Operando Soft X-ray Absorption Spectroscopic Study of an All-solid-state Lithium-ion Battery Using a NASICON-type Lithium Conductive Glass Ceramic Sheet

Keisuke YAMANAKA, a, * Koji NAKANISHI, a Iwao WATANABE, b and Toshiaki OHTA a

a SR Center, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan
b Office of Society-Academia Collaboration for Innovation, Kyoto University, Gokashou, Uji, Kyoto 611-0011, Japan
* Corresponding author: k-yamana@fc.ritsumei.ac.jp

ABSTRACT
An electrochemical cell was developed for operando soft X-ray absorption spectroscopic (XAS) study of an all-solid-state lithium-ion battery. Operando XAS experiments were performed for a battery using LiMn2O4 as a cathode material and a NASICON-type lithium conductive glass ceramic sheet (LICGC) as a solid electrolyte. O K-edge, Mn L-edge and Ti L-edge XAS spectra were taken during the charging process up to 2.2 V. Detailed analysis of the XAS spectra revealed that the valence change from Mn3+ to Mn4+ occurred during charge with simultaneous change in the spectrum of O K-pre-edge region. Ti L-edge spectra revealed a partial change from Ti4+ to Ti3+ in the LICGC at the anode side, indicating a rather dispersed anode formation.

1. Introduction
Rechargeable lithium ion batteries (LIBs) are now widely used for energy sources for mobile phones, laptop computers and electric vehicles. Charge/discharge processes in the practical batteries are generally complicated and a number of techniques have been applied to elucidate their mechanisms. X-ray Absorption Spectroscopy (XAS) is one of the powerful methods for characterization of LIBs because it provides local electronic and structural information around specific elements in batteries. Although ex situ experiments are useful to characterize the charged and discharged states, they can only provide information of the relaxed equilibrium states, which might be different from the real dynamic states. Operando experiments are promising to reveal the dynamic states.

In fact, operando hard XAS has been widely used for rechargeable batteries to investigate local structures and valence states of transition metal ions in cathode materials during charge/discharge processes. Recently, soft XAS has attracted attention since it provides additional valuable information about oxygen and transition metal ions which cannot be obtained by hard XAS only. However, it is difficult to perform operando soft XAS experiment to probe materials in working batteries owing to the very short penetration depth of soft X-rays.

Another inherent problem of the soft XAS experiments is the necessity of the vacuum environment for the sample, which requires a proper film to protect the XAS equipment from leakage of electrolyte materials, especially in the case of liquid electrolyte. Several challenges to perform operando soft XAS experiment have been reported for liquid electrolyte systems.1-4

Recently, all-solid-state batteries have been developed using polymer and/or ceramic ion conductive sheets.7-10 They are regarded as promising rechargeable batteries with greater safety and higher energy density, although their power densities are inherently low because of large resistances between electrodes and solid electrolyte.11,12 One possible way to solve this problem is to generate self-formed anode inside of the solid electrolyte.13,14 The anode formation in solid electrolyte has been reported15-17 using a Li+ conductive glass ceramic (LICGC) solid electrolyte sheet based on NASICON-type structure, Li2O·Al2O3·SiO2·P2O5-TiO2·GeO2. The structure and compositional distribution in the LICGC film were characterized by Hoshina and others.18

From experimental point of view, operando soft XAS experiments of these all-solid-state batteries are much easier than those using liquid electrolyte, because no care is necessary for the leakage of electrolyte into vacuum chamber.9

In this paper, we prepared an all-solid-state battery using the LICGC as an electrolyte and LiMn2O4 as a cathode and performed operando soft XAS experiments to demonstrate how operando experiments are useful for the detailed analysis of charge/discharge mechanisms. LiMn2O4 was selected as the cathode because its behavior in charge/discharge processes are rather simple and straightforward.20

2. Experimental
Mirror-polished LICGC sheets (AG-01) were purchased from OHARA Inc., Kanagawa, Japan21 with a size of 10 mm × 10 mm and a thickness of 180 µm. The cathode material, LiMn2O4 thin film was prepared with the sol-gel method, which has good electrochemical properties in a liquid electrolyte system.22 Raw gel material, containing Li-Mn-O sol were spin-coated on one side of the LICGC sheet and heated at 500°C in air for 30 min to form a thin LiMn2O4 film. By repeating this procedure, three samples were prepared with different cathode thicknesses: 50, 250, and 500 nm. Hereafter, we denote these samples as T50, T250 and T500, respectively. Their thicknesses were estimated by using a scanning electron microscope (SEM) (TM3030, Hitachi), equipped with an electron probe microanalyzer (EPMA). The constitution of the all-solid-state battery is schematically illustrated in Fig. 1(a) and the SEM image of a part of the cathode and LICGC of T500 is also shown. As the current collectors, ca. 10 nm thick Al film was deposited on both sides of each sample. Then, the battery was set in a home-made operando XAS equipment (see Fig. 1(b)).

All the operando soft XAS experiments were performed at the soft X-ray diffraction grating beamline, BL-11 of the SR center in Ritsumeikan University, which covers the photon energy range from...
50 to 1200 eV by replacing three kinds of gratings. In BL-11, three kinds of detection modes are available: (1) partial electron yield (PEY) mode, using a MCP (Micro Channel Plate: Photonics USA Inc.) having a retarding grid in front of it, (2) total electron yield (TEY) mode, monitoring the sample leak current with a pico-ammeter, and (3) partial fluorescence yield (PFY) mode, which uses a silicon drift detector (SDD). For the present experiments, the PFY mode was exclusively used since this is much more bulk-sensitive than the other two modes.

Operando soft XAS measurements were performed continuously during charging process in the constant current mode (0.2 µA/cm² for sample T50, and 0.5 µA/cm² for samples T250 and T500) up to the cut-off voltage of 2.2 V, using an automatic charge/discharge equipment (SD-8, Hokuto Denko). It took about 25 min. to obtain a spectrum in the energy region from 515 to 665 eV covering both O K-edge and Mn L-edge, and about 12 min. for a Ti L-edge spectrum from 435 to 530 eV. We obtained 16 and 17 pieces of O K-edge and Mn L-edge XAS spectra during charge for samples T50 and T250, respectively, and 17 and 21 pieces of Ti L-edge spectra for samples T50 and T250, respectively. Among these three samples, it turned out that T500 was too thick to monitor the spectral change during charge, thus its spectral and electrochemical results will not be given here.

3. Results and Discussion

3.1 Charging curves

Figure 2 shows the charging curves for samples T50 and T250 with the cathode thicknesses of 50 and 250 nm, respectively. These profiles are in good agreement with that of liquid electrolyte cell using LiMn₂O₄ thin film as a cathode. The voltage plateau was observed at 1.5–2.0 V, which is reasonable because the redox potential of a LICGC sheet is 2.35 V (vs. Li/Li⁺) and that of LiMn₂O₄ is 4.0–4.2 V (vs. Li/Li⁺). The charge stored were 1.8 and 4.3 mAh for samples T50 and T250, respectively. Considering the volume of the cathode (10 mm × 10 mm × 50 nm or 250 nm), the estimated charge capacities were 90 and 42 mAh/g for T50 and T250, respectively, corresponding to 61% and 28% of their theoretical capacity of 148 mAh/g.

3.2 Mn L-edge XAS spectra

Figure 3 shows operando XAS spectra at Mn L-edge for samples T50 and T250. For comparison, spectra from MnO, Mn₂O₃, Li₂MnO₃ are also shown as the references of Mn²⁺, Mn³⁺, Mn⁴⁺ compounds. For both samples, the peak at 643 eV was enhanced by charging, indicating the increase of the Mn⁴⁺ component. This means that Mn ion compensates the charge change due to the Li⁺ release. Note that the spectral change is more significant for T50 than T250, even though the current flowed for T250 was much larger than that for T50. This result suggests that the probing depth of Mn L-edge PFY mode is shorter than 250 nm and the spectra obtained do not reflect the chemical state of the whole cathode. No difference was detected between Mn L-edge spectra from T500 before and after charge (not shown). These results indicate that charging reaction does not proceed homogeneously, but preferentially at the interface between the cathode and solid electrolyte, where is the deepest position in the cathode film of the present arrangement.

3.3 O K-edge XAS spectra

Figures 4(a) and (b) show operando XAS spectra at O K-edge for samples T50 and T250, respectively. Two characteristic peaks appear at 529 and 531 eV in the pre-edge region, as shown in Fig. 4(c), whose relative intensity ratios are different between T50 and T250. The peak at 531 eV in the spectrum from T50 is more enhanced, which happens to be the same energy as that for the substrate, LICGC, as shown in the same figure. In contrast, the
**Figure 3.** Evolution of Mn $L_3$-edge XAS spectra with charge for the samples T50 (a) and T250 (b). Mn $L_3$-edge XAS spectra before charge (black line) and after charge (red line) (c), together with those of reference compounds, MnO, Mn$_2$O$_3$, and Li$_2$MnO$_3$.

**Figure 4.** Evolution of O $K$-edge XAS spectra with charge for T50 (a) and T250 (b). O $K$-edge XAS spectra before charge (black line) and after charge (red line) (c), together with that of LICGC.
spectral profile of T250 is quite similar to that of pristine LiMn$_2$O$_4$, reported by Yoon and others, indicating that the probing depth of O K-edge fluorescence XAS is less than 250 nm and the contribution from the LICGC can be neglected.

3.4 Ti L$_3$-edge XAS spectra

According to the previous papers, charging induces Li insertion into the LICGC, and self-formation of the negative electrode, which can be monitored by charge compensation of Ti$^{4+}$ $\rightarrow$ Ti$^{3+}$. Figure 5 shows operando XAS spectra at Ti L$_3$-edge during charge for samples T50 and T250. Spectra were obtained by irradiating X-rays onto the negative electrode side. Comparing the spectra before and after charge, we found almost no change from T50, but significant shift to the lower energy side for those from sample T250.

3.5 Analysis of the charging mechanism

In order to extract the spectral changes induced by the charging reaction, Mn L$_3$- and O K-edge spectra before charge are regarded as the backgrounds and are subtracted from the corresponding raw spectral data obtained during charging process. The background-subtracted Mn L$_3$-edge spectra, as shown in Fig. 6, indicate the increase in Mn$^{4+}$ peak intensity by charge.

Figure 7 shows the background-subtracted O K-edge spectra from T50 and T250. The spectral features of T50 are more complicated than those of T250. This is because the thickness of T50 is smaller than the detection depth of O K-edge fluorescence XAS and the spectra contain the contribution from oxygen in the solid electrolyte LICGC, whose chemical state changes by Li insertion. In the pre-edge region of O K-edge XAS spectra, the peaks at 529 and 531 eV are assigned to the transitions from O 1s to hybridized orbitals of Mn 3d and O 2p, whose intensities are known to be closely related to the amount of Mn 3d vacancy since the charge transfer from O 2p to Mn 3d increases with the Mn 3d vacancy.

Figure 8 shows the intensity plots of the O K-pre-edge peak at 529 eV and Mn$^{4+}$ peak at 643 eV as a function of charge for T50 and T250, together with the charging curves. This result clearly shows that the change of O K-edge spectra is closely related to that of the Mn valence state, indicating that the valence change of Mn is primary responsible for the charge compensation.

The chemical state of the anode was also monitored by using Ti L-edge spectra as shown in Fig. 5. The peaks in T250 spectra shifted to lower energy side by 0.3 eV after the charge, which is much smaller than the spectral shift of ca. 1.5 eV, reported by Yamamoto and others by using EELS technique. Unfortunately, there is no appropriate reference compound for Ti$^{3+}$. If we assume that the peak shift of 1.5 eV obtained by the EELS method corresponds to the change from Ti$^{4+}$ to Ti$^{3+}$ states, our result for T250 indicates a partial reduction of Ti with Li insertion. The distribution of the Li inserted into the electrolyte is not uniform. From a half cell experiment, the Li ion was known to be concentrated at the anode collector side. If it holds for the present experiment, we can expect distinct change even in the sample of T50. However, almost no change was observed for T50 and a slight shift for T250. This indicates the inclination in Li concentration is rather mild even if there is some inhomogeneity. In order to investigate the reaction mechanism of the self-forming anode in more detail, it is necessary to collect the data for the LICGC samples with different thicknesses and with different charges.

3.6 Features of the operando soft XAS experiments

Ex situ experiments have been widely used to characterize the batteries during charge/discharge processes. They are useful to provide information of the averaged chemical states. However, for the ex situ experiments we have to prepare several batteries with different SOC’s (state of charge) and disassemble them to take out samples. Unless the chemical and/or electronic state is homogeneous among the samples, the ex situ experiments are not reliable.

**Figure 5.** Evolution of Ti L-edge XAS spectra with charge for T50 (a) and T250 (b). Ti L-edge spectra before charge (black line) and after charge (red line) (c).

**Figure 8.** Shows the intensity plots of the O K-pre-edge peak at 529 eV and Mn$^{4+}$ peak at 643 eV as a function of charge for T50 and T250, together with the charging curves.
Figure 6. Background-subtracted Mn $L_3$-edge XAS spectra for T50 (a) and T250 (b). The spectra before charge are regarded as the background.

Figure 7. Background-subtracted O $K$-edge XAS spectra for T50 (a) and T250 (b). The spectra before charge are regarded as the background.

Figure 8. Intensity plots of the O $K$-pre-edge peak at 529 eV (red circle) and Mn$^{4+}$ peak at 643 eV (blue circle) as a function of charge for T50 (a) and T250 (b). Corresponding charging curves are also shown in the same figures.
In contrast, a remarkable advantage of the operando XAS experiment is the ability to monitor changes in the chemical and/or electronic state of a sample at the same position. It is easier to detect small changes which occur during charging process and the data are more reliable than those of the ex situ experiments. Another advantage is the capability of monitoring chemically unstable dynamic state. Note that the ex situ experiments provide us the data for chemically relaxed state and it may not be the same as the dynamic state proceeding in the batteries. Thus, it is desirable to confirm the ex situ results by using operando experiments.

4. Conclusions

We performed operando soft XAS experiments for the lithium-ion battery using LICGC as a solid electrolyte and LiMn$_2$O$_4$ as a cathode. O K-edge and Mn L-edge XAS spectra obtained during charge revealed that the increase in the O K-pre-edge peak intensity is concomitant with the oxidation of Mn ion. Ti L-edge spectra from self-formed anode could also be observed which indicated a partial reduction from Ti$^{4+}$ to Ti$^{3+}$. The self-formed anode in LICGC was not concentrated in the electrolyte/collector interphase, but rather diffused in LICGC. The present experiment demonstrated the potential of operando soft XAS measurements for detailed analyses of all-solid-state batteries.

Acknowledgment

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) under the Research and Development Initiative for Scientific Innovation of New Generation Batteries 2 (RISING2) project. The authors thank Dr. Kadono for experimental support of the SEM observation.

References

1. J. Gao, M. A. Lowe, Y. Kiya, and H. D. Abruna, J. Phys. Chem. C, 115, 25132 (2011).
2. M. A. Lowe, J. Gao, and H. D. Abruna, RSC Adv., 4, 18347 (2014).
3. D. A. Torit, M. R. Antonio, P. Schilling, R. Tittsworth, and D. A. Scherson, Electrochim. Acta, 47, 3195 (2002).
4. M. Cuisinier, P. E. Cabedou, S. Evers, G. He, M. Kolbeck, A. Garsuch, T. Bölin, M. Balasubramanian, and L. F. Nazar, J. Phys. Chem. Lett., 4, 3227 (2013).
5. K. Nakamato, D. Kato, H. Arai, H. Tanida, T. Mori, Y. Otikasa, Y. Uchimoto, T. Obta, and Z. Ogumi, Rev. Sci. Instrum., 85, 084103 (2014).
6. K. Nakamato, H. Tanida, H. Komatsu, I. Takahashi, Y. Tamenori, K. Tsuruta, T. Yaji, M. Yoshimura, K. Yamamoto, S. Kitazaki, Y. Otikasa, K. Kojima, K. Yamamoto, Y. Uchimoto, Z. Ogumi, and T. Obta, Adv. X-ray Chem. Anal., Japan, 48, 403 (2017).
7. Y. Inaguma, L. Q. Chen, M. Isb, T. Nakamura, T. Uchida, H. Ikuta, and M. Wakahara, Solid State Commun., 86, 689 (1993).
8. P. Birke, S. Scharner, R. A. Huggins, and W. Weppner, J. Electrochem. Soc., 144, L167 (1997).
9. Y. Iriyama, C. Yada, T. Abe, Z. Ogumi, and K. Kikuchi, Electrochem. Commun., 8, 1287 (2006).
10. C. Yada, Y. Iriyama, T. Abe, K. Kikuchi, and Z. Ogumi, Electrochem. Commun., 11, 413 (2009).
11. N. Ohta, K. Takada, L. Zhang, M. Osada, and T. Sasaki, Adv. Mater., 18, 2226 (2006).
12. A. Sakuda, A. Hayashi, and M. Tatsumisago, Chem. Mater., 22, 949 (2010).
13. Y. Amiki, F. Sagane, K. Yamamoto, T. Hirayama, M. Sudoh, M. Motoyama, and Y. Iriyama, J. Power Sources., 241, 583 (2013).
14. K. Yamamoto, Y. Iriyama, T. Asaka, T. Hirayama, H. Fujita, K. Nonaka, K. Miyahara, Y. Sugita, and Z. Ogumi, Electrochem. Commun., 20, 113 (2012).
15. K. Yamamoto, R. Yoposhida, T. Sato, H. Matsumoto, H. Kurobe, T. Hamaanaka, T. Kato, Y. Iriyama, and T. Hirayama, J. Power Sources., 266, 414 (2014).
16. A. Shimoyamada, K. Yamamoto, R. Yoshida, T. Kato, Y. Iriyama, and T. Hirayama, Microscopy, 1 (2015).
17. K. Yamamoto, Y. Iriyama, and T. Hirayama, Microscopy, 1 (2016).
18. K. Hoshina, K. Yoshima, M. Kotobuki, and K. Kanamura, Solid State Ionics, 209–210, 30 (2012).
19. X. Liu, D. Wang, G. Liu, V. Srinivasan, Z. Liu, Z. Hussain, and W. Yang, Nat. Commun., 4, 2568 (2013).
20. W. S. Yoon, K. Y. Chung, K. H. Oh, and K. B. Kim, J. Power Sources, 119–121, 706 (2003).
21. http://www.ohara-inc.co.jp/jp/product/electronics/licgc.html
22. Y. H. Rho, K. Kanamura, and T. Umegaki, J. Electrochem. Soc., 150, A107 (2003).
23. K. Yamana, M. Yoshimura, K. Nakas, I. Watanabe, and T. Obta, Adv. X-ray Chem. Anal., Japan, 48, 273 (2017).
24. Y. Xia and M. Yoshio, J. Power Sources, 66, 129 (1997).
25. M. F. de Groet, M. Grisoni, and J. C. Fuggle, Phys. Rev. B, 40, 5715 (1989).