

A causal study of the capacity fading of $\text{Li}_{1.01}\text{Mn}_{1.99}\text{O}_4$ cathode at 80°C , and the suppressing substances of its fading

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Abstract

Discharge capacities of the $\text{Li}_{1.01}\text{Mn}_{1.99}\text{O}_4$ cathode and Mn content dissolved from the cathode were examined on the addition of some chemicals, as the storage temperatures and time were changed. On the addition of 1000 ppm of H_2O to 1.0 M LiPF_6 solution in EC/DMC (1:2 in volume), 41% of capacity of the cathode was lost after 24 h storage at 80°C , in contrast to 5% loss in the case of no additive. Water would be responsible for causing the capacity fading of the cathode under such condition as elevated temperatures.

In the EC/DMC solution without LiPF_6 , on the contrary, no capacity fading was observed with H_2O additive at 80°C storage, while the $\text{CF}_3\text{SO}_3\text{H}$ addition resulted in 40% of capacity fading.

These results show that plausible acid derived from the reaction of LiPF_6 with H_2O causes the capacity fading on the lithium manganese oxide at 80°C , relatively high storage temperature. On the other hand, addition of 500–1000 ppm of $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ resulted in less capacity fading of the cathode and made Mn dissolution decrease drastically. Therefore, dehydration and acid-neutralization in the electrolyte solution would restrain the capacity fading of the lithium manganese oxide cathode during high temperature storage, and we confirmed it in some experiments. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Discharge capacity; $\text{Li}_{1.01}\text{Mn}_{1.99}\text{O}_4$ cathode; Capacity fading

1. Introduction

Spinel-type lithium manganese oxides have been extensively studied [1–23] as substitute cathodes for LiCoO_2 in Li-ion batteries in terms of their cost, abundance of cobalt, safety, and toxicity. There are, however, certain problems before this cathode material can be fully exploited in commercial use.

One major problem of the lithium manganese oxide cathode is its capacity fading at high temperatures [7,13,22–32]. There have been no general agreements on the problem, but the following causes have been suggested: Mn dissolution [24–31,38]; structural instability in the charged state [24,32]; electrolyte decomposition [33,34] and the Jahn–Teller effect [35].

In order to improve this situation, the systems should be examined in a simpler way. Roughly to say, the capacity fading could happen in the following two stages: one is during cycling of charge and discharge and another is during

storage at elevated temperatures. As the former would be affected by too many factors, we mainly studied the latter in the present paper.

Pistoia et al. [33] reported the storage characteristics of the lithium manganese oxide. They studied the effects of electrolyte, current collector, voltage range and cathodic additives on the capacity losses, and those of the preparative conditions as well.

In the previous paper [36], we showed that deeper discharge states increased capacity fading and that no evident correlation was observed between the extent of the Mn dissolution and that of the capacity loss.

While the present study was in progress, Du Pasquier et al. [37] reported the results on storage experiments that acids caused the Mn dissolution and resulted in protonated $\lambda\text{-Mn}_{2-y}\text{O}_4$. However, we have not deduced the apparent relation between acids and the capacity fading on storage yet. It is important to confirm if protons actually cause the capacity fading and to clarify the mechanism if any.

In the present study, we report the results of some storage experiments, and discuss the substances causing the capacity fading and the mechanism of the capacity fading.

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2. Experimental

2.1. Materials

Powder of lithium manganese oxides [38] was supplied by Japan Metals & Chemicals (Tokyo). LiF (99%) and CH₃COOH (99%) were those commercially available from Nacalai Tesque (Kyoto, Japan). CF₃SO₃H (98%) and (CH₃)₃SiNHSi(CH₃)₃ (99%) were from Tokyo Kasei (Tokyo) and Chisso Corp. (Tokyo), respectively.

The 1:2 solvent mixtures of EC/DMC with and without 1 M LiPF₆ dissolved were purchased from the Mitsubishi Chemical (Tokyo, Japan) and contained less than 20 ppm of H₂O. The 2:1 mixture of acetylene black binder–PTFE was from Soei Tsusho (Osaka, Japan).

2.2. Measurements

The contents of Li and Mn in the lithium manganese oxide were determined by the conventional method [39] with an Hitachi 180-50 atomic absorption spectrophotometer. Cyclic voltammograms (CVs) were measured with a BAS 100B Electrochemical Analyzer. Charge–discharge profiles and performance tests of the cells 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 limit were fixed at 4.5 and 3.5 V (versus Li/Li⁺), respectively.

2.3. Electrochemical cells

The mixture of 66% of the lithium manganese oxide powder and 33% of conducting binders was pressed carefully at 300 kg/cm² to make a cathode for a cell and was then dried at 150°C for 2 h. The charge and discharge tests were performed on a cell assembled with Li metal/the electrolyte/the cathode. All the processes of assembling and disassembling of the cells were carried out in argon atmosphere in a glove box (Vacuum Atmosphere Co., California, USA).

2.4. Storage tests

The cell consisting of a lithium metal anode, 1 M LiPF₆–EC/DMC (1:2 in volume) electrolyte, and the lithium manganese oxide cathode was used for the storage test. Charging

of the cell was performed galvanostatically at 0.5 mA/cm² up to 4.5 V, and after a 2 h pause, the cell was discharged to 3.5 V. Then, the cell was disassembled.

The discharged cathode was put into a 10 ml of the electrolyte solution (1 M LiPF₆–EC/DMC (1:2 in volume) or EC/DMC (1:2 in volume) without LiPF₆) with some additives at 80°C for 24 h in a Schlenk tube, and then the solution was filtered in a glove box. The Mn contents in the solution were analyzed. The same type of a cell with this cathode was reassembled and was charged up to 4.5 V. It was then discharged down to 3.5 V to measure the discharge capacity of the cathode.

3. Results and discussion

The lithium manganese oxide prepared and used in the present study was analyzed chemically and determined to Li_{1.01}Mn_{1.99}O₄. X-ray diffraction analysis of the powder showed a definite spinel structure. The crystal structure was indexed to a cubic system with a lattice parameter *a*₀ of 8.2387 Å, and then defined to the space group *Fd3m*. The lithium manganese oxide cathode has an initial discharge capacity of 129 mAh/g and shows an ordinary two-step voltage profile. After 70 cycles, the discharge capacities were 120 mAh/g at 25°C and 105 mAh/g at 55°C. This means 7 and 19% of capacity losses at 25 and 55°C, respectively.

3.1. Effect of some additives in the LiPF₆ solution of EC/DMC

In order to identify substances causing the capacity fading, we conducted a series of storage experiments adding some chemicals (additives) to the electrolyte solution at 80°C for 24 h. The added chemicals are H₂O, LiF and CH₃COOH, and each one was added to give 1000 ppm of concentration in the electrolyte solution. These additives were selected because water is a very common contaminant as impurity in the electrolyte, LiF is one of plausible compounds formed by decomposition of LiPF₆, and acetic acid is chosen as an acid.

Table 1 gives the results of the measurements including that of no additive, where capacity fading percentage (CFP)

Table 1
Quantities of dissolved Mn and specific discharge capacities of the electrode after storage in the electrolyte solution with additives^a

Additive compound	Concentration of dissolved Mn (ppm)	Specific discharge capacity (mAh/g)		CFP ^b (%)
		Before storage	After storage	
No additives	5.6	129	123	5
H ₂ O ^c	17.2	129	77	41
LiF ^c	4.9	129	129	0
CH ₃ COOH ^c	7.3	130	119	9

^a The electrode was exposed to 10 ml of 1 M LiPF₆ solution (EC/DMC (1:2 in volume)) with additives at 80°C for 24 h.

^b CFP = [(discharge capacity before storage) – (discharge capacity after storage)]/discharge capacity before storage] × 100.

^c The concentration of the additive in the solution is 1000 ppm.

Table 2
Quantities of dissolved Mn and specific discharge capacities of the electrode after storage in the EC/DMC solution with additives^a

Additive compound	Concentration of dissolved Mn (ppm)	Specific discharge capacity (mAh/g)		CFP ^b (%)
		Before storage	After storage	
No additives	0	129	129	0
H ₂ O ^c	0.8	128	128	0
LiF ^c	0	129	129	0
CH ₃ COOH ^c	0.7	128	124	0
CF ₃ SO ₃ H ^c	146	129	78	40

^a The electrode was exposed to 10 ml of non-LiPF₆ solution (EC/DMC (1:2 in volume)) with additives at 80°C for 24 h.

^b CFP = [((discharge capacity before storage) – (discharge capacity after storage))/discharge capacity before storage] × 100.

^c The concentration of the additive in the solution is 1000 ppm.

is the ratio of the discharge capacity difference between before and after the storage to the discharge capacity before the storage. The very large value of CFP is observed only for the H₂O additive in contrast to the small ones for other additives or nothing.

Thus, it is evident that addition of water to the electrolyte solution causes severe capacity fading but acetic acid gives a slight effect on capacity fading. The Mn content dissolved into the solution is outstanding for the H₂O additive but remain low for other additives or nothing. The important fact is that water causes the largest capacity fading at the elevated temperature storage.

3.2. Effect of some additives in EC/DMC including no LiPF₆

Similar experiments to the above were done under the same condition, but using only EC/DMC (1:2 in volume) solvent including no LiPF₆.

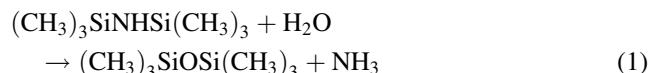
As shown in Table 2, the CF₃SO₃H additive gives the largest CFP, 40% and another acid additive, CH₃COOH, gave only 3% of CFP. However, no capacity fading is observed for H₂O in contrast to the previous result. The Mn concentration in the solution is remarkably high for CF₃SO₃H. On the other hand, only trace amount of Mn ion is detected in the solutions including CH₃COOH and H₂O.

From these experiments, it is found that in the solvent of EC/DMC mixture, water does not cause the capacity fading and dissolve Mn out of the cathode. Acids such as CF₃SO₃H are considered the key substances causing the capacity fading of the lithium manganese oxide cathode, though CH₃COOH addition causes only slight capacity fading. The slight effect of CH₃COOH would be explained by its very weak acid-dissociation.

3.3. Effect of addition of hexamethyldisilazane to the electrolyte solution

From the argument in the above section, acids formed by the reaction of LiPF₆ with H₂O in the electrolyte solution are suspected to cause the capacity fading at elevated temperatures. Thus, removal of water as a contaminant in the

electrolyte solution is expected to suppress the decomposition of LiPF₆. One of the most powerful candidate for dehydration and acid neutralization in the solution is hexamethyldisilazane ((CH₃)₃SiNHSi(CH₃)₃) (HMDS). The compound is widely used as an organic liquid desiccant and it can remove water neutralize acids in solutions as follows:



We did some storage experiments for 24 h at several temperatures of the cathode in electrolyte solutions containing HMDS. As seen in Table 3, less capacity fading is observed and Mn dissolution is drastically decreased. The pH measurement¹ showed about pH = 5 for the HDMS electrolyte solution, while the ordinary electrolyte solution gave pH = 3.

Protons from the decomposition of PF₆⁻ in the reaction with H₂O apparently cause the capacity fading of the lithium manganese oxide. As a result, the suppression of such reaction by dehydration and neutralization is proved effective to reduce capacity fading in the electrolyte solution at the higher temperatures.

3.4. Effect of storage temperature and duration time

We examined effects of the storage temperature and time on the capacity fading and the manganese dissolution at the fully discharged state.

Table 4 summarizes their results after the storage for 48-h storage at the various temperatures from 25 to 100°C. Both Mn ion concentration and CFP value of the cathode increases as storage temperature is raised. However, CFP values go up as in a very different way from Mn concentrations as there seems to be a critical point at 80°C.

Raising the storage temperature over 80°C abruptly increases the CFP value and the CFP value reaches 74%

¹ The pH measurement was done simply by putting one drop of the solution on a piece of wet pH test paper. The error is considered to be about 0.5.

Table 3
Quantities of dissolved Mn and specific discharge capacities of the electrode after storage in the electrolyte solution with $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3^{\text{a}}$

Concentration of $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ (ppm)	Concentration of dissolved Mn (ppm)	Specific discharge capacity (mAh/g)		CFP ^b (%)
		Before storage	After storage	
0 (80°C)	5.6	129	123	5
500 (80°C)	0.3	128	126	2
1000 (80°C)	0.7	129	126	2
1000 (55°C)	<0.1	129	128	1
1000 (100°C)	2.4	129	124	4

^a The electrode was exposed to 10 ml of 1 M LiPF_6 solution (EC/DMC (1:2 in volume)) with the additive for 24 h.

^b $\text{CFP} = [((\text{discharge capacity before storage}) - (\text{discharge capacity after storage}))/\text{discharge capacity before storage}] \times 100$.

Table 4
Storage temperatures, quantities of dissolved Mn, and specific discharge capacities of the electrode after storage^a

Storage temperature (°C)	Concentration of dissolved Mn (ppm)	Specific discharge capacity (mAh/g)		CFP ^b (%)
		Before storage	After storage	
25	1.5	120	120	0
40	1.8	120	120	0
55	2.8	129	127	2
70	5.8	128	120	6
80	10.1	129	66	49
90	13.1	129	54	58
100	25.3	128	33	74

^a The electrode was exposed to 10 ml of 1 M LiPF_6 solution (EC/DMC (1:2 in volume)) for 48 h.

^b $\text{CFP} = [((\text{discharge capacity before storage}) - (\text{discharge capacity after storage}))/\text{discharge capacity before storage}] \times 100$.

at 100°C, whereas the Mn concentration gradually increases up to 25 ppm which is only about 0.8% of Mn contents of the cathode.

Table 5 shows the result of the measurements at various storage periods from 6 to 48 h at 80°C. The CFP value of the cathode increases as the storage period is longer and then the value sharply rises at much longer storage period than 36 h. On the other hand, Mn concentration in the solution shows an increase over all the storage periods.

As seen from both of the storage experiments, the observed Mn concentration in the electrolyte solution is too small to explain the capacity fading in our previous results [36]. In addition, the present results suggests that there is a threshold temperature on the deterioration of the lithium manganese oxide at between 70 and 80°C.

3.5. The deterioration of lithium manganese oxide by acids

To investigate what governs the threshold temperature following experiments were done. The discharge capacities of a cathode are measured after being stored in the electrolyte solution including $\text{CF}_3\text{SO}_3\text{H}$ additive at 70 and 80°C. A large difference in the capacities was found between 70 and 80°C. In other words, for the deterioration of lithium manganese oxide by acids, there certainly is a threshold temperature between 70 and 80°C.

In order to know the extent of decomposed PF_6^- ions, we measured the ^{31}P NMR of the ions in the electrolyte solutions containing 1000 ppm H_2O . The measurements were done of the solution stored for 48 h at 50, 70 and 80°C. Plots of intensities of the ^{31}P NMR signal of the PF_6^- ion versus

Table 5
Storage times, quantities of dissolved Mn, and specific discharge capacities of the electrode after storage^a

Storage time (h)	Concentration of dissolved Mn (ppm)	Specific discharge capacity (mAh/g)		CFP ^b (%)
		Before storage	After storage	
6	<0.2	128	126	2
12	<0.2	129	126	2
24	5.6	129	123	5
36	18.6	129	95	26
48	10.1	129	66	49

^a The electrode was exposed to 10 ml of 1 M LiPF_6 solution (EC/DMC (1:2 in volume)) at 80°C.

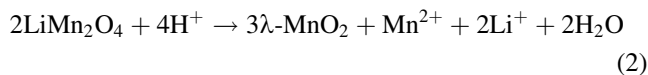
^b $\text{CFP} = [((\text{discharge capacity before storage}) - (\text{discharge capacity after storage}))/\text{discharge capacity before storage}] \times 100$.

$-1/T$ are on a straight line and, therefore, the decomposition of PF_6^- gradually increases between 70 and 80°C. This implies that decomposition of PF_6^- ions due to the reaction with H_2O [40] would not be prompted in the range from 70 to 80°C. Not only acids from decomposition but also other factors are considered effective on the capacity fading of lithium manganese oxide in the storage over 80°C.

3.6. Relation between open circuit voltage (OCV) and the discharge capacity of the cathode after storage

Fig. 1 shows the relation between the OCV values measured and the CFP on the various cathodes. Samples with small capacity fading give about 3.7 V of OCV similar to the empirical value as expected to the discharged sample showing no capacity fading. However, OCV values increases as capacity fading gets larger. This could be well explained if we suppose that manganese ions in the cathode are oxidized in the process of the capacity fading.

Hunter [41] studied the reaction of lithium manganese oxide with acids in aqueous solutions. This reaction produces $\lambda\text{-MnO}_2$ as follows:



The formation of $\lambda\text{-MnO}_2$ would raise the voltage of the cathode if the Mn^{2+} formed in the reaction is electrochemically ignored. However, further study would be required because much still remains unclear about relation between the reaction and the mechanism of the capacity fading.

3.7. Cyclic voltammetry of the lithium manganese oxide cathode after storage

We measured CVs of the lithium manganese oxide cathode after storage. The working electrode was the lithium manganese oxide, and both the counter and the reference electrodes were Li foil.

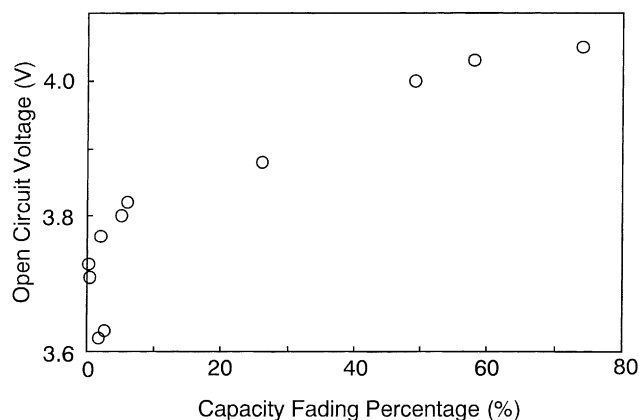


Fig. 1. Plots of CFP vs. initial OCV of $\text{Li}_{1.01}\text{Mn}_{1.99}\text{O}_4$ after storage.

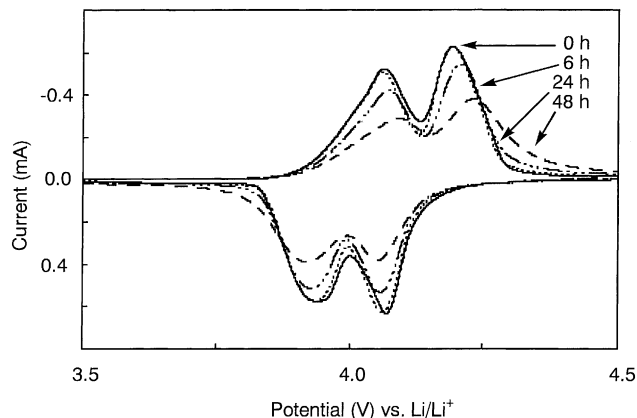


Fig. 2. CV of $\text{Li}_{1.01}\text{Mn}_{1.99}\text{O}_4$ after storage for various storage times at 80°C at a scan rate of 0.1 mV/s. The electrolyte solution is 1.0 M LiPF_6 solution in EC/DMC (1:2 in volume).

The potential was cycled between 3.5 and 4.5 V at 0.1 mV/s. After the measurements of the CV of the lithium manganese oxide cathode, the cathode was stored at 80°C for 6 h and then its CV was measured again. Such a successive storing and following CV measurement were repeated. These CV measured are shown in Fig. 2. Two pairs of well separated redox peaks are observed for each sample. Although the amplitudes of these redox peaks decrease with longer storage times, the each integrated intensity of the higher or lower voltage wave remained the same for every sample.

The appearance of two pairs of redox peaks suggests that lithium ions are extracted from and inserted into the spinel lattice via a two-step process. Lithium ions are first removed from the half of the tetrahedral sites, and then from the rest half of tetrahedral sites. Such peak splitting is characteristic of materials with a high degree of crystallinity. Further, both from the appearance of no other new peaks and from similarity of the CV to each sample, electrochemically active Mn sites would not undergo a great structural change by inactive manganese ions.

Let us consider the peak shifts in the CVs of the cathodes. A larger shift of the oxidation peak was observed as storage time was longer, in contrast with the small shift of the reduction peak. In addition, the oxidation peak positions fully depend on CV sweep rates. This suggests that an increase in the capacity fading could be caused by interference with the extraction or by difficulty in the extraction of lithium ions out of crystal lattices of LiMn_2O_4 on charging.

Du Pasquier et al. [38] have very recently reported the presence of organic coating layers on the lithium manganese oxide cathode, mainly on the basis from their IR measurements. We are now take care of some of our measurements on the lithium manganese oxide cathode from the different point of view. For example, TEM pictures of the cathodes were compared before and after the storage. Some kinds of passive layers are already admitted at surfaces of particles on the cathode after the storage.

We are studying also the stoichiometry of the reaction in the capacity fading process and the structures of the lithium manganese oxide cathodes at various stages of capacity fading after storage using a X-ray diffraction technique with a synchrotron radiation source. The results will be reported in the near future.

4. Conclusions

From storage experiments at 80°C for 24 h on the addition of H₂O, CH₃COOH, or LiF to the electrolyte solution containing LiPF₆, largest capacity fading is observed for the H₂O additive. Water is considered to accelerates the capacity fading of the cathode.

On the other hand, in the absence of LiPF₆ in the solution, no fading is found in the case of H₂O additive, but very large amount of capacity fading is caused by the CF₃SO₃H additive. Acids formed by the reaction of LiPF₆ with H₂O are supposed to be involved in causing the capacity fading of the lithium manganese oxide cathode.

Addition of 500–1000 ppm (CH₃)₃SiNHSi(CH₃)₃ to the electrolyte solution gives rise to less capacity fading and results in a drastic decrease of Mn dissolution even at such a higher temperature as 80°C. This compound could work as a suppressant of the reaction mentioned above by dehydration and acid neutralization in the solution.

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