

Li-Ion Thin-Film Batteries with Nitride and Subnitride Anodes MeN_x (Me = Sn, In)

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Using a crystalline LiCoO_2 cathode, the direct fabrication of thin-film batteries onto polished Si wafers has recently been demonstrated (1, 2) and provides an alternative to the integration of thin-film batteries in electronic circuits using the solder reflow or surface mount technique (1-3). In the search for new, improved Li-ion thin-film batteries that survive solder reflow conditions, we extended our Li-ion anode catalogue beyond silicon tin oxynitride ("SiTON") (3), Sn_3N_4 (1), and Zn_3N_2 (1) to subnitrides of tin and indium as well as to InN .

The nitrated Li-ion anodes MeN_x (Me = Sn, In) were prepared by reactive rf magnetron sputter deposition from a Sn or In target in an Ar- N_2 gas mixture ranging from 0-100 % N_2 . Employing the same deposition technique, the lithium phosphorus oxynitride ("Lipon") electrolyte was deposited from a Li_3PO_4 target in N_2 whereas the LiCoO_2 cathode was deposited from a LiCoO_2 target in Ar-30% O_2 and subjected to a post-deposition anneal at 700 °C in O_2 . Chemical analysis was carried out by Rutherford backscattering spectrometry (RBS: N, O, P, Co, In, Sn) and proton-induced gamma-ray emission (PIGE: Li). The Li-ion thin-film batteries were fabricated on polished Si wafers, quartz glass slides, and polycrystalline $\alpha\text{-Al}_2\text{O}_3$ substrates and cycled at up to 10 mA/cm^2 in the voltage range 4.2 – 2.7 V.

During the initial charge of $\text{MeN}_x\text{-LiCoO}_2$ thin-film batteries, the nitrated Li-ion anode reacts with lithium that is supplied by the LiCoO_2 cathode according to



which is then followed by the reversible de-alloying/re-alloying process during electrochemical cycling



Inferring from equations [1] and [2], the irreversible formation of Li_3N consumes capacity and the reversibly utilized portion of the lithium capacity, which amounts to $y / (y + 3x)$, increases as x becomes smaller. Thus, the main reason for studying subnitride compounds is the decrease in the initial capacity loss, which theoretically should lead to no loss in the case of the pure metals where $x = 0$.

One way to partially compensate for the initial capacity loss is to fabricate cathode-heavy cells which near the end of charge cause lithium to precipitate in the nitrated thin-film Li-ion anodes. In the early stages of discharge, the capacity is then delivered by the precipitated lithium and the discharge profile of the battery looks like a battery with a metallic lithium anode. The supersaturation of the anodes with lithium proved to be highly reversible and significantly increased the capacity of our Li-ion thin-film batteries. The utilization of the precipitated lithium of the anode, which had a stoichiometry of $\text{Li}_{10,0}\text{SnN}_{1,33}$ at the end of charge to 4.2 V, is shown at the left of the dashed line in Fig. 1. As can be seen, this portion of the discharge capacity had a much higher cycle stability over 1000 cycles at 1 mA/cm^2 than the portion delivered by the de-alloying process of Li_ySn shown at the right of the dashed line. The cathode-heavy $\text{SnN}_{1,33}\text{-LiCoO}_2$ thin-film battery of Fig. 1 supplied 7 % less capacity in the second cycle and 38 % less capacity

after 1000 cycles when compared to a thin-film battery that is configured with a metallic Li anode and with the same cathode mass of LiCoO_2 and operated under the same conditions.

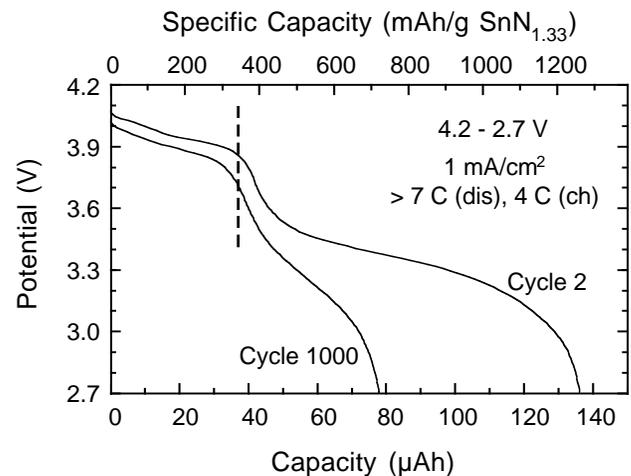


Fig. 1: Discharge profiles of a 1 cm^2 Li-ion thin-film battery having the cell configuration 2000 Å $\text{SnN}_{1,33}$ / 1.5 μm Lipon / 3.0 μm LiCoO_2 .

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