

## Capacity fading of the acid-treated lithium manganese oxides in high-temperature storage

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### Abstract

We have studied capacity fadings of acid-treated lithium manganese oxides in high-temperature storage. The amounts of dissolved lithium and manganese ions and consumed acids were determined in the reaction of lithium manganese oxides with acids. Discharge capacities of the acid-treated samples were measured and the small capacity fadings were observed. X-ray diffraction patterns of the acid-treated samples were almost the same as the one before the acid-treatment.

After the acid-treated samples were stored in the EC/DMC solutions without Mn and Li ions at 80 °C for 24 h, they gave no further capacity fadings. On the other hand, after the storage under the same condition but in the EC/DMC solution containing both Mn and Li ions, the same acid-treated samples as above showed large capacity fadings. Thus, the following mechanism is deduced; the acid-treated lithium manganese oxide would react with Mn and Li ions in the solution, and its spinel structure would partly be fractured to result in the severe capacity fading.

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### 1. Introduction

Lithium manganese oxide (LiMn<sub>2</sub>O<sub>4</sub>) spinels have been extensively investigated [1–14] for the past decade to substitute LiCoO<sub>2</sub> cathodes of conventional Li-ion batteries in terms of their cost, abundance, safety, and toxicity. However, problems come out on mastering its material as the cathode. A critical one is the capacity fading during a high-temperature operation and the capacity fading is caused at the two stages: one is storage, and the other is charge–discharge cycling.

There have been many studies on capacity fading of battery cells with LiMn<sub>2</sub>O<sub>4</sub> cathodes in a high-temperature operation, but it is not thought that general agreements have been reached about its mechanism. The following causes have been suggested; they are Mn dissolution [8,15,16], structural instability [9,10,17–20], electrolyte decomposition [8,11], or Jahn-Teller effect [21,22]. Pistoia and co-workers [23,24] studied the influence of electrolyte, cur-

rent collector, voltage range, and cathodic additives on the capacity loss of lithium manganese oxides, and that of the preparative conditions as well. In the previous study, we demonstrated that lithium manganese spinel gave a large capacity fading at 10% of charged state in high-temperature storage [25] and that acids derived from the reaction of PF<sub>6</sub><sup>−</sup> with H<sub>2</sub>O in the electrolyte solution caused the capacity fading of the cathode [26]. We also reported that capacity fadings in storage and cycling related to each other [25]. Therefore, we consider it important to know about capacity fadings of lithium manganese oxides by acid treatment and those of their acid-treated lithium manganese oxides in high-temperature storage.

Hunter [27] studied reactions of LiMn<sub>2</sub>O<sub>4</sub> with H<sup>+</sup> in acidic aqueous solutions. Ammundsen et al. [28] discussed H<sup>+</sup> insertion into λ-MnO<sub>2</sub> along the following reaction:



Tarascon and co-workers [8] mentioned that an acid-induced Mn dissolution occurred and it lead to the deficient spinel structures oxidizing all the Mn<sup>3+</sup> ions to Mn<sup>4+</sup> followed by the protonic ion-exchange reaction. Then they thought

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that the resulting protonated  $\lambda$ - $\text{Mn}_{2-y}\text{O}_4$  phase reduced the capacity. However, to our knowledge there have been no reports about capacity fadings of acid-treated lithium manganese oxides in high-temperature storage.

In the present study, we report capacity and structural changes of the acid-treated lithium manganese oxides during or after high-temperature storage.

## 2. Experimental

### 2.1. Materials

Powder of lithium manganese oxides [29] was supplied by Japan Metals & Chemicals (Tokyo).  $\text{CF}_3\text{SO}_3\text{H}$  (98%) and  $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$  (99%) were purchased from Tokyo Kasei (Tokyo) and Chisso Corp. (Tokyo).  $\text{LiClO}_4$  (99%) and  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (98%) were commercially available reagents from Nacalai Tesque (Kyoto, Japan).

The 1:2 solvent mixtures of EC to DMC with and without 1 M ( $\text{M} = \text{mol}/\text{dm}^3$ )  $\text{LiPF}_6$  dissolved were purchased from the Mitui Chemical (Tokyo, Japan) and contained less than 10 ppm of  $\text{H}_2\text{O}$ . The 2:1 (by weight) binder mixture of acetylene black to PTFE was the one from Soei Tsusho (Osaka, Japan).

### 2.2. Measurements

The content of the consumed acid was titrimetrically determined after the filtrate was diluted with water. The contents of Li and Mn in the lithium manganese oxide were determined with the conventional method [30] using a Hitachi 180-50 atomic absorption spectrophotometer. X-ray powder diffraction data were collected using a large Debye–Scherrer camera equipped with an Imaging Plate as a detector at the SPring-8 BL02B2 synchrotron. The wavelength of incident X-ray was 0.5 Å. The specific surface area was determined with the BET method using a Quanta Chrome-NOVA 1200. The characterization of samples was performed by a transmission electron microscope (TEM) using a JEOL-100CX operated at 100 kV.

### 2.3. Electrochemical cells

The mixture of sample powder and conducting binders (2:1 by weight) was pressed at  $300 \text{ kg}/\text{cm}^2$  to make a cathode pellet for a cell and it was then dried at  $150^\circ\text{C}$  for 2 h. Charge and discharge tests were performed on a cell assembled with Li metal/the electrolyte/the cathode. All the cells for the present work were assembled in argon atmosphere in a glove box (Vacuum Atmosphere Co.).

### 2.4. Acid treatments, soak and storage experiments

As procedures of the soak and storage experiments are a little complicated, they are figuratively described in Scheme 1.

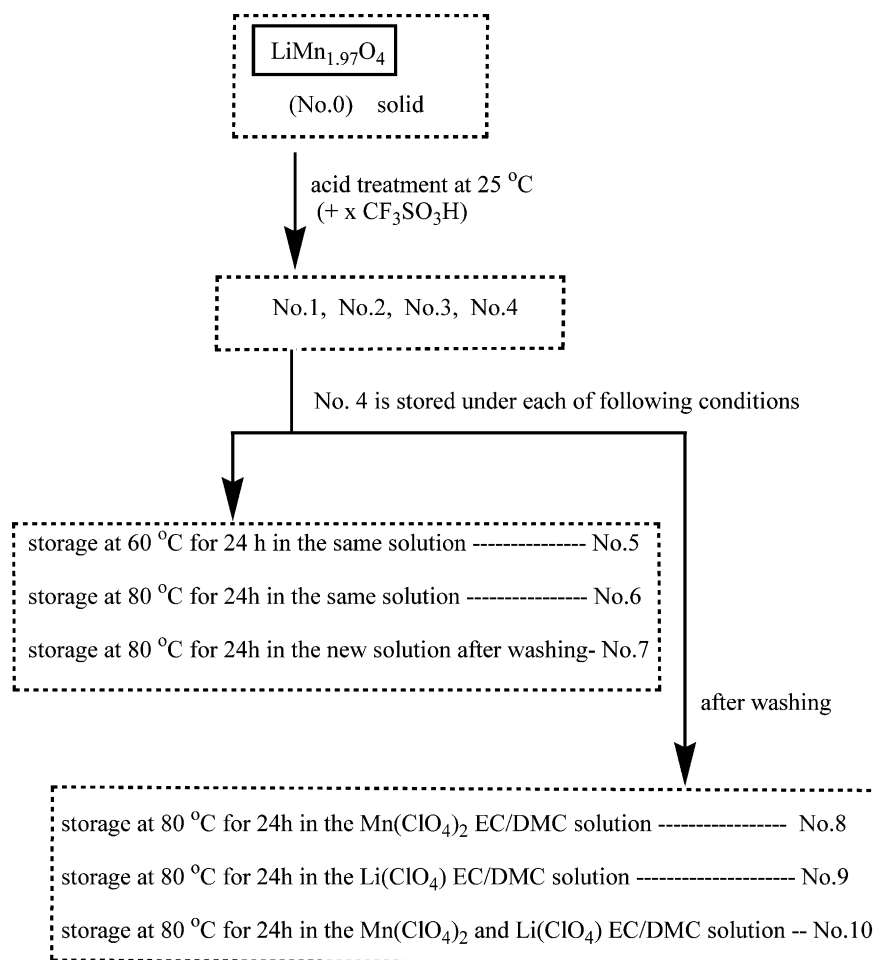
Lithium manganese oxide powders (denoted by sample No. 0, ca. 1.5 g) were put into a 10 ml of the EC/DMC (1:2 in volume) solution in a Schlenk tube, containing  $\text{CF}_3\text{SO}_3\text{H}$  in each concentration of 0.082, 0.16, 0.41, or 0.59 M. The resulting suspension was kept without stirring at  $25^\circ\text{C}$  for 24 h and then it was filtrated. Acid-treated samples are denoted by sample Nos. 1–4 according to the increasing concentration of the acid added. Amounts of the acid consumed during the treatment were determined with a titration method and, at the same time, contents of lithium and manganese ions dissolved were also measured.

A No. 4 sample was kept successively in the same solution for 24 h at either  $60^\circ\text{C}$  (No. 5) or  $80^\circ\text{C}$  (No. 6). After another one of No. 4 samples was washed well with a new EC/DMC solution, this sample was suspended and then kept in a new EC/DMC solution for 24 h at  $80^\circ\text{C}$ . The sample is denoted by No. 7. For these samples, Nos. 5–7, were measured contents of lithium and manganese ions in their solutions, and their charge and discharge capacities.

Further, about 1.5 g of each of No. 4 samples was immersed for 24 h at  $80^\circ\text{C}$  in the EC/DMC solution containing either  $\text{Mn}^{2+}$  ions (0.189 M  $\text{Mn}(\text{ClO}_4)_2$ ) or  $\text{Li}^+$  ions (0.140 M  $\text{LiClO}_4$ ), or both  $\text{Mn}^{2+}$  (0.137 M  $\text{Mn}(\text{ClO}_4)_2$ ) and  $\text{Li}^+$  ions (0.259 M  $\text{LiClO}_4$ ). For the solutions containing  $\text{Mn}^{2+}$  ions,  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  salt was used. In these cases, the equivalent amount of 1,1,1,3,3,3-hexamethyldisilazane was added to remove water included in these manganese perchlorate crystals. The suspension was filtered off. Lithium manganese oxide samples are denoted by Nos. 8–10, as in Table 3. Similarly to the above, contents of lithium and manganese ions in their solutions and their charge and discharge capacities were determined for these samples.

## 3. Results and discussion

The lithium manganese oxide used in an experiment was analyzed chemically and identified to  $\text{Li}_{1.00}\text{Mn}_{1.97}\text{O}_4$ . Its X-ray diffraction pattern showed a spinel structure and the crystal structure was indexed to a cubic system with a lattice parameter  $a_0$  of 8.239 Å, and then defined to the space group  $Fd3m$ . The surface area of this material was determined to be  $4.35 \text{ m}^2/\text{g}$  with a BET method. The cathode with this compound had initial charge and discharge capacities of 134 and 128 mAh/g, respectively, in the range of 3.5–4.5 V and showed an ordinary two-step voltage profile. The discharge capacities after 70 cycles were 120 mAh/g at  $25^\circ\text{C}$  and 105 mAh/g at  $55^\circ\text{C}$  and the capacity losses are 7 and 19% at 25 and  $55^\circ\text{C}$ , respectively. The storage at  $80^\circ\text{C}$  for 24 h resulted in charge and discharge capacities of 97 mAh/g (28% loss) and 85 mAh/g (34% loss) and at the same temperature for 96 h it resulted in 73 mAh/g (45% loss) and 63 mAh/g (51% loss), respectively.



Scheme 1.

### 3.1. The reaction of $\text{LiMn}_2\text{O}_4$ with an acid

The reaction of the lithium manganese oxide with  $\text{CF}_3\text{SO}_3\text{H}$  was studied in the EC/DMC solution. The lithium manganese oxide powder was treated with the acid as shown in Scheme 1. Table 1 summarizes their results and Fig. 1 shows the relation of acid contents consumed with

concentrations of manganese ions and lithium ions in the solutions. A roughly linear correlation is apparent between acid contents and either manganese ions or lithium ions in the whole range and a good correlation is observed in the higher concentration of the acid. The concentration ratios of consumed  $\text{H}^+$  to dissolved manganese ions and to dissolved lithium ions are 4:1 and 5:2, respectively. The OCV

Table 1  
Stoichiometry of the reaction of lithium manganese oxide with  $\text{CF}_3\text{SO}_3\text{H}$  in EC/DMC solution and electrochemical data of their acid-treated samples

	Sample			
	No. 1	No. 2	No. 3	No. 4
Amount of the lithium manganese oxide (g)	1.515	1.511	1.515	1.503
Molar ratio of consumed $\text{CF}_3\text{SO}_3\text{H}$ to the lithium manganese oxide (%)	9.7	19.5	48.5	70.6
Molar ratio of dissolved lithium ion in solution to the lithium manganese oxide (%)	4.8	8.4	20.4	29.6
Molar ratio of dissolved manganese ion in solution to lithium manganese oxide (%)	1.8	2.8	12.3	18.2
Open circuit voltage (V)	2.97	2.98	3.89	3.95
Initial charge capacity <sup>a</sup> (mAh/g) (capacity loss (%))	130 (3.0)	127 (5.2)	108 (19)	102 (24)
Initial discharge capacity <sup>b</sup> (mAh/g) (capacity loss (%))	119 (7.0)	115 (10)	111 (13)	107 (16)

<sup>a</sup> The charge capacity of the sample No. 0 is 134 mAh/g.

<sup>b</sup> The discharge capacity of the sample No. 0 is 128 mAh/g.

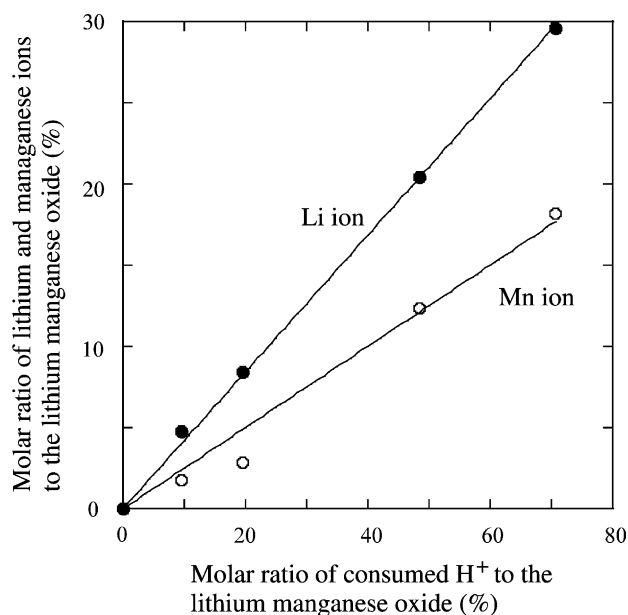


Fig. 1. Acid contents consumed vs. concentrations of Mn and Li ions in the solutions.

values and the discharge capacities increase and decrease, respectively, as an increase of amounts of the consumed H<sup>+</sup>.

### 3.2. Structural change of the acid-treated sample No. 4

Structural studies were carried out for the lithium manganese oxides of sample Nos. 0 and 4 before and after the acid-treatment, respectively. Fig. 2 shows X-ray diffraction patterns of their samples. Both patterns are very similar to each other and give almost the same diffraction line widths. The diffraction lines of sample No. 4 shift higher than those of the sample No. 0, which is explained by a decreasing lattice constant due to the increase of Mn<sup>4+</sup> on the acid-treatment. SEM images of the sample Nos. 0 and 4 are given in Fig. 3. The untreated sample, No. 0, gives a clear image on the edges of particles. On the other hand, the sample No. 4 shows some space looking like pores at peripheral sites of particles. This suggests that the reaction of the sample with acids occurs at the surface of particles where manganese and lithium ions would dissolve into the solution.

### 3.3. Capacity fading of the acid-treated samples in high-temperature storages

We examine capacity fading of the acid-treated samples in high-temperature storages. As described in the above section, acid-treatment causes the lithium manganese oxide cathodes rather small capacity fading. In order to study the successive reaction of the acid-treated sample with lithium and manganese ions in the solution, three kinds of treatments to the sample No. 4 were undergone as described previously and their procedures are drawn in Scheme 1. Table 2 sum-

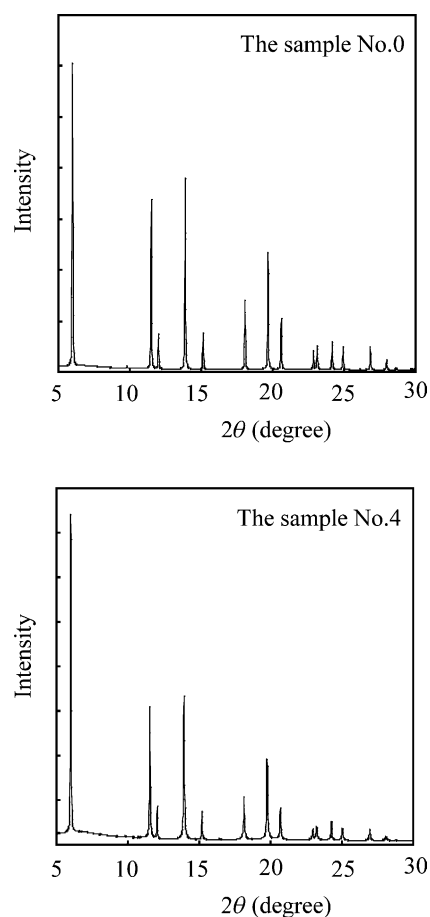


Fig. 2. X-ray diffraction patterns of the sample Nos. 0 and 4 without any treatments and with the acid-treatment, respectively.

marizes the results. In the case of the sample No. 7, no Mn and Li contents were detected in the solution and this sample maintained the same capacities as before. This fact means that the capacity fading of the acid-treated sample is not promoted even at elevated temperatures under the condition without lithium and manganese ions in the solution. However, in two samples of Nos. 5 and 6, stored successively in the same solutions<sup>1,2</sup> without washing, the capacities are 79 and 60 mAh/g, respectively, and the larger capacity fadings are observed. The Li and Mn quantities increase and decrease, respectively, in the high-temperature storage in contrast with the result for the sample No. 4. The decrease of Mn contents in the solutions implies that dissolved Mn ions in the solution react with solid lithium manganese oxide.

Fig. 4 shows an X-ray diffraction pattern of the sample No. 6. The diffraction lines broaden and new lines appear, which can be assigned to be those from Mn<sub>3</sub>O<sub>4</sub>. This may be

<sup>1</sup> In the solution, the acid has been completely consumed after the acid treatment.

<sup>2</sup> For example, a different reaction formula has been obtained for a Li-rich lithium manganese oxide.

Table 2  
Data after the high-temperature storages of the acid-treated sample No. 4

	Sample		
	No. 5	No. 6	No. 7
Storage condition	Storage at 60 °C for 24 h	Storage at 80 °C for 24 h	After washing storage at 80 °C for 24 h
Molar ratio of dissolved lithium ion in solution to lithium manganese oxide (%)	39.0	56.7	Less than 0.02
Molar ratio of dissolved manganese ion in solution to lithium manganese oxide (%)	17.2	9.4	Less than 0.02
Initial charge capacity (mAh/g) (capacity loss (%))	67 (50)	93 (31)	102 (24)
Initial discharge capacity (mAh/g) (capacity loss (%))	79 (38)	60 (53)	107 (16)

due to the reaction of the lithium manganese oxide with Mn ions in the solution, which leads to an decrease of the Mn concentration in the solution during storage. SEM images of the sample No. 6 seen in Fig. 5 demonstrate that the contours of particles are more indistinct in comparison with those of the acid-treated sample No. 4.

#### 3.4. The high-temperature storage of the acid-treated samples in the solutions containing $Mn^{2+}$ and $Li^+$ ions

As described in the previous sections, the acid-treated sample causes no additional capacity fading even in the 80 °C storage in the absence of lithium and manganese ions in the solution. On the contrary, in the solution containing Mn and Li ions, the same sample gives larger capacity fading

in high-temperature storage. This strongly suggests that the presence of Mn and Li ions in the solution induces the severe or significant capacity fading in high-temperature storage. To confirm this, other experiments were done as followed; the acid-treated samples were stored in EC/DMC solutions containing  $LiClO_4$  and  $Mn(ClO_4)_2$ .

Table 3 shows significant effects of quantities of Li and Mn ions in the solutions to the capacities of the sample Nos. 8–10. The discharge capacities of the sample Nos. 8–10

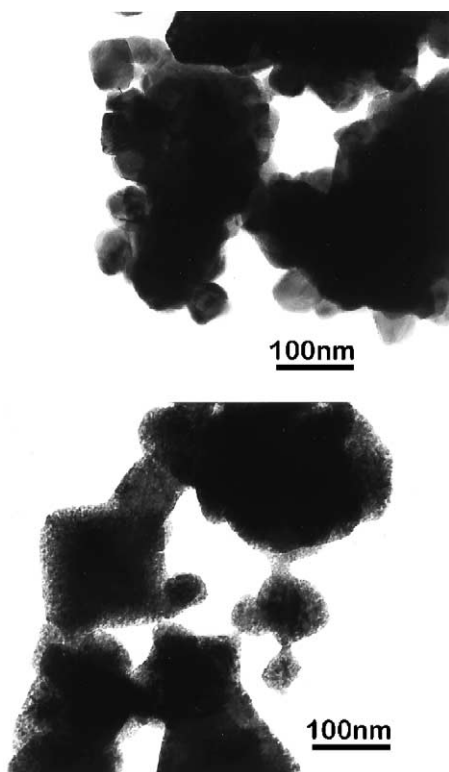


Fig. 3. SEM images of the sample Nos. 0 (top) and 4 (bottom).

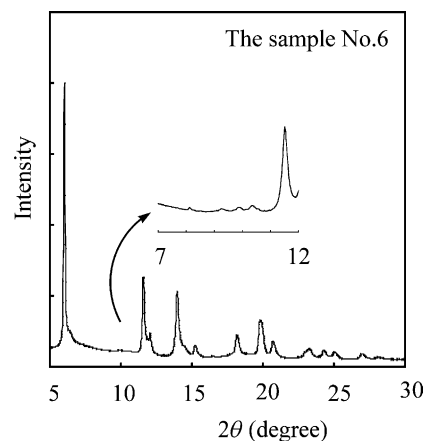


Fig. 4. X-ray diffraction pattern of the sample No. 6 which is the No. 4 kept stored in the same solution at 80 °C for 24 h.

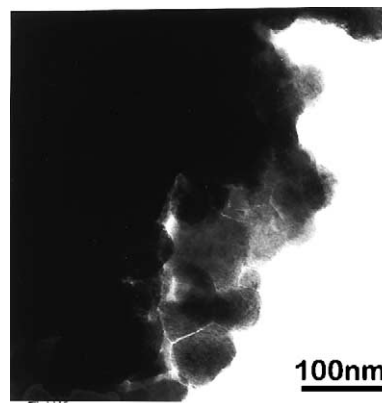


Fig. 5. SEM image of the sample No. 6.

Table 3  
Data after storages in various conditions of the acid-treated sample No. 4

	Sample		
	No. 8	No. 9	No. 10
Storage condition	Storage in $\text{Mn}^{2+}$ solution at $80^\circ\text{C}$ for 24 h	Storage in $\text{Li}^+$ solution at $80^\circ\text{C}$ for 24 h	Storage in $\text{Mn}^{2+}$ and $\text{Li}^+$ solution at $80^\circ\text{C}$ for 24 h
Molar ratio of dissolved lithium ion in solution to lithium manganese oxide (%)	2.3	-6.8 <sup>a</sup>	-10.2 <sup>b</sup>
Molar ratio of dissolved manganese ion in solution to lithium manganese oxide (%)	-0.2 <sup>c</sup>	5.0	-6.9 <sup>b</sup>
Charge capacity (mAh/g) (capacity loss (%))	81 (40)	85 (37)	49 (63)
Discharge capacity (mAh/g) (capacity loss (%))	89 (31)	90 (30)	47 (64)

<sup>a</sup> The sample was soaked in the 0.245 M  $\text{LiClO}_4$  EC/DMC solution. The concentration of  $\text{Li}^+$  decreases during the soak.

<sup>b</sup> The sample was soaked in the 0.259 M  $\text{LiClO}_4$  and 0.137 M  $\text{Mn}(\text{ClO}_4)_2$  EC/DMC solution. The concentrations of  $\text{Li}^+$  and  $\text{Mn}^{2+}$  decrease during the soak.

<sup>c</sup> The sample was soaked in the 0.143 M  $\text{Mn}(\text{ClO}_4)_2$  EC/DMC solution. The concentration of  $\text{Mn}^{2+}$  decrease during the soak.

are 89, 90, and 47 mAh/g, respectively, and their capacity fading reach 31, 30, and 64%, respectively, while they are much larger than 16% for that of the sample No. 4. Thus, the co-existence of Li and Mn ions in the solution turns out to accelerate the capacity fading of the lithium manganese oxide. However, it follows that if solid lithium manganese oxide reacts with Mn ions in the solution, no quantitative correlation will be deduced between quantities of the capacity fading of the cathode and the content of Mn ions in the solution.

Fig. 6 shows the X-ray diffraction of the sample No. 10 which has a distinct feature from those of the others. It is an extensive fracture in the crystal structure of the lithium manganese oxide. As seen in the SEM image and in the X-ray diffraction of the sample No. 10 (Fig. 7), the contours of particles seem unclear and new diffraction lines ascribed to  $\text{Mn}_3\text{O}_4$  appear. These results suggest that Mn ions in the solution are digested into the inactive region on the surface to result in forming  $\text{Mn}_3\text{O}_4$  and this leads to the fact that Mn concentration is maintained almost constant. Thus, Li and Mn ions in the solution would be causal substances to the

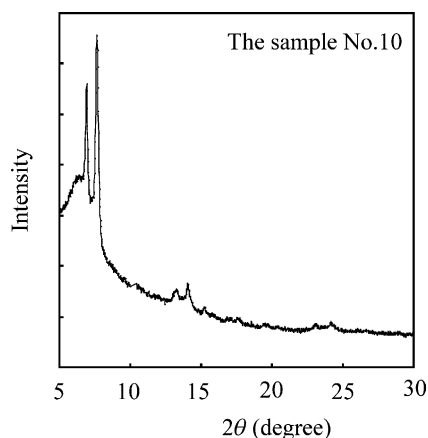


Fig. 6. X-ray diffraction pattern of the sample No. 10 which is the No. 4 kept stored in the EC/DMC solution containing  $\text{Mn}^{2+}$  and  $\text{Li}^+$  ions at  $80^\circ\text{C}$  for 24 h.

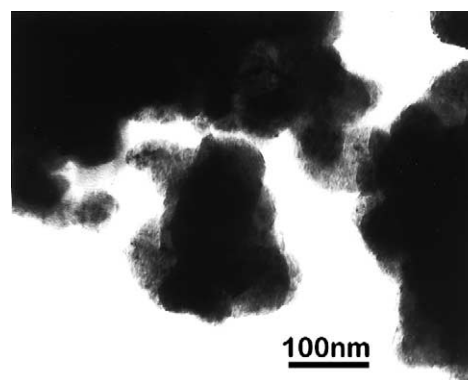


Fig. 7. SEM image of the sample No. 10.

capacity fading at elevated temperatures and as the capacity fading goes on, more  $\text{Mn}_3\text{O}_4$  would be formed.

#### 4. Conclusion

The reaction of the lithium manganese oxide with acids and the storage performance of the acid-treated samples have been studied. The following conclusions have been deduced.

- (1) For the reaction of the lithium manganese oxide with  $\text{CF}_3\text{SO}_3\text{H}$ , amounts of the consumed acid and dissolved Mn and Li were determined. Discharge capacities of the acid-treated samples were measured and small capacity fadings were observed for them.
- (2) The acid-treated samples underwent the storage at 60 and  $80^\circ\text{C}$  for 24 h under a few conditions. For the acid-treated sample washed with a fresh EC/DMC solution, its capacity fading is rather small and not further promoted, after being stored at  $80^\circ\text{C}$  in the absence of lithium and manganese ions in the storage solution. On the contrary, the acid-treated sample kept in the treatment solution itself without washing gives severe capacity fading in the storage at  $80^\circ\text{C}$ . Subsequently, coexisting lithium and manganese ions in the solution

would be involved to a great extent in a larger capacity fading of the acid-treated sample.

- (3) Storage experiments at high temperatures of acid-treated samples were carried out in the solutions containing either manganese ions or lithium ions, or both manganese and lithium ions. Severe capacity fading was found only in the run of the solution containing both manganese and lithium ions. Further studies will be required to elucidate mechanism of such a severe capacity fading.

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