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Variation of stress with charging rate due to strain-rate sensitivity of silicon electrodes of Li-ion batteries

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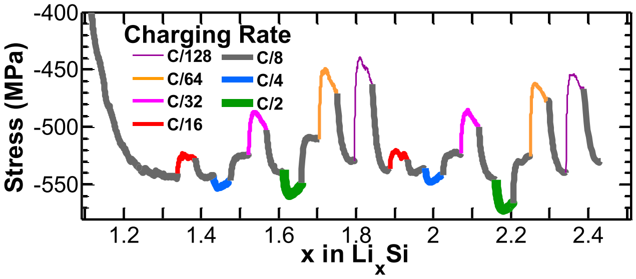
HIGHLIGHTS

- Increasing the charging rate results in an increase in stresses measured in a-Li$_x$Si.
- Observations indicate that rate-sensitive plasticity occurs in a-Li$_x$Si.
- A model of concurrent lithiation and rate-sensitive plasticity is developed.
- Rate-sensitive material parameters are quantified for a-Li$_x$Si.
- Results have important ramifications for rate-capabilities of silicon electrodes.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicon is a promising anode material for lithium-ion batteries due to its enormous theoretical energy density. Fracture during electrochemical cycling has limited the practical viability of silicon electrodes, but recent studies indicate that fracture can be prevented by taking advantage of lithiation-induced plasticity. In this paper, we provide experimental insight into the nature of plasticity in amorphous Li$_x$Si thin films. To do so, we vary the rate of lithiation of amorphous silicon thin films and simultaneously measure stresses. An increase in the rate of lithiation results in a corresponding increase in the flow stress. These observations indicate that rate-sensitive plasticity occurs in a-Li$_x$Si electrodes at room temperature and at charging rates typically used in lithium-ion batteries. Using a simple mechanical model, we extract material parameters from our experiments, finding a good fit to a power law relationship between the plastic strain rate and the stress. These observations provide insight into the unusual ability of a-Li$_x$Si to flow plastically, but fracture in a brittle manner. Moreover, the results have direct ramifications concerning the rate-capabilities of silicon electrodes: faster charging rates (i.e., strain rates) result in larger stresses and hence larger driving forces for fracture.

1. Introduction

Silicon has been identified as a promising anode material for lithium-ion batteries due to its ability to host a large amount of lithium [1]. Lithiation of silicon, however, causes an enormous volumetric expansion of ~300–400%, which under constraint can result in large mechanical stresses and fracture [2]. Fracture of the electrode leads to loss of active material and creates more surface area for solid-electrolyte interphase (SEI) growth, both of which significantly contribute to the fading of the capacity of the system [2-5]. Fortunately, this mechanical damage can be mitigated by nanostructuring the silicon anodes, as has been successfully demonstrated in nanowires [6,7], thin films [8–12], nanoporous structures [13,14], and hollow nanoparticles [15,16]. Specifically,

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recent experiments and theories indicate that one can prevent fracture by taking advantage of lithiation-induced plasticity [11,17–22].

A number of studies have examined plastic deformation in Li_xSi [5,12,18,20–34]. Sethuraman et al. measured stresses during cycling of Li_xSi electrodes, finding plastic flow, which results in dissipation of energy comparable to that of polarization losses [18]. Zhao et al. suggested that plastic flow in a-Li_xSi reduces the energy release rate (i.e., the crack driving force), thus preventing fracture in nano-sized (~100 nm) electrodes [20]. Hertzberg et al. used nanoindentation to measure the hardness of nanocrystalline Li_xSi [23]. They found a linear variation of the hardness with the volume fraction of lithium, decreasing from 5 GPa for pure nanocrystalline silicon to 1.5 GPa for the fully lithiated phase ($Li_{15}Si_4$) [23]. Zhao et al. performed first-principles simulations of a-Li_xSi, attributing plastic flow to the continuous breaking and re-forming of Si—Si bonds [24]. Likewise, Fan et al. performed molecular dynamics simulations, finding lithiation-induced plastic softening due to the decreasing fraction of strong covalent Si—Si bonds and an increase in weak Li—Li bonds that facilitate plastic flow [25]. At large concentrations of lithium, they found that the high mobility of lithium facilitates bond breaking, switching, and re-forming in response to mechanical loading [25].

Beyond these studies, a number of questions remain concerning the nature of plasticity in Li_xSi. For instance, Pharr et al. measured the fracture energy of a-Li_xSi silicon thin films, finding that it demonstrates a peculiar ability to both flow plastically and fracture in a brittle manner [5]. The authors did not, however, speculate as to the physics governing this curious combination of properties. Brassart and Suo have suggested that inelasticity in high-capacity lithium-ion batteries may occur by two processes: flow and reaction [30]. The authors define “flow” as a process driven by deviatoric stress that preserves lithium concentration and volume, similar to plastic flow in a metal. By comparison, the authors define “reaction” as lithium insertion/removal: a process that changes the concentration and volume of the electrode [30]. One result of their theory is that lithium insertion (or removal) may enable flow at a lower stress than that needed for flow under pure mechanical loading. The applicability of this “reactive flow” theory to a-Li_xSi remains an open question. A study from first-principles calculations found the lithiation reaction to markedly reduce the flow stress of a-Li_xSi [27], while a molecular dynamics study found no such effects [25]. There are no experimental studies aimed at investigating these effects.

The purpose of this paper is to provide experimental insight into the nature of plasticity in a-Li_xSi. To do so, we vary the charging rate in amorphous silicon thin-film electrodes, while simultaneously measuring stresses that develop. The stresses are seen to increase monotonically with the charging rate. This observation cannot be explained by the “reactive-flow” effect, as has been suggested in literature [27,30]. Instead, these results indicate that rate-sensitive plasticity occurs at room temperature and at charging rates typical of lithium-ion batteries. These data are well described by a power law relationship between the plastic strain rate and the stress. These results also provide important insight into the unusual ability of a-Li_xSi to flow plastically, while fracturing in a brittle manner.

2. Experimental results

Using the substrate curvature technique, we measure stresses in thin-film electrodes of amorphous silicon during electrochemical testing. Details can be found in the Experimental procedure section. As a brief summary, 100 nm films of amorphous silicon on a glass substrate are lithiated and delithiated galvanostatically at a C/8 rate during the first cycle (8 h to fully lithiate and 8 more to fully delithiate). During the second cycle, the lithiation rate is varied systematically to investigate the effect of the charging rate on the stresses that develop in the electrode.

Fig. 1 shows a typical sequence of the applied charging rate and the response in the measured voltage. During the second lithiation, an increase in the charging rate results in a decrease in the voltage, as is normally observed in Li_xSi electrodes. We should note that the horizontal axis in the figure is constructed by integrating the current during the experiment to get the total charge. The amount of charge does not necessarily represent the concentration of lithium in silicon, as SEI formation may consume lithium during the first cycle. However, the main focus of this paper is related to the stress measurements as a function of charging rate (as shown in Fig. 2). These data are obtained during the second cycle, which minimizes the influence of the SEI on our measurements, as the majority of the SEI is formed during the initial lithiation [11].

Fig. 2 shows the stress measured in the film subject to the electrochemical cycling shown in Fig. 1. Fig. 2b is a zoomed-in view that focuses on the second lithiation. The legend shows the charging rate during each segment as expressed in the C-rate convention. Fig. 2b thus demonstrates that increasing the rate of lithiation results in a quick and sustained increase in the magnitude of the stress (the stress becomes more compressive). In fact, this increase in stress increases monotonically with charging rate — faster charging results in larger stress. We believe that these observations are indicative of a material rate-effect, i.e., plastic deformation of a-Li_xSi is rate sensitive, even at room temperature.

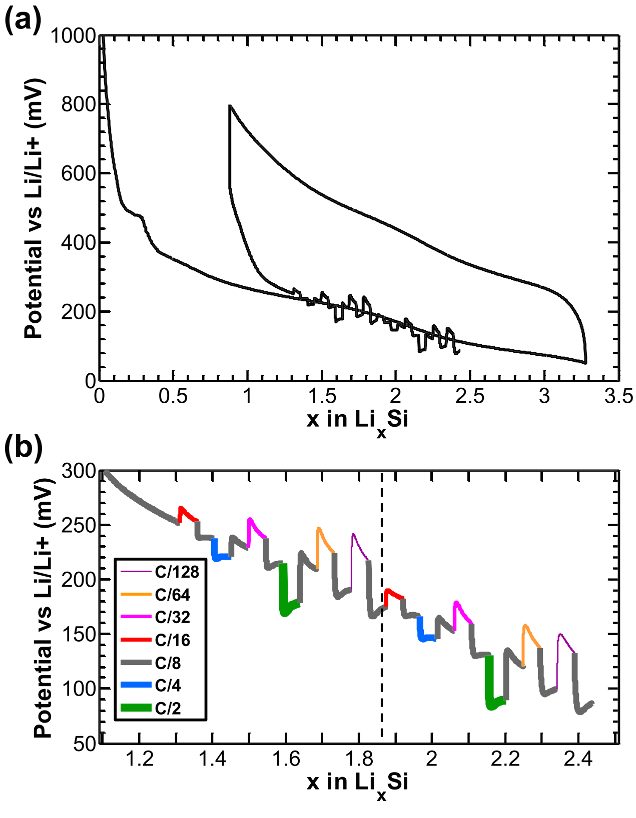

Fig. 1. Results of electrochemical cycling of a 100 nm Si thin-film electrode. (a) Measured potential as a function of lithium concentration. (b) A zoomed-in view that focuses on the second lithiation. The line thickness increases with the charging rate. The vertical dashed line indicates the point at which the set of charging rates is repeated.