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Application News

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Electron Probe Microanalyzer EPMA-8050G

Analysis of Positive Electrode of Lithium Ion Battery

Introduction

Lithium ion batteries (LIB) are storage batteries in which the cell is charged and discharged by desorption/insertion of lithium ions (Li^+) in the structure of the active material. The applications of LIB have expanded dramatically in recent years, and active research is underway with the aims of achieving higher capacity, longer life, lower cost, and improved safety. The main components of a LIB are the positive electrode, negative electrode, separator, and electrolytic solution, and among these, the positive electrode is the key element for enhanced performance. The positive electrode has a structure in which a mixture of the active material, binder, and conductive additive are coated on a collector made of aluminum foil. Evaluation of the distribution of these components is important in improvement of cell performance, quality control, and failure analysis.

This article introduces an example of analysis of the positive electrode of a LIB using a Shimadzu EPMA-8050G EPMA™ electron probe microanalyzer.

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Positive Electrode Materials

In positive electrodes, a material which is capable of maintaining a stable structure during desorption/insertion of Li^+ is used as the active material. The mainstream active materials in the market are lithium nickel cobalt manganese oxide ($Li(Ni\text{-}Co\text{-}Mn)O_2$), lithium nickel cobalt aluminum oxide ($Li(Ni\text{-}Co\text{-}Al)O_2$), spinel-type lithium manganate ($LiMn_2O_4$), and olivine-type lithium iron phosphate ($LiFePO_4$)(1).

Analysis of Positive Electrode Surface

The object of this analysis is a positive electrode of a lithium ion battery cell which was prepared using the materials shown in Table 1, and was disassembled in the 100 % charged condition. The active material of the positive electrode is spinel-type lithium manganate ($LiMn_2O_4$). Because this electrode is inexpensive, offers highsafety, and is suitable for large capacity discharge, it is widely used in rechargeable batteries (secondary batteries) of hybrid electric vehicles.

Fig. 1 is the result of a mapping analysis of the surface of this positive electrode and shows the distribution of the main elements. O and Mn show the distribution of the active material, F shows the binder and supporting electrolyte ($LiPF_6$), C shows the binder and conductive additive, and P shows the supporting electrolyte.

Table 1 Materials of Lithium Ion Battery

Class		Material
Positive electrode	Active material	$LiMn_2O_4$
	Collector	Al
	Binder	PVDF
	Conductive additive	Acetylene black
Separator		3-layer microporous membrane
		Glass filter
Electrolytic solution	Supporting electrolyte	$LiPF_6$
	Solvent	EC/DEC
	Additive	VC

(Sample provided by the National Institute of Advanced Industrial Science and Technology (AIST).)

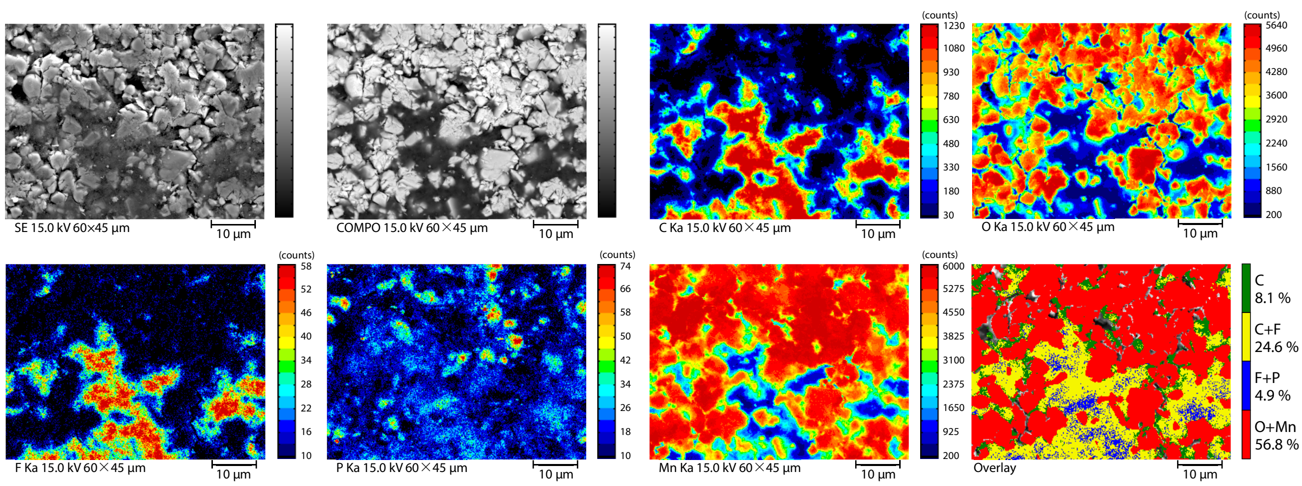

Fig. 1 Mapping Analysis of Positive Electrode Surface

Analysis of Positive Electrode Cross Section

Next, a cross-sectional sample of the positive electrode was prepared and analyzed. Fig. 2 is the result of a mapping analysis of the positive electrode cross section. In all the element distribution images, the upper side is the aluminum foil of the collector and the lower side has a composition consisting mainly of the active material. Comparing the distributions of each element, the distributions of C and F, O and Mn, and F and P are generally in agreement. Therefore, the area ratios of the respective elements can be represented by the overlay at the lower right in Fig. 2, in which areas where C and F overlap (binder) are shown in yellow, areas where O and Mn overlap (active material) are shown in red, areas where F and P overlap (supporting electrolyte) are shown in blue, and other C-rich areas (conductive additive) are shown in green. Although both the binder and the electrolytic solution contain F, if F is identified from the combination of its distribution with C or P, it can be understood that F is concentrated in the collector side as part of the electrolytic solution. Similarly, C is present in both the binder and the conductive additive, but can be identified from the combination of its distribution with F. Fig. 3 shows the result of a mapping analysis in which the area enclosed by the yellowish-green square in the COMPO image in Fig. 2 (top row, center) was magnified 10,000 times. Not only coarse particles with sizes of several µm, but also fine particles with sizes of less than 1 µm, the condition of boundaries and the element distribution can be observed.

Conclusion

A mapping analysis of the surface and cross section of a positive electrode of a lithium ion battery, in which spinel-type lithium manganate ($LiMn_2O_4$) was used as the active material, was carried out by EPMA. The distributions of the active material, binder, conductive additive, and electrolytic solution could be understood, and it was also possible to evaluate the fine particles and boundaries under high magnification. Thus, EPMA is an effective tool for research and development of the various materials of LIB, quality control in the manufacturing process, and failure analysis.

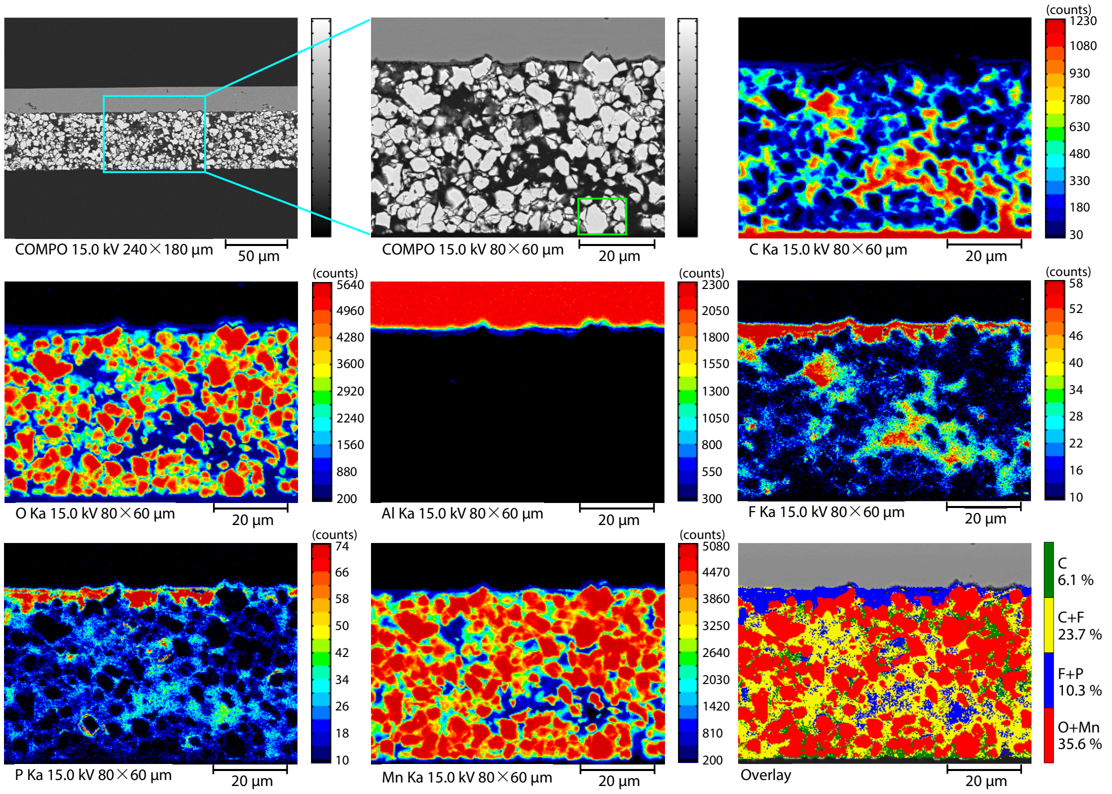

Fig. 2 Mapping Analysis of Full Positive Electrode Cross Section

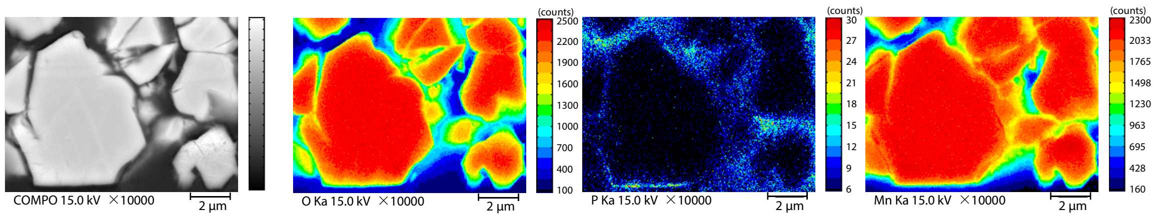

Fig. 3 Enlarged Mapping Analysis of Active Material on Surface Side of Positive Electrode Cross Section

<Reference>
Noboru Oyama, Takuhiro Miyuki, Performance Evaluation of Lithium Ion Secondary Batteries (2019)

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