

Metal Doped Lithium Manganese Oxide Spinel  
as a Cathode for Lithium Secondary Battery

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In the place of  $\text{Li}_x\text{CoO}_2$  utilized as a cathode in a practical rechargeable lithium batteries,  $\text{Li}_x\text{Mn}_2\text{O}_4$  spinel, which was lower cost, safer and less toxic than it, was investigated. The homogeneous phase reaction of  $\text{Li}_x\text{Mn}_2\text{O}_4$  spinel with a continuous lattice parameter change in the region  $1 > x > 0.5$  and then two cubic phases of it in the region  $0.5 > x > 0.13$  were observed on the 4V ( $\text{Li}/\text{Li}^+$ ) plateau. In the latter region,  $\text{Li}_x\text{Mn}_2\text{O}_4$  decomposed through the extraction of lithium to form  $\text{Mn}^{2+}$  compound as a separate phase and its cycling efficiency as a rechargeable cathode was poor. This is due to the weak bonding Mn and O.

The chemical substitution of another cations to the place of  $\text{Mn}^{3+/4+}$  was effective for the improvement of the cycling efficiency.  $\text{Li}^+$  more than 0.2 mol% was doped in a single-phase spinel (e.g.  $\text{LiMn}_{1.8}\text{Li}_{0.2}\text{O}_4$ ). At lithium doped lithium manganese oxide spinels, only homogeneous phase was observed during charge-discharge on 4V region, as in Fig.1(a). Their crystal lattice parameters were reduced, and the differences between primary and charged states were decreased with increasing of the concentrations of dopant, as in Fig.1(b). This means that their covalences of the bonding nature are increased, and the charge-discharge reactions proceed smoothly on a homogeneous phase. Though the capacities were reduced, the cyclabilities during charge and discharge became better by the substitution of  $\text{Li}^+$ , as in Fig.2(a).

Thus, the substitution of +2 or +3 cations to Mn sites of lithium manganese oxide spinels may be better.  $\text{Ni}^{1+}$  and  $\text{Co}^{2+}$ , which were transition metals, were chosen as the substitution metals. These metals more than 0.2 mol% were substituted in a single-phase spinel, and  $\text{Ni}^{2+}$  and  $\text{Co}^{3+}$  were stable during charge and discharge between 4.5 to 3.5 V (vs.  $\text{Li}/\text{Li}^+$ ). Then,  $\text{Li}^+$  was not extracted perfectly from crystal lattice at the charged state. However, since  $\text{Ni}^{2+}$  and  $\text{Co}^{3+}$  were oxidized to  $\text{Ni}^{4+}$  and  $\text{Co}^{4+}$  at the potential more than 4.5V (vs.  $\text{Li}/\text{Li}^+$ ), the cycling efficiencies during charge and discharge between 5.0 to 3.5 V (vs.  $\text{Li}/\text{Li}^+$ ) were poor by the structural degradation. Then,  $\text{Mg}^{1+}$  and  $\text{Al}^{2+/3+}$ , which were nontransition metals, with smaller ionic size than Mn were chosen. Mg and Al more than 0.2 mol%, were substituted for Mn sites in a single-phase spinel. Since manganese oxidation state was increased with the increase of the mol% of dopants, capacities were reduced by such substitution. Such capacity losses were increased with the increase of the concentrations of dopants in order of  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ .  $\text{Li}_x\text{Mn}_{1.9}\text{Al}_{0.1}\text{O}_4$  ( $x = 1 \sim 0.23$ ) with energy of about 4V (vs.  $\text{Li}/\text{Li}^+$ ) and  $0.1\text{Ahg}^{-1}$  (about 65% of  $\text{LiCoO}_2$ ) was better cathode candidate and cycled stably during charge and discharge.

References

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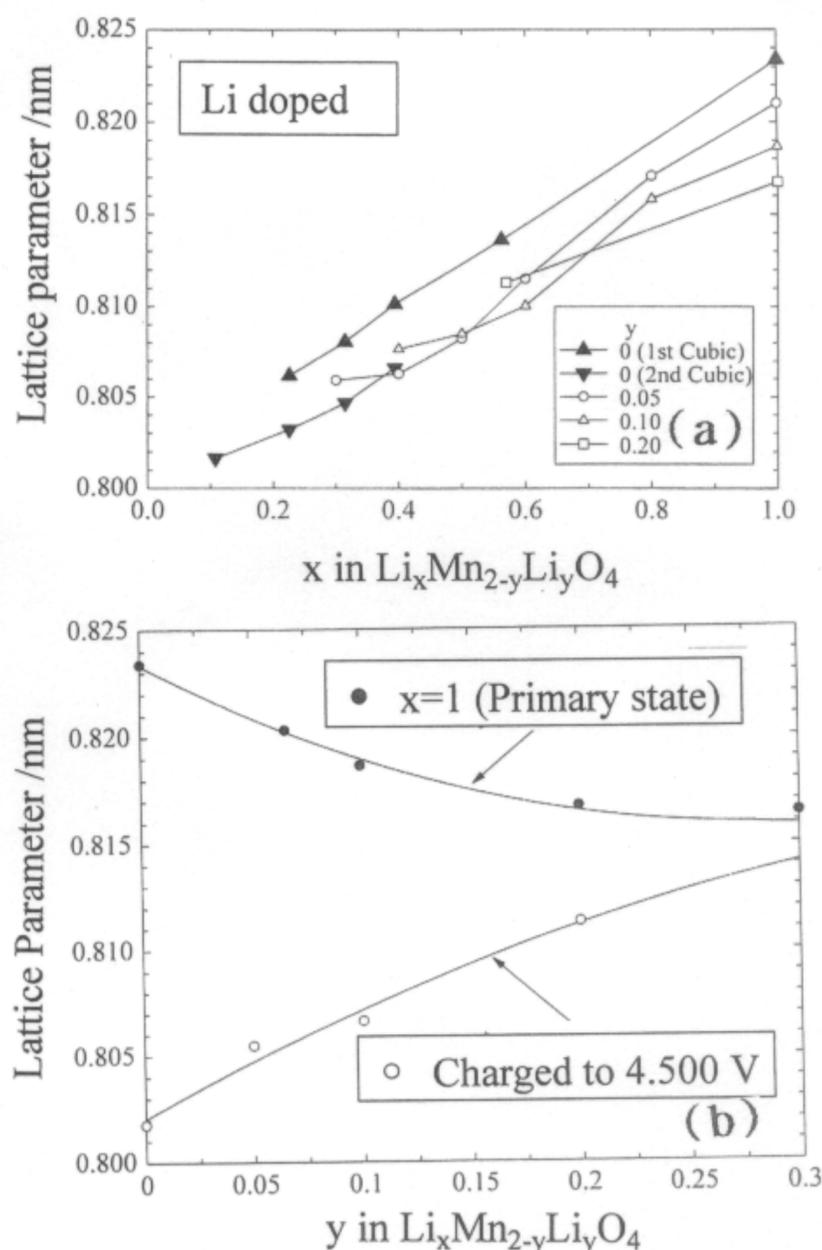


Fig.1 Lattice Parameters of  $\text{Li}_x\text{Mn}_{2-y}\text{Li}_y\text{O}_4$  as a function of x (a) and as a function of y (b), calculated from X-ray diffraction patterns.

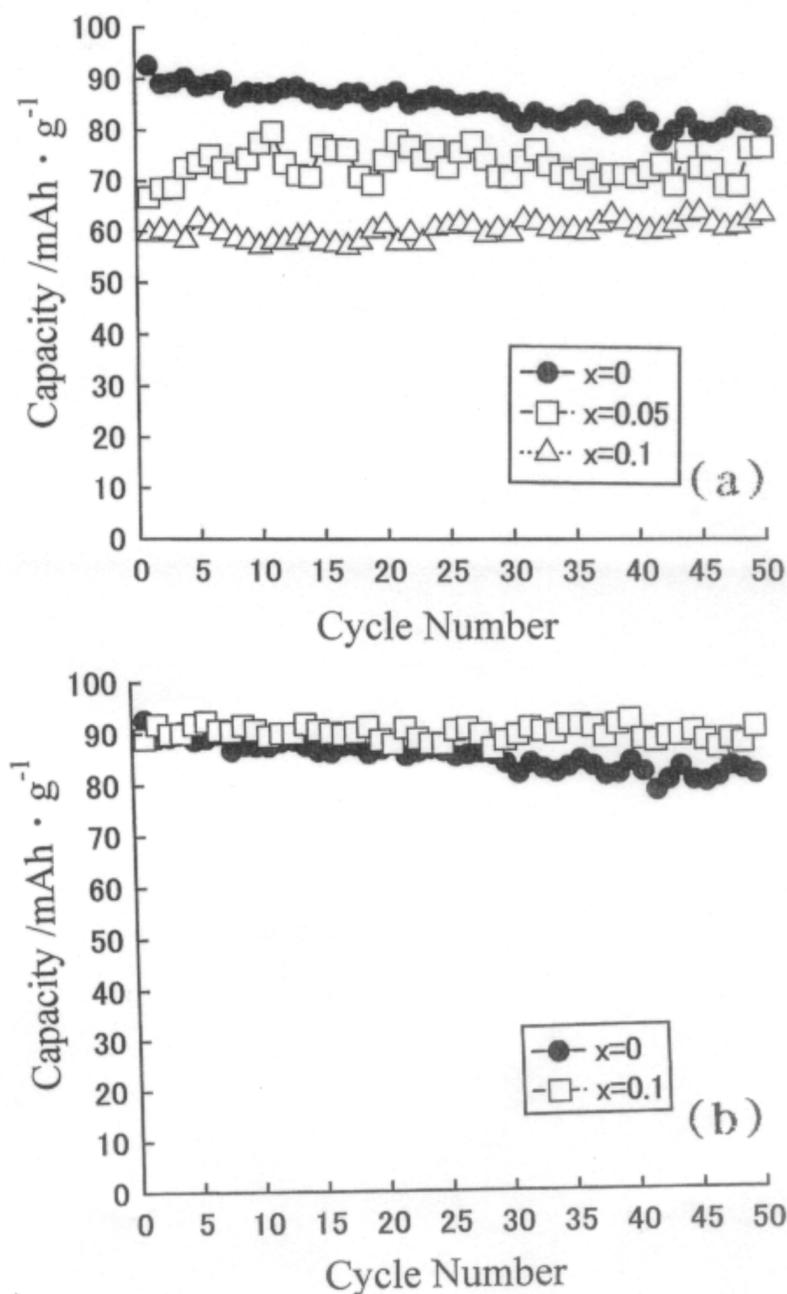


Fig.2 Discharge capacities as a function of cycle number for  $\text{LiMn}_{2-y}\text{Li}_y\text{O}_4$  (a) and  $\text{LiMn}_{2-y}\text{Al}_y\text{O}_4$  (b).