

# The Effects of Defects on Structural Changes and Capacity Fading for $\text{LiMn}_2\text{O}_4$ Type Cathode Materials During Cycling

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## Introduction

It was reported by Ohzuku<sup>1</sup> that stoichiometric  $\text{LiMn}_2\text{O}_4$  undergoes a structural first order phase transition from a cubic (Fd3m) to a cubic structure with the same symmetry but different lattice constant during charge-discharge cycle between 3.5 V and 4.5 V. When the cell was discharged below 3.0 V, the material transfers in to a tetragonal structure. One-phase, two-phase, and three-phase models have been proposed for the structural changes in the 4.0 V and 4.2 V charge plateaus (2). In this paper, we will report the effects of defects on these structural changes in the 4.0 V and 4.2 V plateaus. These defects include those formed during synthesis, thermal treatments, and charge-discharged at different conditions. The relationship between these defect-induced structural changes and the capacity fading will also be discussed.

## Experimental

*XRD studies:* In situ XRD spectra were collected on beam line X18A at National Synchrotron Light Source (NSLS) operated at an energy of 10375 eV ( $\lambda=1.195 \text{ \AA}$ )

*The spectroelectrochemical cell:* All of the *in situ* data reported here were done in a spectroelectrochemical cell that has been described elsewhere (3).

*Preparation of  $\text{LiMn}_2\text{O}_4$  with different O stoichiometries:*  $\text{LiMn}_2\text{O}_4$  with various O stoichiometries were prepared by heat treating  $\text{Li}_{1.07}\text{Mn}_{1.93}\text{O}_4$  at 600°C under Ar. The O stoichiometry was determined from separate TGA measurements.

## Results and Discussion

*Effect of O stoichiometry on low temperature phase transitions in  $\text{LiMn}_2\text{O}_4$ :* DSC results in show that the temperature for the phase transition and kinetics of the conversion from the cubic to the tetragonal phase increased with decreasing oxygen stoichiometry. In the case of stoichiometric materials the conversion occurs in the vicinity of 0°C. For longer heat treatments the conversion

occurred at ambient temperature or above. The oxygen stoichiometry also had major effects on the phase transformations at low temperature. The results indicate that the existence of oxygen vacancies in  $\text{LiMn}_2\text{O}_4$  is a critical condition for formation of the low temperature phase, with the percentage of the low temperature phase proportional to the population of oxygen vacancies. Also, the larger number the oxygen vacancies, the higher the transition temperature. The XRD results at low temperature are more consistent with a mixture of a tetragonal and a cubic phase, rather than a single phase with an orthorhombic structure. The following series of experiments strongly support a mechanism based on oxygen vacancies. At 300K the results show a mixed phase composition for a sample treated at 600°C under Ar for 12 h. After treatment of the sample under  $\text{O}_2$  at 700°C for 10 hours only a single cubic phase is seen at 300K.

$\text{LiMn}_2\text{O}_4$  with low oxygen stoichiometry clearly displayed three cubic phases during charge. Stoichiometric materials and materials with excess lithium stoichiometry display pseudo-single phase behavior in the early stages of charge. This is followed by two-phase behavior towards the end of charge. Preliminary cycling studies indicate that the oxygen stoichiometry also affects capacity maintenance and phase behavior during cycling.

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## References

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