

Application News

State Analysis of Positive Electrode Active Materials and Compounds in Black Mass

Satoshi Yoshimi

User Benefits

- ◆ The distribution of formation products by heat treatment of various components contained in black mass can be confirmed.
- ◆ The types of positive electrode active materials contained in black mass can be identified by using phase analysis and state analysis.
- ◆ The states of compounds contained in black mass can be inferred by state analysis.

■ Introduction

In recent years, use of lithium-ion batteries (LIBs) has increased as a result of widespread adoption of smart devices and electrification of automobiles with the aim of achieving carbon neutrality. While the materials used in batteries are obtained from costly mineral resources, battery recycling also plays an important role in reducing the risks associated with the procurement of raw materials and the environmental impacts accompanying industrial wastes. In particular, the black mass obtained from used LIBs is a core raw material for recycling rare metals such as Li (lithium) and Co (cobalt), and an accurate evaluation of black mass quality is indispensable for enhancing the 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 a state analysis of microregions of the positive electrode mix contained in black mass using an EPMA™ electron probe microanalyzer (EPMA-8050G).

■ Black Mass

Black mass is a powdery black material produced by the upstream processes of battery discharging, crushing and separation of recovered LIBs. Ideally, black mass should contain only the positive electrode active material, but in actuality, it contains various impurities, including Al (aluminum) and Cu (copper) of the current collector foils, and resins in the electrodes, and compounds formed by heat treatment¹⁾.

Fig.1 shows the element distribution images obtained by mapping of the cross section of black mass. Distributions of the Ni (nickel), Mn (manganese), and Co of the positive electrode active material, and C (graphite: carbon) of the negative electrode active material (arrow (1)) can be observed. In the Overlay image of Al-Mn-Ni, the overlaid color hues (arrows (2) and (3)) suggest the possibility that two types of positive electrode active materials exist in the black mass. The distributions of Ni, Mn, and Co indicate the existence of multiple positive electrode active materials with different concentrations, and particles (arrow (4)) with different concentrations in the interior and outside.

In the Overlay image of O-Al-P, the color hues (arrows (5), (6), and (7)) suggest the possibility that the sample contains three types of oxides. The P (phosphorus) of the electrolyte supporting salt (LiPF_6) appears to be a formation product (arrow (7)) formed by reaction with some Al of the positive electrode current collector foil, battery casing, and/or laminated film. Part of the F (fluorine) of the electrolyte supporting salt has become distributed inside a positive electrode active material with a high Co concentration.

The distributions of S (sulfur), which is thought to be an electrolyte additive, and the Cu of the negative electrode current collector foil are consistent with the distribution of some positive electrode active material.

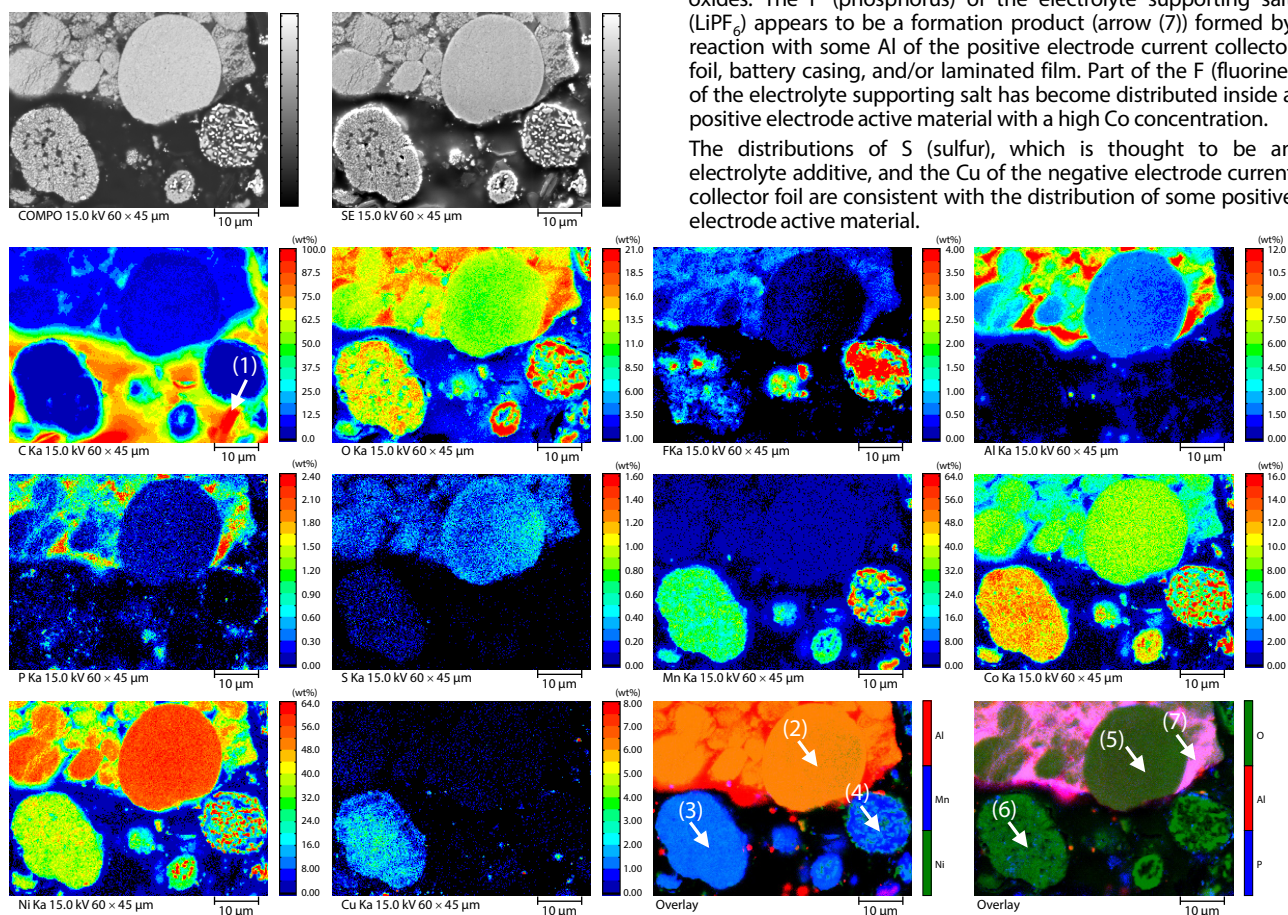


Fig. 1 Element Distribution of Black Mass

■ Phase Analysis of Positive Electrode Active Materials in Black Mass

Since black mass is prepared using LIBs recovered from various types of recycled products as raw materials, it contains various positive electrode active materials. Positive electrode active materials with a ternary system of lithium nickel manganese cobalt oxide (NMC) include multiple types (NMC811, NMC622, NMC523, NMC111) with different properties, and other systems include Ni-based lithium nickel cobalt aluminum oxide (NCA).

Fig. 2 (a) and (b) show ternary scatter diagrams of Ni-Co-Mn and Ni-Co-Al prepared from the element distribution images of Al, Mn, Co, and Ni in Fig. 1 (see related Application 1.). Fig. 2 (a) shows the compound marks by theoretical concentration for ▼NMC811, ✕NMC622, ○NMC523, and □NMC111, while Fig. 2 (b) shows the compound mark by theoretical concentration for ✕NCA. In the ternary scatter diagrams in Fig. 2 (a) and (b), clusters (point-sets) can be observed in the two regions of NMC622 and NCA. Therefore, filters were set in those regions. Fig. 2 (c) is a ternary scatter diagram of O-P-Al prepared from the element distribution images of O, P, and Al in Fig. 1. Here, filters were set in the P- and Al-rich regions.

Fig. 2 (d) is the phase diagram obtained by filter setting, where the blue-green region and the purple region are identified as the positive electrode active materials NMC622 and NCA, respectively, and the magenta regions are formation products of O-Al-P.

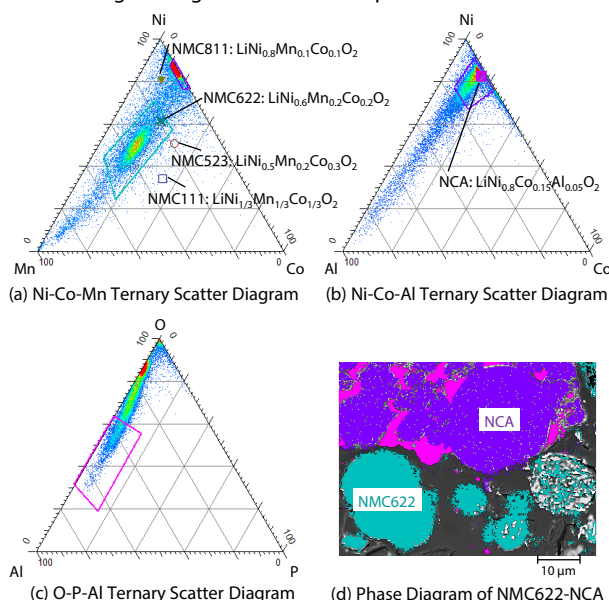


Fig. 2 Phase Analysis of Positive Electrode Active Materials in Black Mass

■ State Analysis of Positive Electrode Active Materials in Black Mass

It is known that state analysis of Ni, Co, and Mn is possible based on the wavelength shift to the short wavelength side when the valence increases, differences in the waveform, and other features. Fig. 3 (b), (c), and (d) show the spectra of standard samples, the raw material NMC811, and Ni, Co, and Mn in the black mass structure normalized by the La spectral intensity. The analysis lines by the midpoint method, which show the region of the peak point of the La peak, indicate the difference in the peak wavelength and waveform by their positions and slopes. It is thought that the Ni of BM-NMC622 and BM-NCA was reduced from the tetravalent state (valence 4) of the raw material NMC811 and reached a valence close to 2⁺. It is also thought that the Co and Mn of BM-NMC622 and BM-NCA were reduced from the tetravalent state of the raw material NMC811²⁾.

For Al and P, it is known that state analyses can be carried out based on the wavelength shift and intensity ratio using the sKa 3,4 spectra. Fig. 3 (e) and (f) are the spectra of standard samples of Al and P and the black mass structure normalized by the sKa 3 spectral intensity. Since the Al sKa 3,4 spectrum of the BM-Al, P-rich structure is consistent with the wavelength and intensity ratio of the standard sample of Al₂O₃, it is considered that Al has formed an oxide. The P sKa 3,4 spectrum of the BM-Al, P-rich structure is similar to the wavelength and intensity ratio of the standard sample of Ca₅(PO₄)₃, suggesting that P exists as part of a phosphide system, and not a phosphate system.

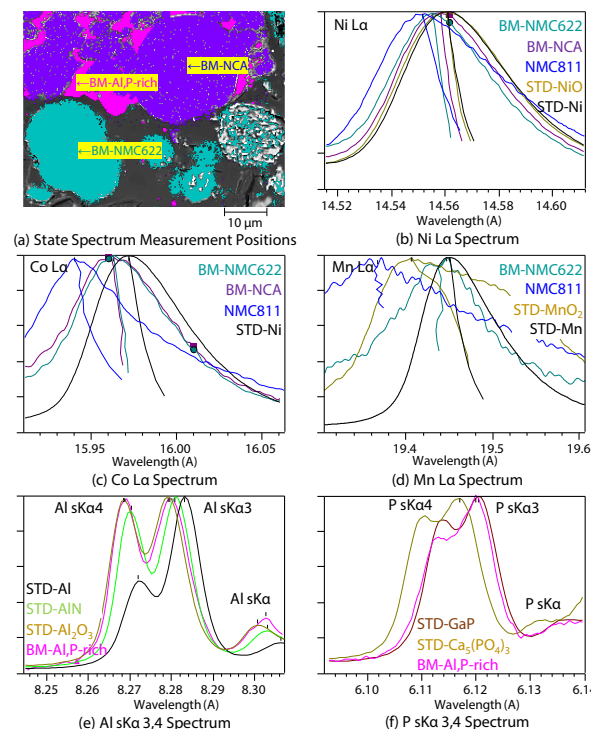


Fig. 3 State Analysis of Positive Electrode Active Materials in Black Mass

■ Conclusion

Lithium-ion batteries recovered from recycled products contain various substances (e.g., active materials, electrolyte supporting salts), and even the positive electrode active materials include multiple types such as LFP, NMC, and NCA, among others. Therefore, an understanding of the formation products and impurities contained in black mass is important for optimizing the battery recycling process. For this, it is possible to analyze the phases of each component by obtaining element distribution images using EPMA. Furthermore, by combining state analysis and phase analysis, it is possible to accurately identify not only the active materials, but also the components, valences, and compound states of the impurities and formation products contained in microregions. 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) Masashi Jinno: The Battery Book, Sogo Kagaku Pub., 113 (2019).

<Related Application>

1. Element Distribution and Phase Analysis of Positive Electrode Active Materials in Black Mass, [Application News No.01-01121-EN](#)

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