Characterization of the Interface between LiMn$_2$O$_4$ Thin-film Electrode and LiBOB-based Electrolyte Solution by Redox Reaction of Ferrocene

Junichi INAMOTO$^{a,b,*}$ Tomokazu FUKUTSUKE$^{a,c}$ Kohei MIYAZAKI$^{a,c}$ and Takeshi ABE$^{a,c}$

$^a$ Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
$^b$ Present address: Graduate School of Engineering, University of Hyogo, Himeji, Hyogo 671-2280, Japan
$^c$ Hall of Global Environmental Research, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

* Corresponding author: j.inamoto@eng.u-hyogo.ac.jp

ABSTRACT

Lithium bis(oxalato)borate (LiBOB) has attracted much attention as an alternative lithium salt in lithium-ion batteries. At positive electrodes, LiBOB is considered to form a protective surface film. However, its protection ability is not understood in detail. In this study, the surface-film formation behavior and the protection ability on a LiMn$_2$O$_4$ thin-film electrode in LiBOB/propylene carbonate (PC) was investigated using spectroscopic methods and a redox reaction of ferrocene. The surface film formed in LiBOB/PC at 55°C is much thinner than that in LiClO$_4$/PC. The redox reaction of ferrocene on cycled LiMn$_2$O$_4$ showed that the electronic passivation did not occur during cycling even at 55°C. On the basis of the results, a degradation behavior of LiMn$_2$O$_4$ was discussed.

Keywords: LiMn$_2$O$_4$ Thin-Film Electrode, Lithium Bis(oxalato)borate, Surface Film, Lithium-ion Battery

1. Introduction

Development in lithium-ion battery (LIB) technology has promoted widespread use of portable devices in these two decades. Recently, LIBs have been also practically applied to large-scale devices such as electric vehicles (EVs) and energy storage systems (ESSs). For the use for EVs and ESSs, over ten-year durability is expected to LIBs. In this regard, the cycleability of LIBs becomes a more severe problem than ever. The side reaction at the electrode/electrolyte interface is thought to be one of the factors for the degradation of LIBs. Therefore, it is important to understand the surface state of the electrodes and design the ideal interface. For graphite negative electrodes, the formation of proper solid electrolyte interphase (SEI) is indispensable for the reversible charge and discharge. To compose the proper SEI, some film-forming additives have been used. One of the effective additives is lithium bis(oxalato)borate (LiBOB). Unlike the other additives such as vinylene carbonate, LiBOB can be used not only as the additive but also as a lithium salt. Therefore, only using LiBOB as the lithium salt, the proper SEI can be formed on the graphite. This means that LiBOB extend the range of applicable organic solvents for LIBs.

As for positive electrode materials, it has been reported that LiBOB also gave positive effect on them, especially on LiMn$_2$O$_4$ at elevated temperatures. Some X-ray photoelectron spectroscopy (XPS) studies revealed that decomposition products of BOB anion formed the surface film on LiMn$_2$O$_4$, and the film was considered to behave as a protective layer like the SEI. We have clarified that propylene carbonate (PC) did not form stable surface film on LiCoO$_2$ and LiMn$_2$O$_4$ at room temperature. Therefore, it is important to understand the properties of the LiBOB-derived surface film on the positive electrode materials in order to reduce the side reactions at the cathode/electrolyte interface. However, the properties of the LiBOB-derived surface film such as compactness and stability have not been understood in detail. There is a room for discussion on to what extent the surface film contributes to the improvement in the cycleability. In this study, we focused on these important properties of the LiBOB-derived surface film. To investigate the surface film, redox reaction of ferrocene was employed. This method was applied to LiCoO$_2$ and LiMn$_2$O$_4$ thin-film electrodes in our previous studies, and it was proved that the method was effective for analyzing surface states of the electrodes such as passivation caused by surface film. From the passivation behavior, the compactness and stability of the LiBOB-derived surface film was discussed.

2. Experimental

LiMn$_2$O$_4$ thin-film electrodes were prepared by pulsed laser deposition (PLD) method according to our previous paper. The fourth harmonic (266 nm) of Nd:YAG laser (Electronics Optic Research, Ltd.) was used as a laser source. As a target material, Li$_{1.4}$Mn$_2$O$_{4+x}$ was used. The thin film was deposited on a mirror-polished platinum substrate heated at 873 K for 1 h. A three-electrode cell was used for electrochemical measurements. A LiMn$_2$O$_4$ thin-film electrode was used as a working electrode, and lithium metals were used as a reference and a counter electrode. Hereafter, all potentials are referenced to Li$^+$/Li. To investigate the change in the redox behavior of ferrocene on the LiMn$_2$O$_4$ thin-film electrode during electrochemical cycle, a series of electrochemical measurements was conducted. Cyclic voltammetry (CV) (1) was measured in 1 mol dm$^{-3}$ LiBOB/PC (Tomiyama Pure Chemical Industries, Ltd.). CV (2) was measured in 1 mol dm$^{-3}$ LiClO$_4$/PC (Tomiyama Pure Chemical Industries, Ltd.) containing 1 mmol dm$^{-3}$ ferrocene (Alfa Aesar, Purity 99%) at 30°C. Note that the electrolyte for CV (2) was not LiBOB but LiClO$_4$ to avoid any possibility of oxidative decomposition of LiBOB and resulting surface-film formation during CV (2). It was confirmed that LiClO$_4$/PC does not form the passivating surface film under 4.2 at room temperature in our previous study. Sweep rates and sweep ranges were 0.1 mV s$^{-1}$ and 3.5–4.2 V for CV (1), and 10 mV s$^{-1}$ and 3.0–3.6 V for CV (2), respectively. First of all, CV (2) was measured on the pristine LiMn$_2$O$_4$ thin-film electrode using the ferrocene-containing solution. After that, the cell was washed with pure PC and electrolyte was changed to the ferrocene-free electrolyte solution to measure CV (1). After the prescribed number of cycle, the cell was washed, the electrolyte solution was changed, and CV (2) was conducted. Following this procedure, CV (2) was measured...
before the 1st cycle and after the 1st, 5th, 10th and 20th cycle of CV (1). To evaluate the redox-reaction rate of ferrocene quantitatively, standard rate constants \( k \) between ferrocene and electrodes at each number of cycle were obtained using simulation of cyclic voltammogram. The simulation procedure was followed to the literature. 20 Electrochemical impedance spectroscopy (EIS) of the LiMn\(_2\)O\(_4\) thin-film electrodes was conducted during cycles of CV (1). EIS was measured at 4.1 V at 30°C or 55°C before the 1st cycle and after the 1st, 5th, 10th, and 20th cycle of CV (1). Frequency range and applied ac voltage were set at 100 kHz–10 mHz and 15 mV. All the electrochemical measurements were carried out in argon filled glove box. In addition to electrochemical measurements, Raman spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR), and XPS were conducted. Raman spectroscopy was performed with a triple monochromator (Jobin-Yvon, T64000) equipped with a CCD detector. As a light source, a 514.5-nm line of argon ion laser (CVI Melles Griot, 543-GS-A03) was used. ATR FT-IR (Bruker Alpha) was conducted in the argon filled glove box to avoid exposure to the air. XPS was conducted with MT-5500 (ULVAC PHI Inc.) using 400 W X-ray of MgK\(_\alpha\). The cycled cells were disassembled in the argon filled glove box and washed with PC, and then obtained electrodes were transported to chamber of the instrument. For depth analysis of LiMn\(_2\)O\(_4\) thin film, Xe-ion sputtering was combined. The obtained spectra were calibrated by C 1s peaks of contamination derived from pump oil at 284.8 eV, and the data was analyzed with analysis software PHI Multipak.

### 3. Results and Discussion

Figure 1 shows cyclic voltammograms of the LiMn\(_2\)O\(_4\) thin-film electrode in 1 mol dm\(^{-3}\) LiBOB/PC at 30°C and 55°C (CV (1)). In Fig. 1, two reversible peaks around 4.0 and 4.15 V, which are characteristic to LiMn\(_2\)O\(_4\), were observed. 21 At 30°C (a), the cyclic voltammogram showed better reversibility. It indicates that the degradation of LiMn\(_2\)O\(_4\) hardly proceeded in LiBOB/PC at room temperature. At 55°C (b), the peak current gradually decreased with increasing cycle number. It indicates that the degradation of LiMn\(_2\)O\(_4\) gradually proceeded in LiBOB/PC at the elevated temperature. In addition, the observed peaks are broader than those at 30°C, and non-negligible background current was observed. This result indicates that the oxidative decomposition of the electrolyte solution (LiBOB and/or PC) proceeded competitively. Since such background current was not observed in LiClO\(_4\)/PC at 55°C in our previous study, 19 it suggests that LiBOB mainly contributed to the current. In addition, if the decomposition products of the oxidation form a stable film on the electrode, it probably passivates the electrode and decreases the background current after several cycles. Since the decrease was not observed in the result, it indicates that the passivating film was not formed on the electrode in LiBOB/PC at 55°C. After the 20th cycle at 55°C, a shoulder peak at 650 cm\(^{-1}\) was observed in Raman spectrum (not shown here), and it was attributed to Mn\(_2\)O\(_3\). 22 This result was similar to that observed in LiClO\(_4\)/PC at 55°C in our previous study. 19 Therefore, it suggests that the similar interfacial side reactions occurred between LiMn\(_2\)O\(_4\) and the electrolyte solutions at the elevated temperature, leading to irreversible structural deterioration of LiMn\(_2\)O\(_4\).

Figure 2 shows Nyquist plots of the LiMn\(_2\)O\(_4\) thin-film electrodes at 30°C and 55°C. The starting points of the semi-circles are rearranged at zero because intercepts of the plots are varied with cycle number. In the Nyquist plots, single semi-circles and following straight lines were observed. The semi-circles are assigned as the charge-transfer (lithium-ion transfer) resistance, \( R_c \), of LiMn\(_2\)O\(_4\). 21 At 30°C, the semi-circle was not clearly observed at the earlier cycles. The semi-circles appeared after the 5th cycle, and the \( R_c \) were evaluated to be 10 \( \Omega \) after the 20th cycle. It suggested that the resistance of the interfacial lithium-ion transfer was increased during cycling in LiBOB/PC. Since no change in the surface region of LiMn\(_2\)O\(_4\) was observed in Raman spectrum, the increase was possibly attributed to the surface-film formation. On the other hand, the semi-circle was clearly observed at 55°C before cycling. This indicates that the resistance increased during potential holding at 4.1 V at 55°C for EIS measurement, and it may be caused by the surface-film formation derived from oxidative decomposition of LiBOB/PC. After the 5th cycle, \( R_c \) became slightly smaller. This result implies that the resistance decreased during cycling, which possibly indicates that the surface film disappeared during cycling. After the following cycles, the diameter became gradually larger, and \( R_c \) increased to 100 \( \Omega \) after the 20th cycle. The increases are attributed to formation of Mn\(_2\)O\(_3\) at the surface region observed in Raman spectrum.

To analyze the surface species on LiMn\(_2\)O\(_4\) cycled in LiBOB/PC, ATR FT-IR and XPS measurements were conducted for LiMn\(_2\)O\(_4\) thin-film electrodes before and after cycling at 30°C and 55°C. Figure 3 shows FT-IR spectra of LiMn\(_2\)O\(_4\) thin-film electrodes before and after the 5th cycle at 30°C and 55°C. For both cycled LiMn\(_2\)O\(_4\), peaks at 1633 and 1317 cm\(^{-1}\) were observed in LiMn\(_2\)O\(_4\). These peaks are consistent with lithium oxalate (1640 and 1320 cm\(^{-1}\)), indicating formation of lithium oxalate. In addition, the weak peak around 1780 cm\(^{-1}\) can be assigned as the decomposition products of PC. 23 For these reasons, the PC decomposition products and lithium oxalate were deposited as the surface film in LiBOB/PC. Figure 4 show C 1s (a), O 1s (b), and B 1s (c) XPS spectra of LiMn\(_2\)O\(_4\) thin-film electrodes before and
after the 5th and 20th cycle at 30°C and 55°C. In C 1s spectra, the strong peak at 284.8 eV which was observed even for the pristine LiMn$_2$O$_4$ was due to the contamination in the chamber. A peak at 289.0 eV was observed in each of the cycled LiMn$_2$O$_4$ and it was attributed to C=O bond.24 It suggested the formation of lithium oxalate derived from LiBOB which was observed in the FT-IR spectra. Since the peak became weaker after the 20th cycle at each temperature, it indicated that the amount of the surface species decreased during cycling. However, since the extent of oil contamination varies with samples, it made difficult the quantitative discussion of the ratio of C=O over C-C. For the quantitative discussion of the amount of the surface film, O 1s spectra of those samples was also analyzed. In O 1s spectra, a peak at 531.5 eV was observed for each of cycled LiMn$_2$O$_4$ and attributed to O=C bond,24 which also supports the formation of lithium oxalate and PC decomposition products. Since a peak at 529.6 eV was observed for LiMn$_2$O$_4$, and the most of metal oxides generally show the peaks around here, the peak was attributed to O atom in LiMn$_2$O$_4$ and also Mn$_2$O$_3$ formed at 55°C. In each of cycled LiMn$_2$O$_4$, the peak was observed, indicating the surface of LiMn$_2$O$_4$ was partially exposed or the surface film was considerably thin. Since relative intensity of the peak at 531.5 eV decreased after the 20th cycle at each temperature, the amount of the surface species decreased during cycling. This is important in considering the passivation behavior of

Figure 3. Attenuated total reflection Fourier transform infrared spectra of pristine LiMn$_2$O$_4$ thin-film electrode and LiMn$_2$O$_4$ thin-film electrodes after the 5th cycle in 1 mol dm$^{-3}$ LiBOB/PC at 30°C and 55°C.

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LiMn$_2$O$_4$ in LiBOB/PC. In B 1s spectra, no peak was observed in LiMn$_2$O$_4$ cycled at 30°C, indicating the surface film did not contain residue of LiBOB and decomposition products containing B atom. As for LiMn$_2$O$_4$ cycled at 55°C, very weak peaks of B 1s were observed, suggesting that the surface film contained little amount of B atom. Figure 4(d) shows the depth profiles of LiMn$_2$O$_4$ thin-film electrodes before and after the 5th cycle in LiBOB at 30°C and 55°C. Both cycled electrodes showed almost the same profile to the pristine LiMn$_2$O$_4$. Since concentrations of C atom rapidly decreased with increasing sputtering time and concentrations of B atom kept quite low value, the surface films are considered to be very thin.

This result is in good agreement with the previous report on the surface film on LiCoO$_2$ thin-film electrode in LiBOB-based electrolyte solution.25 The results also indicated that the thickness and the amount of the surface species were not largely influenced by operating temperatures. In this regard, the surface-film formation behavior at 55°C was quite different from the results of LiMn$_2$O$_4$ in LiClO$_2$/PC, which showed much thicker surface film at 55°C.19 It indicates that the surface-film formation mechanism in the both electrolyte solution is largely different from each other.

As mentioned above, it was suggested that the surface film formed in LiBOB/PC was very thin and the amount of the surface species decreased during cycling. It possibly has strong influence on the passivation behavior of the LiMn$_2$O$_4$ thin-film electrode. To investigate the passivation behavior of the LiMn$_2$O$_4$ thin-film electrode, redox reaction of ferrocene (CV (2)) was performed during cycles of CV (1) at 30°C and 55°C. Figure 5 shows the results of CV (2). Before cycling, reversible redox peaks of ferrocene were observed at the both temperatures. After the initial cycling at the both temperatures, peak-to-peak separation slightly increased, but the peaks were clearly observed during cycling. Based on the results of CV (2), the standard rate constant $k^0$ at each cycle was calculated and the variations of the value were shown in Fig. 5(c). Fitting error of $k^0$ was estimated at ca. 6%. At 30°C, $k^0$ decreased up to the 5th cycle, indicating that some part of active sites for interfacial electron-transfer decreased during cycling process. This means formation of the surface-film. After the 5th cycle, $k^0$ showed minimum value but it was still measurable, indicating that the electrode was not electronically passivated. This result is consistent with the results of XPS which showed the surface film was very thin. After the 10th cycle, $k^0$ slightly increased, indicating disappearance of the surface species. This is also in good agreement with the results of XPS which suggested the amount of the surface species decreased after the 20th cycle. At 55°C, the similar behavior of $k^0$ was observed. The $k^0$ decreased by a factor of
After the initial cycle, but the value was still measurable, indicating the electronic passivation did not occur. The value gradually increased with increasing cycle number. Since Mn2O3 was observed after cycling at 55°C in Raman spectra, there is a possibility that the formation of Mn2O3 in influenced on k0. Since Mn2O3 was an electronic insulator, the formation of Mn2O3 at the surface region of LiMn2O4 would lead to drastic decrease of k0. However, such a drastic decrease was not observed at 55°C. In addition, k0 even increased during prolonged cycling, which was similar to the behavior at 30°C. For these reasons, although the formation of Mn2O3 might make minor change in k0, the variations of k0 was mainly attributed to the formation and decomposition of the surface film. These results indicate that the surface film formed in LiBOB/PC at 55°C was also too thin to passivate the surface of LiMn2O4, and the amount of the surface species gradually decreased with increasing the cycle number.

In our previous study, the formation of thick surface film and the electronic passivation were observed for LiMn2O4 cycled in LiClO4/PC at 55°C. However, in this study, the surface film was very thin and LiMn2O4 was not electronically passivated even at 55°C. Such a unique surface-film formation behavior in LiBOB/PC can be explained considering the oxidation process of the electrolyte solution. A series of density functional theory calculations clearly showed that the electrolyte anions strongly influence the oxidation process of PC. In the literature, the oxidation potential of PC became lower when PC interacted with anions of lithium salts. Therefore, PC molecules near anions were oxidized at lower potential prior to free PC. When LiClO4 and LiPF6 were used as electrolytes, electron was extracted from PC. On the other hand, when LiBOB was used, electron was extracted not from PC but from BOB anion, and BOB anion was decomposed into CO2 gas at last. In this way, since BOB anion was sacrificially oxidized at the electrode/electrolyte interface, the oxidation of PC was suppressed, and consequent formation of the surface film was less likely to occur. Lithium oxalate found in the present result is considered to be an intermediate product or a bi-product of BOB-anion oxidation. In addition, the results of XPS indicated that the amount of lithium oxalate decreased after the 20th cycle at the both temperatures. This may be caused by instability of lithium oxalate toward oxidation. It has been reported that oxalate anion was oxidized to form CO2 at 3.5–4.0 V. Therefore, it is considered that the lithium oxalate formed on the surface was gradually decomposed into CO2 during cycling. At the initial cycle, since the surface film did not exist, the oxidation reaction of BOB anion rapidly occurred. After the surface-film formation, active sites for electron-transfer reaction between BOB anion and the electrode decreased by the film, and the oxidation of BOB anion was suppressed. Simultaneously, the oxidative decomposition of lithium oxalate on the surface of the LiMn2O4 gradually proceeded, resulting in decrease of the surface species and increase of k0 at the later cycles. In this way, since the
compact and stable surface film was not formed on LiMn$_2$O$_4$ in LiBOB/PC even at 55°C, the electronic passivation of LiMn$_2$O$_4$ did not occur. As mentioned above, it has been proposed that the surface film derived from LiBOB protects LiMn$_2$O$_4$ from side reactions such as further oxidative decomposition of electrolyte solution. However, our result clearly indicates that LiBOB had little ability to form the compact and stable surface film. Therefore, the surface film did not contribute to protect LiMn$_2$O$_4$ from interfacial side reactions. It follows that the improvement of cycleability was possibly caused by other factors. Unlike LiPF$_6$-based electrolyte solution, LiBOB-based electrolyte solution is free from impurity HF. As it is pointed out, this HF-free feature of LiBOB probably contributed to the less interfacial side reactions, resulting in the improvement. Since the present result denied the protective effect of the surface film, the indication seems to be more probable explanation of the capacity retention mechanism. Our results also presented a demerit of LiBOB-based electrolyte solutions. Since the compact and stable surface film was not formed on LiMn$_2$O$_4$ in LiBOB/PC, the oxidative decomposition of BOB anion continuously occurred during cycling. The base current observed during cycling at 55°C supports this supposition. In addition, compared the base current observed at each temperature, the continuous oxidative decomposition of the electrolyte solution occurred harder at the elevated temperature. Since the oxidation of LiBOB continuously occurred, the amount of usable lithium salt gradually decreased, resulting in decrease of ionic conductivity and degradation of rate capability in long-term cycles at the elevated temperature. In conclusion, the present results suggest that the film-forming ability of the electrolyte solutions is important in composing stable positive-electrode/electrolyte interface.

4. Conclusion

The surface state of LiMn$_2$O$_4$ thin-film electrode during cycling in LiBOB/PC at 30°C and 55°C was investigated. FT-IR and XPS analysis revealed that the very thin surface film mainly composed of lithium oxalate derived from LiBOB was formed at the both temperatures. The redox reaction of ferrocene on the cycled LiMn$_2$O$_4$ clarified that electronic passivation did not occur after cycling even at 55°C, indicating the surface film has little ability to suppress interfacial side reactions. These results indicated that since the oxidation of BOB anion sacrificially proceeded prior to oxidation of PC during charging process, the compact and stable surface film derived from PC was not formed on LiMn$_2$O$_4$ even at the elevated temperature. It follows that the improvement in capacity retention with LiBOB was caused not by the formation of protective surface film but by HF-free feature of LiBOB. Although the no emission of HF contributed to suppress degradation of LiMn$_2$O$_4$, lack of the surface film led to continuous oxidative decomposition of LiBOB and the solvent during cell operation especially at elevated temperature. Since it decreases the amount of the electrolyte solution and degrades performance of the electrolyte solution such as the ionic conductivity, it should be considered the deterioration of rate capability in long-term cycling in practical LIBs using LiBOB-based electrolyte solution.

Figure 5. Cyclic voltammograms of redox reaction of ferrocene on LiMn$_2$O$_4$ thin-film electrodes during cycling in 1 mol dm$^{-3}$ LiBOB/PC at 30°C (a) and 55°C (b). Variations of standard rate constant $k_0$ between ferrocene and LiMn$_2$O$_4$ thin-film electrode at each cycle evaluated from the voltammograms (c).

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