EPMA-8050G Electron Probe Microanalyzer

Application News

Element Distribution and Phase Analysis of Positive Electrode Active Materials in Black Mass

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User Benefits

◆ EPMA can be used to check for impurities, such as current collector foils, contained in black mass.

◆ Compounds formed by heat treatment can also be investigated by EPMA.

◆ The types of positive electrode active materials contained in black mass can be identified by using phase analysis.

■ Introduction

In recent years, use of lithium-ion batteries (LIBs) has increased as a result of the widespread adoption of smart devices and electrification of automobiles with the aim of achieving carbon neutrality. Although the materials used in batteries are obtained from valuable mineral resources, securing resources by battery recycling is required in order to reduce the risks associated with raw material procurement and the environmental impacts of industrial wastes. In particular, black mass, which is obtained from used LIBs, is a core resource for recycling rare metals such as Li (lithium) and Co (cobalt). An accurate evaluation of the quality of black mass is indispensable for enhancing the metal recovery rate and possibility of reuse. Understanding the metal content and the types and concentrations of impurities in black mass will contribute to optimization of the recycling process and stabilization of product quality.

This article introduces an example of an analysis of positive electrode active materials contained in black mass using an EPMA™ electron probe microanalyzer (EPMA-8050G).

■ Black Mass

"Black mass" refers to a powdery black material which is produced by the series of upstream processes such as battery discharge, crushing, and separation of recovered LIBs. Ideally, black mass would include only the positive electrode active material, but in practice, it is difficult to completely remove various impurities such as Al (aluminum) and Cu (copper) of current collector foils and resins contained in electrodes. However, since mixed impurities and compounds formed by heat treatment have an adverse effect on metal recovery efficiency and quality in the downstream process, careful management is required in process design [1].

Fig. 1 shows element distribution images obtained by mapping of the cross section of a black mass sample by EPMA. The distributions of the positive electrode active materials Ni (nickel), Mn (manganese), and Co, and the negative electrode active material C (graphite: carbon) can be confirmed from these images. It is also possible to observe the distributions of substances considered to be the P (phosphorus) of the electrolyte supporting salt (LiPF$_6$) and the iron (Fe) of the battery casing. Slight amounts of P and Fe (indicated by arrows ①), which seem to have originated from the LiFePO$_4$ positive electrode active material, can also be recognized. It can be understood that distribution of some Al of the positive electrode current collector foil, the battery casing or laminated film matches that of the F (fluorine) of the electrolyte supporting salt, and slight amounts of P, Co, and Ni (indicated by arrows ②) have adhered in surrounded area. In part of the positive electrode composite layer, S (sulfur), which is thought to be an electrolyte additive, displays a different distribution from Al and P. The Cu of the negative electrode current collector foil is distributed in a fibrous form, and is partially oxidized, and very slight amounts have adhered to the P and Fe in the surrounding area. Si (silicon) has formed oxides with Al.
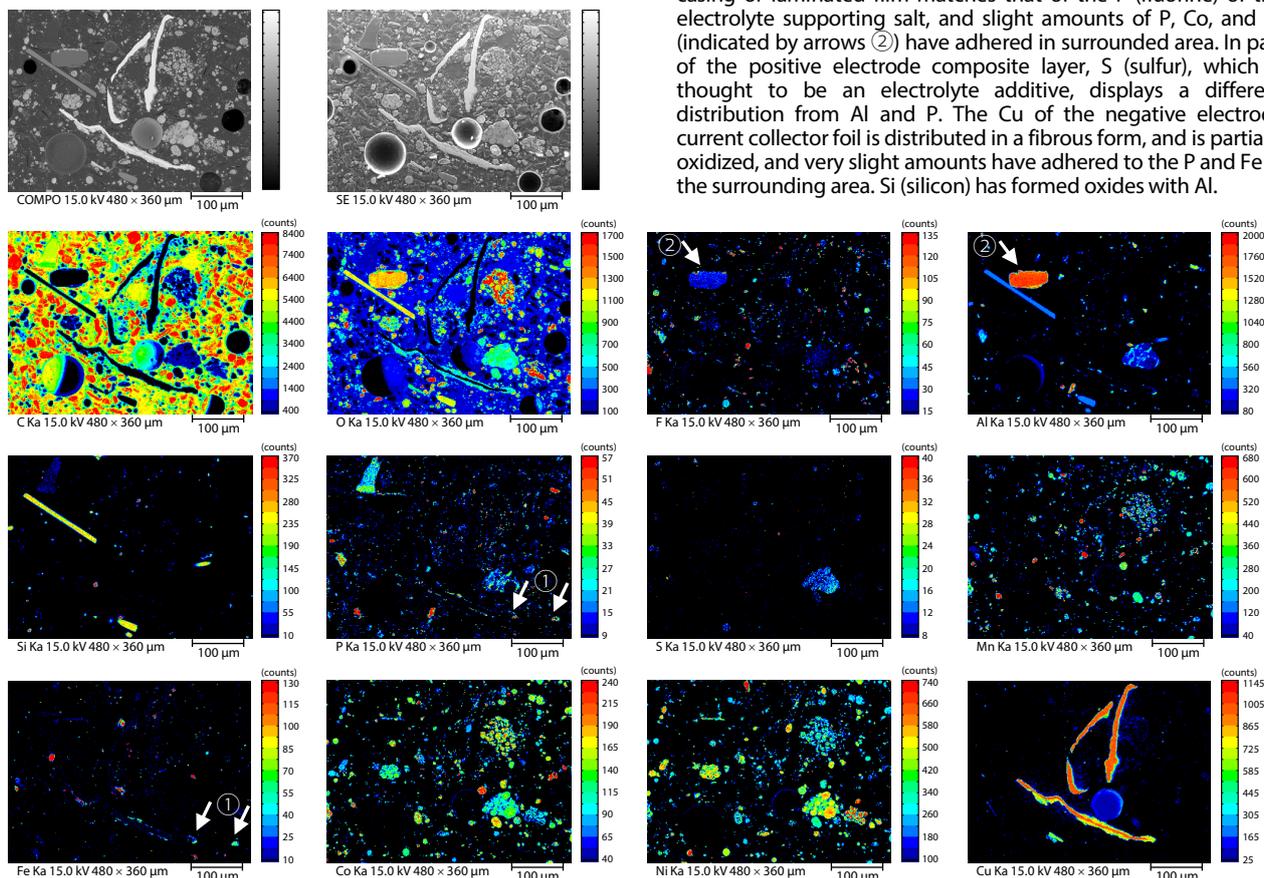

Fig. 1 Element Distribution of Black Mass

■ Active Materials in Black Mass

The compounds used in the positive electrode active materials of LIBs include olivine lithium iron phosphate (LFP: $LiFePO_4$), a ternary system of lithium nickel manganese cobalt oxide (NMC), and Ni-based lithium nickel cobalt aluminum oxide (NCA), among others. The active materials used in negative electrodes include graphite and silicon.

Since black mass is prepared using various types of recovered batteries as raw materials, it contains various positive electrode active materials. Representative NMC systems include multiple types (NMC811, NMC622, NMC523, NMC111), which have different properties (e.g., different energy densities [2]).

Fig. 2 shows a COMPO image and SE image of the black mass cross section, together with the element distribution images of the single elements, expressed by mass percentage concentration (wt%). The flat parts of the SE image and the areas with high concentrations of C (carbon) are the graphite of the negative electrode active material. Multiple active materials with different concentrations exist in the distributions of Ni, Mn, and Co, and particles with different concentrations can also be seen in the interior and exterior. In the Overlay image of Mn-Co-Ni, the overlaid color hues indicate two types of active materials, while the Overlay image of Al-Mn-Ni suggests the possibility of three types of active materials (indicated by the arrows).
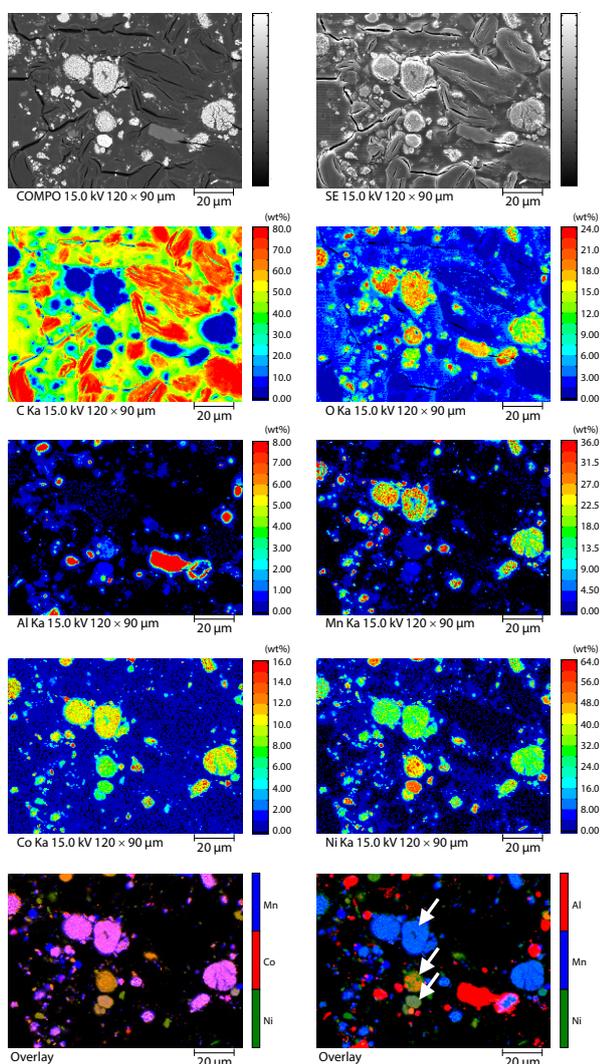

COMPO 15.0 kV 120 × 90 µm   20 µm

SE 15.0 kV 120 × 90 µm   20 µm

C Ka 15.0 kV 120 × 90 µm   20 µm   (wt%)

O Ka 15.0 kV 120 × 90 µm   20 µm   (wt%)

Al Ka 15.0 kV 120 × 90 µm   20 µm   (wt%)

Mn Ka 15.0 kV 120 × 90 µm   20 µm   (wt%)

Co Ka 15.0 kV 120 × 90 µm   20 µm   (wt%)

Ni Ka 15.0 kV 120 × 90 µm   20 µm   (wt%)

Overlay   20 µm

Overlay   20 µm

Fig. 2 Distribution of Active Materials in Black Mass

■ Phase Analysis of Positive Electrode Active Materials in Black Mass

Fig. 3 (a) and (b) are ternary scatter diagram of Ni-Co-Mn and Ni-Co-Al prepared from the element distribution images of Al, Mn, Co, and Ni in Fig. 2. Fig. 3 (a) shows the compound marks by theoretical concentration for ▼NMC811, ✕NMC622, ○NMC523 and □NMC111, while Fig. 3 (b) shows the compound mark by theoretical concentration for ⊠NCA.

In the ternary scatter diagram in Fig. 3 (a) and (b), clusters (point-sets) can be observed in the three regions of NMC811, NMC622, and NCA. Therefore, filters were set in those three regions. Fig. 3 (c) is a binary scatter diagram of Ni-Co shown by the color scheme of those filter settings, and indicates that the clusters of the three types of compounds are distributed from the positions of the compound marks toward the origin (upper left corner), and have the same composition ratios.

Fig. 3 (d) is the phase diagram given by filter setting, where the green region is NMC622, the brown region is NMC811, and purple region is NCA. This diagram demonstrates that it was possible to identify the types of positive electrode active materials in black mass.
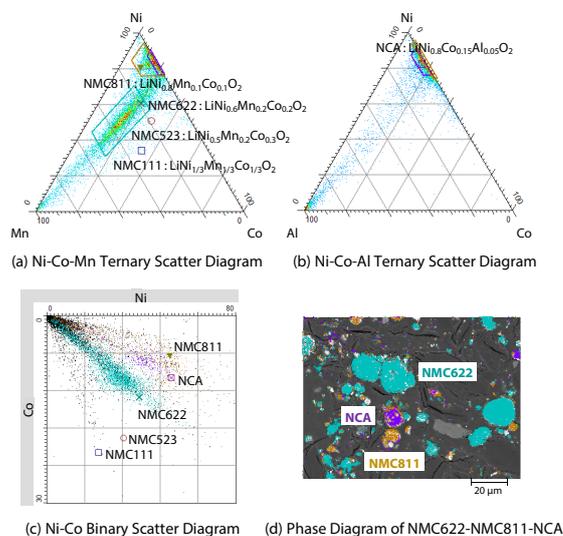

NMC811 : $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$
NMC622 : $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$
NMC523 : $LiNi_{0.5}Mn_{0.2}Co_{0.3}O_2$
NMC111 : $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

(a) Ni-Co-Mn Ternary Scatter Diagram

NCA : $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

(b) Ni-Co-Al Ternary Scatter Diagram

(c) Ni-Co Binary Scatter Diagram

(d) Phase Diagram of NMC622-NMC811-NCA

Fig. 3 Phase Analysis of Positive Electrode Active Materials in Black Mass

■ Conclusion

Recovered lithium-ion batteries contain various substances (e.g., active materials, electrolyte supporting salts), and even among the positive electrode active materials, multiple types exist, such as LFP, NMC, and NCA. Therefore, an understanding of the formation products and impurities contained in black mass is important for optimizing the battery recycling process. In research and development on black mass recycling technologies, the components and compound states of the impurities and formation products contained in black mass can be accurately identified by using a combination of element distribution images and phase analysis. This type of analysis makes it possible to optimize the heating and dissolution treatment conditions in the downstream process, contributing to lower costs and reduced environmental impacts in the recycling process, including wastewater and exhaust gas treatment.

<References>

1) Manabu Nishimura, et al.: Secondary Batteries, Kobelco Research Institute, No. 58, Apr., 17 (2024).
2) Taku Shiraishi: No. 1 Guide to Understanding State-of-the-Art Secondary Batteries, Gijutsu-Hyohron Co., Ltd., 151, 163 (2020).

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