

**State Analysis of Positive Electrode Active Material
in Lithium Ion Battery**

Introduction

Lithium ion batteries are a type of storage battery in which charging and discharging of the battery take place by desorption/insertion of lithium ions (Li⁺) from inside the structure of the active material. In recent years, the applications of lithium ion batteries have expanded dramatically, and active research is underway with the aims of achieving higher capacity, longer life, lower cost, and improved safety. The main materials of a lithium ion battery can be divided into the positive electrode, negative electrode, separator, and electrolytic solution. Among these, the active materials which are the main constituent materials of the electrodes are important elements for improving battery performance.

This article introduces an example of analysis to evaluate the chemical bonding state of the active material of the positive electrode of a lithium ion battery using a Shimadzu EPMA-8050G EPMA™ electron probe microanalyzer.

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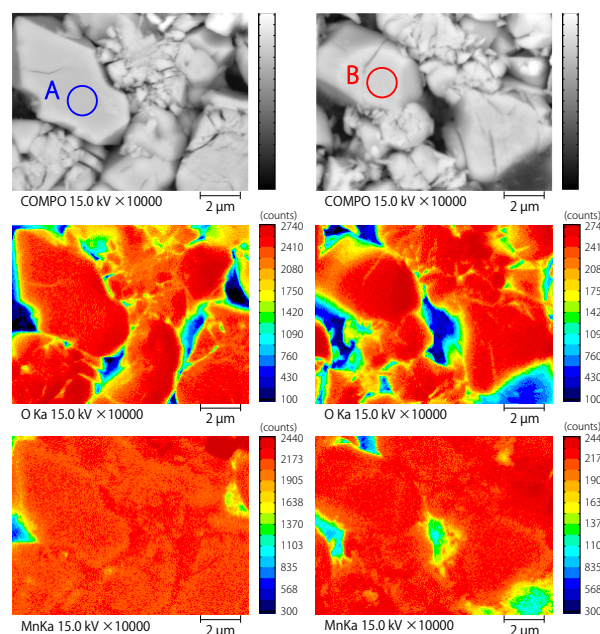
Analysis of Positive Electrode Surface

The object of this analysis was a positive electrode in which spinel-type lithium manganese oxide (LiMn₂O₄) was used as the active material. The separator-side surface of the electrode sheet was analyzed before assembling the cell, that is, in the "initial state" before charging/discharging, and in the "charged state" after the lithium ion battery cell was fabricated and then disassembled in the 100 % charged state.

Fig. 1 is the result of a mapping analysis showing the density distributions of O and Mn on the positive electrode surface in the initial state and the charged state. The left row of the figure shows the initial state, and the right row shows the charged state.

The composition of the active material in the initial state is LiMn₂O₄, but it is known that this composition changes to spinel-type λ-MnO₂ when Li is desorbed by the charging reaction⁽¹⁾. Therefore, in order to investigate the chemical bonding state, a state analysis of O and Mn was carried out for active material A

(initial state) and active material B (charged state). The results for O and Mn are shown in Fig. 2 and Fig. 3, respectively. Comparing the spectra of active materials A and B, a shift in the position of the peak wavelengths can be observed. A comparison in which the spectra of standard samples (STD) of LiMn₂O₄ and MnO₂ were overlaid on these spectra of the active materials revealed that the initial state was close to the peak wavelength position of the spectra of LiMn₂O₄, whereas the charged state was close to the peak wavelength position of MnO₂.



**Fig. 1 Mapping Analysis of Positive Electrode Surface
(Left: Initial State, Right: Charged State)**

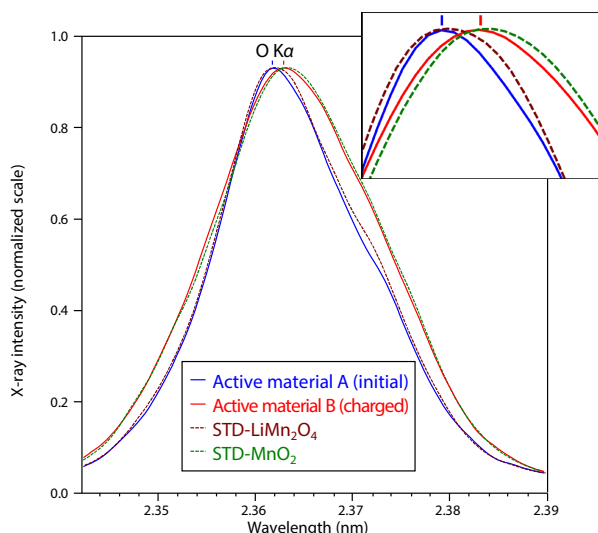


Fig. 2 Spectrum of O on Positive Electrode Surface and Enlarged View of Peak Tops

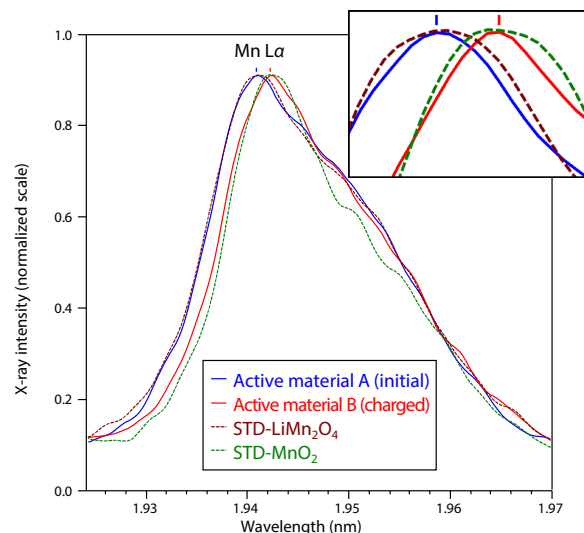


Fig. 3 Spectrum of Mn on Positive Electrode Surface and Enlarged View of Peak Tops

■ Analysis of Positive Electrode Cross Section

Next, the cross section of the positive electrode in the charged state was analyzed. Fig. 4 shows the mapping analysis results, including enlarged views of the active material. Here, in order to target microregions by reducing the primary X-ray emission volume, the accelerating voltage was set to 5 kV, and Mn was measured by using the L α -ray. The difference in contrast in the COMPO image in Fig. 4 is mainly due to a difference in the mean atomic number. However, differences in contrast can also be seen in the region at the upper left, which includes a and b, and in the region at the lower right, which includes c and d, even though the active material particles are the same. In combination with this, the element distribution images of O and Mn also show differences in the intensity values of the respective elements. Moreover, since a fine striated pattern could also be observed in the COMPO image, the possibility that differences in the microstructure appeared in these results is conceivable.

In order to investigate the chemical bonding state, a state analysis of microregions a to d in the COMPO image in Fig. 4 was carried out. Fig. 5 and Fig. 6 show the spectra for O and Mn, respectively. Comparing the peak wavelength positions when the spectra of the standard samples of LiMn₂O₄ and MnO₂ were overlaid on these results, a and b were located at positions close to LiMn₂O₄, and c and d are close to MnO₂. Furthermore, the Mn spectrum of c in Fig. 6 has a spectrum shape that appears to overlap the peak

wavelengths approximating a and b and the peak wavelength approximating MnO₂. This indicates a condition in which multiple chemical bonding states are mixed in the process of Li desorption by the charging reaction. Thus, it is possible to obtain information concerning the chemical bonding state from a designated X-ray spectrum by EPMA, and it is also possible to investigate the differences in the chemical bonding state of microregions within the same active material particle.

■ Conclusion

Using EPMA, a mapping analysis and state analysis were carried out for the surface and cross section of the positive electrode sheet of a lithium ion battery in which spinel-type lithium manganese oxide (LiMn₂O₄) was used as the active material. A high-magnification mapping analysis of the active material particles revealed that differences exist in the component concentration and microstructure. It was also possible to capture the state changes of the component elements that accompany charging by analyzing the chemical bonding state, targeting microregions of the surface (outside) and cross section (interior) of the active material particles. As demonstrated here, EPMA is a useful tool for research and development, quality control in the manufacturing process, and failure analysis of the various materials of lithium ion batteries.

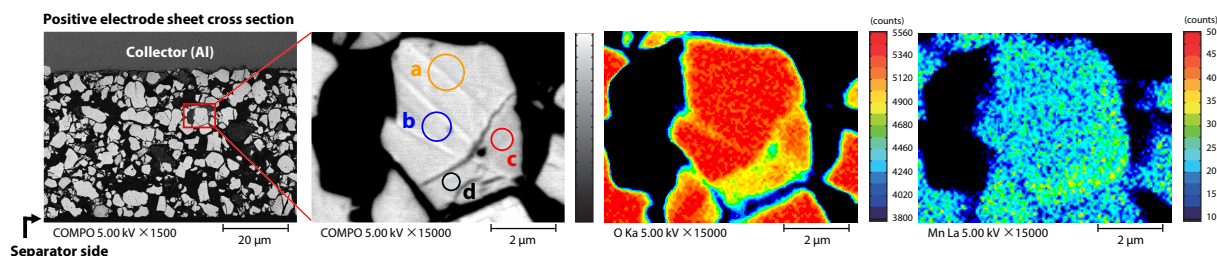


Fig. 4 Mapping Analysis of Positive Electrode Cross Section in Charged State

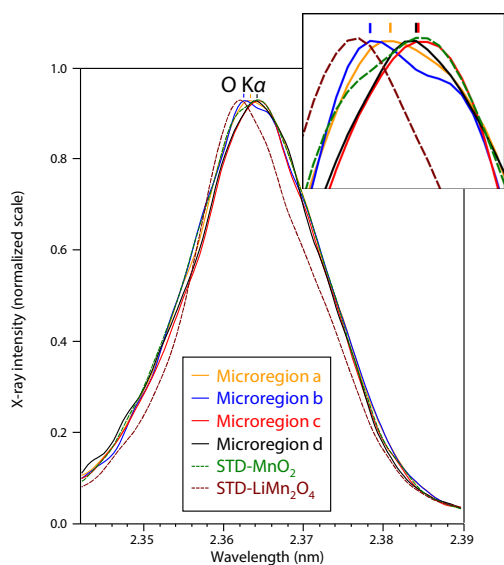


Fig. 5 Spectrum of O in Positive Electrode Cross Section and Enlarged View of Peak Tops

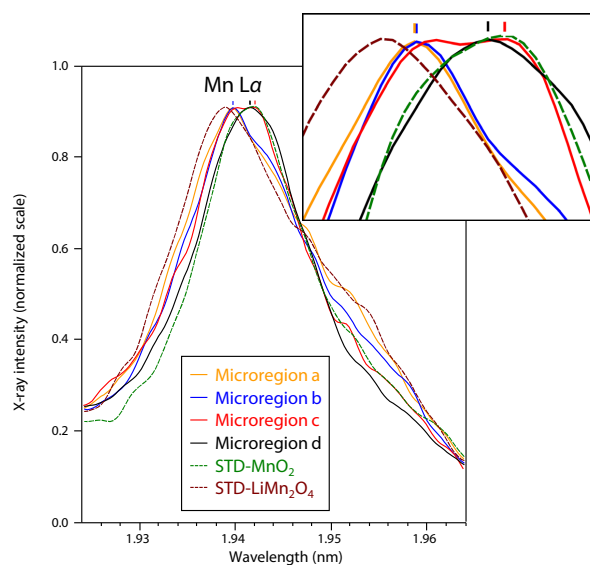


Fig. 6 Spectrum of Mn in Positive Electrode Cross Section and Enlarged View of Peak Tops

(Samples were provided by the National Institute of Advanced Industrial Science and Technology (AIST))

<References>

- (1) Kiyoshi Kanamura, Lithium Ion Batteries for Hybrids Vehicles (2015)

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