In situ X-ray micro-CT characterization of chemo-mechanical relaxations during Sn lithiation

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HIGHLIGHTS

- 3D X-ray tomography is done during lithiation, rest, and delithiation of a Sn wire.
- Lithiation proceeds isotropically and causes wire elongation and diameter increase.
- Damage occurs as cracks on the wire surface and as voids in the unlithiated core.
- Significant fragmentation occurs during delithiation.
- Damage also persists during long-term rest of the lithiated wire.

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ABSTRACT

Sn has been proposed for use as a high capacity anode material. Because of its ductile metallic nature, Sn may exhibit unique stress evolution during lithiation. Here, 2D radiography and 3D tomography are employed to visualize the evolution of geometry, internal structure, alloying, and damage during lithiation, delithiation, and rest of Sn wires with micron scale diameters. Lithiation proceeds isotropically, resulting in geometric and dimensional changes after 25% of total lithiation when the tensile stresses are sufficiently high to exceed the flow stress of the unlithiated Sn core and cause elongation and diameter increase. Damage occurs at later stages in the form of cracks terminating at the wire surface and voids forming in the unlithiated core. Notably, significant fragmentation occurs during delithiation which, due to void formation that accommodates the resulting stresses, does not measurably alter the wire cross-section and length. The distinguishing feature of the chemo-mechanics of Sn compared to Si or Ge is the pronounced creep rate at applied strain rates as high as 10^{-6} s^{-1}, which promotes large strains in the core, eventually leading to void nucleation in the unlithiated core during lithiation, and more importantly, continues driving the deformation of the anode while at rest.

1. Introduction

Alloying electrodes have attracted a great amount of interest because of their high storage capacities of ions such as Li [1–4]. Such electrodes are important in achieving high energy density storage for the next generation of electrified transportation and microelectronic devices [5]. Inherent to very large capacities are the associated large volumetric and crystallographic changes which often induce irreversible capacity fade through a variety of mechanisms, such as mechanical fracture, interface decohesion and loss of percolation, and amorphization [6–10]. A variety of novel nanostructuring and engineering approaches partially overcome these problems and realize efficient high cycle performance from alloying electrodes [6,11]. However, the

scalability and cost of synthesizing many nanostructured materials remain impractical. This motivates the need to develop novel approaches to improve the function of more conventional alloying electrode particles. Approaches that have found some success include controlling the voltage window or developing self-healing electrode matrices [12,13]. However, a limited understanding of the chemo-mechanical response of high-strain alloying electrodes during cycling constrains our ability to engineer new solutions.

The chemo-mechanical response of alloying electrodes is difficult to predict for a number of reasons. In order to make quantitative predictions, both the concentration dependent mechanical properties (*e.g.*, modulus, yield strength, fracture toughness) and the concentration and stress dependent transport kinetics must be known. Limited
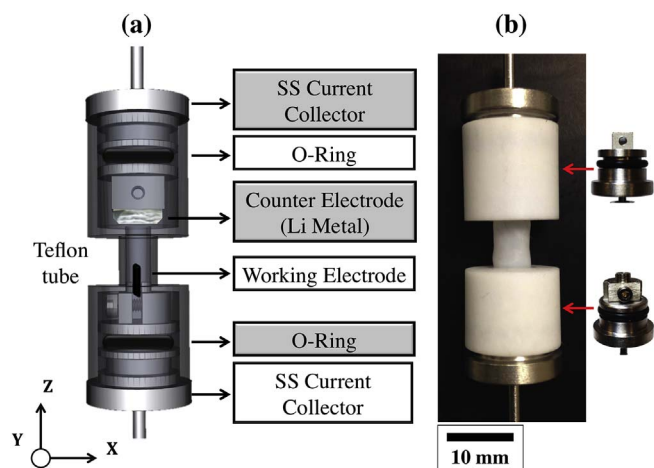

Fig. 1. Reusable *in situ* μCT cell assembled for testing Sn wires: **(a)** rendered design of the cell with transparent Teflon tube encasing to show the internal components, and **(b)** actual cell after assembly.

experimental data exist to define these parameters [14–16], but some information calculated from first principles and molecular dynamics is available [17,18]. Alloying electrodes often undergo numerous sequential solid-solution and two-phase reactions as a function of Li concentration, due to the presence of multiple phases on the relevant equilibrium and non-equilibrium phase diagrams. The stress evolution associated with two-phase reactions versus solid-solution alloying differs dramatically [19]. For two-phase reactions, the largest strain gradient localizes at the interface between the adjacent phases [19,20]. For solid-solutions, the strain gradient couples closely with the concentration gradient [21,22]. Fracture associated with solid-solution alloying reactions is reaction rate dependent, since the rate defines the composition profile that is coupled to the strain gradient [22]. For materials reacting by a two-phase mechanism exhibiting elastic-plastic response, the fracture of electrode materials should not be rate dependent with absent significant concentration gradients in the resulting intermetallic compounds [19,20]. For these systems, fracture depends only on geometric factors, such as particle size, particle shape, and crystallographic orientation. This has been shown experimentally for Si [20], which has received considerable attention due to its status of having the highest gravimetric Li capacity. However, high capacity electrodes suffer from large stresses whose severity has been shown to depend on the lithiating particle size. For example, *in situ* Transmission Electron Microscopy (TEM) experiments have been utilized to demonstrate and measure a critical Si particle size associated with fracture [20]. For systems such as Si, it is argued that during the early stages of lithiation, the surface develops a compressive stress and undergoes irreversible plastic deformation. As the reaction continues, the inner volume of the particle continues to expand and forces the surface into tension. If the particle is sufficiently large that the continued reaction forces this tensile stress to exceed a critical value then fracture will occur [19,20]. Similar *in situ* experiments have been performed using other group IV materials, including amorphous Si, Ge, and Sn where the critical particle size increases in that sequence [10,23,24]. It is interesting to compare these 3 group IV systems because they all react *via* a similar mechanism, accommodate similar amounts of Li per host atom, and exhibit similar strains. For the case of Sn, the particles do not fracture at TEM length scales and their size dependent response has been measured using *in situ* SEM [25]. This work found that the fracture behavior depends on both the particle size and the local lithiation rate. It was argued that, unlike Si, at room temperature Sn is at a high homologous temperature where

diffusional stress relaxation mechanisms (*i.e.*, power-law creep) should have a significant contribution to the overall material deformation at relatively low strain rates. Experimental results matched simulated predictions that employed power-law creep stress-relaxation which introduced both a size and a rate dependent mechanical response [25]. Related micro-pillar mechanics measurements indicated that lithiated Sn creeps at room temperature [26]. The authors used this information to predict a size and rate dependence to Sn fracture similar to what was observed in the *in situ* Scanning Electron Microscopy (SEM) experiments [25,26]. Such stress relaxation phenomena should be an important consideration in a number of low melting point alloying electrode systems of interest for Li$^+$ and non-Li chemistries, such as Al, Sb, Bi, Pb, and Zn. In this work we will further discuss Sn as a model system that forms a very similar phase diagram with Li as Si, but has quite distinct properties.

An anomalous stress relaxation was noted during *in situ* wafer curvature measurements of stress evolution during lithiation of Sn [27]. These results differed significantly from similar experiments on Si [28]. We hypothesize that the observations in Sn are again indicative of a dominant diffusion-mediated stress relaxation mechanism. Diffusion mediated stress relaxation has also previously been observed in Sn electrodes, manifested as porosity evolution during dealloying [8,24,29,30]. Dealloying of Li occurs *via* bulk diffusion that induces a tensile stress gradient near the surface. Surface diffusion relaxes this stress by an evolving pore volume. The wavelength of the resulting porous network depends on delithiation rate and temperature as anticipated for a diffusive process [29]. While clear evidence for diffusion-mediated stress relaxations in alloy electrodes exists in the literature, limited research has been performed investigating the phenomenon qualitatively or quantitatively [25,26,31]. To initially address this knowledge gap, we designed a set of model experiments to probe the extent to which diffusional relaxation occurs after partial lithiation of Sn electrodes. The extent of reaction during different stages of lithiation, delithiation, and relaxation is quantified *via* X-ray absorption and strain is quantified *via* direct X-ray imaging using radiographs and microcomputed tomography (μCT).

2. Experimental procedures

A reusable *in situ* μCT lithium ion battery cell was designed and fabricated from Teflon with stainless steel (SS) current collectors, as shown in Fig. 1. The cell did not require a separator since the electrodes were spaced by a distance greater than 5 mm. The Li-metal anode and Sn wire (1.5–2 mm length and 250 μm diameter, Sigma Aldrich) electrodes were clamped into stainless steel grips, with the Sn wire denoted as the working electrode in Fig. 1a and shown by a black vertical line. A small piece of L-shaped Teflon was placed adjacent to the tip of this Sn wire such that its end was supported during expansion. This Teflon piece may be seen clearly in the subsequent 2D radiographs. The cell was filled with 1:1 ethylene carbonate dimethyl carbonate 1 M LiPF$_6$ electrolyte and assembled inside an argon-filled glove box. The total amount of liquid electrolyte present in the cell as shown in Fig. 1a was about 1.5 ml. A BioLogic SP-200 portable potentiostat was used for *in situ* galvanostatic cycling with potential limitations of 0.01 V during lithiation and 1.5 V during delithiation.

X-ray radiography and microcomputed tomography data were acquired using the Xradia MicroXCT-400. Time-lapse 2D radiographs were captured under *operando* conditions without interrupting the experiment, while 3D μCT were performed *in situ* under open circuit conditions at specific lithiation levels. The full-frame real-time radiographs were taken using a 4× magnification lens and were such as to image the entire length of the wire. At specific lithiation levels, for use in the μCT analysis, 2D radiograph images were taken at 1° increments