

NANOCRYSTALLINE LITHIUM MANGANESE OXIDE CATHODES FOR THIN FILM BATTERIES

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Thin film cathodes, 0.2 to 3 μm thick, have been deposited by radio-frequency magnetron sputtering from a ceramic target of LiMn_2O_4 . [1] When deposited onto substrates at temperatures less than about 100°C , the lithium manganese oxide films are smooth, dense and featureless. Xray diffraction indicates that the films are amorphous, while examination by TEM and electron diffraction reveals films that are at least partially crystalline with spinel nanocrystallites of 4 to 5 nm. [1] Annealing the films at $300\text{--}800^\circ\text{C}$ promotes an increase in the grain size of the spinel phase as revealed by xray diffraction analysis. Typically the film compositions are Mn deficient compared with the LiMn_2O_4 sputter target giving a Li substituted spinel composition which is unaltered by high temperature anneal in an oxidizing atmosphere.

The lithium insertion reactions of the nanocrystalline and well crystallized cathodes has been compared by fabricating and cycling all solid-state thin film batteries. [2,3] The battery is composed of an amorphous lithium phosphorous oxynitride electrolyte, known as lipon, [4] deposited over the cathode film, followed by an evaporated lithium metal anode and a protective parylene coating. The thin film batteries were cycled in an inert atmosphere at temperatures of $25\text{--}100^\circ\text{C}$ using a Maccor battery tester equipped with high impedance test channels.

The accompanying figure shows an overlay of the charge and discharge profiles measured at low currents for the thin film lithium cells with either a nanocrystalline cathode or a fully crystalline spinel cathode. In both cases, there is a significant hysteresis between the charge and discharge curves which has been discussed in earlier work. [5] Because of the Li substituted spinel compositions, extracting all the lithium from the 8a sites of the material requires charging to a cell potential above 4.5V. This must be accompanied by further oxidation of the cathode, presumably giving an average oxidation state for the Mn of $>+4$. Charging to high voltages causes an irreversible change in the spinel cathode.

The behavior of the nanocrystalline material is characterized by a sloping potential profile with less distinct plateaus and steps than observed for the spinel. The overall capacity, however, is just as large as that for the crystalline spinel cathode. While some lithium clearly occupies lattice sites resembling the 8a and 16c of the spinel structure, much of the lithium must be located in disordered sites. Whether these disordered sites should be viewed as a distinct amorphous phase or as disordered sites near the surface of the nanocrystallites has not been determined.

There are tradeoffs in optimizing the cathode composition and in selecting between a nanocrystalline spinel and a coarser grain material. Rate studies indicate that lithium transport in the nanocrystalline film is 100X slower than for the well crystallized material. On the other hand, extended cycling reveals that the nanocrystalline cathode is more stable at both elevated temperatures and when discharged to voltages well below 3V than is a highly crystalline cathode film of the same thickness. The nanocrystalline structure, however, is not completely

stable, as it gradually becomes more crystalline either through grain growth or recrystallization during cycling.

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Fig. 1 Low current discharge and charge cycles of Li - $\text{Li}_x\text{Mn}_{2-y}\text{O}_4$ thin film batteries. One battery has a nanocrystalline cathode (solid line), while the second has a crystalline spinel cathode (dashed line). For both cells, cycling was initiated by equilibration of the cell potential at 4.5V, followed by discharge to 1.5V and then charge to 5.3V, as indicated by the arrows.

