Relationship between cycle life of Li$\left(\text{Mn}_{2-x}\text{Li}_x\right)O_{4-\delta}$ and oxygen deficiency δ

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Abstract

We electrochemically and crystallographically investigated the quantitative details of relationship between cycle life of Li(Mn$_{2-x}$Li$_x$)O$_{4-\delta}$ (nominally $x = 0.02$) spinel and oxygen deficiency δ which was precisely determined by chemical analysis. We found that capacity retention rate after the 100th cycle at 25°C is linearly decreased with increasing oxygen deficiency. The changes in lattice parameter before and after 500 times cycling test were compared with the changes in potential curves. The changes in lattice parameter at the end of discharged state after the 500th cycle depended on oxygen deficiency δ. They were in good accordance with the degradation in the low voltage region of potential curve, which was strongly affected by oxygen loss and rapidly saturated within about the 100th cycle. These results implied the influence of Jahn–Teller ion Mn^{3+} introduced with oxygen deficiency. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Oxygen deficiency; Spinel; Li(Mn$_{2-x}$Li$_x$)O$_{4-\delta}$; Jahn–Teller ion

1. Introduction

Lithium manganese spinel oxides Li(Mn$_{2-x}$Li$_x$)O$_{4-\delta}$ have been extensively studied for cathode material in large capacity rechargeable Li-ion batteries for EV. They are cheap and non-toxic, and have high cell voltage and relatively high specific capacity. Lithium manganese spinel oxide, however, has large capacity fading upon charge and discharge cycling at room and elevated temperature. Many efforts to improve the cycle life have been reported [1–3], however, all the origins of capacity fading have not yet been clarified. Even at room temperature, the mechanism of capacity loss has not been made clear. Therefore, it is important to clarify the mechanism of capacity loss at room temperature in order to improve the cycle life at elevated temperature.

Oxygen non-stoichiometry of LiMn$_2$O$_{4-\delta}$ has been reported [4–8], however, only qualitative relationship between the cycle life of LiMn$_2$O$_4$ and oxygen deficiency has been reported so far. Here, several series of Li(Mn$_{2-x}$Li$_x$)O$_{4-\delta}$ samples which had various oxygen deficiency precisely determined by chemical analysis were studied in order to further understand the quantitative details of relationship between the cycle life of Li(Mn$_{2-x}$Li$_x$)O$_{4-\delta}$ and oxygen deficiency. We electrochemically and crystallographically report the characteristic behaviour of capacity fading caused by oxygen deficiency.

2. Experimental

The starting materials were reagent-grade LiOH · H$_2$O and MnO$_2$ (EMD). They were mixed into the nominal Li/Mn molar ratio at 1.02/1.98. In order to select the heat treatment conditions, oxygen non-stoichiometry was measured by thermogravimetric analysis under various conditions, in advance. Samples of Li(Mn$_{2-x}$Li$_x$)O$_{4-\delta}$ were calcined at 750–800°C for 24–48 h in O$_2$ or air, cooled slowly to 600–300°C in O$_2$ or N$_2$, and then quenched to room temperature.

To determine the chemical composition, Li and Mn concentrations were measured by atomic absorption spectroscopy and chelate back-titration method, respectively, and average Mn valence was measured by iodometry. Following electroneutrality rule, we determined δ by use of average Mn valence and the chemical composition which was assumed that (Li + Mn) = 3.

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Electrochemical measurements were carried out using coin-type cells (CR2032) with $Li(Mn_{2-x}Li_x)O_{4-\delta}$/PTFE/acetylene black (75/20/5 wt.%) as cathode, Li foil with an excess amount against cathode mass as anodes, 1 M $LiClO_4$ dissolved in EC/DME (50/50 vol%) (Mitsubishi Chemical) as electrolyte, and microporous polyethylene separators (25 μm in thickness). Charge–discharge cycling tests were carried out galvanostatically at apparent current density of 1 mA/cm^2 (1 C) in the voltage range between 3.2 V and 4.35 V at 25°C.

Lattice parameters and lattice strain were measured by powder X-ray diffraction (XRD) method. The lattice strain was evaluated by fitting Hall's equation [12] to experimental measurements.

3. Results and discussion

On the basis of thermogravimetric measurement, we prepared samples with various oxygen deficiency. Fig. 1 shows the relationship between oxygen deficiency δ and capacity retention rate after the 100th cycle. Capacity retention rate means the ratio of discharged capacity of the 100th cycle to that of the 1st cycle. Since the amount of excess lithium: x in $Li(Mn_{2-x}Li_x)O_{4-\delta}$ strongly affects cycleability, nominal lithium contents of each sample in Fig. 1 are 1.02 ($x = 0.02$). Average analytical value of lithium obtained from atomic absorption spectroscopy is 1.014 ± 0.008. As shown in Fig. 1, capacity retention rates after the 100th cycle at 25°C linearly decrease with increasing oxygen deficiency δ.

In order to clarify the dependence of oxygen deficiency, we carried out XRD measurement. Fig. 2 shows that both lattice parameter and lattice strain increased with increasing oxygen deficiency. The changes in lattice parameter of samples A and B, of which δ are 0.037 and -0.006, respectively, after charging and discharging in the 1st and 500th cycles are given in Table 1. It shows that the lattice contraction/expansion with Li extraction/insertion of the 1st cycle in oxygen deficient sample A was larger than that
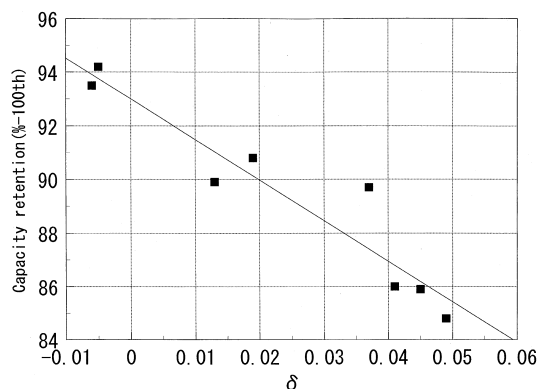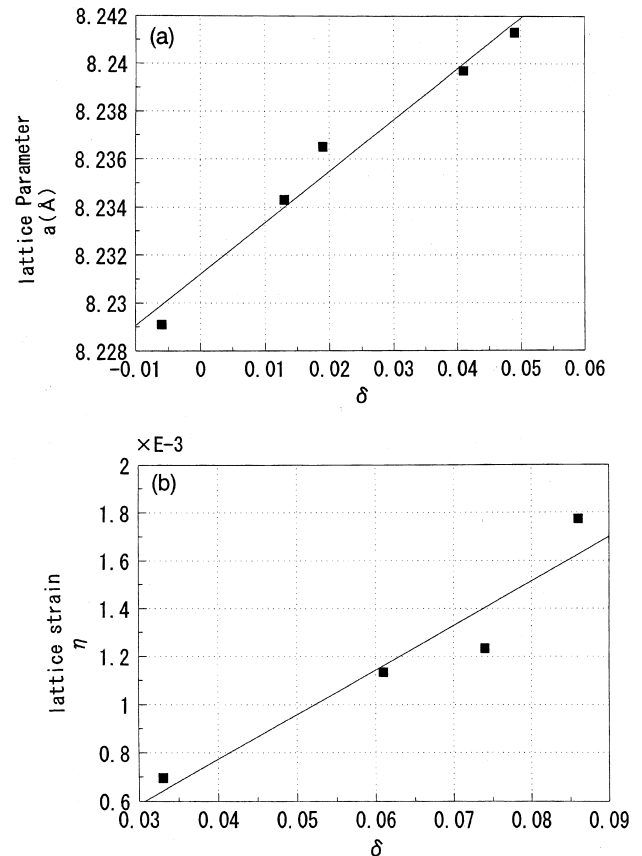
Fig. 2. The relationship between oxygen deficiency δ and lattice parameter (a) and lattice strain (b).

of sample B. After the 500th cycle, both contraction and expansion of lattice with Li extraction and insertion are decreased in both samples A and B, and the rates of decrease in lattice contraction at the end of charged state during 500 cycles are the same in samples A and B. On the other hand, the large rate of decrease in lattice expansion

Fig. 1. The relationship between oxygen deficiency δ and capacity retention rate after the 100th cycle.

Table 1
Change in lattice parameter of samples A (a) and B (b) in the 1st and 500th cycles

	Discharged (Å)	Charged (Å)	DC capacity (mA h/g)
(*a*) A:$Li(Mn_{1.972}Li_{0.028})O_{3.963}$; averaged Mn valence = 3.498			
d(1st)	8.2416	8.0564	129
d(500th)	8.2221	8.0822	97
Δd(1st–500th)	-0.0195	$+0.0258$	
$\Delta d / d$(1st)	-0.24%	$+0.32\%$	
(*b*) B:$Li(Mn_{1.989}Li_{0.011})O_{4.006}$; averaged Mn valence = 3.520			
d(1st)	8.2326	8.0657	124
d(500th)	8.2260	8.0893	102
Δd(1st–500th)	-0.0066	$+0.0236$	
$\Delta d / d$(1st)	-0.08%	$+0.29\%$	

d(1st): lattice constant in the 1st cycle.
d(500th): lattice constant in the 500th cycle.
Δd(1st–500th) = d(1st) − d(500th).
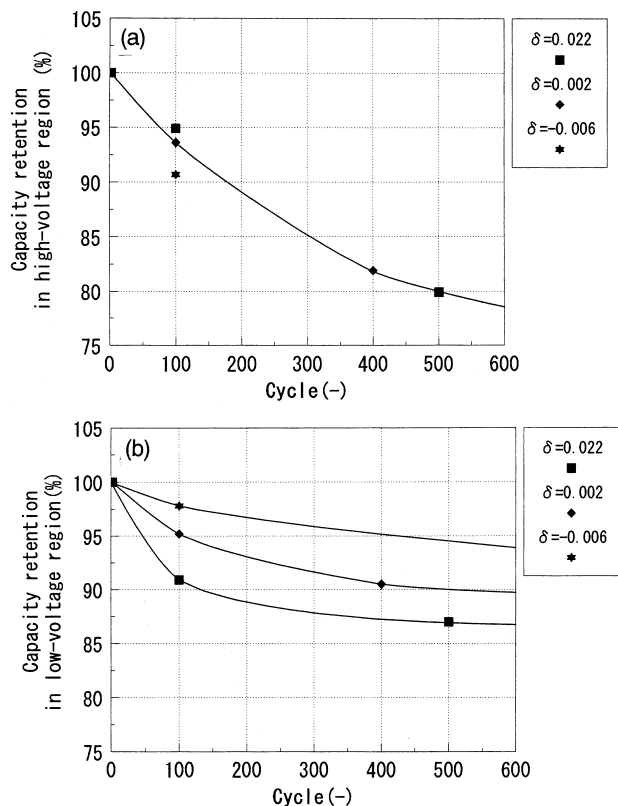$\Delta d / d$(1st) = Δd(1st–500th)/d(1st).

Fig. 3. The changes in capacity retention rate in high (a) and low (b) voltage region of potential curve with charge/discharge cycling times in the samples of which δ are 0.022, 0.002, and -0.006.

at the end of discharged state was shown in A (0.24%), which was three times as large as that of B (0.008%).

The changes in the 'high and low voltage region', which show the 'one-phase and two-phase structure' as mentioned in [9], are compared with the changes in lattice parameter. Fig. 3a and b shows the changes in the high and low voltage regions as a function of cycle numbers. Fig. 3a shows that the capacity retention in the high voltage region monotonously decreased with cycle numbers and was not dependent on oxygen deficiency. On the other hand, Fig. 3b shows that the capacity retention in low voltage region also decreased with cycle numbers, but was strongly affected by oxygen deficiency, and the degradation of the oxygen deficient sample was rapidly saturated within about the 100th cycle. This shows that the capacity fading upon early charge–discharge cycling is predominantly due to oxygen deficiency. Tarrascon et al. [5] also reported the large capacity fading upon early cycles in quenched sample which would be deficient in oxygen. Xia et al. [9] also mentioned that no degradation in the low potential region occurred upon charge and discharge cycling in the stoichiometric and oxygen sufficient $LiMn_2O_4$ system, and capacity fading was predominant in high potential region. The change in lattice parameter after the 500th cycle is in good accordance with that of potential curve, therefore, the

capacity fading in the discharged state is characteristic of oxygen loss.

All the results suggested the influences of Mn^{3+} (Jahn–Teller ions) introduced with the oxygen deficiency. Oxygen extraction induces Mn^{3+} as a result of the change in Mn valence due to charge compensation. Sugiyama et al. [7,8] proposed the cluster model which consisted of a few Mn^{3+} ions bounded a few oxygen vacancies, and Yamada and Tanaka [10] described the Jahn–Teller distortion in $LiMn_2O_4$ suppressed by the dilution effect of Mn^{4+} (non-Jahn–Teller ions). We speculate that the Jahn–Teller distortion of Mn^{3+} around oxygen vacancy would not be suppressed by Mn^{4+}, since the lattice strain and the lattice contraction/expansion with Li extraction/insertion in oxygen deficient samples were larger than those of samples with small oxygen deficiency. Furthermore, Mn^{3+} ions around oxygen vacancies in the charged state would be also oxidized to Mn^{4+}, and the valence of oxygen vacancy is $+2$, therefore, the Mn^{4+} around the oxygen vacancies would be unstable because of locally excess of cation. It can be easily imagine that those unstable Mn^{4+} ion would oxidize electrolyte and would be reduced to Mn^{3+}, and then would be dissolved. However, we need more detailed data to explain the mechanism of capacity fading in the discharged state characteristic of oxygen deficiency. We are pursuing further work along these directions.

We have described the relationship between cycle life and oxygen deficiency so far. It is important to diminish the oxygen deficiency in order to obtain good cycle life. We carried out good cycle performance at room temperature by controlling the oxygen deficiency. Fig. 4 shows the cycle life in the system of $Li(Mn_{1.964}Li_{0.036})O_{4.008}$ as cathode, cokes (MBC-N: Mitsubishi Chemical) as anode, and 1 M $LiClO_4$ in EC/DMC/DEC (40/40/20 vol%) at 25°C in coin-type cell (CR2032). This shows very high performance on 1000 cycles at room temperature. Even this 'good' cathode material, however, shows large degradation in storage or cycle performance at the elevated temperature. Blyr et al. [11] reported the relationship between Mn dissolution in the discharged state at 55°C and cooling rate by which the oxygen deficiency would be
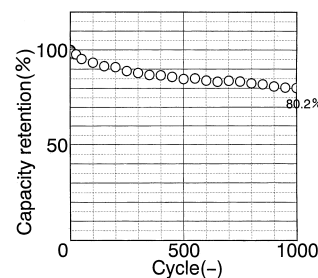

Fig. 4. Cycle performance in the system of $Li(Mn_{1.964}Li_{0.036})O_{4.008}$ as cathode, cokes as anode, and 1 M $LiClO_4$ in EC/DMC/DEC (40/40/20 vol%) as electrolyte at 25°C in coin-type cell(CR2032).

changed. They mentioned that Mn dissolution of the slowly cooled sample in the discharged state is greater than that of quenched sample, which would be more deficient in oxygen than slowly cooled sample. They qualitatively showed the dependence on oxygen deficiency. In any case, more investigations are necessary to clarify what affects the degradation of capacity at the elevated temperature, and this is the top priority item that must be solved.

4. Conclusion

We have investigated the quantitative details of the relationship between cycle life of $Li(Mn_{2-x}Li_x)O_{4-\delta}$ (nominally $x = 0.02$) and oxygen deficiency, which is precisely determined by chemical analysis. We have shown that capacity retention rate after the 100th cycle is linearly decreased with increasing of oxygen deficiency, and the changes in lattice parameter and potential curves in the discharged state after the 500th cycle depend on oxygen deficiency. Capacity fading due to oxygen deficiency may be caused by Jahn–Teller ion Mn^{3+} introduced with oxy-

gen deficiency. However, we need more detailed data to explain the mechanism of capacity fading in the discharged state characteristic of oxygen deficiency.

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