In-situ Observation of Single Silicon Particle during Charging and Discharging

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Introduction
Lithium-ion batteries (LIBs) with high gravimetric and volumetric energy density are very important key devices to encourage the popularization of an environmental friendly energy system, which is consisted of solar cells, wind power generations, smart grid, and batteries. For the application of LIBs, further improvements in the energy density are major issues. Silicon negative electrode is very attractive material because of much higher capacity than current graphite negative electrode. However, the silicon electrode shows very large volume change during charging and discharging, and then the capacity retention drastically decreases due to the cracking and electrically disconnection from current collector. Considering the volumetric energy density of the silicon electrode, it is very significant to understand the real volume change behavior. Here, we demonstrate in-situ microscopic observation with a single particle measurement system, which enables the observation of the drastic volume change behavior of one silicon particle caused by the charging and discharging. The larger volume change invites the reconsidering the actual volumetric capacity of the silicon negative electrode for the commercial use.

Experimental
A Pt microwire with 20 µm diameter was sealed in glass capillary [1]. The tip of the glass-sealed Pt microwire was cut to yield a microdisk, and then polished carefully to a mirror face. Cu was electrodeposited onto the Pt microdisk tip, because of the prevention for the electrochemical reaction of Pt with Li+ ion during the charging. The Cu electrodeposition was carried out at a constant current condition of 62.8 nA for 15 min in 0.6 M CuSO4·5H2O and 5 x 10-4 M H2SO4 aqueous solution. The silicon powders (crystalline/amorphous, 99.9985%, Alfa Aesar) were dispersed on a glass-fiber sheet. The sheet was placed on the glass flitter in the electrochemical cell as shown in Fig. 1. The Cu electrodeposited micro electrode was attached to a silicon particle by using a micromanipulator (QP-2RH, Microsupport) under optical microscope (BX-51, Olympus) observation. The electrolyte was 1 M lithium perchlorate in a mixture of propylene carbonate / ethylene carbonate (PC / EC, 1:1 by volume), from Kishida Chemical Co., Ltd.. and the electrochemical measurements were performed with a two-electrode system. The single particle measurements were conducted in the dry room (< 20 ppm H2O). The temperature was kept 295 K.

Results and Discussion
Silicon particles used in this study was agglutinated by 100 nm size primary particles. The size of silicon secondary particles is between 5 µm to 20 µm. This is very adequate to be attached by the microelectrode.

Fig.2 shows the optical microscope images of lithiating silicon particle in the single particle measurement system. The left picture shows the contact of the micro electrode with a silicon particle (red circle). The tip of the microelectrode is coppery brown because the Cu electrodeposition was conducted onto the tip. The center and right pictures demonstrate the drastic volume expansion of the silicon particle during the 1st charging. The observation indicated that the real volume expansion ratio is larger than theoretical volume expansion (~400%). Such in-situ observation for volume change behavior of silicon electrodes during charging and discharging should help to understand the charging and discharging mechanism of silicon electrodes [2-4]. Furthermore, the finding of real volume change ratio is very important in order to design the negative electrode using silicon based materials for next generation high energy batteries.

References