JFE TECHNICAL REPORT
No. 27 (Mar. 2022)

Advanced Micro-Beam Analysis for Functional Materials Improving EV and FCV

1. Introduction

Development of technologies that reduce loads on the earth environment, beginning with automobile electrification and weight reduction, is indispensable for realizing a sustainable society. In electric vehicles (EVs) and fuel cell vehicles (FCVs), the change from engine drive powered by combustion of fossil fuels to drive by electric motors has fundamentally changed many of the elements of automotive development. Among which the development of secondary batteries, fuel cells and motors, and the inverters and other electronic components that connect them, is particularly important. At the same time, weight reduction is also strongly required in EVs and FCVs. In research and development in these areas, evaluation of structures to the nanometer level is often required, for example, in materials expressing advanced functions and at interfaces between heterogeneous materials. The Nano Analysis Center of JFE Techno-Research Corporation (JFE-TEC) is responding to these needs by developing advanced micro-beam analysis.

2. Advanced Micro-Beam Analysis for Functional Materials

Figure 1 shows an overview of the advanced micro-beam analysis that are objects of work at JFE-TEC for research and development related to functional materials.

The core components of secondary batteries and fuel cells are composites of various functional materials. In Fig. 1, the axis labelled “Into the atomic world” shows the JFE-TEC is putting effort into two-dimensional and three-dimensional structural analysis of these composites, continuing seamlessly from the visual to the atomic level.

The aims of the “Visualize the difference” axis are to achieve even higher sensitivity and to extract more advanced information by controlling detected signals,

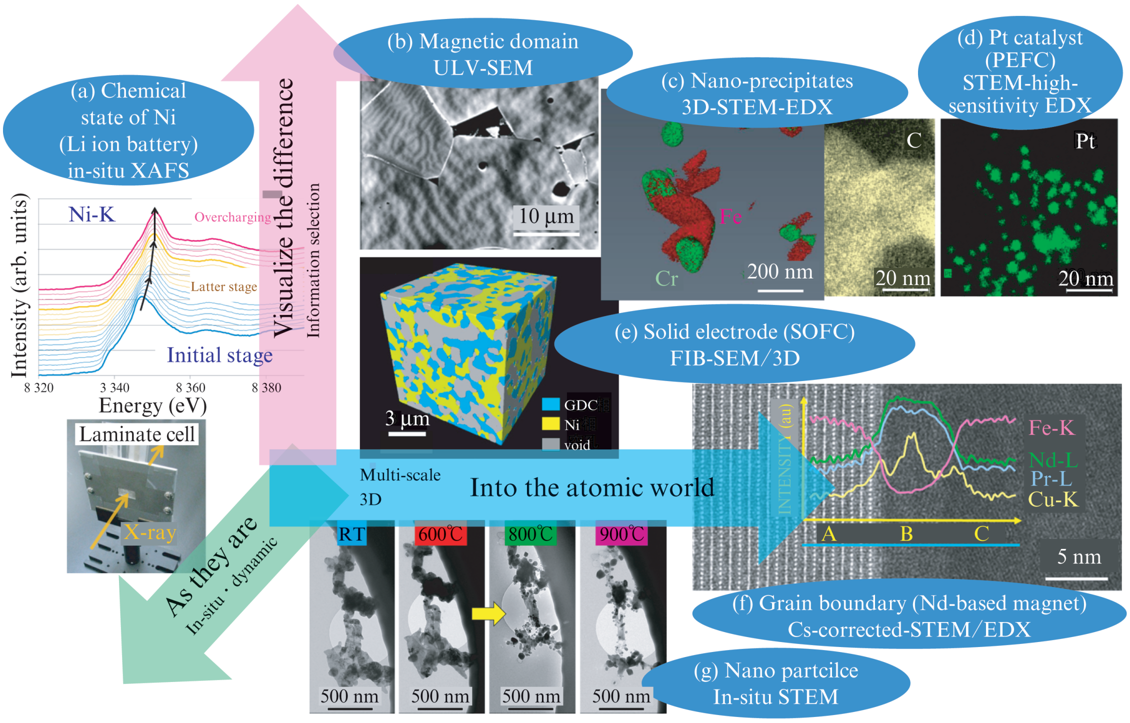

Fig. 1 Advanced micro-beam analysis techniques for improving functional materials

† Originally published in *JFE GIHO* No. 47 (Feb. 2021), p. 62−65

based on advanced micro-beam analysis[1)] such as the spherical aberration corrected scanning transmission electron microscope (Cs-corrected STEM) and the ultra-low voltage scanning electron microscope (ULV-SEM), which were cultivated by the JFE Group.

"As they are" means observation and analysis of materials under their actual environments. On this axis, we are constructing technologies for visualization of the structures and states of materials under high and low temperature environments or under battery operating conditions by utilizing the electron microscope, X-ray and synchrotron radiation techniques.

By integrating these three axes sophisticatedly in line with the Client's needs, we believe that we can provide information that will lead to breakthroughs in the development of functional materials for EVs and FCVs.

3. Advanced Micro-Beam Analysis for EV and FCV Development

3.1 Analysis of Secondary Battery Materials

Many of the materials of secondary batteries which use nonaqueous electrolytes, represented by lithium ion batteries (LIBs), must be analyzed in an environment where they will not be exposed to moisture or air. JFE-TEC has constructed an air protection system for micro-beam analysis[2)], and regularly conducts structural analyses of secondary batteries using electron microscopes and surface analysis devices[3)]. We have also constructed SEM and STEM analysis systems[4)] for all-solid-state batteries using sulfide electrolytes, which are expected to realize high battery performance and safety. JFE-TEC provides integrated services from fabrication[5)] of all-solid-state batteries to detailed structural analysis.

Surface treatment of electrode active materials is important for enhancing performance and extending the life of secondary batteries. **Figure 2** shows the results of ULV-SEM observation of Nb oxides coated on the surface of the positive electrode active material (lithium cobalt oxide) for all-solid-state batteries using sulfide-based solid electrolytes. Although the distribution of the coating layer was difficult to identify under the conventional condition (accelerating voltage: 10 kV), it has been captured clearly as dark contrast under the low accelerating voltage condition of 0.5 kV of the ULV-SEM. Elemental analysis of the extreme surface layer by detecting the Nb-M line has also become possible by using a newly-introduced windowless energy dispersive X-ray spectrometer (EDX)[6)]. From Fig. 2(c), it can be seen that the coating of the sample is localized. In analysis of the thickness and interfacial structure of the coating layer at the nano level, Cs-corrected STEM is used.

For direct observation of changes in materials corresponding to battery reactions, *in-situ* experiments are performed by the X-ray diffraction and X-ray absorption fine structure (XAFS) techniques. In the example in Fig. 1(a), the valence change of Ni in the positive electrode active material accompanying charging of a LIB was clarified by Ni-K edge XAFS[7)].

3.2 Analysis of Fuel Cell Materials

Power generation in polymer electrolyte fuel cells (PEFC), which are applied practically in FCV, is performed by the membrane electrode assembly (MEA). To improve PEFC performance, it is necessary to observe and analyze the structure and properties of the MEA at various size levels. **Figure 3** shows an example of observation of the MEA by electron microscopy. At JFE-TEC, we have achieved multi-scale observation

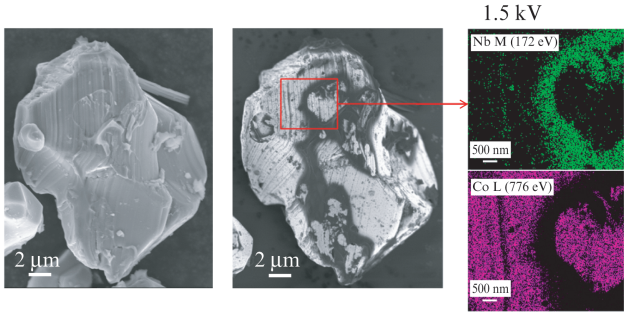

Fig. 2 SEM images of cathode material (lithium cobalt oxide) particle with Nb-base coating observed with accelerating voltage of 10 kV (a) and 0.5 kV (b: ULV-SEM condition) EDX mapping of Nb-M and Co-L lines recorded with accelerating voltage of 1.5 kV (c)

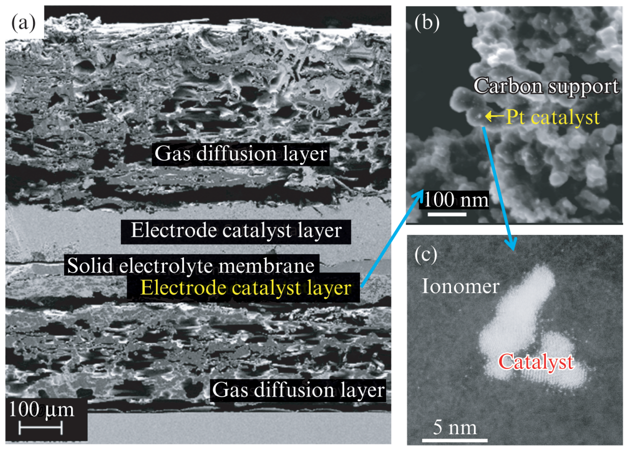

Fig. 3 Multi-scale images of the MEA in a PEFC ULV-SEM images with low magnification (a) and high magnification (b; a catalyst layer) Atomic-scale image of a catalysts and ionomer observed by Cs-corrected STEM (c)

from the overall image of the MEA cross section by ULV-SEM to the Pt catalyst nanoparticles of the catalyst layer by Cs-corrected STEM. In observation of the Pt catalyst nanoparticles of the catalyst layer by Cs-corrected STEM, the ionomer that surrounds the catalyst particles and the Pt atoms which exist in the ionomer can be successfully observed (Fig. 3(c)). JFE-TEC has also established techniques for visualization of the 3-dimensional structure at the micron-level by using a focused ion beam (FIB)-SEM (Fig. 1(e) Example of a solid oxide fuel cell (SOFC)) and at the nano-level by STEM tomography (Fig. 1(c)). For PEFC, the ULV-SEM and surface analysis techniques are applied to the characterization of separator material surfaces in which low cost is desired. In addition, JFE-TEC has established a technique which enables *in-situ* observation of the changes in the microstructures and chemical states of catalysts and other nanoparticles under high temperatures (Fig. 1(g)).

3.3 Analysis of Motor Materials

The development of rare earth sintered magnets is an urgent challenge for achieving low-cost manufacturing of high efficiency motors, and active research and development are underway with the aims of higher efficiency and improved properties. The key point in those research efforts is controlling the composition of crystal phases, the crystal grain size and crystal orientation distributions of the main phase, and the grain boundaries of the rare earth magnet. **Figure 4** shows an example of an evaluation of the distribution of Dy added to a neodymium magnet, separately in the crystal grain (upper part of Fig. 4(b)) and in the crystal grain boundary phases (lower part of Fig. 4(b)). This was achieved by superimposing the distribution of Dy measured with a field emission-electron probe micro-analyzer (FE-EPMA) and the crystal grain map extracted by electron backscatter diffraction (EBSD).

The crystallographic structure and elemental distribution of a grain boundary layer with a thickness of several nm was clarified by a Cs-corrected STEM investigation (Fig. 1(f)). Thus obtained information is critical for suppressing eddy current loss. The ULV-SEM technology has made it possible to observe the magnetic domain structure of neodymium magnets (Fig. 1(b))[8].

3.4 Analysis of Power Device Materials

As a semiconductor material for EV and FCV power devices, which operate at high power, SiC has attracted attention because it has higher withstand voltage and high temperature characteristics than Si, which is currently the main stream material. To investigate the surface quality of SiC as a substrate material for this application, JFE-TEC conducted a quantitative analysis of strain by the EBSD-Wilkinson method[9]. We successfully visualized the existence of a trace amount of N remaining on the SiC/SiO_2 interface in the manufacturing process in device production by using a STEM with a high sensitivity EDX device.

In developing semiconductor component mounting units, it is important to secure durability against temperature changes in use. JFE-TEC succeeded in capturing the structural changes of devices due to temperature changes by using sample stages that enabled heating and cooling in SEM. We have also developed technologies for visualizing the changes in strain and structural changes accompanying temperature changes, tension and compression, etc.

3.5 Analysis of Interface between Heterogeneous Materials for Weight Reduction of Car Bodies

Use of aluminum, carbon fiber reinforced plastic (CFRP) and other lightweight materials is being promoted with the aim of reducing car body weight. Bonding of heterogeneous materials is necessary when using these materials. **Figure 5** shows an example of SEM observation of the interface between an Al-based

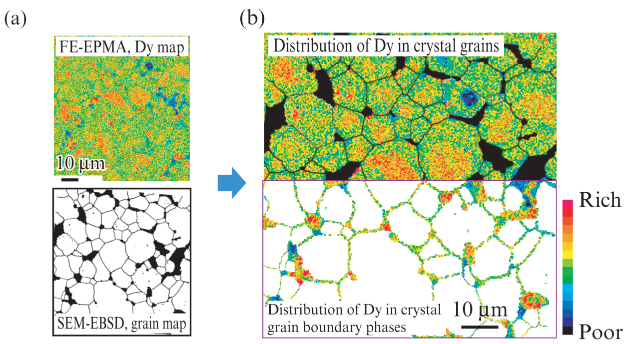

Fig. 4 Dy map measure by FE-EPMA and grain map obtained by EBSD for an identical area of a sintered Nd-based magnet (a) Distribution of Dy in the crystal grain (upper part) and in the crystal grain boundary phases evaluated by superimpose of Dy elemental map and grain map (b)

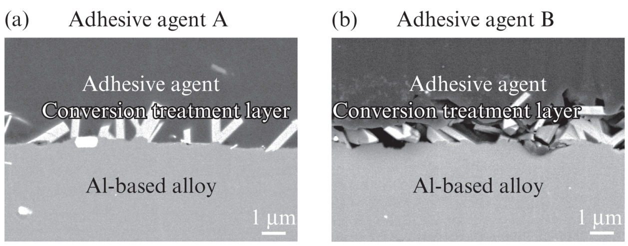

Fig. 5 ULV-SEM images for the cross sections of aluminum alloy/adhesive agent interfaces resulting high (a) and poor (b) adhesive strength

alloy and adhesive agents in a member in which the alloy and CFRP were bonded. Different adhesives were used in Fig. 5(a) and (b). In (a), which showed high shear strength, it is clear that the wraparound of the adhesive in the conversion treatment layer (fine projections shown by bright contrast) formed on the surface of the Al-based alloy is better than that in (b), where shear strength was inferior. In addition to analysis of the interfacial morphology illustrated in this example, we can also conduct investigations of the characteristics that control bond strength by a nano-level analysis of the interface and by surface chemical state analysis and STEM observation of the sample surface before bonding.

4. Conclusion

This paper has described the importance of controlling functional materials and their composites in research and development related to EVs and FCVs, and has introduced a number of micro-beam analysis developed by JFE-TEC for this purpose. Examples of the application of these micro-beam analysis were introduced for each of the key development elements for EVs and FCVs. At present, JFE-TEC is engaged in efforts to extract information from the micro-beam analysis data which will enable a more direct discussion of the characteristics of materials and composites. As examples, we are studying characteristic prediction based on 3-dimensional structural analysis results, and quantitation of the strain distribution of materials from changes in their electron microscope observation images.

We hope to hear the opinions and needs of all concerned for the JFE-TEC technologies introduced in this article. We will also be happy to take on the challenge of difficult problems so as to contribute to the development and practical application of functional materials.

Reference

1) Special Issue on "Analysis and Characterization". JFE Technical Report. 2017, no. 22.
2) Analysis of Secondary Battery Materials Under Low-Humidity or Air-Protected Condition. JFE Technical Report. 2017, no. 22, p. 65–67.
3) Simauchi, Y.; Ohmori, S.; Ikemoto, S. Microscopic Structural Analysis of Advanced Anode Material for Lithium Battery. JFE Technical Report. 2017, no. 22, p. 55–59.
4) Tekkou Shinbun (Japan Metal Daily). 2018.11.8.
5) Fabrication and Evaluation of All-solid-state Lithium Secondary Battery with Sulfide-based Solid Electrolytes. JFE Technical Report. 2022, no. 27, p. 83–85.
6) Nakamura, T.; Sato, K.; Nagoshi, M. ULV-SEM-EDX analysis of fine precipitates in Cr-Mo steel using windowless silicon-drift detector. Journal of Surface Analysis. 2019, vol. 26, no. 2, p. 206–207.
7) Kon, A.; Simauchi, Y.; Makiishi, N.; Takahashi, S.; Ohmori, S.; Ogawa, M.; Sakurada, T. In-situ XAFS study on degradation behavior of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ as a cathode active material for Li ion battery. The 57th Battery Symposium in Japan. 2016, 2A01.
8) Oda, T.; Sato, K.; Kitahara, Y.; Sakurada, T. Optimization of magnetic domain contrast in a commercial SEM. The 73th Annual Meeting of The Japanese Society of Microscopy. 2017, P_I-15.
9) Tsukimoto, S.; Ise, T; Maruyama, G.; Hashimoto, S.; Sakurada, T.; Senzaki, J.; Kato, T.; Jojima, K.; Okumura, H. Local Strain Distribution and Microstructure of Grinding-Induced Damage Layers in SiC Wafer. Journal of Electronic Materials. 2018, vol. 47, no. 11, p. 6722–6730.

For Further Information, Please Contact:

Sales Division, JFE Techno-Research
Phone: (81)3–3510–3833
Nano-scale Characterization Center
Phone: (81)44–322–6181
https://www.jfe-tec.co.jp/en/