# PROPERTIES OF LITHIUM- MANGANESE OXIDE THIN FILMS PREPARED BY A TWO STEP PROCESS

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## INTRODUCTION:

Lithium manganese oxides are being actively pursued for use as cathodes in lithium ion batteries [1.2] Manganese based oxides are usually favoured over cobalt and nickel oxides, primarily for their low cost and non-toxicity. Spinel lithium manganate and layered lithium manganese oxides are among the most promising materials. Extensive studies have been performed on the preparation, structure and electrochemical properties of the bulk material. Thin films have been deposited by electron beam evaporation, magnetron sputtering, pulsed laser deposition and chemical vapour deposition. In this work, thin lithium manganate films were deposited by a two step process consistent of the electrodeposition of Li-Mn alloy followed by oxidation in air.

## EXPERIMENTAL:

The Li-Mn alloy was electrodeposited on SS and Ni substrates in the potentiostatic mode using a potential of – 1.55 V (SCE) at room temperature. The plating time was 30 min. Thickness of the films was 2.0 μm from gravimetry. The films were heat treated at different temperatures in the range 400 - 600°C for 5 minutes in air. The films were characterized by x-ray diffraction studies using Cu Ka radiation and a Phillips x-ray diffractometer. SEM studies were made using JEOL scanning electron microscope. FTIR studies were made in the range of 400 – 4000 $cm^{-1}$ in order to get an idea about the bending, rotating and vibrational modes of the atoms.

## RESULTS AND DISCUSSION:

The films characterized by x-ray diffraction studies. Films heat treated at temperatures below 550° C indicated mixed phases of $LiMn_2O_4$ , $MnO_2$ etc., while those heat treated above 550°C indicated low intense peaks due to reduction in thickness of the films. Films heat treated at 550 ° C indicated the formation of single phase spinel $LiMn_2O_4$. Peaks corresponding to (111),(311) and (222) characteristics of the spinel phase were observed. The lattice parameters calculated as 8.236Å, which is slightly less than the reported value of 8.243 Å for the bulk material. Spinels belong to the cubic symmetry system and are constructed by close space packing of oxygen ions. The oxygen ions occupy each corner of the polyhedron. The chains are connected by cations existing in the tetrahedral sites. When $LiMn_2O_4$ spinel electrodes are deposited as thin films, typically 0.5 mm or more thick be electron beam evaporation or R.F sputtering, structures are formed that provide unusual electrochemical behaviour in solid state lithium cells [3 – 5]. Though by and large thin film electrodes crystallize in the cubic spinel structure, recently two models have been put forward for the structures of thin film $LiMn_2O_4$ electrodes to explain their electrochemical behaviour. One model proposes a spinel structure with strong inverse character, i.e., with some manganese in the tetrahedral 8a sites, but it was subsequently pointed out that partially inverse spinels could not satisfactorily explain all the electrochemical properties. A second model suggests a spinel structure in which a fraction of the manganese ions are located in the 16 c octahedral sites, i.e., outside the $[Mn_2]O_4$ spinel framework. The lattice model is generally used to explain the electrochemical behaviour of thin film $LiMn_2O_4$ electrodes. Scanning electron microscopy studies indicated the uniformity of the films with the crystallites forming a flaky structure. FTIR studies indicated lines at 620,639.90 and 668.30 $cm^{-1}$. The high local symmetry of the parent cubic spinel lithium manganate is reflected by the observation of a strong absorption band at 620 $cm^{-1}$ [6]. Impedance studies are being carried out on these films. Preliminary attempt to prepare a cell using the thin film $LiMn_2O_4$ as cathode and tin oxide thin film as anode and Lithium perchlorate as electrolyte indicated that an open circuit voltage of 1.8V could be obtained. Charge discharge studies indicated that upto 25 cycles the cell output did not decrease. Further steps to improve the cycle life is in progress.

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