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Mechanical behavior of electrochemically lithiated silicon

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HIGHLIGHTS

- The mechanical behavior of lithiated silicon is probed with nanoindentation.
- Young's modulus and hardness are extracted for various Li–Si alloy compositions.
- Young's modulus of fully lithiated silicon is measured to be 41 GPa.
- Lithiated silicon is found to creep readily.
- Creep occurs via viscoplastic flow with large power law creep stress exponents (>20).

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ABSTRACT

The time-independent and time-dependent mechanical behavior of electrochemically lithiated silicon was studied with nanoindentation. As indentation was performed with continuous stiffness measurements during loading and load-hold, new insight into the deformation behavior of lithiated silicon is furnished. Supporting other research, Young's modulus and the hardness of lithiated silicon are found to decline with increasing lithium content. However, the results of this study indicate that Young's modulus of the fully lithiated phase, at 41 GPa, is in fact somewhat larger than reported in some other studies. Nanoindentation creep experiments demonstrate that lithiated silicon creeps readily, with the observed viscoplastic flow governed by power law creep with large stress exponents (>20). Flow is thought to occur via local, shear-driven rearrangement at the scale of the $Li_{15}Si_4$ molecular unit volume. This research emphasizes the importance of incorporating viscoplasticity into lithiation/delithiation models. Additionally, more broadly, the work offers insight into nanoindentation creep methodology.

1. Introduction

In light of the growing need to improve energy storage in electronic devices requiring rechargeable battery power, lithium ion battery research has been widely pursued over the past decade [1–3]. Anode design, in particular, has become a focus in the drive for improved battery performance. Silicon, due to its high theoretical specific capacity for electrochemical lithium incorporation, has emerged as one of the most appealing materials to replace conventional graphitic anodes in lithium ion batteries. However, upon lithium insertion silicon undergoes a large volume expansion (~300%), which promotes fracture of bulk silicon during lithiation/delithiation cycling and thereby causes capacity fading of silicon anodes. Much progress has recently been made in design of silicon nanostructures that are more resistant to lithiation-induced fracture [4–10]. Although nanostructured silicon shows retarded fracture formation during electrochemical lithium cycling relative to bulk silicon, fracture remains an issue.

The problematic capacity fade exhibited by silicon anodes, brought on by fracture processes during electrochemical cycling, has inspired much research into the details of the lithiation behavior of silicon. Experimental studies have provided insight into the mechanisms by which silicon (both amorphous and crystalline) lithiates [11–14]. Mechanistic knowledge, in turn, has enabled formulation of lithiation models [15–19]. Such models, however, depend strongly upon the inputted mechanical properties of lithiated silicon, and the current understanding of these properties lags that of the lithiation process and its underlying mechanisms.

There have been a few attempts to investigate the mechanical behavior and extract the mechanical properties of lithiated silicon. In three related research projects, an electrochemical cell with a silicon anode was constructed, and as the cell was cycled the wafer

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curvature technique was used to measure the biaxial modulus, yield strength, and fracture toughness of lithiated silicon [20–22]. Pharr et al. also employed a wafer curvature approach to estimate the fracture energy of lithiated silicon [23]. Kushima et al. attempted to determine Young's modulus and the fracture strength of lithiated silicon nanowires by first lithiating crystalline silicon nanowires in a transmission electron microscope (TEM) chamber and then deforming the wires in tension with an in situ TEM piezo device [24]. An x-ray diffraction experiment, wherein a lithiated silicon specimen was subjected to in situ hydrostatic compression, was used by Zeng et al. to establish the bulk modulus of the material [25]. With nanoindentation, Ratchford et al. measured Young's moduli of various equilibrium lithium–silicon alloy phases synthesized at high temperatures [26,27]. Hertzberg et al. performed nanoindentation studies, instead on electrochemically lithiated silicon samples, and the authors extracted the modulus and hardness as a function of state-of-charge [28].

Literature on the mechanical properties of lithiated silicon is informative, yet there still exists some uncertainty in the accuracy of the obtained parameters. Specifically, there is substantial variation in the Young's modulus values reported throughout the literature. More important, little is known about the creep behavior of lithiated silicon. Existing models for the process of lithiation of silicon often ignore time-dependent deformation behavior. In view of these remaining issues, we have carried out ex situ nanoindentation studies to characterize the mechanical behavior of lithiated silicon. We have developed a nanoindentation holder that allows nanoindentation to be performed on samples immersed in mineral oil and enables precise lateral positioning of indents via a high-magnification fluid immersion optics system. The utilized nanoindenter possesses continuous stiffness mode (CSM) capabilities, making this work the first known lithiated silicon indentation study with CSM-based results. In addition to allowing particularly thorough and reliable hardness and modulus testing, our modified CSM indentation setup gives us the ability to critically assess the nanoindentation creep characteristics of lithiated silicon. We show that Young's modulus of fully lithiated silicon is likely markedly larger than reported in a few previously published studies. Lithiated silicon is found to creep rapidly during constant-load-hold nanoindentation experiments. Using a standard model for thermally activated stress-driven processes, we infer some physical meaning from the observed large power law creep exponents. Our research suggests that models must take into account viscoplastic flow behavior in order to more realistically describe silicon anode lithiation and delithiation.

2. Experimental

2.1. Sample preparation

Lithiated silicon samples suitable for nanoindentation testing were prepared by depositing silicon films onto molybdenum substrates. The choice to use molybdenum substrates was made in light of molybdenum's lack of reactivity with lithium and its high yield strength. The substrates were cut from a swaged molybdenum rod with wire electrical discharge machining. Residue from the machining process was removed by etching the pieces in a dilute hydrogen peroxide (5%) bath, and the resulting scale was removed by etching in concentrated hydrochloric acid. The clean molybdenum discs (6.3 mm in diameter and ~480 μm thick) were mechanically polished to a mirror finish, and organic mounting debris was removed by immersion into a bath of concentrated sulfuric acid. Finally, the samples were thoroughly cleaned by sonication in solvents (acetone, methanol, and then ethanol), oxide was etched with concentrated sulfuric acid and then concentrated hydrochloric acid, and one final ethanol rinse was administered. The above-mentioned, extensive sample preparation measures were followed to reduce surface contamination of the molybdenum, thereby promoting a strong silicon–molybdenum interface and helping to discourage film delamination during lithiation.

Amorphous silicon films were deposited onto the substrates by sputtering with dual-target AC magnetron sputtering at a constant power of 300 W. Some sputtering batches included an in situ argon ion gun pre-clean to remove native molybdenum oxide prior to deposition; however, pre-etching did not appear to affect the subsequent lithiation behavior of the deposited films. The deposited silicon films were ~1.4 μm thick, though there was some variation in the film thickness from sample to sample. An x-ray diffraction scan of a film [Fig. 1(a)]—showing only diffracted peaks corresponding to the molybdenum substrate—confirmed that the sputtering recipe produced amorphous silicon films.

After film deposition, electrochemical half-cells were assembled. A polyethylene separator was placed between the working electrode (silicon-coated molybdenum samples) and the counter/reference electrode (lithium foil). A solution of 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1; Merck) was used as the electrolyte. The pouch cells were hermetically sealed and then removed from the glovebox for electrochemical testing. For samples that were to be fully lithiated (ie. lithiated to $Li_{15}Si_4$), lithiation was performed galvanostatically (7 μA current) until the voltage reached 10 mV vs. Li/Li^+, at which the voltage was subsequently held for some time—at least 40 min and up to 10 h—to further encourage full lithiation. Samples prepared for creep testing ("heavily lithiated" silicon) were perhaps very close to but slightly under the fully lithiated composition. A current of 7 μA provided lithiation rates for fully lithiated samples near C/50. Electrochemical data for a fully lithiated sample is shown in Fig. 1(b).

Partial lithiation was also performed galvanostatically at 7 μA; lithiation was terminated once the total charge transferred reached a specified value corresponding to the desired silicon anode lithium fraction. In order to determine the cutoff charge for partial lithiation, all as-deposited samples were assumed to have the same total mass of amorphous silicon as the first sample subjected to full lithiation. Following lithiation, partially lithiated samples were held under open circuit conditions for at least 10 h to allow lithium concentration gradients to dissipate by lithium diffusion. Upon completing electrochemical lithiation, the pouch cells were returned to the argon glovebox. The lithiated samples were extracted, rinsed in acetonitrile, and then mounted onto aluminum pucks using Crystalbond 509 adhesive. Inside the glovebox, the mounted samples were placed into vials filled with paraffin oil prior to being transferred to the nanoindenter system. Samples were kept immersed in paraffin oil during nanoindentation, so the air-sensitive lithium-containing samples were never exposed to ambient air.

Although sample preparation procedures were designed to limit film delamination during lithiation, delamination was not entirely avoided. During lithiation, film blistering developed in both fully lithiated and partially lithiated films. Such blistering is depicted in Fig. 2, which is a scanning electron microscope image (52° stage tilt) of an amorphous silicon film on molybdenum that was fully lithiated potentiostatically. As performing nanoindentation on blistered film regions would provide uninterpretable data, it was necessary to selectively indent the film between blisters, where the film remained adhered to the substrate.

2.2. Nanoindentation

Because lithium rapidly oxidizes in humid air, nanoindentation was performed on samples immersed in a protective paraffin oil