

Application News

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

Surface Potential Measurement at the Electrode-Electrolyte Interface of a Charged All-Solid-State Lithium-Ion Battery

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User Benefits

- ◆ Enables SPM (AFM) observation and analysis of a charged battery in an inert atmosphere without exposure to ambient air
- ◆ Enables the visualization of the surface morphology and distribution of surface potential at the electrode-electrolyte interface of an all-solid-state lithium-ion battery.
- ◆ Enables the visualization of the charged state of active materials in an all-solid-state lithium-ion battery.

■ Introduction

With the growing demand for renewable energy to meet 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 due to ASSLiBs having excellent characteristics that include a long lifespan, excellent safety, and high energy density, with even greater power output and performance improvements expected in the future. One of the challenges facing the practical adoption of ASSLiBs is resistance at the electrode-electrolyte interface. High resistance has a detrimental effect on the movement of lithium ions at the electrode-electrolyte interface, reduces battery capacity and power output, and prevents fast charging. Improving the electrode-electrolyte interface is key to improved ASSLiB performance. However, these interface phenomena and mechanisms of performance deterioration are not yet understood and methods of assessing these issues have yet to be established.

Scanning probe microscopy (SPM [AFM]) offers one potential method of collecting microscopic-scale measurements and evaluating the electrode-electrolyte interface. This article describes an example application in which a scanning probe microscope is used to measure surface potential (Kelvin probe force microscopy [KPFM] mode) at the electrode-electrolyte interface of a charged ASSLiB.¹⁾

■ SPM-Nanoa and Glove Box

Measurements were performed using 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 box is designed to continuously circulate and purify argon gas inside the box and maintain the box at moisture and oxygen levels as low as 1 ppm and below. 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.

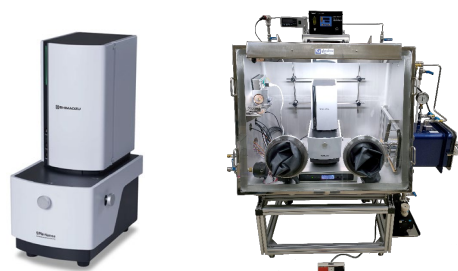


Fig. 1 SPM-Nanoa and Glove Box

■ Samples

The battery cell was a NASICON-type ASSLiB with oxide-based solid electrolytes. The battery cell used LiFePO_4 active cathode material, TiO_2 active anode material, $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) solid-state electrolyte, and acetylene black (AB) as a conductive agent.

Current collectors serving as electrode terminals were bonded to the sample battery cell with silver paste, the entire sample was strengthened by an epoxy resin covering, and after cross-section polishing, light ion milling was performed from directly above to remove the contamination of surface layer (Fig. 2). The battery cell was then charged for 50 hours inside a glove box. Charging was performed in an environment with a moisture concentration of 10.6 ppm (dew point: -60°C) and an oxygen concentration of 0.4 ppm. Since NASICON-type ASSLiBs are relatively stable when exposed to air, moisture concentrations of 1 ppm or above should not pose a problem. The charged battery cell was then placed in SPM-Nanoa installed in the glove box and the electrode-electrolyte interface was observed under the conditions shown in Table 1.

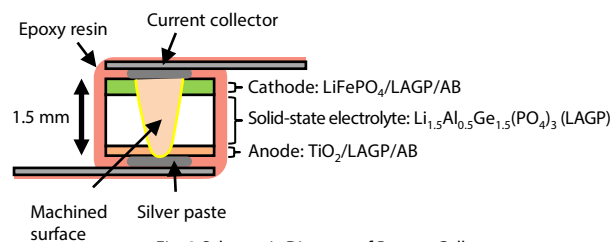


Fig. 2 Schematic Diagram of Battery Cell

Table 1 Observation Conditions

Instrument:	SPM-Nanoa Scanning Probe Microscope
Scanner:	Large-Range Scanner (XY: 125 μm , Z: 7 μm)
Observation Mode:	Surface Potential (KPFM) Mode
Field-of-Observation:	30 \times 30 μm (Fig. 3) 5 \times 5 μm (Fig. 4)
Pixel:	256 \times 256

■ Topographical Observation of Electrode-Electrolyte Interface

The surface shape of the electrode-electrolyte interface was observed. Voids were observed at the interface as indicated by the white arrows in Fig. 3. Voids hinder the transfer of lithium ions and contribute to resistance at the interface.

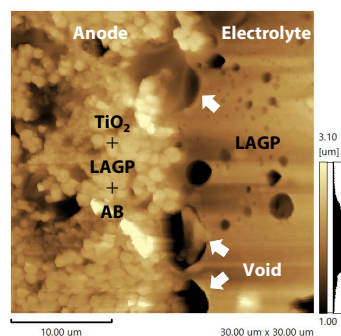


Fig. 3 Topographical Image of Electrode-Electrolyte Interface

■ Evaluating the Charged State of Active Anode Materials

The surface shape observation and KPFM measurements were performed at three sites on the anode: (a) Current collector side, (b) Center area, and (c) Solid electrolyte side. Fig. 4 shows an optical microscope image indicating measurement points on the anode and measurement results at each site. Examining the topography images reveals AB particles (several 100 nm diameter) and TiO₂ particles (approx. 1 μm diameter) at (a), TiO₂ particles across the entire field of view at (b), and LAGP and TiO₂ particles at (c). In the KPFM images, TiO₂ particles are labeled by mean potential with circles indicating a mean potential of 0.48 V, triangles indicating a mean potential of 0.57 V, and crosses indicating a mean potential of 0.67 V.

While charging, lithium ions (Li⁺) transfer from the cathode to the anode via LAGP, and electrons (e⁻) transfer from the current collector to the inside of the anode via AB (Fig. 5). TiO₂ also reacts with the transferring Li⁺ and e⁻, converting it into Li_xTiO₂. On KPFM images, the lower the surface potential the greater the number of electrons, thus the lower the potential of a particle the more charged it is. Accordingly, the TiO₂ particles labeled with circles in Fig. 4 are more charged while the TiO₂ particles labeled with triangles and crosses are less charged. Comparing sites (a), (b), and (c) shows the center area (b) is more charged than the other two sites. This indicates that Li⁺ and e⁻, which travel from the current collector side and the solid electrolyte side, are probably present in appropriate amounts in the center area (b). Similarly, the current collector side (a) has charged less due to insufficient Li⁺ and the electrolyte side (c) has charged less due to insufficient e⁻. These results suggest there are insufficient conduction paths for Li⁺ and e⁻ in the anode.

This article used KPFM measurements to understand the charged state of active anode materials and identify which active materials play an effective role in charging/discharging and which do not.

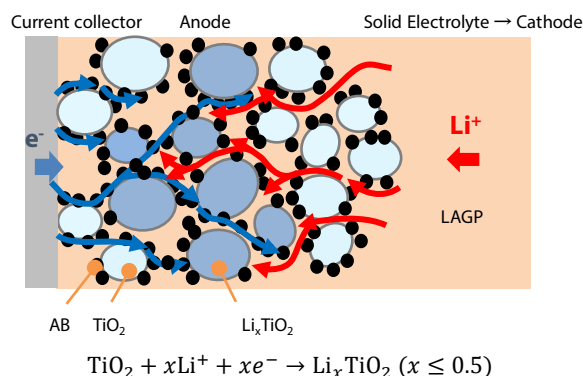


Fig. 5 Simplified Model of Lithium Ion and Electron Movement during Charging

■ Conclusion

Scanning probe microscopy of the electrode-electrolyte interface of a charged ASSLiB performed in an inert atmosphere revealed voids at the interface and enabled an evaluation of the charged state of active anode materials. This analysis is expected to help elucidate mechanisms of reactions at the electrode-electrolyte interface and resolve the issue of interface resistance in ASSLiBs.

< Acknowledgments >

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< References >

- 1) E. Iida, T. Miyamoto, A. Kogure, H. Mukohara, N. Morimoto, R. Yamasaki, H. Yamada, SPM/AFM Evaluation of Interface of All-Solid-State Lithium-Ion Batteries., IVC-22, Sep 13, 2022; Sapporo, Japan.

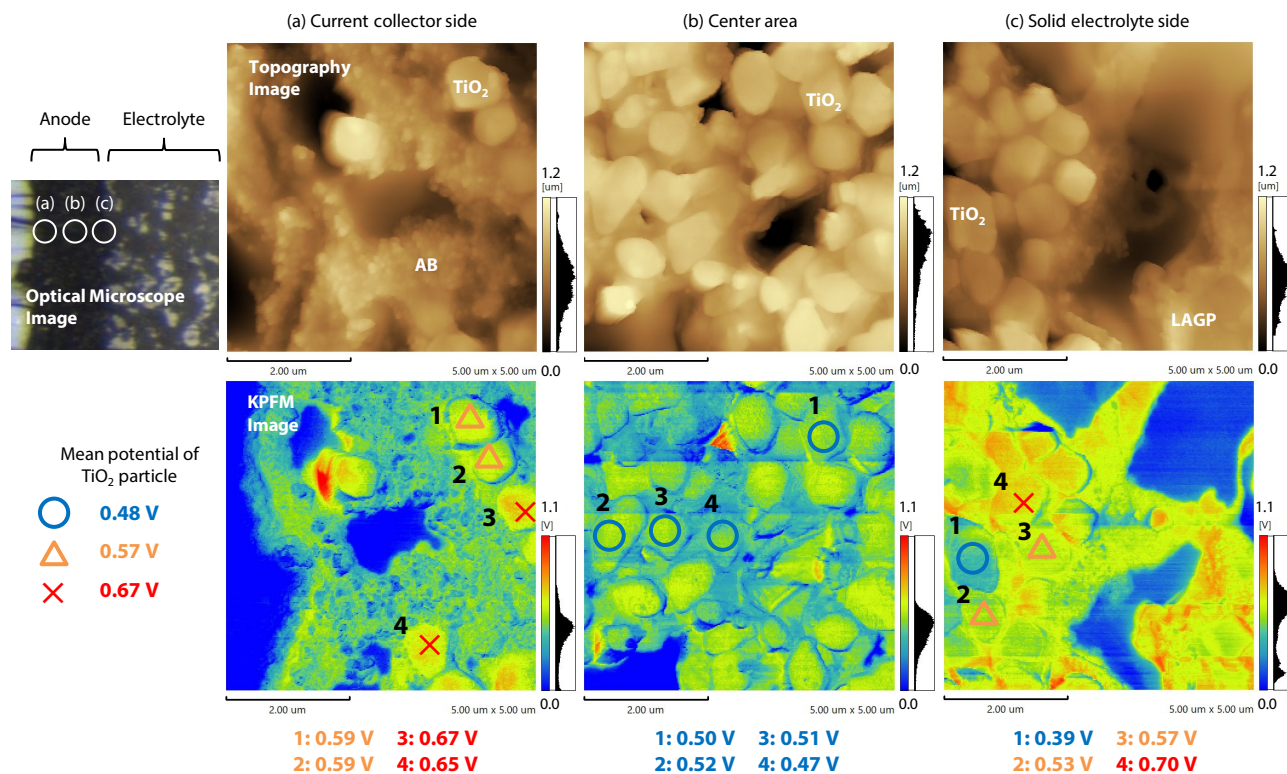


Fig. 4 Evaluation of the Charged State of Active Anode Materials

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