



## Short communication

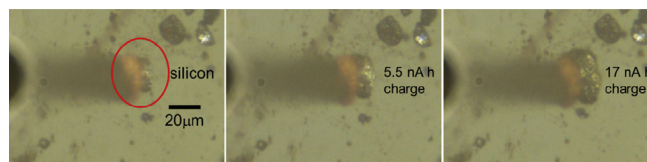
## In-situ observation of one silicon particle during the first charging

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## HIGHLIGHTS

- Single particle measurement was performed for silicon secondary particle.
- The volume expansion behavior of silicon particles was in-situ observed successfully.
- The apparent volume expansion ratio of silicon was larger than the theoretical expectation.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The understanding of volume change mechanism of silicon electrode is necessary to design a new negative electrode using silicon-based active materials. Here, the drastic volume expansion of one silicon secondary particle with  $\mu\text{m}$ -size was in-situ observed in order to find apparent volume expansion ratio during the first charging by using single particle measurement technique. The apparent volume expansion accompanied with the first lithiation is much larger than theoretical expectation due to the agglutination state and anisotropic property. The importance of direct observation with the single particle measurement has been affirmed for understanding the characteristics of silicon electrodes.

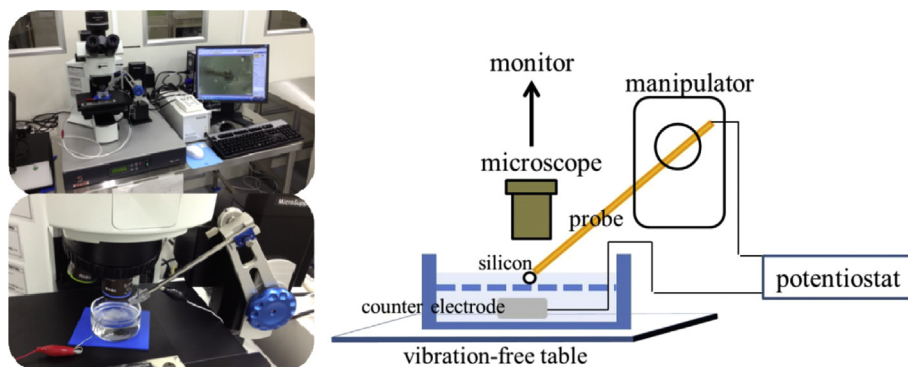
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## 1. Introduction

Lithium-ion batteries (LIBs) with high gravimetric and volumetric energy density are very important key devices to encourage popularization of an environmental friendly energy system which is consisted of solar cells, wind power generations, smart grid, and batteries. In addition, the batteries are extensively expected for a power supply of plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs). Further improvements in the energy density are major issues in order to increase the mileage per

charge [1]. New negative electrode materials with high capacity are of great concern, for example, tin based materials [2–4], lithium metal [5,6] and silicon based materials [7–26]. Compared with current negative electrode material, graphite ( $840 \text{ mA h cm}^{-3}$ ), the theoretical specific capacity of these materials is much larger; tin ( $1520 \text{ mA h cm}^{-3}$ ), lithium metal ( $1980 \text{ mA h cm}^{-3}$ ) and silicon ( $2440 \text{ mA h cm}^{-3}$ ). The energy density per volume not weight is very important because the standards of LIBs have been set for mobile phones, PHVs, and EVs. These materials alloying with lithium shows volume change more or less during charging (lithiation) and discharging (delithiation). The theoretical volume expansion of silicon electrode reaches by up to 400% during charging [7]. In other hands, discharging causes contraction of the lithiated silicon. The repeats of the volume expansion and

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**Fig. 1.** A photograph (left) and a schematic diagram (right) of a single particle measurement system in the dry room. The probe of micro electrode was controlled by a micromanipulator to contact the probe with a silicon particle.

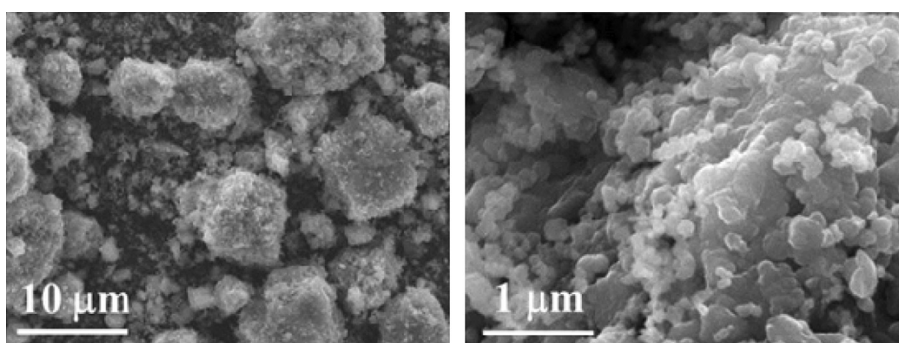
contraction induce an electrode failure due to the occurrence of cracking in the active materials and the electrical disconnection with a current collector. Numerous investigations have focused on how to restrict or avoid the volume change of silicon based active materials during cycles [7–26]. The improvements of the electrical connection during charging and discharging have been reported by using a new binder [12]. Liu et al. reported that new polyfluorene (PF)-type polymer binders could accommodate the volume change of silicon to achieve good stability and cyclability. The other researches have focused to reduce the material size to nanometer range [13–22]. The nano-sized silicon electrodes show better electrode performance because the strain in silicon nanostructure is allowed by using surrounding free space. Lee et al. discussed the anisotropic volume change behavior of silicon nanopillars by scanning electron microscope (SEM) observation [15]. Liu et al. reported in-situ transmission electron microscope (TEM) observation of silicon nanowires (NWs) and nanoparticles during the lithiation, and the anisotropic volume change behavior [16,17]. These in-situ TEM researches have revealed anisotropic property of the lithiation of silicon electrode and a size dependence of cracking in the nano-sized silicon particle during the lithiation. Some researchers have compared theoretical studies with those researches for the lithiation mechanism of silicon electrodes [20,21]. Dahn et al. have researched the volume change of amorphous silicon and silicon-tin alloy thin film electrodes during charging and discharging by using in-situ atomic force microscopy technique [23,24]. Such in-situ measurement techniques help to understand the volume change mechanism. Although thin film electrode is very popular electrochemical model system to examine some basic properties and is applicable for some in-situ measurements, actual electrodes in current LIBs are composed of the powder active materials with  $\mu\text{m}$  size, conductive agents and

binders. It is very important to reveal the electrochemical characteristics and the volume change behavior of not only primary nm-size silicon particles but also the agglutinated secondary particles with  $\mu\text{m}$  range in the liquid electrolyte as well as practical battery system. In this study, we introduce, for the first time, in-situ observation for the volume expansion behavior of a  $\mu\text{m}$ -sized silicon secondary particle during the first lithiation by a single particle measurement technique.

The single particle measurement system is a very powerful equipment to evaluate the electrochemical characteristics of active materials themselves in the practical battery electrolyte. Nishizawa and Uchida demonstrated the micro electrode system for the characterization of battery materials [27]. They utilized the system to investigate some positive electrode materials for LIBs [28,29]. The previous works of our group have revealed excellent electrochemical properties of  $\text{LiCoO}_2$ , graphite and  $\text{LiFePO}_4$  single particle [30–32]. In this study, the single particle measurement system described schematically in Fig. 1 was located in a dry room. The dew point of the dry room was under 223 K with human, and under 203 K without human. Thus, the moisture contamination was ignorable during the electrochemical measurement. Compared with the conventional single particle measurement system located in a globe box filled in purified Ar gas, the system in the dry room has much better operation performance.

## 2. Experimental

A Pt microwire with 20  $\mu\text{m}$  diameter was sealed in glass capillary [31]. 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  $\text{Li}^+$  ion during the



**Fig. 2.** SEM images of silicon particles at different magnification. Primary silicon particles size is about 100 nm, and these particles agglutinate to secondary particles with about from 5  $\mu\text{m}$  to 20  $\mu\text{m}$  diameter.

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