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AFM Evaluation of Different-Sized Active Materials and Interface of All-Solid-State Lithium-Ion Batteries

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Introduction

With recent global warming, improving energy use efficiency with high-performance storage batteries is an important issue. All-solid-state lithium-ion batteries (ASSLiB) with excellent safety, long life, and high energy density have been proposed as a candidate for high-performance batteries.

Problem

The electrode and solid electrolyte form a solid-solid interface, which significantly increases the interface resistance and remarkably lowers the battery performance for the following reasons.

- ✓ Deterioration of contact state between the electrode active material and solid electrolyte
- ✓ Depletion of Li^+

In our previous work, voids were observed at the interface of ASSLiB using TiO_2 with average particles size of 1 µm as the negative active material. These voids may prevent the movement of Li^+ and contribute interfacial resistance [1].

In this study we investigated ASSLiB using TiO_2 with a particle size of 150 nm with Atomic Force Microscope (AFM) to evaluate the effect of degradation by charge-discharge tests.

Materials & Methods

◆Materials

Oxide-based NASICON (Na Super Ionic Conductor) type ASSLiB

✓ As assembled : (A) ✓ After charge-discharge tests : (B)

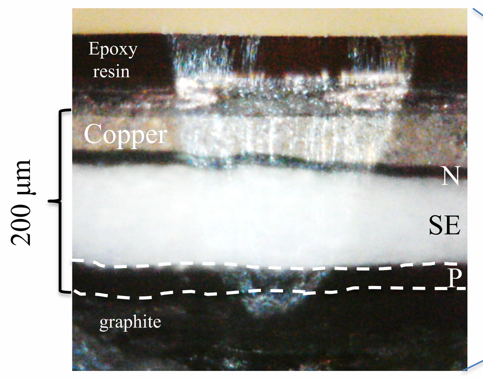


Fig.1 Optical microscope image of (A)

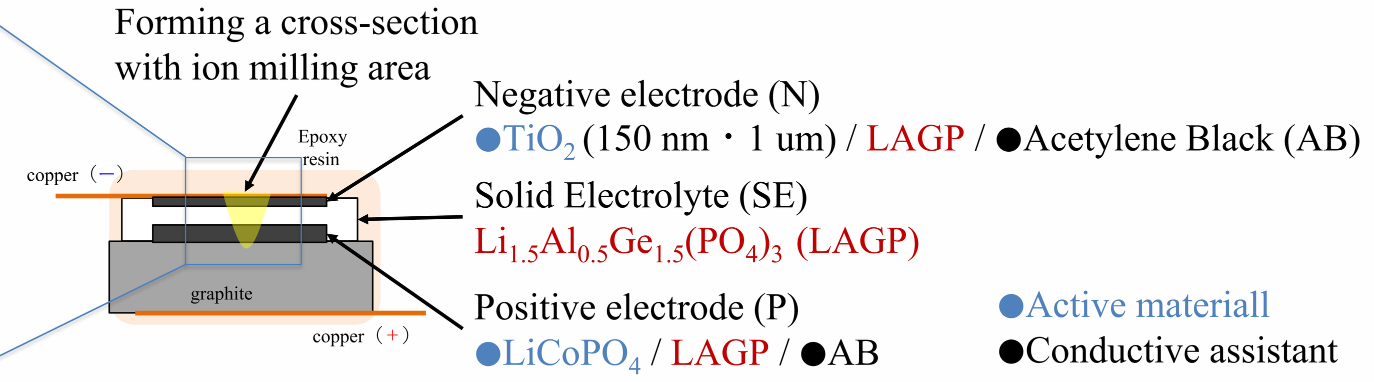


Fig.2 Overview of assembled ASSLiB

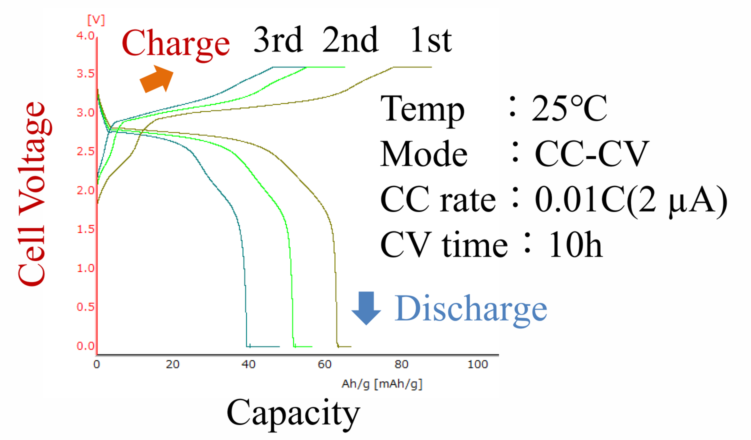


Fig.3 Charge-discharge characteristic of ASSLiB

After the surface of ASSLiB was cross-sectioned, charge-discharge tests were performed. The theoretical capacity of this ASSLiB piece is 150mAh/g, but the actual charge capacity is about half. And the performance was degraded by the charge-discharge tests.(Fig.3).

◆Methods

SPM / AFM measurement in the glove box

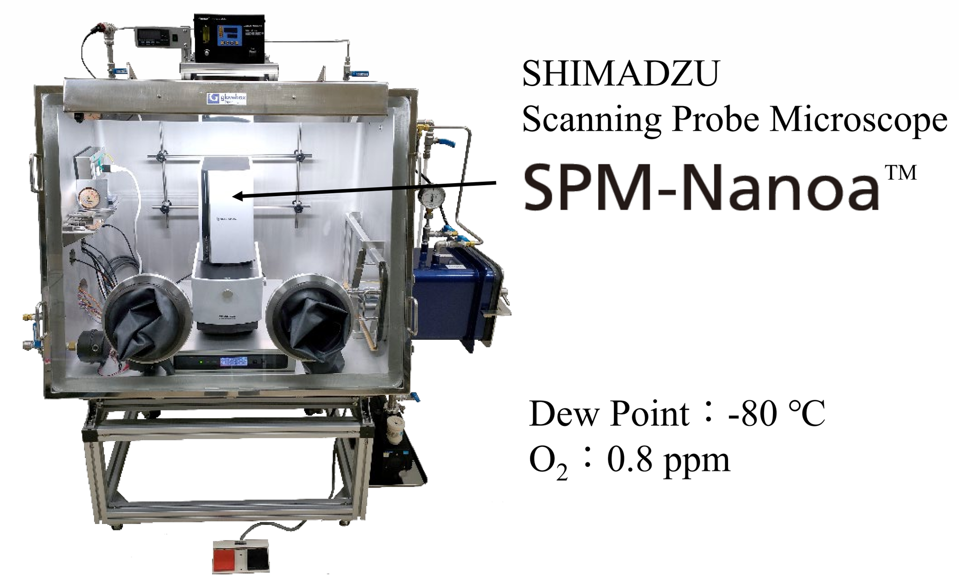
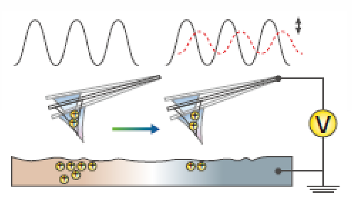


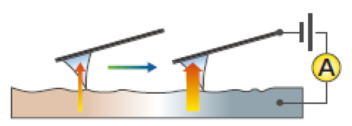
Fig 4. Flow-type glove box (made by Glovebox Japan inc.)

✓ Kelvin Probe Force Microscope (KPFM)



Surface electric potential is observed by detecting the static electric force acting on the cantilever.

✓ Current



Electrical properties of surfaces are observed by detecting the current flowing through the cantilever.

Results & Discussion

◆Size evaluation of the negative active materials

The shape of the negative active material as assembled was observed.

Different particle sizes of TiO_2 can be clearly seen (Fig.5). When the width of any 4 particles was measured from the topography, the average value was close to the nominal value of the material (Table 1).

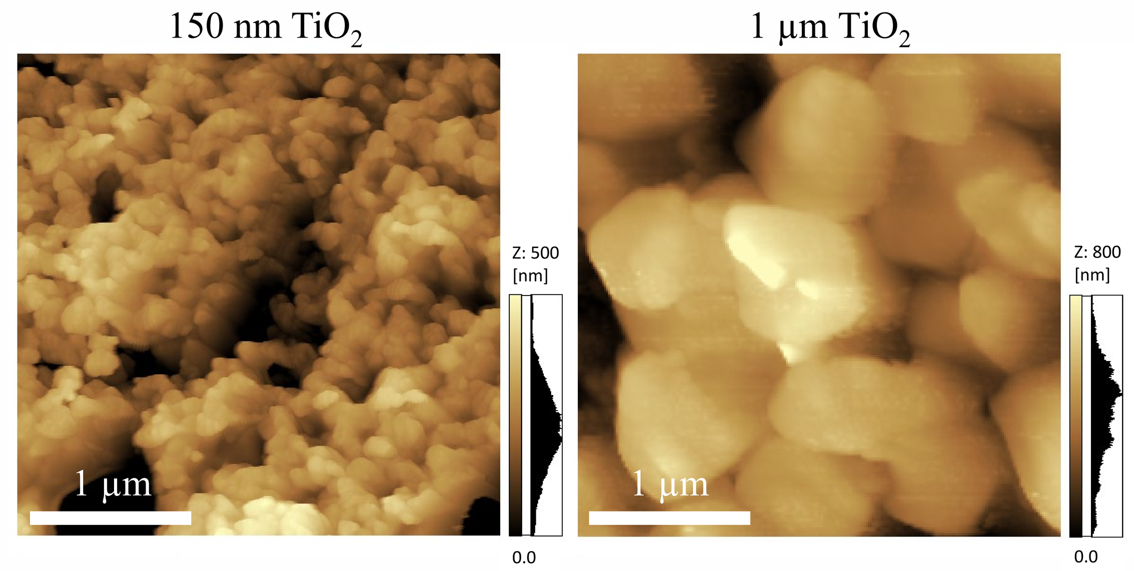


Fig.5 Topography of the negative active materials

Table 1 Size measurement of TiO_2 particles

	150 nm TiO_2	1 µm TiO_2
Average particle sizes [nm]	160.1	1005

◆Visualization of the conductive path at the positive electrode

The current distribution in 150 nm TiO_2 battery operating conditions was evaluated.

Active material and solid electrolytes have high resistance, so current does not flow very much. Therefore, we can see that the area through which the current flows is the conductive assistant (Fig. 7). From this figure, we can consider the following:

- ✓ As assembled and after charge-discharge tests, no deterioration in the current path can be confirmed.
- ✓ The distribution of the conductive assistants was uneven with respect to the 150nm TiO_2 particles. The conductive path to the active material was insufficient.
- ✓ In order to improve the charge/discharge characteristics, it is necessary to improve the dispersion state of the conductive assistant.

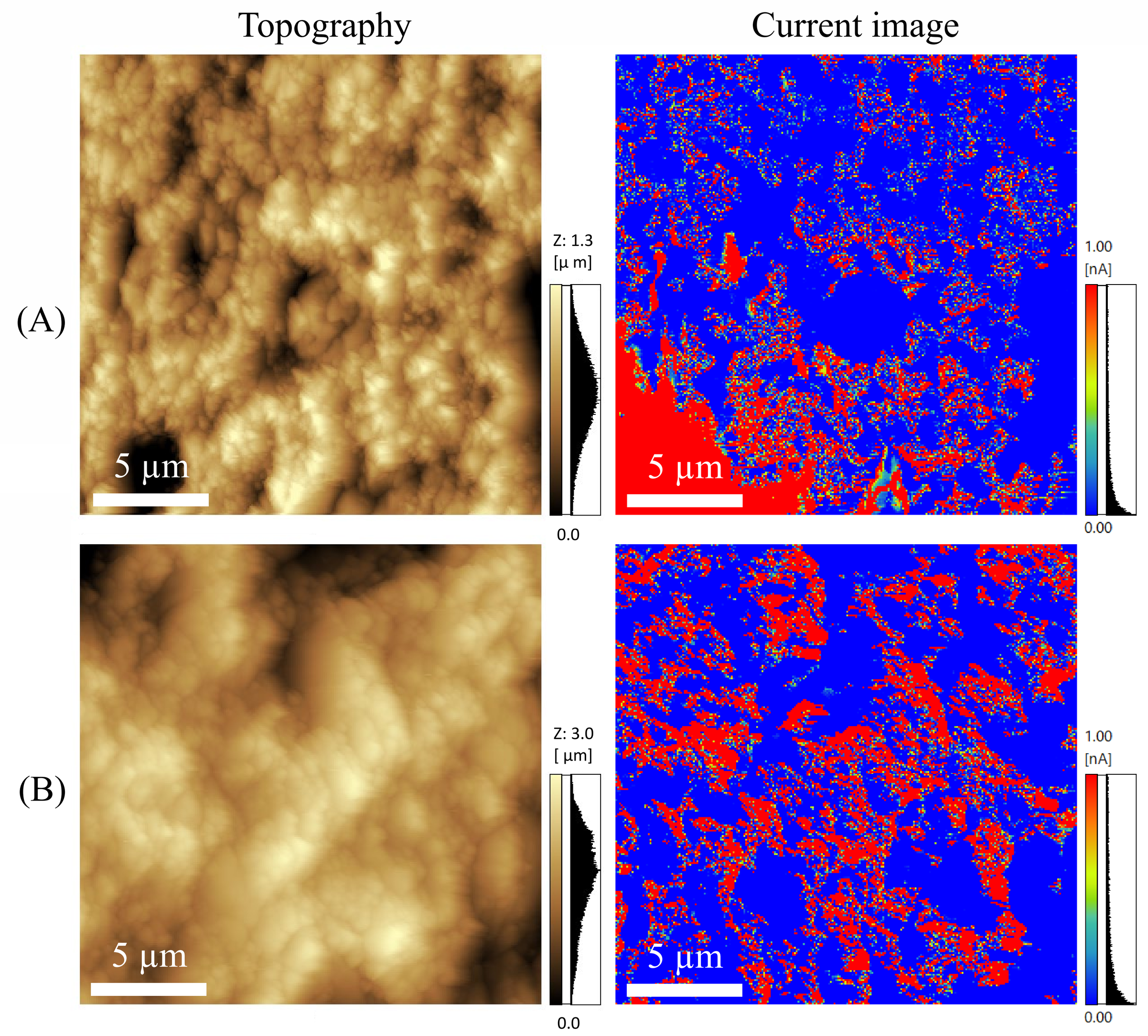


Fig.7 Conductivity of positive electrode

◆Improvement of the bonding state of the interface

The shape of the negative electrode-solid electrolyte interface as assembled was observed.

There are voids at the interface when the hot press is not used. When hot pressing was used, there were no voids at the interface, which was successfully improved to a dense structure.

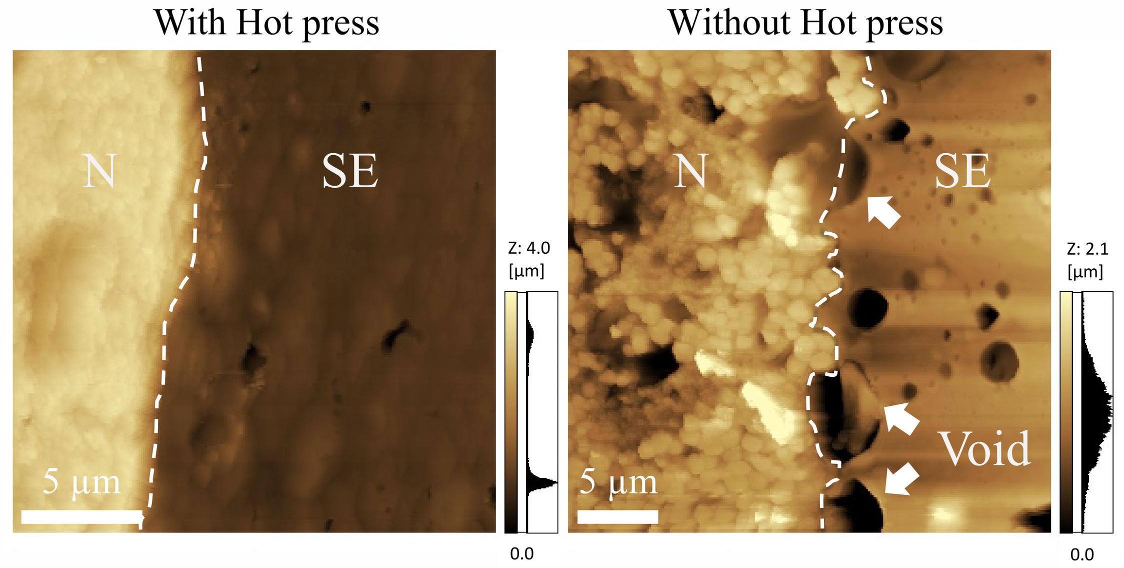


Fig.6 Topography of interface of (A)

◆Visualization of the degradation state of positive active material

KPFM measurements were performed on the 150nm TiO_2 positive electrode as assembled and after the tests.

The average potential is 0.75 V before charging and 2.98 V after charging/discharging (Fig. 8). Originally, the potential after discharge should approach 0 V, but the charge remains in this sample. As shown in Fig. 8, there is no deterioration of the electron conduction path, suggesting that a problem occurred in the ion conduction path.

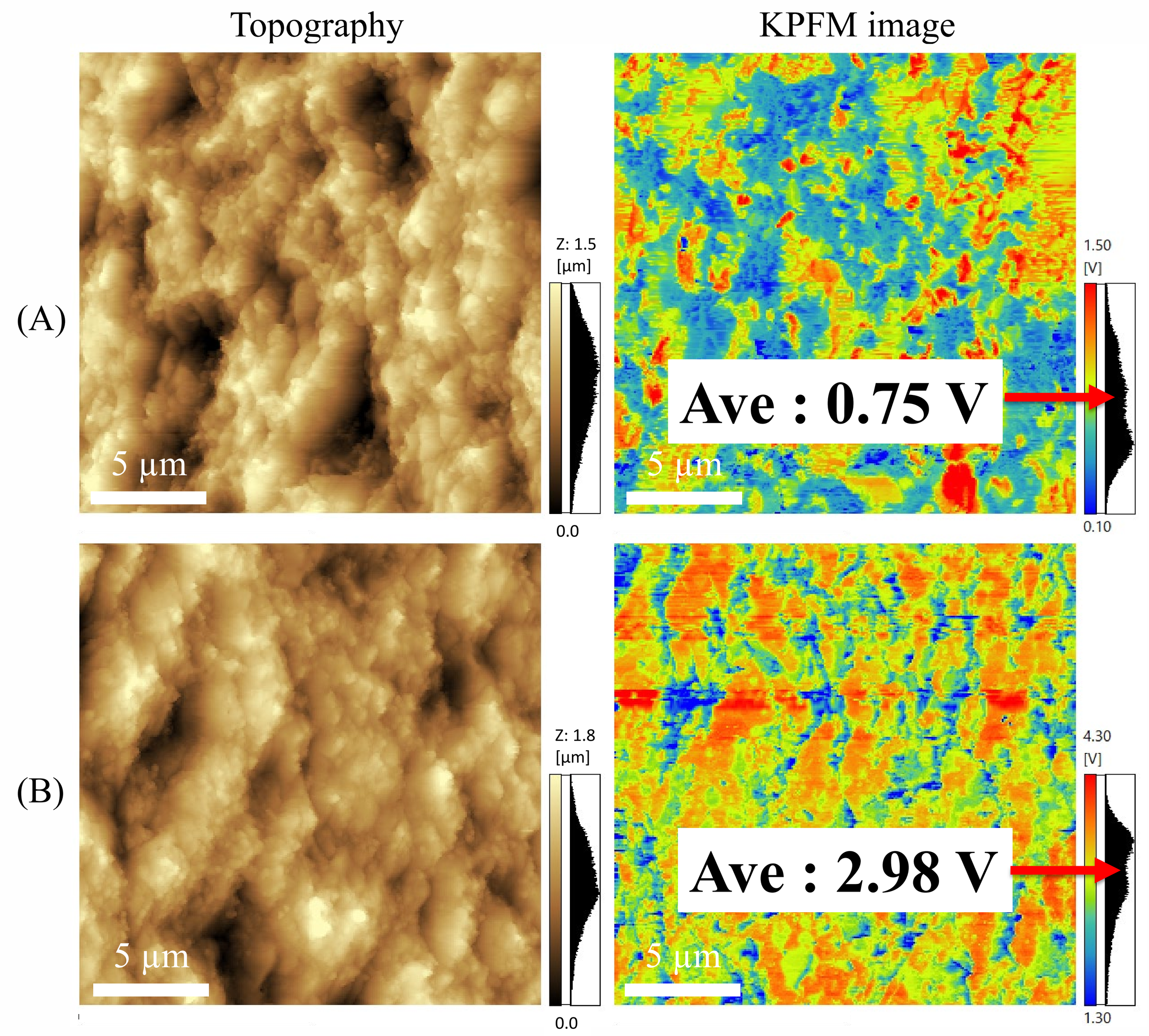


Fig.8 Surface potential of the positive electrode

Conclusion

- ✓ The shapes of different particle sizes of TiO_2 were observed with high resolution by SPM/AFM.
- ✓ We were able to improve the bonding state of the interface by hot pressing.
- ✓ The conductive assistant was distributed unevenly, and improvement of the dispersion state was necessary.
- ✓ Degradation caused by charging and discharging can be captured by KPFM measurement.

Reference

1) E. Iida et al., “SPM/AFM Evaluation of Interface of All-Solid-State Lithium-Ion Batteries”, IVC-22, Sapporo, Japan (September 13, 2022)