Application News

High-Resolution Scanning Probe Microscope (Atomic Force Microscope) SPM-8100FM

SPM (AFM) Measurements of Cathode and Anode Materials from All-Solid-State Lithium-Ion Batteries without Exposure to Air

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User Benefits

- SPM (AFM) observations and measurements can be performed without exposure to air.
- The cathodes and anodes of all-solid-state lithium-ion batteries can be observed and measured.
- Shapes can be observed at the microscopic scale, and current and electrical forces can be visualized.

■ Introduction

Further improvements to battery performance are called for due to policies promoting electric vehicles (EV). This includes expectations for the commercialization of all-solid-state lithium-ion batteries because of their advantages including safety, high energy density, and resistance to degradation. One issue in the practical utilization of such batteries is the difficulty of reducing the interface resistance between the electrodes and the solid electrolyte. However, it is believed that shape observations and measurements of current at the microscopic scale will lead to a better understanding of interface reaction mechanisms leading to the resolution of this issue. This article introduces examples of surface observations of cathode and anode materials and measurements of current in all-solid-state lithium-ion batteries using SPM.

■ SPM-8100FM and Glove Box

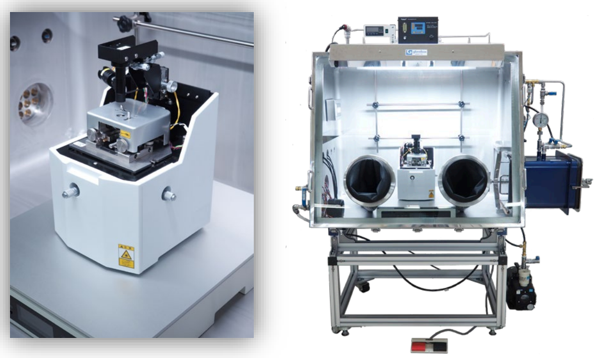
These measurements were performed using the SPM-8100FM high-resolution scanning probe microscope [SPM (AFM)], and a gas flow type glove box (Fig. 1). The features of this equipment are as follows.

SPM

(1) It can operate in frequency modulation (FM) in addition to amplitude modulation (AM).
(2) ZXY measurement enables the acquisition of 3-dimensional data, including current and electric forces (hereafter: ZXY data).

Glove Box

(1) Oxygen and water vapor concentrations are both 1 ppm or less.



(a) SPM-8100FM (b) Gas Flow Type Glove Box

Fig. 1 SPM-8100FM and Glove Box

■ All-Solid-State Lithium-Ion Batteries and Related Issues

Fig. 2 is a schematic of an all-solid-state lithium-ion battery (hereafter: All-solid-state LiB). All-solid-state LiBs use a solid electrolyte, so they are safer than LiBs that use a normal combustible liquid electrolyte. However, the contact between the solid electrolyte and the electrodes is poor, so the interface's electrical resistance is large, making high-speed charging and discharging difficult. The SPM can measure the distribution of current and electric forces at the microscopic scale, so it holds promise as one method for evaluating the interface between solid electrolytes and electrodes.

In this article, sintered compacts of commercially available electrode material were observed and measured, in anticipation of the analysis of electrodes in contact with a solid electrolyte. The materials used were lithium cobaltite ($LiCoO_2$: hereafter LCO) for the cathode and lithium titanate ($Li_4Ti_5O_{12}$: hereafter LTO), both of which are used in all-solid-state LiBs. Fig. 3 shows an overview of the observations. Note that the electrode material used here was in its initial state, before charging or discharging.

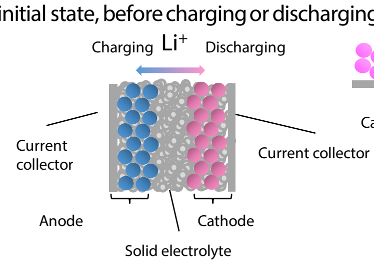


Fig. 2 Schematic Diagram of All-Solid-State LiB

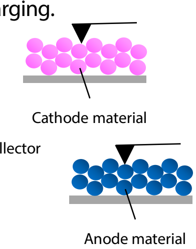
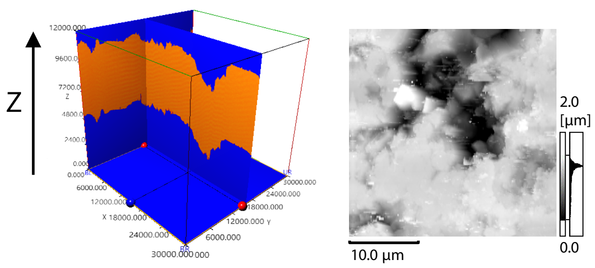


Fig. 3 Observation of a Sintered Compact of Commercially Available Electrode Material

■ ZXY Current Measurements and Image Construction

Observations and measurements were performed by measuring the ZXY-current. Fig. 4 shows a typical height image and ZXY data for LCO measurements, and Table 1 shows the measurement conditions. Normal shape measurements use planar data with Z information for each point with X and Y coordinates. However, the ZXY measurement method is based on force curve measurements, in which there is data for all three axes, Z, X, and Y. As a result, a variety of images can be constructed including height images and adsorption force images, based on the acquired ZXY data.[1), 2), 3), 4)]



(a) ZXY Data (b) LCO Height Image

Fig. 4 LCO ZXY Data and Constructed Height Image

Table 1 Measurement Conditions

Instrument:	Scanning Probe Microscope SPM-8100FM
Scanner:	Deep type scanner (maximum operation range XY: 55 µm, Z: 13 µm)
Holder:	Micro current holder Measurement range: ±10 nA
Observation Mode:	ZXY measurement
Pixel Number:	Z : 1024 X : 256 Y : 256
Purge Gas:	Argon
Atmosphere:	Oxygen 0.7 ppm or less, water vapor 0.75 ppm or less

■ Image Construction and Inspection

The images in Fig. 5 (a) to (j) were constructed from ZXY data in the measurement range from XY: 30 µm Z: 12 µm to XY: 5 µm Z: 6 µm.

(1) Height Images

The 30 µm LCO height image (a) and the 30 µm LTO height image (c) showed irregularities on the order of 2 µm, and the roughness (Sa) analysis showed surface roughness at 341.5 nm and 333.6 nm. Several gaps in the LCO were also found. In contrast, no gaps were found in the LTO, but residual marks from sample formation were evident on the samples in the vertical direction.

The 5 µm LCO height image (e) showed that the grains in the electrode material were about 1 µm in size, and that there were small gaps between them. There were also grains several hundred nm in size as indicated by the arrows. The LTO height image (h) showed plate-like crystal structures as indicated by the arrows.

(2) Current Images

In the 30 µm LCO current image (b), the current distribution was not uniform, and the current was detected over 41.7 % of the area (as analyzed using particle analysis software). In the 30 µm LTO current image (d), no current was detected, but this was likely because of the high resistance of the LTO in the uncharged state.

In the 5 µm LCO current image (f), it was found that the direction of current flow was different on the left and right sides of the yellow dotted line. On checking the 5 µm LCO height image (e), the yellow dotted line was found to be the boundary of a crack. In addition, it was evident that there was no current flow at the grains several hundred nm in size, indicated by the arrows.

As in the 30 µm LTO current image (d), no current was detected in the 5 µm LTO current image (i).

(3) Attractive Force Images

Normally, attractive forces in force curves are said to be caused by meniscus forces, van der Waals forces, or electrical forces due to water adsorption on the surface of a sample. In these measurements, however, the water vapor concentration was 75 ppm or less, so the effect of meniscus forces was likely small. Taking the above into consideration, it was found that the 5 µm LCO attractive force image (g) was correlated with the distribution in both the 5 µm LCO height image (e) and the 5 µm LCO current image (f). It was also found that the 5 µm LTO attractive force image (j) was correlated to the distribution of plate-like crystals in the 5 µm LTO height image (h) (arrows). It is therefore likely that the attractive force images represent van der Waals forces or electrical forces, and that these indicate the compositional distribution of the electrode material.

From the information above, it is likely that the LCO current distribution reflects the compositional distribution of the material, and that the path of the current is due to cracks or gaps between the grains. Regarding the LTO, for which current images could not be obtained in this case, there are plans to measure the anode of an actual battery after charging.

■ Conclusion

The surfaces of all-solid-state LiB electrode materials LCO and LTO were measured without exposure to air, and height images, current images, and attractive force images were obtained. It is expected that such measurements will be applicable to the resolution of issues with resistance at the interface in all-solid-state LiBs.

References
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3) Application News No. S 57 Visualization of Distribution of Electrostatic Force in Electrolyte Clarifying Corrosion and Cell Reactions
4) Application News 01-00256-EN Visualization of Current Distribution by ZXY Measurement: Current Measurement of Graphite Sample

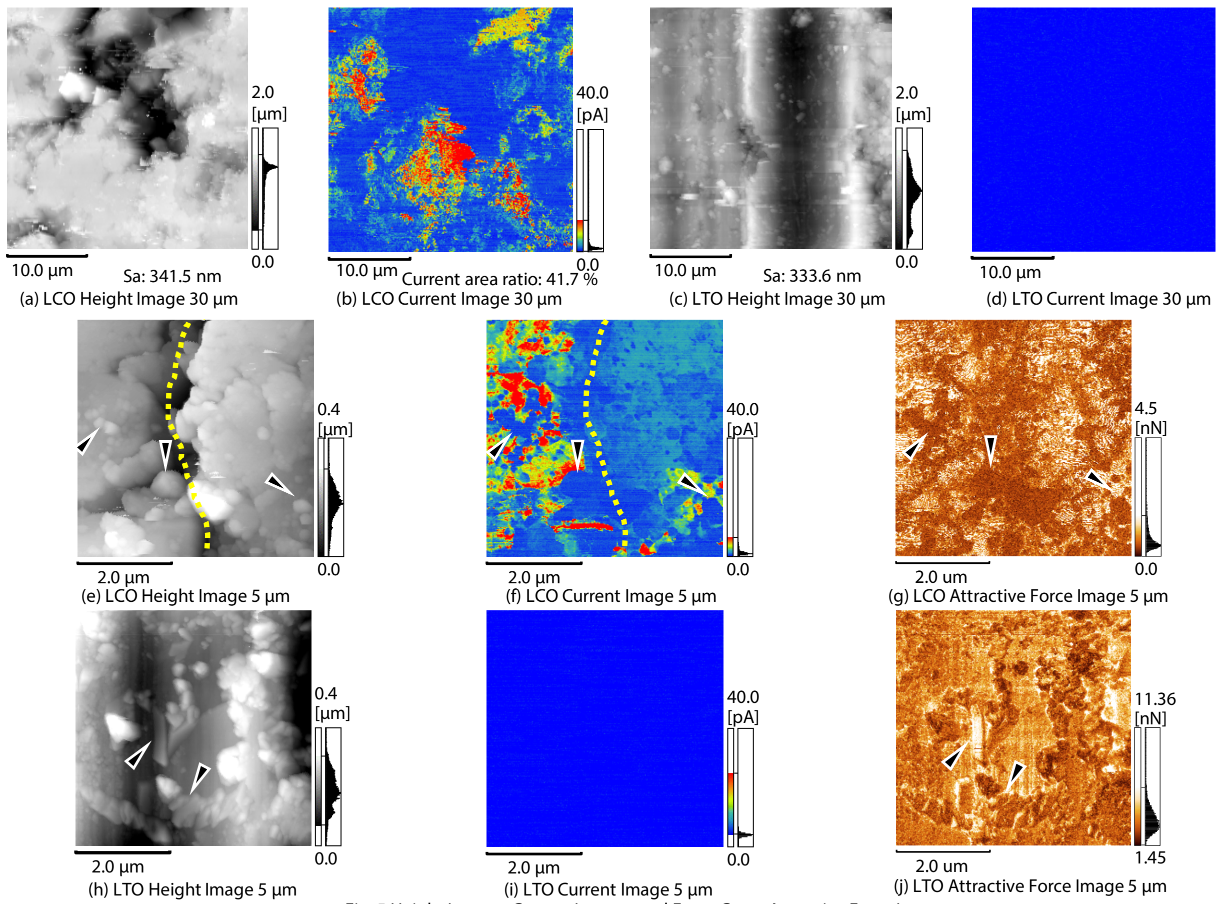

Fig. 5 Height Images, Current Images, and Force Curve Attractive Force Images

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