

Supporting Information

Figures

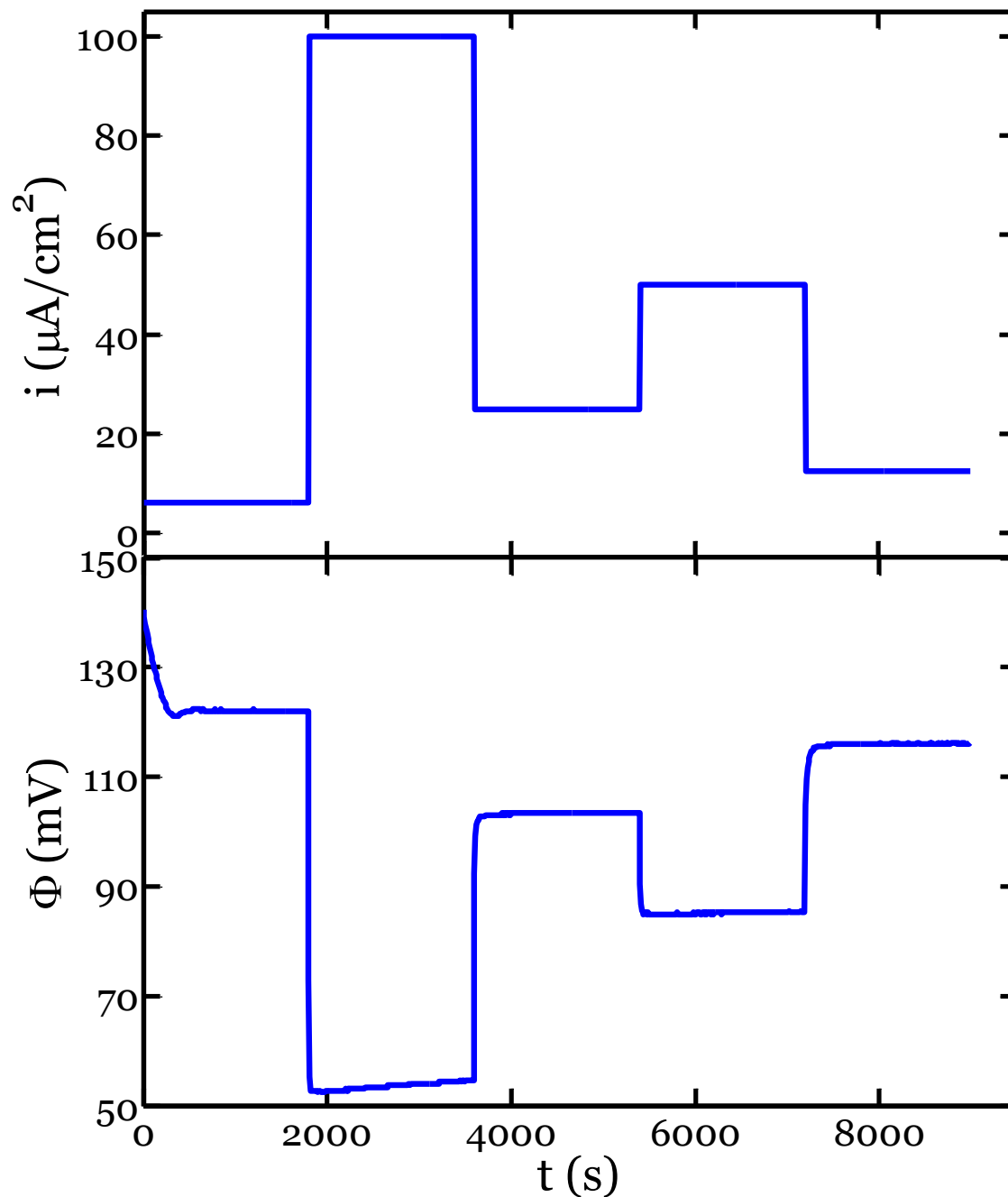


Figure S1. Typical sequence of applied current density, i , and measured response of the potential vs. Li/Li^+ , Φ , for a $\{100\}$ Si wafer.

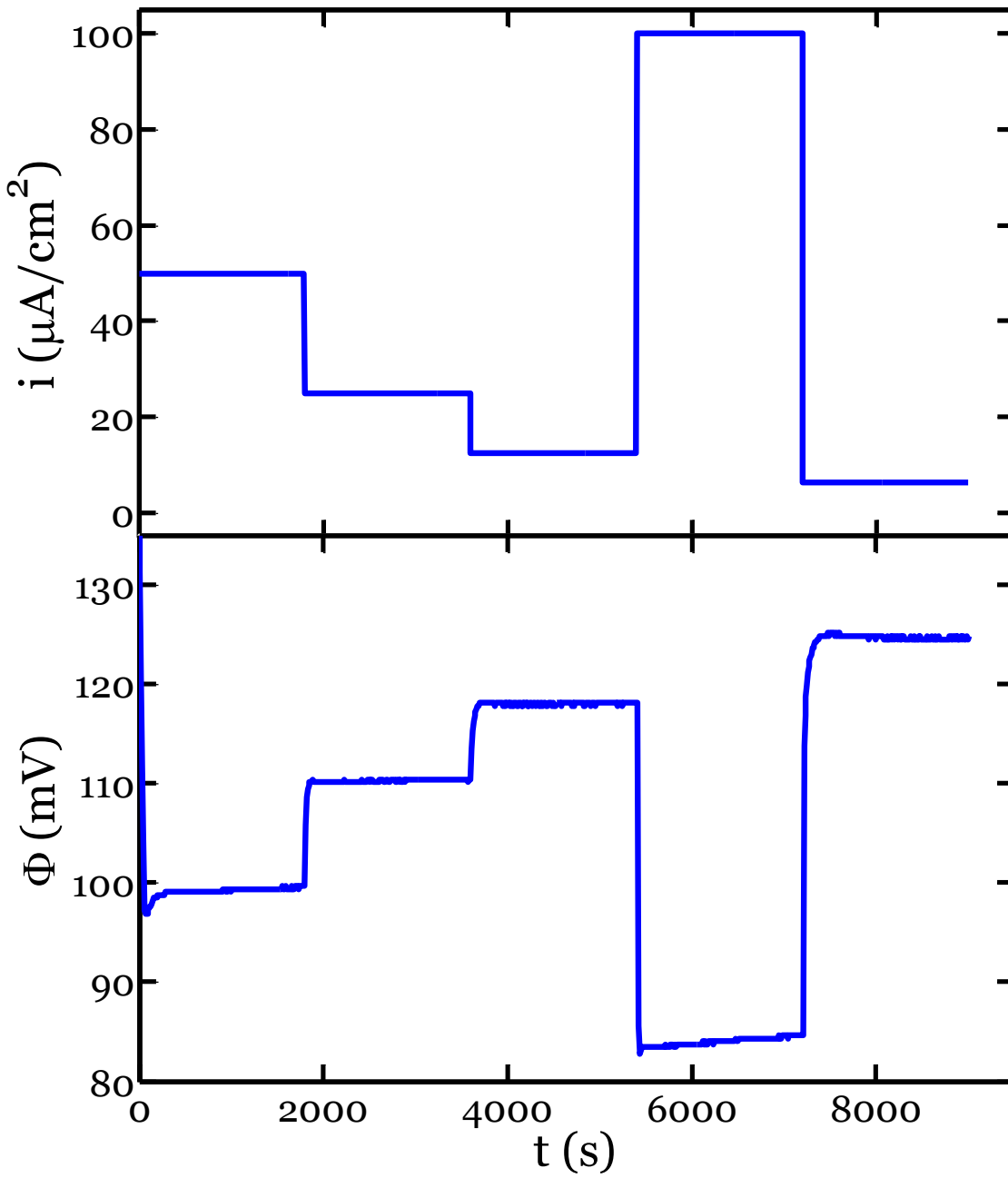


Figure S2. Typical sequence of applied current density, i , and measured response of the potential vs. Li/Li^+ , Φ , for a $\{111\}$ Si wafer.

Derivation of the Kinetic Model

The redox reaction at the electrolyte/ a-Li_ηSi interface is given by



Associated with this redox reaction, we take the current density through the electrolyte/ a-Li_ηSi interface as given by the Butler-Volmer equation:

$$i = i_o \left[\exp\left(-\frac{\alpha F}{RT} [\Phi - \Phi_{eq}^{curr}]\right) - \exp\left(\frac{[1-\alpha]F}{RT} [\Phi - \Phi_{eq}^{curr}]\right) \right], \quad (\text{S2})$$

where i is the current density, i_o is the exchange current density, α is the charge transfer coefficient, F is Faraday's constant, R is the ideal gas constant, T is the temperature, Φ is the potential of the electrode (i.e., the measured voltage), and Φ_{eq}^{curr} is the equilibrium potential in the current state, corresponding to the lithium concentration in the electrode near the electrolyte/ a-Li_ηSi interface. Here, we have neglected mass transport through the electrolyte, i.e., we do not consider the concentration polarization. For comparison to our experiments, we believe this assumption should be valid because of the relatively small currents in our tests. Additionally, in general the exchange current density can be a function of the lithium concentration in the electrode near the electrolyte/ a-Li_ηSi interface. However, in this model, we will examine small changes in concentration from a metastable phase, a-Li_ηSi, and hence i_o will be taken as a constant. Also, since the redox reaction involves one electron per lithium atom, the flux is given by $J = i/q$, where q is the elementary charge. Taking $\alpha = 1/2$ for simplicity, we get

$$J_1 = 2 \frac{i_0}{q} \sinh \left[-\frac{F}{2RT} (\Phi - \Phi_{eq}^{curr}) \right]. \quad (S3)$$

In the lithiated phase, $\eta + \delta$ is the number of lithium atoms hosted by each silicon atom. We regard η as a constant and δ as a small deviation, $\delta \ll \eta$. As a result, the diffusion of lithium atoms in the lithiated silicon phase is driven by the position-dependence of the composition, $\delta(y)$, where y is the position as shown in Figure 3. Let C be the concentration of lithium in the lithiated phase (i.e., the amount of lithium per unit volume of the lithiated phase). The concentration of lithium in this phase relates to the composition by $C = (\eta + \delta) / \Omega_{Li, Si}$, where $\Omega_{Li, Si}$ is the atomic volume of the lithiated phase. We take the flux, J_2 , to be driven by the gradient in the concentration of lithium through the thickness of the lithiated silicon:

$$J_2 = -D \frac{\partial C}{\partial y}, \quad (S4)$$

where D is the diffusivity of lithium in the lithiated silicon. Because $\delta \ll \eta$, D is taken to be a constant, independent of the concentration. In general, the flux of lithium is driven by the gradient in chemical potential. In writing Equation (S4), we have taken the concentration gradient as the sole driving force, i.e., we have neglected any other driving forces such as those due to stress gradients. This assumption should be valid for a planar geometry for which the stress is constant through the thickness of the lithiated silicon.¹ In support of this hypothesis, Chon, et al. experimentally observed a constant stress, independent of time, during the lithiation process for {100} Si wafers.²

In the steady state, the flux is independent of position, and the concentration is linear in the position, so that

$$J_2 = D \frac{C_1 - C_2}{y_0}, \quad (\text{S5})$$

where C_1 is the concentration of lithium in the lithiated silicon at the interface between the electrolyte and the lithiated silicon, C_2 is the concentration of lithium in the lithiated silicon at the interface between the lithiated silicon and crystalline silicon phases, and y_0 is the thickness of the lithiated silicon.

At the interface between the lithiated silicon and the crystalline silicon phases, a chemical reaction occurs:



The reaction is driven by the excess lithium δ_2 in the lithiated silicon at this interface.

The rate of reaction controls the flux of lithium across the interface. For simplicity, we take the flux corresponding to this reaction to be given by the first-order relation:

$$J_3 = k \frac{\delta_2}{\Omega_{\text{Li},\text{Si}}}, \quad (\text{S7})$$

where k is the rate of the reaction. In general, the flux, J_3 , may have a nonlinear dependence on δ_2 . However, Equation (S7) should be valid to first order for $\delta \ll \eta$. Additionally, we propose that k is a function of the crystallographic orientation, as is consistent with the experiments in this paper.

In the steady state, all of the fluxes are equal: $J_1 = J_2 = J_3$. In a unit time, dt , the number of atoms that react to form new lithiated silicon is $J_3 \cdot A \cdot dt$, where A is the cross-sectional area of the planar interface. During this time, dt , the reaction increases the volume of the a-Li $_{\eta}$ Si layer by $J_3 \cdot A \cdot dt \cdot \Omega_{\text{Li},\text{Si}} / \eta$. As a result, the thickness of the

lithiated silicon phase increases by $dy_o = J_3 \cdot dt \cdot \Omega_{\text{Li}_\eta\text{Si}} / \eta$ so that the instantaneous velocity of phase boundary is given by

$$\frac{dy_o}{dt} = \frac{\Omega_{\text{Li}_\eta\text{Si}}}{\eta} J_3, \quad (\text{S8})$$

We will take the quantity $\Omega_{\text{Li}_\eta\text{Si}} / \eta$ as a constant, which is valid for small changes in composition, $\delta \ll \eta$. In fact, more generally, this quantity has been found to be constant for large values of $\eta + \delta$.³

Since $J_1 = J_3$ in the steady state, the velocity of the phase boundary is given by:

$$\frac{dy_o}{dt} = 2 \frac{\Omega_{\text{Li}_\eta\text{Si}}}{\eta} \frac{i_o}{q} \sinh \left[-\frac{F}{2RT} (\Phi - \Phi_{eq}^{curr}) \right]. \quad (\text{S9})$$

From the Nernst equation, the equilibrium potential, Φ_{eq} , is given by

$$\Phi_{eq} = -\frac{RT}{F} \ln(\gamma x_1), \quad (\text{S10})$$

where the reference electrode is taken to be that of pure metallic Li. The parameter γ is the activity coefficient, which in general can be a function of the concentration, and x_1 denotes the mole fraction of lithium atoms in $\text{a-Li}_\eta\text{Si}$ at the interface with the electrolyte. If the composition of the amorphous lithiated region at the interface with the electrolyte is given by $\text{Li}_{\eta+\delta_1}\text{Si}$, the mole fraction is

$$x_1 = \frac{\#\text{Li atoms}}{\#\text{Li atoms} + \#\text{Si atoms}} = \frac{\eta + \delta_1}{\eta + \delta_1 + 1}. \quad (\text{S11})$$

Let Φ_{eq}^{ref} denote the equilibrium potential in the reference state, corresponding to a-Li_ηSi. Noting that $\Phi - \Phi_{eq}^{curr} = \Phi - \Phi_{eq}^{ref} - (\Phi_{eq}^{curr} - \Phi_{eq}^{ref})$, and combining with Equation (S10):

$$\Phi - \Phi_{eq}^{curr} = \Phi - \Phi_{eq}^{ref} - \left[-\frac{RT}{F} \ln \left(\gamma \frac{\eta + \delta_1}{\eta + \delta_1 + 1} \right) + \frac{RT}{F} \ln \left(\gamma \frac{\eta}{\eta + 1} \right) \right]. \quad (S12)$$

Expanding this equation for $\delta_1 \ll \eta$ to first order gives:

$$\Phi - \Phi_{eq}^{curr} = \Phi - \Phi_{eq}^{ref} + \frac{RT}{F} \left[\frac{\delta_1}{\eta(\eta + 1)} \right]. \quad (S13)$$

Since $C = (\eta + \delta)/\Omega_{Li_\eta Si}$ and $J_2 = J_3$ in the steady-state:

$$\delta_1 = \left(\frac{ky_o}{D} + 1 \right) \delta_2. \quad (S14)$$

Combining Equations (S7)-(S9), (S13) and (S14) we obtain:

$$\frac{dy_o}{dt} = 2 \frac{\Omega_{Li_\eta Si}}{\eta} \frac{i_o}{q} \sinh \left\{ -\frac{F}{2RT} \left(\Phi - \Phi_{eq}^{ref} + \frac{RT}{F} \left[\frac{1}{(\eta + 1)} \left(1 + \frac{ky_o}{D} \right) \frac{1}{k} \frac{dy_o}{dt} \right] \right) \right\}. \quad (S16)$$

This is an implicit equation for the instantaneous velocity of the phase boundary, dy_o/dt , as a function of measured potential, Φ . Recalling that $J = i/q$, we get an implicit relationship between the applied current density and the measured potential:

$$\frac{i}{i_o} = 2 \sinh \left\{ -\frac{F}{2RT} \left(\Phi - \Phi_{eq}^{ref} + \frac{RT}{F} \left[\frac{\Omega_{Li_\eta Si}}{q\eta(\eta + 1)} \left(1 + \frac{ky_o}{D} \right) \frac{1}{k} i \right] \right) \right\}. \quad (S17)$$

References

1. Zhao, K. J.; Pharr, M.; Wan, Q.; Wang, W. L.; Kaxiras, E.; Vlassak, J. J.; Suo, Z. G. *Journal of the Electrochemical Society* **2012**, 159, (3), A238-A243.
2. Chon, M. J.; Sethuraman, V. A.; McCormick, A.; Srinivasan, V.; Guduru, P. R. *Physical Review Letters* **2011**, 107, (4), 045503.
3. Zhao, K. J.; Tritsarlis, A. G.; Pharr, M.; Wang, W. L.; Okeke, O.; Suo, Z. G.; Vlassak, J. J.; Kaxiras, E. *Nano Letters* **2012**, DOI: 10.1021/nl302261w.