Failure Modes of $LiMn_2O_{4-\delta}$ for Cathode Materials in Lithium Secondary Batteries

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Layered $LiCoO_2$, $LiNiO_2$ and spinel $LiMn_2O_4$ could be used as the cathode materials of the lithium batteries because of their high voltage (about 4V) and good rechargeability. Among these materials, $LiMn_2O_4$ is most favored because of low cost and no harmful for the environment [1]. For the past ten years, the spinel $LiMn_2O_4$ has been studied extensively as a positive electrode material for rechargeable lithium and lithium ion cells[2-5]. However, the $LiMn_2O_4$ electrodes have showed capacity fading during cycling. In the present study, we have adapted the modified Pechini process to the synthesis of $LiMn_2O_4$. The process is based on the ability of certain weak acids to form poly-basic acid chelates with various cations.

Using this method, it is possible to obtain phase-pure ultra-fine crystalline spinel phases after firing the polymeric precursors at low temperatures.

This paper aim to failure mechanism by control Mn valence state and oxygen nonstoichiometry

Figure 1 shows the XRD pattern of un-doped $LiMn_2O_4$ synthesized at 800°C for 4 hours. It shows Mn reduction and also accompanies oxygen loss steps. In order to obtain high Mn valences state, we doped Ga at 0.1mol % in stead of Mn. High Mn valence state guarantee reversibility of Li ion secondary battery[2]. Synthesized sub micron-sized particle distribution is shown in Figure 2.

Cycling result shown in Figure 3. It shows good reversibility.

Therefore, Ga doping is a useful method to make $LiMn_2O_4$ powder without capacity loss. Reduced Mn generates lattice distortion that so called Yahn-Teller [6] distortion during cycling. Ga doping prevent reduction of Mn. The advantages of doping in this work are very effective to prevent capacity loss.[6]

References

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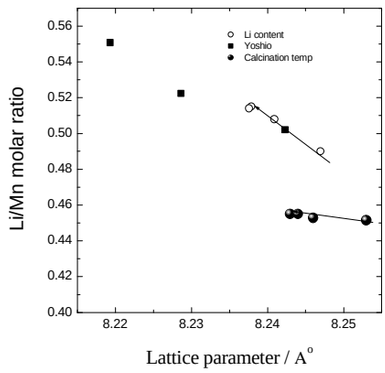

Fig. 1. The lattice constant vs. Li/Mn content of the of the $LiMn_2O_4$ powder

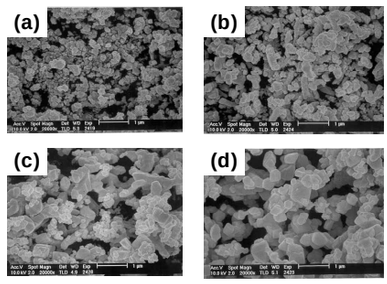

Fig. 2. Scanning electron microgrphs of Ga doped powder heated at different temperature :
(a) 600℃ for 4hrs (b) 700℃for 4hrs
(c) 800℃ for 4hrs (d) 800℃ for 24hrs

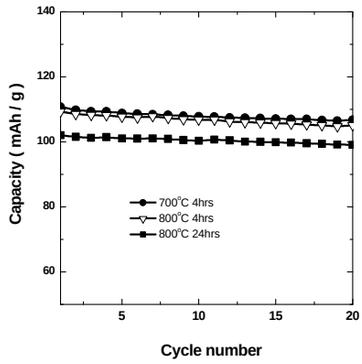

Fig. 3. Cycling result of Ga doped (0.1mol) spinel.