



Measurements of stress and fracture in germanium electrodes of lithium-ion batteries during electrochemical lithiation and delithiation



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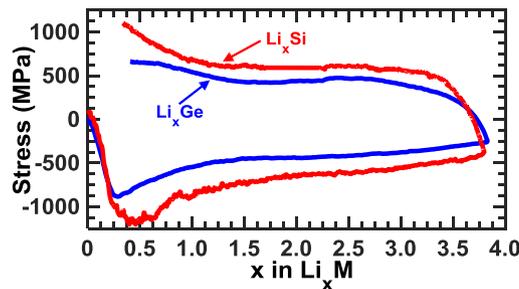
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HIGHLIGHTS

- Stresses were measured in-situ in a-Li_xGe during electrochemical cycling.
- a-Li_xGe was found to flow plastically at significantly lower stresses than a-Li_xSi.
- The elastic modulus was measured in a-Li_xGe as a function of lithium concentration.
- The fracture energy of a-Li_xGe was measured, indicating a brittle material.
- a-Li_xGe exhibits an unusual combination of plastic flow and brittle fracture.

GRAPHICAL ABSTRACT



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ABSTRACT

We measure stresses that develop in sputter-deposited amorphous Ge thin films during electrochemical lithiation and delithiation. Amorphous Li_xGe electrodes are found to flow plastically at stresses that are significantly smaller than those of their amorphous Li_xSi counterparts. The stress measurements allow for quantification of the elastic modulus of amorphous Li_xGe as a function of lithium concentration, indicating a much-reduced stiffness compared to pure Ge. Additionally, we observe that thinner films of Ge survive a cycle of lithiation and delithiation, whereas thicker films fracture. By monitoring the critical conditions for crack formation, the fracture energy is calculated using an analysis from fracture mechanics. The fracture energies are determined to be $\Gamma = 8.0 \text{ J m}^{-2}$ for a-Li_{0.3}Ge and $\Gamma = 5.6 \text{ J m}^{-2}$ for a-Li_{1.6}Ge. These values are similar to the fracture energy of pure Ge and are typical for brittle fracture. Despite being brittle, the ability of amorphous Li_xGe to flow at relatively small stresses during lithiation results in an enhanced ability of Ge electrodes to endure electrochemical cycling without fracture.

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1. Introduction

Lithium ion batteries provide power for an increasing number of applications, particularly in portable electronic devices and elec-

tric vehicles [1–4]. On the anode side, silicon has received much attention due to its extremely high specific capacity ($\sim 3579 \text{ mAh g}^{-1}$) [5], which is almost ten times larger than that of the commercial anode of choice, graphite ($\sim 372 \text{ mAh g}^{-1}$) [5–8]. However, lithiation of silicon causes an enormous increase in volume of $\sim 280\%$, which can result in large stresses and fracture under constraint [9–45]. Fracture leads to loss of active material and creates more surface area for solid-electrolyte interphase (SEI) growth, both of which substantially contribute to capacity fade in the system [9–13]. This

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mechanical degradation has been mitigated to varying degrees of success via nano-structuring of the electrodes, but it remains an important issue in constructing practical silicon anodes [14–24]. Germanium, another group IV element, has garnered relatively little attention as an anode material despite its comparatively large theoretical charge density: $\sim 7370 \text{ mAh cm}^{-3}$ for $\text{Li}_{15}\text{Ge}_4$ versus $\sim 8330 \text{ mAh cm}^{-3}$ for $\text{Li}_{15}\text{Si}_4$ [46]. Furthermore, both the electronic conductivity of Ge and the diffusivity of Li within Ge have been reported to be much larger than those of Si, thereby making Ge a promising candidate for high-rate applications (e.g., high-power applications) [14,47]. Still, prior to implementation of Ge as a practical anode material, it is important to evaluate its mechanical performance during electrochemical cycling.

To date, relatively few studies have examined mechanical characteristics of germanium anodes. Using *in-situ* transmission electron microscopy in Ge nanowires, Liu et al. found the volumetric expansion upon lithiation to be nearly isotropic and highly reversible upon delithiation [48]. Liang et al. also found highly reversible isotropic swelling and de-swelling of crystalline Ge nanoparticles upon lithiation and delithiation [49]. Moreover, they observed no fracture, even during multiple cycles, for particles with an initial diameter as large as 620 nm [49]. This resistance to fracture was attributed to the isotropic nature of lithiation [49], which is in stark contrast to the highly anisotropic lithiation observed in crystalline silicon electrodes [9,10,25,26]. The anisotropic lithiation of c-Si leads to stress concentrations, thereby increasing the driving force for fracture relative to the isotropic (e.g., Ge) case. Lee et al. found a critical pillar diameter of 1.2 μm for fracture of $\langle 111 \rangle$ axially oriented Ge nanopillars [50]. They also attributed this larger critical size than that of Si nano-pillars ($\sim 300 \text{ nm}$) to the nearly isotropic lithiation of Ge [50]. Overall, these studies suggest improved mechanical robustness of crystalline Ge electrodes compared to their crystalline Si counterparts. However, studies aimed at experimental quantification of mechanical properties of Li_xGe are lacking. In particular, measurements of quantities such as the elastic modulus, the fracture energy, and the stresses that develop during electrochemical cycling are essential for enabling practical designs of Ge electrodes that avoid mechanical degradation.

In this study, we have performed mechanical measurements of a- Li_xGe electrodes *in-situ* during electrochemical cycling. In particular, we have measured the stresses that develop during lithiation and delithiation as a function of lithium concentration. The a- Li_xGe electrodes were observed to flow plastically and develop smaller stresses than their a- Li_xSi counterparts. These *in-situ* stress measurements also allowed for quantification of the elastic modulus of a- Li_xGe . Furthermore, we observed that thinner films of germanium survive a cycle of lithiation and delithiation, whereas thicker films fracture. The fracture energy was calculated based on the critical conditions for crack formation using an analysis from fracture mechanics. Overall, these measurements indicate an enhanced ability of Ge electrodes to endure electrochemical cycling without fracture relative to their silicon counterparts.

2. Experimental procedures

Glass substrates with a thickness of 1 mm were cleaned with acetone and isopropanol, and placed into a sputter deposition system (AJA Int. ATC 1800) with a base pressure of $< 10^{-8}$ Torr. All depositions were performed at room temperature (22°C), using sputtering targets with a 50.8 mm diameter. First, the substrates were plasma-cleaned in Ar at 20 mTorr using an RF power of 24 W for 5 min. Next, 15 nm of Ti was sputtered onto the substrates using a pressure of 3 mTorr of Ar and a DC power of 100 W for 5 min. A 300 nm layer of Cu was then deposited using a pressure of 5 mTorr of Ar and a DC power of 100 W for 15 min. The Cu film served as current collector, while the Ti under-layer was used to improve the adhe-

sion between the Cu film and the glass substrate. Finally, films of Ge with varying thickness were deposited using a pressure of 5 mTorr of Ar and a DC power of 100 W. The working area of each Ge electrode was 8 mm by 30 mm.

Electrochemical cells were assembled in a glove box maintained at a moisture level of less than 1 ppm, using a 1M solution of LiPF_6 in 1:1:1 (weight %) ethylene carbonate: diethyl carbonate: dimethyl carbonate as the electrolyte. Electrochemical measurements were performed with a VersaSTAT 3 galvanostat from Princeton Applied Research. The electrodes were lithiated at a C/16 rate (assuming a specific capacity of 1384 mAh g^{-1} for $\text{Li}_{15}\text{Ge}_4$ and a density of pure Ge of 5.32 g cm^{-3} [51,52]) to a cutoff voltage of 50 mV. Delithiation was performed at the same rate to a cutoff voltage of 2 V.

Stresses in the Ge films were measured by monitoring the curvature of the substrate during lithiation and delithiation. The stresses in the films were calculated using Stoney's equation [53,54],

$$\sigma = \sigma_r + \frac{E_s h_s^2}{6h_f(1-\nu_s)} \Delta K, \quad (1)$$

where σ represents the average stress in the film, σ_r is the residual stress in the as-deposited Ge film, E_s is the elastic modulus of the substrate, h_s is the thickness of the substrate, ν_s is Poisson's ratio of the substrate, and ΔK is the change in curvature of the substrate induced by changes in the stress in the film. The residual stress in the as-deposited Ge film was determined by measuring the curvature of the glass substrate before and after Ge deposition. In the calculations, values of $E_s = 72 \text{ GPa}$ and $\nu_s = 0.23$ were used for the glass substrate [55].

The change in curvature of the substrate was monitored with a multi-beam optical sensor (MOS) from k-Space Associates. For more details on this method, please see Ref. [29]. The change in the curvature of the substrate was calculated from the geometric relation,

$$\Delta K = \frac{d_0 - d}{d_0} \left[\frac{\cos \alpha}{2L} \right] \frac{n_a}{n_e}, \quad (2)$$

where d is the distance between two adjacent laser spots measured on the CCD camera of the sensor, d_0 is the initial distance between the laser spots, α is the angle of reflection of the laser beams, L is the distance between the electrochemical cell and the CCD camera, and n_a and n_e are the indices of refraction of air and the electrolyte, respectively. In the calculation of the stress, we took $n_e = 1.42$ for the electrolyte [56] and $n_a = 1$ for air.

Since the Ge thin-film electrodes were constrained in the plane of the film by the relatively thick substrate, lithium insertion was accommodated entirely by expansion in the thickness direction. As a result, we take the thickness of the film as linear in the state of charge,

$$h_f = h_f^0(1 + \beta s), \quad (3)$$

Where h_f^0 is the initial thickness of the film, β is related to the atomic volumes (Ω) of Ge and the lithiated phase by $\beta = (\Omega_{\text{Li}_{3.75}\text{Ge}} - \Omega_{\text{Ge}}) / \Omega_{\text{Ge}} = 2.6$, 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 $\text{Li}_{3.75}\text{Ge}$ with a capacity of 1385 mAh g^{-1}). The state of charge was inferred from the experimental time during the galvanostatic experiments. The value of 2.6 was taken from Liang et al., who found that germanium undergoes a 260% increase in volume upon full lithiation [49].

Each of the thin-film electrodes was scratched with a diamond scribe to introduce imperfections off of the sidewalls of the cracks with sizes on the order of the film thickness. This technique initiates channel cracks through the thickness of the film so that the fracture analysis by Beuth [57] (analyzed in the Results and Dis-

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