

Preparation and Its Electrochemical Properties of Li_xMnO_2 Material

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Introduction

The layered oxide materials, LiMO_2 (M=Co, Ni, Mn...) and the LiMn_2O_4 spinel are the most widely studied 4 V cathode materials for lithium secondary batteries with high energy density. The Mn-based materials have attracted wide attention as intercalation cathode materials because of their low cost and nontoxicity. Orthorhombic LiMnO_2 (herein referred to as *o*- LiMnO_2) of the ordered rock salt structure described by Johnston¹ and Hoppe et al.² has been studied many research groups. The low temperature synthesis (170~450°C) first reported by Ohzuku et al.³ showed a large rechargeable capacity above 190mAh/g.² Reimers et al. also reported a new ion exchange method and revealed an irreversible structural change to the spinel phase using in-situ XRD.³ Croguennec et al. and other groups⁴ reported a different synthetic route at mid-range temperatures (600~750°C). They contributed to reveal the capacity loss mechanism and improve the cycleability of the *o*- LiMnO_2 material. However, the results showed a reduced initial discharge capacity (about 130mAh/g) and the elevated temperature performance of *o*- LiMnO_2 has not been reported.

Recently, Y.S. Lee et al. reported a new synthetic method using quenching process, which could synthesize a well-crystallized *o*- LiMnO_2 material at high temperature (1000 °C) by one-step method. This work showed a couple of new indications as follows; First, the unique quenching effect for obtaining the pure orthorhombic LiMnO_2 phase, which showed no structural transformation to the spinel-like phase during the cooling process. Second, *o*- LiMnO_2 material with an excellent cycling performance at room and high temperature (55 °C) could be obtained easily without the exchange reaction of Li^+/Na^+ or maintaining the sensitive synthetic condition. Last, it clearly revealed the marvelous relation between particle size (or surface area) and initial discharge capacity of *o*- LiMnO_2 compound by adopting the grinding process. However, the *o*- LiMnO_2 obtained at high temperature needs a grinding process for 12 hrs, which improve initial discharge capacity by enlarging a contact area and a surface area of powders.

Therefore, we reports here a new cathode material obtained at low temperature (350 °C), Li_xMnO_2 , which shows a high initial discharge capacity over 200 mAh/g with excellent cycle performance without grinding process.

Experimental

Li_xMnO_2 material was synthesized using $\text{LiOH} \cdot \text{H}_2\text{O}$ and $\gamma\text{-MnOOH}$ by the melt impregnation method. The mixture of LiOH and $\gamma\text{-MnOOH}$ was precalcined at 200 °C for 5 h in Ar and then post-calcined at various temperatures (250-350 °C) for 20 h in Ar. The powder X-ray diffraction (XRD) using $\text{CuK} \alpha$ radiation was employed to identify the crystalline phase of the synthesized material. The Li and Mn contents in the

resulting materials were determined using an inductively coupled plasma-atomic emission spectrometry. The particle morphology of Li_xMnO_2 material was observed using a scanning electron microscope.

The electrochemical characterizations were performed using CR2032 coin-type cell. The test cell was made of a cathode and a lithium metal anode separated by a porous polypropylene film. The electrolyte used was a mixture of 1M $\text{LiPF}_6\text{-EC/DMC}$ (1:2 by vol.). The charge/discharge current density was 0.4 mA/cm^2 with a voltage of 2.0 to 4.3 V at room temperature.

Results and Discussion

Li_xMnO_2 was synthesized using LiOH and Mn_3O_4 starting materials at various temperatures (250-350 °C). X-ray diffraction revealed that Li_xMnO_2 calcined at 350 °C showed a well-defined orthorhombic phase of a *Pnam* space group. The $\text{Li/Li}_{0.7}\text{MnO}_2$ obtained at 350 °C showed the increase of capacity on cycling and it delivered a fairly high discharge capacity of 200 mAh/g after 50 cycles.

We found that the cycling performance of Li_xMnO_2 was very related to its surface area and structural transformation using TEM and other analytical tools.

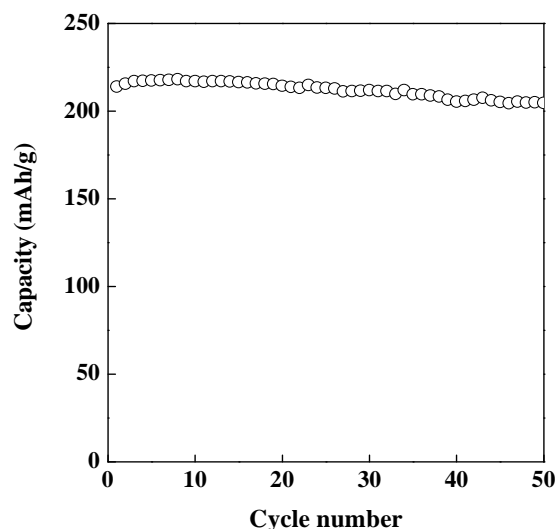


Fig. 1. Charge/discharge curves for the $\text{Li}/1\text{M LiPF}_6\text{-EC/DMC/Li}_{0.7}\text{MnO}_2$ cell obtained at 350 °C.

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