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Application News

Scanning Probe Microscope (Atomic Force Microscope) SPM-Nanoa™

Evaluating Electrochemical Activity and Electric Potential inside Cathodes in All-Solid-State Lithium-Ion Batteries

Eiji Iida and Akinori Kogure

User Benefits

- The SPM (AFM) can observe and measure charged batteries that are not exposed to ambient air.
- It enables visualization of electron conduction pathways in cathode materials during the operation of all-solid-state lithium-ion batteries.
- Also, it can visualize electric potential changes in cathode materials during charging/discharging of all-solid-state lithium-ion batteries.

■ Introduction

With the growing demand for renewable energy to meet the United Nation's Sustainable Development Goals (SDGs), using high-performance battery storage to improve energy efficiency is becoming an important issue. All-solid-state lithium-ion battery (ASSLiB) development is primarily aimed at electric vehicle applications. This is because ASSLiBs have excellent characteristics, such as long lifespans, excellent safety, and high energy density, and even greater power output and performance improvements are expected in the future. However, one issue that needs to be resolved for achieving their practical adoption is the performance drop of active materials due to charge-discharge cycles. Such performance drops reduce electron/ion mobility and can decrease battery capacity and output and prevent high-speed charging and discharging. Clarifying the mechanism that reduces the performance of active materials will provide the key to improving battery performance.

One way to evaluate the status of materials inside electrodes is to use a scanning probe microscope (SPM/AFM) to measure the materials on a microscopic scale. This Application News describes an example[1] of using an SPM to evaluate the effect of ASSLiB performance drops caused by charge-discharge cycles.

■ SPM-Nanoa and Glove Box

Measurements were performed using an SPM-Nanoa in a flow-type glove box (Fig. 1). Scanning probe microscopes use a microscopic probe to scan the sample surface and observe and measure the three-dimensional shape and local physical properties of the sample at high resolutions. Flow-type glove boxes are designed to continuously circulate and purify argon gas inside the box to maintain the box at moisture and oxygen levels of 1 ppm or lower. ASSLiB charging and analysis must be performed in an inert atmosphere without exposure to ambient air because the lithium ions in the battery cell react and degrade in the presence of oxygen and water.

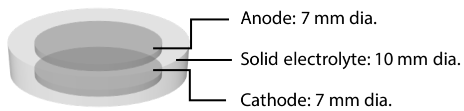
(a) SPM-Nanoa™ (b) Flow-Type Glove Box

Fig. 1 SPM-Nanoa and Glove Box

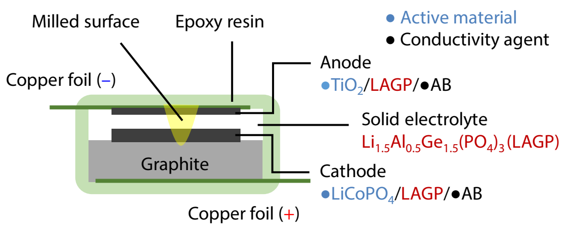
■ Measurement Sample

An ASSLiB battery with an oxide-based NASICON solid electrolyte was used for the measurements. The battery cell was composed of cathodes containing a $LiCoPO_4$ active material (5 to 10 µm diameter particles), anodes containing TiO_2 (60 nm particles), a solid electrolyte containing $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP), and an acetylene black (AB) conductivity agent. Its overall construction is shown in Fig. 2 (a). After splitting the cell into two parts, graphite and copper foil materials were attached, and the overall composition was solidified in an epoxy resin.

The cut surface was processed by ion milling before charge-discharge testing (Fig.2 (b)), and the surface contamination layer was removed using light ion milling treatment immediately before the measurements. The battery cell was mounted in the SPM-Nanoa installed inside the glove box, and the electrode surface was measured using the observation condition settings shown in Table 1.



(a) Overview before Milling



(b) Cross Section after Milling

Fig. 2 Diagram of Battery Cell

Table 1 Observation Conditions

Instrument:	SPM-Nanoa scanning probe microscope
Scanner:	Large-range scanner (XY: 125; Z: 7 µm)
Observation Mode:	Current mode and surface potential (KPFM) mode
Field-of-View:	20 µm × 20 µm
Pixels:	256 × 256
Dew Point:	-80 °C
Oxygen Concentration:	0.8 ppm

■ Evaluation of Localized Electrochemical Activity in the Cathode

Electrochemically active regions in the battery cell were evaluated by creating battery operating circuits (Fig. 3) and measuring the electrical current flow between the cathode cross section and the anode current collector. The measurement results are shown in Fig. 4.

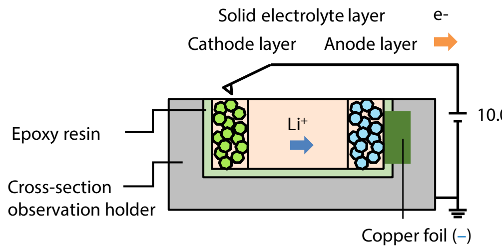


Fig. 3 Circuit Configuration for Current Measurements

The following describes how the combination of electrical current information for the entire battery cell, including electron conduction inside the cathode, the interface surface status between the solid electrolyte and active material, and the network effects of the solid electrolyte were obtained. In the current image, the red areas indicate high current flows, and the blue areas low current flows. Electrical current flows easily through a conductivity agent where resistance is low, while little current flows through active and solid electrolyte materials where resistance is high. Therefore, we can assume that the red areas mainly consist of conductivity agents and the blue areas active materials or solid electrolytes. A comparison of the current images from before and after charge-discharge testing shows no major changes in the distribution of electron conduction pathways. The current image from before charge-discharge testing shows that the conductivity agents were distributed unevenly, as shown below on the left. Therefore, one way to improve charge-discharge characteristics would be to improve the distribution of conductivity agent distribution.

■ Evaluation of Surface Electric Potential inside the Cathode

The surface potential (KPFM) inside the cathode was measured before and after the charge-discharge test. Those measurement results are shown in Fig. 5. A comparison of the KPFM images from before and after the test shows an average in-plane electric potential of 0.75 V before the charge-discharge test and 2.98 V after the test. Normally, the electric potential should approach 0 V after discharging, but the results show that there was an electric charge remaining in the sample, indicating that the charge-discharge performance decreased. Considering that Fig. 4 shows no major changes in the distribution of electron conduction pathways before and after the charge-discharge test, it suggests a degradation in the ion conduction pathways or the interface surface between the solid electrolyte and the active material.

■ Conclusion

This Application News describes how the phenomena of electron conduction pathway formation inside cathodes, which can lead to lower active material performance in ASSLiB, can be visualized and how changes in surface electric potential can be measured before and after charge-discharge testing. These results are expected to lead to improvements in ASSLiB performance by providing feedback about materials and the manufacturing process.

Acknowledgments

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Reference Documents

1) E. Iida, A. Kogure, T. Miyamoto, H. Nakajima, H. Mukohara, N. Morimoto, R. Yamasaki, H. Yamada, C. J. Macey, AFM Evaluation of Different-Sized Active Materials and Interface of All-Solid-State Lithium-Ion Batteries., M&M2023, July 23-27, 2023; Minneapolis, MN, USA.

Related Application News

1. Surface Potential Measurement at the Electrode-Electrolyte Interface of a Charged All-Solid-State Lithium-Ion Battery [Application News No. 01-00490-EN]

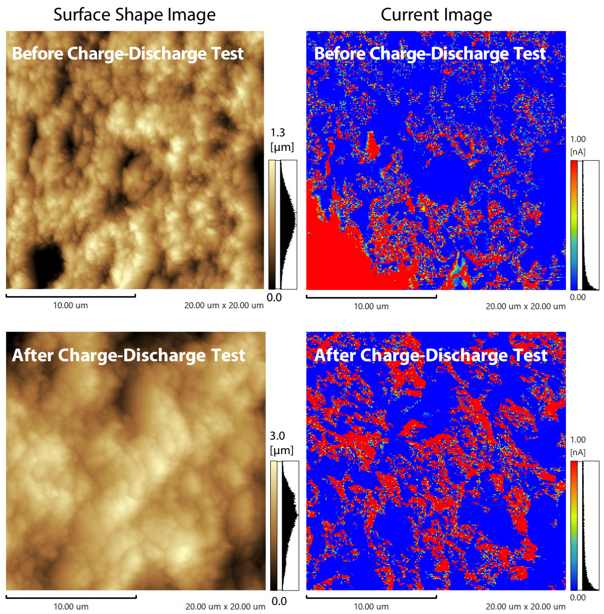

Fig. 4 Evaluation of Electrochemical Activity inside Cathode

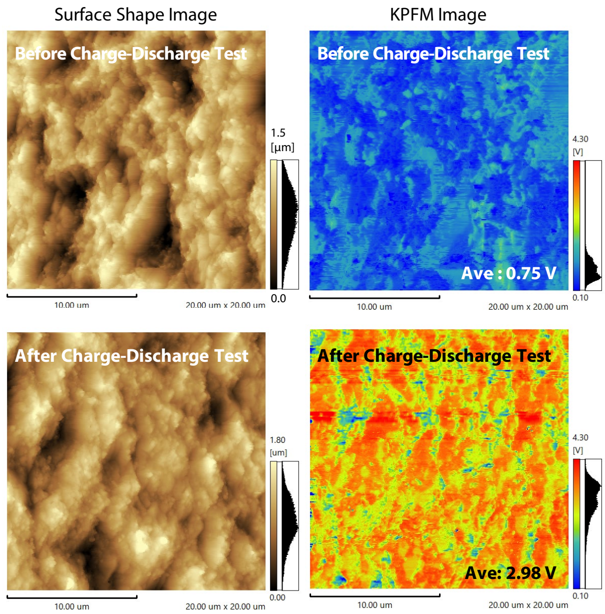

Fig. 5 Evaluation of Surface Electric Potential inside Cathode

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