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Magnetic susceptibility study on Li-Mn spinel oxides

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Li-Mn spinel oxide particles were prepared by the solid state reaction using Mn_3O_4 particles and Li-hydroxide monohydrate, and the effects of the reaction temperature on the produced phase were studied with the powder X-ray diffraction and the magnetic susceptibility measurement. From the lattice constant variation versus the reaction temperature, it was found that the spinel oxides prepared by low temperature reaction were cation deficient type, and that the cation deficient degree decreased with an increase in the reaction temperature. The asymptotic Curie temperature (Weiss constant), derived from the temperature dependent magnetic susceptibility, was always negative, and it implied that the antiferromagnetic coupling among Mn ions is dominant. The absolute value of the Weiss constant increased with the reaction temperature, took a maximum at the reaction temperature around 750°C, and then decreased with a further increase in the reaction temperature. These were attributed to the variation of the average valence of Mn ions. At the reaction temperature, where the absolute value of the Weiss constant takes a maximum, the non-stoichiometry of Li-Mn spinel oxide becomes minimum. In the specimen prepared above the temperature, it was likely that there existed oxygen vacancy, and the phase transformation between cubic and orthorhombic structures was found in the DSC curves. © *2003 Kluwer Academic Publishers*

1. Introduction

Scientific and commercial interest in lithiated transition metal oxide as high energy density and rechargeable cathode materials has recently increased considerably. The commercialization of lithium ion batteries, using a carbon anode and $LiCoO_2$ cathode, was initiated in 1990. An alternative intercalation cathode material under intense development for use in 4 V battery system is $LiMn_2O_4$ spinel oxide. Because it offers several advantages with regard to both toxicity and cost, $LiMn_2O_4$ spinel oxide has already been demonstrated to be the most promising 4 V cathode material for lithium ion batteries.

These cathode materials have been synthesized mainly by the solid state reaction [1–5]. In general, the solid state synthesis of ceramic powders has advantages of low cost of production and high productivity: the precursors are ground and mixed together, and the mixtures are calcined at a suitable temperature. However, less compositional homogeneity including by-product, strong aggregation and important particle size distribution restrict its applicability for advanced ceramics. These disadvantages may be improved by selecting highly reactive constituents to enhance the reaction rate and reduce the reaction temperature, or by confining well-mixed constituents into finely sized reaction zone so as to limit the unnecessary diffusion. Especially for Li-Mn spinel oxide synthesis, some advanced processes have been proposed, such as the melt impregnation method and the Pechini process etc. [5–7].

The charge/discharge behaviour of the cell using the Li-Mn spinel oxide as the cathode material, depends strongly on the preparation conditions such as starting material, reaction temperature, reaction atmosphere and cooling rate [8–12]. For a good understanding of the electrochemical properties as a function of the preparation conditions, it is particularly important to characterize the oxidation state of Mn. It is known that the Mn oxidation state can be easily changed with the preparation conditions [10–14], and that the change in the average Mn valence state provides several kinds of defect structure [14–17]. It has been considered that the Li-Mn spinel oxide synthesized at a relatively low temperature includes the cation vacancy where the average Mn valence is higher than the expected value. It is likely that the Li-Mn spinel oxide releases the lattice oxygen without the phase decomposition at high temperature [16–18].

In these lithiated transition metal oxides, the magnetic properties are determined by the interactions between the transition metal ions, which in turn depend on the valence distribution. Therefore, it is thought that the magnetic measurements are potential tools for the material characterization of these compounds. In this study, we clarified the relationships between the preparation conditions and structural property of the Li-Mn spinel oxide from the viewpoint of the magnetic susceptibility.

2. Experiments

Reagent grade Li-hydroxide monohydrate ($Li(OH)H_2O$) was utilized as Li raw material. Mn_3O_4 particles were synthesized by the thermal decomposition of Mn-oxalate dihydrate at 400°C in air. Li-Mn spinel oxides were synthesized using the solid state reaction technique. The obtained Mn_3O_4 particles were thoroughly mixed with predetermined amounts of Li-hydroxide monohydrate (the molar ratio of $Li/Mn = 0.500$ and 0.505) by dry milling. The well-mixed powders were pressed into disks at a pressure of 500 kg/cm^2 (green density of approximately 2.5 g/cm^3), calcined in static air at the temperature range from 500 to 900°C for ten hour, then subjected to furnace cooling down to room temperature.

The powder X-ray diffraction patterns were measured on a RIGAKU RINT-1500 diffractometer, where Cu K_α radiation (40 kV and 200 mA) monochromatized with a graphite monochromator was used. The full diffraction patterns of the products were measured in the 2θ range of 10° to 90° with 0.02° steps and used to identify the produced phases. The lattice constants were determined with the Nelson-Relay extrapolation method.

The magnetic susceptibility of the powder specimen was measured using the magnetic balance on the heating process in the temperature range from 77 K to 300 K. The samples were placed in glass tubes, and the empty glass tube was used as a reference. The external applied magnetic field was changed within the range from 1 to 10 kOe, and it was certified that the magnetic susceptibility is independent of the magnetic field within the experimental errors. The linear part between the inverse of the magnetic susceptibility and the temperature was found at above 160 K, and therefore, the magnetic susceptibility data was fitted to the Curie-Weiss expression and the asymptotic Curie temperature (Weiss constant) was numerically evaluated.

Thermal properties were studied using differential scanning calorimetry (DSC) with RIGAKU DSC-8230D apparatus. The samples were placed in aluminum crucibles, and the empty aluminum crucible was used as a reference. The measurements were performed on both cooling and heating of the samples in the temperature range from 200 to 400 K with heating and cooling rate of 10 K/min.

3. Results and discussion

All the calcined products were identified as a single phase of cubic spinel structure from powder X-ray diffraction. The impurity phases such as unreacted Mn_3O_4 and Li_2CO_3 were not detected in the X-ray diffraction pattern. The line-width of the X-ray diffraction became sharper as the calcinations temperature was raised. It is likely that the narrowing of the line-width is attributed to the improvement of the crystallinity and to the grain growth of the Li-Mn spinel oxide particle.

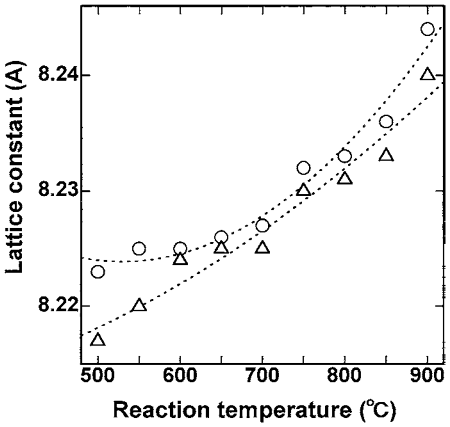

Figure 1 The lattice parameter versus the reaction temperature with the Li/Mn molar ratio of 0.500 (open circle) and 0.505 (open triangle). The dotted lines are drawn as a guide for the eye.

The lattice parameters of the cubic spinel oxide strongly depended on the preparation conditions. Fig. 1 shows the variations of the lattice parameters versus the reaction temperature for $Li/Mn = 0.500$ and 0.505. For the fixed reaction temperature, the lattice parameter decreased with an increase in the Li/Mn molar ratio. It is thought that this variation of the lattice parameter was caused by the cation distribution over the 8a tetrahedral and 16d octahedral sites. Li^+ ion has a strong preference for the tetrahedral coordination of the oxygen, and excess Li^+ ions are located on the 16d octahedral site after the full occupation of the 8a tetrahedral site. Mn ions are located only on the 16d octahedral site, and the average valence of Mn ions increases with the Li/Mn molar ratio, since the charge compensation is attained. The ionic radius of Mn^{4+} is smaller than that of Mn^{3+}, and it results in the smaller lattice parameters.

For the fixed molar ratio of Li/Mn, the lattice parameter gradually increased with the reaction temperature. This trend coincides with the previously reported result [14]. In general, it is known that the oxygen activity decreases with an increase in the temperature. From this fact, it is considered that the low-temperature calcinations brings the formation of higher valence Mn ions, and that the cation deficiencies are created for the charge compensation. Therefore, the cation deficiency, generated at relatively low reaction temperature, is an origin of the smaller lattice parameter. The lattice parameter variation with the reaction temperature implied that the cation deficient degree is decreased as the reaction temperature is raised. It is thought that the cation deficiency vanishes and the stoichiometric compounds are formed at a certain reaction temperature. Above the critical temperature, the further lowering of the Mn ionic average valence may cause the oxygen vacancy in the oxygen sublattice. It is thought that the presence of the oxygen vacancy may generate the spinel oxide with larger lattice parameter, which was prepared at higher reaction temperature [16–18].

Next, the variation of the Weiss constant derived from the magnetic susceptibility versus the reaction

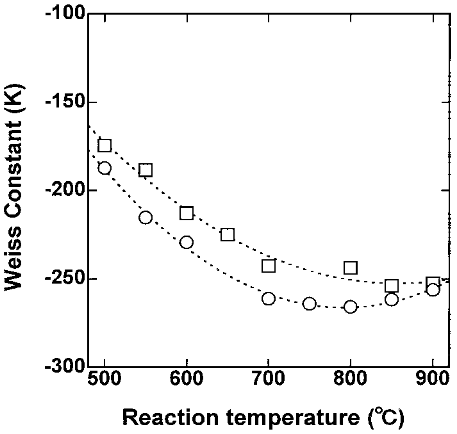

Figure 2 The variation of the Weiss constant with the reaction temperature for the Li/Mn molar ratio of 0.500 (open circle) and 0.505 (open square). The dotted lines are drawn as a guide for the eye.

conditions was examined and then plotted in Fig. 2 for Li/Mn = 0.500 and 0.505. The Weiss constant was always negative, irrespective to the reaction conditions. It means that the antiferromagnetic coupling among Mn ions is dominant in the Li-Mn spinel oxide. For the samples with Li/Mn = 0.500, the Weiss constant shifted toward more negative value, as the reaction temperature is raised up to 750°C, and it took a minimum value of approximately −265 K at the reaction temperature of approximately 750°C. A further increase in the reaction temperature brought a slight shift of the Weiss constant toward positive direction. The same tendency was observed for the samples with Li/Mn = 0.505, but it was found that the absolute value of the Weiss constant was smaller than those of the samples with Li/Mn = 0.500.

These variations are atributed to the magnetic coupling among Mn ions, which is affected by the distribution of Mn valence state. In the Li-Mn spinel oxide, the coupling angles of two Mn magnetic ions through oxygen anion are close to $\pi/2$, since the magnetic Mn ions are located only on the octahedral 16d site. Therefore, the magnetic Mn ions are coupled magnetically by the direct Mn-Mn interactions as well as the interaction through oxygen anions, that is, by the super-exchange interaction. According to the Kanamori-Goodenough rule on the super-exchange interactions [19–21], the super-exchange interactions of both Mn^{3+}-Mn^{3+} and Mn^{3+}-Mn^{4+} pairs with the coupling angle of $\pi/2$ are antiferromagnetic, since the contributions of the Mn^{3+}(e$_g$)-O^2-Mn^{3+}(t$_{2g}$) and Mn^{3+}(e$_g$)-O^{2-}-Mn^{4+}(t$_{2g}$) interaction are dominant and antiferromagnetic. On the Mn^{4+}-Mn^{4+} super-exchange interaction with the coupling angle of $\pi/2$, the direct interaction of Mn^{4+}(t$_{2g}$)-Mn^{4+}(t$_{2g}$) is large and ferromagnetic. It makes the Mn^{4+}-Mn^{4+} coupling to be ferromagnetic. At the reaction temperature lower than 750°C, the Weiss constant shifted toward negative direction with an increase in the reaction temperature. The experimental fact coincides with the previous result [14], and is explained as the reduction of the Mn average valence, that is, the formation of antiferromagnetic Mn^{3+}-Mn^{4-} pairs with the expense of the ferromagnetic Mn^{4+}-Mn^{4+} coupling. However, at the reaction temperature higher than 750°C, the Weiss constant shifted toward positive direction with an increase in the reaction temperature. It is seen that this is in contradiction to the previous result [14], where the Weiss constant shifted toward negative direction with an increase in the reaction temperature. It is thought that the differences of the sample preparation such as the utilization of the different Mn sources caused the different results. Y. Jang *et al.* said that the electromechanically-lithiated Li$_2$Mn$_2$O$_4$ had the Weiss constant of approximately −770 K, while the LiMn$_2$O$_4$ had the Weiss constant of approximately −250 K [22]. It means that both Mn^{3+}-Mn^{3+} and Mn^{3+}-Mn^{4+} super-exchange interactions provide antiferromagnetic couplings, and that the interaction of Mn^{3+}-Mn^{3+} is stronger than that of Mn^{3-}-Mn^{3+}. However, the electromechanically-lithiated Li$_2$Mn$_2$O$_4$ has no oxygen vacancy and tetragonal-distorted structure, and the high-temperature synthesized Li-Mn spinel oxide has some oxygen vacancy and cubic symmetry, in which some interstitial oxygen exist in addition to some lattice oxygen loss [18]. It is thought that the oxygen lattice framework may importantly affect the magnetic exchange interaction and two Mn^{3+} ions are trapped in the vicinity of the oxygen vacancy, due to the lowering of the electrostatic Coulomb energy. Only the direct interaction of Mn^{4+}-Mn^{4+} needs to be considered, and the contribution of the Mn^{3+}(e$_g$)-O^{2-}-Mn^{3+}(t$_{2g}$) antiferromagnetic coupling is negligible. Therefore, the loss of the lattice oxygen brings about the weakening of the antiferromagnetic contribution, and consequently, the Weiss constant shifts toward positive direction.

Namely, when the fraction of the Mn^{4+}-Mn^{4+} coupling pair increases with the expense of the Mn^{3+}-Mn^{4+} coupling pair or some lattice oxygen are lost, the Weiss constant shifts toward positive direction and its absolute value becomes smaller. Subsequently, it was seen that the specimen prepared at 750°C has the most negative Weiss constant. That is, the specimen had the minimum value of the non-stoichiometric degree. Combining the magnetic results with the lattice parameter variation, it was shown that the samples prepared at temperature lower than 750°C have a larger fraction of Mn^{4+}-Mn^{4+} coupling pair and that they are cation-deficient spinels. In addition, it was thought that the specimen prepared at temperature higher than 750°C have a larger fraction of Mn^{3+}-Mn^{3+} coupling pair and that some lattice oxygen are lost in the spinel framework.

For the samples with Li/Mn = 0.500 prepared at various temperatures, the DSC curves were shown in Fig. 3. For the sample prepared at temperature higher than 750°C, there were an exothermic peak on the cooling and an endothermic peak on the heating below room temperature, and their onset temperatures were different from each other. This thermal effect is atributed to the first order structural transition between high-temperature cubic phase and low-temperature orthorhombic phase [23]. On the other hand, for the sample prepared at 750°C, there was no anomaly on the DSC curve, and accordingly there is no first order phase transition. It is known that this structural transition is

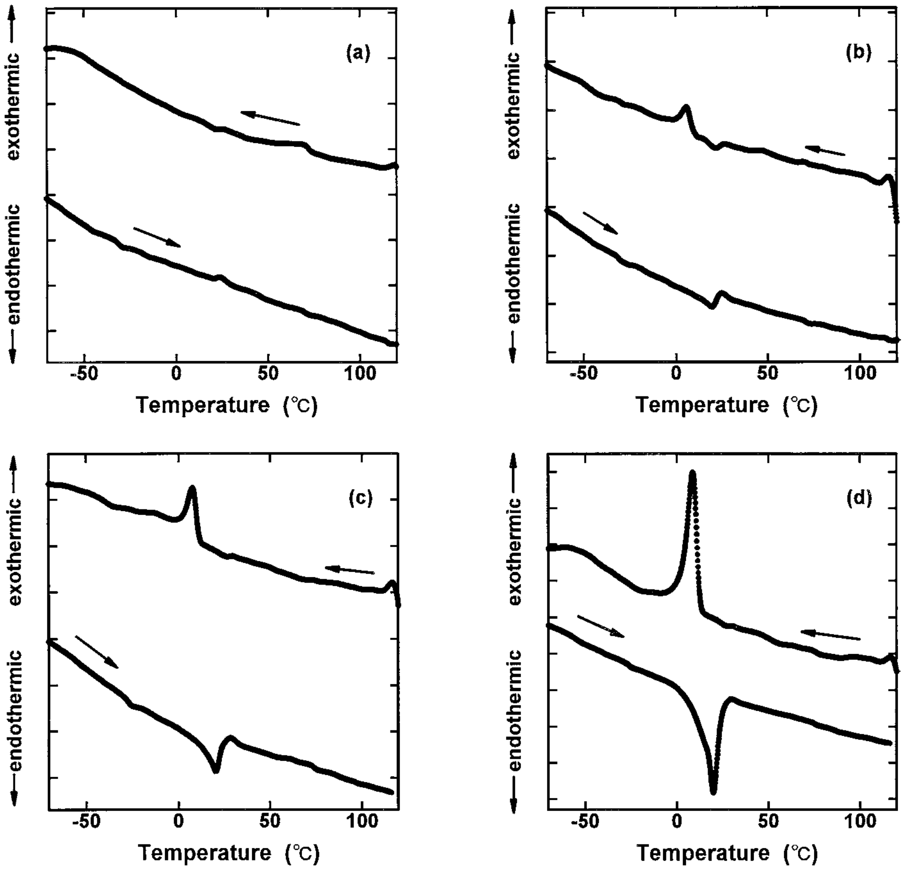

Figure 3 The DSC curves of Li-Mn spinel oxides prepared at 750°C (a), 800°C (b), 850°C (c), and 900°C (d).

related to the cooperative Jahn-Teller distortion of Mn^{3+} ions in the 16d octahedral site, and that the phase transition is induced with an increase in the fraction of the Jahn-Teller active Mn^{3+} ion. From the above results, it is likely that the phase transition is related to the Mn^{3-} fraction and the presence of the oxygen vacancy enhances the phase transition. It means that the phase transition requires more than 50% Mn^{3+} fraction on 16d site and it is absent in the stoichiometric sample.

4. Conclusion

Li-Mn spinel oxide particles were prepared by the solid state reaction. The effects of the reaction temperature on the produced phase were studied. It was found that the lattice parameter of the spinel oxide increased with the reaction temperature. The lattice parameter variation was related to the variation of the average Mn valence. The Weiss constant, derived from the temperature-dependent magnetic susceptibility, was always negative. The absolute value of the Weiss constant increased with the reaction temperature, took a maximum at the reaction temperature around 750°C, and then decreased with a further increase in the reaction temperature. The variation of the Weiss constant was also attributed to the variation of the average valence of Mn ions. The spinel oxide prepared by low temperature reaction was cation deficient type and the Mn^{3+} fraction on 16d site was greater than 50%. In the specimen prepared above the critical temperature, it was likely that there existed oxygen vacancy, the Mn average valence was less than 3.5, and the cubic-orthorhombic phase transition below room temperature was found in the DSC curves. For the Li-Mn spinel oxide synthesized at the critical reaction temperature, which was approximately 750°C in our experiment, the absolute value of the Weiss constant took a maximum, the non-stoichiometry of Li-Mn spinel oxide becomes minimum and the phase transition is not detected in the DSC curve.

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