MoO₃ Thin Film Cathodes for Elevated Temperature Applications

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Introduction

One of the important advantages Li thin film batteries offer beyond outstanding cycle life and shelf life is the robustness inherent in the solid-state design; *viz.* the ability to tolerate temperature extremes, mechanical shock, and moderate flexure far better than conventional Li-ion or Li polymer cells.

However, a critical limitation of state-of-art Li thin film batteries is the sensitivity to elevated temperature cycling. Cells incorporating LiCoO2 cathodes, the most widely employed cathode for this type of battery, can be charged and discharged at 25°C over tens of thousands of cycles and experience capacity losses of only about 0.002% per cycle. In contrast, $LiCoO_2$ based cells that are operated at 60°C experience a factor of ten greater capacity loss per cycle.¹ Experimentation in our laboratories indicate that at higher temperatures, the capacity fade per cycle is even more severe, with cells capacity fading to 50% of initial values after only 100 cycles when operated at temperatures of 150°C. We are currently examining alternative cathode materials for elevated temperature cycling, and to this end have identified MoO₃ as a promising candidate material.

Experimental

All solid-state Li thin film battery cells were fabricated on glass slides. The deposition of all the films (except the anode layer) was carried out in a planar RF magnetron sputtering chamber. The cell design was a Ti/Pt current collector, MoO_3 cathode (0.3 \Box m thick), LiPON electrolyte (1 \Box m thick) and a thermally evaporated Li anode film.

 MoO_3 film crystallinity was characterized via x-ray diffraction, and surface morphology was studied using scanning electron microscopy (SEM). The electrochemical characterization of the cells was performed using a Princeton Applied Research 273A potentiostat, and cycling experiments were carried out using an Arbin battery cycler. For elevated temperature testing, the cells were placed on a hot plate in the glovebox with the temperature monitored using a thermocouple.

Results

As deposited, the MoO_3 films were amorphous. Following an anneal at 280°C for one hour, the MoO_3 film crystallized as mixed phases of layered \Box -MoO₃ and monoclinic \Box -MoO₃.

The cells were tested at 150°C, with a charge/discharge current density of 0.7 mA/cm². The first discharge shows two distinct plateaus, yielding an areal specific capacity of 89 \square Ahr/cm² \square m (Figure 1). On recharge and subsequent discharges, these plateaus disappear and become broad, smoothly sloping profiles with specific areal capacity of about 140 \square Ahr/cm² \square m.



Fig. 1. First three discharges of MoO_3 cells.

The rate capability of the cells is very good at 150° C, as shown in Figure 2. The cells retained about 60% of the low discharge rate capacity when discharged at 3.6 mA/cm². At very low discharge rates of 0.014 mA/cm², the areal specific capacity from 3.5V – 1V was approximately 180 \square Ahr/cm² \square m.



Fig. 2. Rate capability of MoO_3 cells.

The cycle life of the MoO_3 thin film batteries depends on a number of factors including charge/discharge cutoff voltages and temperature. However, preliminary results indicate that the capacity retention of the MoO_3 based thin film batteries is significantly better than conventional LiCoO₂ based thin film batteries.

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References

¹ B. Wang, J. B. Bates, F. X. Hart, B. C. Sales, R. A. Zuhr, and J. D. Robertson, *J. Electrochem. Soc.*, **143**, 3203 (1996).