

X-ray Absorption Spectroscopic Analysis on Photo-lithium Insertion of Silicon

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Light energy as an alternative energy source is utilized for energy conversion devices such as solar cells. Solar cells convert light energy into electrical energy, which has been widely used in our society. However, both of the light and electrical energies cannot be stored in their form; thus, it requires the energy conversion from the electrical to the chemical energy using rechargeable batteries. The development of the devices for converting light energy to chemical energy was expected to drastically improve energy efficiency. The photo-electrochemical reaction of lithium-ion insertion and deinsertion has been reported by employing dye-sensitized battery material under light irradiation [1]. The light energy generates electron-hole pairs with the holes aiding the chemical conversion. This concept is not new but was initially proposed by H. Tributsch in 1983 [2] before the commercialization of lithium-ion batteries. The light energy can induce the transfer of ions between the electrode and electrolyte when there is a difference in Fermi level between electrolyte and electrodes in semiconductor materials. However, there is a lack of fundamental studies for the photo-lithium intercalation reaction. In this study, we examine the photo lithiation reaction of silicon crystal by Si K-edge X-ray absorption spectroscopy (XAS).

Photo-lithiation reactions were conducted using three electrode-cell with LiFePO₄ as the working electrode, silicon p-type as the counter electrode and lithium metal as the reference electrode. The LiFePO₄ composite electrode was prepared by mixing the LiFePO₄ with acetylene black, ruthenium dyes, and polyvinylidene difluoride. N-methyl 2-pyrrolidone was added to adjust the viscosity of the slurry, and then it was coated to the aluminum sheet. The pre-treated silicon single crystal was used after removing the surface film. The electrolyte was 1M LiClO₄ with propylene carbonate (PC). Xenon lamp (300 W) was used as the light source with a constant current of 10 A. The current and potential in the system were measured at the same time using a digital multimeter. Si K-edge XAS of the silicon after the irradiation of light energy was measured in fluorescence mode at BL-10, SR Center, Ritsumeikan University.

The current and the potential of the cell changed significantly as the light irradiated. Upon the light irradiation, the electron-hole pairs were generated at

the semiconductor electrode involving ion insertion/deinsertion from the electrolyte due to potential difference [2]. For the p-type semiconductor, lithium insertion reaction can be induced by the light irradiation. Figure 1 shows Si K-edge X-ray absorption near edge structure of the initial state and the light irradiated sample. The white line peak was broadened, and the edge energy was shifted towards lower energy. This trend agrees with the spectrum change during the electrochemical lithium insertion of the silicon electrode [3]. Therefore, lithium is inserted to the silicon electrode without electrical energy. This result demonstrates that light energy can be stored as chemical energy.

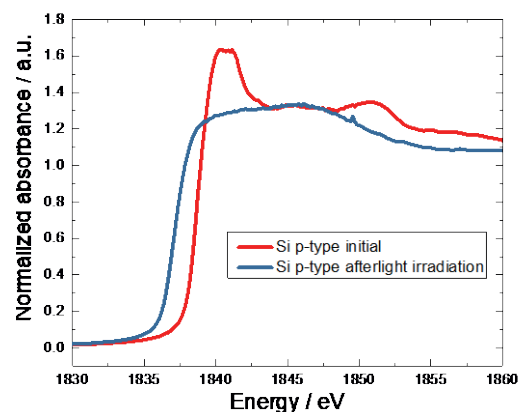


Fig.1 Si K-edge X-ray absorption near edge structure of p-type silicon single crystal before and after the light irradiation in photochemical cell.

References

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