

Ultra-low voltage SEM observation for battery materials

Ph.D. Yutaka Nagaoka¹, Dr. Yoichiro Hashimoto¹, Mr. Toru Aiso¹, Mr. Shuhei Yabu², Mr. Masahiro Sasajima³

¹Solution Development Dept., Hitachi High-Tech Corporation, Hitachinaka, Japan, ²Electron Microscope Systems Design Dept., Hitachi High-Tech Corporation, Hitachinaka, Japan,

³Software Design Dept., Hitachi High-Tech Corporation, Hitachinaka, Japan

Background incl. aims

The scanning electron microscope (SEM) observation at an ultra-low accelerating voltage can visualize strictly superficial surface of the sample with a little electron beam irradiation damage, since the electron scattering volume into the sample is extremely small. However, interpretation of the captured image becomes complicated because the voltage contrast (VC) depending on emitted electron yield changes its behavior under the ultra-low accelerating voltage conditions [1]. Previously, the VC between binders and active materials of lithium-ion battery (LIB) anodes under ultra-low accelerating voltage conditions below 50 V were studied. As the result, we reported that the VC between the binder and the active material was dramatically changed among the ultra-low accelerating voltage conditions [2]. Especially, particle-like unique contrast, which was thought to reflect the binder structure, was observed at 20 V. Although this VC was presumed to be formed by the surface potential at the specific accelerating voltage, the formation mechanism was unknown. In this study, a simplified experiment simulating the binder on the LIB anode was performed to elucidate the binder VC formation mechanism.

Methods

Styrene-butadiene-rubber (SBR) particles: the primary material of the binder, were dispersed in water. The solution with the dispersed particles were dropped onto an osmium (Os) coated Si substrate. The solution was dried at the room temperature. The SBR particles were observed at accelerating voltages below 50 V using a Hitachi SU8700 field emission SEM [3]. The correlative observation with SEM and atomic force microscope (AFM) was performed using a Hitachi AFM5300E for surface potential measurements after electron beam irradiation. The "Air protection" sample holder was used to retain the sample in vacuum at the transfer between SEM and AFM.

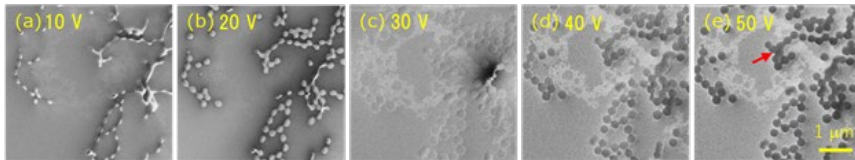
Results

The graphic shows the observation results of the SBR particles, representing the "binder", on the Os-coated Si substrate at the same area captured at accelerating voltages from 10 to 50 V. The SBR showed darker signal (indicated by the red arrow in image (e)) compared to the surrounding Si substrate at 50 V. As the accelerating voltage gradually decreased to 30 V, the contrast between the SBR and the substrate was almost disappeared. When the accelerating voltage decreased to 20 V, the SBR was observed with particle-like contrast. At the accelerating voltage of 10 V, mirror phenomenon, in which the primary electrons bounced off before impacting the sample surface, occurred. This result showed that the VC of the SBR on the Si substrate showed same manner of the binder on the active material in the previous work in spite of different substrate material. To clarify the principle of the VC formation mechanism, correlative AFM observations of the SEM observed area were also executed to measure the residual surface potential. As the result, the residual surface potential of the SBR, the "binder", was confirmed to be varied by the accelerating voltage.

Conclusion

VC formation mechanism of the binder was investigated with the simplified specimen. The surface appearances of the “binder” were observed with the SEM and the surface potentials were also measured with the AFM correlatively, and SEM accelerating voltage dependency of the residual surface potential was found.

Graphic:



Keywords:

Ultra-low-voltage observation, Voltage contrast, Correlative observation

Reference:

- [1] I. Müllerová, Scanning Microscopy 13. 1., 7-22. (1999).
- [2] Y. Hashimoto et al., Microscopy and Microanalysis 29 (Suppl 1), 499-500 (2023).
- [3] Y. Hashimoto et al., Microscopy Vol. 70, No. 4, 375-381 (2021).