Electrochemical Surface Analysis of LiMn_2O_4 Thin-film Electrodes in LiPF_6 /Propylene Carbonate at Room and Elevated Temperatures

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ABSTRACT

Degradation of LiMn_2O_4 in LiPF_6 -based electrolyte solution is complicated due to the influence of PF_6^- anion. Decomposition of PF_6^- anion accelerates both of dissolution of manganese ion and surface-film formation. In this study, surface states of LiMn_2O_4 thin-film electrodes in LiPF_6 /propylene carbonate (PC) derived from the surface-film formation were investigated using redox reaction of ferrocene and spectroscopic analyses. The spectroscopic analyses suggested that properties of the surface film depended the operation temperature (30 °C and 55 °C); a thinner surface film composed of LiF and PC decomposition products formed on LiMn_2O_4 at 30 °C and a thicker surface film was formed at 55 °C. The redox reaction of ferrocene clearly showed that LiMn_2O_4 was completely passivated at 30 °C, while it was partially passivated at 55 °C, indicating the surface film formed at 55 °C was not compact and LiMn_2O_4 was exposed to the electrolyte solution. It was one of the causes of the rapid degradation of LiMn_2O_4 at elevated temperatures in LiPF_6 -based electrolyte solution.

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1. Introduction

Recent advancement in lithium-ion batteries (LIBs) technology has enabled practical use of electric vehicles (EVs). Since the energy density of the LIB determines the cruising distance of the EV, the LIB with high energy density is required. In addition, they are also required low cost and high reliability to avoid thermal run away. Concerning these required features, LiMn_2O_4 is one of the most attractive materials for positive electrode because manganese is relatively abundant transition metal and the material is thermally stable. Therefore, the material has been widely used in LIBs for EVs. Although LiMn_2O_4 shows such ideal properties, it suffers from severe capacity fading during its operation especially at elevated temperatures,^{1–5} which is a crucial shortcoming for long-term use of the LIBs.

Thus far, degradation mechanisms of LiMn_2O_4 have been extensively studied for over two decades, and various degradation phenomena such as Jahn–Teller distortion,^{6–8} dissolution of manganese ion,^{1–5,9–13} structural changes^{3–5,10,14–17} and surface film formation^{15,17–29} have been reported. In particular, the dissolution is the most severe problem for LiMn_2O_4 . In the practical LIBs, LiPF_6 has been commonly used as a lithium salt. However, PF_5 , decomposition products of PF_6^- anion, reacts with impurity water in the solution to form HF, which accelerates the dissolution of manganese ion.^{2–5,9} In addition, the surface-film formation is also a severe problem in LiPF_6 -based electrolyte solution because F^- forms LiF, which has low conductivity of lithium-ion, on the surface of LiMn_2O_4 .^{15,17–22,29} Moreover, since PF_5 is a strong Lewis acid, it triggers polymerization of organic solvent to form organic surface film, resulting in large interfacial resistance.^{30–32} Furthermore, these degradation phenomena brought by LiPF_6 are

accelerated at elevated temperature because of thermal instability of LiPF_6 . For these reasons, the degradation mechanism at the surface region of LiMn_2O_4 in LiPF_6 -based electrolyte solution should be quite complicated.

Since the dissolution of manganese ion and formation of the surface film competitively occur, these processes possibly influence on each other. Hirayama et al. reported that the compact surface film formed in LiPF_6 -based electrolyte solution protected the surface of LiMn_2O_4 from attack by HF, resulting in suppression of dissolution of manganese ion.¹⁷ In addition, it was also suggested that non-uniform surface film did not completely suppress the degradation of LiMn_2O_4 .¹⁷ This study clearly showed that the properties of the surface film affected the other degradation phenomena occurring at the surface region of LiMn_2O_4 . Based on this suggestive study, it is considered that the compact surface film which uniformly covers LiMn_2O_4 is ideal for protecting it from the side reactions. Thus far, a large number of surface analyses of LiMn_2O_4 were conducted using X-ray photoelectron spectroscopy (XPS), which is one of the most powerful tools for the surface analysis. However, since an area of X-ray beam spot is larger than micrometer scale, it was not suitable to analyze the compactness of the surface film along the in-plane direction. Since the side reactions takes place at the interface between LiMn_2O_4 and electrolyte solution, it is important to analyze the surface in much smaller scale. In general, there are few spectroscopic methods which can analyze the surface region of the sample in such scale. As for microscopic analysis such as transmission electron microscope (TEM), the surface region of the sample can be analyzed in atomic scale. However, since TEM is conducted after pre-treatment of the sample in high vacuum condition, it is difficult to observe fragile or volatile components in the surface film.

Therefore, in this study, we employed redox reaction of ferrocene as a probe for surface analysis of LiMn_2O_4 . In our previous study, it was investigated that the surface-film formation behavior on the LiMn_2O_4 thin-film electrode in LiClO_4 /propylene carbonate (PC) using redox reaction of ferrocene.³³ As the result, it was clarified that

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the electronic passivation of the electrodes did not occur during charge–discharge cycles at room temperature, and it occurred only at elevated temperature. Using this method, the coverage of the surface film formed in LiPF_6 -based electrolyte solution can be discussed in much smaller scale than XPS. In order to investigate the effect of operating temperature on the surface states of LiMn_2O_4 , the cycling test was carried out at 30 °C and 55 °C. Analyzing the changes in the surface state of LiMn_2O_4 thin-film electrodes during cycling using redox reaction of ferrocene together with spectroscopic analyses, the degradation phenomena at the surface region of LiMn_2O_4 was investigated.

2. Experimental

2.1 Preparation of LiMn_2O_4 thin-film electrode

LiMn_2O_4 thin-film electrodes were prepared by pulsed laser deposition (PLD) method using the fourth harmonic of Nd: YAG laser (Electronics Optic Research Ltd.). The energy density of the laser beam was set at 1.08 J cm^{-2} . The repetition frequency was 10 Hz. $\text{Li}_{1.4}\text{Mn}_2\text{O}_{4+x}$ was used as a target material. The chamber pressure was kept at 27 Pa by flowing O_2 gas during the deposition. The thin film was prepared on a mirror-polished platinum substrate heated at 873 K for 1 h. The resulting thin film was characterized with X-ray diffraction measurement and Raman spectroscopy.

2.2 Electrochemical measurements and spectroscopic analysis

Using the LiMn_2O_4 thin-film electrode as a working electrode, three-electrode cell was composed for electrochemical measurements. As a reference and a counter electrode, lithium metal was employed. Hereafter, all potentials are referenced to Li^+/Li . Lithium-ion extraction/insertion reaction was conducted by cyclic voltammetry in 1 mol dm^{-3} LiPF_6/PC (lithium battery grade, purchased from KISHIDA CHEMICAL Co., Ltd.) at 0.1 mV s^{-1} in the range of 3.5–4.2 V at 30 °C and 55 °C. Redox reaction of ferrocene was conducted in 1 mol dm^{-3} LiClO_4/PC (Tomiya Pure Chemical Industries, Ltd.) containing 1 mmol dm^{-3} ferrocene (Alfa Aesar, purity 99 %). Cyclic voltammetry of ferrocene was carried out at 10 mV s^{-1} in the range of 3.0–3.6 V at 30 °C before and after the 1st, 5th, 10th, and 20th lithium-ion extraction/insertion reaction. In addition, the electrochemical impedance spectroscopy (EIS) was conducted at 4.1 V before and after the cyclic voltammetry for the lithium-ion extraction/insertion reaction. Applied ac voltage and frequency range were set at 15 mV and 100 kHz–10 mHz. All the electrochemical measurements were conducted in argon filled glove box using HSV-100 (HOKUTO-DENKO) or Solartron1470E + 1255 (Solartron Analytical).

To evaluate redox behavior of ferrocene quantitatively, electrochemical surface area A and a standard rate constant k^0 between ferrocene and electrode at each cycle were obtained by fitting a simulated voltammogram to the experimental one. The simulation procedure was followed to the literature,³⁴ and the simulation condition was shown in our previous work.³³ Modifying k^0 and A until the simulated voltammogram fitted to the experimental ones, these values were obtained.

As the structural characterization after the lithium-ion extraction/insertion reaction, Raman spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR), and XPS measurement were conducted. Raman spectroscopy was measured with a triple monochromator (Jobin-Yvon, T64000) equipped with a CCD detector. As a light source, 514.5-nm line of argon ion laser (CVI Melles Griot, 543-GS-A03) was used. ATR FT-IR was conducted with Bruker Alpha in Ar-filled glove box. XPS measurements were carried out ex-situ with MT-5500 (ULVAC PHI, Inc.). Prior to XPS analysis, the cell was deconstructed in Ar-filled glove box to obtain cycled electrodes, and the electrodes were

transferred in Ar-filled vessel to side chamber of the XPS instrument.

3. Results and Discussion

3.1 Characterization of a LiMn_2O_4 thin film prepared with PLD

Figure 1 shows XRD pattern of a LiMn_2O_4 thin film prepared with PLD. All the peaks were consistent with reported ones in previous reports,⁵ and no other peak was observed. In addition, relative peak intensities were similar to those of powder one, indicating that the film did not have any specific crystalline orientation. It also suggested that the film was composed of polycrystalline LiMn_2O_4 . Therefore, using this thin film as an electrode, the information independent from crystalline orientation at the surface can be obtained.

Figure 2 shows Raman spectrum of the thin film. Peaks around 500, 580, and 625 cm^{-1} were attributed to F_{2g} , F_{2g} and A_{1g} modes of LiMn_2O_4 , respectively.⁸ Since no other peak was observed in the spectrum, the thin film was composed only of LiMn_2O_4 and did not contain impurity phase. From the results of XRD and Raman spectroscopy, it was found that the prepared LiMn_2O_4 thin film was desirable for a model electrode.

Figure 1. X-ray diffraction pattern of a prepared thin film on Pt substrate. Number on peaks denotes index hkl . * indicates peaks of sample holder.

Figure 2. Raman spectrum of a prepared thin film.

Figure 3. Cyclic voltammograms of LiMn₂O₄ thin-film electrodes in 1 mol dm⁻³ LiPF₆/PC at 30 °C (a) and 55 °C (b).

3.2 Electrochemical properties of LiMn₂O₄ thin-film electrodes

Figure 3 shows cyclic voltammograms of the LiMn₂O₄ thin-film electrodes in 1 mol dm⁻³ LiPF₆/PC at 30 °C and 55 °C. Around 4.0 and 4.15 V, two reversible peaks which are unique to LiMn₂O₄ were observed in each voltammogram. At 30 °C, peak current gradually decreased with increasing cycle number. This result was slightly different from the results in LiClO₄/PC of our previous report.³³ Therefore, it indicated that the degradation of LiMn₂O₄ was accelerated in LiPF₆/PC even at room temperature. At 55 °C, the peak current decreased more rapidly, indicating that the degradation of LiMn₂O₄ was accelerated at the elevated temperature. Many reports suggested that LiMn₂O₄ suffered from severe capacity fading in LiPF₆/PC at elevated temperatures.^{1–5,35} The present result was in good agreement with these reports.

Figure 4 shows the Nyquist plots of the LiMn₂O₄ thin-film electrode at 30 °C and 55 °C. A semi-circle and a following straight line were observed in each Nyquist plot. The semi-circle was attributed to charge-transfer (lithium-ion transfer) resistance R_{ct} at the electrode/electrolyte interface, and the straight line was assigned to lithium-ion diffusion in LiMn₂O₄.³⁶ In the both Nyquist plots, the diameters of the semi-circles increased with increasing the cycle number. For LiMn₂O₄ cycled at 30 °C, R_{ct} increased by a factor of 15 during 20 cycles. In addition, small semi-circles were also observed at high frequency region in the plots. This semi-circle possibly attributed to lithium-ion transfer in surface layer on LiMn₂O₄ (note that the pristine LiMn₂O₄ was charged to 4.1 V to conduct EIS measurement, and surface film might be formed during the process). On the other hand, R_{ct} increased by a factor of ca. 3000

Figure 4. Nyquist plots of LiMn₂O₄ thin-film electrodes at 4.1 V vs. Li^+/Li during cycling in 1 mol dm⁻³ LiPF₆/PC at 30 °C (a) and 55 °C (b). An enlarged view is inserted in (b). The value indicates the frequency at the top of the semi-circles.

during 20 cycles at 55 °C, which was much larger increasing rate than that obtained at 30 °C. The results possibly suggests that a large number of the active sites decreased during the cycling process at 55 °C, which was consistent with the variations of cyclic voltammograms. The decrement of the active sites would be discussed in detail based on the results of redox reaction of ferrocene and X-ray photoelectron spectroscopy in the next sections.

3.3 Redox reaction of ferrocene on LiMn₂O₄ thin-film electrodes

Since the degradation behaviors of LiMn₂O₄ thin-film electrodes remarkably depended on the operation temperatures in LiPF₆/PC, the surface state of the LiMn₂O₄ thin-film electrodes at the temperatures were investigated with the redox reaction of ferrocene. Figure 5 shows the cyclic voltammograms of ferrocene on the LiMn₂O₄ thin-film electrodes. Before the 1st cycle of the lithium-ion extraction/insertion, clear reversible peaks of ferrocene were observed. At 30 °C, the peaks completely disappeared after the 1st cycle. In the case at 55 °C, although the peak currents decreased after the 1st cycle, the peaks were still slightly observable even after the 20th cycle. The standard rate constant k^0 and ratio of the surface area to the initial value A/A_0 were evaluated by fitting the simulated voltammograms to the experimental ones, and they were summarized in Table 1. At 30 °C, A/A_0 could not be evaluated because the

Figure 5. Cyclic voltammograms of redox reaction of ferrocene on LiMn_2O_4 thin-film electrodes during cycling in 1 mol dm^{-3} LiPF_6/PC at 30°C (a) and 55°C (b).

peaks completely disappeared. After the 1st cycle, k^0 drastically decreased by a factor of almost one thousand at 30°C , indicating complete electronic passivation of the LiMn_2O_4 thin-film electrode. Therefore, it was suggested that the film compactly covered the surface. It might suppress side reactions such as oxidation of electrolyte solution and H^+ attack to LiMn_2O_4 , resulting in contribution to capacity retention. However, since the increase of R_{ct} was observed in Nyquist plots at 30°C , it was suggested that the surface film also decreased the number of the reaction sites for lithium-ion transfer at the electrode/electrolyte interface. In contrast, at 55°C , A/A_0 drastically decreased after the 1st cycle, whereas k^0 kept similar values to the pristine one. It indicated that LiMn_2O_4 was not completely electronically passivated. There were two possible causes for the incomplete passivation of LiMn_2O_4 ; one is a part of LiMn_2O_4 was not covered by the surface film, and the other is exposure of platinum substrate resulted from massive dissolution of manganese ion. However, if platinum substrate was exposed by the dissolution of LiMn_2O_4 , the redox current of the ferrocene must increase with increasing the cycling number. In Fig. 5(b), the redox current decreased with increasing the cycle number. Therefore, it is considered that the surface film formed at 55°C did not completely cover the surface and a slight part of the surface was still exposed to the electrolyte solution. The incomplete formation of the surface film would be caused by the harsh dissolution of manganese ion at the elevated temperature. During the following cycles, the value of A/A_0 continuously decreased, indicating that the surface film grew after the 1st cycle and the exposed area of LiMn_2O_4 gradually

Table 1. Ratio of surface area to the initial value A/A_0 and standard rate constant k^0 between ferrocene and LiMn_2O_4 thin-film electrodes.

number of cycle	30 °C	55 °C	
	$k^0/\text{cm s}^{-1}$	$k^0/\text{cm s}^{-1}$	A/A_0
0	6.5×10^{-4}	2.0×10^{-3}	1.0
1	$<3.1 \times 10^{-7}$	1.7×10^{-3}	9.6×10^{-2}
5	$<3.1 \times 10^{-7}$	2.1×10^{-3}	7.2×10^{-2}
10	$<3.1 \times 10^{-7}$	1.7×10^{-3}	7.6×10^{-2}
20	$<3.1 \times 10^{-7}$	1.7×10^{-3}	3.4×10^{-2}

decreased during cycling. It should be the reason of the continuous increase of R_{ct} observed in EIS. The present results are consistent with the previous report in terms of the thickness of the surface film after the prolonged cycles.²⁰ Since the surface film did not completely cover the surface of LiMn_2O_4 at the elevated temperature, side reactions such as further oxidation of electrolyte solution and H^+ attack to LiMn_2O_4 possibly occurred at the exposed area of LiMn_2O_4 . It should be one of the reasons that capacity fading of LiMn_2O_4 rapidly and continuously proceeded at elevated temperatures.

3.4 Characterization of surface species on LiMn_2O_4 after cycling in LiPF_6/PC

To investigate the surface-state changes before and after the cycles, LiMn_2O_4 thin-film electrodes were analyzed with Raman spectroscopy, XPS and ATR FT-IR. Figure 6 shows Raman spectra of pristine and cycled LiMn_2O_4 thin-film electrodes. No new peak emerged after cycling, indicating other impurity phase did not exist in the LiMn_2O_4 thin-film electrodes. In our previous report, a new peak of Mn_2O_3 at 650 cm^{-1} was observed for LiMn_2O_4 cycled in LiClO_4/PC at 55°C . However, the peak was not observed in the present results in LiPF_6/PC . It was reported that Mn_2O_3 was easily dissolved into LiPF_6 -based electrolyte solution at elevated temperature.³ Therefore, Mn_2O_3 might be once formed on LiMn_2O_4 at 55°C in LiPF_6/PC , but it immediately dissolved into LiPF_6/PC . This may be the reason of no observation of Mn_2O_3 . It should be emphasized that structural change at the surface region of LiMn_2O_4 was not the reason of the increase of R_{ct} .

Figure 7 shows the depth profiles of the atomic concentrations at the surface region of pristine and cycled LiMn_2O_4 thin-film electrodes calculated from the results of XPS. In both profiles of cycled LiMn_2O_4 , a large concentration of Li and F were observed at

Figure 6. Raman spectra of LiMn_2O_4 thin-film electrodes before cycling and after the 20th cycle in 1 mol dm^{-3} LiPF_6/PC at 30°C and 55°C .

Figure 7. Depth profile of LiMn_2O_4 thin-film electrodes before cycling and after the 5th cycle in 1 mol dm^{-3} LiPF_6/PC at 30°C and 55°C evaluated from the results of X-ray photoelectron spectroscopy.

short sputtering time. Since the LiMn_2O_4 cycled at 55°C showed higher concentrations of Li and F at 486-s sputtering, the thicker LiF was formed on the surface. The results clearly indicated that the thickness of the LiF surface film increased with increasing temperature, and it is in good agreement with the previous report on surface film on LiMn_2O_4 .²⁰ In addition, C and a slight amount of P were also observed, which were attributed to decomposition products of PC and PF_6^- , respectively. Comparing variations of C and F in depth profile, concentration of F kept almost the same value during 162 s of sputtering, while that of C gradually decreased. It indicated that organic species derived from PC was formed on top surface of the electrode, and LiF was formed near the surface of LiMn_2O_4 . Since the formation of LiF on LiMn_2O_4 decrease active sites for lithium-ion extraction and insertion, it could cause the large increase of R_{ct} observed in EIS.

In addition to XPS, ATR FT-IR was conducted to analyze organic species on the surface of LiMn_2O_4 . Figure 8 shows the ATR FT-IR spectra of the pristine LiMn_2O_4 and LiMn_2O_4 after the 5th cycle at 30°C and 55°C . For the both cycled LiMn_2O_4 , new peaks around 1780 cm^{-1} appeared. According to the report by Matsui et al., $\text{C}=\text{O}$ double bond in decomposition products of PC showed peak at 1780 cm^{-1} .³⁷ Therefore, decomposition products of PC precipitated on the surface of the cycled LiMn_2O_4 . In our previous study, surface film derived from decomposition products of PC was not observed on LiMn_2O_4 cycled in LiClO_4/PC at 30°C in FT-IR spectrum. In contrast, in the present results, the organic surface film was observed at 30°C in LiPF_6/PC . It was reported that PF_5 , decomposition products of LiPF_6 , was a strong Lewis acid and acted as an initiator of polymerization of carbonates.^{30,32} Therefore, such a difference in formation of PC-decomposition products at 30°C was possibly resulted from instability of PF_6^- anion. As for decomposition products of PF_6^- , no peak corresponding to them were observed in the spectra. However, it does not follow that the result denies the formation of the surface species derived from the decomposition products of PF_6^- . Since total amount of the surface film formed on the thin-film electrode should be smaller than that formed in composite electrodes, it might be difficult to detect the minor species with FT-IR. From the result of XPS, there was a slight amount of P atom on the surface region. Therefore, there should be a small amount of the species from PF_6^- on the surface.

Figure 8. Attenuated total reflection Fourier transform infrared spectra of LiMn_2O_4 thin-film electrodes before cycling and after the 5th cycle in 1 mol dm^{-3} LiPF_6/PC at 30°C and 55°C .

From these results, the surface states of LiMn_2O_4 in LiPF_6/PC were summarized as follows. After the cycling at 30°C , LiMn_2O_4 was covered with the compact surface film composed of LiF and PC-decomposition products, and it led to complete passivation of LiMn_2O_4 . In this regard, the surface film contributed to suppression of further side reactions such as the dissolution of manganese ion to a certain extent. However, since the charge-transfer resistance also largely increased by the surface film, the film also hindered interfacial lithium-ion transfer. In our previous report,³³ it was revealed that the surface film derived from PC hardly hindered the interfacial lithium-ion transfer. Therefore, such low lithium-ion conductivity of the surface film was caused by LiF, which is known as a poor lithium-ion conductor. At 55°C , although the thicker surface film was formed, it was not compact and LiMn_2O_4 was partially exposed to the electrolyte solution. It was probably because the emission of HF was accelerated at the elevated temperature and dissolution of manganese ion rapidly proceeded. The continuous dissolution of manganese ion occurred at the exposed area of LiMn_2O_4 , preventing from formation of compact surface film, and resulted in severe capacity degradation of LiMn_2O_4 . It is, namely, a vicious cycle of surface degradation. This shows marked contrast to the surface state of LiMn_2O_4 in LiClO_4/PC at 55°C .³³ The surface film formed in LiClO_4/PC completely electronically passivated LiMn_2O_4 and it prevented LiMn_2O_4 from the interfacial side reactions during cycling. The contrast clearly showed the intrinsic difficulties of LiPF_6 -based electrolyte solution for long-term cycling of LiMn_2O_4 . Even at 30°C , the interfacial lithium-ion transfer was much slower because of the low lithium-ion conductive surface film. In addition, at 55°C , the surface film could not suppress the severe interfacial side reactions. Although LiPF_6 is widely used in commercialized LIBs, alternative electrolytes which are safe and stable are required for further improvement of the long-term cycleability of the LIBs.

4. Conclusion

The electronic passivation behavior of LiMn_2O_4 cycled in LiPF_6/PC was strongly influenced by its operation temperature; At 30°C , complete electronic passivation was brought by compact surface film composed of LiF and decomposition products of PC. The electronic passivation possibly suppressed further side reactions at the interface such as dissolution of manganese ion and oxidation of electrolyte solution, leading to suppression of capacity fading. However, it also hindered interfacial lithium-ion transfer, resulting in worse rate capability. On the other hand, at 55°C , the surface film

was thick but not compact, and it did not completely electronically passivate LiMn_2O_4 . Therefore, LiMn_2O_4 was partially exposed to the electrolyte solution, and further side reactions such as dissolution of manganese ion continuously occurred during cycling, leading to instability of the surface film. This vicious cycle of surface degradation should be one of the causes of rapid degradation of LiMn_2O_4 at elevated temperatures.

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