



Studies of Capacity Losses in Cycles and Storages for a $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ Positive Electrode

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A spinel-type of lithium-rich lithium manganese oxide, $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$, was prepared and studied electrochemically and structurally as a positive electrode of a Li-ion battery. In cycle performance tests, capacity losses were 3 and 11 mAh/g after 75 cycles at 25 and 55°C, respectively, corresponding to 15 and 50 mAh/g for a normal lithium manganese oxide, LiMn_2O_4 . Their losses were divided into two parts; one resulting from the deterioration of the active material itself and the other due to the poor conduction of the active material to the collector. The former and latter contributions to the losses at 55°C were 2 and 9 mAh/g, respectively for the Li-rich spinel, and 18 and 32 mAh/g, respectively for the normal spinel. The capacity loss by the poor conduction was apparently much larger for both spinels of positive electrodes. Cycle performance tests in each region of the charge states divided into five regions show that relatively larger capacity losses were observed in lower potential states. However, in every region, a capacity loss for the Li-rich spinel was much smaller than that of the normal spinel. There was a close relation found between capacity losses in the storage and those in the cycle. Electron densities spreading between manganese and oxygen atoms were larger in the Li-rich than in the normal spinels. Thus, it turned out that the structure of the Li-rich spinel was made more stable because of strong Mn-O bonds.

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Lithium-ion batteries are currently and widely used in mobile phones because they have advantages over other kinds of batteries, such as high potential and specific energies. Thus demands are climbing. Further developments of large-sized lithium-ion batteries are strongly required for electric and hybrid vehicles. So the higher performance in terms of safety, environment friendliness, and cost, are to be expected. In these respects, a spinel-type of lithium manganese oxide for lithium-ion batteries is much safer, much lower in cost, richer in natural resources, and more permissible in an environmental standard as a positive electrode, when it is compared with the conventionally used LiCoO_2 positive electrode.

However, lithium manganese oxide positive electrodes are known to lose their capacity to a great extent at such a high temperature as 55°C.^{1,2} For the past several years, many studies have been done about the causes of the loss and to develop a positive electrode with less capacity loss at high temperatures.³ Among these, there has been the preparation of partially substituted manganese spinels, $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$, where M is a metal atom such as Li, Al, or Cr.⁴ Some of these examples of lithium-rich lithium manganese oxides showed better cycle performance to some extent.

We have already done some studies on the mechanisms of capacity loss in lithium manganese oxide positive electrodes.^{2,5,6} They included cycle and storage performance tests in each state of charge and capacity recovery tests with the addition of a conductor to a positive electrode after cycles. Through these studies, it was understood highly significant it is for improvement of lithium manganese oxide positive electrodes to know how the capacity losses are improved particularly in lithium-rich lithium manganese oxides. Moreover, it seems that Mn ions, dissolved out of a lithium manganese oxide positive electrode, cause a severe capacity loss of a carbon negative electrode.⁷ However, with respect to the lithium-rich lithium manganese oxides showing good cycle performances there have been few studies yet on the Mn dissolution out of the electrode.

In the present study, we report a series of electrochemical characteristics of a lithium-rich $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ positive electrode and amounts of Mn dissolved from the electrode at high temperature

cycles and storages. We discuss capacity losses of the lithium manganese oxide positive electrodes and electron densities around Mn-O bondings measured by X-ray diffractions.

Experimental

Materials.—A lithium-rich manganese oxide was prepared according to the self-reaction method by the Japanese Metal and Chemical Co., Ltd. (JMC).⁸ First, 7.58 g of LiNO_3 (99%, Wako Pure Chemical Industries, Ltd) and 58.54 g of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Wako Pure Chemical Industries, Ltd.) were dissolved together in a 20 mL of distilled water to form an aqueous mixture. Into the solution was added 33 g of 20% polyvinyl alcohol (Wako Pure Chemical Industries, Ltd) aqueous solution with stirring. Then the mixed solution was heated at 150°C to react. The black powders obtained were ground and were then calcined in an alumina crucible at 750°C for 6 h, with them kept in a conventional electric furnace. For comparison, LiMn_2O_4 was also synthesized.

The 1:2 solvent mixture of ethylene carbonate (EC) to dimethylcarbonate (DMC) with 1 M LiPF_6 dissolved was given by the Mitsui Chemical (Tokyo, Japan) and contained less than 10 ppm of H_2O . The 2:1 mixture (CB-2) of acetylene black binder to poly(tetrafluoroethylene) was available from Soei Tsusho (Osaka, Japan).

Measurements.—Elemental analyses of the sample was done with a fluorescent X-ray spectrometric method. The contents of Li and Mn in the lithium manganese oxide and Mn on Li negative electrodes were obtained with the conventional method⁹ using an Hitachi 180-50 atomic absorption spectrophotometer. Cyclic voltammograms (CVs) were measured with a BAS-100B electrochemical analyzer at a scan rate of 0.1 mV/s. The working electrode was the mixture of 2/3 of the lithium manganese oxide powder and 1/3 of the conductor, CB-2, and both the counter and reference electrodes were lithium foil.

The powder sample was sealed in a silica glass capillary (0.3 mm inner diam). To collect an X-ray powder pattern with good counting statistics, the synchrotron radiation X-ray powder experiment with a large Debye-Scherrer camera equipped with an imaging plate was carried out at SPring-8 (Hyogo, Japan) BL02B2.¹⁰ The exposure time was 1 h. The wavelength of incident X-rays was 0.497 Å. The X-ray powder pattern was obtained from 5.0° to 43.0° in 2θ , which corresponds to 0.68 Å resolution in d spacing.

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Electrochemical cells and cycle performance tests.—The mixture of 2/3 of the lithium manganese oxide powder and 1/3 of CB-2 was pressed carefully at 200 kg/cm² to make it into a disc for a positive electrode of a cell and was then dried at 150°C for 6 h. Cycle performance tests in charge/discharge were done on a coin-type cell (CR-2032) assembled with Li metal/the electrolyte (ethylene carbonate/dimethyl carbonate, EC/DMC = 1/2 with 1 M LiPF₆)/the positive electrode and Celgard 2400 as a separator. Charge/discharge curves were recorded galvanostatically with a Nagano BTS-2004 at a current density of 0.5 mA/cm². The cutoff potentials for the charge and discharge limits were fixed at 4.5 and 3.5 V (vs. Li/Li⁺), respectively. All processes of assembling and dismantling the cells were carried out in an argon atmosphere in a glove box (Vacuum Atmosphere Co., CA).

Addition of the conductor to the positive electrode after cycles.—Positive electrodes were taken out of the coin-cells after cycles. The active material was kneaded enough with an additional conductor, CB-2 (consequently, the final weight ratio of the lithium manganese oxide to CB-2 was about 1:1). The mixture was pressed carefully at 200 kg/cm² to make it into a disc for the positive electrode of the cell and was then dried under vacuum for 3 h. Then each positive electrode pellet was assembled again into a coin-cell consisting of Li metal as the negative electrode, the electrolyte (EC/DMC = 1/2 with 1 M LiPF₆), and the positive electrode.

Cycle performance in each state of charge.—Figure 1a is a cycle order diagram of the experiment. Firstly, the positive electrode was charged up to a cutoff high voltage limit (4.5 V) and successively discharged down to 3.5 V after a short stop to evaluate its discharge capacity. The cutoff voltages were determined with the capacity divided equally in five; they were 4.5, 4.159, 4.124, 4.056, 3.997, and 3.5 V for the Li-rich, and 4.5, 4.146, 4.137, 4.040, 4.002, and 3.5 V for the normal. Secondly, it was charged to each higher cutoff voltage and discharged to each lower cutoff voltage in each region, and then such charge-discharge cycles were repeated eight times in each region of five divisions of the discharge capacity. In the eleventh cycle, it was fully charged to the cutoff voltage (4.5 V) and then discharged to 3.5 V to measure the discharge capacity and such cycles were successively repeated. Figure 1b shows the results of the sequence of measurements described above. In the first cycle, the full discharge capacity was measured; from the second to tenth cycles the discharge capacities in each higher and lower cutoff voltages in each region were obtained, and in the eleventh cycle the full discharge capacity was measured. Thus, this procedure led to an estimate of the capacity in each region during charge/discharge cycles.

Storage experiment of the lithium manganese oxide as a positive electrode at each constant potential.—A cell was charged up to 4.5 V and then discharged down to 3.5 V to measure its discharge capacity. It was charged up again to each voltage with each state of charge; the voltage was 3.939, 3.976, 4.003, 4.038, 4.077, 4.111, 4.134, 4.155, or 4.194 V for the 10, 20, 30, 40, 50, 60, 70, 80, or 90%, respectively. Each cell was stored galvanostatically at 55°C for a week at each constant potential maintained by using a Nagano BTS-2004. Similar procedures were also done at 3.5 V for the 0% charged state and at both 4.3 and 4.5 V for the 100% charged state. After storage, the cell was charged up to 4.5 V and discharged down to 3.5 V to measure its discharge capacity at room temperature. After the storage experiment was finished, each cell was dismantled and the Li metal as a negative electrode in the cell was taken out to measure its Mn contents on the Li metal.

Maximum entropy method (MEM) analysis from powder XRD.—The charge densities were obtained by the MEM/Rietveld method. The detail of the method is described elsewhere.¹¹

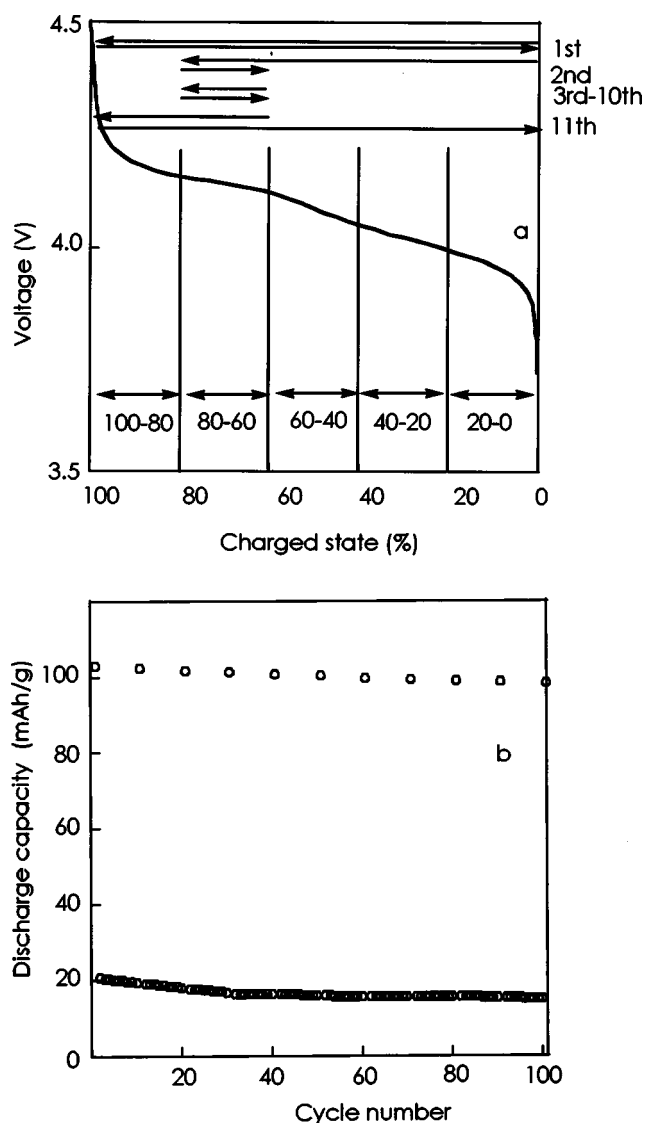


Figure 1. Cycle order diagram (Fig. 1a) and discharge capacities (Fig. 1b) at each state of charge of the sample.

Results and Discussion

The prepared lithium manganese oxide was analyzed chemically and identified as Li_{1.10}Mn_{1.90}O₄ which is a Li-rich lithium manganese oxide. XRD analysis of the sample definitely indicates its spinel structure and the crystal structure is indexed to a cubic system with a lattice parameter a_0 of 8.2088 Å, and then is defined to the space group $Fd\bar{3}m$. The surface area of the material is estimated to 3.28 m²/g with a Brunauer-Emmett-Teller method. A normal LiMn₂O₄ spinel was also prepared with the similar method in order to compare with the Li-rich lithium manganese oxide and was chemically identified to Li_{1.00}Mn_{2.00}O₄ with a lattice parameter a_0 of 8.2387 Å.

For a comparison of electrochemical properties of the prepared Li-rich spinel with those of a normal spinel, LiMn₂O₄, their CVs were measured at cutoff voltages between 3.0 and 4.5 V, as shown in Fig. 2. The CV of the Li-rich spinel shows two gentle redox peaks, while there are two sharp redox peaks at about 4.00 and 4.16 V for the normal spinel.

The initial charge capacity measured was 105 mAh/g for the Li-rich spinel. The theoretical capacity can be estimated from the chemical composition with or without oxygen deficiency. However, no oxygen deficiency in Li_{1.1}Mn_{1.9}O₄ is suggested from the result of

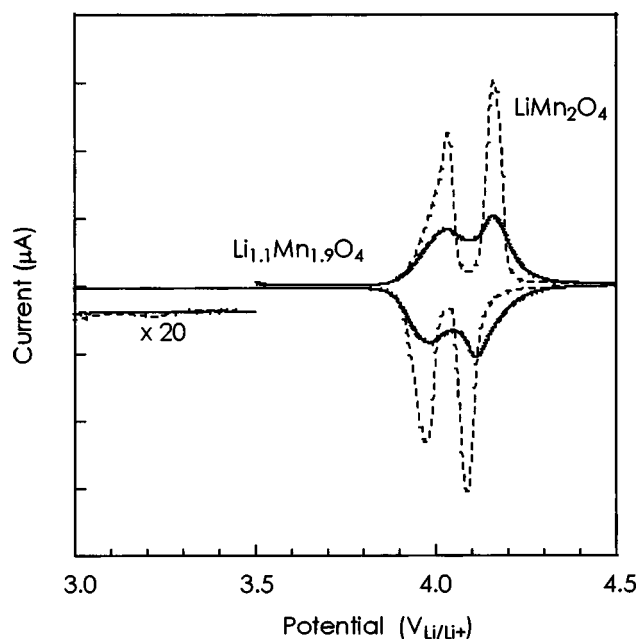


Figure 2. Cyclic voltammograms of (solid line) $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and (broken line) LiMn_2O_4 .

CV measurements showing no apparent redox peaks at 3.3 V.¹² Thus, the theoretical capacity was estimated to 106.6 mAh/g, and this is in good agreement with the observed capacity above.

Performances of charge/discharge cycles and Mn dissolutions after the cycle.—Figure 3 shows the cycle performances of the Li-rich and normal spinels as positive electrodes at 25 and 55°C. First, all the cells were charged and discharged 5 times at 25°C and then cycle performances tests were done at 25 and 55°C, respectively, for 75 cycles. The results are shown in Table I together with other data. Discharge capacities of the Li-rich spinel were 100 and 92 mAh/g at 25 and 55°C, respectively, after the cycles. Capacity losses at 25 and 55°C were found to be 3 and 11%, respectively. On the other hand, discharge capacities of the normal spinel were 117 and 83 mAh/g, and their corresponding capacity losses were 12 and 38% at 25°C and 55°C, respectively. Therefore, better cell performance is expected for the cell with a lithium-rich lithium manganese oxide as a positive electrode than that with a normal spinel at either 25 or 55°C. While the positive electrode of a lithium-rich spinel has a lower initial capacity than a normal spinel, it is noted that the cycle performance of the Li-rich spinel is better than that of the normal spinel after 30 cycles at 55°C.

After the cycle performance tests were finished, the amounts of manganese deposited onto the lithium metal negative electrode were

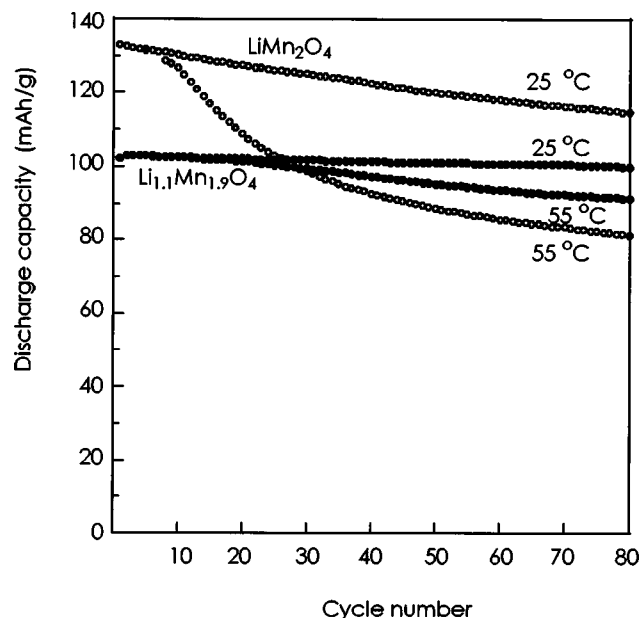


Figure 3. Cycle performances of the discharge capacities for $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and LiMn_2O_4 at 25 and 55°C.

measured. These contents were assumed to be equal to the amounts of manganese ions dissolved into the solution out of positive electrode material. For the Li-rich spinel, the amounts of dissolved manganese after the cycle were 0.3 and 1.0% by weight at 25 and 55°C, respectively, while those of dissolved manganese for the normal spinel after the cycle were 0.5 and 2.0% at 25 and 55°C, respectively. Consequently, manganese contents from the Li-rich spinel were about a half of those from the normal spinel.

The recovery of capacities by the addition of the conductor after the cycles.—In order to acquire more information about the causes for the capacity loss during the cycles, each positive electrode was taken out of the cells after the cycles at 25 or 55°C and each active material was kneaded enough with additional conductive material, CB-2. Then a positive electrode pellet from the above mixture was assembled again into a cell and its discharge capacity was measured.

The results are given in Table I and Fig. 4 and compared with those of the normal spinel. The capacities increased to 102 from 100 mAh/g, and to 101 from 92 mAh/g after the cycle at 25 and 55°C, respectively. Similar capacity recoveries were already observed in our previous study as well.⁶ Such recovery of capacity is a result of the improvement of the poor conductivity with the addition of conductive material to the active material of the positive electrode. Therefore, it is understood that ionic or electric conduction in the positive electrode decrease during cycles and they are recovered

Table I. Recoveries of capacities by the addition of the conductor to the cathodes after the cycle at 25 and 55°C.

| | $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ 25°C | LiMn_2O_4 25°C | $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ 55°C | LiMn_2O_4 55°C |
|--|--|-----------------------------------|--|-----------------------------------|
| Initial discharge capacity (mAh/g) | 103 | 133 | 103 | 133 |
| Discharge capacity after the cycle at 25°C (mAh/g) | 103 | 132 | 103 | 132 |
| Discharge capacity after the cycle (mAh/g) | 100 | 117 | 92 | 83 |
| Recovery of the capacity (mAh/g) | 102 | 128 | 101 | 115 |
| Capacity loss from deterioration of the active material itself (mAh/g) | 1 | 5 | 2 | 18 |
| Capacity loss from the poor conduction (mAh/g) | (33) ^a | (31) | (18) | (36) |
| | 2 | 11 | 9 | 32 |
| | (66) | (69) | (82) | (64) |
| Mn dissolution (%) | 0.3 | 0.5 | 1.0 | 2.0 |

^a The parenthesis is the ratio (%) to the total capacity loss.

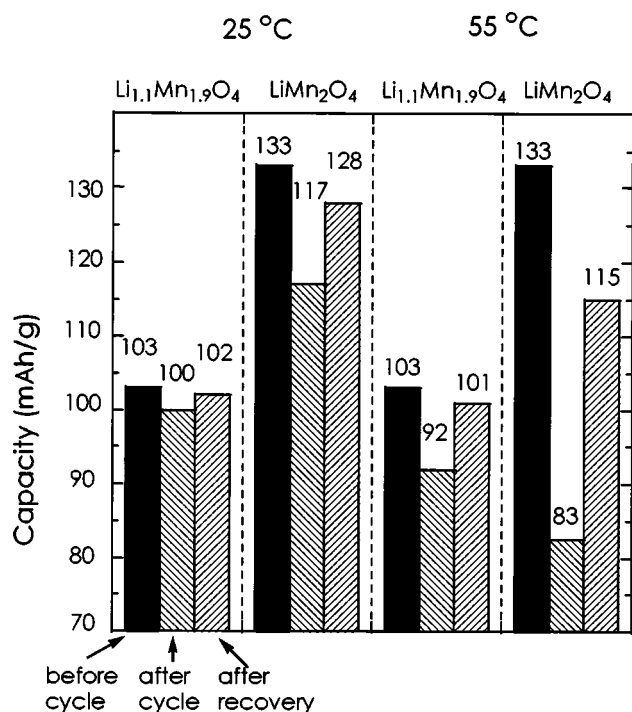


Figure 4. Recoveries of the capacities with the addition of the conductor to the positive electrode of $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and LiMn_2O_4 after cycling at 25 and 55°C.

with the above procedure. However, the capacity loss still remaining after the addition of the conductor is thought due to the deterioration of the active material itself. So, we propose that the cause of the capacity loss of a positive electrode during the cycles can be divided into two major ones; the deterioration of the active material itself and the poor conduction between the active material and collector; the conduction lessening.

For the Li-rich spinel at 55°C, the capacity loss due to the deterioration of the active material itself was 2.0 mAh/g and this is much lower, as seen from a comparison with 18 mAh/g for the normal spinel. On the other hand, the capacity loss resulting from the conduction lessening was 9 mAh/g and this was also much smaller than the 32 mAh/g of the normal spinel. Ratios of the capacity loss due to the former cause to that from the latter one were found to be 1:2 and 5:11 at 25°C for the Li-rich and the normal spinels, respectively, and 2:9 and 18:32 at 55°C. The capacity loss by the conduction lessening was apparently much larger for both spinels. The deterioration of the active material itself and the conduction lessening between the active material and collector could depend on the strength of Mn—O bond and the reactivity of surfaces of lithium manganese oxides. Thus, this suggests that for the Li-rich spinel, Mn—O bonds and reactivity of the surface would be stronger and lower than those of the normal spinel.

Cycle performance at each state of charge.—To specify in what region the capacity loss was caused, cycle performance was examined at each state of charge.⁶ The whole range of charge capacities was divided into five parts between 3.5 and 4.5 V as shown in Fig. 1. Within each of the divisions, a cycle test was carried out to measure the rate of the capacity loss so that it was possible to specify the region where a particular capacity loss was observed. Table II and Fig. 5 show the results of the Li-rich and the normal spinels at 25 and 55°C. Less capacity losses are observed for the Li-rich spinel. The order of the good performances at 55°C was as follows; 80-100 > 60-80 ≅ 40-60 > 0-20 ≅ 20-40. This order is roughly the same as that for the normal spinel.⁶ It is noted that the

Table II. Cycle performances in each state of charge after 100 and 150 cycles at 25 and 55°C, respectively.

| State of charge (%) | Ratio of capacity loss (percent) | | | |
|---------------------|--|---------------------------|--|---------------------------|
| | 25°C | | 55°C | |
| | $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ | LiMn_2O_4 | $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ | LiMn_2O_4 |
| 0-20 | 1.4 | 12.2 | 5.6 | 30.8 |
| 20-40 | 1.5 | 14.1 | 5.9 | 24.1 |
| 40-60 | 1.4 | 9.2 | 4.6 | 22.7 |
| 60-80 | 1.7 | 9.0 | 4.4 | 17.4 |
| 80-100 | 1.5 | 4.8 | 2.8 | 12.9 |

decrease of the capacity losses at the lower voltage regions contributed to improving the cycle performance of the Li-rich spinel.

Storage performances of positive electrodes at constant potentials.—We previously observed potential shifts of lithium manganese oxide electrodes to higher voltages in high temperature storage.² Therefore, it was difficult to specify in what regions the capacity loss appeared. Then in the present work, we performed storage experiments in the following way; a cell was charged until the potential reached the expected charge state, and then it was kept at a constant potential at 55°C for a week. After the storage, the cell was cycled several times to measure the capacity at 25°C and then it was dismantled to take out the electrodes and the electrolyte solu-

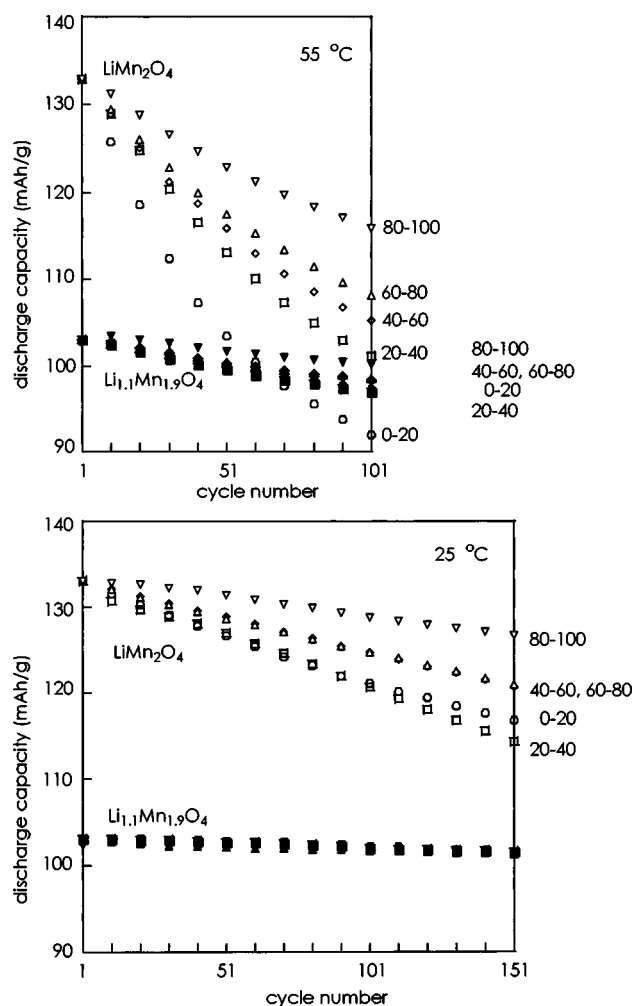


Figure 5. Cycle performances of discharge capacities at each state of charge in $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and LiMn_2O_4 at 25 and 55°C.

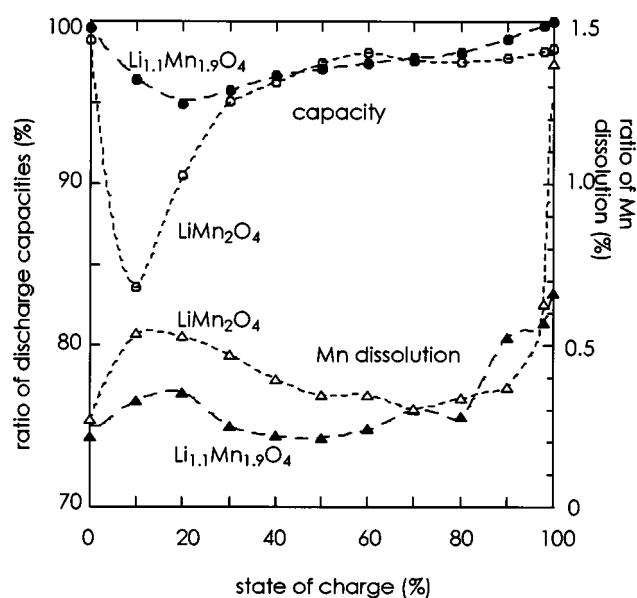


Figure 6. Storage performances and Mn dissolution of $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and LiMn_2O_4 at each constant potential at 55°C for a week.

tion. Mn contents deposited on a Li metal negative electrode were also measured and estimated as the amounts of Mn ion dissolved out of the positive electrode.

Figure 6 summarizes the results together with those of the normal spinel. For the Li-rich spinel, there was the largest capacity loss at 20% of the state of charge (SOC) and almost no capacity losses were observed at both 0 and 100% of SOC. Although the results of the Li-rich spinel were similar to those of the normal spinel, the rate of the capacity losses was significantly less than in the normal spinel. It should be noted that for the Li-rich spinel, the order of the good cycle performances is as described above; at 80-100% of SOC $>$ at 40-60 and at 60-80 $>$ at 0-20 $>$ at 20-40%. The order roughly agrees with the order of the capacity loss in the storage experiments. For the normal spinel, the largest capacity loss observed at 10% of SOC also agrees with the worst cycle performance at 0-20% of SOC. Thus, the capacity loss in the storage is thought to have a large effect on the cycle performance.

We will briefly mention the relation between the capacity loss and the Jahn-Teller effect. Little capacity loss was observed at 0% of SOC. At this state, Mn^{3+} ions are expected to reach their maximum quantity from a point of the chemical formula, in which the largest Jahn-Teller effect will be anticipated. This suggests that there is no apparent connection of the capacity loss in the storage with the Jahn-Teller effect.

Then, let us describe the Mn dissolution in the storage and consider its relation to the capacity loss. Amounts of manganese ions dissolved into the solution for the Li-rich spinel were less than those for the normal spinel. The Mn dissolution from the positive electrode was prevented more effectively in the Li-rich manganese oxide than in the normal spinel. The maximum Mn dissolution were found at the highest potential region, that is, at 100% of SOC, while amounts of dissolved Mn ions were relatively small in other regions. However, almost no capacity loss is observed for the Li-rich spinel at 100% of SOC. Therefore, no apparent relationship existed between them and it suggests a close relation between solvent decompositions and Mn dissolutions. As means to suppress the Mn dissolution, it is suggested to set a cutoff voltage lower than 4.5 V at 100% of SOC.

Storage performances of a graphite negative electrode were examined using the Li-rich or the normal spinel as a positive electrode at a high temperature. After a graphite negative electrode was left for 1 week at 55°C , the charged graphite was then discharged and

Table III. Storage performances of the graphite negative electrodes with $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and LiMn_2O_4 positive electrodes for 7 days at 55°C .

| | $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ | LiMn_2O_4 |
|---|--|---------------------------|
| Initial discharge capacity (mAh/g) | 277 | 279 |
| Discharge capacity after the storage (mAh/g) | 193 | 179 |
| Ratio of the capacity loss (%) | 30 | 36 |
| Quantity of Mn dissolution ($\mu\text{g}/\text{mg}$ of the graphite) | 1.05 | 1.54 |

the capacity was measured. The result is shown in Table III. The rate of the capacity loss of the negative electrodes was 30 and 36% for the Li-rich and the normal spinels, respectively, and Mn dissolution for the Li-rich spinel is about 2/3 of that for the normal spinel. Although the extents of the decrease of the Mn dissolution and the capacity loss of the negative electrode were larger in the Li-rich spinel than in the normal spinel, such results are not considered to be satisfactory enough with respect of the improvement in batteries.

Electron density on Mn—O bonds estimated from the structural analyses with the XRDs.—As seen above, the Li-rich spinel showed less capacity losses in storage and cycling, and less Mn dissolutions as well. This is considered partly due to stronger Mn—O bonds in a Li-rich lithium manganese oxide.¹³ Then, precise charge densities of both the Li-rich and normal spinels were analyzed by the MEM/Rietveld method and the Mn—O bonding electron distributions were measured. The weighted profile reliability factor, R_{wp} , and the reliability factor based on integrated intensities, R_1 , of the Rietveld analyses were 3.4 and 3.9% for the Li-rich and 4.9 and 5.1% for the normal, respectively. The MEM calculation was carried out in $64 \times 64 \times 64$ pixels per cubic unit cell using the computer program ENIGMA.¹⁴

The MEM electron density mapping of {100} plane is shown in Fig. 7 for both spinels. The contours of electron densities are drawn at every 0.1 ($e/\text{\AA}$) step from 0.0 to 2.0 $e/\text{\AA}$. The electrons looked more densely distributed between Mn and oxygen atoms in the Li-rich spinel; while they were relatively dispersed in the normal spinel. As a result, Mn—O bonds of the Li-rich spinel were relatively strong and such stronger Mn—O bonds would make the main framework of the spinel structure tighter. More rigid framework of the Li-rich spinel resulted in disturbing Mn dissolution out of the spinel. No obvious relation was found between the Mn dissolution and the capacity loss as described above, but it should be pointed out that the crystal structure of lithium-rich spinel was a little harder to collapse due to its more rigid framework than that of a normal manganese spinel.

Mn—O bond strength estimated from the measurements of IR spectra.—IR spectra was measured with KBr discs and the strength of Mn—O bonds in the spinels was estimated. A band appearing at 617 cm^{-1} was assigned to that of the Mn—O stretching of LiMn_2O_4 according to the literature¹⁵ and this band shifted to 625 cm^{-1} for the Li-rich spinel. As the amounts of substituted lithium in the spinels increased, these peaks shifted to higher wavenumbers. This also confirms that Mn—O bonds in a Li-rich spinel are stronger than those in a normal spinel.

Here we briefly consider why the covalent bonding of Mn—O is tightened more in the Li-rich spinel. The chemical composition of this compound is $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and it can be expressed as $\text{Li}_{1.1}\text{Mn}^{3+}_{0.7}\text{Mn}^{4+}_{1.2}\text{O}_4$. Quantities of Mn^{4+} and Mn^{3+} increase and decrease, respectively, in comparison with the normal spinel of $\text{LiMn}^{3+}_{1.0}\text{Mn}^{4+}_{1.0}\text{O}_4$, where the σ -type covalent bond of Mn—O strengthens as frequently observed in coordination compounds.¹⁶

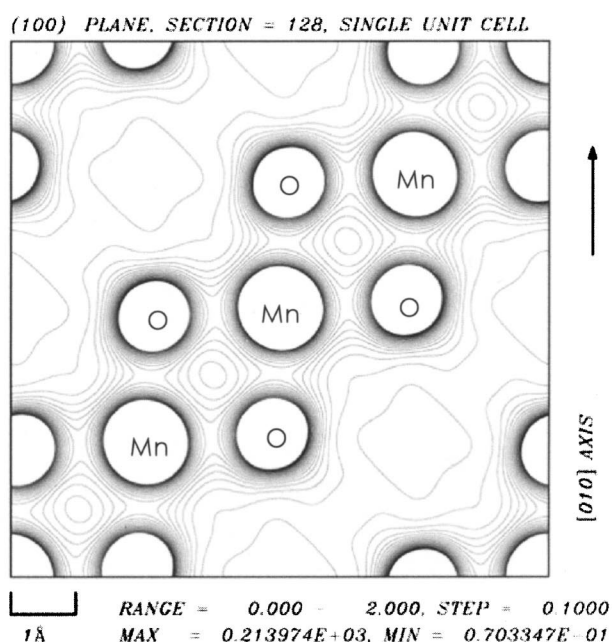
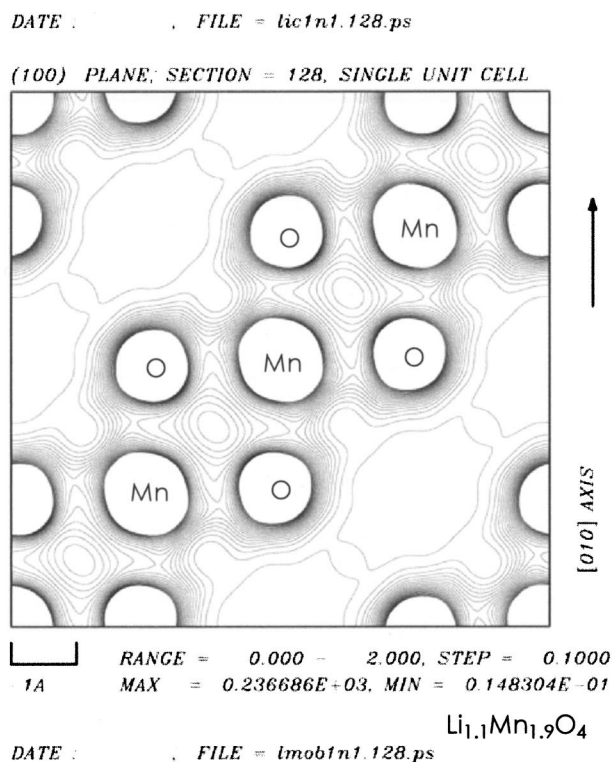


Figure 7. Electron distribution maps in $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ and LiMn_2O_4 with the MEM/Rietveld method.

Conclusions

The lithium-rich $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ was prepared and studied from electrochemical and structural points of view and the following conclusions are drawn.

The lithium-rich $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ shows two superior performances; one is as a very low capacity loss, 11% at 55°C as compared with 38% for the normal LiMn_2O_4 ; and the other is as a low Mn dissolution, 1.0%, after the 75 cycles at 55°C as compared with 2.0% for

the normal spinel. From the cycle performance tests, the capacity loss during cycles was found to be divided into two kinds; one was a capacity loss resulting from the deterioration of the active material itself and the other was from the conduction loss of the active material to the collector. The former capacity losses were 2 and 18 mAh/g at 55°C, and the latter ones are 9 and 32 mAh/g at 55°C for the Li-rich and normal spinels, respectively. The capacity loss by the poor conduction is apparently much larger for the positive electrode material.

Cycle performance tests in each region of the charge states divided into 5 regions show that relatively larger capacity losses are observed in lower potential states. However, in every region, a capacity loss for the Li-rich spinel was much smaller than that of the normal spinel. There was a close relationship found between capacity losses in the storage and those in the cycle. Electron densities spreading between manganese and oxygen atoms were larger in the Li-rich than in the normal spinels. Thus, it turned out that the structure of the Li-rich spinel was made more stable by strong Mn—O bonds.

Acknowledgments

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