



COMMUNICATION

In situ measurement of lithiation-induced stress in silicon nanoparticles using micro-Raman spectroscopy



Zhidan Zeng^{a,b,c,1}, Nian Liu^{d,1}, Qiaoshi Zeng^{a,b,c}, Seok Woo Lee^d,
Wendy L. Mao^{a,e,*}, Yi Cui^{d,e,**}

^aDepartment of Geological Sciences, Stanford University, Stanford, CA 94305, USA

^bCenter for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, PR China

^cHPSynC, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439, USA

^dDepartment of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

^ePhoton Science and Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

Received 15 December 2015; received in revised form 27 January 2016; accepted 1 February 2016
Available online 9 February 2016

KEYWORDS

Silicon anode;
Stress;
Raman spectroscopy;
Lithium ion batteries;
High pressure

Abstract

Stress is a long standing challenge for the applications of silicon (Si) anodes in lithium (Li) ion batteries. Nanostructured Si are important materials to address mechanical stress issues in batteries although their stress was only calculated and no experimental data are available. Using in situ Raman microscopy to monitor the shift of the first-order Raman peak of Si, we were able to measure for the first time the lithiation-induced stress in Si nanoparticles. The shift of Raman peak of Si under hydrostatic stress was calibrated via an in situ high pressure Raman experiment. We observed a tensile-to-compressive transition of the stress in Si core of nanoparticles during lithiation. At the beginning of lithiation, the reduction of the surface native oxide on the Si particle results in a tensile stress of approximately 0.2 GPa in Si. During the formation of amorphous Li_xSi in the outer layer of the nanoparticles, an increasing compressive stress up to 0.3 GPa is built up in the Si core. This stress evolution explains the cracks that developed in the amorphous Li_xSi layer during lithiation of the Si nanoparticles, and is also consistent with modeling results. These results improve our understanding of

*Corresponding author at: Department of Geological Sciences, Stanford University, Stanford, CA 94305, USA. Tel.: +1 650 723 3718; fax: +1 650 725 2199.

**Corresponding author at: Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA. Tel.: +1 650 723 4613; fax: +1 650725 4034.

E-mail addresses: wmao@stanford.edu (W.L. Mao), yicui@stanford.edu (Y. Cui).

¹These authors contributed equally to this work.

lithiation-induced stress in nanostructured Si anodes, and provide valuable information for their computational study and rational engineering.

© 2016 Elsevier Ltd. All rights reserved.

Introduction

Lithium ion batteries (LIBs) are an important energy storage system due to their high capacity, long lifetime, environmental friendliness, etc. However, the capacities of current electrode materials are too low to meet the need of high energy density storage for portable electronics and electric vehicles applications. Therefore high capacity electrode materials are critical for next generation batteries. In terms of anode materials, Si has the highest theoretical specific capacity of 3579 mAh/g (formation of $\text{Li}_{15}\text{Si}_4$), near ten times higher than the currently used graphite (370 mAh/g) [1]. To achieve this high capacity, each Si atom hosts more than three Li ions during lithiation, forming amorphous Li_xSi ($\alpha\text{-Li}_x\text{Si}$, $x=3.4\pm 0.2$) or crystalline $\text{Li}_{15}\text{Si}_4$ [1,2]. Alloying and de-alloying with large amount of Li ions result in dramatic volumetric changes in the Si anodes, and consequently lead to enormous internal stress during battery operation [3].

Stress in electrode materials affects the performance of LIBs in many ways [4]. It can cause fracture and pulverization of electrode materials, which lead to their loss in contact to each other or to the current collectors [5-7]. Fracture of the electrode materials also exposes fresh surfaces to the electrolyte, which consumes extra Li ions to form new solid electrolyte interphase (SEI) layers during battery cycling [8]. These two factors are the main reasons that account for the decay in capacity of LIBs. The stress status determines the failure mode of the electrode materials. For instance, a tensile stress in the core of a Si particle leads to fracture starting from the core; while a tensile stress in the outer layer of the particle causes cracks on its surface. In addition, stress would also change thermodynamics and kinetics of the electrochemical reaction in LIBs, and alter the effective potential window for electrochemical cycling [9-11].

To mitigate stress and fracture associated with battery operation, different nanostructured Si anodes have been intensively studied, e.g. nanoparticles, porous nanoparticles, nanowires, double-walled hollow tubes, core-shell, yolk-shell, pomegranate structures [12-23]. Compared with bulk Si anodes that usually fail within a few cycles, nanostructured Si anodes can maintain their integrity after hundreds of cycles [12,19,24]. This significant improvement in performance is attributed to the release of stress in the nanoscale. Although the stress in bulk Si anodes has been experimentally determined, the stress in nanostructured Si anodes has never been measured, which is crucial for understanding of their behavior and further optimization of their performance.

By measuring stress induced substrate curvature, Chon et al. determined the stress in $\alpha\text{-Li}_x\text{Si}$ layer of a 425-450 μm thick Si wafer (diameter 50.8 mm) [3]. They found an almost constant compressive stress of approximately 0.5 GPa in the $\alpha\text{-Li}_x\text{Si}$ during lithiation. The lithiation-

induced stress in Si nanoparticles is expected to be different, as they show highly improved battery performance compared with their bulk counterpart. Theoretical studies suggest that the hoop stress in the $\alpha\text{-Li}_x\text{Si}$ layer of Si nanoparticles changes from compression to tension during lithiation, and a similar stress transition is reported in Ge nanopillars [25,26]. However, no experimental results have been available.

In this study, the lithiation-induced stress in Si nanoparticle anodes was investigated using in situ Raman microscopy. A tensile stress of 0.2 GPa was observed in Si at the beginning of lithiation, followed by a transition to a compressive stress up to 0.3 GPa upon further lithiation. These results not only reveal the stress evolution in Si nanoparticles during lithiation, but also can validate theoretical models for nanostructured Si anodes.

Experimental

Electrochemical cell fabrication

Si nanoparticles (MTI Corporation, ~ 100 nm) were mixed with carbon black (Super P, TIMCAL, Switzerland) and sodium carboxymethyl cellulose (Sigma-Aldrich, Mw $\sim 90,000$) with a mass ratio of 45:45:10 and stirred in deionized water overnight. A piece of stainless steel mesh (400 mesh, TWP Inc.) was dip-coated with this slurry and baked in a vacuum oven at 90 $^\circ\text{C}$ for > 3 h to obtain a Si nanoparticles electrode. The mass of the Si nanoparticles in an electrode (ca. 0.1 mg) was determined using a microbalance (Sartorius SE2, 0.1 μg resolution).

Figure 1a and b shows the schematic and photograph of the electrochemical cell respectively. The cells were assembled using a Si nanoparticles electrode, Li metal as the counter electrode, and a Celgard separator soaked in electrolyte, similar to previous reports [27,28]. The electrolyte was 1.0 M LiPF_6 in 1:1 (w/w) ethylene carbonate/diethyl carbonate (BASF). The cells were assembled inside an Ar-filled glovebox and sealed in 0.11 mm thick transparent polyester pouches (Kapak Corporation). For efficient sealing of the battery cells, pretaped Ni current collectors (MTI Corporation) were used. In situ battery cycling was performed using a MTI eight-channel battery analyzer (0.002-1 mA). The voltage cutoff was set to 2.0 V and 0 V versus Li/Li^+ , and the cycling rate was C/10 in terms of the theoretical capacity of Si (4200 mAh/g). A cycling rate of C/10 means charge/discharge in 10 h.

High pressure sample preparation

For in situ high pressure Raman experiment, a crystalline Si sample was loaded into a symmetric diamond anvil cell (DAC). The sample chamber was a 120 μm diameter hole

Download English Version:

<https://daneshyari.com/en/article/7953747>

Download Persian Version:

<https://daneshyari.com/article/7953747>

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