In situ measurement of biaxial modulus of Si anode for Li-ion batteries

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ABSTRACT

We report in situ measurement of biaxial moduli of a Si thin-film electrode as a function of its lithium concentration. During lithiation, biaxial compressive stress is induced in the Si film and it undergoes plastic flow. At any state-of-charge (SOC), a relatively small delithiation–relithiation sequence unloads and reloads the film elastically. From the stress and strain changes during a delithiation–relithiation cycle, the biaxial modulus of the film is calculated. Stress change is obtained by measuring the change in substrate curvature using a Multi-beam Optical Sensor; the elastic strain change is obtained from the change in SOC. By repeating these measurements at several different values of SOC, the biaxial modulus was seen to decrease from ca. 70 GPa for $Li_{0.32}Si$ to ca. 35 GPa for $Li_{3.0}Si$. Such a significant reduction in elastic modulus has important implications for modeling stress evolution and mechanical degradation in Si-based anodes.

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1. Introduction

Silicon's high lithiation capacity of 3579 mAh/g [1] makes it an attractive choice for use as negative electrodes in lithium-ion batteries. A large body of literature exists on the electrochemical and mechanical performance of anodes made of pure silicon and composites in which silicon is one of the constituents [2]. It is well known that Si undergoes large volume expansion (ca. 370%) upon complete lithiation, which results in generation of stresses as high as 1–2 GPa [3]. The large stresses lead to mechanical damage and consequently, capacity fading. In order to model the mechanics of electrode materials and predict their cycle life, it is essential to know their mechanical properties (elastic moduli, flow stress and its rate dependence, ductility, fracture toughness, etc.) and how they vary with SOC. When Si is fully lithiated, the number of solute atoms is about 3.5 times that of the solvent atoms; hence, it is reasonable to expect significant changes in mechanical properties with SOC. However, little data is available in literature on the mechanical properties of lithiated silicon. Recently, using density-functional-theory (DFT) calculations, Shenoy et al. estimated the elastic moduli of Li–Si system as a function of lithium concentration [4], and noted that they decrease linearly with increasing lithium concentration. For example, they predict that the Young's modulus of amorphous silicon decreases from about 90 GPa for α-Si to less than 40 GPa for α-$Li_{15}Si_4$. If the reduction in elastic moduli is any indication of increased ductility due to alloying, one can

expect significant changes in other mechanical properties as well. In this paper, we present an experimental effort, the objective is to directly measure the biaxial modulus of silicon thin-film electrode as a function of lithium concentration.

2. Experimental

2.1. Electrochemical cell

Si wafers [double-side polished, 50.8 mm diameter, nominally 425–450 μm thick, (111) orientation, with 200 nm thermal oxide on all sides] were used as substrates for electrode fabrication. The oxide layer isolates the silicon wafer from participating in the electrochemical reactions. A 50 nm Ti layer was first sputtered (Lesker-Lab18 Sputtering System) on one of the sides of the Si wafer followed by deposition of ca. 250 nm thick Cu layer and ca. 250 nm thick silicon layer (see Fig. 1). Film thicknesses were measured using a surface profilometer (Dektak) and a white-light interferometer (Zygo). Ti and Cu layers were prepared by DC-sputtering of Ti and Cu targets (2 in. diameter, 0.25 in. thick discs, 99.995%, Kurt Lesker Company) at 150 W and a pressure of 0.266 Pa of Ar. The Ti layer improves adhesion between the wafer and the Cu underlayer provides uniform current distribution in the Si thin film. Previous studies have shown that the Cu underlayer is critical to the cycling of Si thin films [5]. Si thin films were prepared by RF-magnetron sputtering of a Si target (2 in. diameter, 0.25 in. thick disc, 99.995% Si) at 180 W power and at a pressure of 0.266 Pa of Ar. Previous studies have shown that the sputter-deposited Si films are amorphous in nature [5]. The sample wafer (with Ti, Cu and Si layers) is then assembled into an electrochemical cell, which is shown schematically in Fig. 1, in ultra-high-pure (UHP) Ar atmosphere. Li metal (50.8 mm

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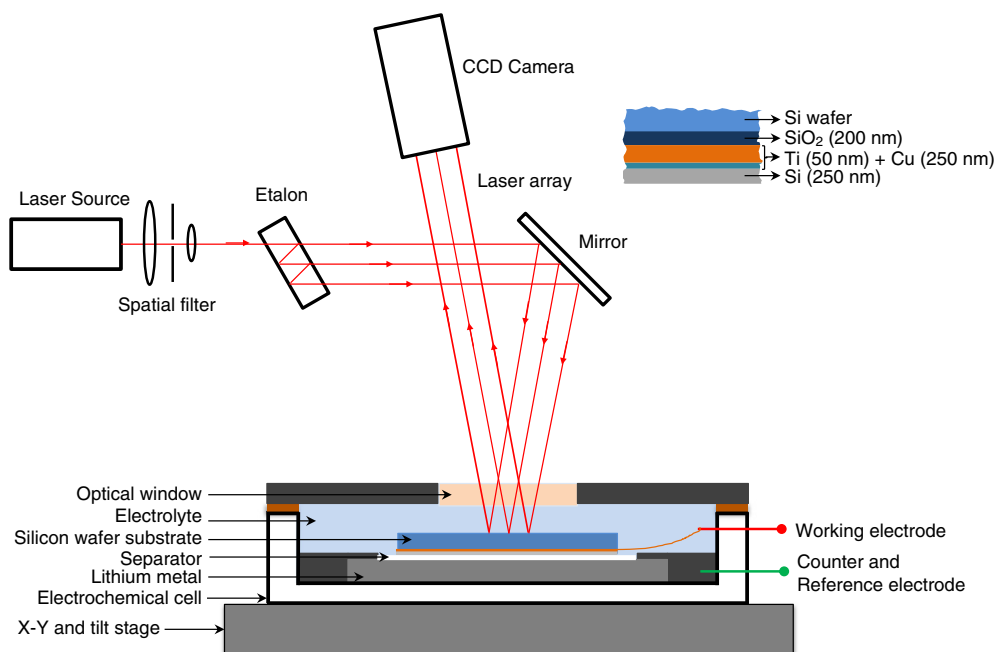Pradeep_Guduru@Brown.edu (P.R. Guduru).

Fig. 1. Schematic illustration of the electrochemical cell and the MOS setup used to measure substrate curvature. In this two-electrode configuration, Si thin film is the working electrode, and Li metal is the counter and reference electrode. Above right: layered configuration of the working electrode on Si-wafer substrate is shown. Cell-schematic is not drawn to scale.

diameter, 1.5 mm thick) was used as counter and reference electrode, which is separated from the Si electrode by a woven Celgard C480 separator (62 mm diameter, 21.5 μm thick). 1.2 M lithium hexa-fluoro-phosphate in 3:7 (wt.%) ethylene carbonate:diethyl carbonate with 10% fluoro-ethylene carbonate was used as the electrolyte.

2.2. Electrochemical measurements

Electrochemical measurements were conducted in UHP Ar atmosphere at 25 °C (± 1 °C) using a Solartron 1470E MultiStat (Solartron, Oak Ridge, TN). The Si thin-film electrode was lithiated galvanostatically at a current–density of 5 μA/cm^2 (ca. C/24 rate) for 1 h followed by an open-circuit relaxation for 1 h. The electrode was then delithiated galvanostatically at the same rate for 8 min followed by an open-circuit relaxation for 5 min (see Fig. 2a for a representative sequence). These lithiation–relaxation–delithiation–relaxation–relithiation sequence of steps was repeated at several different values of SOC until a lower cut-off potential of 0.01 V vs. Li/Li$^+$ was reached.

2.3. In situ stress measurements

Stress in the Si film was measured by monitoring the substrate-curvature changes during electrochemical lithiation and delithiation. The relationship between the biaxial film stress, σ, and the substrate-curvature change $\Delta \kappa$, is given by the Stoney equation [6,7],

$$\sigma = \sigma^r + \frac{E_s h_s^2 \Delta \kappa}{6 h_f (1 - \upsilon_s)} \qquad 1$$

where E_s and υ_s are the Young's modulus and the Poisson's ratio of the substrate respectively, σ^r is the residual stress in the Si film due to sputter deposition, and h_s and h_f are the substrate and the film thickness respectively. Values for E_s and υ_s were obtained from Brantley's work [8]. Residual stresses were measured by tracking the substrate curvature before and after each film-deposition (Ti/Cu, Si) step.

Based on in situ observations of height and volume changes during lithiation/delithiation in thin-film Si electrodes [9] reported in the literature, it is reasonable to assume that the film thickness (also volume) increases linearly with SOC,

$$h_f = h_f^0 (1 + 2.7z) \qquad 2$$

where h_f^0 is initial film thickness, and z represents the SOC, which can vary between 0 and 1. Here, $z = 1$ corresponds to a charge capacity of 3579 mAh/g, which corresponds to a volume expansion of 370%.

Substrate curvature was monitored with a multi-beam optical sensor (MOS) wafer curvature system (k-Space Associates, Dexter, MI), which is illustrated schematically in Fig. 1. The MOS system uses a parallel array of laser beams that get reflected off the sample surface and captured on a camera. The relative change in the spot spacing is related to the wafer curvature through

$$\kappa = \frac{\left(d - d^0 \right)}{d^0} \frac{1}{A_m} \qquad 3$$

where d is the distance between two adjacent laser spots on the camera (see Fig. 1(b) in Ref. [3]), d^0 is the initial distance and A_m is the mirror constant, given by $2L/\cos(\theta)$; L is the optical path length of the laser beam between the sample and the array and θ is the incident angle of the laser beam on the sample. The mirror constant A_m is measured by placing a reference mirror of known curvature in the sample plane and measuring the relative change in the spot spacing. Data acquisition rate was 1 Hz for all the experiments.

At any SOC, when the film is delithiated by a small amount, the in-plane strain change ($\Delta \varepsilon$) is given by $\Delta \varepsilon = \Delta \sigma / Y + \Delta \varepsilon^*$, where σ is the equi-biaxial stress in the film, Y is the biaxial modulus of the film, $Y = E/(1 - \nu)$, where E is the Young's modulus and ν is the Poisson's ratio of the film; and ε^* is the compositional strain due to lithiation. If
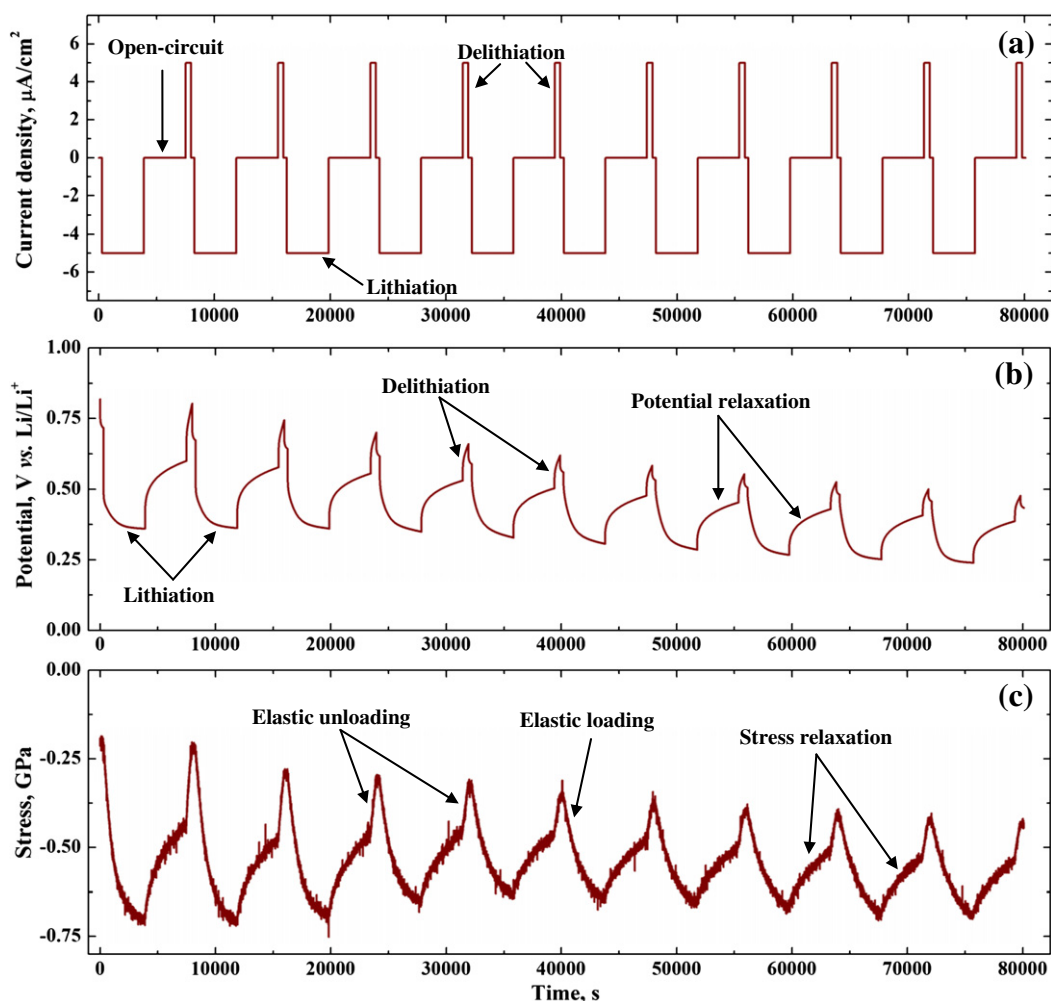
Fig. 2. Representative current–density, potential and stress transience obtained *in situ* from the experiments designed to measure biaxial moduli of a lithiated-silicon electrode.

we assume that the volumetric strain of the film due to lithiation is proportional to z, ε^* is given by

$$\varepsilon^* = (1 + 2.7z)^{1/3} - 1 \qquad\qquad 4$$

Since the in-plane strain change is zero due to substrate constraint, *i.e.*, $\Delta\varepsilon = 0$ the biaxial modulus can be written as $Y = -\Delta\sigma/\Delta\varepsilon^*$. During the delithiation–relithiation perturbation at each SOC, the stress change $\Delta\sigma$ is obtained from the substrate-curvature change, and $\Delta\varepsilon^*$ is obtained from Eq. (4), from which the evolution of the biaxial modulus with z can be inferred.

3. Results and discussion

It was shown earlier that the Li–Si electrodes undergo cycles of compressive and tensile stress during lithiation and delithiation, respectively [3]. Since full delithiation can result in large tensile stresses and film cracking, the elastic constants are best measured during the first lithiation, when the stress is known to be compressive and cracks do not form.

A representative history of current–density, potential and stress (which is a fraction of a long sequence SOC perturbation cycles) is shown in Fig. 2a–c. The stress–strain data in the elastic unloading region was used to estimate the biaxial modulus of the Li–Si system. Note the rapid stress relaxation immediately after the current interrupted, possibly due to double layer discharge. Ideally, the stress should reach a steady state during the open-circuit step before delithiation

commences so that viscoplastic stress relaxation does not contribute to the stress drop. However, in the Li–Si system, side reactions slowly and continuously remove Li from Si, resulting in a corresponding continuous change in stress; hence the stress does not reach a steady-
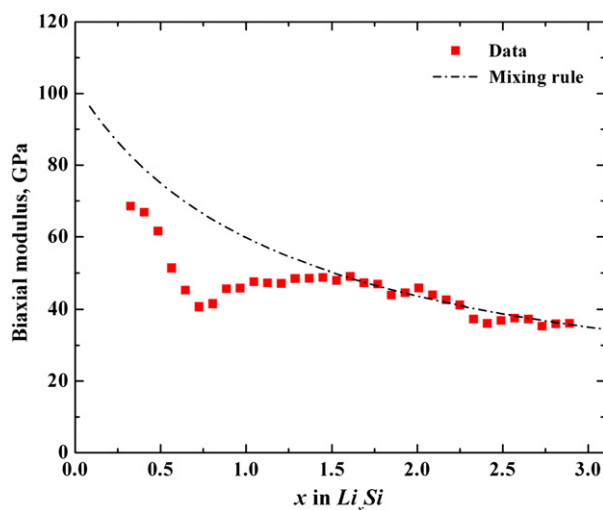

Fig. 3. Biaxial moduli of silicon thin-film as a function of lithium concentration obtained using the data shown in Fig. 2. The dotted line represents biaxial modulus calculated using a linear mixing rule.

Table 1
Parameters used for the stress and biaxial-modulus calculations presented in this study.

Parameter	Definition	Value	Comments
d_f	Diameter of a-Si film (Si-wafer diameter)	5.08 cm	Measured
E_{Li}	Young's modulus of Li	4.91 GPa	Ref. [11]
E_s	Young's modulus of Si (111) wafer	169 GPa	Ref. [8]
E_{Si}	Young's modulus of a-Si film	80 GPa	Ref. [7]
h_f^0	Initial film thickness	256 nm	Measured
h_s	Wafer thickness	450 μm	Measured
$2L/\cos(\theta)$	Mirror constant	2.7 m	Measured
σ_f^r	Residual stress in a-Si film	0.232 GPa	Measured
v_{Li}	Poisson's ratio of Li	0.36	Ref. [11]
v_s	Poisson's ratio of Si (111) substrate	0.26	Ref. [8]
v_{Si}	Poisson's ratio of a-Si film	0.22	Ref. [7]
ρ_f	Density of a-Si film	2.33 g/cm³	Ref. [8]

state value even after days [10]. In this investigation, we assume that 1 h of open-circuit relaxation is sufficient to minimize the contribution of viscoplastic relaxation to the stress drop during delithiation.

The biaxial moduli of Li–Si calculated from the data set shown in Fig. 2b–c, and the results are shown in Fig. 3. The experiments reveal that the biaxial modulus decreases significantly, from around 70 GPa to about 35 GPa, as the Li fraction is increased. Hence, it becomes essential to consider the change in elastic moduli while modeling stress evolution and mechanical damage in Si anodes. We note that the DFT calculations of Shenoy et al. [4] agree well with our experimental measurements. For example, they show that the elastic constants of amorphous Li–Si are well described by a simple rule of mixtures between the properties of pure Si and pure Li. Using such a rule of a mixture, the biaxial modulus as a function of x can be estimated to be

$$Y_{est} = \frac{x_{Li}E_{Li} + x_{Si}E_{Si}}{1 - (x_{Li}v_{Li} + x_{Si}v_{Si})} \qquad 5$$

where $x_{Li}(= 1 - x_{Si})$ is the fraction of Li atoms in the Li–Si electrode, E_{Li}, E_{Si}, and v_{Li}, v_{Si}, represent the Young's modulus and Poisson's ratio of amorphous-Si film and bulk Li, respectively. Parameters used for the calculations are listed in Table 1. Biaxial-modulus estimates from

Eq. (5) are shown in Fig. 3 as a dotted line, which seems to agree with the experimental measurements remarkably well.

4. Conclusions

We report an *in situ* method to measure the change in the biaxial modulus of Si anodes as a function of Li concentration. It involves perturbing the SOC of the anode through a small delithiation–relithiation cycle, while measuring the change in film stress with a MOS wafer curvature system. The measurements show that the biaxial modulus drops substantially from *ca.* 70 GPa for $Li_{0.32}Si$ to *ca.* 35 GPa for $Li_{3.0}Si$. A simple rule of mixtures was seen to agree well with the measurements. Hence, it may be reasonable to expect that other relevant mechanical properties (*e.g.*, ductility and fracture toughness) would also change substantially, which has implications for realistic modeling of the mechanics of Si anodes to predict their cycle life. The methodology presented here can be applied to characterize the biaxial modulus of other lithium-ion-battery electrodes of interest as well.

Acknowledgements

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