THIN-FILM Li-LiMn$_2$O$_4$ BATTERIES

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Abstract
Thin-film rechargeable Li-LiMn$_2$O$_4$ batteries have been fabricated and characterized. Following deposition by electron beam evaporation of LiMn$_2$O$_4$, the amorphous as-deposited cathode films 1 cm$^2$ in area by 0.3 to 4 μm thick were annealed at 700°C to 800°C in oxygen in order to form the crystalline spinel phase. The capacity of the cells between 4.5 V to 3.8 V depended on the annealing conditions and ranged from 50 pAh/mg to 120 pAh/mg. When cycled over this range, the batteries exhibited excellent secondary performance with capacity losses as low as 0.001% per cycle. On charging to 5.3 V, a plateau with a median voltage of 5.1 V was observed. The total charge extracted between 3.8 V to 5.3 V corresponded to about 1Li/Mn$_2$O$_4$.

Introduction
Thin-film rechargeable lithium batteries have been under investigation in this laboratory for several years (References 1-3). Previous studies focused on cells with amorphous V$_2$O$_5$ (aV$_2$O$_5$) cathodes deposited at ambient temperatures. While having large specific capacities of over 400 μAh/mg when discharged from 3.5 V to 1.5 V, the slow diffusion of Li$^+$ in the cathodes limits the practical operating current density to about 50 μA/cm$^2$ depending on the cathode thickness. Recently, thin-film lithium batteries with crystalline LiMn$_2$O$_4$ cathodes have been fabricated. Depending on cathode thickness, these cells could sustain current densities of several mA/cm$^2$ when cycled between 4.5 V and 3.8 V with 60% cathode utilization. In this paper, we summarize our investigations of Li-LiMn$_2$O$_4$ cells and report some preliminary results obtained on cycling to 5.3 V.

Experimental Procedures
With the exception of the cathode, the Li-LiMn$_2$O$_4$ batteries were fabricated using the methods described previously for thin-film Li-V$_2$O$_5$ cells (References 1-3). Cathode films ~1 cm$^2$ in area and 0.3-μm to 4-μm thick were deposited over Pt current collectors on alumina substrates by electron beam evaporation of LiMn$_2$O$_4$ in ~10$^{-5}$ Torr of O$_2$. The source material was synthesized by reacting Li$_2$CO$_3$ and Mn$_2$O$_3$ at 600°C. After deposition, the amorphous cathode films were annealed in O$_2$ at temperatures of 700 and 800°C in order to form a highly crystalline cubic spinel phase. The crystalline films were characterized using x-ray diffraction and scanning electron microscopy; their thickness was measured using a profilometer. The cathode films were covered with about 1 μm of the amorphous lithium phosphorus oxynitride electrolyte (Reference 1) deposited by rf magnetron sputtering of Li$_3$PO$_4$ in N$_2$, and the lithium anode films about 3-μm thick were deposited by evaporation of lithium metal at 10$^{-6}$ Torr. In a few cases, the cells were sealed with a multilayer protective coating, but usually they were sealed in vacuum-tight weighing bottles.

Constant current cycling experiments were performed with a Maccor 2000 battery test system, and ac impedance measurements were made between 10 mHz and 10 Mhz (References 1,2). Most of the experiments were performed at 25°C, but measurements on one of the cells were made at 0°C and -20°C. The as-deposited open circuit voltage of the cells was about 3 V. After charging to 4.5 V, the cells were usually cycled between the fixed limits of 4.5 V and 3.8 V which is the range for optimum current densities and secondary performance. After their performance between 4.5 V and 3.8 V was determined, several cells were cycled to 5.3 V.

Results and Discussion
An example of the first charge from the as deposited initial voltage of ~ 3 V to 4.5 V and the first few cycles between 4.5 V and 3.8 V for a Li-LiMn$_2$O$_4$ cell is shown in Figure 1. Assuming a film density of 4.2 g/cm$^3$, the specific capacity of this 800°C annealed cathode was 77 μAh/mg, which corresponds to about 0.5 Li/Mn$_2$O$_4$. The discharge curves in Figure 2 show that better than 60% cathode utilization was achieved with this battery at a current density of mA/cm$^2$. From the iR loss measured between the 80 μA/cm$^2$ and the 250 μA/cm$^2$ curves, the resistance of this cell was about 150 Ω. This is more than 100 times lower than the resistance of Li-aV$_2$O$_5$ cells with cathodes of comparable thickness. As in the case of the Li-aV$_2$O$_5$ cells, an analysis of ac impedance data...
Figure 1. Initial charge and first few cycles of a Li-LiMn$_2$O$_4$ cell. The cathode was annealed at 800 °C.

Figure 2. Discharge at different current densities for the cell of Fig. 1.

confirmed that lithium diffusion in the cathode is the main current limiting factor in the thin film Li-LiMn$_2$O$_4$ batteries.

Cycle data at two current densities are shown in Figure 3. On the charge cycle, the voltage was held constant at 4.5 V and the current allowed to decay to 1 μA before the following discharge cycle. The origin of the sudden increase in capacity for a few cycles near cycle 250 is not certain, but is believed to have been caused by a temporary instrument malfunction. The dashed lines in the figure are graphs of equation (1) where C is the capacity remaining after n cycles, $C_0$ is the initial capacity, and $\delta$ is the fraction of charge lost per cycle. The parameters $C_0$ and $\delta$ were fit by least squares to the observed data. As shown in the figure, the capacity loss per cycle is smaller at the higher current density, possibly due to the smaller amount of Li$^+$ ions cycled through the cathode. The coulombic efficiency in these experiments was about 100%.

Except for the capacity loss, which depends on the amount of charge cycled, the cells examined to date were relatively insensitive to the charge/discharge conditions. In one case, no change in the cycle performance was observed when the charge condition was changed from a constant rate to a short circuit rate. The charge current, limited by the internal cell resistance, peaked at about 1 mA as the cell was rapidly driven to the upper cutoff at 4.5 V.

The specific capacities of the LiMn$_2$O$_4$ cathodes annealed at 800°C were typically lower than those annealed at 700°C. A comparison is shown in Figure 4. In addition to the difference in capacity, the transition from one cubic spinel phase to another is clearly evident in the discharge curve of the cathode annealed at 700°C, characteristic of bulk LiMn$_2$O$_4$ (Reference 4), whereas no evidence of a transition was observed for the cathode annealed at 800°C. Based on the iR loss, the resistivity of the cell with the 700°C annealed cathode

\[ C = C_0(1-\delta)^n \] (1)
was about 20 times higher than that of the cell with the 800°C annealed cathode. In most of the cells fabricated to date, there appears to be a trade-off between specific capacity and cell impedance in the 4.5 V to 3.8 V range.

An example of the first charge cycle from 3.8 V to 5.3 V is shown in Figure 5. This cell with an 800°C annealed cathode had one of the lower specific capacities in the 4.5 V to 3.8 V range, about 60 μAh/mg, corresponding to about 0.4 Li/Mn$_2$O$_4$. On charging to 5.3 V, a plateau with a median voltage of 5.1 V was observed, and after holding the voltage constant at 5.3 V until the current decreased to 1 μA, the amount of charge extracted corresponded to about 1Li/Mn$_2$O$_4$. Within experimental error which includes the assumed film density, all of the Li was extracted from the cathode. The 5.1 V plateau seen in the curve might be due to the removal of tightly bound Li ions occupying octahedral sites in the spinel structure (Reference 5). We speculate that the differences in the capacities observed between 4.5 V to 3.8 V with the cathodes annealed under different conditions are caused by differences in the Li occupancy of octahedral sites vs. tetrahedral sites in the spinel structure.

Conclusions

Thin-film rechargeable Li-LiMn$_2$O$_4$ batteries with well-crystallized cathodes can deliver currents 100 times higher than those previously achieved using amorphous V$_2$O$_5$ cathodes of comparable dimensions. The cells exhibit excellent secondary performance with small capacity losses when cycled between 4.5 V and 3.8 V. The specific capacity of the cells in this range varied from about 50 μAh/mg to 120 μAh/mg depending on the post deposition annealing conditions. A previously unidentified plateau at about 5.1 V was observed and, within experimental error, the charge extracted on a slow charge to 5.3 V corresponded to 1Li/Mn$_2$O$_4$ removed from the cathode. Several prototype Li-LiMn$_2$O$_4$ batteries for different kinds of low current electronic devices are presently under development.

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