Hydrothermal Synthesis of Lithium Manganese Oxide with α -NaFeO₂ Structure

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α -NaFeO₂ 型リチウムマンガン酸化物の水熱合成

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Hydrothermal synthesis of lithium manganese oxide with α -NaFeO₂ structure has been studied. A Li_xMnO₂·*n*H₂O, (Li-birnessite), with rhombohedral symmetry was used as a starting material. When the molar ratio of Mn/Al was smaller than 0.9/0.1, spinel type lithium manganese oxides were obtained. On the other hand, when the molar ratio of Mn/Al was larger than 0.85/0.15, metastable lithium manganese oxides with α -NaFeO₂ structure formed at 80°C, and the capacity fade of the Li-ion cell with cathodes made of these oxides was very small in comparison with that of cathodes made of layered Li-manganese oxides, as previously reported.

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1. Introduction

LiCoO₂ with layered α -NaFeO₂ structure (Space group: $R\bar{3}m$) has been developed as a cathode material for rechargeable lithium ion batteries, and used in the industrial practice.¹⁾ LiMnO₂ compounds have been attractive as intercalation materials for rechargeable batteries because of their large theoretical capacity (285 mAh/g), which is about twice that of LiMn₂O₄, and low cost compared with LiCoO₂.^{2),3)} However, it has been generally known that the structure of LiMnO₂ is rather an orthorhombic polymorph (*o*-LiMnO₂), which belongs to the space group *Pmnm*, rather than an α -NaFeO₂ structure.⁴⁾ Li_{1.09}MnO₂ with rhombohedral ($R\bar{3}m$) structure has been synthesized from Li₂MnO₃ by acid treatment following Li doping.⁵⁾ Recently, the monoclinic polymorph of LiMnO₂ (*m*-LiMnO₂) with space group *C2/m*, in spite of a layered rock salt structure, has been synthesized by soft chemistry.^{2),3)} Because Mn exists as Mn³⁺ in LiMnO₂, the coordination polyhedron around the Mn³⁺ ions undergoes a distortion from a regular octahedron shape, consisting of MnO₆, due to the Jahn-Teller effect, and *m*-LiMnO₂ has a tendency to have an α -NaMnO₂ (*C2/m*) structure rather than α -NaFeO₂ ($R\bar{3}m$) structure. It is well known that both *o*- and *m*-LiMnO₂ are electrochemically active, and their reversible capacities are as high as 200 mAh/g.³⁾ However, both LiMnO₂ structures irreversibly transform to a spinel-like structure during electrochemical cycling, and significant capacity fade and changes in charge-discharge curve are observed.

The structure of LiMeO₂ (Me: transition metals) strongly depends on the size of the MeO₆ octahedron, that is, the ionic radius of the transition metal ions Me³⁺. LiMeO₂ containing transition metals with small ionic radius, such as V, Cr, Co and Ni, show an α -NaFeO₂ structure. On the other hand, that containing Sc shows a γ -LiFeO₂ structure.⁶⁾ Among transition metals, Mn is especially interesting because both *o*-LiMnO₂ and *m*-LiMnO₂ structures can be obtained, depending on the preparation procedure. A soft chemical synthesis method for lithium manganese oxide with the α -NaFeO₂ structure from Al-doped Li-birnessite was studied in this paper.

2. Experimental procedure

Al-doped Li-birnessite was prepared by pouring a solution of 150 ml with molar ratio H₂O₂/LiOH = 1/10 into an 1 M Mn(NO₃)₂ and 1 M Al(NO₃)₃, 30 ml solution with molar ratio Mn/Al = 1/0–0.85/0.15.⁷⁾ After stirring the solution with Al-doped Li-birnessite, dispersed in LiOH at room temperature for 30 min, the solution was sealed into a Teflon container, and then a hydrothermal treatment was conducted at 80°C for up to 48 h. The lithium manganese oxides formed after treatment were separated and washed with water, and then dried in air at 80°C. Reaction products were identified by X-ray diffraction (XRD) using a monochromatic Cu K α radiation. Their chemical compositions were determined by the inductively coupled plasma (ICP) method, and average Mn oxidation states were determined by redox titration using ferrous ammonium sulfate/KMnO₄. The particle size and microstructure were observed by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Electrochemical tests were conducted by using 2016 coin type-cells. The working electrode consisted of a mixture of 70 mg lithium manganese oxides, 25 mg acetylene black and 5 mg Teflon powders. The mixture was pressed into a tablet 13 mm in diameter. The negative electrode was a lithium metal foil 15 mm in diameter and 400 μ m in thickness. The separator was a microporous polyethylene sheet, 25 μ m in thickness. The electrolyte was a mixture of ethylencarbonate (EC) and diethylcarbonate (DEC), 1 mol·dm⁻³ LiPF₆ was used as supported electrolyte. The cell was constructed in an argon-filled glove box. Cycling performance was evaluated between 4.2–2.5 V at 20°C, the current density was 1C.

3. Results and discussion

The results of an X-ray diffraction analysis an Al-doped Li-birnessite, prepared by solutions with various molar ratios of Mn/Al, are shown in Fig. 1. A birnessite phase was obtained when the molar ratio of Mn/Al was less than 0.9/0.1. The basal spacing along the *c*-axis was about 0.7 nm, which agrees well with previously reported data.⁷⁾ Birnessite-type lithium manganese oxide has a layered structure with a single sheet of crystal water between the MnO₆ octahedral sheets.⁷⁾ The diffraction peak assigned to the MnO

Fig. 1. XRD patterns of Al-doped Li-birnessite prepared at various mixed molar ratios of Mn/Al. ▼ located the position of MnO(OH) peaks.

Fig. 2. XRD patterns of lithium manganese oxides hydrothermally obtained from Al-doped birnessite at 80°C for 16.5 h.

(OH) phase was observed at $2\theta = 18^\circ$ for a mixture with a molar ratio of Mn/Al = 0.85/0.15, as shown Fig. 1. This suggests that the solubility limit of Al in Mn sites is about 15%. Moreover, because the diffraction peaks became broad with increasing the amount of Al, the crystallinity of birnessite is thought to become lower. Figure 2 shows the X-ray diffraction patterns of lithium manganese oxides ob-

Fig. 3. XRD patterns of lithium manganese oxide prepared at 80°C for different hydrothermal reaction times, in the condition Mn/Al = 0.85/0.15. ▼ located the position of $(\text{Li, Al})\text{MnO}_2(\text{OH})_2$ peaks.

tained from Al-doped birnessite by a hydrothermal treatment at 80°C for 16.5 h. In the range of molar ratio $\text{Mn/Al} \leq 0.95/0.05$, all diffraction peaks were sharp and assigned to the spinel phase. On the other hand, the shape of the diffraction peak became broad in the range of $\text{Mn/Al} \geq 0.9/0.1$. Chemical analysis also reveals important difference (Table 1). When molar ratios of Mn/Al were 1/0 and 0.95/0.05, chemical analysis showed that those compounds had a spinel structure with excess Li. When Mn/Al ratios were 0.9/0.1 and 0.85/0.15, these structures were estimated to arise from LiMnO_2 rather than LiMn_2O_4 with spinel structure. More importantly, there are vacancies on the Mn sites. Although it is well known that the space group of LiMnO_2 is $Pnmm$ or $C2/m$, the crystal structure of Al-doped lithium manganese oxide obtained in this study is thought to be similar to that of LiCoO_2 with the space group $R\bar{3}m$, according to X-ray diffraction patterns.

In order to examine the process of crystal growth of these lithium manganese oxides, the hydrothermal treatment was conducted on Al-doped birnessite with a molar ratio of Mn/Al = 0.85/0.15 at 80°C up to 48 h. The X-ray diffraction patterns of the lithium manganese oxides treated for various hours are shown in Fig. 3. The main peak of the birnessite

Table 1. Composition of Lithium Manganese Oxide Hydrothermally Obtained from Al-Doped Birnessite at 80°C for 16.5 h

Nominal Al content	Composition	Average valence of Mn	Percent of Mn site vacancies
0.00	$\text{Li}_{1.08}\text{Mn}_{1.91}\text{O}_4$	3.62	1
0.05	$\text{Li}_{1.12}\text{Mn}_{1.82}\text{Al}_{0.07}\text{O}_4$	3.66	0
0.10	$\text{Li}_{0.71}\text{Mn}_{0.81}\text{Al}_{0.08}\text{O}_2$	3.77	11
0.15	$\text{Li}_{0.76}\text{Mn}_{0.75}\text{Al}_{0.12}\text{O}_2$	3.84	13

phase used as starting material was found to be about $d=0.7$ nm when the treatment time was shorter than 1.5 h. However, the diffraction pattern of lithium manganese oxides became similar to that of LiCoO₂, except for the small peaks indicated by a close circle, when the treatment was 1.75 h. The composition of lithium manganese oxide, prepared with treating for 1.75 h, was determined as Li_{0.58}Mn_{0.79}Al_{0.14}O₂ by chemical analysis. The main peak of (Li, Al)MnO₂(OH)₂ newly appeared around $d=0.9$ nm when the treatment time was longer than 2 h. Figure 4 shows a TEM photograph of the lithium manganese oxide Li_{0.58}Mn_{0.79}Al_{0.14}O₂ with Mn/Al=0.85/0.15. It is clear that the lithium manganese oxide has a layered structure with a 0.46

Fig. 4. TEM photograph (a) and selected area electron diffraction pattern (b) of lithium manganese oxide. The sample was prepared in the same condition as for the sample, in Fig. 3 that the treatment was for 1.75 h.

nm distance between the layers. The selected-area electron diffraction pattern was indexed by a hexagonal unit cell with $a=0.29$ nm and $c=1.39$ nm, and the index obeyed the extinction law, $-h+k+l=3n$. Therefore, the structure of lithium manganese oxide obtained herein appears to be of a α -NaFeO₂ structure mixed with LiCoO₂.

In order to examine the growth mechanism, hydrothermal treatment of samples with various amount of Al were conducted for different hours. Figures 5(a)–(e) show SEM photographs of the detained sample. It was revealed that the particles of birnessite are randomly shaped before hydrothermal treatment, and became smaller from about 50 to 30 nm with increasing the amount of Al (Figs. 5(a) and (c)). This result corresponds to the increase of the half-height width detected by X-ray diffraction as shown in the Fig. 1. Particles with octahedral shape, which is considered to be automorphic of spinel, were observed after hydrothermal treatment of birnessite without Al at 80°C (Fig. 5(b)). It was also revealed that relatively highly crystallized lithium manganese oxides with automorphic spinel structure were obtained at temperature as low as 80°C. On the other hand, when the Mn/Al ratio was 0.85/0.15, the particle shape changed from a roundish one to platelets with increasing the reaction time. The particle size of lithium manganese oxide with α -NaFeO₂ structure, prepared by hydrothermal treatment for 1.75 h, was about 30 nm, which is the same size as those of the precursor (Fig. 5(d)). These results suggest that the crystalline water between the MnO₆ octahedral sheets of birnessite was dehydrated by hydrothermal treatment, and Li topotactically lied in between the layers in place of water. Plate like particles with a diameter larger than 80 nm formed when the hydrothermal treatment was conducted up to 48 h (Fig. 5(e)). Platelets of (Li, Al)MnO(OH)₂ were considered to grow by diffusion

Fig. 5. SEM photographs of lithium manganese oxides hydrothermally obtained at 80°C.

Fig. 6. Charge and discharge curves of a $\text{Li}_{0.58}\text{Mn}_{0.79}\text{Al}_{0.14}\text{O}_2/\text{Li}$ cell. Current density was $0.2 \text{ mA} \cdot \text{cm}^{-2}$ and the operating temperature was 20°C .

of Al in MnO_6 layer to the space between the MnO_6 octahedral sheets. The lithium manganese oxide with $\alpha\text{-NaFeO}_2$ structure was estimated to be an intermediate phase during transformation from Li-birnessite to $(\text{Li}, \text{Al})\text{MnO}(\text{OH})_2$.

Figure 6 shows the charge-discharge curves of the $\text{Li}_{0.58}\text{Mn}_{0.79}\text{Al}_{0.14}\text{O}_2$ cell used as cathode ($\text{Mn}/\text{Al}=0.85/0.15$) with $\alpha\text{-NaFeO}_2$ structure and lithium metal as anode. The specific capacity on charge (ca. 110 mAh/g) is smaller than that of $m\text{-LiMnO}_2$ (ca. 210 mAh/g) reported previously.³⁾ During the first discharge, a plateau was observed at 3.0 V , and the discharge capacity was about 150 mAh/g . On the first discharge curve, two plateaus were

found at 3.0 V and 3.8 V because $m\text{-LiMnO}_2$ irreversibly transformed to a material with a spinel-like order. Therefore, the charge-discharge behavior after the 2nd cycle is like that of a spinel structure. The lithium manganese oxide with $\alpha\text{-NaFeO}_2$ structure obtained in this study enables no change of the charge-discharge behavior up to 10 cycles in the range $2.5\text{--}4.2 \text{ V}$. The mean oxidation number of Mn in this sample, calculated from the composition, was approximately $+3.8$. Therefore, it is thought that the stabilization of the layered structure can be attributed to the formation of Mn^{4+} .

4. Conclusion

Lithium manganese oxides with $\alpha\text{-NaFeO}_2$ structure were obtained from Al-doped Li-birnessite by hydrothermal reaction using a LiOH solution. It is shown that lithium manganese oxides were intermediate phases during transformation from the Li-birnessite containing Al to layered $(\text{Li}, \text{Al})\text{MnO}_2(\text{OH})_2$. The lithium manganese oxide obtained was electrochemically active, its specific capacity was about 150 mAh/g ($2.5\text{--}4.2 \text{ V}$), and no transformation was observed during cycling.

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