

Superlattice Formation and Lithium-Ordering in the Delithiated LiMn_2O_4 Spinel

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Single-crystals of LiMn_2O_4 spinel have been synthesized and investigated by X-ray diffraction. On the basis of the systematic absences, the cubic space-group $\text{Fd}\bar{3}\text{m}$ was chosen with $a = 8.245(4)$ Å. The crystals were then delithiated electrochemically to two different voltages: 4.25 and 4.08 V vs. Li/Li^+ (Fig. 1).

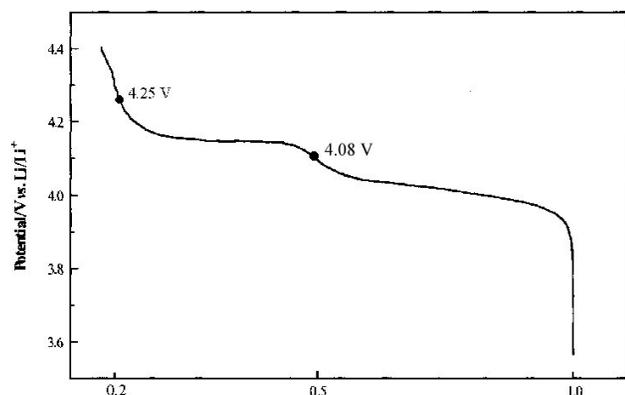


Figure 1. The discharge curve for a $\langle \text{Li} | \text{liq. el.} | \text{LiMn}_2\text{O}_4 \rangle$ cell.

The reduction mechanisms at 4.08 V and 4.25 V of the LiMn_2O_4 has by several researchers [1-4] been ascribed to different phase transitions, including lithium ordering, but insufficient experimental techniques have made it difficult to prove such behavior. At 4.08 V, the crystals show a $3 \times 3 \times 3$ superlattice with $a = 24.41(1)$ Å. The lithium-depleted single-crystals obtained at 4.25 V exhibited a $7 \times 7 \times 7$ superlattice cell with $a' = 56.49(2)$ Å and $57.13(3)$ Å, respectively. These superlattices can be ascribed to the ordering of lithium ions followed by a charge-ordering of manganese ions with different oxidation-states, which will be discussed.

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