Anneal Temperature Effect on Crystallite Size and Electric Conductivity of LiMn_2O_4

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Abstract

Powder samples of LiMn_2O_4 have been prepared by solid state reaction of LiOH and MnO_2 . Neutron scattering experiments at room temperature and conductivity measurement have been performed on the samples. Anneal temperature effect on the crystallite size and electric conductivity of LiMn_2O_4 is analyzed. The average crystallite size is obtained from the full width at half maximum (FWHM) of Bragg lines using Scherrer equation. The average crystallite size increases with the increase of anneal temperature. Activation energy and conductivity prefactor increase with anneal temperature.

Keywords: Neutron scattering, LiMn_2O_4 , Crystallite size, Electric conductivity

1. Introduction

Lithium-based metal oxides are well known promising materials for cathode in next generation of rechargeable lithium-ion batteries due to their high energy densities. At present, LiCoO_2 is widely used as commercial product for cathode in lithium-ion batteries. However the cobalt in LiCoO_2 is a relatively rare metal, expensive and toxic. Nowadays, LiNiO_2 and LiMn_2O_4 are studied as alternative materials because they are relatively cheaper and less toxic. LiMn_2O_4 is electrochemically more stable than LiNiO_2 .

In recent years, there is a great interest in the synthesis of nanosized materials for development of cathode in lithium-ion batteries^{1,2)}. It has been reported that anneal process is important to control the crystal size in the lithium-based metal oxide³⁾. It is known that charge-discharge characteristics of lithium cells are mainly depend on the physical and chemical properties of the cathode materials such as crystallite size, purity and homogeneity^{4,5)}. Effect of annealing on the charge-discharge properties of LiMn_2O_4 has been reported⁶⁾. The synthesis process is important to obtain the materials with desired properties. From the point of possible application of LiMn_2O_4 in lithium ion batteries, it is important to understand the formation process of crystal LiMn_2O_4 by anneal treatment and its relation to the electrical properties. In this paper we report the anneal temperature effect on crystallite size of LiMn_2O_4 and its relation to the electric conductivity.

2. Experimental

Powder sample of LiMn_2O_4 was from starting materials LiOH and MnO_2 . The mixture was milled by

high-energy planetary milling for 3 hours at frequency 2 Hz to perform a ground product. After that, it was heated at temperature 200°C for 16 hours. In order to analyze the anneal temperature effect to the crystallite size and electric conductivity of LiMn_2O_4 , the whole sample was divided into three parts: sample A which was annealed at 400°C for 3 hours, sample B annealed at 500°C for 3 hours and sample C annealed at 800°C for 3 hours.

Neutron scattering experiments have been performed on LiMn_2O_4 (sample A, B and C) at room temperature using HRPD (High Resolution Powder Diffractometer) installed at Japan Research Reactor 3 in Japan Atomic Energy Agency (JAEA). The experimental set-up was including a 12' collimator in front of monochromator. Incident neutron wavelength of 1.823 Å which was monochromatized by Ge (331) was used and the data were collected in the 2θ range from 10° to 150° with step angle 0.05°.

Powder samples for conductivity measurements were pressed between conductive silver powder layer at 700 kg/cm² for about 1 hour into cylindrical pellets of 1.3 cm in diameter and ~1 mm in thick. The entire cell was clamped with non-conductive plate and inserted into a special vacuum vessel. The measurements were done using KOKUYO KC-605 LCR Meter at temperature range from room temperature to 100°C.

3. Results and Discussion

Figure 1 shows neutron scattering intensity from sample A, B and C after experimental time correction. Neutron scattering intensity of sample A shows very weak and wide Bragg peaks of LiMn_2O_4 around $2\theta \sim 45^\circ$, 95° and 118° . These three peaks

become stronger and narrower in the sample B. Other clear Bragg peaks of LiMn_2O_4 also appear at 52.5° , 57.5° , 70° and 77° in the scattering intensity of sample B. The strongest and narrowest Bragg peaks is observed in the sample C.

Figure 1. Neutron scattering intensities of powder LiMn_2O_4 at room temperature by HRPD.

In the former report of another lithium-based metal oxide LiNiO_2 , the diffuse scattering intensity

decreases drastically with increasing the annealing temperature. The strong diffuse neutron scattering intensity is related to the amount of starting material LiOH in the powder samples, because atom H has large incoherent scattering cross section by neutron beam³⁾. However, in the case of LiMn_2O_4 the diffuse scattering intensity does not change so much in sample A, B and C as shown in Fig. 1. It is concluded that the amount of starting material LiOH is very small even in sample A. Furthermore, this means that the solid state reaction to perform LiMn_2O_4 is almost completed by annealing the sample at 400°C .

Rietveld refinement analysis has been performed on the neutron scattering intensities of sample A, B and C using RIETAN-2000⁷⁾. Crystal of LiMn_2O_4 is assumed to belong to cubic type structure with the space group $Fd\bar{3}m$ ⁸⁾. It is obtained that our structure model fitted well with the experimental data. In Table 1, R factors and structure parameters obtained from refinement analysis are shown.

Table 1. Reliability factors R , goodness of fit parameter S , lattice constant a , coordinate fraction of atom O x , and temperature parameters B obtained from refinement analysis.

sample	R_{wp} [%]	R_{I} [%]	R_{F} [%]	S	a [Å]	x	B_{Li} [Å ²]	B_{Mn} [Å ²]	B_{O} [Å ²]
A	8.87	5.34	2.19	1.91	8.234	0.3875	0.110	0.520	0.980
B	8.01	4.16	3.48	1.82	8.236	0.3880	0.119	0.644	1.079
C	11.42	5.60	4.17	2.27	8.236	0.3880	0.458	0.723	1.161

Table 2. Values of instrumental correction D_{inst} , full width at half maximum (FWHM) from refinement analysis D_{meas} and corrected FWHM D of Bragg peaks in sample A, B and C which were used in the calculation of Scherrer equation.

(hkl)	2θ [deg.]	D_{inst} [deg.]	D_{meas} [deg.]			$D = (D_{\text{meas}}^2 - D_{\text{inst}}^2)^{1/2}$ [deg.]		
			A	B	C	A	B	C
(400)	52.6	0.245	1.904	0.926	0.391	1.888	0.893	0.305
(331)	57.7	0.235	2.360	0.860	0.334	2.348	0.827	0.237
(622)	94.5	0.265	3.829	0.875	0.529	3.820	0.834	0.458

The average crystallite size of LiMn_2O_4 formed in the annealing process from ground product is analyzed from the full width at half maximum of Bragg line using Scherrer equation:

$$t = \frac{K\lambda}{D \cos \theta}, \quad (1)$$

where t is the average crystallite size in angstrom, K is a constant and equal to 0.9, λ the wavelength of incident neutron beam, D the FWHM (full width at half maximum) of Bragg line and 2θ the scattering angle of Bragg line. For each value of hkl -reflection, the value of t is interpreted as an average crystal

dimension perpendicular to the reflecting planes. The full width at half maximum of Bragg line D_{meas} which is obtained from measurements should be corrected with the instrumental resolution D_{inst} . The corrected FWHM D is obtained by using the relation:

$$D^2 = D_{\text{meas}}^2 - D_{\text{inst}}^2. \quad (2)$$

The value of D_{meas} was obtained from Rietveld refinement analysis.

The crystallite size of LiMn_2O_4 in samples A, B and C are calculated using three Bragg peaks (400), (331) and (622). The values of FWHM from refinement D_{meas} for these three Bragg peaks and

instrumental resolution D_{inst} at 2θ of the peaks are shown in Table 2. The average crystallite sizes of LiMn_2O_4 are ~5, 14 and 37 nm for sample A, B and C, respectively as shown in Fig. 2. From the analysis of crystallite size using Scherrer equation, it is shown that the average size increases almost linearly with annealing temperature.

Figure 2. Average crystallite size of LiMn_2O_4 in powder samples. Inset shows the resolution curve of the instrument.

Figure 3 shows the DC conductivity σ_{DC} of sample A, B and C. The temperature dependence of σ_{DC} is analyzed using Arrhenius relation:

$$\sigma_{\text{DC}} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right), \quad (3)$$

where σ_0 is conductivity prefactor, E_a activation energy, k Boltzmann constant and T temperature in Kelvin. DC conductivity shows clearly temperature dependence and obeys Arrhenius relation. Our results on DC conductivity agree with the previous report¹²⁾. Anneal temperature also affects to the value of DC conductivity. DC conductivity of sample B at one specific temperature is higher than that of sample A and C as shown in Fig. 3(a). In Fig. 3(b) the DC conductivities of sample A, B and C at room temperature are shown. In addition to the DC conductivity data of sample A, B and C, the DC conductivities at room temperature for samples which were annealed at 700 and 900°C are also checked. The values of DC conductivity of these two additional samples are marked with (#) in Fig. 3(b). Solid line in Fig. 3(b) is figured for the reader's eye to show the tendency of DC conductivity. Based on the anneal temperature dependence of DC conductivity data, it might be possible to suggest that there is an optimum annealing temperature between 500 and 800°C to obtain high DC conductivity. This might be related to the crystallite size and grain boundary resistivity. However, further analysis is needed to confirm this.

Figure 3. (a) Arrhenius plot of conductivity of LiMn_2O_4 samples, (b) DC conductivity of LiMn_2O_4 samples at room temperature.

The conductivity prefactor σ_0 and activation energy E_a are obtained by linear least squares fitting to the observed DC conductivity data using eq. (3) and its values are shown in Fig. 4. A relatively small variation of activation energy between 0.30 – 0.39 eV were obtained for sample A, B and C. It is obtained that the values of conductivity prefactor and activation energy increase with increasing anneal temperature.

Figure 4. Conductivity prefactor σ_0 and activation energy E_a of LiMn_2O_4 .

4. Conclusions

Nanosized LiMn_2O_4 has been successfully prepared by solid state reaction of LiOH and MnO_2 . The average crystallite sizes of LiMn_2O_4 in powder samples increases with increasing anneal temperature. From the conductivity measurements, it was concluded that there is an optimum anneal temperature to obtain high DC conductivity at room temperature from powder LiMn_2O_4 .

Acknowledgements

Financial supports from The Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research on Priority Area, 17041001, 2006 and from Ibaraki Prefecture are gratefully acknowledged. One of the authors (KB) expresses his thanks to Ibaraki Prefecture, Hitachi, Ltd. and Ibaraki University for research fellowship by Renkei Jigyō.

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