Li-ION THIN-FILM BATTERIES WITH TIN AND INDIUM NITRIDE AND SUBNITRIDE ANODES MeNₓ (Me = Sn, In)

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ABSTRACT

Nitride and subnitride thin-films of Sn or In were prepared by reactive rf magnetron sputtering of the metals in appropriate Ar-N₂ gas mixtures. Inferred from X-ray diffraction studies, the tin subnitrides consisted of a solid solution of N in nanocrystalline tetragonal Sn and the indium subnitrides represented two-phase mixtures of crystalline hexagonal InN and crystalline tetragonal In. Using a LiCoO₂ cathode and a Lipon electrolyte, Li-ion thin-film batteries with MeNₓ (Me = Sn, In) anodes were cycled over 1000 times between 4.2 and 2.7 V or 2.0 V at current rates up to 10 mA/cm² and at a charge rate of 10 C. The inherent, initial capacity loss of the MeNₓ anodes due to the formation of the irreversible Li₃N matrix was greatly reduced by applying two concepts. First, the use of subnitrides with low N/Me ratios resulted in less Li₃N formation, and second, supersaturating the MeNₓ anodes with Li of cathode-heavy cells produced less Li₃N per unit capacity of LiCoO₂ and precipitated metallic Li, which was found to be electrochemically highly reversible.

INTRODUCTION

There are two major options for integrating Li-ion thin-film batteries into electronic circuits. First, the batteries can be deposited directly onto the circuit components serving as the battery substrate, such as chips or the circuit board itself. Recently, we demonstrated the feasibility of this option by fabricating thin-film batteries having a crystalline LiCoO₂ directly onto polished Si wafers.¹ In the second option, the batteries are fully prepared on a separate substrate, such as a thin ceramic plate or a thin metal foil, which is subsequently attached to the circuit board in a single step along with all of the other electronic components using the solder reflow or surface mount technique. To accomplish this, the thin-film batteries have to survive typical solder reflow conditions which are 250°C in air for a few minutes. Our Li-ion thin-film batteries consisting of a crystalline LiCoO₂, a lithium phosphorus oxynitride (“Lipon”) glass electrolyte, and a nitrided anode, such as silicon tin oxynitride (“SiTON”),²,³ Zn₃N₂,⁴,⁵ or Sn₃N₄,⁴,⁵ not only survived solder reflow conditions but were found to even improve their electrochemical properties after such a heat treatment. In search for new, better Li-ion thin-film batteries,
we extended our Li-ion anode catalogue in this paper to subnitrides of Sn and In as well as InN.

EXPERIMENTAL

Thin-film batteries were fabricated by sequential layer deposition of the cell components using rf magnetron sputtering, except for the metal current collectors which were deposited by dc magnetron sputtering. Our standard thin-film cell configuration and the latest preparation conditions for the LiCoO₂ cathode and for the lithium phosphorus oxynitride ("Lipon") electrolyte have been reported in greater detail in previous papers.¹,⁶ All of the Li-ion thin-film batteries were fabricated with a gas-tight Lipon overlayer ¹ and subsequently heated at 250°C in air for 10 min in order to decrease the internal cell resistance and also to simulate solder reflow conditions.¹,²,⁶ Films were typically deposited at rates of 90 Å/min for LiCoO₂, 180 Å/min for Lipon, and about 100 Å/min for MeNₓ (Me = Sn, In). No additional heating of the substrates was applied during film deposition. The stoichiometry of the MeNₓ films was controlled by reactive sputtering from a metallic Sn or In target in specific Ar-N₂ gas mixtures at 5 mTorr. To determine their stoichiometry, MeNₓ films were prepared on graphite and Be substrates and analyzed by Rutherford Backscattering Spectrometry (RBS).

Thin-film phases were identified by X-ray diffraction (XRD) in theta-theta geometry using CuKα radiation. Employing a specially designed vacuum-tight transfer system with electrical feedthroughs and specimen stage, we were able to execute scanning electron microscopy during electrochemical cycling (in-situ SEM). Common electrochemical tests of the thin-film cells connected to a battery cycle system were performed under Ar inside sealed stainless steel jars with electrical feedthroughs. The mass of the LiCoO₂ and the MeNₓ electrodes was calculated from the steady state deposition rate and the deposition time. During electrochemical cycling, the Li-stoichiometry of both electrodes was computed from their mass and the amount of charge transferred.

RESULTS AND DISCUSSION

XRD and SEM Studies

The XRD patterns of SnNₓ for 0.48 ≤ x ≤ 1.33 are shown in Fig. 1. Only the fully nitrided films, where x = 1.33 or Sn₃N₄, crystallized well in the as-deposited state and the observed Bragg peaks could entirely be indexed to the hexagonal space group P 3m1 with a = 3.7148(4) Å and c = 5.2560(8) Å. As noticed in Fig. 1, only a slight decrease in x was needed to destroy the long-range order of Sn and N found for SnN₁.₃₃, and N was forced to form a solid solution with nanocrystalline tetragonal Sn instead. The latter becomes evident from the broad but gradually narrowing Bragg peaks assignable to metallic β-Sn with decreasing x. Because of that, the stoichiometric range Δx of the binary compound
SnN_{1.33-D_x} seems to be very small, so that typical tin subnitrides represent a solid solution of N in nanocrystalline β-Sn. Also, the XRD patterns, including peak widths, and the Sn/N ratio of all SnN_x films remained virtually unchanged after heating at 250°C in air for 10 min. As indicated in the experimental section, the inertness of the bulk of the SnN_x films to such a treatment enabled us to significantly improve the performance of our Li-ion thin-film batteries because this treatment, we believe, “cured” both electrolyte interfaces.

In contrast to SnN_x, as-deposited InN_x had a stronger tendency to crystallize. Since hexagonal InN (space group P6_3mc) films were highly textured showing a very strong intensity in (002) direction (insert of Fig. 2), the XRD patterns of InN_x are better compared on a semi-logarithmic scale which enhances the visibility of weaker Bragg peaks (Fig. 2). As x deviates from unity, InN_x immediately co-precipitates metallic In. At x = 0.44, the XRD pattern is dominated by this phase although the remainder of the InN (002) peak at 2θ_{corr} = 31.18° is still visible. Thus, the indium subnitride InN_{0.44} consists of a two-phase mixture of tetragonal In (I4/mmm, a = 3.2527(1) Å, c = 4.9436(3) Å) and hexagonal InN (P6_3mc, a = 3.529(1) Å, c = 5.750(2) Å). Due to the very good agreement of the refined lattice parameters with the literature, the In phase seems to consist of almost pure In metal rather than a solid solution of N in In. Despite the very low melting point of In (mp 156°C), InN_{0.44} thin films did not melt during the heat treatment at 250°C in air for 10 min, and the refined lattice parameters after cooling remained virtually unchanged.

Fig. 1: XRD patterns of as-deposited SnN_x (0.48 ≤ x ≤ 1.33) on pyrex glass substrate whose pattern is included for comparison. The patterns are offset in intensity for clarity.
When MeNₓ is initially lithiated, in-situ XRD measurements suggest the concurrent formation of a nanocrystalline Li₃N matrix and alloying of the metal Me according to

\[ \text{MeN}_x + (3x + y) \text{Li} \rightarrow \text{Li}_y\text{Me} + x \text{Li}_3\text{N} \]  

[1]

Obtained from in-situ SEM studies on Li-ion thin-film cells, the thickness of the MeNₓ anodes increased by a factor of 330 % when \( y = 4.4 \) for SnN₁.₃₃ and \( y = 4.33 \) for InN. Exceeding the saturation limits of the alloys, i.e. \( y > 4.4 \) for Sn and \( y > 4.33 \) for In, causes metallic Li to precipitate as an additional phase thus further increasing the thickness of these lithiated MeNₓ electrodes.
During cell operation, the lithium alloys reversibly de-alloy and re-alloy inside the Li$_3$N matrix, which is believed to be a mixed conductor under the changing electrode potential due to a possible stoichiometry variation such as Li$_{3\pm\delta}$N. The reversible electrochemical process is formally described by

\[
\text{Li}_y\text{Me} = y\text{Li} + \text{Me} \quad [2]
\]

and, as observed for SnN$_{1.33}$ and InN by in-situ SEM, causes the electrode thickness to vary between 330% and 160% of its initial value. Verified by XRD during electrochemical cycling (in-situ XRD), reaction [2] proceeds via nanocrystalline lithium alloys and nanocrystalline Sn or In. Due to the nanocrystallinity, elements from the alloy phase and the matrix phase share a high surface area which, as $y$ changes, probably alleviates the transition from one alloy phase to the next inside the matrix. In contrast, electrodes consisting of pure and crystallized lithium alloys are known to cycle poorly (see below and refs. 8 and 9).

Reducing the inherent, initial capacity loss

Analogously to the recently proposed tin oxide based anodes for Li-ion batteries,$^{2,3,10-12}$ MeNx anodes show a significant, inherent capacity loss during their initial lithiation due to the formation of the Li$_3$N matrix according to equation [1]. Since this capacity loss is paid by the Li-ion cell's heaviest and most voluminous cell component, the LiCoO$_2$ cathode which is also the cell's only initial lithium source, it is of utmost importance to minimize this loss.

Two strategies have successfully been applied in this work. First, Li-ion thin-film cells were fabricated "cathode-heavy" in which the mass ratio of MeNx to LiCoO$_2$ was decreased thus resulting in the formation of less irreversible Li$_3$N matrix per unit capacity of LiCoO$_2$. Moreover, at the end of the battery charge the MeNx anode became supersaturated with Li causing metallic Li to precipitate. As noticed from the voltage profile of "InN (cathode-heavy)" in Fig. 3 between 56 and 69 $\mu$Ah/(cm$^2 \times \mu$m LiCoO$_2$), the precipitated Li could reversibly be stripped on battery discharge thus improving the ratio of reversible to irreversible capacity as compard to InN. Of course, the irreversible capacity loss could further be reduced to less than the given 35% by increasing the cathode heaviness of the cell. The other strategy to combat the inherent capacity loss is to decrease the N/Me ratio leading to the fabrication of subnitride anodes MeNx, in which $x < 1.33$ for Sn or $x < 1.0$ for In and where less irreversible Li$_3$N matrix is formed during the initial lithiation. As demonstrated in Fig. 3, this resulted in a substantial improvement of the reversible capacity of InN$_{0.44}$ over InN.

Both strategies, cathode-heaviness and subnitride fabrication, do not need to be combined, since the concept of cathode heaviness alone is good enough to reduce the initial capacity loss so efficiently that the capacity difference, at least in early cycles,
between a Li-LiCoO$_2$ and a cathode-heavy SnN$_{1.33}$-LiCoO$_2$ thin-film battery becomes satisfyingly small (Fig. 4). In addition, comparing cycle 2 and cycle 1000 of the cathode-heavy SnN$_{1.33}$-LiCoO$_2$ cell clearly reveals that the capacity portion obtained from precipitating and stripping of Li metal at the supersaturated anode is much more reversible than the capacity portion delivered by the de-alloying and re-alloying process. Taking this concept of supersaturating the anode with Li to an extreme, the MeN$_x$ anode material could be omitted altogether. This led to the development of our “Li-free” thin-film batteries which have an inherent anode capacity loss near zero.$^1$

![Fig. 3: Capacity loss during the first 1.5 cycles of selected InN$_x$-LiCoO$_2$ thin-film cells between 4.2 and 2.7 V at 0.1 mA/cm$^2$ where the InN$_x$ potential ranged from 0 V to 1.2 V vs. Li/Li$^+$. The capacity loss is expressed in percent of the maximum achievable capacity of LiCoO$_2$ that has been normalized to 1 µm and 1 cm$^2$ or 1 g. The potential profiles given as InN$_x$ vs. Li/Li$^+$ are offset by 1.3 V for clarity.](image1)

![Fig. 4: Comparison of the capacity as a function of cycle number of a cathode-heavy SnN$_{1.33}$-LiCoO$_2$ (bold lines) and a Li-LiCoO$_2$ (fine lines) thin-film battery between 4.2 and 2.7 V at 1 mA/cm$^2$. Charge time was 15 min (4 C rate). Both LiCoO$_2$ cathodes were 3.0 µm thick. The gravimetric capacity of SnN$_{1.33}$ is given within the plot. At the left of the dashed line: Discharge capacity is obtained from Li stripping of the supersaturated SnN$_{1.33}$ anode. At the right of the dashed line: De-alloying process prevails.](image2)
Cell Performance

At high current rates such as 5 mA/cm², the difference in capacity, but not in energy, between MeNₓ-LiCoO₂ and Li-LiCoO₂ thin-film cells having the same LiCoO₂ dimensions becomes virtually zero. This is demonstrated in Fig. 5 for SnN₀.₉₂-LiCoO₂ and cathode-heavy SnN₀.₄₈-LiCoO₂ thin-film batteries. As a conclusion, the degree of cathode heaviness and/or subnitridation, and therefore the degree of the initial capacity loss, becomes less and less important as the current density is increased.

Fig. 5: Discharge profiles of a SnN₀.₉₂-LiCoO₂, a cathode-heavy SnN₀.₄₈-LiCoO₂, and Li-LiCoO₂ thin-film battery between 4.2 and 2.7 V at 0.1 mA/cm² (left figure) and 5 mA/cm² (right figure). The LiCoO₂ cathodes were 1.0 µm thick and had an area of 1 cm².

During this work we found that all of our thin-film batteries with crystalline LiCoO₂ cathodes, at least up to 3.5 µm in thickness, accommodated 96% of their theoretical charge capacity at a 10 C charge rate (charge time of 6 min) between 2.7 and 4.2 V. Comparative tests at much lower charge rates did not yield better cycle stabilities, and the discharge capacity of the early cycles, which was higher by about 4%, vanished as cycling proceeded.

In Fig. 6, the cycle stability of selected SnNₓ-LiCoO₂ thin-film batteries operated at 1 mA/cm² between 4.2 - 2.7 V and at a 10 C charge rate are compared to a Li-LiCoO₂ thin-film battery having the same cathode dimensions. The following information is gathered from this figure: (i) It is evident that the Li-LiCoO₂ thin-film battery has a better cycle performance than the Li-ion counterparts. (ii) Inferred from the SnN₀.₉₂-LiCoO₂ thin-film battery which was cycled at 10 mA/cm² in the extended potential window of 4.2- 2.0 V, such extreme conditions do not seem to adversely affect the cycle stability, since the capacity fade over 1000 cycles is similar to that of the other SnNₓ-LiCoO₂ thin-
film cells in that figure. (iii) The poor cycle stability of the Sn-LiCoO$_2$ thin-film battery was caused by the Sn anode which, representing the most extreme subnitride MeN$_x$ possible where x = 0, completely lacked of a Li$_3$N matrix. It was reported that, during electrochemical cycling, the Li$_2$O matrix of tin oxide based anode materials is beneficial in delaying the detrimental aggregation of Sn nanoparticles into large clusters thus improving the cycle stability as the amount of matrix was increased.$^{13}$ However, the amount of matrix present in the anode seems to be only one factor determining the cycle stability. Other factors such as the ductility of the active, lithiated anode material itself seem to also play a role. For instance, in our new "Li-free" thin-film batteries,$^1$ in which the entire, very ductile Li anode is electroplated in-situ in the absence of any matrix, we achieved high cycle stabilities over 1000 cycles although much higher volume changes occurred compared to a Sn anode.

In the case of InN$_x$-LiCoO$_2$ thin-film batteries (Fig. 7) cycled under the same conditions as the SnN$_x$-LiCoO$_2$ thin-film batteries in Fig. 6, the cycle performance was not satisfactory due to their large capacity fade during the first 200 cycles. As suggested by in-situ XRD measurements, indium gradually agglomerated into electrically insulated particles inside the InN$_x$ anode during early cycles which was probably the reason for the poor performance. This result was corroborated by pseudo-OCV measurements performed after 1000 cycles where about 30% of the theoretical capacity of the anode was found to be electrochemically inactive under these conditions.
The inherent, initial capacity loss of Li-ion thin-film cells fabricated with nitrided tin and indium anodes can efficiently be reduced by:

(i) the use of subnitrides, which contain less N per Sn or In and therefore form less irreversible Li$_3$N matrix during the initial lithiation and

(ii) supersaturating the anodes with Li by means of cathode-heavy cells in which less Li$_3$N matrix is formed per unit capacity of LiCoO$_2$ and where metallic Li is reversibly precipitated and stripped thus improving the ratio of reversible to irreversible capacity.

Both strategies were combined in cathode-heavy Sn$_N$-LiCoO$_2$ thin-film cells in which gravimetric capacities of the anode between 1400 and more than 700 mAh/g were obtained in the early cycles and after 1000 cycles, respectively. These Li-ion cells were operated at 1 mA/cm$^2$ between 4.2 and 2.7 V corresponding to a potential range of Sn$_N$ between 0 and 1.2 V vs. Li/Li$^+$. Charging was done at a 10 C rate (6 min charge). This was particularly useful, since discharge capacities and cycle stability remained virtually the same when using much lower charge rates, i.e. longer charge times.

The cycle stability of strongly subnitrided anode materials, such as Sn$_{N0.48}$ and In$_{N0.44}$, is still comparable to the fully nitrided materials Sn$_{N1.33}$ and InN, respectively. In contrast, metallic Sn representing the most extreme tin subnitride possible shows a very poor cycle performance. Thus, there has to be lower limit where x is so small that Sn$_N$ becomes a poor anode material.

Increasing the current density in the potential range between 4.2 and 2.7 V significantly decreases the difference in capacity supplied by a Sn$_N$-LiCoO$_2$ and a Li-LiCoO$_2$ thin-film cell having the same LiCoO$_2$ dimensions. At a current density as high as 5 mA/cm$^2$, this difference is virtually zero.

The capacity portion obtained from the precipitated/stripped metallic Li in supersaturated Sn$_{N1.33}$ shows a higher reversibility than the capacity portion delivered by the alloying/de-alloying process of Li$_y$Sn within the Li$_3$N matrix. This result suggest that the Li-ion anode material could be omitted altogether. Recently, we have successfully demonstrated this concept through the fabrication of our “Li-free” thin-film batteries with in-situ electroplated Li anodes.$^1$

As far as the cycle stability is concerned, Sn$_N$ anodes are superior to In$_N$ anodes.

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