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Kim, Yeongae; Sim, Soojin; Kang, Sujin; Yun, Jeonghun; Lee, Hyun-Wook; Lee, Seok Woo

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Highly robust silicon bimorph plate anode and its mechanical analysis upon electrochemical lithiation

Abstract

As the need for smaller, lighter, and longer lasting energy storage increases, silicon (Si) rises as a promising anode material of lithium (Li) ion batteries due to large specific capacity. However, the Si undergoes severe volume expansion causing mechanical fracture and electrochemical degradation. The use of nanostructured Si prevents mechanical fracture, but its large surface area enables irreversible side reaction. Therefore, understanding the mechanical behavior of lithiated Si (Li_xSi) is essential for designing robust Si structures with less surface area. Here, we estimate the stress in Li_xSi on crystalline-Si (c-Si) and copper bimorph plate and study its fracture resistance. When Li_xSi and c-Si coexisted, Li_xSi exhibits $\sim 50\%$ of the full lithiation and compression of ~ 0.55 GPa, which is smaller than its yield strength. After c-Si is removed, it is predicted that plastic deformation of Li_xSi would occur on the open surface of the plate, but most of the structure would remain in the elastic behavior regime. The low stress in the Li_xSi plate allows it to bear fractures up to much larger size ($\sim 2\ \mu\text{m}$) than that of Si nanoparticles and nanopillars. It suggests using the robust micron-scale silicon structure for highly reversible and cost effective anode of Li-ion batteries.

Keywords: lithium ion battery; silicon anode; lithiation; stress; fracture

1. Introduction

Lithium (Li) ion batteries have become an indispensable part of daily life as a mobile power-supply solution. Despite the satisfaction of market demand for Li-ion batteries, higher-performance batteries with larger energy density, faster charging, and lower cost are still required for various applications such as electric vehicles and mobile electronic devices [1-3]. Silicon (Si) is considered a promising candidate for the anode of Li-ion batteries because of its abundance, low cost, and outstanding specific capacity of 3,580 mAh/g, which is about ten times higher than commercial graphite anodes [4-7]. However, the Si anode undergoes significant volumetric expansion up to 300% when alloyed with Li, and the swelling leads to mechanical fracture, in turn causing electrochemical degradation [8-10]. To avoid or minimize fractures, Si nanostructures such as nanoparticles, nanowires, and nanotubes have been introduced [11-15]. Nanoscale Si structures bring the advantage of larger fracture resistance, but also bring disadvantages caused by their large surface area. In particular, a solid electrolyte interphase (SEI) layer is formed on the Si anode surface via the electrochemical reduction of the electrolyte, and functions as a passivation film that prevents further decomposition of the electrolyte while allowing only ion transfer [16, 17]. The formation of SEI on Si nanostructures causes irreversible consumption of Li-ions and low initial coulombic efficiency of 65–80% [12, 18]. Moreover, the repeated expansion and contraction of the Si electrode during long-term electrochemical reduction and oxidation hinders the formation of a stable SEI layer, which repeatedly undergoes fracture and reformation [19-21]. Therefore, the Si anode must have either a sufficiently low surface area or a fixed outer surface in order to maintain a stable SEI layer for stable cycling of batteries. Considering the aforementioned factors together, strong fracture resistance of the Si anode requires a smaller feature size but stable SEI formation needs a larger feature size to reduce the surface area-to-volume ratio. To overcome this conflict, it is necessary to optimize the design of Si anode structures to reduce strain while increasing the

critical dimension of fractures. This will allow stable SEI formation on the minimized surface of the Si anode structure while securing its mechanical stability against fracture.

For the optimal design of stress-resistant large structures, understanding the lithiation process of the Si anode and measuring the induced stress should take precedence. Several previous studies have measured the stress on the Si anode during its lithiation/delithiation. In situ Raman spectroscopy has been used to measure the stress induced in the crystalline core of a Si nanoparticle during its lithiation [22]. During the process of lithiation, the stress was found to alter from tensile to compressive stress, the latter of which was too weak to risk causing fracture in the crystalline core of Si. Studies have revealed that fracture most commonly occurs in lithium-silicon alloys (Li_xSi). Therefore, understanding the mechanical behavior of Li_xSi and measuring its mechanical properties are important for optimizing the design of Si anode structures with high fracture resistance. Multi-beam optical sensors have been used to measure the induced stress in Li_xSi lithiated from amorphous Si (a-Si) thin film or crystalline Si (c-Si) wafer [23-25]. The compressive stress in fully lithiated a-Si remains below 1.2 GPa after plastic deformation. Lithiated c-Si exhibited relatively smaller compressive stress of 0.5 GPa, but such small stress is not fully understood yet. Because the most widely used Si anodes are crystalline particles and nanowires, rather than a-Si, further understanding of the mechanical behavior of Li_xSi formed from c-Si is necessary to improve the design of robust Si anode structures [26]. In particular, it is important to know the preferred lithiation of c-Si at the $\{110\}$ surface, and accurately determine the Li composition, in the measurement of the stress of lithiated c-Si.

In this study, we estimated stress in the Li_xSi lithiated from various crystalline surfaces of c-Si using vertically aligned single crystalline Si plates and present highly robust c-Si/Cu bimorph plate structure for which the critical dimension is increased 2 μm . For the partially lithiated Si plate at various applied potentials, an analytical model estimated the induced stress in Li_xSi

and c-Si, based on the thickness of each phase when the lithiation terminated at thermodynamic equilibrium between the Gibbs free energy of lithiation, influence of induced stress, and applied external potential. For the fully lithiated Si plate, the stress in Li_xSi was estimated by measuring the bending curvature of the $\text{Li}_x\text{Si}/\text{Cu}$ bimorph plate, and numerically analyzing the effect of an increase of Li in Li_xSi . The fracture resistance of the c-Si/Cu bimorph plate anode was evaluated by ex-situ scanning electron microscopy (SEM) for various thicknesses of the plate.

2. Results and discussion

2.1 Lithiation of single crystalline silicon (c-Si) plate

A vertically aligned Si plate provides well-defined dimensions and crystalline orientation. Because it is fixed on the rigid substrate, cross-sectional observation of the partially or fully lithiated Si plate allows clear identification of the thickness of Li_xSi , amount of consumed c-Si, and remaining c-Si for precise analysis, giving a well-defined Li composition of Li_xSi . In this study, c-Si plates with three different surface orientations were fabricated to observe their mechanical behaviors during the first stage of lithiation: $\{110\}$, $\{100\}$, and $\{111\}$ (see Methods and Fig. S1 in Supporting Information). Fig. 1a shows a cross-section of the fabricated c-Si plate with an aspect ratio of ca. 10. The left side of the plate is exposed to allow lithiation and the other side is covered with Cu thin film to block Li insertion. Hence, Li_xSi is formed on the left side of the plate upon electrochemical Li insertion (Fig. S2). In the formula Li_xSi , the x is the stoichiometric ratio of Li and Si atoms. The maximum value of x is 3.75 at room temperature, and the volume of $\text{Li}_{3.75}\text{Si}$ is 4 times that of c-Si. We assumed that the mechanical properties would change depending on the x value during lithiation from c-Si (Li_0Si) to $\text{Li}_{3.75}\text{Si}$ (see Fig. S3 and Table S1). It is well known that compressive stress is induced by volume expansion of Li_xSi , and is counteracted by tensile stress in c-Si upon lithiation of a flat surface,

and such stresses cause bending of the plate (Fig. 1b). Fig. 1c shows cross-sectional SEM images of the lithiated $\{110\}$ plate at various cut off voltages (COVs), recorded to study the dependence of stress on the degree of lithiation. There are two distinct stages of lithiation of the c-Si plate. In the first stage, the c-Si and Li_xSi (c-Si/ Li_xSi) coexist with distinct interfaces between c-Si, Li_xSi , and Cu, and the growth in thickness of Li_xSi is terminated at thermodynamic equilibrium with a given COV. As the COV decreases, the thickness of the Li_xSi layer increases. In contrast to the intuitive assumption that lithiated c-Si would immediately become fully lithiated $\text{Li}_{3.75}\text{Si}$, the volume expansion of Li_xSi is significantly lower than 400%, that is, the value of full lithiation. In the second stage, the COV is lower than 80 mV vs. Li/Li^+ , which allows complete consumption of the c-Si, and the elimination of rigid c-Si induces deformations of the Li_xSi plate upon further expansion. The expansion ratio of Li_xSi was measured to determine how many Li atoms reacted with one Si atom at various COVs (Fig. 1d). The expansion ratio was calculated based on the area of the Li_xSi versus the area of the consumed c-Si, and the calculated ratios were used to determine the x value in Li_xSi (Fig. S3). The volume change of lithiated Si is mainly observed as the height change in the normal direction due to the constraint by the rigid substrate and it is proportional to state of charge [27]. Therefore, we assume that the volume change of Li_xSi is directly correlated to the value of x in Li_xSi . In the first stage, during the coexistence of c-Si/ Li_xSi , the expansion ratios of Li_xSi were similar for the various COVs and thicknesses of Li_xSi ; specifically, the ratios were 2.48 at 120 mV vs. Li/Li^+ and 2.49 at 85 mV vs. Li/Li^+ . Assuming a proportional relation between the stoichiometric ratio of Li atoms and the expansion ratio, the x values were 1.85 and 1.86 (~ 50% of the full lithiation) at COVs of 120 mV and 85 mV vs. Li/Li^+ , respectively. For comparison, we calculated x from the video of a lithiated Si nanopillar in a previous in situ TEM study as shown in Fig. S4 [28]. In that study, x converged to about 2 during the lithiation of the pillar, which was in good agreement with our experiment. In the second stage of lithiation,

without c-Si, an isotropic expansion occurs in amorphous Li_xSi (a- Li_xSi), and the constraint of the Cu thin film induces significant bending of the plate. As COV is decreased, further Li insertion causes the expansion of Li_xSi and increase of the curvature. When COV is decreased to 10 mV vs. Li/Li^+ , a common value of COV in Si anode testing, the expansion ratio and x are very close to the theoretical values of fully lithiated Si.

The $\{100\}$ and $\{111\}$ plates were lithiated and characterized in the same manner as the $\{110\}$ plate as shown in Fig. 2. At the first stage of lithiation, the x value was 1.48 and 1.43 in the $\{100\}$ and $\{111\}$ plates, respectively, when the COV was 80 mV vs. Li/Li^+ . These lower x values were maintained during the second stage of lithiation as well. Although the Li was fully inserted at a COV of 10 mV vs. Li/Li^+ , the measured Li_xSi compositions were $\text{Li}_{3.02}\text{Si}$ and $\text{Li}_{2.15}\text{Si}$ for the $\{100\}$ and $\{111\}$ plates, respectively. In situ optical microscopy (OM) confirmed the bending of the $\text{Li}_x\text{Si}/\text{Cu}$ bimorph plate at the second stage of lithiation (Fig. S5) [29]. The experimental setup was the same as the half-cell for electrochemical lithiation as shown in Fig. S5a. When the COV of 10 mV vs. Li/Li^+ was applied to the $\{100\}$ c-Si, the plate started to display curvature after a certain time, and the curvature increased as the lithiation progressed.

2.2 Analytical model

An analytical model was used to estimate the induced stress in Li_xSi during the first stage of lithiation assuming thermodynamic equilibrium of lithiation, expressed by a modified Gibbs free energy equation including the influence of stress [30, 31].

$$\Delta G = \Delta G_r^{\text{Li}_x\text{Si}} - e\Phi + \Delta G_\sigma \quad (1)$$

where ΔG is the change of Gibbs free energy of lithiation, $\Delta G_r^{\text{Li}_x\text{Si}}$ is the change of free energy of lithiation without applied voltage or mechanical stress, Φ is the applied voltage, and ΔG_σ

is the change of free energy due to mechanical stress. The direction of reaction can be inferred from the sign of ΔG . A negative value of ΔG drives lithiation, and a greater negative value brings a larger driving force. In contrast, a positive ΔG leads to delithiation, with a driving force that also depends on the absolute value of ΔG . When the three terms in Eq. (1) are balanced during lithiation, ΔG becomes zero and lithiation is terminated. In the analysis of the first stage of the lithiation, the change of free energy ($\Delta G_r^{Li_xSi}$) is assumed to be a constant value of -0.18 eV because of a two phase reaction with reaction front between c-Si and a-Li_xSi [31, 32]. The applied voltage Φ is the measured value in the experiment. Therefore, the change of free energy due to mechanical stress (ΔG_σ) can be determined at the moment of self-termination of lithiation using Eq. (1). The ΔG_σ is defined as the induced mechanical stress at the reaction interface of c-Si and Li_xSi, expressed as follows [28, 31]:

$$\Delta G_\sigma = \frac{1}{x} (\sigma_m^{Si} \cdot \Omega^{Si} - \sigma_m^{Li_xSi} \cdot \Omega^{Li_xSi}) \quad (2)$$

where x is the number of Li atoms reacting with one Si atom, σ_m^{Si} and $\sigma_m^{Li_xSi}$ are the mean stress in the c-Si and the mean stress in the Li_xSi at each reaction front, respectively, Ω^{Si} is the volume per Si atom, and Ω^{Li_xSi} is the volume per unit Li_xSi. To estimate the stresses, the cross-sectional dimensions of parts of the lithiated Si plate are defined as shown in Fig. 3a. The thickness of the pristine c-Si plate and deposited Cu are t_o and t_{Cu} , respectively. The Li_xSi is formed by alloying with the consumed c-Si (t_1) as the result of lithiation, and the thickness of c-Si and Li_xSi are defined t_{Si} and t_{Li_xSi} , respectively. The t_{Li_xSi} is defined as the sum of t_1 and t_2 , and the ratio of t_2 versus t_1 is the expansion ratio.

In the analysis, two kinds of stresses, that is, those caused by force equilibrium ($\sigma^{Li_xSi/Si/Cu}$) and bending moment ($\sigma_{bend}^{Li_xSi/Si/Cu}$), were considered to estimate σ^{Li_xSi} , the induced stress in Li_xSi. Fig. 3b shows these stresses in the unit length structure. Assuming force equilibrium,

σ^{Si} and σ^{Cu} as a function of σ^{Li_xSi} were derived as follows:

$$\sigma^{Si} = -\frac{E_{Si} \cdot \sigma^{Li_xSi} \cdot t_{Si}}{E_{Cu} \cdot t_{Cu} + E_{Si} \cdot t_{Si}}, \quad \sigma^{Cu} = -\frac{E_{Cu} \cdot \sigma^{Li_xSi} \cdot t_{Li_xSi}}{E_{Si} \cdot t_{Si} + E_{Cu} \cdot t_{Cu}} \quad (3)$$

where E is the Young's modulus of the superscripted material (Table S1 in Supporting information). The t_{Cu} and E_{Cu} are 700 nm and 128 GPa, respectively. Bending stress by moment was represented as:

$$\sigma_{bend} = \frac{(t - t_{NA})}{I_{NA}} M \quad (4)$$

where M and I are the moment and moment of inertia, respectively, and the subscript NA means neutral axis. The moment was calculated as follows:

$$M = \int_{t_{Cu}+t_{Si}}^{t_{Cu}+t_{Si}+t_{Li_xSi}} -\sigma^{Li_xSi} (t - t_{NA}) dt \quad (5)$$

The above calculations are expanded in detail in Note S1.

The mean stresses at the reaction front in c-Si and Li_xSi were represented as follows:

$$\sigma_m^{Si} = \frac{\sigma_1^{Si} + \sigma_2^{Si} + \sigma_3^{Si}}{3}, \quad \sigma_m^{Li_xSi} = \frac{\sigma_1^{Li_xSi} + \sigma_2^{Li_xSi} + \sigma_3^{Li_xSi}}{3} \quad (6)$$

where the subscripts 1, 2, and 3 mean direction of height, longitudinal direction, and direction of thickness, respectively. In our experimental model, $\sigma_3^{Li_xSi} = \sigma_3^{Si} = 0$ because Li_xSi swelled without any constraints along the normal direction. σ_1 takes the stresses caused by both the force equilibrium and bending moment, while σ_2 has only the stress from the force equilibrium along the longitudinal direction in each material. Finally, the mean stresses at the reaction interface in c-Si and Li_xSi were expressed as:

$$\sigma_m^{Si} = \frac{\sigma^{Si} + \sigma_{bend}^{Si} + \sigma^{Si}}{3}, \quad \sigma_m^{Li_xSi} = \frac{\sigma^{Li_xSi} + \sigma_{bend}^{Li_xSi} + \sigma^{Li_xSi}}{3} \quad (7)$$

Fig. 3c-e shows the dimensionless stress profiles at the reaction interface between Li_xSi and c-Si and the change of free energy due to mechanical stress for the consumed c-Si ratio (t_1/t_0) on the {110} plate with COV of 85 mV vs. Li/Li^+ . The thickness of each part measured in the experiment was inserted into the derived equations of stresses for force equilibrium (σ^{Si} and σ^{Li_xSi}) and bending moment (σ_{bend}^{Si} and $\sigma_{bend}^{Li_xSi}$). Then, each stress was divided by the σ^{Li_xSi} to plot normalized values, as σ^{Li_xSi} was the unknown value to be estimated. Considering the bent structure toward the Cu side, bending moment induces compression from the open surface of Li_xSi to the neutral axis, and then the direction is changed to tensile stress since the bending moment is zero at the neutral axis. Therefore, the stress due to bending moment at the reaction interface (blue lines) becomes zero when the neutral axis is located on the reaction interface as shown in Fig. 3c. Then, sign conversion of the stress occurs as the neutral axis located in Li_xSi upon further lithiation. The lithiation was halted at $t_1/t_0 = 0.45$ (vertical gray dash line) in the experiment, although the stresses were calculated until the entire consumption of c-Si. These calculated stresses were used to plot the mean stresses (σ_m^{Si} and $\sigma_m^{Li_xSi}$) normalized by σ^{Li_xSi} in Fig. 3d. In Fig. 3e, ΔG_σ for t_1/t_0 is plotted for various σ^{Li_xSi} . The horizontal gray dash line represents $e\Phi - \Delta G_r^{Li_xSi}$ when the applied voltage (Φ) is 85 mV and the free energy of Li deposition versus lithiation of Si ($\Delta G_r^{Li_xSi}$) is -0.18 eV [32]. According to Eq. (1), termination of lithiation occurred when the plot of ΔG_σ crossed the horizontal gray dash line. Then, the location of the crossing point indicated the t_1/t_0 of self-termination of lithiation for a given Φ . In the opposite manner, we defined the self-termination point of lithiation from the experimental data and estimated the value of σ^{Li_xSi} at which ΔG_σ crossed the point. The red dot is the self-termination point of lithiation determined by the experiment, and is located where ΔG_σ is 0.095 GPa and t_1/t_0 is 0.45. The dash line in Fig. 3e is ΔG_σ when σ^{Li_xSi} is assumed to be -1 GPa, widely considered as the yield strength of fully lithiated Si. This line does not have

a crossing point with the horizontal gray dash line, indicating that σ^{Li_xSi} was expected to be less compressive than -1 GPa. Consequently, ΔG_σ (black line) crosses the red dot when σ^{Li_xSi} is assumed to be -0.55 GPa. In the same manner, we estimated σ^{Li_xSi} for various COVs and crystalline surfaces of the c-Si plate as shown in Fig. 3f. On each c-Si surface, the extent of consumed c-Si at thermodynamic equilibrium was different, but the induced stresses were similar. In the analytical model, we considered only elastic behavior, without plastic deformation. Nevertheless, the estimated stress in Li_xSi lithiated from c-Si is about a half of widely considered yield strength of fully lithiated Si, 1 GPa. This might indicate elastic deformation of Li_xSi on c-Si rather than plastic deformation, with the induced stress dependent on the yield strength due to the inherent anisotropic lithiation of c-Si.

2.3 Finite element method (FEM) analysis

A finite element method (FEM) analysis was conducted to explore how deformation progressed and the stress was distributed during the second stage of lithiation after the disappearance of c-Si. In this analysis, heat conduction and thermal stress considering plastic deformation were treated analogously to that of Li diffusion in Li_xSi as reported in previous studies [28]. The initial structure consists of Li_xSi and Cu thin film, where the initial x is obtained from the experiment of the first stage of lithiation for each crystalline surface. The estimated stress in Li_xSi at the first stage of lithiation was applied as the initial stress, and the mechanical properties were derived in accordance with x , which itself was derived from the expansion ratio at each COV. Fig. 4a shows the calculated first principal stress of the {110} plate for various depths of lithiation. As the structure was increasingly lithiated, it exhibited continual expansion and bending of the plate, as demonstrated in the experiment (Movie S1). Plastic deformation was expected only in the open (exposed) surface rather than in the overall structure. The maximum tension was found at the open side close to the interface between Li_xSi and substrate,

where fracture occurred in the experiment, as discussed in the next paragraph. The radius of curvature of the {110} plate obtained from FEM analysis was analogous with the experimental data below 40 mV vs. Li/Li⁺, as shown in Fig. 4b. (See Fig. S6 for the detailed measurement of the radius of curvature.) Fig. 4c compares the calculated radius of curvature of the {100} and {111} plates with the experimental data. Because x of the {100} and {111} plates in the first stage of lithiation was smaller than that of the {110} plate, the former swelled more in the second stage of lithiation and consequently bent more than the {110} plate, as shown in the experimental data. The FEM analysis accounted for such behavior by show the smaller radius of curvature on the {100} and {111} plates than the {110} plate. Results in the radius of curvature were similar between the experimental data and simulation data as the lithiation progress, while the results are not matched well at the beginning. It is because the materials properties for x was obtained from the result of the first state of lithiation instead of the second stage due to experimental limitation and small deformation at the beginning of the second stage caused large error of the measurement of the radius of curvature. At lower cut off voltages (< 40 mV vs. Li/Li⁺), the results of FEM analysis was in good agreement with experimental date due to similar x value and large deformed structure.

2.4 Fracture of micro-sized structures

To study the fracture resistance of the c-Si/Cu bimorph plate and its size effect, micron-scale {110} c-Si plates were fabricated with thicknesses of 2, 4, 6, and 8 μm , and Cu thin film was deposited on one side of the plate. The Si plate was lithiated to 10 mV vs. Li/Li⁺ to create fully lithiated Li _{x} Si. The cross-sectional SEM images of the structures are shown in Fig. 5 before and after the lithiation. After the lithiation, the plates showed remarkable volumetric expansion. Visible cracks were observed in the cross-sectional view of all but one of the lithiated Si plates with various thicknesses (Fig. 5a). Only the 2 μm thick plate exhibited no visible crack, while

all of the thicker plates were fractured as shown in Fig. 5b. The 2 μm plates without crack and cracked plates of the 4 μm are shown in Fig. S7 as well. This was a significant improvement compared with the critical fracture size of Si nanoparticles and Si nanopillars, which ranged from 150 to 300 nm as reported in previous studies [11, 33]. The improvement could be attributed to the flat interface of lithiation in the Si plate, which induced compressive stress in Li_xSi , while Si particles and pillars had curved interfaces that induced tension in Li_xSi as described by the pressurized vessel model [11, 30]. Moreover, a larger fracture resistance is expected when the Si plates are randomly dispersed, without constraint, in the anode structure; fractures occurred at the interface with the Cu substrate during lithiation which would not be present in a practical anode. The stress concentration at the interface calculated by FEM is shown in Fig 4a. Delithiation was conducted to observe reversibility of c-Si/Cu bimorph plate after the lithiation. After the delithiation of the {110} c-Si plate, there was no significant fracture on the delithiated Si, but delamination was found between the Si and Cu due to weak adhesion as shown in Fig. S8. The previous study also reported large fracture resistance of a-Si during lithiation and delithiation but delamination occurred at the interface with heterogeneous structure [34]. Therefore, further design of the Si anode structure is necessary to increase the adhesion with the bimorph layer while Si structure maintains large fracture resistance.

3. Conclusions

In summary, we investigated the deformation and induced stress of Li_xSi lithiated from various crystalline surfaces of c-Si using vertically aligned c-Si/Cu bimorph plates. We found that Li insertion occurred in two stages, rather than reaching the fully lithiated Li_xSi immediately after lithiation of c-Si. At the first stage of lithiation, Li_xSi and c-Si coexisted while c-Si was

consumed to form Li_xSi by electrochemical lithiation. The measurement of the thickness of each layer in the cross-sectional view revealed that the stoichiometric ratio of Li in lithiated c-Si, x , was uniform, but much less than in the fully lithiated state. x showed a dependency on the preferred crystal orientation following the lithiation of c-Si, reaching its highest level for the $\{110\}$ plane, followed by the $\{100\}$ and $\{111\}$ planes. Through analytical modeling, the lithiation induced compression in Li_xSi was estimated to be ~ 0.55 GPa in the first stage of lithiation, much lower than the widely assumed yield strength of Li_xSi , 1 GPa. It is interesting that such a low stress was estimated by an elastic model without considering plastic deformation. Furthermore, the yield strength of Li_xSi in the first stage was larger than that of fully lithiated Si due to the smaller x . Therefore, we conclude that Li_xSi might not have shown plastic behavior throughout the entire structure due to the inherent anisotropic lithiation of c-Si in the first stage. Nevertheless, plastic deformation might have occurred in the microscopic region around the reaction interface between Li_xSi and c-Si. In the second stage of lithiation, c-Si disappeared and Li_xSi expanded isotropically until Li was fully inserted. Each plane showed a different extent of volume expansion in the second stage due to the different amounts of inserted Li in the first stage, resulting in a variable curvature of these plates. FEM analysis of the second stage of lithiation indicated that tension was applied at the open surface of Li_xSi , but that the maximum stress was not sufficiently large to cause severe fracture. Such low stress in the plate structure during the first and second lithiation stages allowed lithiation of a plate up to ~ 2 μm thick without any fractures, more than 6 times larger than the size of fracture for Si nanoparticles and nanopillars. The structure demonstrated here could provide a fracture resistive Si anode with a minimized surface area for highly efficient Li-ion batteries using cost effective fabrication methods such as large scale microfabrication or metal assisted catalytic etching. Furthermore, future studies of this well-defined Si structure and its analytical/numerical modeling should contribute to understanding the fundamental behavior of

lithiated Si anodes and improve the design of Si anode structures with mechanical and electrochemical stability for high-performance Li-ion batteries.

4. Methods

4.1 Fabrication of c-Si plates and Preparation of half-cell

Three kinds of standing c-Si plates were fabricated from c-Si wafers to expose the {110}, {100}, or {111} surface on the side wall by photolithography and dry etching. Inclined e-beam evaporation was used to deposit a Cu thin film on one side of the plate to allow lithiation only on the other, open side of the structure (see Fig. S1a). For the electrochemical lithiation of the fabricated sample, half-cells were assembled with the fabricated c-Si plate sample as a working electrode and Li foil as a counter electrode (Fig. S1b).

4.2 Electrochemical lithiation and Structural characterization

The assembled cell was connected to a potentiostat (VMP3, Bio-Logic Inc.) for electrochemical lithiation. COV were applied in range from 120 mV vs. Li/Li⁺ to 10 mV vs. Li/Li⁺ because Si starts reaction to Li below 200 mV vs. Li/Li⁺ and the formation of Li_xSi is completed near 30 mV vs. Li/Li⁺ [35]. Voltage was linearly swept from open circuit voltage to 500 mV vs. Li/Li⁺ with a sweep rate of 5 mV/s and then swept to the desired COV with a sweep rate of 0.1 mV/s. COV was set to 10 mV vs. Li/Li⁺ for full lithiation and higher voltages for the partial lithiation of the c-Si plates. These COVs were maintained for 10 h to ensure complete reaction and thermodynamic equilibrium. After the electrochemical lithiation, the cells were disassembled in an Ar-filled glove box to prevent oxidation. The c-Si was rinsed in acetonitrile to wash off residual electrolyte and the SEI layer. The cleaned c-Si samples were transferred to SEM equipment (LEO 1550, Zeiss) to observe their lithiation status.

4.3 Finite Element Method (FEM) Analysis

A finite element package (COMSOL Multiphysics, COMSOL Inc.) was used to depict the deformation of the c-Si plate at the second stage of lithiation considering a model of isotropic, elastic, and perfectly plastic deformation with Von Mises criteria. To model Li insertion, heat conduction and thermal stress analysis were used by defining an artificial temperature profile. The x value at the starting point of the second stage of lithiation was set as the initial temperature and the final x value was set as the final temperature. The heat was applied through the open side of the plate and propagated across the plate while the other sides were thermally insulated. Isotropic expansion was induced by defining a thermal expansion coefficient derived from the measured volumetric change. Mechanical and thermal properties were also derived according to the x values within the defined range of temperature (Fig. S3 and Table S1). In addition to these, the estimated stress at the first stage of lithiation was applied as the initial stress.

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Supplementary Materials

Supporting information and movie accompany this paper.

Figures

Fig. 1. Lithiation of crystalline-silicon and copper (c-Si/Cu) bimorph plate. (a) Pristine c-Si/Cu plate. (b) Schematic views of c-Si/Cu plate during electrochemical lithiation. Induced stresses and deformation are represented. (c) Schematic views and SEM images of lithiated {110} plate. (d) Calculated x value in Li_xSi from the measured expansion ratio versus cut off voltages. (Scale bar: 5 μm)

Fig. 2. Measured x value in Li_xSi and expansion ratio depending on cut off voltages and corresponding SEM images. (a) {100} plate and (b) {111} plate. (Scale bar: 5 μm)

Fig. 3. Analytical model of the c-Si/Cu bimorph plate to calculate stress on each material. (a) A schematic view of c-Si plate before and after electrochemical lithiation with deposited Cu. The scheme represents defined dimensions. (b) A schematic view of the force and stress distribution when the c-Si is lithiated. In the upper scheme, stress represents from force balance. The lower scheme means induced moment from bending stress. (c-e) Dimensionless stresses in the c-Si and Li_xSi change of free energy due to mechanical stress on {110} plate when cut off voltage is 85 mV vs. Li/Li^+ . x axes are the lithiation ratio (t_1/t_0) in these graphs and vertical dash line represents a stop point of the lithiation. (c) Dimensionless stresses from the force balance and moment at the reaction front of each material. (d) Mean stresses normalized by stress in the Li_xSi . (e) Change of free energy due to mechanical stress (ΔG_σ) when induced stresses on the Li_xSi are -0.55 GPa compare with -1 GPa. (f) Stresses in the Li_xSi from experimental data.

Fig. 4. Finite element method (FEM) analysis. (a) Deformed {110} plate and stress distribution data corresponding to experimental conditions. Legend is corresponding to a range of elastic modulus at COV of 80 mV vs. Li/Li⁺ and a plastically deformed region is a gray color. (b,c) Comparison of radius of curvature between experimental and simulation data of (b) {110} and (c) {100} and {111} plate structures.

Fig. 5. SEM images of the lithiated {110} c-Si/Cu plate of various micro scale thickness. Cut off voltage of 10 mV vs. Li/Li^+ was applied for 10 h to observe fully lithiated structures. (a) Groups of the fully grown Li_xSi structures. (b-e) Comparison between pristine c-Si/Cu plates and fully lithiated plates. The thicknesses of pristine plates are (b) 2 μm , (c) 4 μm , (d) 6 μm , and (e) 8 μm . Fractures are found in every structure except for the 2 μm structures. (Scale bar: 50 μm for Fig. 5a, 5 μm for Fig. 5b-e)