

# Synthesis and reaction mechanism of 3 V $\text{LiMnO}_2$

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## Abstract

$\text{LiMnO}_2$  with orthorhombic structure (Pm2m) was synthesized by hydro-thermal method using gamma-MnOOH and lithium hydroxide as starting material. A process for the synthesis was proceeded by an ion exchange reaction, obtaining 190 Ah/kg of reversible capacity in 2 h lithiation and 160 Ah/kg in half an hour lithiation. Investigation for the changes of host material on each steps of lithiation process was carried out in view of crystal structure, chemical state of lithium and proton in connection with electrochemical behavior. When the orthorhombic phase appeared, a spectrum of solid-echo proton-NMR (H-NMR) on gamma-MnOOH became diminished, while a spectrum of solid-echo lithium-NMR ( $^7\text{Li}$ -NMR) emerged with three different kinds signals which is accompanied by spinning side band at around 37 ppm, 74 ppm and 1, ppm respectively. As longer lithiation in process, the ratio of intensity of each peaks was changing, implying an occupation of lithium site might be changed in process. After cycling test on  $\text{LiMnO}_2$ , it was hard to have a look of phenomenon of spinel frame transition which might be seen in spinel material at low temperature synthesis showing chemical shift of Li-NMR at around 600 ppm. We have tried to elucidate the mechanism of ion exchange reaction and also propose a method to enhance a rate for the process effectively in a short time. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Synthesis; Reaction mechanism;  $\text{LiMnO}_2$

## 1. Introduction

Many manganese oxides have been studied, including spinel type, and among them  $\text{LiMnO}_2$  with Li/Mn ratio of almost 1 has attracted a great deal of its functional characteristic that can be expected to have high capacity [1–3]. Orthorhombic type structure of  $\text{LiMnO}_2$  is expected to work at 3 V class with high capacity and reduce a strain on decomposition of electrolyte because a restriction to oxidize electrolyte might be expected to be more relaxed. Preparation for  $\text{LiMnO}_2$  has been reported by many researchers. Some of mechanisms for the reaction have been explained by ion exchange reaction between proton in a solid of manganese compound and lithium ion from lithium compound [4].

Supposing a mechanism for the preparation support this hypothesis of ion exchange mechanism, it is considered that a more effective method for preparation must exist. We aimed to use a method that lithium species within activated vapor attack on the surface of a manganese compound. We have tried to prepare  $\text{LiMnO}_2$  effectively

in a short time by hydrothermal method using activated vapor including lithium under a preparation condition of stoichiometry in the ratio of Li/Mn, different from the method using excess amount of lithium to manganese that has been used in general. According to this method, since vapor at least higher than 100°C can dissolve lithium species more than in boiled water, dissolved lithium within vapor would be more activated, giving ion exchange reaction being more enhanced. We have used gamma-MnOOH as manganese compound to maintain the oxidation state during the process, and lithium hydroxide as lithium compound so as to dissolve in vapor easier and exclude any other formation except water.

It is interesting to know how ion exchange reaction proceeds, or how the chemical state of proton and lithium ion changes. There are few reports suggesting the evidence for the change of chemical state of proton and lithium ion, and for the explanation on this.

In this paper, we discuss the process for ion exchange reaction between proton and lithium ion in view of the chemical state of proton and lithium ion by solid NMR measurement, crystal structure change of gamma-MnOOH connected with electrochemical characterization on each step of reaction process.

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## 2. Experiment

Samples were prepared as follows. Designated amount of gamma-MnOOH and  $\text{LiOH} \cdot \text{H}_2\text{O}$  were mixed in order to obtain the orthorhombic structure of  $\text{LiMnO}_2$  with stoichiometry, and made some pellets by press machine. After that, these pellets were put into autoclave under a condition of temperature at about  $130^\circ\text{C}$ , pressure at about 3 bars, reaction time for a half-hour to 4 h at maximum. After finishing the hydrothermal process, samples were dried in a vacuum system, temperature at  $110^\circ\text{C}$  for about 12 h. Then, samples were examined by solid NMR of proton and lithium, XRD and other methods to see how these materials were changing. We have previously reported that the NMR measurement was very useful to analyse the chemical state of lithium in a solid matrix [5]. NMR measurements were carried out at room temperature on Varian INOVA-400 by using solid echo method (frequency: 400 MHz for proton and 155 MHz for  $^7\text{Li}$ , d1: 1.0 s for proton and 3.0 s for lithium, pulse width:  $4.1 \mu\text{s}$  for proton and  $3.9 \mu\text{s}$  for lithium, spinning speed: mainly 15.5 kHz). XRD measurements were carried out on RINT 2500. The ratio of Li/Mn was determined by ICP after rinsing the material by methanol.

Electrochemical behavior of charge/discharge was examined by a two-electrode cell with lithium as counter electrode by constant current of  $0.5 \text{ mA}/\text{cm}^2$ , for the range of 2.0 to 4.3 V. vs. Li at room temperature. EC/DMC 1 M LiPF<sub>6</sub> was used as electrolyte.

## 3. Results and discussion

Fig. 1 shows solid-echo profiles of H-NMR on gamma-MnOOH before/after lithiation. As can be seen, before lithiation there was a broad signal at around 250 ppm. This chemical shift is considered to be an attribution of being strongly influenced by paramagnetism of manganese. After a half-hour of lithiation, the intensity of this peak became reduced in comparison with that of the initial state, and after 2 h lithiation, no signal attributed to proton could be seen.

Fig. 2 shows solid-echo profiles of Li-NMR on gamma-MnOOH after a half-hour and 4 h lithiation, respectively. It was found that in a half-hour lithiation, there were three kinds of profiles, for instance, SSB (spinning side band) of main peak A at around 37 ppm, small SSB of peak B at around 74 ppm and SSB of peak C at around 1 ppm. Interestingly, the ratio of intensity on peak A and C was changed inversely in comparison with the case of a half-hour lithiation and the case of 2 h lithiation. On the other hand, peak B started to appear after an half hour lithiation and the intensity of this peak was maintaining from in case of a half-hour lithiation to 4 h lithiation without drastic changes. It was shown that peak C tended to be diminished gradually while peak A was growing as a main signal.

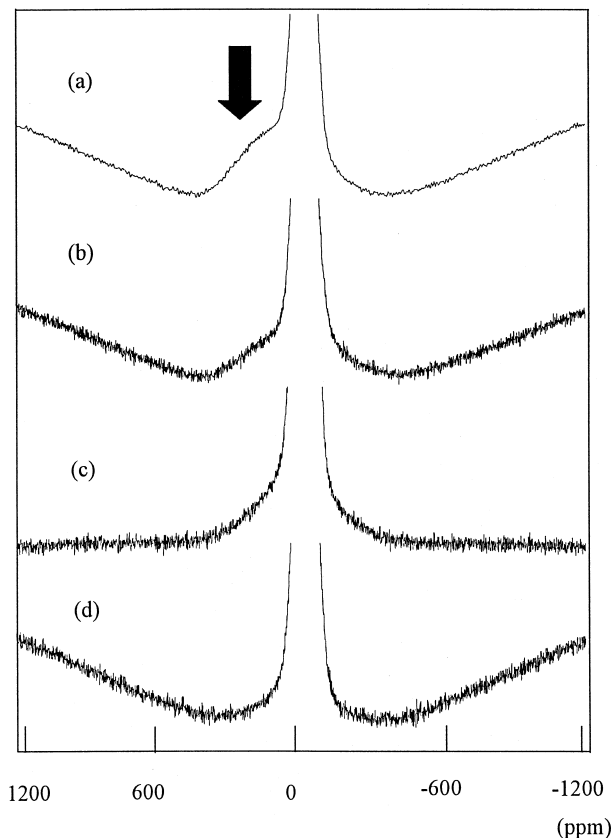


Fig. 1.  $^1\text{H}$ -NMR (solid-echo) spectra of the change in process on  $\gamma$ -MnOOH. (a) after half-hour lithiation, (b) after 1 h lithiation, (c) after 2 h lithiation, and (d) after 4 h lithiation.

Fig. 3 shows the XRD patterns for lithiation time from half-hour to 4 h. From this figure, even in a half-hour lithiation, we could find the diffraction patterns reflecting orthorhombic structure in its major part which was formed as a result of lithiation, while the rest remain as the original patterns attributed to gamma-MnOOH. When the lithiation time was longer than 2 h, most of the diffraction patterns turned to orthorhombic phase and formed almost one phase.

Fig. 4 shows the result of the relation between chemical analysis for the ratio of Li/Mn in solid matrix and lithiation time. The ratio of Li/Mn was increased as lithiation proceeded; a rapid increase was seen at the beginning stage of half-hour to an hour of lithiation. When it is longer than 1-h lithiation, the ratio of Li/Mn did not show drastic changes, keeping at a constant position. The position, however, was not the value corresponding to stoichiometry, meaning there might have existed some lithium which were not able to contribute to lithiate.

From Figs. 1–4, it seemed that almost all of the process for proton–lithium ion exchange reaction proceeds at the initial stage of hydro-thermal reaction from the evidences that in a half-hour lithiation, spectrum in solid-echo of H-NMR was reduced and inversely spectrum profile, suggesting that incorporation of lithium in solid-echo of Li-

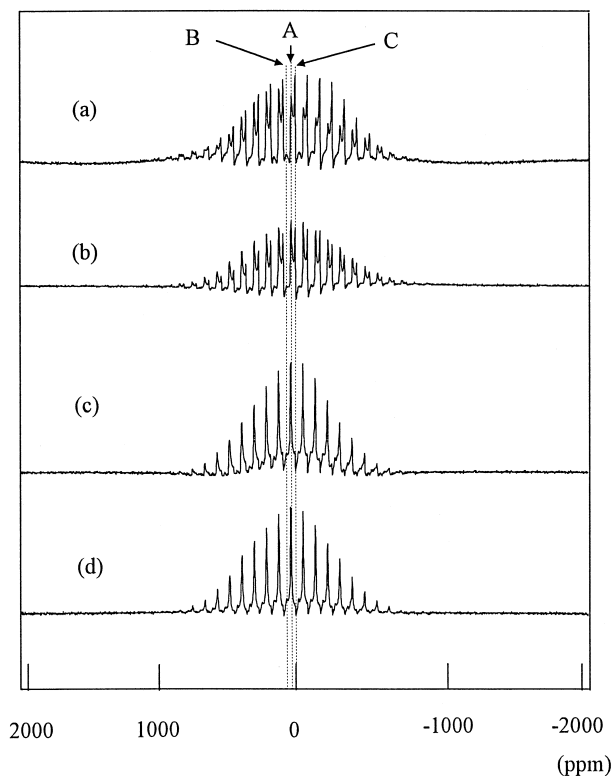


Fig. 2.  $^7\text{Li}$ -NMR (MAS/echo) spectra of the change in lithiation process on  $\gamma\text{-MnOOH}$ . (a) after half-hour lithiation, (b) after 1 h lithiation, (c) after 2 h lithiation, and (d) after 4 h lithiation.

NMR appeared, corresponding to the appearance of the XRD patterns of orthorhombic phase. After that, spectrum of proton in H-NMR was disappeared completely and the

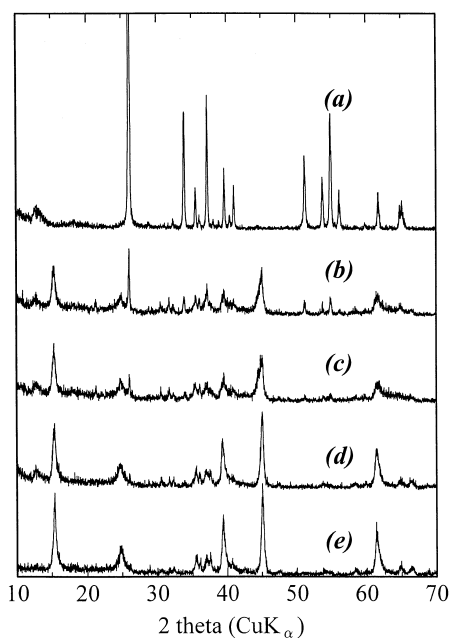


Fig. 3. XRD patterns of the change in lithiation process on  $\gamma\text{-MnOOH}$ . (a)  $\gamma\text{-MnOOH}$  (starting material), (b) after half-hour lithiation, (c) after 1 h lithiation, (d) after 2 h lithiation, and (e) after 4 h lithiation.

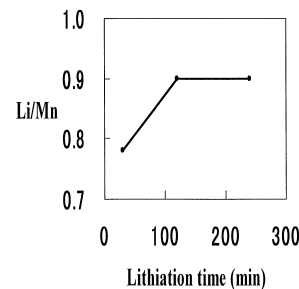


Fig. 4. Chemical analysis on the ratio of Li/Mn in the lithiation process.

profile reflecting incorporation of lithium in Li-NMR was changing of its intensity on each three spectrum, corresponding to the appearance of the XRD patterns of orthorhombic phase being almost one phase. These results inevitably allow us to think about the ion-exchange reaction. We believe that the ion-exchange reaction in this system is as follows. At first, vapor arising from excess water out of this reaction system in an autoclave attack the particles of lithium hydroxide, which was involved in the  $\gamma\text{-MnOOH}$  and lithium hydroxide mixture, dissolving lithium species into its vapor. Under the condition of over  $100^\circ\text{C}$  and 3 bars in an autoclave, vapor can accommodate lithium species as  $\text{Li}^+$  and  $\text{OH}^-$  within dispersed water mist. Since the vapor within lithium species under these conditions can accommodate more lithium than in boiled water system, in which the total amount of dissolution is limited to about 6 mol/l, they can attack on the surface of  $\gamma\text{-MnOOH}$  particles actively. We think that the proton in the  $\gamma\text{-MnOOH}$  is extracted by a neutralization reaction in an activated vapor which is adsorbed at the surface of  $\gamma\text{-MnOOH}$ , after that, lithium ion might be inserted to obey the electric neutralization rule. Therefore, all lithium contributed to insertion reaction should start at the surface on the  $\gamma\text{-MnOOH}$ , so it is considered that peak C at around 1 ppm in Li-NMR is assigned to be adsorbed lithium species at the surface, of which chemical state is thought to be ionic because the chemical shift is almost the same as standard material of LiCl, meaning it is not so much influenced by paramagnetism of manganese. Instead of decreasing the intensity of proton spectrum in H-NMR, lithium ion in the solid matrix occupy octahedral site in the space group of Pm2m, and this gives peak A or peak C showing different chemical shift in the Li-NMR spectrum. It is considered that lithium in an interstitial site is more influenced by the paramagnetism of manganese than that of adsorbed state at the surface because of the difference in the distance of lithium to manganese in case of the state of adsorbed and that of inserted in matrix, and difference in chemical circumstance whether a lithium is present in an oxygen octahedral packing or not. So, the difference in the surroundings of lithium induce chemical shift.

In orthorhombic type of  $\text{LiMnO}_2$  [space group Pm2m], since there are two kinds of Mn–Mn distance as well as

Mn–O distance due to be considered of existing Jahn–Teller distortion, an effect of the structural configuration of lithium on chemical shift might be complicated. A explanation for the presence of peak A and peak B, or the difference of chemical shift in both peaks should be introduced by the term of paramagnetism of manganese or in view of microstructure configuration. In our previous work [5], the chemical shift in manganese spinel material have been shown at over 500 ppm, quite different to this work in spite of almost the same condition for the paramagnetism of manganese; of course, there is a difference in oxidation state between spinel material and orthorhombic material, and also in structural type. It should be taken into consideration that for the differences of crystal structure in a micro domain, electron configuration in 3d orbit and Madelung potential strongly relate with the three-dimensional factor of cubic structure. We presume, at the moment, that the big difference in spinel and orthorhombic type is attributed to an isotropic characteristic in orthorhombic structure due to be a lower crystallized state in a micro domain, this gives the chemical shift positively shifted. Anyway, further work for the elucidation of physical meaning of these chemical shifts will be necessary.

Fig. 5 shows the electrochemical behavior of charge/discharge characterization. As is expected, the longer lithiation process, the higher reversible capacity was obtained at the third cycle. Reversible capacity in a half-hour lithiation showed over 160 Ah/kg, supporting the fact that the presence of orthorhombic structure, the presence of peak A with coexistence of peak C in Li-NMR, and being in the state halfway of the process occurred because the ratio of Li/Mn was not completed to stoichiometry. Meanwhile, the reversible capacity in 2 h lithiation showed over 190 Ah/kg, supporting the fact that the presence of orthorhombic structure, which is almost one phase, the presence of main peak A in Li-NMR with no proton, and being the state of saturation for the process occurred because the

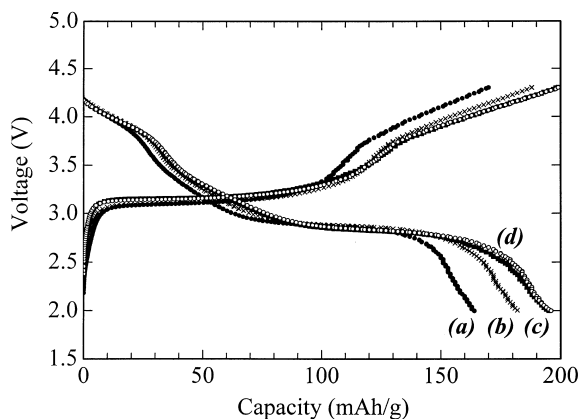


Fig. 5. Charge/discharge curves of  $\text{LiMnO}_2$  prepared in various conditions, (the third cycle) (a) after half-hour lithiation, (b) after 1 h lithiation, (c) after 2 h lithiation, and (d) after 4 h lithiation.

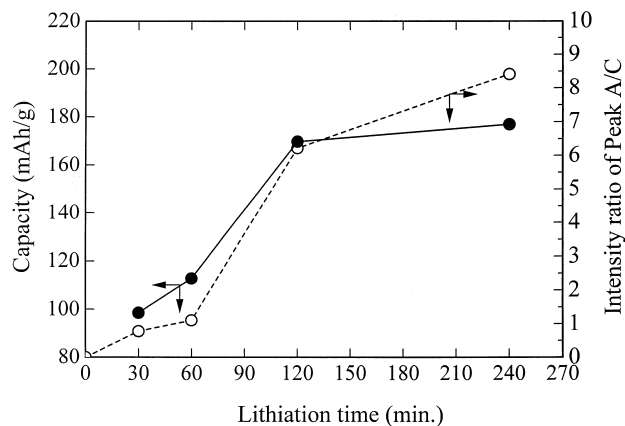


Fig. 6. Relation between charge capacity at first cycle and the intensity of peak ratio of peak A/C to lithiation time.

ratio of Li/Mn appeared at a constant position which is lower than stoichiometry.

Fig. 6 shows the relation of capacity at the first charge and the ratio of intensity of peak A and peak C in the process to lithiation time. As can be seen, an electrochemical characteristic and a NMR information to lithiation time was closely correlated. At the first cycle, charge capacity of 100 Ah/kg in half-hour lithiation and 170 Ah/kg in 2 h lithiation were obtained.

It is quite important to have the first charge capacity for a cathode material in a rocking chair type battery. As longer lithiation, capacity of the first charge was increasing corresponding to the ratio of NMR intensity, meaning a main peak A suggested an important information for the charge capacity to be more increased.

Fig. 7 shows the cycle performance of all samples synthesized by the hydrothermal method. For samples in longer lithiation, degradation of cycle behavior was relatively serious, while the reversible capacity was obtained higher than others. Electrochemical behavior is closely related to how much lithium could be incorporated into the matrix of manganese oxide during process.

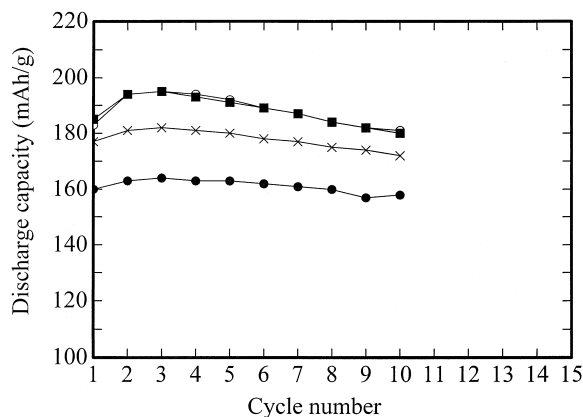


Fig. 7. Cycle behavior of  $\text{LiMnO}_2$  prepared in various conditions. ● after half-hour lithiation, × after an hour lithiation, ■ after 2 h lithiation, and ○ after 4 h lithiation.

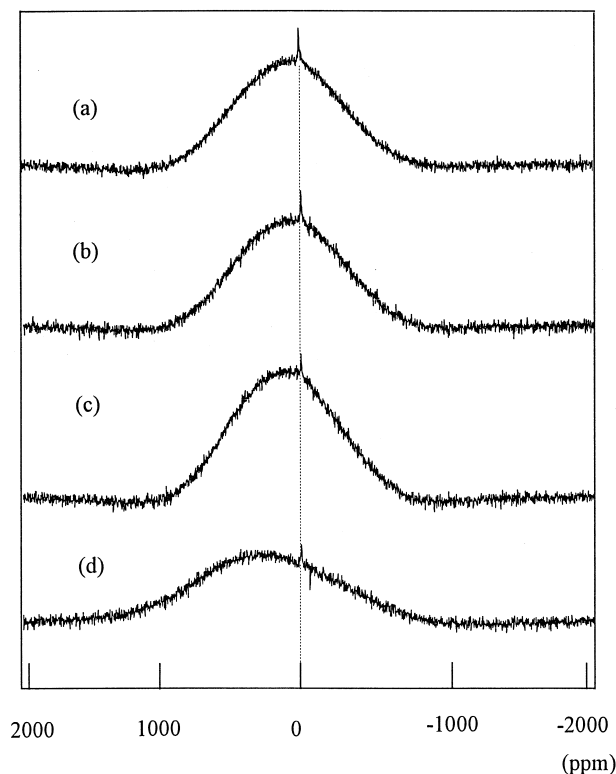


Fig. 8.  $^7\text{Li}$ -NMR (solid-echo) spectra of  $\text{LiMnO}_2$  prepared in various conditions after 10 cycles. (a) after half-hour lithiation, (b) after 1 h lithiation, (c) after 2 h lithiation, and (d) after 4 h lithiation.

Generally speaking, the orthorhombic type of  $\text{LiMnO}_2$  is changed to spinel frame after cycling. We also saw spinel transition in samples of longer lithiation but hardly saw it in samples of shorter lithiation. This is supported by the Li-NMR profiles of each sample.

Fig. 8 shows the profiles of Li-NMR in a static measurement on each samples after cycling test. As can be seen, a peak top of broad spectrum of sample in 4-h lithiation showed negatively shifted, while the sample in the half-hour lithiation showed almost 0 ppm. The position of a peak top on this broad spectrum was dependent on lithiation time. We have managed to do peak fitting on these profiles and had a speculation that a spectrum of 4 h lithiation could be divided into two peaks; for instance, one was at around 0 ppm and the other one was at around 500 ppm. It might be possible to think the latter was

attributed to spinel frame because almost the same description was obtained, which was already reported in previous paper [5], that spinel material synthesized even in a condition of low temperature of below than  $400^\circ\text{C}$  revealed a broad spectrum at around 600 ppm of chemical shift. It is considered that the sample lithiated considerably enough in the process is easy to change to spinel frame and deteriorate in cycle performance despite having high reversible capacity at the beginning stage. As previously mentioned, it seems to be significantly influenced on spinel transition by the factors of how the crystal structure was growing and how the spectrum occupied by peak A was obtained.

#### 4. Summary

The mechanism of  $\text{LiMnO}_2$  with orthorhombic structure synthesized by hydrothermal method was explained by ion exchange reaction as follows. When the orthorhombic phase appeared in the lithiation process, a spectrum of solid-echo H-NMR on gamma- $\text{MnOOH}$  diminished, while a spectrum of solid-echo Li-NMR emerged showing three different kinds of signals, accompanied by spinning side band at around 37 ppm, 74 ppm and 1 ppm. For longer lithiation in the process, the ratio of intensity of each peaks was changed, meaning that an occupation of lithium site is changed and this gives influence on electrochemical activity, especially the charge capacity at the first cycle, which is closely related to the amount of accommodated lithium in the material. After the cycling test on  $\text{LiMnO}_2$ , it was hard to see the phenomenon of spinel frame transition, which might be seen in spinel material at low temperature synthesis showing chemical shift of Li-NMR at around 600 ppm.

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