Robustness of amorphous silicon during the initial lithiation/delithiation cycle

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HIGHLIGHTS

- We probe the lithiation and delithiation behavior of amorphous silicon micropillars.
- No isolated cohesive, lithiation- or delithiation-induced pillar fracture is seen.
- Amorphous silicon is robust with respect to lithiation/delithiation.
- A diffusion-induced stress analysis supports experimental observations.

ARTICLE INFO

ABSTRACT

Recent research on the electrochemical lithiation of amorphous silicon nanoparticles shows that amorphous silicon is more fracture resistant than crystalline silicon during lithiation. Nanoparticles of amorphous silicon can be lithiated and delithiated without any fracture at all. To fully exploit the potential of using amorphous silicon as electrodes for lithium ion batteries it is important to determine if larger, micron-sized, amorphous silicon structures can be lithiated and delithiated without fracture. Here we study the morphologies of initially amorphous silicon micropillars (∼2.3 μm tall) both before and after electrochemical lithiation and delithiation. No internal or external cohesive cracking is detected in lithiated pillars for any of the pillar sizes studied. Delithiated pillars exhibit some delamination at the interface between the pillar and the underlying nickel substrate. For larger diameter pillars, the initiated interfacial crack is driven upward into the delithiated pillar as the crack propagates radially inward. However, no cohesive fracture unrelated to interfacial cracking is seen in even the largest delithiated pillars. Finite element modeling provides support for the observation that the cohesive fracture resistance of amorphous silicon micropillars is representative of the fracture resistance of amorphous silicon microparticles of comparable dimensions.

1. Introduction

Lithium ion batteries have become the most widely used battery technology in applications requiring lightweight and high-power rechargeable energy storage [1,2]. With recent interest in electric vehicles, and accompanying the trend in increasing power consumption of rechargeable consumer electronic devices, the need for higher capacity Li-ion batteries has become a key technological issue. For the most part, commercial Li-ion battery anodes have been composed of carbonaceous material. Recently, however, silicon has received significant attention as a possible anode material, as the theoretical charging capacity of silicon is about ten times greater than that of commercialized carbon anodes [3]. Although Si offers a considerable increase in charging capacity, Si anodes suffer from large capacity fade during cycling and low cycle life. Such problem stems, in large part, from the substantial volume expansion (∼300%) and contraction that Si undergoes upon Li alloying/dealloying. Due to the large volume changes, lithiation and delithiation are mechanically powerful processes that produce large stresses in Si anodes. The noted poor characteristics of Si anodes arise because such stresses give rise to anode failure, which can occur by cohesive rupture and delamination, among other mechanisms.

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Shortcomings of Si anodes in Li-ion batteries have been ameliorated by utilizing nanostructured Si anodes, as nanostructures are much more robust with respect to fracture than bulk material [4—8]. Great progress in nanostructure synthesis, particularly in preparation of crystalline Si (c-Si) nanostructures, has enabled researchers to probe the lithiation and delithiation behavior of anodes comprised of various c-Si geometries, including pillars, spheres, and wires [9—13]. Though these crystalline nanostructures offer improvement in anode performance, such nanostructures are still susceptible to fracture during cycling, and thus capacity fade remains an issue. This outcome has prompted research into the mechanisms by which c-Si lithiates. It has now been widely observed that c-Si lithiates via a two-phase mechanism whereupon pure Si is consumed by reaction with Li, forming a heavily lithiated amorphous Li_xSi phase behind the path of the phase front, and a fully lithiated $Li_{15}Si_4$ phase is occasionally observed [14—16]. As indicated by the highly anisotropic volume expansion of c-Si upon lithiation, the velocity of the phase front depends strongly upon crystallographic orientation, with the <110> directions reacting most rapidly [17—19]. This behavior has been accounted for in some modeling research that has shed light onto the lithiation-induced stress states in crystalline silicon nanoparticles [20,21]. Some recent modeling supports empirical evidence for the presence of a critical size below which c-Si nanostructures do not fracture upon lithiation [21].

For some time, it has been widely recognized that the lithiation behavior of amorphous Si (a-Si) is substantially different from that of c-Si. Indeed, a-Si nanoparticles have recently been observed to be quite robust to fracture during cycling [22,23]. For example, using an in situ transmission electron microscopy (TEM) technique, McDowell et al. observed that hydrogenated a-Si nanoparticles are much more fracture resistant than c-Si nanoparticles, noting that a-Si spheres originally 870 nm in diameter did not fracture upon lithiation [22]. These authors also made the surprising observation that a-Si appears to lithiate by a quasi-two-phase mechanism and not single-phase diffusional insertion of Li. Wang et al. separately provided TEM evidence supporting two-phase lithiation of a-Si [25]. These observations provide a framework from which models describing the lithiation of a-Si can be developed.

The observation that nanoparticles do not fracture during lithiation is not altogether surprising, as one can expect that fracture by electrochemical shock might not occur for such small nanoparticles [9,11,24]. However, based on simple considerations of electrochemical shock one might expect fracture to occur for larger particles. An aim of this work is to explore the robustness of a-Si during lithiation/delithiation at larger size scales. Here, we present experimental and computational research on lithiation/delithiation of a-Si nano- and micro-pillars. We demonstrate that, during the initial lithiation/delithiation cycle, patterned a-Si is resistant to fracture even at the micron scale. Although we observe delamination at the pillar/substrate interface in some cases, there is no evidence of isolated internal or external cohesive fracture in the top portion of any of the pillars studied. In light of the findings of recent studies, we develop a new phenomenological finite element model for diffusional lithiation of a-Si that takes account of a steeper concentration profile than captured by a standard diffusional approach [22,25]. The modeling shows that plastic yielding severely limits the stresses that can be generated during electrochemical shock and even changes the sign of the stresses at different points in the lithiation/delithiation cycle relative to the expectations based on electrochemical shock of elastic particles. In particular, tensile stresses are generated at the surfaces during lithiation while compressive stresses are generated there during delithiation, the opposite of what might be expected based on the thermal shock analogy. Furthermore, the triaxial tensile stresses in

the interior during delithiation are limited by yielding near the surface and evidently are insufficient to initiate fracture. The modeling results support our experimental findings and provide new insight into the lithiation/delithiation behavior of both a-Si and c-Si.

2. Experimental

2.1. Sample preparation

With an e-beam evaporation apparatus, a-Si films approximately 2.3 μm thick were deposited onto polished, nickel squares (purity >99.9%) with side length 5 mm and thickness 450 μm. The deposition recipe was confirmed by X-ray diffraction (Supplementary data Fig. S1) to produce amorphous films when utilized on silicon-coated nickel substrates. It is expected that films evaporated with this recipe, when deposited on uncoated nickel substrates, would similarly be amorphous. Following film deposition, pillars were milled into the a-Si films using an FEI Strata 235DB focused ion beam (FIB) with 30 keV gallium ions and concentric circle milling patterns. By performing final milling steps at low ion beam currents, pillar taper was minimized and Ni that had been redeposited onto the pillar sidewall was removed. The final pillar height was determined by the initial thickness of the film at the pillar location. Pillar heights varied from 2340 nm to 2380 nm for lithiation studies and from 2100 nm to 2460 nm for delithiation. In order to explore potential size effects, multiple pillars with diameters ranging from 600 nm—2930 nm for lithiation and 780 nm—5850 nm for delithiation were patterned onto each sample. Prior to lithiation, each pillar was imaged with the electron beam using the dual-beam FIB/SEM apparatus.

2.2. Electrochemical lithiation/delithiation

Following micromachining with the FIB, electrochemical half cells were constructed in an argon-filled glove box. In each half cell, an a-Si pillar sample served as the working electrode, and a polymer separator was placed between the working electrode and the Li foil counter/reference electrode. A solution of 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1; Merck) was used as the electrolyte. After the cells were hermetically sealed in pouches, they were removed from the glove box and the leads were connected to an Arbin BT2000 battery tester. The half cell containing pillars for lithiation was subjected to 10 mV vs. Li/Li^+, and the voltage was held at this value for 10 h. Samples with pillars that were to be delithiated were first lithiated for 10 h at 10 mV vs. Li/Li^+ and were then held at 2 V vs. Li/Li^+ for another ten hours. Some electrochemical testing results are shown in Supplementary data Fig. S2.

2.3. Characterization

Once lithiation or delithiation was completed, the sealed pouch cells were transferred back into the glove box, whereupon the pouches were opened and the pillar samples were extracted. The samples were gently washed in acetonitrile, mounted on a puck, and then sealed in vials. The argon-filled vials containing the lithiated or delithiated samples were carried to the FIB for observation. To minimize the time during which samples were exposed to the atmosphere, vials were kept sealed until the FIB chamber was fully vented. The samples were rapidly loaded into the chamber, and the chamber was then immediately pumped down. All pillars were imaged with the electron beam. Subsequent to imaging the external surfaces of the pillars, the pillars were sliced into cross sections with the ion beam to evaluate the interior morphology,