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Effect of Cr-substitution on the Electrical Properties of $LiMnO_2$

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Cathode materials composed of $LiMnO_2$ with Cr substituted for Mn were prepared using a hydrothermal method, and their electrochemical properties were studied. Solid solution powders (SSP) of $Mn_{2-x}Cr_xO_3$ prepared by firing mixtures of MnO_2 and $Cr(NO_3)_3 \cdot 9H_2O$ were hydrothermally treated in LiOH or KOH-LiOH solutions at 180-260 ℃ for 1-5h. The resultant products were washed with distilled water, filtered, and dried at 100 ℃. The product, monoclinic $LiMnO_2$ with small amounts of orthorhombic $LiMnO_2$, was successfully prepared. The powder was mixed with acetylene black, polytetrafluoroethylene and droplets of toluene, and then kneaded into a sheet of cathode material. Lithium metal foil was used as the anode, and $LiPF_6$ in a mixture of ethylene carbonate and diethylcarbonate (1:1 in volume) was used as the electrolyte. The charge-discharge characteristics were evaluated between voltage limits that ranged from 4.3 to 2.0 V. The characteristics of the Cr-substituted products were more stable than those of $LiMnO_2$ without Cr. Furthermore, the gradual degradation of discharge capacity with increasing cycles of charge-discharge previously observed in $LiMnO_2$ without Cr could scarcely be observed.

Key words: lithium-manganate, cathode, substitution.

1. INTRODUCTION

The increasing demand for the miniaturization of electronic appliances has stimulated the development of small lightweight batteries [1]. Rechargeable lithium-ion batteries, which have received a great deal of attention for their high energy density, use a carbon or graphite anode and a lithium transition metal oxide cathode separated by a liquid electrolyte. The performance of a battery depends on the properties of its electrodes [2], and the selection of cathode materials, particularly, becomes one of the most important steps for determining the overall performance of rechargeable lithium-ion batteries [3]. Commercial batteries using $LiCoO_2$ are now widely used, and a search for new cathode materials is being conducted because of the high cost of cobalt and diminishing resources. Manganese oxide with its low cost and non-toxicity has received attention recently among these new materials [4]. Many studies on the preparation of $LiMnO_2$ have been published, and the electrochemical properties of $LiMnO_2$ have been studied. Lithium manganate, $LiMnO_2$, has two crystal forms, orthorhombic (*o*-) and monoclinic(*m*-). These forms have been found to have a high capacity and stable cyclibility. The latter, especially, has been found to have better electrochemical properties than the former[5, 6]. Therefore, the preparation of *m*-$LiMnO_2$ has been investigated [7]. It was found that a hydrothermal synthesis is one of the most effective ways for producing this compound [8]. Its charge-discharge properties showed that its structure during electrochemical cycling collapses in a manner similar to that previously observed in *o*-$LiMnO_2$ [9]. This variation in charge-discharge characteristics has been ascribed to the Jahn-Teller effect in transitional elements [10]. The substitution of an element which cannot undergo a Jahn-Teller distortion has been found to stabilize the charge-discharge characteristics and increase the energy density because this structural change of the cathode materials has been suppressed [11, 12]. In this study, therefore, Cr was selected to substitute for Mn, and the preparatory conditions of $LiCr_{1-x}Mn_xO_2$ were investigated. In addition, the electrochemical properties of the resultant batteries using the powders were studied.

2. EXPERIMENTAL

Mn_2O_3 mixed with Cr_2O_3 was prepared by firing mixtures of MnO_2 and $Cr(NO_3)_3 \cdot 9H_2O$. One-half gram of $(Mn, Cr)_2O_3$ with 50 ml of KOH-LiOH solution was hydrothermally treated at 180-260 ℃ for 1-5 h. The resultant products were washed with distilled water, filtered, and dried at 100 ℃. The cathode was prepared by mixing 0.4 g of the products with 0.08 g acetylene black, 0.02 g polytetrafluoroethylene powder and droplets of toluene, followed by kneading into a sheet around 0.14 mm thick. The anode was lithium metal foil 0.5 mm thick, and the electrolyte was 1M $LiPF_6$ in a mixture of ethylene carbonate and diethylcarbonate (1:1 in volume). The cells were constructed in an argon-filled glove box to avoid moisture and oxygen. The charge-discharge characteristics were evaluated at a current of 30 mA/g between voltage limits that ranged from 4.3 to 2.0 V. Phase identification was carried out by XRD before and after the charge-discharge measurements.

3. RESULTS AND DISCUSSION

3.1 Selection of starting materials

The hydrothermal preparation of $LiMnO_2$ with lithium salts and manganese salts or oxides was attempted, but no powder was produced. The use of lithium hydroxide, however, brought about the formation of powders. Figure 1 shows the XRD patterns of powders hydrothermally prepared in 4 mol/l LiOH at 260 ℃ using manganese oxides. Single-phase *o*-$LiMnO_2$ was obtained when Mn_2O_3 was used, and only Li_2MnO_3 was confirmed when MnO_2 was used. The use of Mn_3O_4 resulted in the formation of $LiMnO_2$ but slight amounts of Li_2MnO_3 and unreacted Mn_3O_4 were observed. These findings lead to the speculation that Mn_2O_3 is an appropriate source for preparing $LiMnO_2$. Figure 2 shows the XRD patterns of powders prepared in various LiOH solutions at 260 ℃. The crystallinity of *o*-$LiMnO_2$ increases with increasing concentration of LiOH, and single-phase *o*-$LiMnO_2$ was synthesized in 4 mol/l solution. Table I summerizes the phases present in powders synthesized using Mn_2O_3 at 180-260 ℃ in 1-4 mol/l LiOH solutions. Unreacted Mn_2O_3 was confirmed in all samples prepared at 180 ℃, and the amount of undesired products decreases with increasing preparation temperature. These results, however, indicated that the desired material, *m*-$LiMnO_2$ might not form in pure LiOH solutions. Tabuchi et al. found that m-$LiMnO_2$ was successfully synthesized by a hydrothermal method in LiOH-KOH or LiCl-KOH

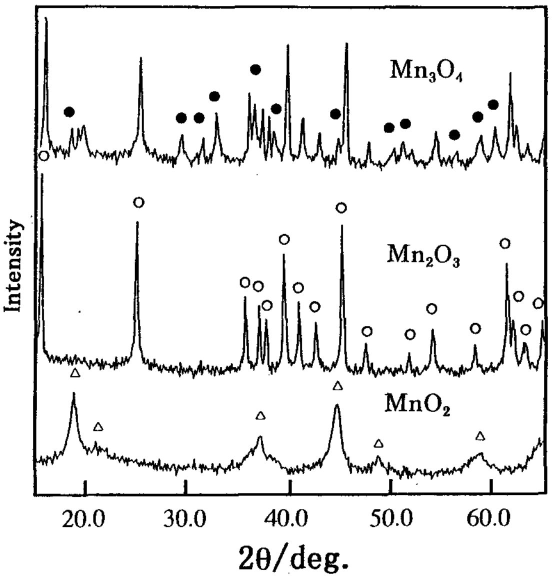

Fig. 1. XRD patterns for products hydrothermally prepared with manganese oxides in 4 mol/l LiOH solution(○:*o*-$LiMnO_2$, ●:Mn_3O_4, △:Li_2MnO_3).

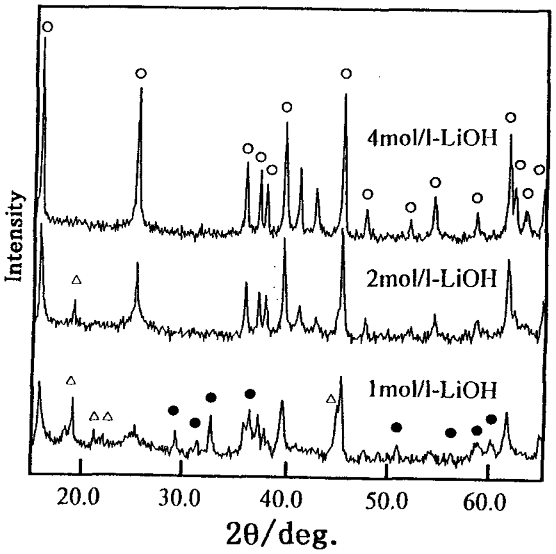

Fig. 2. XRD patterns of products hydrothermally prepared with Mn_2O_3 in 1-4 mol/l LiOH(○:*o*-$LiMnO_2$, ●:Mn_3O_4, △:Li_2MnO_3).

Table I Phases detected by XRD for products hyrdothermally prepared with Mn_2O_3 at 180-260 ℃ in LiOH solutions.

LiOH concentration	synthetic temperature (℃)		
	180	220	260
1 mol/l	◆○●△	◆○△●	○△●
2 mol/l	◆○●△	○△●	○△
4 mol/l	◆○●△	○	○

○:*o*-$LiMnO_2$, △:Li_2MnO_3, ●:Mn_3O_4, ◆: Mn_2O_3

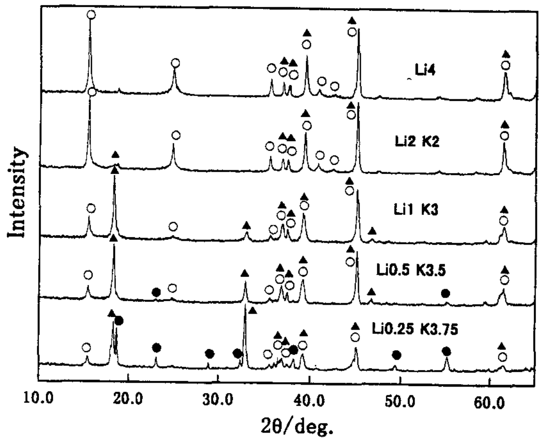

Fig. 3. XRD patterns of products hydrothermally prepared at 240 ℃ for 5 h in a) 4.0 mol/l LiOH, b) 2.0 mol/l LiOH + 2.0 mol/l KOH and c) 1.0 mol/l LiOH + 3.0 mol/l, d) 0.5 mol/l LiOH + 3.5 mol/l KOH and e) 0.25 mol/l + 3.75 mol/l KOH(▲:*m*-$LiMnO_2$, ○:*o*-$LiMnO_2$, ●:Mn_3O_4).

solutions [8], but they did not describe any detailed conditions for the preparation. Therefore, the effect of KOH on the formation of *m*-$LiMnO_2$ was studied in detail. Figure 3 shows phases present in the samples hydrothermally prepared in various LiOH-KOH solutions. Two crystalline forms of $LiMnO_2$ were recognized, and the amount of *m*-$LiMnO_2$ increased and that of *o*-$LiMnO_2$ decreased with increasing content of KOH in the solutions. The sample containing the maximum amount of *m*-$LiMnO_2$ was obtained by carrying out the reaction in a mixed solution of 1.0 mol/l LiOH and 3.0 mol/l KOH. The effect of the alkaline concentration on the nature of the phases formed was investigated, and the crystallinity of the phases formed and the relative amounts of the phases were found to be somewhat changed. The influence of the alkaline concentration was, however, negligibly small and the concentration of the solutions to be used in this study was determined to be 4 mol/l.

3.2 Synthesis of monoclinic $LiCr_xMn_{1-x}O_2$

Kanno mentioned that ionic radius is one of the most important factors for determining the structure of cathode materials [12]. Furthermore, Okada et al. suggested that the substitution of an element without a Jahn-Teller effect for Mn yields better cyclibility [13]. Therefore, Cr was chosen as the substitution element and the preparation of m-$LiCr_xMn_{1-x}O_2$ powders was attempted using $Mn_{2-x}Cr_xO_3$ solid solution powders. Figure 4 shows the XRD patterns of $Mn_{2-x}Cr_xO_3$ powders, showing that the maximum value of x for forming solid solutions is x=0.3. The preparation of m-$LiMnO_2$ powders was attempted in a mixed-solution of 1.0 mol/l LiOH and 3.0 mol/l KOH using these powders, and the XRD patterns of the products are shown in Fig. 5. The electrode material with maximum relative amount of m-$LiMnO_2$ was prepared when $Mn_{1.7}Cr_{0.3}O_3$ powder was used. The relative amount of m-$LiMnO_2$ in the powder was calculated to be 0.95 by comparing the heights of the strongest peaks for m- and o-$LiMnO_2$. These results indicated that the substitution of Cr for Mn favors the formation of m-$LiMnO_2$.

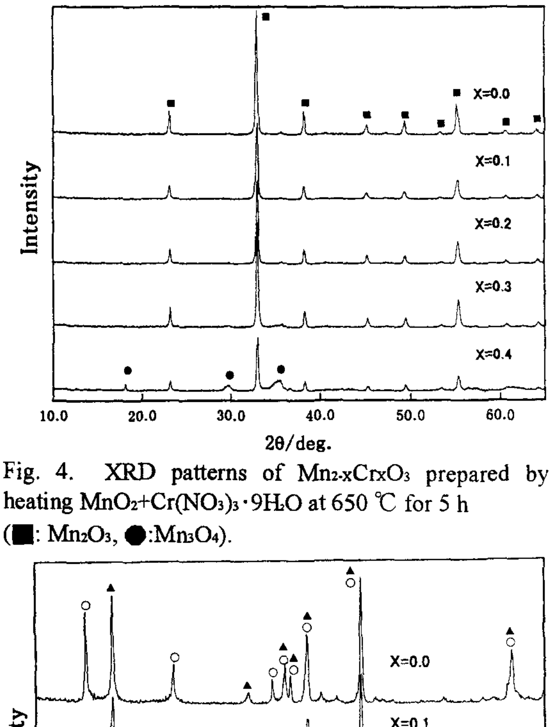

Fig. 4. XRD patterns of $Mn_{2-x}Cr_xO_3$ prepared by heating MnO_2+$Cr(NO_3)_3 \cdot 9H_2O$ at 650 ℃ for 5 h (■: Mn_2O_3, ●:Mn_3O_4).

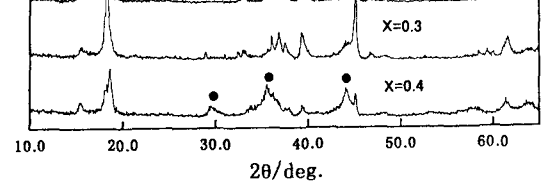

Fig. 5. XRD patterns of products hydrothermally prepared at 240℃ for 5 h in 1.0 mol/l LiOH + 3.0 mol/l KOH by the use of a) Mn_2O_3, b) $Mn_{1.9}Cr_{0.1}O_3$, c) $Mn_{1.8}Cr_{0.2}O_3$, d) $Mn_{1.7}Cr_{0.3}O_3$ and e) $Mn_{1.6}Cr_{0.4}O_3$(▲:*m*-$LiMnO_2$, ○:*o*-$LiMnO_2$, ●:Mn_3O_4).

3.3 Electrochemical properties

Charge-discharge curves of m-$LiCr_xMn_{1-x}O_2$ are shown in Fig. 6. The discharge curves for $LiMn_{1.7}Cr_{0.3}O_2$ and $LiMn_{1.6}Cr_{0.4}O_2$ were a little different from those for others. The most remarkable feature, distinct voltage step at 2.5-3.0 V [14], is scarecely observed for $LiMn_{1.7}Cr_{0.3}O_2$ and $LiMn_{1.6}Cr_{0.4}O_2$. This step was determined to be attributable to the evolution of the spinel phase, $LiMn_2O_4$, and there is no trace of the formation of $LiMn_2O_4$ for these two products. Therefore, the electrochemical stability of these materials seems to be excellent. The variation of the discharge capacity with cycle number for $LiCr_xMn_{1-x}O_2$ (x=0.0-0.4) is shown in Fig. 7. An initial decrease in capacity, which seems to be a typical feature of o-$LiMnO_2$, is scarcely observed, and the stability of the discharge characteristics increased with increasing amounts of Cr. Furthermore, the phases present in $LiMn_{1.7}Cr_{0.3}O_2$ and $LiMn_{1.6}Cr_{0.4}O_2$ after charge-discharge measurements were the same as the ones before the measurement. These facts indicate that the substitution of Cr for Mn has a favorable effect on the stabilization

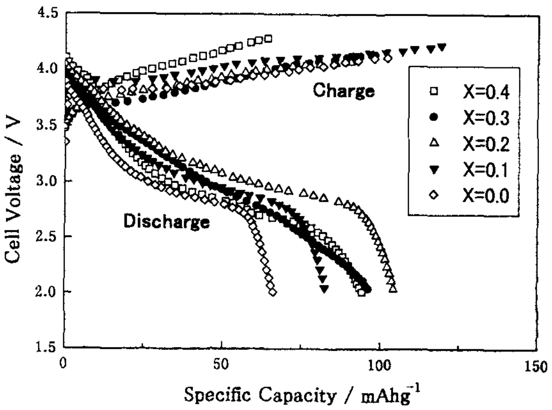

Fig. 6. Charge-discharge curves for $LiMn_{1-x}Cr_xO_2$ hydrothermally prepared at 240 ℃ for 5h.

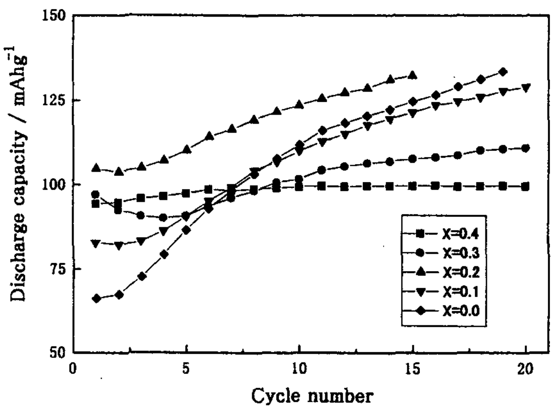

Fig. 7. Variation of the specific capacity with the number of cycles for $LiCr_xMn_{1-x}O_2$.

of the m-$LiMnO_2$ structure, and that an intermediate stage of cation ordering [2] might be excluded in Cr-substituted *m*-$LiMnO_2$.

4. CONCLUSION

The preparation of the cathode material for the rechargeable lithium ion batteries, $LiMnO_2$ with substitution of Cr for Mn was studied with various starting materials by a hydrothermal method. Monoclinic $LiMnO_2$ powders with small amounts of orthorhonbic $LiMnO_2$ were successfully prepared using $Mn_{2-x}Cr_xO_3$. The charge-discharge characteristics of the materials were evaluated and the stability of the charge-discharge characteristics was found to increase with increasing amounts of Cr.

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