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The Synthesis and Electrochemical Properties of Lithium Manganese Oxide (Li_2MnO_3)

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ABSTRACT :

The layered lithium-manganese oxide (Li_2MnO_3) as a cathode material of lithium ion secondary batteries was prepared and characterized the physico-chemical and electrochemical properties. The morphological and structural changes of MnO(OH) and Li_2MnO_3 are closely connected to the changes of electrochemical properties. The crystallinity of Li_2MnO_3 is enhanced as the annealing temperature increase, but its capacity is reduced due to the easier structural changes of less crystalline Li_2MnO_3 than highly crystalline one. Moreover, the addition of buffer material such as MnO(OH) into cathode causes to reduce the morphological and structural changes of layered Li_2MnO_3 and increase the discharge capacity and cycleability.

Keywords: *Li_2MnO_3, manganese oxyhydroxide (MnO(OH)), hydrothermal reaction, structure changes, spinel $LiMn_2O_4$*

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1. Introduction

The materials affiliated with lithium transition metal oxides are mainly used for the cathode active materials of the lithium secondary batteries (LIB), and the electrochemical properties are attributed to the oxidation number changes of the transition metal in the active materials. Specifically, the oxidation number of the transition metal ion is changed as lithium ions are inserted and extracted (intercalation/deintercalation), and the average voltage depends on the oxidation/reduction of the each element. However, in the layered structure Li_2MnO_3, the oxidation number of manganese is +4 in the discharging state (lithium ions are intercalated) and is +5 in the charging state (lithium ions are extracted), and therefore, it becomes electrically inactive.[1-2] However, the recent studies have shown high capacities by acid treatment which makes deficiencies in the material and induces spontaneous redox reactions or by Li_2O elimination from Li_2MnO_3. It allows Li ions existing between $[Li_{1/3}Mn_{2/3}]$ layers to participate in electrochemical reactions.[3-5] Moreover, it has been shown that Li_2MnO_3-$LiMO_2$ (M = Mn, Co, Ni, Cr, etc.) composite electrodes have different polymorphs and reduce structural changes during charge/discharge cycles.[6-7]

In this study, we investigated physico-chemical and electrochemical properties of the Li_2MnO_3 as a cathode material. The Li_2MnO_3 is known as an electrical inactive material, but its layered structure was partially changed into spinel structure after charge/discharge cycles. It makes the manganese redox reaction to be possible and allows doing electrochemical activation. In addition, we investigated the role of the MnO(OH) as a buffer material for the Li_2MnO_3 and discuss the improvement of electrochemical properties.

2. Experimental

The manganese precursor of Li_2MnO_3 is MnO(OH)

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and it is synthesized by hydrothermal reaction. After preparing the mixture of $KMnO_4$ (5 g) and ethanol (5 mL) in deionized water (DIW, 400 mL), ~30 mL of stock solution was added into autoclave bomb and performed reaction with stirring at various temperatures (100-150°C) for 24 hours.[8] The obtained product was washed with DIW and ethanol several times and then dried at 80-100°C for 3 days. To prepare Li_2MnO_3, MnO(OH) and $LiOH{\cdot}H_2O$ (Aldrich) were mixed (Li : Mn = 2.1 : 1), and annealed at the various temperatures (600-900°C) in air atmosphere.

The physico-chemical properties of the samples were characterized by X-ray Diffraction (XRD, Rigaku DMAX-III diffractometer), scanning electron microscopy (SEM, Hitachi S-4300, Japan) and Fourier transform infrared spectroscopy (FT-IR, Nicolet 380). The electrode for the coin cell was prepared using 10 mg of the cathode material, 4 mg of TAB (Welcos) and isopropyl alcohol. The coin cell (CR2032 type) was assembled in Ar-filled glove box and the cell consists of Li_2MnO_3, lithium metal, separator (polypropylene, Welcos) and electrolyte (1 M $LiPF_6$ in dimethyl carbonate (DMC)/ethylene carbonate (EC) (1 : 1 v/v), TECHNO Semichem Co.). Charge/discharge tests were performed by WBCS 3000 (WonA Tech, Korea) after aging the coin cell for 10 hours. In order to investigate the structural change of the cathode material after charge/discharge tests, the tested coin cell was disassembled in Ar-filled glove box and dried at room temperature. Then, XRD is measured after washing them with DMC (dimethyl carbonate) for removing $LiPF_6$ electrolyte.

3. Results and Discussion

The manganese precursor, MnO(OH), of Li_2MnO_3 was prepared by hydrothermal reaction method.[8] The morphology of prepared MnO(OH) was investigated by SEM. Fig. 1 shows the SEM images of MnO(OH) synthesized at various temperatures. The reaction at the low temperature results in the formation of spherical nanoparticles. The particle size of MnO(OH) prepared at 100-120°C is ~70-80 nm. However, the morphology of MnO(OH) is significantly different from the reaction at the higher temperature. Fig. 1 (d)-(f) show the SEM images of MnO(OH) synthesized at 130-150°C. The shapes of prepared MnO(OH) are micro-sized nano-rod (about 100 nm in diameter). The particle size and the degree of agglomeration increase as the reaction temperature rises.

The crystallinity of the prepared manganese precursor,

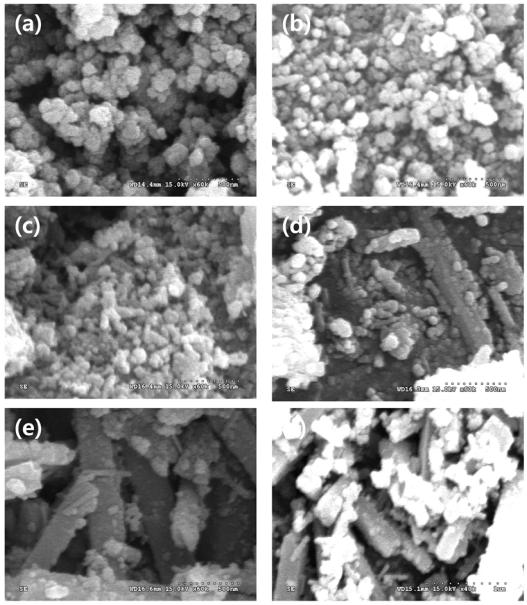

Fig. 1. SEM images of MnO(OH) synthesized at (a) 100°C, (b) 110°C, (c) 120°C, (d) 130°C (e) 140°C, and (f) 150°C.

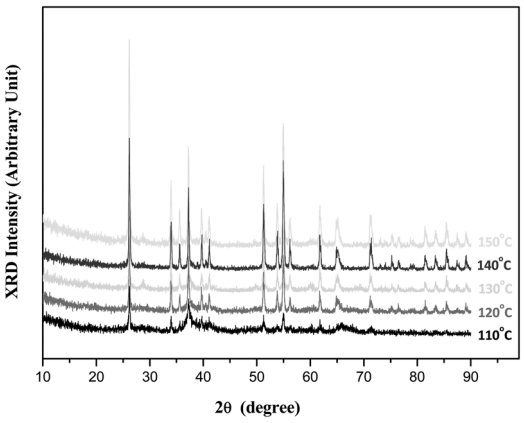

Fig. 2. XRD patterns of MnO(OH) synthesized at 110 – 150°C.

MnO(OH), is characterized by XRD. Fig. 2 shows XRD results of the sample prepared at various temperatures. The X-ray scattering features of MnO(OH) synthesized at 100°C are very broad and not intense due to the formation of nano-sized amorphous particle. However, as the reaction temperature increases, the scattering features become more intense and sharper. It indicates that MnO(OH) prepared at high temperature has good crystallinity. In addition, as shown in Fig. 1 (SEM images),

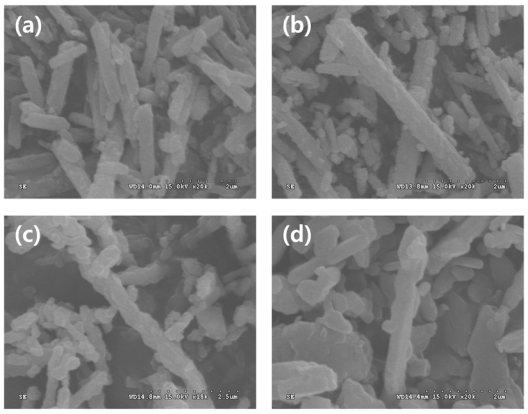

Fig. 3. SEM images of Li_2MnO_3 synthesized at (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C.

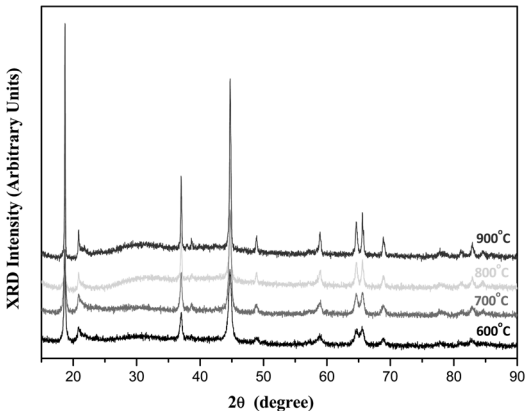

Fig. 4. XRD patterns of Li_2MnO_3 synthesized at 600 – 900 °C.

because the morphology of MnO(OH) has a rod-type shape and large domain as the reaction temperature increases, X-ray scattering features become more intense. The characteristic scattering features are consistent with the published literatures.[8-9] Even though the minor impurity (Mn_3O_4) is observed at ~28 and ~60 degrees, it is evident that the as-prepared MnO(OH) samples are well crystallized.

In order to prepare Li_2MnO_3, thus-prepared nano-rod shaped MnO(OH) synthesized at 140°C was used. The mixture of MnO(OH) synthesized at 140°C and $LiOH{\cdot}H_2O$ (1 : 2.1 mole ratio) was annealed at various temperatures (600-900°C) for 4 hours. Fig. 3 shows SEM images for the prepared Li_2MnO_3. Different from the sample prepared by solid state reaction, the shape of our sample is a rod-type, and this rod-type morphology is the same as that of MnO(OH) which we used as the manganese precursor. This phenomenon is called "chimie-douce effect".[10-11] The chimie-douce reactions are topotactic reactions that the both of a reactant and product have the equivalent structure, which is the one of the methods to control the shapes of a compound. The synthesized Li_2MnO_3 has about 100-150 nm in diameter and micro-sized length similar to the morphology of MnO(OH).

The crystallinity of the prepared Li_2MnO_3 samples is investigated by XRD, and the results are shown in Fig. 4. The XRD patterns shown in Fig. 4 indicate that all of the Li_2MnO_3 samples prepared at 600-900°C have monoclinic structure. These monoclinic structure peaks are attributed to the cation ordering of Li^+ and Mn^{4+} ions existing in the transition metal layers in the Li_2MnO_3. The charge differences induce a different cation distribution of Li_2MnO_3 and simultaneously symmetry lowering from hexagonal *R 3m* to the monoclinic *C2/m*.[1-3] For the sample annealed at 600°C, the superlattice feature of Li_2MnO_3 positioned at ~21 degree completely disappears due to the staking disorder with low crystalliniy.[12] However, the characteristic scattering features of monoclinic structure are clearly seen at 64.5 and 65.5 degree assigned to (135) and (060) reflections even for the sample annealed at low temperature. With further annealing, the scattering features at ~21, 64.5, and 65.5 degree become more intense and shaper as the annealing temperature increases. It indicates that the crystallinity of the Li_2MnO_3 is enhanced with an increase in the annealing temperature.

The electrochemical properties of the prepared Li_2MnO_3 sample are investigated. The charge/discharge tests are performed at 0.2 C-rate with 2.5-4.5 V cut-off condition. The results of charge/discharge tests are shown in Fig. 5. From the results of the charge/discharging tests, discharge capacities monotonically increase as the number of cycle increases, and it decreases after a certain maximum point. It can be explained that these rapid changes are contributed to the irreversible phase transition.[13-14] The results of the cell with Li_2MnO_3 annealed 600°C show relatively stable capacities and the difference between the minimum and the maximum discharge capacities is the smallest among the samples annealed at various temperatures. The cell with Li_2MnO_3 annealed at 700°C shows the best maximum discharge capacity which is larger than that of the sample annealed at 600°C. However, the initial capacity is smaller than the sample annealed at 600°C. On the other hands, the cells with Li_2MnO_3 annealed at 800 and 900°C show the significantly low initial discharge capacities, but their cycleabilities are improved with respect to the cells with

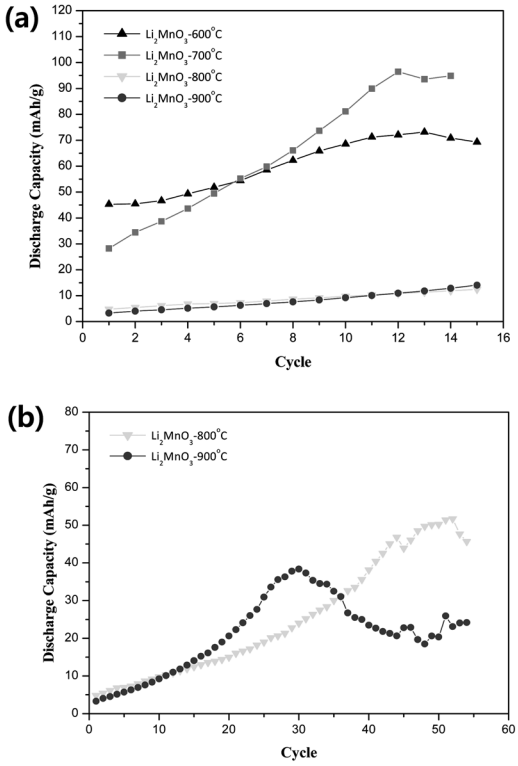

Fig. 5. Discharge capacities of (a) Li_2MnO_3 synthesized at 600-900°C cells (after 15cycles) and (b) Li_2MnO_3 synthesized at 800 and 900°C (after 54cycles).

Li_2MnO_3 annealed at 600 and 700°C. Practically, the stoichiometric Li_2MnO_3 shows no electrochemical reactions because it is difficult for the lithium ions to diffuse into the Mn layer. Hence, the lithium ion diffusion is probably enhanced in less crystalline particles. Even if the maximum discharge capacities of the samples annealed at various temperatures are different for the annealing temperature, the overall change of the discharge capacity for the different samples follows the same trend. It means that structural change of the active materials, annealed at different temperature, follows the same mechanism during the repeated lithium ion intercalation/deintercalation processes. To investigate the structural change after cell tests, the cathodes of the tested cells were washed with DMC, dried and then performed the X-ray diffraction experiments. Fig. 6 shows the XRD results of the cathode material after cell tests. As shown in the figure, the superlattice scattering features of the layered structure Li_2MnO_3 at ~21 degree completely disappears and one of the pair of the monoclinic features at ~65.5 degree significantly reduced. It is evident that the layered structure of the rock-salt Li_2MnO_3 partially collapsed.[3] Besides the change of main feature, some minor scattering feature appears at ~40 and ~58 degree after the cell test. These minor scattering features are assigned to spinel $LiMn_2O_4$. Hence, the rock-salt Li_2MnO_3 gradually changes the structure to spinel $LiMn_2O_4$ and this result is consistent with previous publication.[15] Due to the influences of the Mn^{3+} of thus-

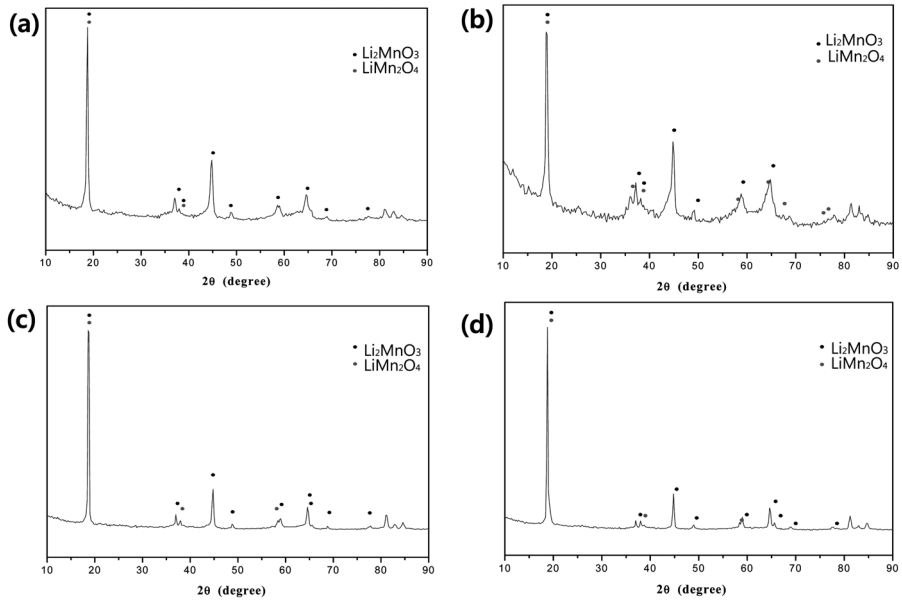

Fig. 6. XRD data for structure changes after cycle tests of Li_2MnO_3 synthesized at (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C.

formed $LiMn_2O_4$, the transition between manganese ions with +3/+4 oxidation numbers is probably possible, and therefore, electrochemically inactive Li_2MnO_3 becomes active as well as increases the discharge capacity. Therefore, the low crystalline Li_2MnO_3 annealed at the lower temperature, having high stacking fault rate,[16] shows relatively high discharge capacities due to the easier structural changes than highly crystalline Li_2MnO_3 annealed at the high temperature. Moreover, because the structure changes of well-crystalline Li_2MnO_3 annealed at 800 and 900°C are proceeded slowly, it probably takes longer time to reach the state that the redox reactions of the manganese can be activated. In order to elucidate the transition between manganese ions with +3/+4 oxidation numbers, the discharge capacity - voltage curves of Li_2MnO_3 annealed at 700°C are plotted in Fig. 7. At the initial several cycles, ~4.0 V plateau related to the manganese +3/+4 redox reaction is too short. However, as increasing the number of cycle, the plateau range around 4.0 V gradually increases and the total discharge capacity is enhanced corresponding to the results as mentioned above.

As already mentioned, the layered Li_2MnO_3 experiences the structural changes as charge/discharge cycles proceed. In order to reduce the morphological and structural change of this cathode material, MnO(OH) used as the manganese precursor is blended with layered Li_2MnO_3. The spherical MnO(OH) nano-particle prepared at 100°C probably acts as a buffer against the morphological and structural change of layered Li_2MnO_3 because MnO(OH) nano-particle not only has the smaller particle size than layered

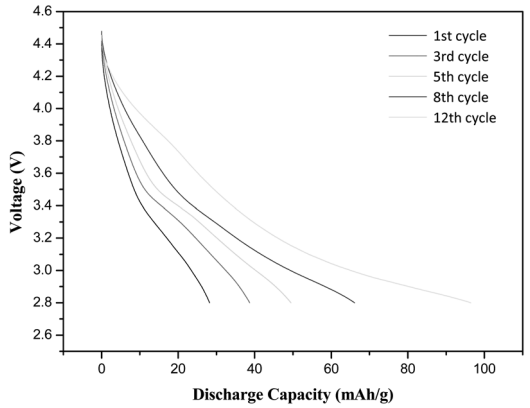

Fig. 7. Structure changes of each Li_2MnO_3 after cycle tests at 2nd, 5th, 8th,and 12th cycles; (a) Discharge capacities of Li_2MnO_3-700°C at the each step and (b) XRD data of the Li_2MnO_3-700°C cell after cycle tests at the each step.

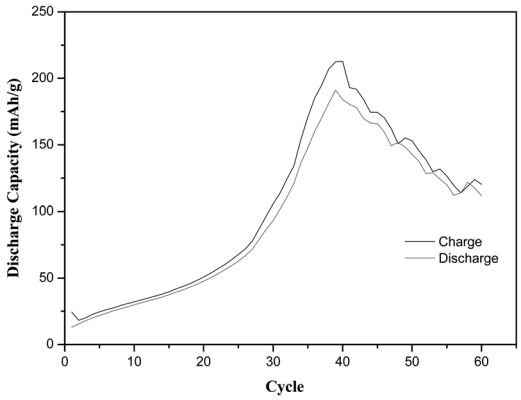

Fig. 8. Charge/discharge performances of the Li_2MnO_3-MnOOH composite.

Li_2MnO_3 but also is converted to an active material, lithium manganese oxide, after intercalation of lithium ion into MnO(OH). To prepare the cathode, MnO(OH) synthesized at 100°C and Li_2MnO_3 (1 : 1 mole ratio) are mixed to make an active material. The charge/discharge tests are performed to investigate the electrochemical property and the results are shown in Fig. 8. The overall cycle performances show the volcano shapes for the discharge capacity with a maximum point, and the initial capacities are gradually increased. However, unlike the case that Li_2MnO_3 is used alone, the maximum discharge capacity is greatly enhanced and appears at ~40th cycle. It demonstrates that the structural changes from layered to spinel are slowly proceeded by the addition of MnO(OH) as a buffer. It also indicates that the slow structural changes during lithium-ion intercalation/deintercalation can be occurred and increases the capacities.

4. Conclusion

We synthesized the manganese oxyhydroxide (MnO(OH)) by hydrothermal reaction and Li_2MnO_3 cathode material was prepared by solid-state reaction of LiOH with as-prepared MnO(OH). The electrochemical performances and structural changing properties of the electrochemically inactive and layered Li_2MnO_3 was investigated. The prepared MnO(OH) shows different morphologies and crystallinity as a function of reaction temperature. However, the morphology of Li_2MnO_3 is not significantly changed with an increase in the annealing temperature, and it has the same morphology as the manganese precursor, MnO(OH). The crystallinity of

Li_2MnO_3 is enhanced as the annealing temperature increases, but its capacity is reduced due to the easier structural change than highly crystalline Li_2MnO_3 annealed at the high temperature. The layered structure of the Li_2MnO_3 is partially changed into $LiMn_2O_4$ spinel structure after charge/discharge cycles and the electrochemical properties are enhanced because the manganese redox reaction in the Li_2MnO_3 can be possible. Moreover, the addition of buffer material such as MnO(OH) into cathode causes to reduce the morphological and structural changes of layerd Li_2MnO_3 and increases the discharge capacity and cycleability.

Acknowledgements

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