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Development of Mn-based Cathode Materials for lithium Secondary Battery

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Among the intercalation materials, lithiated transition metal oxides such as $LiMO_2$ (M = Co, Ni, Mn) and $LiMn_2O_4$ have been widely studied as the cathode materials for lithium secondary battery.

$LiAl_xMn_{2-x}O_4$ (x = 0.03-0.3) has been synthesized using various aluminum starting materials, such as $Al(NO_3)_3$, $Al(OH)_3$, AlF_3 and Al_2O_3 at 800 °C for 20 h in air or oxygen atmosphere. The Al-doped content and the intensity ratio of (311)/(400) peaks can be important parameters in synthesizing Al-doped spinel which satisfies the requirements of high discharge capacity and good cycleability at the same time. The decrease in Mn^{3+} ion by Al substitution induces a high average Mn oxidation state in the $LiAl_xMn_{2-x}O_4$ material. Especially, the initial and last discharge capacity of $LiAl_{0.1}Mn_{1.9}O_4$ using LiOH, Mn_3O_4 and $Al(OH)_3$ complex were 129 mAh/g and 112 mAh/g after 100 cycles, respectively. The Al substitution in $LiMn_2O_4$ was an excellent method of enhancing the cycleability of stoichiometric $LiMn_2O_4$ spinel during electrochemical cycling.

From a series of electrochemical experiments and cycling test, we found many unique characterizations of Al-doped spinel ($LiAl_{0.1}Mn_{1.9}O_4$) in the various voltage region. $LiMn_2O_4$ and $LiAl_{0.1}Mn_{1.9}O_4$ materials were synthesized using LiOH, $Al(NO_3)_3$, and different Mn sources (Mn_3O_4 and γ-MnOOH). XRD patterns showed that all the prepared materials had the same identical crystalline phase ($Fd\overline{3}m$). Two materials using the Mn_3O_4 source exhibited quite different cycle characteristics depending on the cycling voltage range.

However, the two materials using the γ-MnOOH source showed an identical cycling performance in both the 3 V and 4 V regions. A transmission electron microscope (TEM) analysis revealed that the materials using γ-MnOOH consisted of two kinds of structures of cubic and tetragonal in the resulting powders although these were shown as a pure cubic spinel structure in the XRD diagram. This indicated a more stable state for the two Mn-based materials using γ-MnOOH when the transformation from the cubic to tetragonal phase occurred in the 3 V region. Orthorhombic $LiMnO_2$ was synthesized using LiOH and γ-MnOOH starting materials at 1000 °C in an argon atmosphere by quenching method. XRD diagram revealed the $LiMnO_2$ compound in this study showed a well-defined orthorhombic phase of a space group with *Pmnm*. The lattice constants of resulting compound were a = 2.806 Å, b = 5.750 Å, and c = 4.593 Å. The compound was composed of particles of about 5 - 15 μm diameter with a bar-shape and small spherical one of about 1 - 2 μm. After grinding, $LiMnO_2$ delivered 201 mAh/g in the first cycle and still delivered 200 mAh/g after 50 cycles at room temperature. We confirmed that the initial discharge capacity of $LiMnO_2$ agreed well with its specific surface area. The well-defined $LiMnO_2$ obtained by the quenching method exhibited an excellent cycle performance even for the high temperature test by maintaining its original structure upon cycling.