

Preparation and Electrochemical Characterization of Li_2MnO_3 Material

Y-S Lee^{a,*}, M. Miyamoto^b, K. Kobayakawa^b,
and Y. Sato^b

^aHigh-Tech Research Center and

^bDepartment of Applied Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Yokohama 221-8686, Japan

Introduction

Layered lithium metal oxide materials have been studied as preferred cathode materials for lithium secondary batteries. Layered lithium metal oxide with the general formula LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}$) has a rock salt structure ($R\bar{3}m$) where lithium and transition metal cation occupy alternate layers of octahedral sites in a distorted close-packed oxygen ion lattice. The layered MO_2 framework provides two-dimensional interstitial spaces, which allows for easy extraction of lithium ions.

A different type of layered Li_2MnO_3 (monoclinic, $C2/c$, $a=4.932\text{ \AA}$, $b=8.537\text{ \AA}$, $c=9.60\text{ \AA}$, $\beta=99.15^\circ$, $V=404.2\text{ \AA}^3$) could be easily obtained at high temperature using solid-state method. Because Mn oxidation state of this material is 4+ state, it is known to be electrochemically inactive material since the Mn could not be oxidized over the 4+ oxidation state when lithium was extracted from Li_2MnO_3 structure.^{1,2}

One of the useful methods which possible to insert/ extract of lithium ion into the Li_2MnO_3 structure, some research groups have tried to prepared $\text{Li}_{2-x}\text{MnO}_{3-x/3}$ ($0 < x < 2$) material, which obtained by acid-leaching Li_2O from the rock-salt structure.³ They intended to synthesize a stabilized layered lithium manganese oxide which could not convert spinel as well as fully is possible to charge/ discharge process. A similar trial was attempted by Tang et al. that a new type of Li_2MnO_3 was obtained by selective lithium extraction from its structure. They successfully synthesized Li_2MnO_3 using LiCl -flux method and it has the polyhedral crystal with fairly large particle sizes 10-30 μm . It was conducted Li ion extraction into the Li_2MnO_3 in H_2SO_4 solution in a hydrothermal condition. After Li^+ extraction process, Li_2MnO_3 was remarkably changed into plate-like particle with 1-3 μm , which consisted of an aggregate of very thin plates 20-50 nm. Furthermore, Li/Li^+ -extracted Li_2MnO_3 cell presented a very high initial capacity of 191 mAh/g in the first cycle.⁴ Most recently, Robertson and Bruce have reported the electrochemical reaction of Li_2MnO_3 and its cycling characterization in the conference of IMLB 11.⁵

From a review of previous studies, we found that Li_2MnO_3 could be a prospective cathode material with stable layered structure during cycling. We report here a new type of Li_2MnO_3 material by solid-state method, which is possible to fully charge/discharge process and presents a fairly higher discharge capacity at room temperature

Experimental

Li_2MnO_3 material was synthesized using $\text{LiOH} \cdot \text{H}_2\text{O}$ (Kishida Chemical, Japan) and Mn_3O_4 (Tosoh chemical, Japan) by the melt impregnation method. The mixture of LiOH and Mn_3O_4 was precalcined at 470 and 530 $^\circ\text{C}$ for 5 h in air and then post-calcined at various temperatures (600-1000 $^\circ\text{C}$) for 20 h in air. The powder X-ray diffraction (XRD, Rint 1000, Rigaku, Japan) 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 (ICP-AES, SPS 7800, Seiko Instruments Inc., Japan). The particle morphologies of Li_2MnO_3 materials were observed using a scanning electron microscope (SEM,

JSM-5300E, Japan Electron Ltd., Japan). The electrochemical characterizations were performed using CR2032 coin-type cell. The cathode was fabricated with 20 mg of accurately weighed active material and 12 mg of conductive binder (8 mg of Teflonized acetylene black (TAB) and 4 mg of graphite). The test cell was made of a cathode and a lithium metal anode (Cyprus Foote Mineral Co.) separated by a porous polypropylene film (Celgard 3401). The electrolyte used was a mixture of 1M LiPF_6 -ethylene carbonate (EC)/ dimethyl carbonate (DMC) (1:2 by volume). The charge and discharge current density was 0.4 mA/cm^2 with a voltage of 2.0 to 4.5 V at room temperature.

Results and Discussion

Li_2MnO_3 was synthesized using LiOH and Mn_3O_4 starting materials at various temperatures (600-1000 $^\circ\text{C}$). X-ray diffraction revealed that Li_2MnO_3 showed a well-defined monoclinic phase of a $C2/c$ space group although it showed some differences such as super lattice $2\theta = 20-25^\circ$. The $\text{Li}/\text{Li}_2\text{MnO}_3$ obtained at 600 $^\circ\text{C}$ showed the increase of capacity on cycling and it delivered a fairly high discharge capacity of 160 mAh/g after 10th cycle.

We found that the cycling performance of Li_2MnO_3 was very related to its surface area and structural transformation.

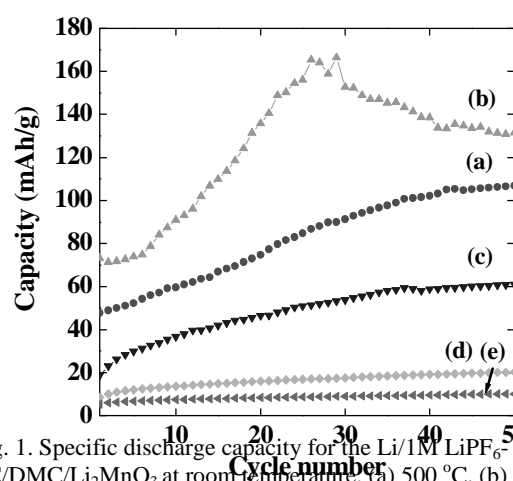


Fig. 1. Specific discharge capacity for the $\text{Li}/1\text{M LiPF}_6\text{-EC/DMC/Li}_2\text{MnO}_3$ at room temperature: (a) 500 $^\circ\text{C}$, (b) 600 $^\circ\text{C}$, (c) 700 $^\circ\text{C}$, (d) 800 $^\circ\text{C}$, and (e) 900 $^\circ\text{C}$.

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