



In-situ observation of volume expansion behavior of a silicon particle in various electrolytes



Kei Nishikawa ^{a,*}, Jinhee Moon ^b, Kiyoshi Kanamura ^{b,c}

^a International Center for Young Scientists, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

^b Global Research Center for Environment and Energy Based on Nanomaterials Science, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

^c Department of Applied Chemistry, Graduate School of Urban Environmental Science, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

HIGHLIGHTS

- Volume expansion of a silicon particle was measured in actual battery electrolytes.
- The apparent volume expansion ratio is larger than theoretical value.
- The apparent volume expansion ratio is independent of Li salts and solvents.
- The applied charging current does not affect the apparent volume expansion ratio.

ARTICLE INFO

Article history:

Received 21 August 2015

Received in revised form

5 October 2015

Accepted 7 October 2015

Available online xxx

Keywords:

Silicon negative electrode

Apparent volume expansion

Initial charging

Single particle measurement technique

Lithium secondary batteries

ABSTRACT

The understanding of volume change behavior of a silicon particle is necessary to design a new negative electrode using silicon active materials. Here, the drastic volume expansion behavior of a silicon particle with μm -size was in-situ observed in order to find apparent volume expansion ratio during the first lithiation in several kinds of electrolytes by using single particle measurement technique. This technique is very useful not only to find the intrinsic electrochemical properties but also to observe the volume change behavior of one electrode active materials particle. The apparent volume expansion ratio of a silicon particle was larger than theoretical expectation because the measured silicon particles were secondary particles which contained some space between the primary particles. In addition, the volume expansion behavior during the first charging was independent on the Li salt, solvents and the applied charging current density.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries (LIBs) with high gravimetric and volumetric energy density are very important key devices for the establishment of sustainable energy system. LIBs are expected to be utilized for the energy storage and the electric load leveling in the energy system. In addition, the utilization of LIBs to plug in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) has started. From the viewpoint of such applications, much higher energy density is strongly demanded to increase the mileage per charge [1]. The current commercial graphite negative electrode shows very

good cycle performance, but the theoretical capacity (840 mAh cm^{-3}) is not enough. The graphite electrode uses the intercalation reaction with one Li atom per six C atoms (LiC_6). Compared with graphite, silicon electrode shows larger theoretical capacity because one silicon atom can react with 3.75 Li atoms to form $\text{Li}_{15}\text{Si}_4$ alloy phase. Thus, the silicon negative electrode is very attractive candidates for next-generation LIBs from the viewpoint of the capacity. However, the silicon electrodes have a fatal problem. Silicon shows very large volume expansion and shrinkage during the lithiation and delithiation, respectively. The theoretical volume expansion accompanied with the lithiation reaches by up to 280% [2]. In other hands, the delithiation induces the extensive volume shrinkage. The repeat of such volume expansion and shrinkage causes very fast capacity fading due to the occurrence of cracks in the particle and the electrical disconnection between

* Corresponding author.

E-mail address: NISHIKAWA.Kei@nims.go.jp (K. Nishikawa).

active materials and the current collector.

Many researches have been reported in order to utilize silicon based active materials for next-generation high capacity batteries [2–36]. Nano-sized silicon has been paid much attention in order to decrease the volume change and the inner stress of each particles for preventing the occurrence of cracks [9–27]. Cui et al. studied volume change characteristics of nano-silicon materials by using in-situ TEM technique, and proposed the threshold size for the occurrence of cracks [18,19]. They also showed the anisotropic volume expansion behavior of silicon pillars. Such anisotropic behavior was also demonstrated by the theoretical calculation [28,29]. Many studies about composite materials with carbon or other elements were also reported [9,12,21,31,32]. They focused to decrease the volume change by using the framework of the composite materials. New binders are also very important key materials for utilization of the silicon electrode. Liu et al. reported that new polymer binder can accommodate the volume change of silicon during the cycle [33,34]. Thus, many researches has been done for the improvement of the cycle performance of silicon electrode, however, only a few researches focuses on the dynamic volume change behavior of silicon particles with micro-meter scale in actual LIBs electrolyte [22,36]. It is very important to understand the volume change behavior of the micro-silicon particles in the battery electrolyte from the view point of the battery industry because nano-sized silicon particles often agglutinate to micro-sized particles. Our group reported in-situ observation of volume expansion behavior of one micro-sized silicon particle by single particle measurement technique in previous paper [36]. The single particle measurement technique is very useful to investigate the intrinsic property of active materials in actual battery electrolyte. It doesn't need composite electrodes which include the conductive agents and the binders. Only one particle of active materials is working electrode in this measurement. In addition to that, in-situ observation by an optical microscope can be applied with this measurement. Therefore, it is very powerful to understand the volume expansion behavior of one silicon particle in the actual battery electrolyte during the first charging. In this research, the volume expansion behavior of one silicon particle in various electrolytes is focused in order to understand the volume expansion mechanism of the micro-sized silicon particle.

2. Experimental

The characterization of silicon powders (crystalline/amorphous 99.9985%, Alfa Aesar) was conducted by field emission scanning electron microscope (FE-SEM) (JSM-7800F, JEOL), transmission electron microscope (TEM) (JEM-ARM200F, JEOL) and micro-Raman spectroscopy (LabRam, Horiba-JobinYvon). The micro-probe was used for electrical connection to one particle in the single particle measurement. The detailed fabrication procedure of the micro-probe was described in previous paper [36]. Fig. 1 shows the microscope image of the micro-probe. The tip was covered by electrodeposited Cu. In this study, micro-probes with two tip shape were used for stable contact between the probe and the particle. The single particle measurement setup was located in super-dry room. The dew point of the dry-room was kept under 223 K. The electrolytes used in this study were 1 M LiPF₆-PC, LiBF₄-PC, LiBETI-PC, LiClO₄-EC:DEC = 1:1, and LiPF₆-EC:DMC = 1:1 (Kishida Chemical Co., Ltd.). The electrochemical cell had two electrodes system and the counter electrode was Li metal (Honjo Metal Co., Ltd.). The galvanostatic charging tests were carried out by a potentiostat (SP-150, BioLogic) with a small current probe. The cut-off voltage for the charging was 0.01 V against Li metal counter electrode. All measurements were conducted in room temperature (295 K).

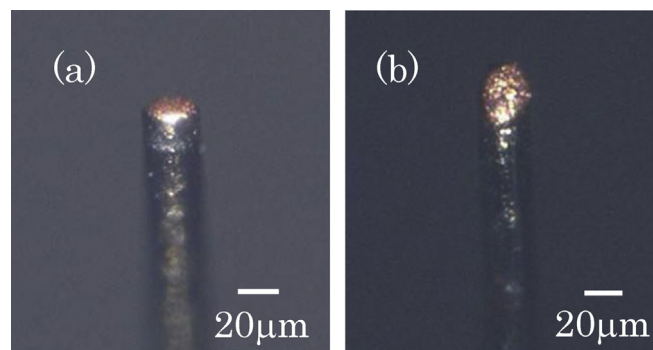


Fig. 1. Microscope images of micro-probes with different tip shape for single particle measurement.

3. Results and discussion

Fig. 2 shows the FE-SEM images of the silicon particles. As mentioned in previous research [36], the size of primary particle is about one hundred nm, and the primary particles agglutinate to secondary particles with ten μm scale. Based on EDS analysis shown in Fig. 2(d), the surface of the particles is covered by thin oxide layer. Fig. 3 demonstrates the cross sectional TEM images and electron diffraction pattern of the silicon particle. The images show that there is some space inside the silicon secondary particle. High magnification images indicate that the small crystal domains with lattice pattern exist inside of the particle (Fig. 3(b)), and the amorphous phase and oxide layer also exists especially at the surface of the particle (Fig. 3(c)). The electron diffraction pattern also indicates that there is the amorphous phase in the surface layer (Fig. 3(d)). Fig. 4 shows the Raman spectra of the silicon particles. The strong peak at 521 cm⁻¹ which is assigned to crystalline silicon was observed, in addition to that, the weak broad peak for amorphous silicon at 480 cm⁻¹ was also detected. Therefore, it is confirmed that the silicon particles used in this study include both crystalline and amorphous phases.

The volume expansion behavior of the silicon secondary particles accompanied with the first lithiation in various electrolytes were in-situ observed by the single particle measurement technique. Fig. 5 demonstrates the typical electrode potential response during the first lithiation in 1 M LiPF₆-PC and the microscope images of the silicon particle before and after the lithiation. The applied current was 2 nA in this case. After the current was started to apply, the electrode potential dropped to about 0.15 V vs. Li metal electrode and then gradually decreased. At about 0.06 V, the inflection point was appeared. After that, the electrode potential gradually approached to cut off voltage of 0.01 V. This potential response is typical of crystalline silicon, which was reported by Dahn et al. [7]. According to their in-situ XRD research, amorphous Li-Si phase is converted Li₁₅Si₄ crystalline phase at about 0.06 V. The inflection point of V-t curve shown in Fig. 5 corresponds the alloy formation reaction. During the lithiation reaction, very large volume expansion was observed as shown in inset of Fig. 5. The volume expansion of the silicon particle during the first lithiation reached about 490% because the average diameter of the lithiated silicon particle increased by 1.7 times. The theoretical value of volume expansion ratio for the lithiation to form Li₁₅Si₄ is about 280%. The difference between the measured and theoretical value may be caused by the existence of the space between each primary particles as shown in Figs. 2 and 3, actually the BET surface area of the silicon powder is 8.59 m²/g. And, the anisotropic volume expansion behavior of a crystalline silicon may enhance making such space inside the secondary particles [13,14,28]. In addition to

Download English Version:

<https://daneshyari.com/en/article/7729904>

Download Persian Version:

<https://daneshyari.com/article/7729904>

[Daneshyari.com](https://daneshyari.com)