Synthesis and Electrical Properties of $Li_{1-2x}Cu_xMn_2O_4$

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$Li_{1-2x}Cu_xMn_2O_4$($x \leqq 0.10$) were synthesized and x dependence of the lattice constant and the electric conductivity were studied. For $x \leqq 0.05$, Li-O bond length and AC conductivity were decreased by substitution of Cu for Li, and Mn-O bond length was increased with x. Conductivity for x=0.10 is higher than that for $LiMn_2O_4$.

The spinel $LiMn_2O_4$ is a cathode material for the rechargeable lithium battery and many studies have been carried out because of its low cost and low toxicity.[1-4] The capacity of this cathode, however, decreases with cycling in the 4V range.[5] This capacity loss is caused by the structural distortion due to a Jahn-Teller effect of Mn^{3+} ion. In recent work, several dopants such as Al, Ni, Zn and Fe were added to reduce a Jahn-Teller distortion and improve the cycling stability.[6,7]

It was reported that $LiMn_2O_4$ is a small-polaron semiconductor and the mobility of e_g electrons on Mn^{3+} ions carries an activation energy.[8] An investigation on the electrical conduction is much important because it is one of the most essential functions for application as the cathode material. In this paper, the effect of the substitution of copper for lithium on the structure and electric conduction in $Li_{1-2x}Cu_xMn_2O_4$ ($0 \leqq x \leqq 0.10$) has been investigated.

$Li_{1-2x}Cu_xMn_2O_4$ ($0 \leqq x \leqq 0.10$) was prepared by reacting the required stoichiometric amounts of Li_2CO_3, CuO and MnO_2, respectively. The mixed powders were calcined at 750 ℃ in air and slowly cooled down to room temperature. Powder X-Ray diffraction patterns were recorded using Cu-K_α radiation. The diffraction data were analyzed by Rietveld method.[9] AC conductivity was measured by a four terminal method at 11 frequencies between 100 Hz and 100 kHz in a dry nitrogen atmosphere(YHP LCR meter 4274A). Complex-plane impedance analysis was carried out to obtain the bulk conductivity.

Table 1. Results of the Rietveld analysis of X-Ray diffraction data for $Li_{1-2x}Cu_xMn_2O_4$

x	R_{wp} / %	S	R_I / %	Coordinates of O [a]
0.0	19.33	1.272	3.08	0.3869(2)
0.01	19.16	1.245	2.60	0.3863(2)
0.03	19.47	1.274	2.87	0.3860(2)
0.05	17.02	1.177	2.57	0.3854(2)
0.07	19.35	1.30	3.02	0.3855(3)
0.10	16.66	1.261	3.16	0.3865(3)

[a] O atom occupies at (x,x,x).

Figure 1 shows the results of Rietveld analysis of powder X-Ray diffraction patterns for $Li_{1-2x}Cu_xMn_2O_4$ (x=0, 0.05 and 0.10). Each sample showed the pattern of the single phase of a cubic spinel structure. In this analysis, Li and Cu atoms were distributed in 8a sites and Mn atom was in 16d sites for all samples. The refined parameters and *R*-values obtained by this method are summarized in Table 1. Acceptable *R*-values were obtained and S ($=R_{wp}/R_e$) were within 1.3 for all samples.

The variance of lattice constant and bond lengths of Mn-O and Li-O in $Li_{1-2x}Cu_xMn_2O_4$ against x was obtained by the results of Rietveld analysis as shown in Figure 2. The lattice constant was increased with x between x=0 and x=0.05, and decreased between 0.05 and 0.10. Considering from the ionic radius,[10] the lattice constant may be decrease monotonically with

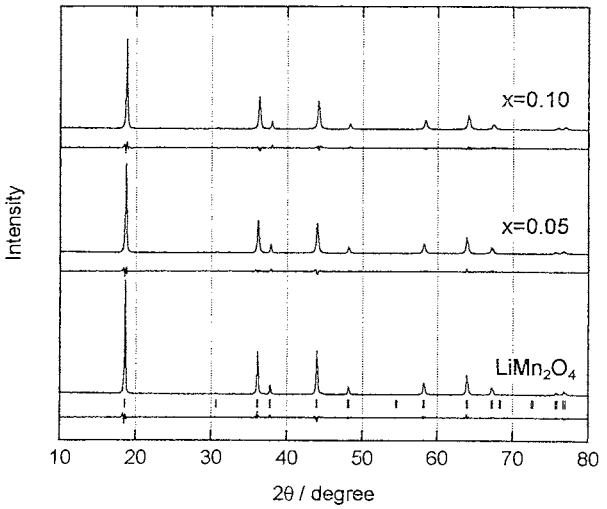

Figure 1. The results of the Rietveld analysis of X-Ray diffraction patterns for $Li_{1-2x}Cu_xMn_2O_4$ at 297 K.

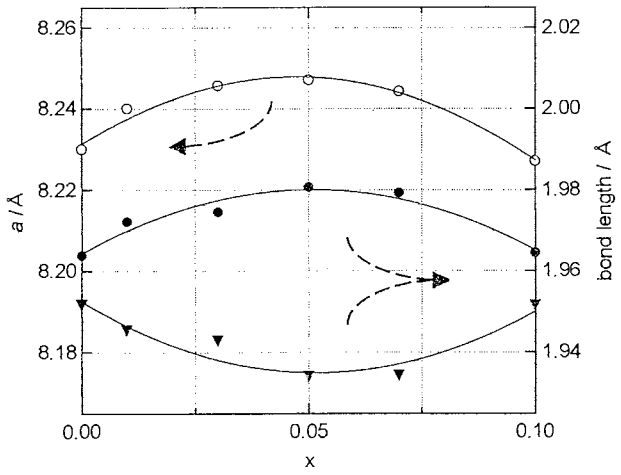

Figure 2. Plots of Lattice constant(○) and bond lengths of Mn-O(●) and Li-O(▼) in $Li_{1-2x}Cu_xMn_2O_4$ against x. Solid lines are fitting curves.

increasing x since the radius of Cu^{2+} ion is smaller than that of Li^{+} ion. It is not known why the lattice constant is increased with x between x=0 and x=0.05 and has the maximum at x=0.05. The bond lengths of Mn-O and Li-O were also varied with x. At x=0.05, Mn-O length has the maximum value and Li-O has the minimum. Lattice constant and the bond lengths for x=0.10 were almost the same value as those for the original $LiMn_2O_4$, respectively.

A plot of the AC conductivity for $Li_{1-2x}Cu_xMn_2O_4$ at 300 K against x is shown in Figure 3. The conductivity was also

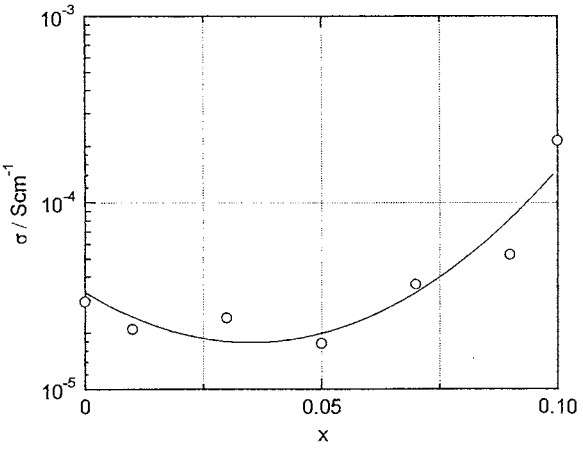

Figure 3. x dependence of AC conductivity in $Li_{1-2x}Cu_xMn_2O_4$ at 300 K. Solid line is a fitting curve.

varied with x. It has the minimum at x=0.05 and increased with x between x=0.05 to 0.10. Furthermore, the conductivity for x=0.10 was about ten times as high as that of the original $LiMn_2O_4$. It was considered that the variance of the conductivity was produced by the effect of both Mn-O bond length and amount of copper ions occupied the tetrahedral sites instead of Li^{+} ions. The conductivity for $LiMn_2O_4$ is mainly governed by the electronic conduction due to the e_g electron of Mn^{3+}. Thus, the conductivity for the compounds from x=0 to 0.05 is decreased due to the increase of Mn-O bond length. At x=0.10, Mn-O length is nearly equal to that of $LiMn_2O_4$ but the conductivity is much higher than that of $LiMn_2O_4$ because the electron of Cu^{2+} ion substituted for Li^{+} ion contributes to the electric conduction in addition to electron of Mn^{3+} ion. When temperature was increased, the conductivity for each sample was increased monotonously. The activation energy for the conduction was evaluated by the following equation:

$$\sigma T = A \exp(-E_a / RT). \qquad (1)$$

where σ and A are the conductivity and the pre-exponential parameter, respectively. The E_a values for $Li_{1-2x}Cu_xMn_2O_4$ are decreased with increasing x, which may be also produced by the additional conduction due to Cu^{2+} ion in the tetrahedral site.

The interesting variance on the conductivity was observed by substituting Cu for Li in $LiMn_2O_4$. A small amount of Cu substitution($x \leqq 0.05$) causes the increase of Mn-O bond length and decrease of the electric conductivity in $Li_{1-2x}Cu_xMn_2O_4$. On the other hand, the conductivity of x=0.10 is higher than that of $LiMn_2O_4$, which may be produced by the electronic conduction for Cu-O bond in addition to Mn-O bond.

References and Notes

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