Lithium manganese oxides for rechargeable lithium batteries

Yoshiaki Nitta *, Kazuhiro Okamura, Masatoshi Nagayama, Akira Ohta

Technology Laboratory Matsushita Battery Industrial Co., Ltd., 1, Matsushita-cho, Moriguchi City, Osaka 570, Japan

Abstract

Lithium manganese spinel compounds HT-LiMn$_2$O$_4$ (HT means high temperature) synthesized at > 700 °C have high capacity in the 4 V range (Li$_x$Mn$_2$O$_4$, $x \leqslant 1$), However, lithium manganese oxides LT-LiMn$_2$O$_4$ (LT means low temperature) synthesized at temperatures lower than 400 °C, resemble to the spinel structure and tend to have a reduced capacity in the 4 V range. We investigated the factor of potential difference between the 4 V type and the 3 V type by using ^{7}Li nuclear magnetic resonance (NMR) and electron spin resonance (ESR) measurements. It was found by using ^{7}Li-NMR that there were two kinds of spectrum in these materials; in the 4 V type, the spectrum having about 530 ppm of chemical shift with spinning side band was mainly observed. On the other hand, in the 3 V type, the broad spectrum having about 760 ppm of chemical shift without spinning side band was mainly observed. There are two different lithium sites in the manganese spinel compound (space group of $Fd3m$), one is at the 8a site located far from the manganese ion and the other one is at the 16c site located close to the manganese ion. It is presumed that the spectrum having 530 ppm of chemical shift with spinning side band is corresponding to the 8a site, and the broad spectrum having 760 ppm of chemical shift without spinning side band is corresponding to the 16c site, with taking into consideration the influence of paramagnetic character of manganese on the lithium site which is closely related to the distance from the manganese ion. © 1997 Elsevier Science S.A.

Keywords: Lithium rechargeable batteries; Manganese oxides; Lithium

1. Introduction

These days, lithium manganese oxides as the cathode materials for lithium secondary battery has been studied intensively [1,2]. These materials are divided into two groups with regard to their potential: (i) a 4 V type such as spinel compounds (space group of $Fd3m$; Li$_x$Mn$_2$O$_4$, $x \leqslant 1$), and (ii) a 3 V type such as spinel-like compounds or a compound which crystallized in an orthorhombic system. A lot of work on lithium manganese oxides have been done by many researchers, but the difference in properties between these two groups has not yet been elucidated.

The HT-LiMn$_2$O$_4$ spinel compound synthesized at > 700 °C as the 4 V type, and mainly LT-LiMn$_2$O$_4$ spinel-like compound synthesized at < 400 °C as the 3 V type, were prepared. We have tried to observe the differences of these compounds by using thermal analysis, crystal structural analysis, magnetic properties and chemical analysis. When we discuss the potential, it is necessary to take into consideration at least which site should be occupied as alternative available lithium sites and also the oxidation state of manganese during charge/ discharge. In order to find out the selective site of lithium ion

related with the electrochemical reduction/oxidation state, ^{7}Li-NMR analysis were performed, and the oxidation state of manganese was measured by means of electron spin resonance (ESR), magnetic moment measurement and chemical analysis. Moisture content which can compensate for the charge of manganese was measured carefully by using the thermogravimetric–differential thermal analysis (TG–DTA) and the Karl–Fischer method. Finally, the crystal structural analysis of synthesized material were examined by X-ray diffraction (XRD) and the Rietveld method.

In this report we discuss the close relation between electrochemical behavior and the lithium sites in consideration with the paramagnetic character of manganese.

2. Experimental

The HT-LiMn$_2$O$_4$ spinel was prepared at 700–900 °C in an oxidizing atmosphere using γ-MnOOH or electrolytic manganese oxide as the manganese compound and Li$_2$CO$_3$ as the lithium compound. On the other hand, spinel-like LT-LiMn$_2$O$_4$ was prepared at 350 °C in an oxidizing atmosphere using electrolytic manganese oxide and Li$_2$CO$_3$ as the lithium compound. Spinel-phase LS-LiMn$_2$O$_4$ (LS means low tem-

* Corresponding author.

perature synthesis and it has a real spinel structure) was prepared at the same condition as that of spinel-like LT-LiMn$_2$O$_4$ using γ-MnOOH as the manganese compound and LiOH·H$_2$O as the lithium compound. Specimen obtained were examined by using XRD and Rietveld method (DBWS) as structural analysis, and also examined by using ^{7}Li-NMR, ESR, magnetic balance as magnetic properties. Thermal analysis were carried out by using TG and the Karl–Fischer method in order to detect existence of water. ^{7}Li (S = 3/2) NMR measurements were carried out at room temperature on Chemagnetics CMX-300 (frequency: 116.75 MHz). The procedure of measurement was a combination of high speed MAS shifts. Lithium chloride was used as a standard material to compare chemical shifts. ESR measurements were carried out at room temperature on Bruker ESP-350E (0–1 T and microwave frequency; 9.45 GHz). The amount of spin from the ESR spectrum was determined by using a standard specimen CuSO$_4$·5H$_2$O single crystal.

Charge/discharge properties of the specimen were obtained by measuring with a two-electrode method at constant current, at current density of 0.33 mA/cm^2, charge/discharge range of 3.5–4.3 V (Li standard) in the case of HT-LiMn$_2$O$_4$ (Fd3m; Li$_x$Mn$_2$O$_4$, $x \leqslant 1$) and that of 2.0–4.3 V (Li standard) in the case of spinel-like LT-LiMn$_2$O$_4$ and spinel phase LT-LiMn$_2$O$_4$ at room temperature. 1.0 M LiPF$_6$ in ethylene carbonate–diethyl carbonate (EC–DEC) mixed solvent was used as the electrolyte.

3. Result and discussion

3.1. Comparison between HT-LiMn$_2$O$_4$ and LT-LiMn$_2$O$_4$

3.1.1. Electrochemical behavior

Fig. 1 shows the first cycle charge and discharge curves of HT-LiMn$_2$O$_4$ and LT-LiMn$_2$O$_4$. The HT type shows two plateaus, and it is possible to charge and discharge in the 4 V range. When the discharge capacity is more than 120 mAh/
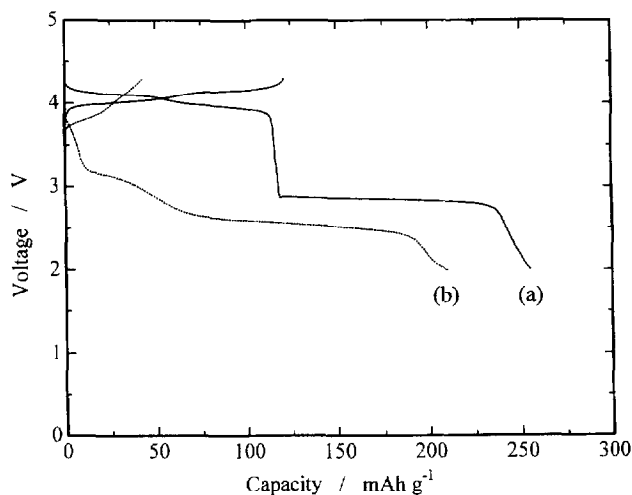
g, there is an abrupt potential drop, and then the 3 V range appears. On the other hand, the LT type shows only a limited 4 V range. The discharge capacity is high, that is, over 200 mAh/g approximately in the 3 V range. However, the charge capacity is only 50 mAh/g approximately. It is possible to charge and discharge in the 3 V range in the second and following cycles. The reason why these samples of the similar composition have different potential behavior is discussed below.

3.1.2. Characterization of materials

Table 1 shows the comparison of the material properties between both samples of the HT type and the LT type. According to Table 1, they are almost the same in lithium wt.%, manganese wt.%, and Li/Mn ratio. The LT type is higher in the oxidation state of manganese oxides (x value) obtained in the chemical analysis. When the analytical result is compared with the oxidation state of manganese oxides calculated from the stoichiometric composition, the x value of HT type was 1.76 and the x value of LT type was 1.85. The ratio of manganese ($4 + (d^3)$) to the whole amount of manganese obtained from the ESR measurement is 52% for the HT type. This means that the state of mixed valences of manganese ($3 + (d^4)$) and manganese ($4 +$) is supported. A magnetic moment obtained from the magnetic susceptibility measurement at room temperature is very usuful to determine the oxidation state of manganese in a solid, for instance, if an electron state of manganese is d^3, then the magenetic moment should be 3.8 μB and in the case of d^4, it should be 4.9 μB theoretically. In the case of the HT type, the magnetic moment is 4.3 μB. It shows almost the mean value and is a reasonable one as above mentioned. For the LT type, however, Mn^{4+} is 35% and the magnetic moment is 3.4 μB. The ratio of Mn^{4+}, which is expected to be higher from the result of chemical analysis, is not reflected in both of them. Also, the magnetic moment is too low to consider all manganese species as Mn^{4+}. This suggests that the existence of highly oxidized manganese species over Mn^{4+} or the exsistence of low spin arrangements is undeniable, though it is necessary to examine repeatedly and fully in consideration of oxygen defect and proton participating.

Fig. 1. Electrochemical behavior of (a) HT and (b) LT-LiMn$_2$O$_4$.

Table 1
Material properties of HT- and LT-LiMn$_2$O$_4$

Chemical analysis

Sample	Li (wt.%)	Mn (wt.%)	Li/Mn	MnO$_x$
HT-LiMn$_2$O$_4$	4.1	60.1	0.54	1.76
LT-LiMn$_2$O$_4$	3.9	59.3	0.52	1.85

Magnetic analysis

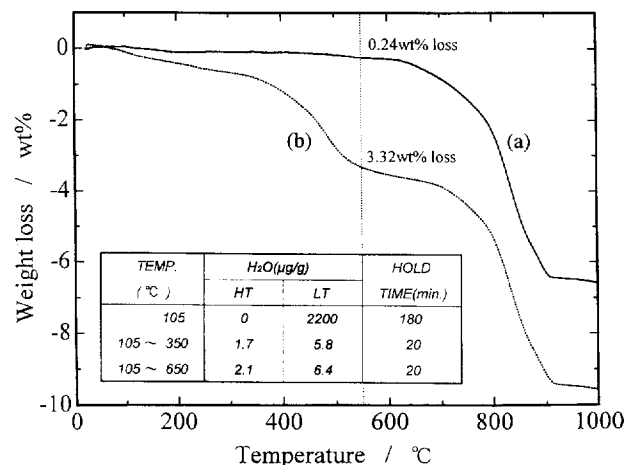| Sample	ESR (Mn^{4+}) (%)	Magnetic moment (μB)
HT-LiMn$_2$O$_4$	52	4.3
LT-LiMn$_2$O$_4$	35	3.4

Fig. 2. Thermogravimetry curves of (a) HT- and (b) LT-LiMn₂O₄. Measurement conditions: heating rate; 10 °C/min, atmosphere: argon, and water content of HT- and LT-LiMn₂O₄ by the Karl–Fischer method.

Next, the water content in the samples was examined by thermal analysis (TG) and the Karl–Fischer method because the samples are dependent on the heating temperature and the starting material. Fig. 2 shows the result. As shown in the figure, the weight reduction of the HT type is 0.24 wt.% at temperatures up to 550 °C. The reduction of the LT type is 3.32 wt.%, corresponding to about 14 times as much as that of the HT type. The Karl–Fischer method showed that most of the weight reduction was due to water since this method is applicable for only for the detection of water. This supports that there exist a large amount of proton impurity. The results of Karl–Fischer method showed that the majority of the water was already removed from the oxides at temperatures below 105 °C. The different results between the TG method and Karl–Fischer method is considered to be the rate of rising the temperature. The way of measurement in the Karl–Fischer method is kept at least 3 h at the proper temperature and in order to detect all the water. Therefore, it is considered to be hard to remove the water from the ramsdellite phase in the LT type material, it is rather stable with containing water. It means to be difficult for exchange from protons to lithium ions in process.

3.1.3. Crystal structural analysis

Powder XRD and Rietveld method (DBWS) [3] were used to analyze the crystal structure of the compounds. Fig. 3 shows the results. As shown in the figure, the HT type has the cubic system (space group $Fd3m$) with the lattice constant of $a = 8.223$ Å and the R factor of 7.16%. On the other hand, the LT type is supposed to have a complicated structure, of which a part of the cubic phase (space group $Fd3m$) are mixed with the ramsdellite phase which has an orthorhombic system (space group $Pnam$), where the ramsdellite is not considered to be pure ramsdellite but having almost the same structure as that present in EMD. The R factor of the LT type is 8.0 1% with a lattice constant of $a = 8.155$ Å in the cubic system and that of $a = 9.471$ Å, $b = 4.938$ Å, $c = 2.836$ Å in
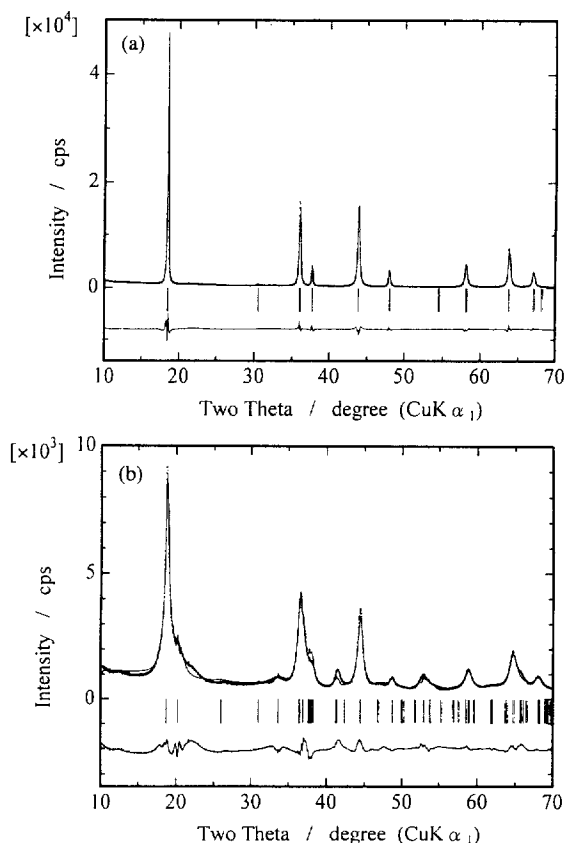

Fig. 3. Powder X-ray diffraction patterns and the results of Rietveld analysis of (a) HT-LiMnO₄ (R factor = 7.16%) and (b) LT-LiMn₂O₄ (R factor = 8.01%).

the orthorhombic system. It has been reported that the rutile structure favors spinel formation [4]; it is considered that the rutile structure in EMD tends to react with lithium, giving a spinel phase, but for the ramsdellite phase it is difficult to react with lithium directly due to the occupied proton. Therefore, it needs to exchange between proton and lithium to obtain partly lithiated manganese oxide in the ramsdellite phase. From the thermal analysis, it was shown that the LT type contained a large amount of moisture. It may be mainly caused by the existence of this ramsdellite phase.

Supposing that protons exist, ⁷Li solid NMR measurement was carried out to examine how the lithium-ion site were influenced by the presence of protons.

3.1.4. ⁷Li-NMR measurement

Usually the high-speed MAS method is used to observe the state of the lithium ion in a transition metalic oxide containing lithium. However, lithium in a transition metalic oxide is influenced by paramagnetism of the transition metal when measured by the MAS method only. It is very difficult to analyze the state of the lithium ion. Accordingly, the pulse-spin-echo method was adopted together with the MAS method to examine the state of lithium species in detail from the point of view of the relaxation time.
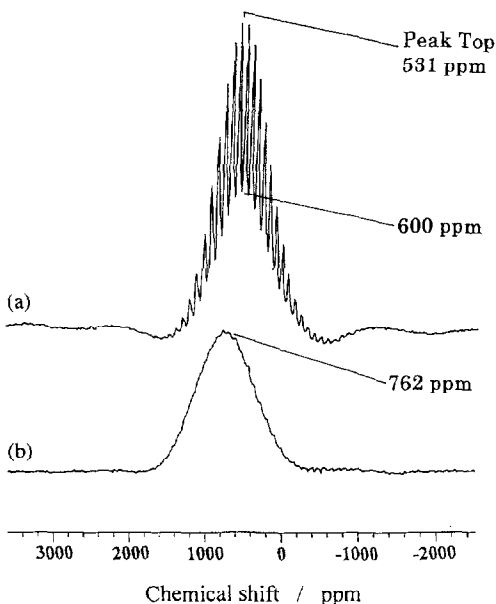
Fig. 4. ⁷Li-NMR (MAS/spin-echo) spectra of (a) HT- and (b) LT-LiMn₂O₄ (starting materials).

Fig. 4 shows the spectra of the HT and LT types obtained in the MAS/spin-echo method. As shown in the figure, the spectrum of the LT type has a broad signal with the peak top at 762 ppm. Another signal is put together on the signal. The line width of the signal put together is narrow, and it has an extremely weak spinning side band (denoted as SSB). On the other hand, the spectrum of the HT type has a broad signal with the peak top at about 600 ppm where chemical shift appears more positively shifted than that of LT type (define right direction as the possitive direction in NMR spectrum). Another signal is put together on the signal with strong SSB. The line width of the signal put together is narrow having high intensity, and the central line of SSB is in the position of 531 ppm where chemical shift is more positively shifted than that of the peak top of broad signal (600 ppm).

The HT type is different from the LT type with regard to the NMR spectrum. It is a well-known fact that the spinel structure (space group $Fd3m$) has two types of lithium site, the 8a site with coordination number of 4 and the 16c site with coordination number of 6. They are different in their distance to the manganese. In consideration of the influence on these two lithium sites at different distances from manganese with high paramagnetism, we think that the 16c site, which is located in closer to the manganese, is more influenced by high paramagnetism and that the chemical shift is negatively shifted. We also think that the 8a site is not so much influenced by high paramagnetism and that the chemical shift is positively shifted. Accordingly, different types of lithium site may be distinguished in the NMR analysis. Next, this NMR method was used to examine how each lithium site changed when the electrochemical redox reaction occurred.

3.1.5. ⁷Li-NMR measurement (at the electrochemical redox reaction)

Figs. 5 and 6 show the NMR spectra under the conditions of oxidization and reduction according to charge/discharge capacity. For the HT type, little spectra are observed when charged at 4.3 V. However, the narrow peak with SSB can be observed at the discharge capacity of 50 mAh/g where the higher potential plateau of the two-stage discharge curves in
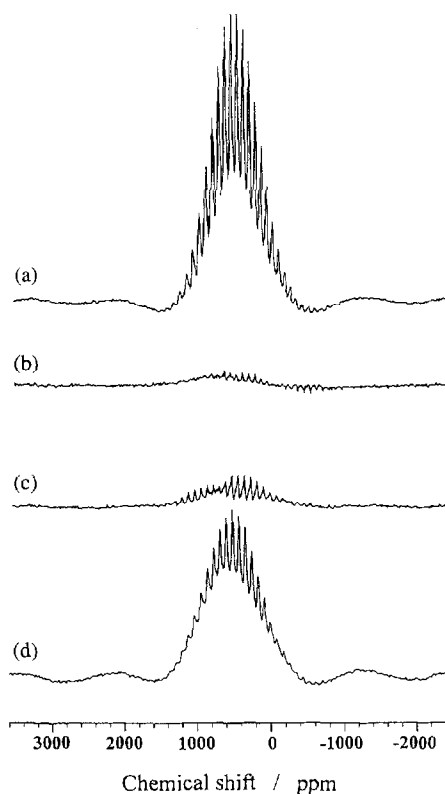

Fig. 5. ⁷Li-NMR (MAS/spin-echo) spectra of HT-LiMn₂O₄: (a) starting material; (b) 4.3 V charge; (c) 50 mAh/g of discharge capacity, and (d) 3.5 V discharge.
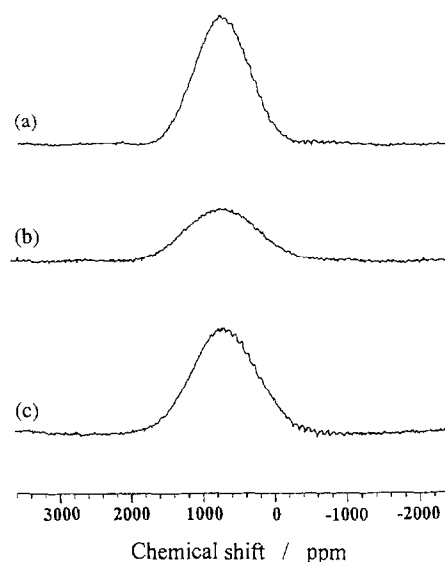

Fig. 6. ⁷Li-NMR (MAS/spin-echo) spectra of LT-LiMn₂O₄: (a) starting material; (b) 4.3 V charge, and (c) 100 mAh/g of discharge capacity.

the 4 V range almost ends, and the same spectrum as the original synthetic one is observed at 120 mAh/g where the last half plateau ends. On the other hand, for the LT type, the spectrum form changes little under the charge and discharge conditions. A broad signal is dominant, and only the peak intensity decreases parallel with the reduction of absolute amount of lithium at the 4.3 V charge.

Accordingly, though the broad spectrum of the HT type dischargeable in the 4 V range grows with discharging, the narrow spectrum with SSB is mainly observed, that is, 8a site lithium may mainly respond. The spectrum of the LT type which has mainly the possibility to discharge in the 3 V range is broad, that is, 16c site lithium may mainly respond, though some narrow spectra with SSB are observed.

We examined if the above supposition of the causal relation between electrode potential and specific lithium site could be applied to other samples. A manganese oxide with a spinel structure synthesized at low temperature (denoted as LS) was selected. It has the same synthesis temperature as that of the LT type. In this case, γ-MnOOH which has mainly the rutile structure and easy to obtain spinel phase was used as a starting material. Its moisture content was lowered to reduce the influence by proton to a minimum.

3.2. Characterization and electrochemical behavior of LS-LiMn₂O₄

3.2.1. Characterization of materials

Table 2 shows the material properties. As shown in the Table, the Li wt.% and Mn wt.% of LS-LiMn₂O₄ are less than those of the HT type. The Li/Mn ratio shows the stoichiometric composition. The x value of manganese oxides is almost the same as that of the LT type, that is 1.82. The crystal structure of the LS type was confirmed to be classified into the single-phase cubic system (space group $Fd3m$) by the XRD and the Rietveld analysis. The lattice constant is 8.197 Å, and the R factor is 8.57%. The moisture reduction at temperatures up to 550 °C is 0.88 wt.%, which is approximately 3.6 times higher than that of the HT type.

Table 2
Material properties of LS-LiMn₂O₄

Chemical analysis

Sample	Li (wt.%)	Mn (wt.%)	Li/Mn	MnO$_x$
LS-LiMn₂O₄	3.7	58.3	0.50	1.82

Magnetic analysis

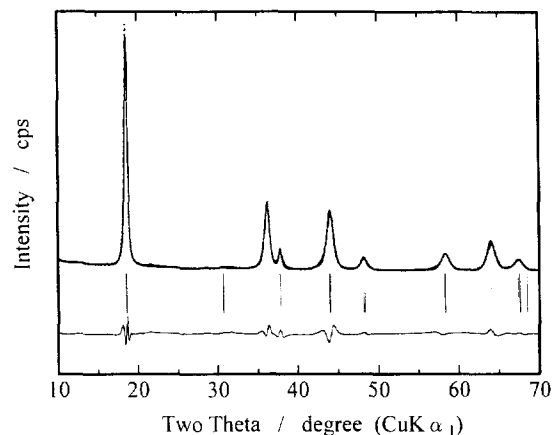| Sample	ESR (Mn^{4+}) (%)	Magnetic moment (μB)		
LS-LiMn₂O₄	32	3.1		

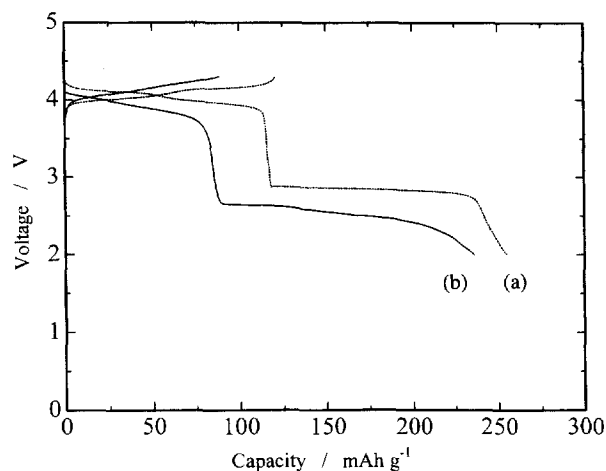Fig. 7. Powder X-ray diffraction patterns and the results of Rietveld analysis of LS-LiMn₂O₄ (R factor = 8.57%).

Fig. 8. Electrochemical behavior of (a) HT- and (b) LS-LiMn₂O₄.

3.2.2. Crystal structure analysis

Fig. 7 shows results of the powder XRD and Rietveld method (DBWS). As shown in the figure, this material has the cubic system (space group $Fd3m$) with the lattice constant of $a = 8.197$ Å and the R factor is 8.57%. No other peaks were observed different from those of LT-LiMn₂O₄.

3.2.3. Electrochemical behavior

Fig. 8 shows the first cycle charge and discharge curves of HT-LiMn₂O₄ and LS-LiMn₂O₄. The LS type shows the capacity of about 80 mAh/g in the 4 V range, and then there occurs an abrupt potential drop. The discharge capacity of about 140 mAh/g is observed in the 2.5 V range. The reason why such a discharge capacity is observed in the 4 V range may be that the lithium site generating the 4 V range can be obtained due to the single-phase having a cubic system and the structural frame not including so much water though it is under the same condition of synthetic temperature of 350 °C as that of the LT type. Therefore, NMR spectra of the synthesized material and samples that were charged/discharged reaction were measured to find the relation between potential and lithium site as discussed for the HT and LT type.
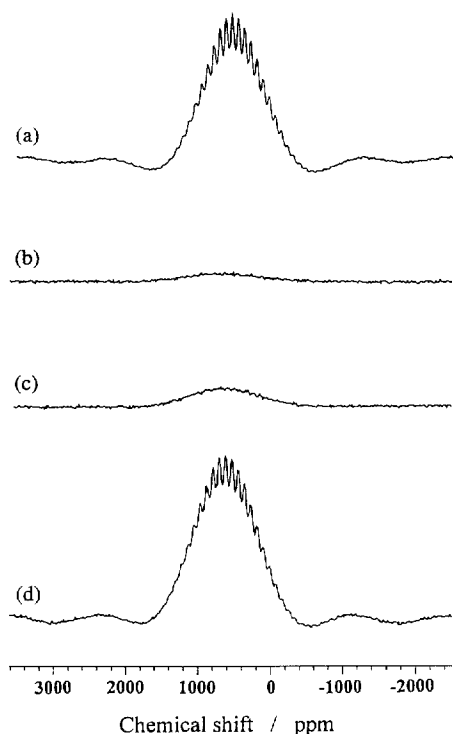
Fig. 9. ^{7}Li-NMR (MAS/spin-echo) spectra of LS-LiMn$_2$O$_4$: (a) starting material; (b) 4.3 V charge; (c) 50 mAh/g of discharge capacity, and (d) 3.0 V discharge.

Fig. 10. ^{7}Li-NMR (MAS/spin-echo) spectra of (a) HT-, (b) LS-, and (c) LT-LiMn$_2$O$_4$ (starting materials).

3.2.4. NMR measurement of electrochemical redox process

Fig. 9 shows the NMR spectra of the LS-type material and those of the redox state according to charge/discharge reaction. The spectra of the new material show hardly any peaks at a 4.3 V charge like in the case of the HT type. When it is discharged at 50 mAh/g in the 4 V range, a broad signal is observed. When it is discharged at 3 V, the same spectrum as that of the original synthetic material is observed. This LS-type sample, as well as the case of HT type, has a spectrum with a broad signal and narrow signal with SSB, of which has a posibility of electrochemical reaction in the 4 V range though the capacity is less than that of the HT type. The peak intensity of SSB is relatively less than that of HT type. The lithium may exist in the same environment as that of the HT type, that is, the LS type has two types of lithium sites like the HT type. The narrow spectrum with SSB of which central line is positively shifted in comparison with the broad one may correspond to the 8a site, and it may be considered to have a close relation with the discharge capacity in the 4 V range. The supposition of the relation between potential and lithium site discussed for the HT and LT types were also confirmed in the case of the LS type.

3.3. Comparison among the NMR spectra of synthetic materials

Fig. 10 shows the NMR spectra of HT, LT, and LS type manganese oxides collectively. As shown in the figure, HT,
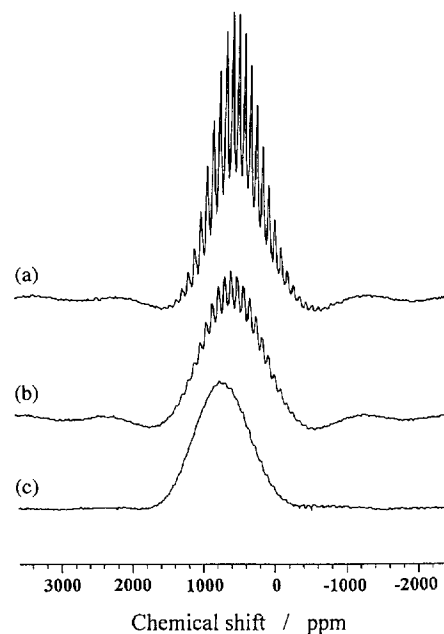
LS, and LT types are in the order of the SSB signal intensity. This order is almost the same as that of the charge/discharge capacity in the 4 V range. This order might be related with the number of 8a site which is occupied by the lithium ion to activate the 4 V operation. In fact, in spite of almost the same oxidation state in both of the LT and the LS samples obtained from the ESR results of Table 1 and 2, the reason why the capacity difference between them in the 4 V range can occur is attributed to the occupied 8a site which can be activated in the 4 V range but is not simply dependent on the degree of oxidation state itself such as the amount of Mn^{4+}. Consequently, we think that the electrochemical behavior of the material can be examined by using the NMR method.

4. Summary

A different type of lithium site can be detected in the solid by analyzing a lithium manganese oxide with the ^{7}Li-NMR (MAS/spin-echo) method.

It was confirmed that the spectrum reflecting the site makes a reversible change by an electrochemical redox reaction.

In combination with the electrochemical behavior, the following may be considered. The dominant lithium site participating in charge and discharge in the 4 V range has a sharp spectrum with SSB of which central line is positively shifted. It was regarded as the 8a site in consideration of the distance from the paramagnetic type of manganese. The dominant lithium site participating in charge and discharge in the 3 V range has a broad spectrum of which peak top is negatively shifted. It was regarded as the 16c site in consideration of the distance from manganese.

The manganese oxide started from EMD and synthesized at the low temperature of 350 °C has a form of a composite oxide with no single phase spinel structure but partly mixed with an orthorhombic phase.

The moisture content in this material is dependent on the domain of ramsdellite phase including proton. The ^{7}Li-NMR spectrum has no sharp signal with SSB, which corresponds to indicate low electrochemical activity in 4 V range. On the other hand, the manganese oxide started from γ-MnOOH and synthesized at the same temperature as that of LT-type has a form of single phase spinel structure. The moisture content in this material is extremely low and the ^{7}Li-NMR spectrum has sharp signal with SSB, meaning a electrochemical activity in 4 V range.

References

[1] T. Ohzuku, M. Kitagawa and T. Hirai, J. Electrochem. Soc., 137 (1990) 769.
[2] R.J. Gummow, A. de Kock and M.M. Thackeray, Solid State Ionics, 69 (1994) 59.
[3] R.A. Young, The Rietveld Method, Oxford University Press, London, 1993.
[4] M.M. Thackeray, M.H. Gummow, D.C. Liles, K. Pearce and A. de Cock, Electrochim. Acta, 38 (1993) 1259.