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Si K-edge X-ray Absorption Spectroscopy of Si Particles

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Silicon (Si) is one of negative electrode materials for next-generation lithium-ion batteries due to its extremely high theoretical capacity. However, Si has several major drawbacks including heavy volume changes during lithiation/delithiation, particle fragmentation, loss of contact with electrolyte, reduced Coulombic efficiency, resulting to capacity degradation. Nano-scale silicon (n-Si) has been shown to mitigate some of these issues by effectively absorbing volume expansion [1]; however, previous studies have primarily focused on the behavior and electrochemical performance of Si within composite electrodes, and to the best of our knowledge, no systematic investigation has been conducted to elucidate the electronic structure of µm-sized Si particles depends on particle size. In this study, we investigated commercially available Si particles with six different average diameters (1, 3, 5, 8, 18, and 45 µm) using Si K-edge X-ray absorption spectroscopy (XAS).

All Si samples were purchased from Japan Natural Energy & Resources Co., Ltd. Si powder was fixed to a sample holder using carbon tape. Si K-edge XAS measurements were conducted at the beamline BL-10 of the SR Center, Ritsumeikan University using total electron yield (TEY) and partial fluorescence yield (PFY) modes.

Figure 1(a) and (b) show Si K-edge X-ray absorption near edge structure spectra of Si particles measured in TEY and PFY modes. In the TEY data, a prominent absorption edge structure of crystalline Si appears near 1841 eV. In addition, the low energy shift is observed in the 1 µm Si particle, suggesting an amorphous structure formation. This is consistent with the XRD results, which show a broad peak alongside the crystalline peak in this sample. The additional peak observed around 1847 eV in the TEY spectra of all samples can be attributed to SiO_2. However, this oxide peak is not present in the PFY spectra. This reflects the fact that the detection depth of PFY (submicron) is much deeper than that of TEY (approximately 70 nm) [2]. This suggests that a thin silicon oxide layer (≤100 nm) covers the surface of each particle but does not penetrate into the interior.

Furthermore, features associated with oxides are most strongly observed in particles of 45 µm and gradually weaken as particle size decreases. This trend indicates that micrometer-sized Si particles form thicker oxide layers on their surfaces compared to larger particles, emphasizing the importance of particle size when considering surface chemistry and long-term electrode stability.

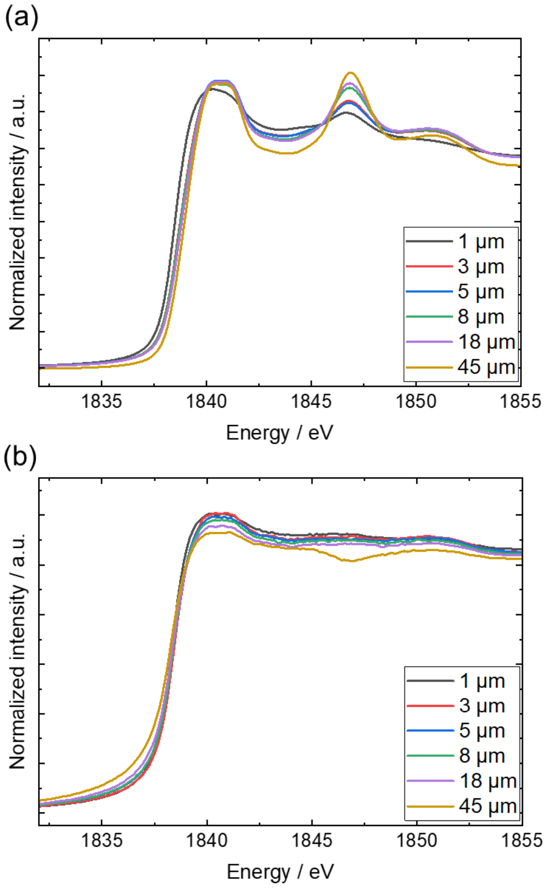

Fig. 1 Si K-edge X-ray absorption near edge structure spectra of Si particles with various particle sizes measured in (a) TEY and (b) PFY modes.

References

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