Synthesis of Solid Solutions in a System of $LiCoO_2$-Li_2MnO_3 for Cathode Materials of Secondary Lithium Batteries

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Lithium-manganese-cobalt oxide, $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2$ ($0 \leq x \leq 1$) was prepared as a solid solution between the two kinds of layer structured end members, $LiCoO_2$ and Li_2MnO_3. Excess lithium carbonate or lithium hydroxide should be added to the mixture on calcination at 900 - 1000 °C to obtain the solid solutions. The resulting layer structured solid solutions can be used as a cathode material for secondary lithium batteries.

Since the success of the development of $LiCoO_2$ as a cathode material for lithium ion battery, much attention has been paid to the improvement of this cathode.[1-3] $LiCoO_2$ has a layered structure with the α-$NaFeO_2$ type with lithium atomic layers sandwiched between the CoO_2 octahedral layers. The interlayer lithium ions are deintercalated and intercalated in the charge and discharge process, respectively. However, only about 70% of Li ions are used as an active part for the cathode.[4] More lithium ions could be deintercalated, but a higher charge voltage should be applied, which would result in the decomposition of electrolyte solutions. In addition, the higher level of Li deintercalation causes the degradation of the cathode due to the higher concentration of reactive Co^{4+}.[5]

In an effort to lower the charge voltage for deintercalation and to stabilize the $LiCoO_2$ electrode against the higher deintercalation, substitution of cobalt with other transition metals has been attempted. Stoyanova et al.[6] reported the effect of Mn-substitution for Co. They tried to synthesize solid solutions in a system of $LiCoO_2$-$LiMnO_2$, and showed that the crystal structure varied with the increase of x in $LiMn_xCo_{1-x}O_2$; trigonal layered structure (α-$NaFeO_2$ type) for $x \leq 0.2$, a rock salt structure for $0.2 < x < 0.7$, and a tetragonal structure for $x \geq 0.7$. In this study, attention is paid to prepare a new solid solution system of $LiCoO_2$-Li_2MnO_3 as a lithium battery cathode. As shown in Figure 1, Li_2MnO_3 is isostructural with α-$NaFeO_2$[7] where Li and ($LiMn^{4+}_2$) layers alternately occupy the octahedral sites between the oxygen packed layers of Na and Fe, respectively. $LiCoO_2$ also has an α-$NaFeO_2$ structure, and the formation of the solid solutions in the system $LiCoO_2$-Li_2MnO_3 is expected. In addition, manganese is much more abundant and less expensive than cobalt, the substitution of Mn for Co may be favorable in the cost of the fabrication of cathode.

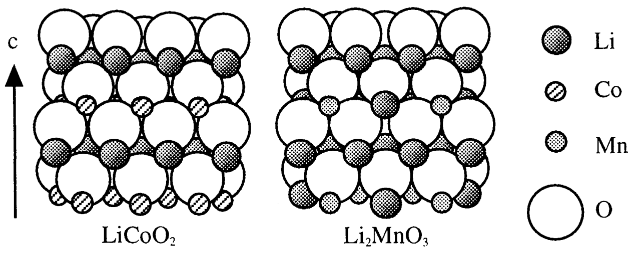

Figure 1. Crystal structure models of $LiCoO_2$ and Li_2MnO_3.

The solid solutions $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2$ ($0 \leq x \leq 1$) were prepared by calcination of the stoichiometric mixtures of lithium carbonate, basic cobalt carbonate, and manganese carbonate with excess amount of lithium carbonate or lithium hydroxide at 900 and 1000 °C for 20 h in an alumina crucible. The compositions of the product will be designated by the formula $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2 \cdot yLi_2O$, where y denotes the excess amount of lithium added.

The X-ray powder diffraction (XRD) patterns of the samples were measured by a diffractometer with graphite monochromated Cu-Kα radiation. Chemical analysis was performed by an ICP (inductively coupled plasma) method after dissolving the sample in a mixed solution of conc. HCl and conc. HNO_3 (3 : 1). The obtained solid solution was compressed into a cathode disk (10.4 mm in diameter) with 4 wt% of polytetrafluoroethylene powder and 6 wt% of acetylene black. A lithium battery cell was constructed with lithium metal anode, and porous fiber separator soaked with 1 M (1 M = 1 mol dm^{-3}) $LiBF_4$ solution in a mixture of propylene carbonate and dimethoxy ethane. The cells were charged and discharged at a constant current density of 1 mA/cm^2.

When a simple mixture of the constituents which correspond to solid solution $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2$ was calcined at temperatures ranging from 900 to 1000 °C, only a mixture of two crystalline phases of $LiCoO_2$ and Li_2MnO_3 was obtained in the whole composition range of $0 < x < 1$. However, when excess amount of lithium was added before the calcination, solid solutions were obtained over the whole composition range. Figure 2 shows typical XRD patterns with a nominal composition of $x = 0.4$. The samples with $x > 0.2$ had some

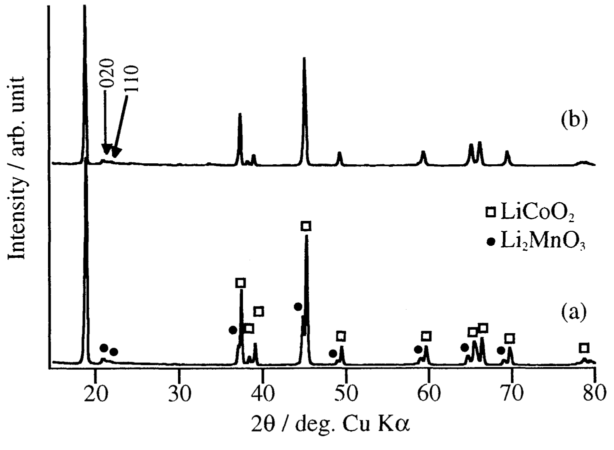

Figure 2. X-ray diffraction patterns of the products obtained by calcination of a mixture with composition of $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2 \cdot yLi_2O$ ($x = 0.4$) at 1000 °C, followed by washing with water : (a) $y = 0$ ($LiCoO_2 + Li_2MnO_3$) and (b) $y = 1/12$ (solid solution).

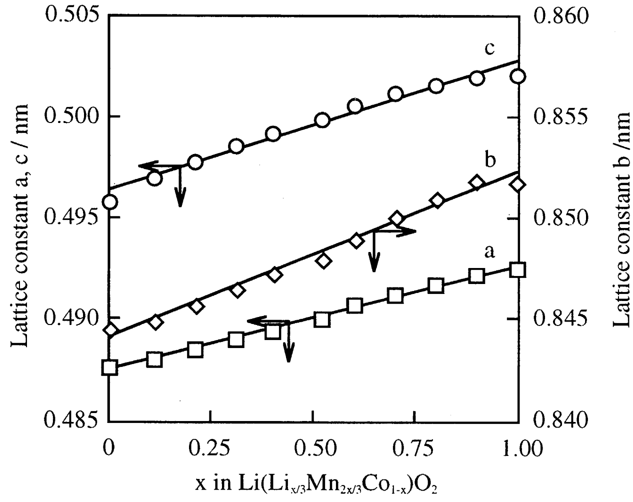

Figure 3. Dependence of the lattice constants against x in $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2$ for the solid solutions obtained by calcination at 1000 °C.

XRD peaks characteristic of the Li_2MnO_3 structure such as 020 and 110 reflections in a range of 20 - 30° in 2θ (Figure 2 (b)). These peaks disappeared for the samples $x \leq 0.2$ with the $LiCoO_2$ structure by systematic extinctions. The XRD reflections of $LiCoO_2$ can also be indexed by a monoclinic symmetry like Li_2MnO_3. The solid solutions have a monoclinic symmetry over the whole composition range, and they can have a higher symmetry, trigonal one, when $x \leq 0.2$. The amount of excess lithium, y in $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2 \cdot yLi_2O$ required to obtain solid solution varied with the composition x and the calcination temperature. In the preparation of the solid solution with x = 0.4, for example, at 900 °C, the amount y was about 1/6, but at higher temperature of 1000 °C, addition of only 1/12 of lithium in y was sufficient. Excess lithium could be added in a form of lithium carbonate or lithium hydroxide $LiOH \cdot H_2O$. On calcination, these compounds form molten phases. It is likely that the liquidous phase enhances the mutual diffusion to form the solid solutions. The excess lithium was removed by washing with water after calcination.

Figure 3 shows the lattice parameters determined on the basis of a monoclinic symmetry for the solid solutions obtained by calcination at 1000 °C. The parameter β was 109.2 ± 0.1° for every sample. As can be seen from the figure, the lattice constants change continuously with the composition, indicating the formation of uniform solid solutions. It is interesting to note that in the solid solution system of $LiCoO_2$-$LiMnO_2$, or $LiCo_{1-x}Mn_xO_2$, the solid solutions with a layered structure were formed only in a region of $x < 0.2$; the solid solutions with $0.2 < x < 0.7$ adopted the rock salt structure. In the system of this study, all of the solid solutions have a layered structure.

Table 1. Chemical analysis data of $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2$

x	Found/(Calculated) (wt%)			Total
	Li_2O	Co_2O_3	MnO_2	
0.11	16.60/(16.17)	76.20/(77.26)	6.48/ (6.57)	99.28
0.31	18.31/(17.94)	62.84/(62.68)	19.42/(19.37)	100.6
0.52	20.10/(20.02)	45.48/(45.65)	34.21/(34.32)	99.79
0.71	22.72/(22.10)	28.79/(28.57)	49.72/(49.33)	101.2
0.90	24.91/(24.33)	10.37/(10.25)	66.20/(65.42)	101.5

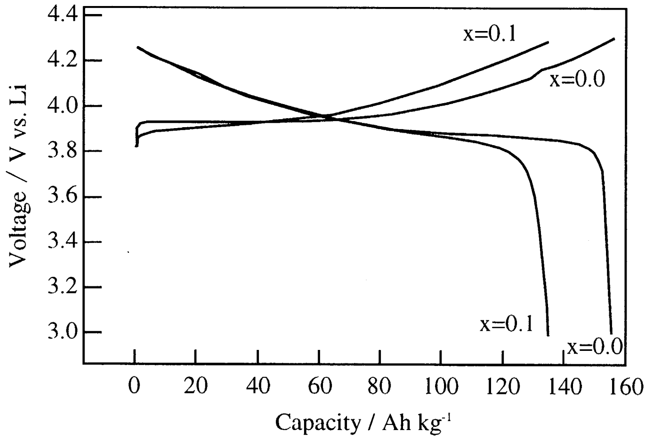

Figure 4. Charge-discharge curves for the sample with composition of x = 0 ($LiCoO_2$) and 0.1 for $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2$.

Table 1 shows the chemical analysis data of the solid solutions. It is assumed that cobalt cations were trivalent and manganese cations were tetravalent. The compositions determined were in good agreement with those calculated on the basis of the solid solutions $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2$.

The performance of the solid solution as the cathode of the lithium battery was examined. Figure 4 shows the charge and discharge curves for the sample with a composition of x = 0.1 for $Li(Li_{x/3}Mn_{2x/3}Co_{1-x})O_2$ in comparison with those of $LiCoO_2$. Two samples were charged up to 4.3 V and discharged down to 3.0 V. $LiCoO_2$ showed a small jump at about 4.1 V in the discharge curve due to a transformation from trigonal to monoclinic.[8] This change was not observed by the formation of the solid solution. It should be noted that a remarkable high discharge and charge rates of $LiCoO_2$ were kept after the formation of solid solutions, though the discharge capacity decreased by 10 %. The maintenance ratio of discharge capacity at the tenth cycle was 98 % for two samples shown in Figure 4.

More detailed electrochemical and physical characteristics of the solid solutions are under investigation and will be reported near future.

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