

X-ray absorption spectroscopy of silicon for lithium-ion battery anode

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Silicon anode used as lithium-ion batteries exhibits a theoretical capacity of 4200 mA h g^{-1} , which is about ten times higher than that of currently used graphite anode. Because of the highly abundant of silicon and the chemical stability of lithium silicide, there is an advantage using silicon anode in the point of cost and safety [1]. Therefore, silicon anode is expected for the next generation battery anode material. The reaction mechanism of silicon anode has been analyzed by X-ray diffraction (XRD) [2]. For the charge reaction in silicon anode, silicon active materials accommodate lithium-ions by forming an alloy with lithium, which transforms an amorphous phase. Although XRD analysis cannot provide enough information about the amorphous phase, X-ray absorption spectroscopy (XAS) is a powerful tool to analyze the electronic and local structural information of the amorphous phase. However, to our knowledge, XAS studies on silicon anode are not sufficiently performed. In this study, we measured Si K-edge XAS of charged silicon anodes.

The charged silicon anodes were electrochemically prepared by using a half-cell in which the electrode mixture using silicon particles was used as a working electrode and lithium metal was used as a counter electrode. The state of charge (SOC) of the sample for XAS measurement was 0%, 50%, and 100%. Si K-edge XAS was measured by fluorescence mode at BL-13, SR Center, Ritsumeikan University.

Fig. 1 shows Si K-edge X-ray absorption near edge structure of the initial state (SOC 0%) and the charged states. In the initial state, the sharp peaks were observed at around 1840 eV and 1847 eV. The former is a peak derived from silicon, and the latter is derived from SiO_2 [3,4], which indicates that a part of the silicon particles is oxidized. As the alloying reaction of silicon with lithium proceeds, the peak at 1840 eV drastically decreases and the absorption edge shifts towards lower energy. On the other hand, the decrease in peak intensity at 1847 eV is small, implying that the contribution of SiO_2 is little to the charge reaction. Fig. 2 shows the radial structure function obtained by Fourier transforming from extended X-ray absorption fine structure (EXAFS) oscillation. The extracted oscillation was weighted by k^2 , and the Fourier transform was performed on $k = 3.0$ to 11.2 \AA . The peak at 2.0 \AA was observed in the initial state and this peak disappeared after charging. The alloying reaction with lithium by the initial charge induces the drastic

distortion in the first shell from the Si-Si bond.

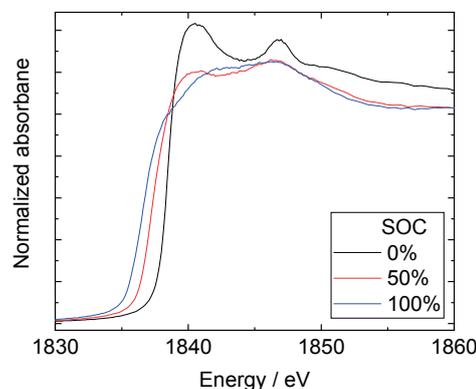


Fig. 1 Si K-edge XANES of charged silicon anodes.

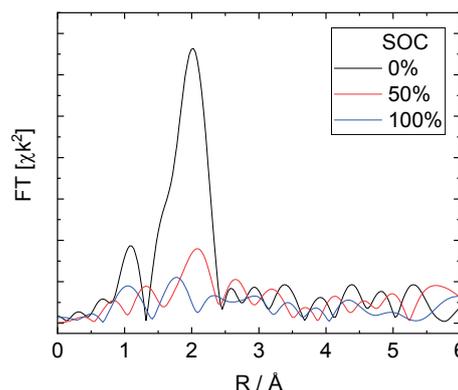


Fig. 2 Radial structure function of Si K-edge EXAFS for charged silicon anodes.

References:

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