Electrodeposition of mesoporous tin films

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Mesoporous metallic tin has been electrodeposited, from the homogeneous hexagonal mesophase of a series of amphiphilic non-ionic surfactants, with a controllable repeat structure in the range of 5–10 nm.

It has been reported that mesoporous silica may be prepared by a sol–gel route from silicon alkoxides in the presence of a low concentration of a cationic surfactant.[1] Similarly the formation of several mesoporous metal oxides has been reported.[2] It has also been shown that nanostructured silica may be formed in the presence of surfactant concentrations high enough to form homogeneous liquid crystalline mesophases.[3,4] Under these conditions the nanostructure of the silica was a cast of the architecture of the liquid crystalline phase in which it was formed. In other words the liquid crystal phase acted as a direct template for the silica.

There have been very few reports of the formation of nanostructured metals although Attard *et al.* have used a direct templating method to prepare mesoporous platinum as both a powder[5] and coherent film.[6] The platinum film was electrodeposited from a homogeneous hexagonal (H_I) mesophase of a range of octaethylene glycol monoalkyl ethers with aqueous hexachloroplatinic acid. The following work reports on the electrochemical synthesis of mesoporous tin films (H_I-eSn) using a route similar to that employed for platinum. Mesoporous tin could be expected to offer advantageous properties over existing negative electrodes in lithium ion batteries.

Tin was electrodeposited from five electrolytes containing oligoethylene glycol monoalkyl ether surfactants (E1–E5, Table 1) and one electrolyte without surfactant (N1).† After deposition the cells were disassembled and the electrodes bearing the electrodeposited tin (H_I-eSn) were repeatedly washed with *ca.* 200 ml of absolute ethanol to remove the electrolyte. Gravimetric measurements of the deposits revealed that the current efficiency was > 94%, based on the two electron reduction of Sn^{II} to Sn.

Small angle X-ray diffractograms of the tin deposits were recorded over the range 2θ 0.7–3.0° (Cu-Kα radiation), which revealed a single peak for each film prepared from the templating electrolytes E1–E5, but not for the reference electrolyte N1, Table 2. Hence the X-ray peak may be taken to indicate that the templated electrodes possessed a spatially periodic structure with a characteristic repeat distance in the range 5–10 nm which was not an artefact of the X-ray technique. The repeat distance was noted to depend on the type of surfactant used and to be increased by the presence of *n*-heptane. As may be expected, if a direct templating mechanism were operating, the repeat distances of the tin films were similar to those obtained for the respective electrolytes from which they were deposited, Table 2. In addition, the repeat distance for tin deposited from E1 was of the same order of magnitude as that observed for H_I-ePt using $C_{16}EO_8$.[6]

Table 1 Electrolyte compositions

		Electrolyte composition (w/o)		
Electrolyte	Surfactant	0.2 M $SnSO_4$, 0.3 M H_2SO_4	*n*-Heptane	Surfactant
E1	$C_{16}EO_8$	50	0	50
E2	$C_{18}EO_{10}{}^a$	50	0	50
E3	$C_{18}EO_{20}{}^a$	40	0	60
E4	$C_{16}EO_8$	47	5	48
E5	$C_{18}EO_{10}{}^a$	50	3.5	46.5

[a] Nominal surfactant formula.

Table 2 Repeat distances of electrolytes and corresponding tin films based on XRD measurements. Also shown are the second cycle lithium extraction capacities of the films from electrochemical measurements

Electrolyte	Repeat distance of electrolyte/Å	Repeat distance tin film/Å	Lithium extraction capacity/C g^{-1}
E1	58 ± 3	60 ± 6	2510
E2	61 ± 3	66 ± 6	2080
E3	82 ± 4	81 ± 8	2060
E4	63 ± 3	63 ± 5	2570
E5	84 ± 4	85 ± 9	2120
N1	—	—	1260

Transmission electron microscopy (TEM) revealed mesoporosity in the samples, although a regular structure could not be assigned unambiguously, Fig. 1.

Further analysis of tin samples with a loading of 1.2 mg cm^{-2} was undertaken after drying under vacuum at 100 °C for 24 h. The dried samples were used as the working electrodes of non-aqueous electrochemical cells with lithium foil counter and reference electrodes and a 1 M $LiCF_3SO_3$–ethylene carbonate–diethyl carbonate electrolyte.

Using these cells ac impedance measurements were carried out over the frequency range 5 kHz to 5 Hz with a dc bias potential of 2 V *vs.* Li–Li$^+$ and oscillator level of 15 mV p–p.

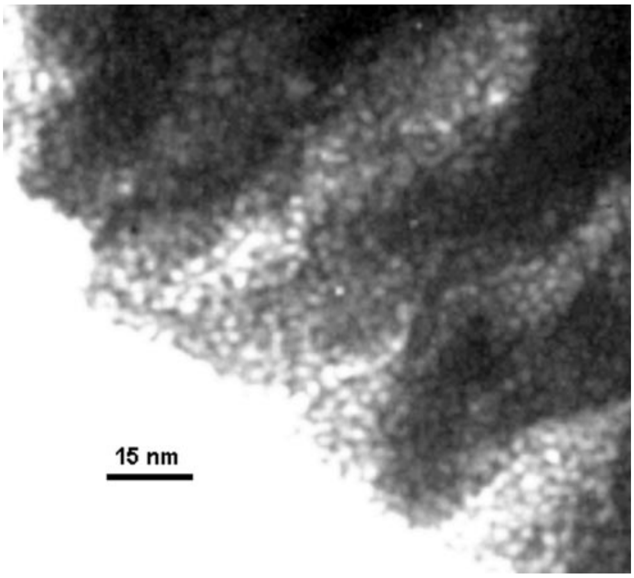

Fig. 1 Typical TEM image of a tin sample deposited from a templating electrolyte (E4).

These measurements showed the tin to act as a blocking electrode at low frequencies, as would be expected in the absence of faradaic reactions. From the values of the electrode capacitance it appeared that the samples prepared from the $C_{16}EO_8$-based electrolytes (E1 and E4), had a surface area 35 ± 10 times greater than that of rolled tin foil (9.0 μF cm^{-2}, Advent metals) of the same geometric surface area. However, an E1 sample dried at 180 °C under vacuum had a surface area enhancement of only 2 ± 1. Such a decrease in surface area may be understood in terms of a reduction in the number of accessible mesopores, which might occur by a surface melting phenomenon at below the bulk melting point of tin (232 °C).[9,10] For comparison tin deposited from the Brij-based electrolytes (E2, E3 and E5) had surface areas only slightly larger than the reference sample (N1), with surface enhancements of 8 ± 3 and 6 ± 2 respectively.

It has been noted previously that the electrochemical alloying of lithium may cause tin to undergo a volume expansion of up to 259%.[11] This expansion and any subsequent contraction, on removal of lithium, tends to create stresses within the tin alloy, leading to disintegration of the structure.[12] As loose tin–lithium particles would not be expected to be in good electrical contact with the bulk of the sample the amount of lithium that may be extracted should give an indication of the extent of pulverisation. It would be expected that extensive mesoporosity would significantly reduce internal stresses during expansion and thus decrease the mechanical degradation of the electrodes.

In order to examine the electrodeposited tin, lithium was inserted and extracted using a pulsed coulometric titration regime,[13] between the potential limits of 0.05 and 0.95 V *vs.* Li–Li^+. The magnitude of the insertion and extraction current densities was 350 μA cm^{-2} (equivalent to 290 mA g^{-1} of tin). The second cycle extraction capacities are shown in Table 2, from which it may be noted that the H_I-eSn samples all showed higher extraction capacities than the non-templated tin (from N1). The samples prepared from the mixed chain length surfactants (E2, E3 and E5) had similar extraction capacities to one another, *ca.* 2100 C g^{-1}. However, the single chain length surfactants (E1 and E4) provided tin samples with the highest extraction capacities, although still below the theoretical maximum of 3570 C g^{-1}.[14] Nevertheless, it may be noted that the H_I-eSn extraction capacities were much higher than those of commercial lithium battery negative electrode materials (coke and graphite) which are typically < 1350 C g^{-1}.[15]

In conclusion mesoporous H_I-eSn films were prepared from a series of templating electrolytes. In addition tin deposited from the $C_{16}EO_8$-based electrolytes (E1 and E4) holds promise for use as a negative electrode material for rechargeable lithium ion batteries.

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Notes and references

† Electrodeposition procedure: of the surfactants, octaethylene glycol monohexadecyl ether ($C_{16}EO_8$, $> 98\%$ Fluka), had a narrow distribution of both alkyl and oxyethylene chain lengths, whereas the others contained a broader mixture of chain lengths: Brij 76 (average composition of $C_{18}EO_{10}$, Aldrich) and Brij 78 (average composition of $C_{18}EO_{20}$, Aldrich). Templating electrolytes were prepared by mixing the surfactants with an aqueous solution of ≈ 0.2 M $SnSO_4$ and ≈ 0.3 M H_2SO_4. E4 and E5 also contained *n*-heptane which was expected to act as a swelling agent, increasing the radii of the cylindrical aggregates of the H_I phase and hence the pore size in the templated electrodeposit. The concentrations of surfactant, aqueous solution and *n*-heptane (Table 1) were chosen such that a H_1 phase of each lyotropic liquid crystal was formed, as verified from the characteristic optical textures when viewed through a polarising microscope.[7]

Although the $C_{16}EO_8$-based electrolytes (E1 and E4) were used at room temperature (22 ± 2 °C) the $C_{18}EO_{10}$-based electrolytes (E2 and E5) required heating to 45 °C, and the $C_{18}EO_{20}$-based electrolyte (E3) to 50 °C, in order to improve ionic conductivity and ensure that a homogeneous H_I phase was formed. All solutions and electrolytes were freshly prepared immediately prior to commencing electrodeposition of tin.

Reference samples were prepared from a non-templating plating electrolyte, N1, with the composition, 0.15 M $SnSO_4$, 0.6 M H_2SO_4, 0.28 M 4-hydroxybenzene sulfonic acid and 0.055 M *p*-cresol.[8] Tin was deposited galvanostatically from N1 with a current density of 5 mA cm^{-2}. Tin was deposited potentiostatically from E1–E5 by applying -100 mV across a two-electrode cell, with a tin counter electrode and copper or gold working electrode of area *ca.* 0.5 cm^2.

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