hence the pore size in any templated electrodeposit.

The concentrations of surfactant, aqueous solution and *n*-heptane were chosen such that a hexagonal (H_1) phase of the lyotropic liquid crystal was formed, as verified from the characteristic optical textures when viewed through a polarising microscope [30].

The first templating electrolyte, T1, consisted of 50 w/o $C_{16}EO_8$, 50 w/o of an aqueous solution of 0.15 M $SnSO_4$ and 0.6 M H_2SO_4 . The second templating electrolyte, T2, consisted of 50 w/o $C_{18}EO_{10}$, 50 w/o of an aqueous solution of 0.5 M $SnSO_4$ and 0.3 M H_2SO_4 . T3 consisted of 5 w/o *n*-heptane, 48 w/o $C_{16}EO_8$ and 47 w/o of an aqueous solution of 0.15 M $SnSO_4$ and 0.6 M

H_2SO_4 . T4 consisted of 3.5 w/o *n*-heptane, 46.5 w/o $C_{18}EO_{10}$ and 50 w/o of an aqueous solution of 0.5 M $SnSO_4$ and 0.3 M H_2SO_4 .

Although the $C_{16}EO_8$ electrolytes (T1 and T3) were used at room temperature ($22 \pm 2^\circ C$) cells containing the $C_{18}EO_{10}$ electrolytes (T2 and T4) required heating to $45^\circ C$ in order to improve ionic conductivity and ensure that the $SnSO_4$ was completely dissolved. It was observed that a pale yellow precipitate formed gradually over a period of days in acidified aqueous solutions of $SnSO_4$. Therefore all solutions and electrolytes were freshly prepared immediately prior to commencing electrodeposition of tin.

2.2. Electrode preparation

Two non-templating plating electrolytes were used to prepare reference samples: (R1) de-ionised water containing 0.15 M $SnSO_4$, 0.6 M H_2SO_4 and (R2) de-ionised water containing 0.15 M $SnSO_4$, 0.6 M H_2SO_4 , 0.28 M 4-hydroxybenzene sulfonic acid and 0.055 M *p*-cresol [31]. Non-templated electrodes were prepared in a two-electrode cell, with a tin foil counter electrode. Tin was electroplated, at room temperature, onto a 25- μm thick copper foil (99.999%, Aldrich). The active area of which was defined by masking with polyimide tape. For electrodes prepared from solutions R1 and R2, tin was plated galvanostatically. From R1 the current densities were between 5 $mA\ cm^{-2}$ to 30 $mA\ cm^{-2}$, from R2 the current density was 10 $mA\ cm^{-2}$.

As the ionic conductivity of the templating electrolytes (T1–4) was relatively low a two-electrode thin layer cell geometry was used for the electrodeposition with an electrode separation of 250 μm . Tin was deposited potentiostatically, by applying $-100\ mV$ across the cell. After deposition the cells were disassembled and the templated tin electrodes were repeatedly washed with absolute ethanol to remove the electrolyte. For cells containing the $C_{18}EO_{10}$ -based electrolytes (T2 and T4) warmed ethanol ($\sim 50^\circ C$) was used for washing the electrodes.

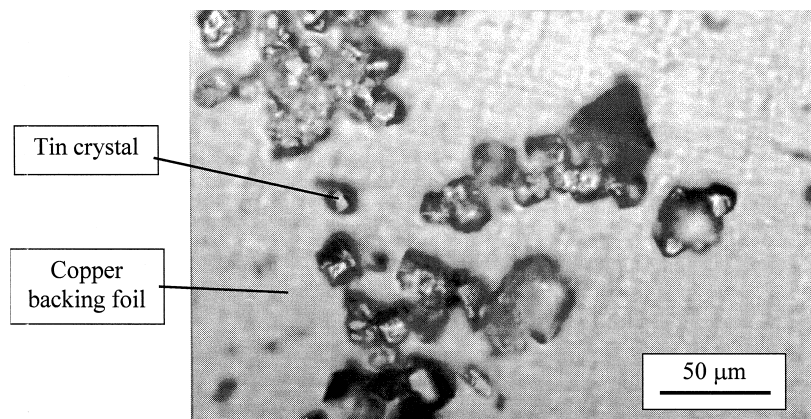


Fig. 1. Tin deposit on copper, from electrolyte R1 at 5 $mA\ cm^{-2}$.

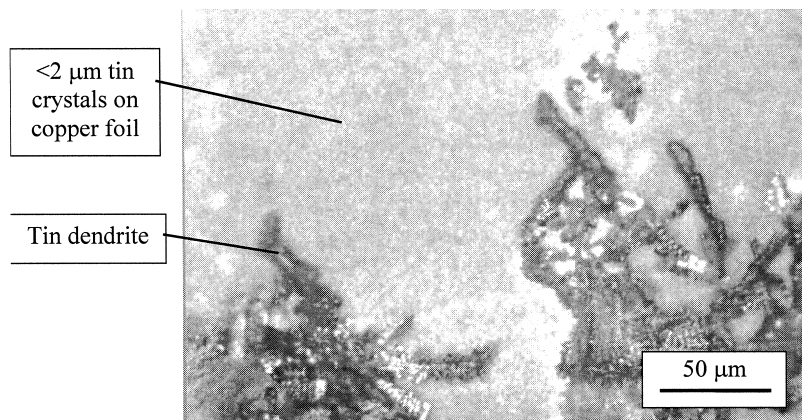


Fig. 2. Tin deposit on copper, from electrolyte R1 at 20 mA cm^{-2} .

For the templated and non-templated electrodes, intended for lithium insertion, the total amount of charge passed per unit area was kept constant at $2.0 \pm 0.1 \text{ C cm}^{-2}$. For samples prepared for X-ray diffraction the charge per unit area was $\sim 0.5 \text{ C cm}^{-2}$. Gravimetric measurements on electrodeposits from the R1 and R2 reference electrolytes revealed that the current efficiency was greater than 95%, based on the two electron reduction of Sn(II) to Sn. A current efficiency of 95% was assumed in order to calculate the insertion capacities of the templated tin electrodes.

2.3. Characterisation of electrodes

After deposition and washing the tin electrodes were dried under vacuum for 24 h. Subsequently non-aqueous electrochemical cells were constructed in an argon-filled dry box with lithium foil counter and reference electrodes and $1 \text{ M LiCF}_3\text{SO}_3/\text{ethylene carbonate (EC)/diethyl carbonate (DEC)}$ electrolyte.

AC impedance measurements were performed, prior to lithium insertion, using a HP 4192A impedance analyser.

The working electrode was held at 2 V vs. Li/Li^+ , where it was anticipated that there would be negligible lithium insertion. The oscillator level was 10 mV p-p and the frequency range $100 \text{ kHz to } 5 \text{ Hz}$.

Lithium was inserted into and extracted from the tin electrodes using a pulsed coulometric titration regime [32]. The overall insertion/extraction rate was $\text{C}/12$; in other words the total time required to pass 991 mAh g^{-1} (tin) would have been 12 h. The potential limit for the insertion was $0.05 \text{ V vs. Li/Li}^+$ and for extraction $0.95 \text{ V vs. Li/Li}^+$.

The small angle X-ray reflections of tin samples, electrodeposited from the R2, T1, T2, T3 and T4 electrolytes, were also recorded over the range $0.7\text{--}3.0^\circ$ in 2θ (CuK_α radiation). In order to accurately align the samples tin was deposited onto gold-coated glass slides which were mounted in a precision-milled aluminium sample holder.

Tunnelling electron microscopy (TEM) of one sample (obtained from the T1 electrolyte) was performed, using a JEOL 2000fx instrument with an accelerating voltage of 200 kV .

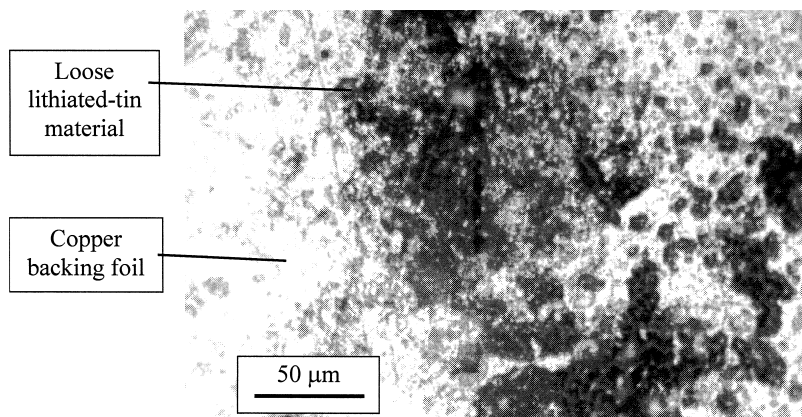


Fig. 3. Tin deposit on copper, from R1 electrolyte at 5 mA cm^{-2} , after insertion and extraction of lithium.

3. Results and discussion

Optical microscopy revealed that the morphology of tin plated from the reference solution R1 was strongly dependent on the current density, over the range 5–30 mA cm⁻². At 5 mA cm⁻² (Fig. 1), widely separated crystals (of ~20 μm length) and clusters of crystals were apparent on the copper backing foil. At 10 mA cm⁻² (not shown), the copper surface was almost entirely covered with tin crystals which were predominantly <5 μm in length. At 20 mA cm⁻² (Fig. 2), and 30 mA cm⁻² (not shown) the copper surface was again almost completely covered by small crystals (<2 μm in length), however relatively long (>50 μm) tin dendrites were also visible. These dendrites were found to be fragile and easily detached from the electrode surface.

After repeatedly inserting and extracting lithium from the electrodes as described above the electrodes were removed from the cell and examined under an optical microscope. By comparison of a tin electrode deposited at 5 mA cm⁻² before and after cycling (Figs. 1 and 3, respectively) it may be seen that average particle size had decreased and that the particles no longer possessed distinct crystal faces. Much of the material coating the electrode surface was loose and effervesced slightly with de-ionised water. This may lead to the assumption that by insertion and extraction of lithium partial fragmentation of the tin crystals had occurred leaving loosely bound lithiated tin powder, as may be anticipated if pulverisation had occurred during cycling. In addition for the tin electrode deposited at 20 mA cm⁻² the tin dendrites (Fig. 2) were no longer apparent after lithium insertion and extraction (Fig. 4).

Fig. 5 shows the lithium extraction capacities of electrodes prepared from R1, at various current densities, with cycle number. It may be seen that for each electrode there is a decrease in extraction capacity with cycle number. The decrease is most notable for the sample prepared at 5 mA cm⁻², which contained the largest tin crystals. The sam-

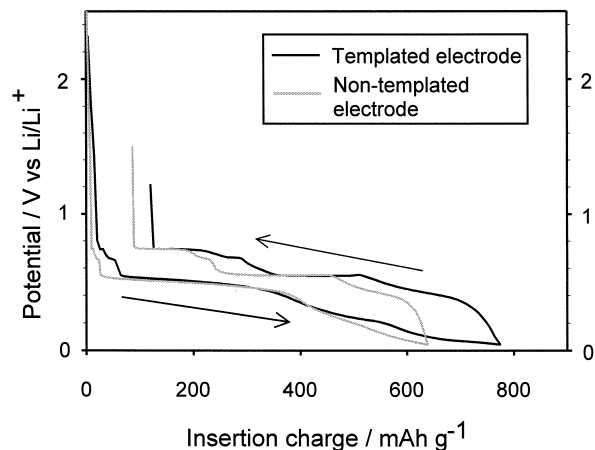


Fig. 5. Typical insertion and extraction profiles of a templated (T1) and non-templated (R1, 5 mA cm⁻²) electrodes.

ples prepared at 20 and 30 mA cm⁻², consisting of a mixture of small crystals and dendrites, showed the lowest first cycle extraction capacities, but less decrease in capacity than the electrode prepared at 5 mA cm⁻². The initially low capacity is probably due to dislocation of the tin dendrites, as observed by optical microscopy. However, the lower capacity fade of the samples containing the smaller tin crystals (prepared at 10, 20 and 30 mA cm⁻²) than large ones (prepared at 5 mA cm⁻²) is in good agreement with previous literature results [18,20].

Tin deposited from the R2, T1, T2, T3 and T4 electrolytes appeared smooth and specularly reflective, with no dendrites. However, from capacitance values, calculated from ac impedance measurements, it appeared that the samples prepared from T1 and T2 (the only samples examined in this manner) had surface areas of between 25 and 50 times greater than tin foil of the same geometric surface area. In addition, TEM (Fig. 6) revealed that the sample prepared from T1 was mesoporous.

Small angle X-ray diffraction of tin samples prepared from the templating electrolytes, T1–4, revealed a single

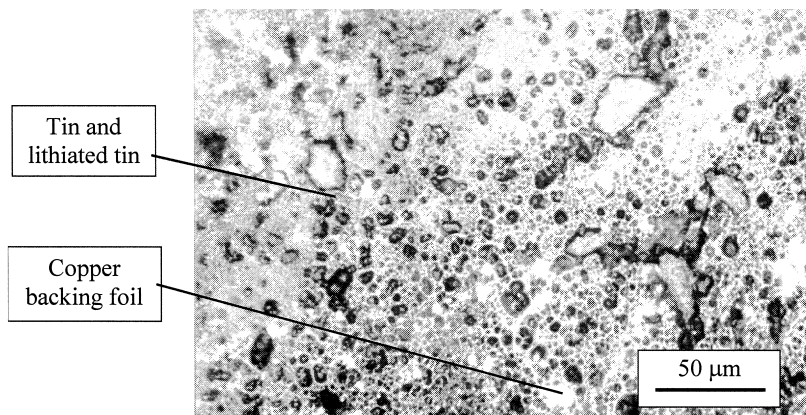


Fig. 4. Tin deposit on copper, from R1 electrolyte at 20 mA cm⁻², after insertion and extraction of lithium.



Fig. 6. TEM image of a tin sample prepared from templating electrolyte T1.

reflection but none for the sample prepared from the reference electrolyte, R2. This indicates that the repeat structure is due to the templating effect of the liquid crystal and is not just a passive effect of surfactant in the electrolyte, or an artefact of the X-ray technique. The position of the peaks and corresponding repeat distance, from the Bragg equation, are summarised in Table 1. From this evidence, it appears that the tin deposited from the templating solutions (T1–4) had some repeat nanostructure. It may also be seen from Table 1, that the presence of a relatively small amount of *n*-heptane in the templating electrolytes caused a significant increase in the repeat distance.

The insertion and extraction profiles of the templated electrodes were similar to those of the crystalline samples (Fig. 7). The insertion profiles show that little charge was passed at < 0.8 V vs. Li/Li^+ which could be associated with reduction of tin oxides [24].

The lithium extraction capacities of the smooth tin samples, prepared from R2, T1, T2, T3 and T4 are shown in Fig. 8. The first extraction capacities for the samples

Table 1
Small angle X-ray diffraction peak positions and corresponding repeat distances for tin deposits from various electrolytes

Electrolyte	Peak position, 2θ ($^\circ$)	Corresponding repeat distance (\AA)
R2	–	–
T1	1.55 ± 0.10	58 ± 5
T2	1.35 ± 0.10	66 ± 6
T3	1.40 ± 0.10	63 ± 5
T4	1.05 ± 0.10	85 ± 9

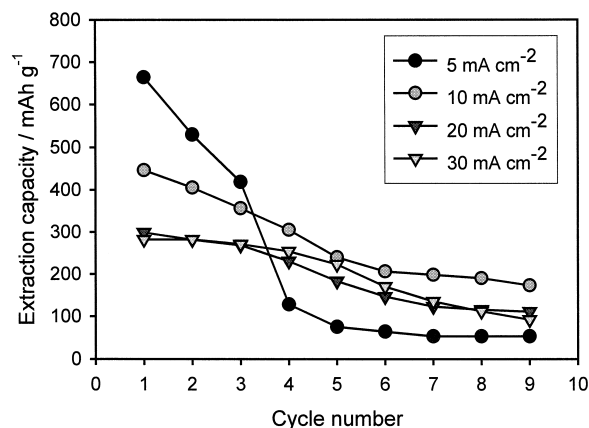


Fig. 7. Extraction charge dependence on cycle number for crystalline tin electrodes prepared from R1 over the range of current densities 5–30 mA cm^{-2} .

prepared from the C_{16}EO_8 electrolytes (T1 and T3) are higher than those prepared from the $\text{C}_{18}\text{EO}_{10}$ electrolytes (T2 and T4) which may be attributed to incomplete removal of the $\text{C}_{18}\text{EO}_{10}$. Any $\text{C}_{18}\text{EO}_{10}$ remaining in the electrode after assembly of the non aqueous cell may be expected to hinder expansion of the electrode material and react, via the hydroxyl end group, with the lithiated tin compounds. This could also account for the low final cycle capacities of the T2 and T4 samples. However, it should be noted that in the initial cycles (2–4) all of the templated samples showed higher extraction capacities than either the crystalline (Fig. 7) or smooth (Fig. 8) reference samples. In addition the samples prepared from the C_{16}EO_8 electrolytes (T1 and T3) showed higher extraction capacities than any of the reference samples at any given cycle number. Visual examination of the templated electrodes after cycling revealed that the electrodes were primarily intact but that the colour had darkened, possibly due to surface roughening.

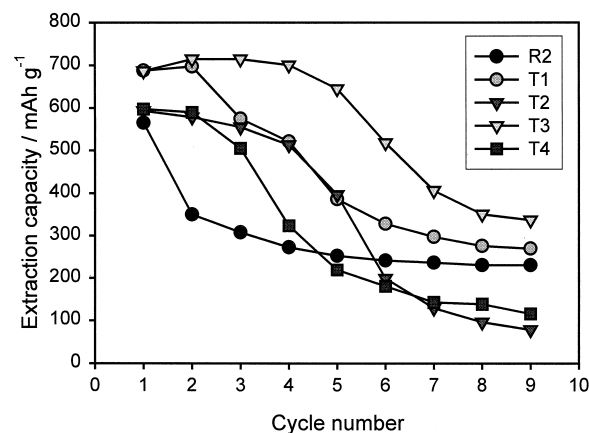


Fig. 8. Extraction charge dependence on cycle number for smooth tin electrodes prepared from electrolytes R2, T1, T2, T3 and T4.

4. Conclusions

It has been demonstrated that mesoporous tin may be deposited from lyotropic liquid crystal electrolytes. The resulting tin deposits had characteristic repeat distances in the range 3–10 nm which is consistent with previous observations for electrodeposited platinum. The lithium extraction capacities of tin deposited from $C_{18}EO_{10}$ -based electrolytes were found to be higher than reference samples over the second, third and fourth cycles. Electrodes prepared from $C_{16}EO_8$ -based electrolytes showed higher extraction capacities than non-templated electrodes at each cycle.

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