

**Layered O3 Lithium Manganese Oxide Cathode  
Materials for Secondary Lithium Batteries –  
Recent Developments**

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Lithium-ion batteries are one of the major technological success stories of the last decade. The pace at which portable electronic devices are developing drives the need for more advanced lithium-ion cells. New positive electrode materials are critical to the success of these advanced batteries. Manganese oxide-based systems have been extensively studied recently due to their attractive characteristics i.e. low cost, low toxicity and good safety in the charged state compared with other transition metal oxides such as  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ . There have been major advances in the performance of lithium manganese oxide spinels, however, good cycling has traditionally been limited to the 4 volt region with practical capacities of around  $110\text{mAhg}^{-1}$ .

In the search for new lithium manganese oxide based positive electrode materials with greater capacities, compounds based on layered  $\text{LiMnO}_2$  have been studied (1-10). Extensive doping is possible by replacing, in part, manganese by a variety of other ions, and research on these materials is expanding rapidly.

We have prepared a range of  $\text{LiMnO}_2$  materials based on the layered O3 structure ( $\text{LiCoO}_2$  structure type). These materials are formed by first preparing the sodium phase then ion exchanging sodium by lithium. Rich variations in the synthesis conditions for these materials are possible. We have exploited this to introduce subtle but important differences in the composition and structure of the materials resulting in considerable variations in their electrochemical properties. Layered lithium manganese oxides with the O2 structure are under investigation by others (11,12).

We have studied a range of systems based on O3  $\text{Li}_x\text{Mn}_y\text{O}_2$  where  $x \cong 0.67$  and  $0 \leq y \leq 0.1$ . Both "pure" materials and a variety of doped materials have been considered and their electrochemical performance investigated over a range of charge/discharge rates at room temperature and  $55^\circ\text{C}$ . Stable capacities in excess of  $200\text{mAhg}^{-1}$  at 1C and at  $55^\circ\text{C}$  are possible.

During cycling, all the materials undergo an irreversible phase transformation to a spinel-like structure that forms as domains within each particle creating nanostructured particles. This is one feature that distinguishes these materials from directly prepared spinels and is also related to their superior cycling behaviour (10,13-16). Orthorhombic  $\text{LiMnO}_2$  also converts to a nanostructured spinel as has been elegantly demonstrated (15,16).

The influence of synthesis conditions and dopants upon electrochemical performance will be discussed in more detail.

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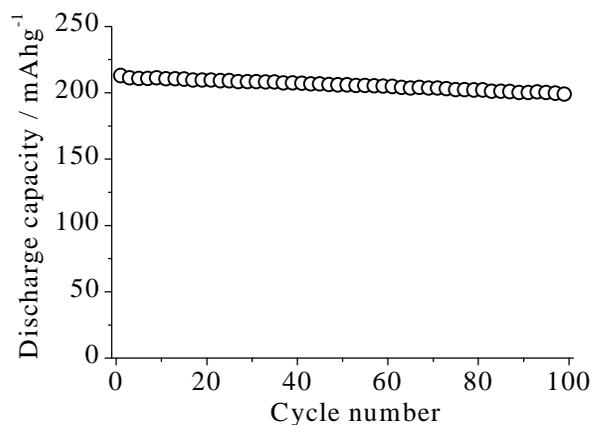


Figure 1.  $55^\circ\text{C}$  cycling data for doped layered  $\text{Li}_x\text{Mn}_y\text{O}_2$ . Rate = 1C,  $200\text{mAhg}^{-1}$ .

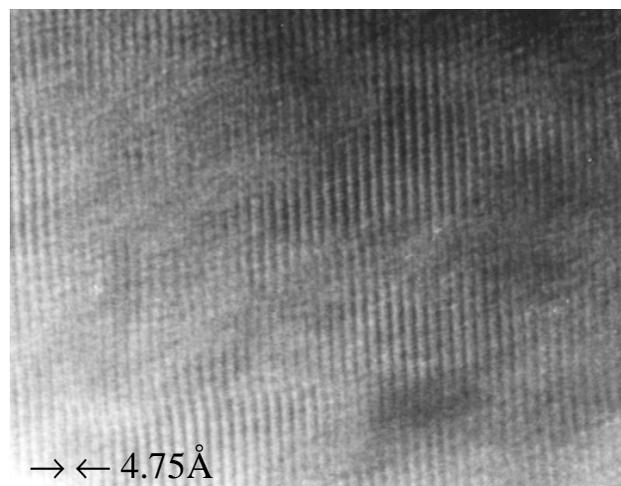


Figure 2. HREM image of layered  $\text{Li}_x\text{Mn}_{0.975}\text{Co}_{0.025}\text{O}_2$  (Ethanol  $80^\circ\text{C}$ ) at deep discharge post 40 cycles showing a nanodomain structure.