Featured Articles

Rapid Detection and Element Identification of Fine Metal Particles for Underpinning Battery Quality

—X-ray Particle Contaminant Analyzer EA8000—

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OVERVIEW: Along with measures for reducing the load on the environment, development of fuel cells and electric vehicles using rechargeable batteries has proceeded with the aim of reducing CO_2 emissions. For the LIBs, fuel cells, and other components used for this purpose, greater safety and quality is required particularly in automotive applications. Metal particle contamination in batteries is one cause of degrading reliability and quality, making this an important aspect of quality control. To satisfy this new demand, Hitachi High-Tech Science has developed X-ray technology and equipment to detect and identify fine metal particles.

INTRODUCTION

USE of technologies such as lithium-ion rechargeable batteries (LIBs) and fuel cells is growing in a variety of fields to help reduce the load on the environment. However, the presence of metal particle contaminants in LIBs and fuel cells is a cause of decreased safety and performance. For this reason, controlling metal particles in the manufacturing process is important for maintaining product safety and performance. These metal particles are also a cause of decreased manufacturing yield. With the growing use of LIBs and fuel cells in automotive applications over recent years, dealing with metal particles is seen as particularly important. So, battery manufacturers have adopted a variety of measures for quickly identifying metal particle contamination in order to maintain battery quality and yield.

To overcome these challenges, Hitachi High-Tech Science Corporation released an X-ray particle contaminant analyzer (the EA8000) for detecting metal particles and analyzing their composition (see Fig. 1).

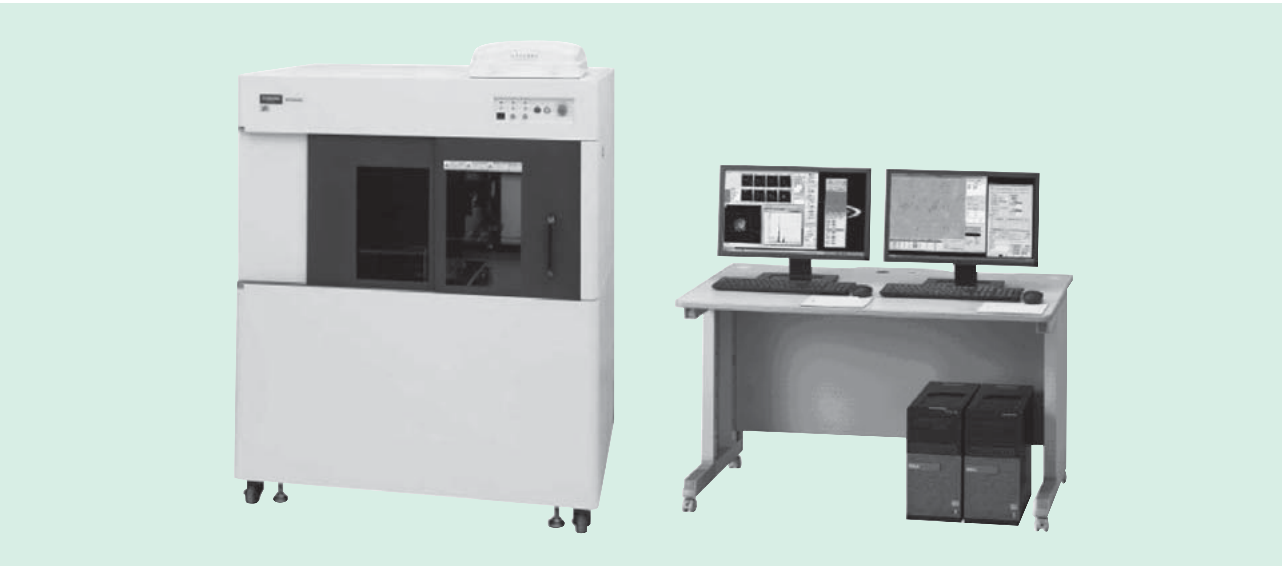

Fig. 1—X-ray Particle Contaminant Analyzer EA8000.
The photograph shows the EA8000 developed by Hitachi High-Tech Science Corporation.

This article describes the EA8000 and some example measurements with particular reference to the control of metal particles in LIB manufacturing.

RAPID DETECTION AND ELEMENT IDENTIFICATION OF FINE METAL PARTICLES

Customer Requirements, Existing Techniques, and Associated Challenges

LIB manufacturing sites need a way to detect contamination by metal particles in materials or intermediate processes. For example, there is a requirement for the detection of metal particles of 20 μm or more in the cathode plates of A4-size LIBs, and the rapid analysis of their number, size, and composition. In some cases, the requirements include detection and analysis of internal as well as surface contaminants.

One method for determining the level of contamination and particle composition is inductively coupled plasma (ICP) analysis[*1]. Unfortunately, this method cannot distinguish between cases with a large number of sub-micron particles and those with a single large contaminant with potential to cause performance degradation and heat generation. Similarly, it is difficult to detect internal metal particles using scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX)[*2] because the electron beam only penetrates a few micrometers into the sample surface.

X-ray fluorescence (XRF) analysis identifies elements using the secondary (fluorescent) X-rays generated when a material is exposed to X-rays. μXRF, in which the analysis is performed over a very small area, obtains an element map that can be used to determine the number, size, and composition of metal particles near the surface and in the interior. Unfortunately, μXRF is impractical because scanning over the entire surface of a sample to detect fine metal particles can take 10 hours or more just to identify particles on the surface, with even more time being required to identify particles in the interior.

Features of the EA8000

The EA8000 uses X-ray transmission imaging, which takes advantage of the differences in the X-ray transparency of different materials to detect fine metal particles in a short amount of time. Hitachi High-Tech Science has also developed an element mapping system that uses XRF with increased sensitivity in a minute area to analyze the contaminants. By mounting both of these on the same XYZ stage, the system can rapidly detect metal particles on the order of 20 μm over an A4-size area and perform element identification[(1)] (see Fig. 2).

*1 A type of emission spectrochemical analysis that is widely used for the analysis of inorganic elements. Samples are put in solution and the type and quantity of the elements they contain are determined by spectrochemical analysis using plasma.

*2 An instrument that observes a sample using a scanning electron microscope (SEM) while at the same time performing an elemental analysis based on the distinctive X-rays emitted by the sample in response to the electron beam. It can be used to obtain a two-dimensional element mapping images.

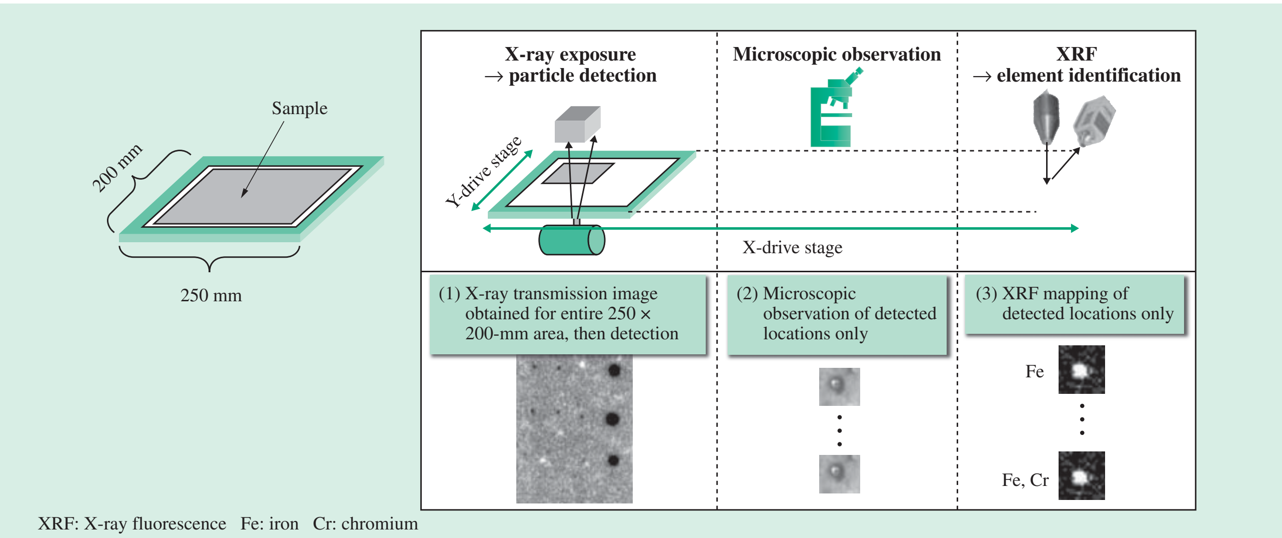

Fig. 2—Sequence of Steps in EA8000 Measurement.
(1) Particle detection, (2) microscopic observation, and (3) element identification can all be performed automatically with the sample on the same stage.

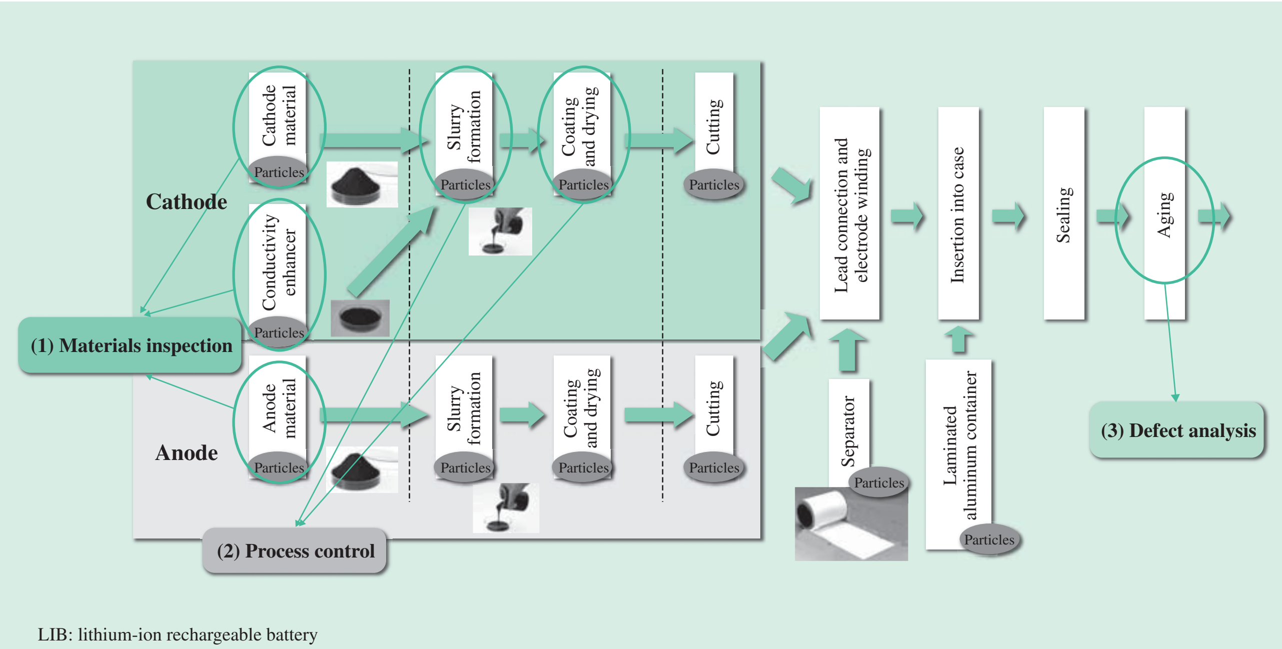

Fig. 3—LIB Manufacturing and Suitable Applications for EA8000 Analysis.
There are applications for the EA8000 at various stages in the LIB manufacturing process.

X-ray transmission imaging

Different materials have different X-ray transparency. Metal, for example, has low X-ray transparency compared to plastic. If metal particles are present in plastic, they appear as dark shadows in an X-ray transmission image. The location of these can then be determined by image processing.

Hitachi High-Tech Science developed an X-ray transmission imaging system for the EA8000 that achieves high spatial resolution and high sensitivity through enhancements such as optimization of the X-ray detector, enabling it to rapidly detect metal particles on the order of 20 µm. The time taken to perform detection ranges from several minutes up to around 20 minutes (depending on the type of sample).

Element identification by XRF

The XRF analysis of contaminants is able to identify their elemental composition quickly by only performing XRF mapping for those locations where contaminants were detected in the X-ray transmission image.

To make the analysis faster, XRF analysis also incorporates an X-ray system with a polycapillary lens that makes the beam sharper and more intense, and a silicon drift detector (SDD) with excellent count rate performance (number of X-rays that can be counted per unit of time). Thanks to these features, it takes only one to three minutes to perform element identification of detected fine metal particles.

EXAMPLE ANALYSES USING EA8000

Fig. 3 shows an overview of how LIBs are manufactured. The EA8000 is suitable for analytical work in the materials inspection, process control, and defect analysis steps within this process. This chapter presents measurement examples using simulated samples from these three applications.

Materials Inspection (Carbon-based Powder Measurement Sample)

To provide an example of materials inspection, measurements were performed on a sample of carbon-based powder of the sort used in anodes and to enhance conductivity.

Commercially available graphite was used for the sample. As shown in Fig. 4 (a), the measurement was performed on graphite placed in a zippered polythene bag that was spread out over a 250 × 200-mm area.

The measurement took approximately 13 minutes to obtain an X-ray transmission image, and XRF mapping was performed at locations where material was detected in this image, taking 50 seconds per location (see Fig. 4).

Fig. 4 (b) shows the transmission image of the entire bag. Variations in thickness are visible depending on the amount of graphite powder present at different places. Fig. 4 (c) shows an enlargement of one such region in which a location is visible that is

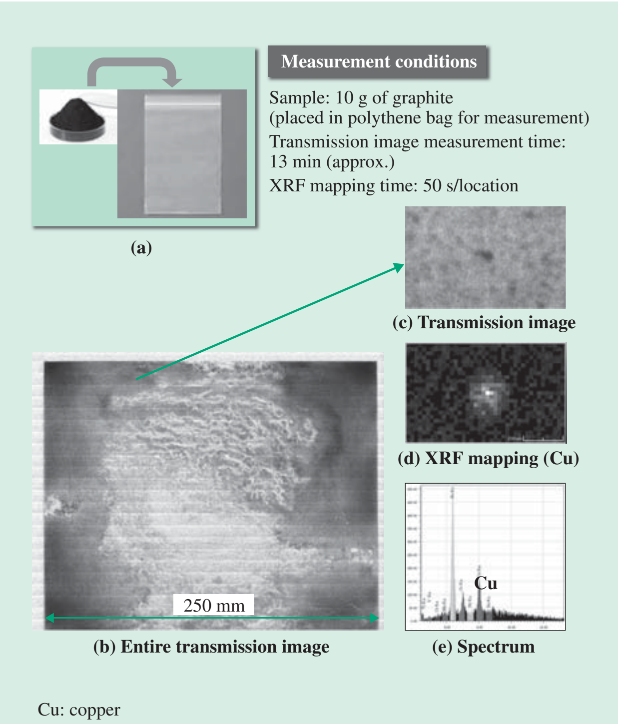

Fig. 4—Example Analysis of Carbon-based Powder Sample.
Carbon-based powder can be measured with just simple sample preparation.

darker than its surroundings. The size of this particle is approximately 100 μm. Locations like this can be identified by image processing. XRF mapping of the particle indicates that it is made of copper (Cu) [see Fig. 4 (d) and (e)].

This technique can perform measurements on carbon powder with only simple sample preparation and, in doing so, can prevent loss of quality or yield by quantifying the presence of large contaminants with sizes in the tens of micrometers range that have the potential to cause defects.

Process Control (Measurement Results for Dust-generated Particle Control Technique)

As an example of use in process control, this section describes a measurement for dealing with dust emitted by production machinery or other sources.

Placing adhesive film next to a production machine and routinely taking it away for measurement provides a way to identify problems such as a deterioration in the condition of the machine that is accompanied by a sudden increase in the amount of dust it emits. To simulate this situation, a measurement was performed on an adhesive film that had been sprinkled with metal powder. XRF mapping for particular elements [iron (Fe) and Cu] was performed over the entire surface of

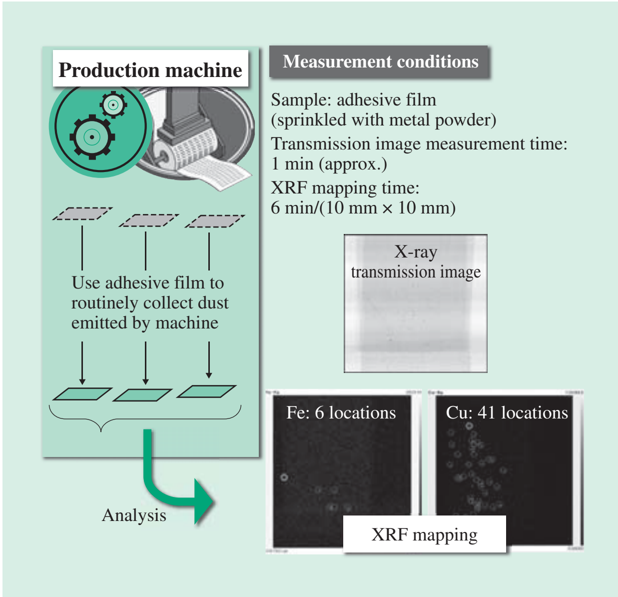

Fig. 5—Example Analysis of Sample for Dust Emitted by Production Machinery or Other Sources.
Analysis can determine the elemental composition, number, and size of metal particles adhering to adhesive film.

the film and the number of such particles was counted (see Fig. 5). Note that this could also be performed by taking measurements at the particle locations identified in the X-ray transmission image.

This method provides a simple way to determine the elemental composition of the particles, and it can be used to monitor for problems in a production machine based on the trend in the amount of dust it emits.

Defect Analysis (Sample for Analysis of Separator)

As an example of defect analysis, this section describes a measurement that might be used in the analysis of particles in and particles adhering to the surface of a separator.

The sample was created by sprinkling stainless steel (SUS) powder on polyethylene terephthalate (PET) film with a thickness of 100 μm.

The measurement took approximately four minutes to obtain a transmission image of the 250 × 200-mm area, and XRF mapping took approximately 40 seconds per location (see Fig. 6).

A particle was detected at the edge of Fig. 6 (a). The measurement found a coin-shaped SUS particle with a known diameter of 20 μm at the top right of Fig. 6 (a). Fig. 6 (b) to (d) show the analysis results for this particle. The particle is visible in the transmission image [Fig. 6 (b)], and the Fe mapping [Fig. 6 (c)] shows a high intensity for Fe at that location, indicating that Fe is present. Fig. 6 (d) shows the spectrum from the center of the particle. Although the measurement was completed in a short amount of time (approximately 40 seconds), it shows peaks for Fe, chromium (Cr), and nickel (Ni).

This demonstrates how the EA8000 can perform automatic measurements of tiny amounts of material, and that it can conduct defect analyses that are automatic (with minimal variation due to the operator performing the test) to identify particles that may have escaped by physical action from a separator.

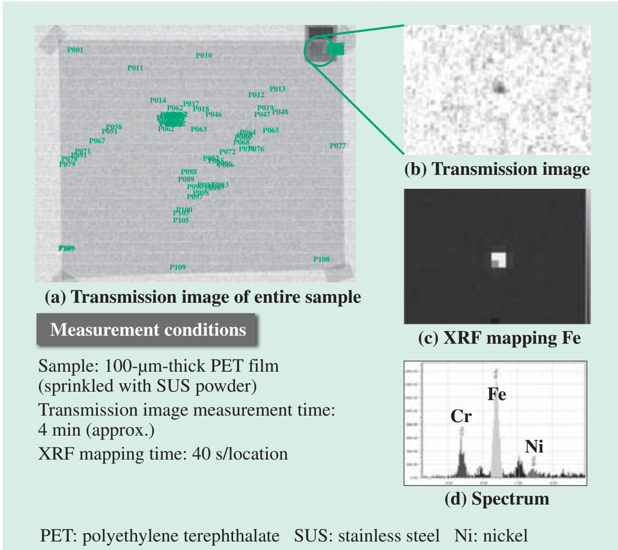

Fig. 6—Defect Analysis Sample for Analysis of Separator.
(a) shows the full transmission image of the sample sprinkled with SUS powder, and (b), (c), and (d) show the analysis results for a particle of known size.

BENEFITS OF USING EA8000

The following summarizes the benefits that can be obtained at LIB manufacturing sites by performing the measurements described in the chapter above.

(1) Increases in defect rates can be prevented by performing materials inspection to quantify the presence of large particles with the potential to cause defects.

(2) Monitoring of production machinery for abnormal conditions can be performed by regularly checking coated electrodes or dust emission by machines. It is also possible to determine the scope of any problems that occur in order to minimize the number of batteries that are rejected.

(3) Defect analysis can be performed automatically, with minimal variation due to the operator performing the test. There is also potential for determining defect causes that could not be identified in the past.

CONCLUSIONS

The market for LIBs and similar products is growing. This article has described examples of how the EA8000 can be used to deal with problems associated with the production of these products, and the associated benefits.

Hitachi High-Tech Science intends to draw on the knowledge it gained in the development of the EA8000 to develop inline models that are capable of higher throughput and utilize them in other fields.

REFERENCE

(1) Y. Matoba et al., “X-ray Technology for Green Innovation, Food Safety, and Hazardous Substances Management of Electronic Components,” Hitachi Hyoron **95**, pp. 610–615 (Sep. 2013) in Japanese.

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