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ORIGINAL PAPER

Formation of an SEI on a $LiMn_2O_4$ cathode during room temperature charge–discharge cycling studied by soft X-ray absorption spectroscopy at the Fluorine K-edge

**Kyung Yoon Chung · Won-Sub Yoon ·
Kwang-Bum Kim · Byung-Won Cho ·
Xiao-Qing Yang**

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Abstract The solid electrolyte interface (SEI) formation on the surface of $LiMn_2O_4$ electrodes during room temperature charge–discharge cycling was studied using soft X-ray absorption spectroscopy at the Fluorine (F) K-edge. $LiMn_2O_4$ electrodes without any binder were prepared by electrostatic spray deposition to eliminate the signal originating from the PVDF binder in the F K-edge X-ray absorption spectra. The F K-edge absorption spectra show that the SEI layer forms at a very early stage of cycling. SEI growth takes place during discharge. In addition, LiF formation is accelerated if the discharge step follows a charge step. The F K-edge absorption spectra suggest that the major component of the SEI is LiF.

Keywords $LiMn_2O_4$ · SEI · LiF · Soft X-ray absorption spectroscopy · Lithium secondary batteries

1 Introduction

$LiMn_2O_4$ has been studied extensively as an alternate cathode material for lithium secondary batteries. However, poor cycling performance (capacity fading) of $LiMn_2O_4$, especially at elevated temperature, limits the broader application of this material in fields such as portable electronics. Despite this limitation, $LiMn_2O_4$ is a very attractive alternative cathode material for large scale batteries that power environmentally friendly vehicles such as HEV, PHEV, and EV or stationary energy storage applications due to the material's low cost, environmental benignity, and better safety characteristics.

Several issues cause capacity fading of $LiMn_2O_4$ during cycling. One cause is manganese dissolution into the electrolyte during cycling, especially at elevated temperature [1–3]. Unfavorable Jahn–Teller distortion also leads to capacity fading, even in the 4 V range [4–6]. In addition to those reasons, the formation of an unfavorable solid-electrolyte interface (SEI) layer is detrimental to cycling performance [7–11]. Previously, it was shown that certain cycling conditions, such as elevated temperature, overcharging to 5.2 V at room temperature, and multiple charge cycles at room temperature, promote the decomposition of the electrolyte as well as cause the degradation of electrochemical performance of $LiMn_2O_4$ [8]. In that work, the decomposition of the electrolyte led to the formation of a LiF layer, and the LiF layer was proposed to be responsible for the deterioration of the electrodes. In addition to that work, previous studies show that an unfavorable SEI including LiF forms on $LiMn_2O_4$ during cycling at elevated temperature and it is detrimental to the $LiMn_2O_4$ cathode material [7–10, 12–14]. Thus, it can be concluded that the LiF layer is one of the factor for the degradation of $LiMn_2O_4$ at elevated temperature. Though an SEI layer,

K. Y. Chung (✉) · B.-W. Cho
Energy Storage Research Center, Korea Institute of Science and Technology, Seoul 136-791, Korea
e-mail: kychung@kist.re.kr

W.-S. Yoon
Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea

K.-B. Kim
Division of Materials Science and Engineering, Yonsei University, 134 Shinchon-dong, Seodaemun-gu, Seoul 120-749, Korea

X.-Q. Yang
Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, USA

especially LiF, may cause degradation of the electrode, its formation on $LiMn_2O_4$ during cycling at room temperature is not yet thoroughly understood.

In this study, Fluorine (F) K-edge soft X-ray absorption spectroscopy was used to study a $LiMn_2O_4$ electrode cycled at room temperature using a partial electron yield (PEY) detector. Because the sample probing depth for this detector is approximately 5 nm, it is an ideal tool to study the SEI layer [15]. The formation process of the SEI layer was studied, and the major component of the SEI layer on the cathode was identified.

2 Experimental

$LiMn_2O_4$ samples were prepared by electrostatic spray deposition (ESD) [5, 6]. The precursor solution consisted of 0.025 M $CH_3CO_2Li \cdot 2H_2O$ and 0.05 M $Mn(NO_3)_2 \cdot 4H_2O$ in ethanol. The substrates used were platinum metal sheets. The distance between the spraying needle and the substrate was set to 4 cm. The voltage applied between the needle and the substrate was 12 kV, and the surface temperature was set to 300 °C during deposition. The flow rate of the precursor solution was fixed at 2 mL/h, and a total amount of 2 mL was sprayed. After deposition, the samples were annealed at 400 °C in air for 2 h and then cooled to room temperature in the furnace. No other additives (e.g., a conducting agent or binder) were added to the electrode. The thickness of the samples ranges around 0.7–1 μm [5, 16, 17].

The samples were charged or discharged to a preset cutoff voltage in a coin cell. The electrolyte used was a commercially available solution of 1 M $LiPF_6$ in a 1:1 ethyl carbonate (EC)/dimethyl carbonate (DMC) solvent (LP 30 from EM Industries Inc.). After charge/discharge to a certain charge/discharge state, the coin cell was disassembled, and the electrode was retrieved and washed repeatedly in tetrahydrofuran (THF) to remove the electrolyte. All steps for electrode recovery were completed in an Ar-filled dry glove box. Since the THF is very volatile, it dries very fast in the Ar-filled dry glove box. When the samples were thoroughly dried, they were carried to the beamline in a hermetically sealed container and put in a high vacuum chamber at the beamline. The samples were exposed to air for a very short time (less than a few minutes) to minimize their contamination.

The F K-edge soft X-ray spectra were taken using a PEY detector at beamline U7A at the National synchrotron light source (NSLS) at Brookhaven National Laboratory in NY, USA. The beam size was 1 mm in diameter. Monochromator absorption features and beam instabilities were normalized by dividing the detected PEY signals by the photoemission current (I_o) of a clean gold mesh standard placed in the incident beam. Energy calibration was carried out by initially calibrating the principal monochromator I_o oxygen absorption feature to 531.2 eV using an oxygen gas phase absorption cell. An additional I_o mesh of Ni was also placed in the incident beam to insure energy calibration (based on the oxygen calibration above) and energy scale reproducibility of the multiple PEY spectra collected. The data were recorded using a channel electron multiplier.

3 Results and discussion

Figure 1 shows the cyclic voltammogram (CV) of $LiMn_2O_4$ prepared by ESD. It shows a typical curve shape with two pairs of current peaks, indicating that the $LiMn_2O_4$ sample was successfully prepared by ESD. The small separation between the anodic and cathodic peaks indicates that the electrode does not experience severe polarization despite the absence of conducting additives and binders.

Figure 2 shows the reference X-ray absorption spectra of polyvinylidene fluoride (PVDF) and LiF that were collected using powder samples. Because both samples contain Fluorine, the spectra show an absorption edge near 690 eV. To eliminate any ambiguity of the signals from PVDF and LiF, samples without PVDF binder are prepared. However, the absorption spectra of PVDF and LiF show very distinctive features. PVDF shows relatively flat spectra near 705 eV, whereas LiF shows a deep valley. In addition, the main edge peak positions are 688 and 691 eV for PVDF and LiF, respectively. These features are quite helpful to distinguish the LiF signal from the signal of the sample.

In order to investigate the formation of the SEI layer, nine different samples were prepared. Figure 3 shows the charge/discharge conditions for six samples. Sample #1 is

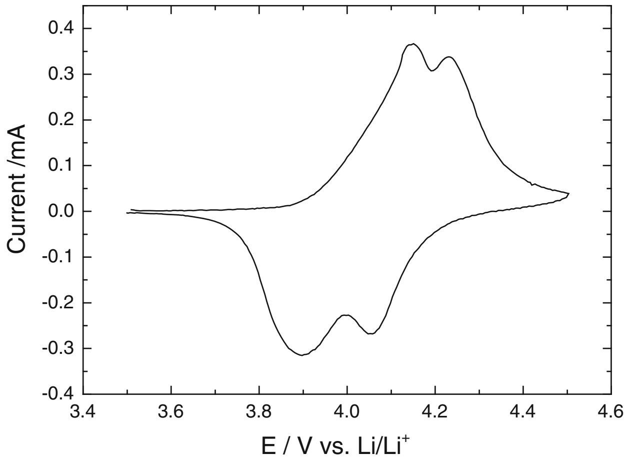


Fig. 1 Cyclic voltammogram of a $LiMn_2O_4$ electrode prepared by ESD. Cutoff voltage: 3.5–4.5 V; scan rate: 0.5 mV/s

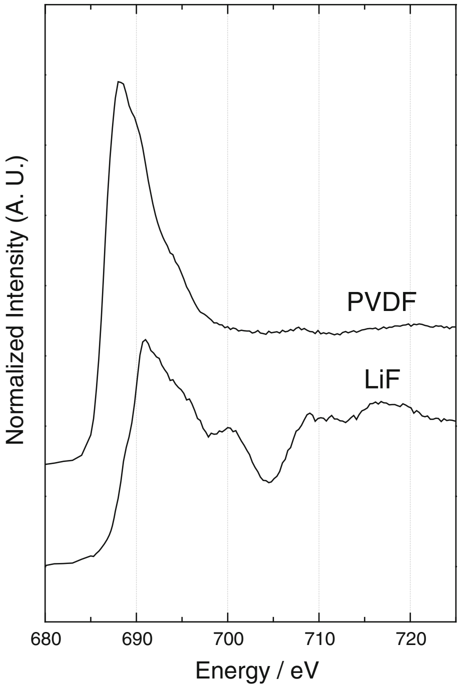


Fig. 2 Normalized F K-edge X-ray absorption spectra of LiF and PVDF

the as-prepared $LiMn_2O_4$ sample. For samples #2–#6, the charge or discharge cutoff was controlled by voltage. When the sample reached a preset voltage, the charge/discharge process was terminated, and the samples were recovered from the coin cell in an Ar-filled glove box. The preset voltages for the samples were 4.1, 4.5, 4.05, 3.0, and 2.0 V for samples #2–#6, respectively. The other three samples, which had different cycling processes with samples #1–#6, had the following charge/discharge conditions: (a) directly charged to 5.2 V, (b) directly discharged to 2.0 V, and (c) cycled seven times between 3.0 and 4.5 V. The charge/discharge curves for those three samples are not shown. The a–c notations correspond to those in Fig. 5.

Figure 4 shows the soft X-ray absorption spectra of samples #1–#6. The pristine sample (#1) shows a weak feature of Fluorine. The origin for the Fluorine feature of sample #1 is not clear. During charging (sample #2), the LiF feature becomes more distinctive (i.e., the valley grows deeper), but the valley near 705 eV flattens at the end of charge (sample #3), indicating that LiF is not the only component of the SEI layer. It is speculated that other components of the SEI layer dominate at the end of charge and cover the LiF formed in sample #2. This coverage results in the reduced feature of LiF in the soft X-ray absorption spectra. It should be noted that the sampling depth of the PEY mode is only approximately 5 nm, and the spectra are easily diminished when the LiF is covered by other components. In addition, the difference between the energy positions of the F K-edge X-ray absorption spectra of LiF in Fig. 2 and the energy positions from the samples in Fig. 4 also supports that LiF is not the only component of the SEI layer. The slightly higher energy positions from the samples in Fig. 4 are due to the combined signal from LiF and other components of the SEI or electrolyte salt containing Fluorine. In addition, the difference in the energy position among the samples #1–#6 indirectly indicates that the component of the SEI layer varies during charging and discharging.

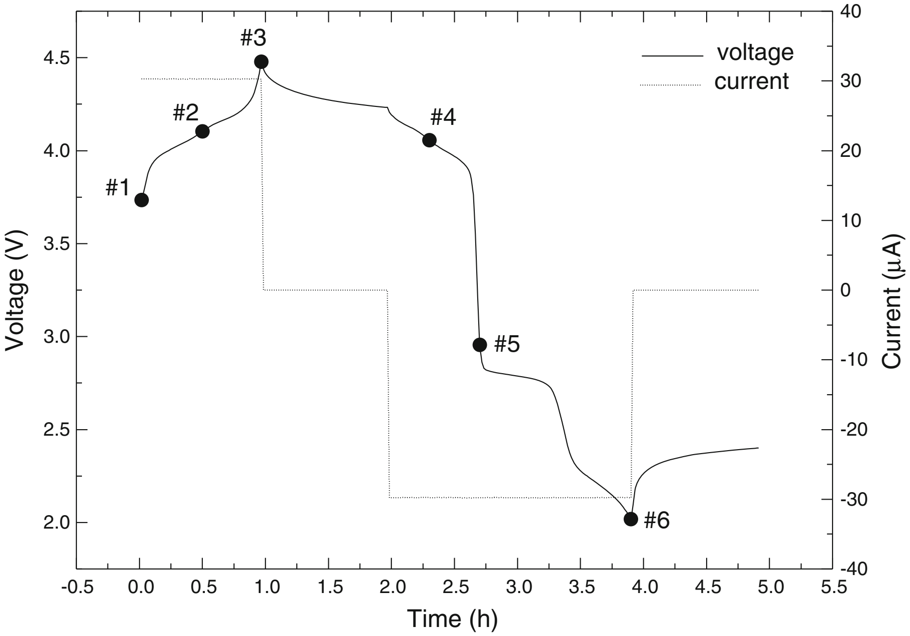
In the subsequent discharge, the LiF feature gradually increases, and the spectrum resembles that of LiF in Fig. 2 very closely when it reaches 3.0 V (sample #5). After further discharging to 2.0 V, the spectrum does not change much. There are two possibilities that might explain why the spectra do not change between samples #5 and #6. The first possibility is that the formation process is terminated after discharge to 3.0 V (sample #5). The second possibility is that the spectra will remain the same if the thickness of the LiF layer exceeds 5 nm (the sampling depth of the PEY mode).

Figure 5 shows the soft X-ray absorption spectra of the samples a–c. As mentioned previously, the samples a, b and c experienced different cycling processes compared with samples #1–#6, i.e., (a) directly charged to 5.2 V, (b) directly discharged to 2.0 V, and (c) cycled seven times between 3.0 and 4.5 V. The soft X-ray absorption spectrum of the sample #6 is included for comparison.

When $LiMn_2O_4$ was charged to an extreme voltage of 5.2 V, the LiF feature almost disappeared (Fig. 5, a), and the valley near 705 eV was very much diminished. The main edge, however, still remained near 691 eV. It may originate from the combined signal from LiF and other components of the SEI containing Fluorine. On the other hand, the sample directly discharged to 2.0 V (Fig. 5b) shows a clear valley near 705 eV. The valley near 705 eV becomes clearer when the sample is cycled multiple times between 3.0 and 4.5 V (Fig. 5c). From the spectra in Figs. 4 and 5, it is reasonable to state that LiF formation mainly takes place during discharge. In addition, LiF formation is accelerated if the discharge step follows a charge step. During charging, electrolyte decomposition is promoted, and the decomposition products may provide the necessary ingredients for LiF formation.

Previously, it was demonstrated that LiF forms at the surface of a $LiNi_{0.85}Co_{0.15}O_2$ electrode after cycling for 2–8 weeks at elevated temperature [18]. The SEI formation on the $LiMn_2O_4$ was also presented in other literatures and one of the components of SEI layer is LiF, but it was cycled at elevated temperature [7–9, 12, 13]. Other literature reporting on the SEI layer of $LiMn_2O_4$ cycled at room temperature mainly discuss only about the composition of

Fig. 3 Charge/discharge curve of a $LiMn_2O_4$ electrode prepared by ESD



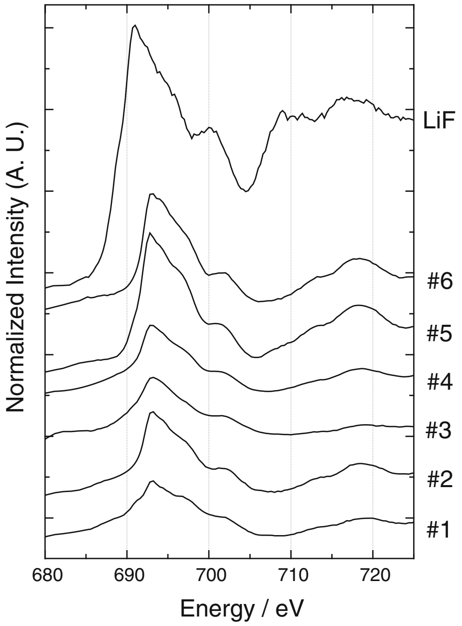


Fig. 4 Normalized F K-edge X-ray absorption spectra of $LiMn_2O_4$

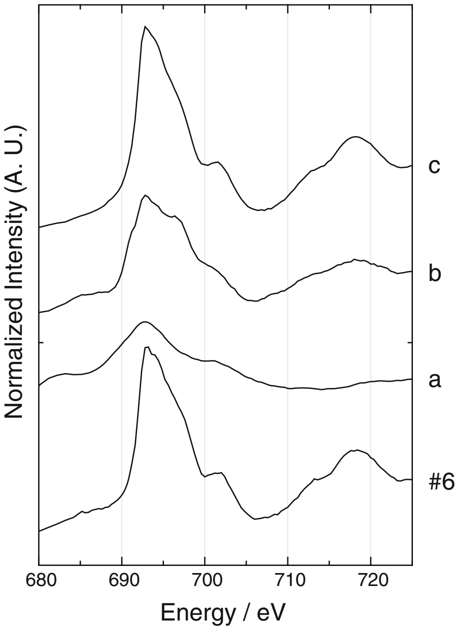


Fig. 5 Normalized F K-edge X-ray absorption spectra of $LiMn_2O_4$: (*a*) charged to 5.2 V, (*b*) directly discharged to 2.0 V, (*c*) cycled seven times between 3.0 and 4.5 V

SEI layer [3, 10]. However, in this study, it is shown that the LiF layer is present not only in the aged samples but also in the samples cycled only once at room temperature. Further, this study mainly focused on the formation process of LiF layer. The LiF formation takes place at a very early stage of cycling, and it agrees very well with previous results that have used in situ bending beam method (BBM) and electrochemical quartz microbalance (EQCM) [17] to show that the SEI layer is formed during the first charge and discharge cycle.

4 Conclusion

The formation of LiF at the surface of $LiMn_2O_4$ electrodes was investigated by soft X-ray absorption spectroscopy at the F K-edge. By using ESD, the X-ray absorption spectra originating from PVDF binder was eliminated. The F K-edge spectra collected from samples charged/discharged to different charging states showed that LiF formation mainly takes place during discharge. In addition, LiF formation is accelerated if the discharge step follows a charge step. This study shows that LiF is present not only in the aged samples but also in the samples cycled only once. LiF formation takes place at a very early stage of cycling.

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