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A simple technique for measuring the fracture energy of lithiated thin-film silicon electrodes at various lithium concentrations

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HIGHLIGHTS

- The fracture energy of lithiated Si was measured at various states of charge.
- A bending test was performed to determine the critical strain for crack initiation.
- The elastic modulus decreased from 113 GPa for a-Si to 31.6 GPa for $Li_{3.28}Si$.
- The fracture energies were determined to be 12.0 J m^{-2} (a-Si) and 10.0 J m^{-2} ($Li_{3.28}Si$).

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ABSTRACT

We have measured the fracture energy of lithiated silicon thin-film electrodes as a function of lithium concentration using a bending test. First, silicon thin-films on copper substrates were lithiated to various states of charge. Then, bending tests were performed by deforming the substrate to a pre-defined shape, producing a variation of the curvature along the length of the electrode. The bending tests allow determination of the critical strains at which cracks initiate in the lithiated silicon. Using the substrate curvature technique, we also measured the elastic moduli and the stresses that develop in the electrodes during electrochemical lithiation. From these measurements, the fracture energy was calculated as a function of lithium concentration using a finite element simulation of fracture of an elastic–plastic substrate. The fracture energy was determined to be $\Gamma = 12.0 \pm 3.0$ J m^{-2} for amorphous silicon and $\Gamma = 10.0 \pm 3.6$ J m^{-2} for $Li_{3.28}Si$, with little variation in the fracture energy for intermediate Li concentrations. These results provide a guideline for the practical design of high-capacity lithium ion batteries to avoid fracture. The experimental technique described in this paper also provides a simple means of measuring the fracture energy of brittle thin-films.

1. Introduction

Lithium ion batteries have been developed to power an increasingly diverse range of applications, such as portable electronic devices and electric vehicles [1–4]. Silicon is considered one of the best candidates as an anode material for the next generation of lithium ion batteries due to its enormous capacity of 3579 mAh g^{-1} ($Li_{15}Si_4$) compared to that of graphite (372 mAh g^{-1}), which is currently the anode of choice [5–8]. However, lithium ion insertion and extraction results in a 200–300% increase in volume, which can lead to fracture of the silicon anode during electrochemical cycling [9,10]. Since fracture of the anode can cause a loss of electrical contact and the creation of more surface area for solid electrolyte interphase (SEI) growth, mechanical stability is a key issue in commercial battery applications [11–15].

A number of studies have reported mechanical properties of silicon electrodes. Mönig and colleagues [16,17] investigated the elastic modulus of lithiated silicon nanowires by uniaxial tensile testing. Hertzberg et al. [18] measured the hardness and the elastic modulus of lithiated silicon films using depth-sensing indentation measurements. They found that the hardness decreases from 5 to 1.5 GPa and that the elastic modulus decreases from 92 to 12 GPa in changing from the as-deposited silicon to the fully lithiated silicon ($Li_{15}Si_4$). Also, Sethuraman et al. [19] performed *in-situ* stress measurements of thin-film silicon electrodes using the substrate-curvature technique, finding a biaxial elastic modulus of 70 GPa

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for $Li_{0.32}Si$ and 35 GPa for $Li_{3.0}Si$. Pharr et al. [20] evaluated the fracture energy Γ of lithiated silicon by monitoring the stress and morphological development of cracks during electrochemical cycling. They measured a fracture energy of 8.5 ± 4.3 J m^{-2} at small concentrations of lithium (~$Li_{0.7}Si$), and established bounds of 5.4 ± 2.2 J m^{-2} to 6.9 ± 1.9 J m^{-2} for Γ at large concentrations of lithium (~$Li_{2.8}Si$). In addition, Nadimpalli et al. [21] estimated an upper bound of 9–11 J m^{-2} for the fracture energy of $Li_{0.4}Si$ based on stress data and electron microscopy observations. However, these measurement techniques have limitations due to the difficulty of determining the critical stress at which cracks initiate on the surface of the electrode. Furthermore, experimental measurements of fracture energy over a range of lithium concentrations are lacking. In order to design durable silicon electrodes, it is essential to know the fracture energy as a function of state of charge.

In this study, we introduce a simple technique for measuring the fracture energy of thin-film silicon electrodes as a function of lithium concentration. We first lithiate amorphous silicon (a-Si) thin-film electrodes on copper substrates to different states of charge. We then perform a bending test by deforming the substrate to a pre-defined shape that allows for a variation in the curvature along the length of the sample. After bending, the electrodes are examined using a focused ion beam (FIB) to obtain both the critical strain for crack initiation and the thickness of the electrodes after lithiation. Using the substrate curvature technique, we measure both the elastic modulus of the lithiated silicon and the stress induced by lithiation. Combining these results, we quantify the fracture energy using a fracture mechanics analysis. The simple technique presented here is not only useful for lithiated-silicon thin-film electrodes but is also generally applicable for measuring the fracture energy of thin-films and coatings.

2. Experimental procedures

All electrochemical measurements were performed using a standard three-electrode configuration in a custom-fabricated, hermetic, Teflon cell with a glass window. Both the reference and counter electrodes consisted of lithium foil, while the working electrode was a thin-film of amorphous silicon on a copper substrate (McMaster-Carr, annealed electrolytic tough pitch copper). To fabricate the working electrode, mechanically polished copper substrates (10 mm × 70 mm) with a thickness of 0.8 mm were electro-polished (2 V, 15 min) in phosphoric acid (85 wt%) and placed in a sputter deposition system (ATC 1800, AJA Int., Scituate). Immediately before deposition, the substrates were plasma cleaned for 5 min in 20 mTorr of argon using an RF power of 24 W. Then, 20 nm of copper was deposited onto the substrates using an argon working pressure of 5 mTorr and a DC power of 200 W. The purpose of this copper film was to provide a fresh surface for silicon film deposition. The silicon film was then deposited directly onto the copper film using an argon pressure of 5 mTorr and a DC power of 100 W. The working area of each silicon electrode was 10 mm × 35 mm, and the silicon electrode thickness was 550 ± 15 nm.

The electrolyte consisted of a 1 M solution of $LiPF_6$ in 1:1:1 (wt%) ethylene carbonate:diethyl carbonate:dimethyl carbonate. The electrochemical cells were assembled in a glove box in an ultrahigh purity argon atmosphere with a moisture content of less than 0.1 ppm. Electrochemical measurements were performed with a VersaSTAT 3 galvanostat from Princeton Applied Research. The silicon electrodes were lithiated at a constant current density of 100 μA cm^{-2} (a C/16 rate assuming a capacity of 3579 mAh g^{-1}), and then potentiostatically held until the current dropped to less than 4% of its original value to reach diffusive equilibrium at four different states of charge: 1/4 (895 mAh g^{-1}), 1/2 (1790 mAh g^{-1}), 3/4 (2684 mAh g^{-1}), and full (3579 mAh g^{-1}). All lithiation processes were conducted within a voltage window of 0.05–3.0 V. After lithiation, the electrodes were removed from the cell, rinsed in dimethyl carbonate (DMC), and dried for 5 min inside the glove box.

Bending tests on the working electrodes were performed inside the glove box 15 min after removing the electrodes from the cell. The tests were performed using a Delrin mandrel (Fig. 1a) that consisted of a male and a female part. The female part had the shape of an ellipsoid, described in x-y coordinates by $9x^2 + y^2 = 9$ (cm), to impose a variable curvature along the length of the sample; the male part had a similar shape, accounting for sample thickness. The strain in the surface of the substrate is then given by [22]:

$$\varepsilon = \frac{h_{sub}}{2\rho}, \tag{1}$$

where h_{sub} is the thickness of substrate and ρ is the local radius of curvature of the substrate. The strain imposed on the electrode film is tensile and varies from 11% in the center of the sample to 0.9% at the edge, as illustrated in Fig. 1b. Prior to bending, the silicon electrodes were scratched with a diamond scribe to introduce imperfections with sizes on the order of the film thickness [20]. Also, marks were drawn at 1 mm increments along the specimen to quantify the position of crack initiation. Then, the samples were placed between the male and female parts of the mandrel and deformed to the shape of the mandrel. Two sets of samples were tested under identical conditions to examine the reproducibility of the experiments. The mandrels are quite stiff, which ensures reproducible deformation of the sample as long as it is in full contact with the surfaces of the mandrel. After the bending test, the samples were sealed in an airtight container inside the glove box and immediately transferred to a focused ion beam (FIB, Zeiss NVision 40) chamber to examine the electrode surfaces. During transfer, the samples were exposed to air for less than 30 s. The elastic modulus of the pure silicon film was measured by performing nano-indentation tests using a Hysitron Tribolab nano-indentation system. Indentation tests were performed in load control at a constant loading rate of 200 μN s^{-1}. A total of 25 indentations were made in a 5 × 5 array with a spacing of 5 μm between the indentations.

3. Results and discussion

Since the silicon thin-film electrodes are constrained in the plane of the film by the relatively thick substrate, lithium insertion is accommodated entirely by expansion of the electrodes in the thickness direction. Thus, it is reasonable to take the thickness of the film, h_f, to be linear in the state of charge,

$$h_f = h_o(1 + \beta s), \tag{2}$$

where h_o is the initial thickness of the film, β is related to the atomic volumes (Ω) of silicon and the lithiated phase by $\beta = (\Omega_{Li3.75Si} - \Omega_{Si})/\Omega_{Si} = 2.8$ (silicon undergoes a 280% increase in volume when it is fully lithiated), and s is the state of charge of the electrode, with a value of 0 representing pure silicon and a value of 1 representing the fully lithiated state (assumed to be $Li_{3.75}Si$ with a capacity of 3579 mAh g^{-1}) [20,23]. It should be noted, however, that SEI formation consumes lithium and thus affects both the thickness of the film and the apparent state of charge [11,24]. In order to examine the effects of SEI formation, we measured the thickness of Li_xSi after different lithiation times using FIB cross-sectioning. Fig. 2 shows the thickness of a Li_xSi thin-film as a function of time for a constant charge rate. The initial thickness of the amorphous silicon