

# Advanced Analysis of Lead-Acid Batteries

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## 1 Abstract

Since their invention in 1859, lead-acid batteries have been used in automobiles, and in emergency and power-storage batteries. The market for these batteries has been expanding recently. On the other hand, Idling Stop System (ISS) vehicles are attracting attention as environmental friendly vehicles. The development of batteries for ISS has progressed to increase durability. However, the analysis of lead-acid batteries is very difficult because the conditions and structure of each component are changed by discharging and charging. Accordingly, we newly developed analytical methods to elucidate the two-and three-dimensional nanostructure, crystalline distribution and dispersion state of ingredients of lead-acid batteries.

## 2 Character of the analytical technology

- New analytical technologies suitable for various fields (**Figure 1**)
- Elucidation of deterioration mechanism in lead-acid batteries (lattice corrosion, dendrite shorting, muddy state of the positive electrode, etc.)

As individual cases of accomplishments,

- 1) In-situ observation of corrosive layer produced on the surface of a positive electrode grid according to 2D-mapping of chemical composition.
- 2) In-situ observation of the cross section of corrosive layer produced on the surface of a positive electrode grid through crystal structure distribution analysis using EBSD\*<sup>1</sup>.
- 3) 3D-structural analysis of crystalline salt deposition growth inside of a separator in a battery after short circuit using high-resolution X-ray CT technique.

\*<sup>1</sup> EBSD: Electron Backscatter Diffraction

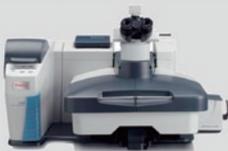
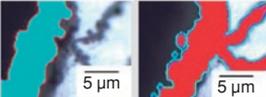
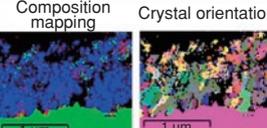
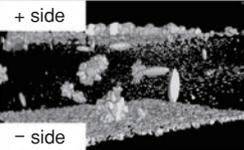
| Field              | 2D Composition   | 2D Crystal Structure  | 3D Structure  |
|--------------------|--|---|---|
| Equipment          | <br>Raman microscope                                  | <br>SEM-EBSD   | <br>High definition X-ray CT                       |
| Observation Object | Mapping of chemical state in sub-micro scale   | Mapping of crystal structure in sub-micro scale   | 3D-observation of lead-acid batteries' separators in sub-micro scale  |
| Output             | <br>Distribution of composition on grid cross-section | <br>Distribution of crystal structure on grid cross-section | <br>3D-CT image of separator after hydration short |

Figure 1 New analytical technologies suitable for various fields

## 3 Background of the development

Compared to lead-acid batteries for conventional vehicles, those for ISS vehicles have a tendency to become low due to continuing power supply while the engine is shut down or discharging power during restart. Therefore, batteries for ISS vehicles require excellent durability for charge and discharge cycles, high charge acceptance and high dendrite short circuit resistance. Although development at our company to improve charge acceptance and other attributes are under way<sup>2)</sup>, elucidating the deterioration mechanism for a lead-acid battery is important to further promote development. However, degraded state analysis through

conventional analytical methods remains difficult and there are many unsolved questions as temperature, specific gravity and the surface condition of active material greatly change due to the reactions between active material and electrolyte during charge/discharge cycles of lead acid batteries. So, we tried new multi-analytical approaches with high level capability to elucidate characteristic functions (visualization, quantification).

## 4 Technical details

In this research work, we newly developed the following multiple analytical methods enabling in situ observation and quantification of 2D- and 3D-nanostructure, crystal distribution and dispersion state of specific ingredients of lead-acid batteries. (1) Component distribution analysis: Visualization of component distribution in the corrosive layer produced on the surface of a positive electrode grid. (2) Distribution analysis of crystal structure: Crystal state visualization of the corrosive layer produced on the surface of a positive electrode grid. (3) 3D-structural analysis: In-situ observation of the microstructure inside a battery separator after short circuit. By applying these new analytical methods, the following facts about lattice corrosion, which is a degradation mode of lead acid battery, and dendrite-induced short circuit were revealed.

- 1) By visualizing 2D-component distribution, change in composition during the process of corrosion was clarified. In the past, elemental distribution analysis was performed using EPMA<sup>\*2</sup> but identification of chemical compounds was still difficult. So, by newly applying a mapping technique using Raman spectroscopy, it was elucidated that components of the corroded layer were composed of two different layers.
- 2) By visualizing 2D-crystal structure distribution, change in crystal structure during the process of corrosion was clarified. In the past, crystal structure in the surface layer was analyzed using X-ray diffraction technique, but evaluation of the crystal distribution was still difficult. So, we applied EBSD crystal structure distribution analysis. SEM<sup>\*3</sup> images of the cross section of the corroded layer and EBSD results are shown in **Figure 2**. It was revealed from observations including band contrast enhancing the outline of crystal particle images, crystal phase color to show crystal component distribution, and Euler color indicating the crystal orientation that corroded layer was polycrystalline and particle size became smaller toward the surface.
- 3) By visualizing the 3D-structure, deposition during short circuit was clarified. In the past, SEM was used to analyze the cross-section structure of a separator, but stereoscopic analysis of the deposition during short circuit was difficult. So, we newly applied a 3D-analytical method using X-ray CT technique. SEM images of the cross-section of a separator and 3D-images of the deposit using X ray CT technique are shown in **Figure 3**. By applying X-ray CT technique, it was revealed that SEM images of the deposit in Battery A were squamous and a minutely small deposit, which had not been confirmed by SEM imaging, was present in Battery B. This visualization technique to observe short circuited state by X-ray CT technique can contribute to the development of improved dendrite short circuit resistance.

\*2 EPMA: Electron Probe Micro Analyzer \*3 SEM: Scanning Electron Microscope

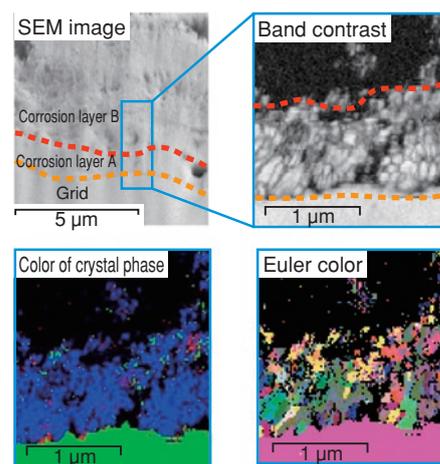


Figure 2 SEM image and dispersion state of crystal structure

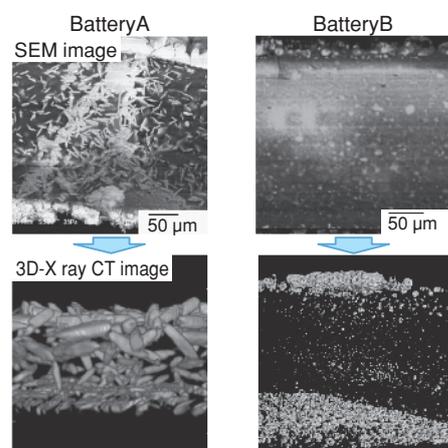


Figure 3 Cross-sectional SEM image and three dimensional structure analysis of separators after hydration short by X-ray CT

## 5 Future Business Development

- Technology deployments in the fields of electrical energy storage devices and related materials
- Detailed elucidation of the functional mechanism of inorganic/organic, solid/liquid composite materials for use in the fields of information/communication and life science

### [References]

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