

Operando Si K-edge XAFS study of the reaction mechanism of SiO anode for lithium ion battery during charge-discharge cycling

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Silicon monoxide (SiO), which was comprised the mixture of nano-sized silicon and amorphous SiO₂¹, is an attractive material as an anode for lithium ion battery due to its high theoretical capacity, and better cycle stability than pure Si materials. However, SiO electrode exhibits a large irreversible capacity at the first charge-discharge cycling. SiO₂ domains in SiO were reacted with lithium to produce lithium silicate and Li₂O which were electrochemically inactive materials during the initial charging.² Although products resulting from the reaction with lithium was studied, the irreversibility of these products have not been clarified. In this study, the reversibility of the reaction products in SiO electrode was analyzed during charge-discharge cycling by *operando* Si K-edge XAFS.

Operando measurement was performed by spectro-electrochemical cell. Picture of the cell was shown in Fig.1. Polyimide film coated with copper was adopted as the X-ray window and the current collector. Composite electrode was comprised of a composite mixture of the SiO, carbon, and polyimide binder with a weight ratio of 75:15:10. Lithium foil was used as the counter electrode, and 1M LiPF₆ dissolved in ethylene carbonate: diethyl carbonate (70:30) v/v% was done as the electrolyte. Si K-edge XAFS measurements were conducted at BL-13 of the Synchrotron Radiation Center (Ritsumeikan University). The partial fluorescence yield mode was used for XAFS measurements, and the incident X-ray beam was monochromated by InSb (111) crystal. The absolute photon energy of Si K-edge was calibrated to the white lines of SiO₂ at 1846.71 eV. The measurement time of a XAFS spectrum was about 9 min.

Figure 2 shows the *operando* Si K-edge XAFS spectrum of SiO with potential profile during the charge-discharge cycling. During initial charging, the lowering energy shift of Si K-edge at 1838 eV was confirmed indicating the Si was reacted with lithium and alloyed. Although the energy shift was reversibly occurred until 2nd discharging, the energy state has not been initialized after discharged. Then the inactive Si part was formed during initial charging.

The Si K-edge peaks at 1846.8 eV, which indicate the SiO₂ part in SiO, were broadened during initial

charging. Then the SiO₂ part was also reacted with lithium. However, the spectral features of them was not changed during initial discharging and subsequent charge-discharge cycling. Then the SiO₂ was not reacted with lithium at subsequent charge-discharge cycling. After initial charging, the peak top energy at 1846.8 eV was not changed. If Li-silicate compounds was formed during charging, the peak top energy could be shifted to lower energy. It is indicated that the SiO₂ has remained in SiO electrode. Then the irreversible reaction of SiO₂ was not all the initial irreversible capacity of SiO electrode.

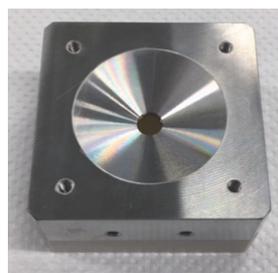


Fig.1. Picture of the spectro-electrochemical cell for Si K-edge XAFS measurements.

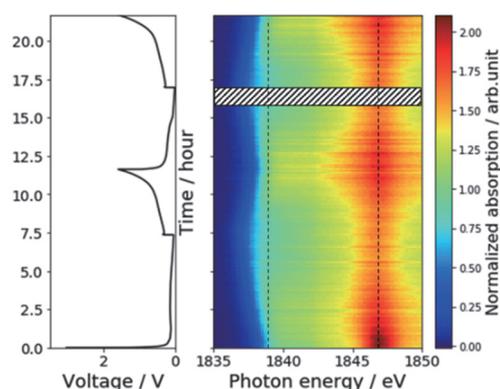


Fig.2. *Operando* Si K-edge XAFS spectra of SiO with potential profile during the charge-discharge cycling. The squared region was no data of Si K-edge XAFS because of beam time ended.

References

1. A. Hirata et al., *Nat. Commun.*, **7**,11591 (2016).
2. T. Kim, S. Park, and S. M. Oh, *J. Electrochem. Soc.*, **154**(12), A1112-A1117(2007).