Li-ion batteries are the most widely used secondary batteries. Researchers have been aiming for larger capacity and energy density, better cycling performance, and safer operation. Also, in response to the trend toward miniaturized device development in the electronic and health industries, all-solid-state planar microbatteries have received special attention because they can be integrated with complementary metal–oxide–semiconductor (CMOS) technology and offer improved safety since no liquid electrolyte is used. Among known anode materials, Si is a promising candidate for applications in microbatteries. It has extraordinarily high volumetric and gravimetric capacities (8375 Ah/cm$^3$, 3579 Ah/kg), along with a low discharge potential and thus a high energy density. The reason that Si exhibits such high capacities is related to its alloying mechanism during lithiation and delithiation. Quite different from conventional intercalation anodes, the lithiation of amorphous Si proceeds by bond breakage and formation of new atomic scale structures in a series of phase transformations. Unfortunately, this mechanism also leads to a large volume expansion and can lead to battery failure. To explore the alloying lithiation process of Si thin-films and better understand the reaction mechanisms and the potential for material optimization, electrochemical methods and material analysis were used to study the irreversible phase transition that occurs in the first lithiation cycle and the change in transformation mechanisms between cycles.

It was found that the current vs. time plot for the first lithiation in the first charge-discharge cycle (Figure 1, black curve) during potentiostatic lithiation shows a step feature that cannot be explained using the single phase diffusion model that is often envisioned for the lithiation process. The time at which the step occurs increases with increasing film thickness, suggesting a transformation mechanism involving the motion of a planar interface, as shown in Figure 2a. The behavior leading to the step can be divided into two regimes, with the curve before the step showing a square root of time dependence and the curve after the step fitting an exponential decay. This division is consistent with diffusion limited thickening of the lithiated phase (Figure 2a), followed by elimination of the Li concentration gradient in the fully transformed film. In the second lithiation cycle, the step feature is absent (Figure 1, red curve). This absence suggests that after the transformation in cycle 1, the single phase diffusion model applies (Figure 2b). Therefore, it is concluded that the two-phase coexistence and interface propagation process that occurs in cycle 1 leads to an at least partly irreversible expansion of the Si structure during cycle 1. Modification of this process might allow optimization of battery performance in subsequent cycles.

![Figure 1: Current density vs. time plots for a 315-nm-thick amorphous Si (a-Si) thin-film in cycle 1 and cycle 2 in potentiostatic tests.](image1)

![Figure 2: (a) Cycle 1 and (b) Cycle 2 lithiation models under a constant potential for a 315-nm-thick a-Si thin-film.](image2)