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Fracture Toughness Characterization of Lithiated Germanium as an Anode Material for Lithium-Ion Batteries

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Germanium (Ge) is a promising candidate anode material for next-generation, high-performance lithium-ion batteries. Despite its apparent promise, the mechanical properties of lithiated Ge including its fracture characteristic are largely unknown. In this paper, we report the first experimental measurement of the fracture toughness of lithiated Ge using an in-house developed nanoindentation system. The fracture toughness of lithiated Ge is found to increase monotonically with increasing lithium content, indicating a brittle-to-ductile transition of lithiated Ge as lithiation proceeds. We also compare the fracture energy of lithiated Ge with that of lithiated Si and show that, despite a slightly lower fracture energy of Ge than that of Si in the unlithiated state, Ge possesses much higher fracture resistance than Si in the lithiated state. These findings suggest that Ge anodes are intrinsically more resistant to fracture than their Si counterparts, thereby offering substantial potential for the development of durable, high-capacity, and high-rate lithium-ion batteries. The quantitative results from this work provide fundamental insights for developing new electrode materials and help to enable predictive modeling of high-performance lithium-ion batteries.

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Rechargeable lithium-ion batteries (LIBs) are the current dominant energy storage solution for portable electronics and electric vehicles. The growing demand in these applications, however, requires next-generation LIBs with an unprecedented combination of low cost, high capacity, and high reliability. To significantly enhance the LIB performance, much of the research effort to date has been devoted to developing new electrode materials that can store more Li ions than the current available technology. In today's commercial LIBs, graphite of 372 mAhg⁻¹ capacity is being widely used as the anode material.^{1,2} There has been a strong tendency to replace graphite with other high-capacity anode materials such as silicon (Si) of 3579 mAhg⁻¹ capacity^{3,4} and germanium (Ge) of 1384 mAhg⁻¹ capacity.⁵

Compared with carbon- and Si-based anodes, Ge-based ones have not been studied as much, primarily because of the higher manufacturing cost of Ge at present. Nevertheless, Ge possesses several advantages over Si as a high-performance anode material. Due to the smaller bandgap of Ge (bandgap energy $E_g = 0.66$ eV at 300 K) than that of Si ($E_g = 1.12$ eV at 300 K), Ge has a four orders of magnitude higher electronic conductivity.⁶ Besides, the Li diffusivity in Ge is much higher than in Si (400 times faster).^{5,7} Fast transport of both electrons and Li ions enable a high charging/discharging rate for LIBs.⁸⁻¹⁰ Although Ge is less earth abundant than other highcapacity anode materials, the price of Ge could potentially decrease with increased interest in Ge anodes and technical improvements in the production of Ge. Furthermore, by alloying Ge with other elements such as Si, Sn, and carbon, it is possible to reduce the manufacturing cost and in the meantime to enhance the overall electrochemical and mechanical performance.

Despite the superior characteristics of Ge as a promising anode material, Ge undergoes colossal volume expansion of nearly 400% when fully lithiated.¹¹ This large volumetric deformation, when occurring inhomogeneously or under mechanical constraint, can cause high tensile stress to develop, resulting in massive electrode cracking and capacity fade of the battery. To minimize the mechanical stress induced by volume change, various nanostructures of Ge electrodes, such as nanowires,¹² nanotubes,¹³ nanoparticles,^{8,9} and thin films,^{10,14} have been studied for improvement in capacity retention. For instance, Park et al. used a high-yielding synthetic method to fabricate Ge nanotubes, which exhibited high rate capability and capacity retention of more than 1000 mAhg⁻¹ over 400 cycles.¹³ Besides engineering nanostructured Ge anodes to mitigate mechanical degradation, Ge alloyed with other elements such as Si, Sn, Cu, and carbon has also

been studied. Song et al. developed a Si/Ge double-layered nanotube array electrode and showed that this type of electrode demonstrated improved cyclability (capacity retention of 85% after 50 cycles) and rate capability (doubled capacity at a 3C rate) compared with homogeneous Si systems.¹⁵

Recently, in-situ transmission electron microscopy (TEM) has been employed to investigate the fundamental mechanisms of electrochemical reaction, microstructural evolution, and mechanical degradation in various rechargeable battery electrodes at the nanoscale.^{11,16,17} Ge nanoparticles (GeNPs) have been found to expand isotropically upon lithiation and undergo no visible cracking after multiple chargedischarge cycles,¹⁸ in distinct contrast to the size-dependent fracture of SiNPs upon the first lithiation.¹⁹ More recently, it has been reported that Ge pillars exhibited slight anisotropic expansion and sizedependent fracture upon lithiation, which, however, displayed a much greater critical size for fracture than their Si counterparts.^{20,21} The robust mechanical behaviors of Ge electrodes offer substantial potential for the development of durable, high-capacity, and high-rate LIBs. However, it remains largely unclear why the Ge nanoparticles and pillars are more resistant to damage and fracture. In this study, we address this issue by investigating the intrinsic fracture toughness of lithiated Ge at various levels of Li content. The fracture toughness of a material (commonly denoted by K_{IC}) is one of the key parameters describing the ability of a material to resist fracture. In the present work, the direct measurement of the fracture toughness of lithiated Ge is performed by applying a nanoindentation method that we have previously developed.²² Furthermore, we compare the fracture resistance of lithiated Ge with that of lithiated Si²² and assess the suitability of the materials for use in high-performance LIBs. The quantitative fracture characteristics obtained in our work provide fundamental insights for engineering new Ge-based electrodes and optimizing the microstructures of advanced LIBs.

Experimental

Electrochemical cell.— All Ge electrodes used in this study were fabricated in a thin-film form on a single-side-polished titanium (Ti) substrate with dimensions of 10 mm \times 10 mm \times 0.5 mm. The thin-film architecture allowed the Ge electrode to be lithiated/delithiated nearly homogeneously and tested by means of nanoindentation. The conductive Ti substrate served as a structural support for the electrode film as well as a current collector for electrochemical measurement. Prior to the thin film fabrication, the Ti substrate was cleaned using 5% hydrogen chloride (HCl) to remove the oxidized layer on the Ti



Figure 1. Schematic illustration of the architecture of a custom-built lithiumion battery cell. The cell consists of a Ge thin-film electrode, a liquid electrolyte, and a lithium-foil counter electrode. The glass window at the top of the cell enables optical access for the in-situ measurement of film stress.

surface. A 20 nm thick Ti layer was prepared by direct-current (DC) sputtering onto the polished side of the Ti substrate at a power of 1.2 W/cm² and a pressure of 0.84 Pa in an argon environment. Subsequently, a 350 nm thick Ge film was sputtered by radio frequency (RF) magnetron at a power of 4.4 W/cm² and an argon pressure of 0.67 Pa. It is reported that Ge sputtered under similar conditions is amorphous.⁵ The presence of the Ti interlayer was necessary to improve the adhesion between the Ti substrate and the Ge film. After the film sputtering, a thin electrically insulating layer of polydimethyl-siloxane (PDMS) was coated on the back side of the Ti substrate to prevent the formation of solid electrolyte interphase (SEI) on the back surface.

The Ge thin-film electrode was subsequently assembled into a custom-fabricated Teflon electrochemical cell (Fig. 1). The assembling was performed inside an argon-filled glove box which was maintained at less than 0.1 ppm of O_2 and H_2O to minimize air and moisture exposure. A lithium foil was used as the counter electrode, and 1 M of lithium hexafluorophosphate (LiPF₆) in a solution of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) with a weight ratio of 1:1:1 was used as the electrolyte.

Electrochemical measurement.— Electrochemical measurement was conducted with a battery tester (UBA 5, Vencon Technologies, Ontario, Canada). During the electrochemical testing of an electrode, an SEI layer tends to form on the electrode surface during initial lithium insertion.²³ This process consumes lithium, thus causing errors in the determination of the true lithium concentration in the electrode. To minimize these errors, all Ge thin-film electrodes used in this study were first lithiated (discharged) to 0.7 V and delithiated (charged) to 1.2 V at a constant current density of 20 μ A/cm². During this initial lithiation/delithiation cycle, SEI layers were pre-formed without introducing any appreciable lithium in the electrodes. One of the Ge electrodes was then cycled galvanostatically at a current density of 20 µA/cm² between 0.01 V and 1.5 V for five cycles. A digital CMOS camera (DFK 72AUC02, Imaging Source, Charlotte, NC) equipped with a 35 mm focal length lens (HF35HA-1B, Fujinon, Stamford, CT) was used to monitor the morphological changes of the Ge electrode surface during cycling. To obtain more details of the surface morphology, the Ge electrode was further imaged with an optical microscope of higher magnification after the electrochemical testing.

To prepare lithiated Ge electrodes for fracture toughness measurement, four Ge electrodes were lithiated at a constant rate of $20 \,\mu$ A/cm² to a pre-determined cutoff potential. The lithiation was followed by delithiation at the same current density to a target potential that is 0.3 V higher than the cutoff potential. After the target potential was reached, the delithiation was continued potentiostatically to homoge-

nize the distribution of lithium until the current density fell below 0.2 μ A/cm². As discussed later, this delithiation process was necessary to alter the stress state in the electrodes to facilitate fracture toughness measurement. To obtain lithiated Ge electrodes with varying lithium concentrations, four Ge samples were electrochemically tested to different Li/Ge molar ratios of 0.15, 0.33, 0.72, and 0.83. The lithium concentrations in the lithiated Ge samples were calculated from the equation of $x = \frac{1}{Fn_{Ge}}(I_{\text{Lith}}t_{\text{Lith}} - \int_{0}^{t_{\text{Delith}}} I_{\text{Delith}}(t)dt)$, in which I_{Lith} and I_{Delith} are the lithiation and delithiation currents, t_{Lith} and t_{Delith} are the lithiation and delithiation time, F is the Faraday constant, and n_{Ge} is the number of moles of Ge in the electrode. The second term in the square brackets accounts for a small amount of lithium extraction during the delithiation step. Note that I_{Lith} in all the experiments is held to be constant, whereas I_{Delith} is time-varying due to a potentiostatic step applied at the end of delithiation. After the electrochemical testing, the lithiated Ge electrodes were taken out from the Teflon cell and rinsed with DMC to remove the remaining lithium salt on the electrode surfaces. To minimize the effect of SEI on mechanical testing, the lithiated Ge electrodes were submerged in anhydrous DMC for five hours to dissolve the SEI components.

In situ film stress measurement.— Lithium insertion and extraction during the electrochemical cycling of a thin-film electrode induce mechanical stress in the film due to the substrate constraint. This stress plays an important role in the evaluation of fracture toughness and therefore needs to be accurately measured. In the present work, a Michelson interferometer was employed to measure the film stress evolution by monitoring the stress-induced curvature change of the substrate. A similar optical setup based on the multi-beam optical sensor (MOS) technique was used by Sethuraman et al.²⁴ and Bucci et al.²⁵ to measure the stress evolution in lithiated Si electrodes. The glass window of the electrochemical cell (Fig. 1) provides optical access for the stress measurement. The film stress was evaluated via Stoney's equation²⁶ in the form of

$$\sigma = \frac{E_s h_s^2}{6h_f (1 - \upsilon_s)} (\kappa_1 + \kappa_2), \qquad [1]$$

where σ is the average in-plane biaxial stress in the film, E_s and υ_s are the Young's modulus and Poisson's ratio of the substrate, h_s is the thickness of the substrate, and κ_1 and κ_2 are the curvature changes in the substrate induced by the film sputtering and electrochemical lithiation/delithiation processes, respectively. The thickness of the lithiated Ge film (h_f) is given by

$$h_f = h_f^0 (1 + 0.72x),$$
[2]

Where h_f^0 is the initial thickness of the film, and *x* is the molar ratio of Li to Ge (x = 0 for pristine Ge; x = 3.75 for fully lithiated Ge). This expression reflects the fact that the volume expansion is 370% at full lithiation^{17,18} and assumes a linear relationship between the volume expansion and the lithium concentration.

Fracture toughness measurement by nanoindentation.— An inhouse developed nanoindentation system situated inside an argonfilled glove box²² was employed to measure the fracture toughness of lithiated Ge electrodes. Fracture indentation tests were performed using a diamond cube-corner tip and monitored by a long working distance (WD) microscope. The sharp cube-corner tip was chosen over other types of nanoindentation tips because it has a greater acuity and is more effective in generating radial cracks for fracture toughness assessment.²⁷ Peak loads ranging from 1 to 93 mN at constant loading and unloading rates of 500 µN/s were used for all nanoindentation tests. Ten indents at each load were made on each LixGe electrode sample to verify repeatability of the measurement. All of the indents were sufficiently spaced (100 μ m or more apart) to avoid interference with each other. The indented Li_xGe electrodes were imaged by a Zeiss Ultra60 field-emission scanning electron microscope operated at an accelerating voltage of 5 kV. During the sample transfer from the glove box to the SEM chamber, the lithiated Ge electrodes were



covered with a thin layer of anhydrous dimethyl carbonate (DMC) to avoid the reaction of lithiated Ge with ambient air.

The fracture toughness of the lithiated Ge electrodes was deduced from the peak indentation loads, the indent sizes, the dimensions of indentation-induced radial cracks, and the measured film stress and thickness using the Morris model.^{27,28} Many nanoindentation models, such as the well-known Oliver-Pharr model²⁹ and Lawn-Evans-Marshall (LEM) model,³⁰ have been developed for the mechanical property characterization of bulk materials. When these models are applied for thin film measurement, the indentation depth should be limited to a small fraction of the film thickness. However, the Morris model used in this work has been developed taking the substrate effect into consideration, and is therefore suitable for fracture toughness measurement of thin films without any constraint on the indentation depth. The validity and accuracy of this indentation model have been demonstrated by both theoretical analysis and experimental results.^{27,28}

In the Morris model, thin film cracking caused by a sharp indenter tip is governed by the pre-existing film-stress field and two elastic stress fields due to indentation, i.e., a short-range "wedging" stress field and a long-range elastic-contact stress field. The fracture toughness of the test material is comprised of three components arising from these stress fields:

$$K_{IC} = K_{IC}^F + K_{IC}^W + K_{IC}^E.$$
 [3]

The three components are then calculated by the following formulas:

$$K_{IC}^F = \Psi \sigma(h_f)^{1/2}, \qquad [4]$$

$$K_{IC}^{W} = \chi^{W} \frac{P}{c^{3/2}} \left[\frac{c}{a} + \frac{a}{c} \ln \frac{2c}{a} \right],$$
 [5]

$$K_{IC}^{E} = \chi^{E} \frac{P}{c^{3/2}} \left[\frac{c}{a}\right],$$
[6]

where *P* is the peak indentation load, and χ^W and χ^E are semiempirical constants relating the wedging and elastic-contact components to the probe acuity and the Poisson's ratio of the material. Ψ is a factor related to the elastic mismatch ratio between the substrate and the film. Parameter *a* refers to the center-to-corner distance of the indent, and *c* refers to the average radial crack length measured from the center of the indent to the ends of the radial cracks.

Figure 2. Voltage profiles of a thin-film Ge electrode during electrochemical lithiation/delithiation cycling. The arrows in the figure indicate the cycling direction. (a-d) Optical images of the Ge electrode surface corresponding to the points labeled in the figure during cycling. The zoom-in image is an optical micrograph that shows cracks in image d. The scale bars are 500 μ m in (a-d) and 100 μ m in the zoom-in image.

Results and Discussion

A plot of the voltage profiles from a Ge film electrode is shown in Fig. 2. At the initial stage of the first lithiation, the cell potential abruptly drops to below 0.7 V due to the SEI formation and irreversible lithiation of the surface GeO₂ layer. The voltage subsequently decreases slowly, indicating that the lithiation of Ge begins approximately at below 0.7 V. This trend is consistent with the previously reported data.⁵ During the lithiation and initial delithiation of the first cycle, no obvious morphological changes are observed for the Li, Ge thin films (image a, pristine Ge and image b, Li₂, Ge). However, cracks start to form on the lithiated Ge electrode at the end of the first delithiation cycle (image c, Li_{0.5}Ge). Further lithiation/delithiation of the Ge electrode causes massive cracking (image d). As previously stated, the cracking is induced by high tensile stress developed due to the colossal volumetric deformation of the electrode during cycling. Cracking of the electrode leads to loss of electrical contact and results in more surface area for SEI growth. Both factors cause rapid capacity fading of the system. It is worth noting that Nadimpali et al. have recently studied the mechanical response of Ge thin-film electrodes during electrochemical cycling and have shown that their Ge films experience no cracking after the first lithiation/delithiation cycle.¹⁴ Such discrepancy might be attributed to a variety of factors such as difference in film thickness, cycling rates and cutoff voltages, and pre-existing defects in the film and at the interface. Compared with the Ge films in their work, the films used in this work have a two times larger thickness, and are cycled with a three times faster rate and an 80% lower cutoff voltage during lithiation, all of which may facilitate crack formation and fracture.31-

Figure 3a shows the electrochemical profiles of four tested Ge film electrodes for fracture toughness measurement. The corresponding stress evolution in the Li_xGe films during the electrochemical testing are plotted in Fig. 3b. The SEI formation on the electrode surfaces during initial lithiation is reported to have a negligible effect on the film stress,³⁴ so its effect is not considered here. All the stress curves start with an initial compressive film stress of 0.3 GPa resulting from the sputtering process. During lithiation of the Ge films, lithium ions are inserted into the films and cause volume expansion. However, the substrate constrains the Ge films from in-plane expansion, resulting in a dramatic increase in the compressive film stress. As the lithiation proceeds, the compressive film stress first increases linearly, revealing the elastic deformation of the films. After reaching a maximum compressive stress, the Li_xGe films lithiated beyond x = 0.33



Figure 3. (a) Voltage profiles of four thin-film Ge electrodes lithiated/delithiated to various lithium concentrations. (b) Film stress evolution in the electrodes corresponding to the electrochemical testing in (a). The two insets in (b) illustrate the development of compressive and tensile stresses during lithium insertion into and extraction from the Ge electrodes, respectively.

show a slower rate of stress change due to plastic deformation. The large compressive stress present in the films, if left unmanaged, could retard crack growth during nanoindentation and therefore impede the fracture toughness evaluation. To circumvent this problem, the Ge electrodes were delithiated for a short period immediately following the lithiation process. During the delithiation process, the substrate constrains the contraction of the films, causing the compressive film stress to be relieved to promote crack formation during subsequent nanoindentation. To minimize possible lithiation-rate effects, we used the same lithiation rate for preparing the lithiated thin film electrodes. Because the focus of this work was primarily on the lithium-concentration-dependent fracture property, no additional effort was made to quantitatively examine the effects of lithiation rate on the stress generation. Furthermore, it was observed that the film stress kept evolving when the lithiation/delithiation process was completed. Therefore, upon the completion of lithiation/delithiation of each electrode specimen, the stress evolution in the electrode was monitored until the stress value became stabilized. The vertical rising portion of each stress curve shown in Fig. 3b is due to this stress stabilization.

It is worth noting that recent lithiation experiments of silicon micropillars have shown that micro- and nano-crack formation during deep lithiation can expose new surface area and cause the formation of new SEI layers, leading to an overestimate of the lithium content in the electrode.³⁵ Unlike these micropillars in which large lithiationinduced hoop stress of a few GPa can promote crack formation, the thin film electrodes used in our experiments were under large compressive in-plane stress during lithiation. Following the lithiation process, the electrodes were slightly delithiated in order to alter their stress state to facilitate fracture toughness measurement. Such delithiation would induce tensile stress of 100–400 MPa, but it was not high enough



Figure 4. Indentation-induced crack patterns under different indentation loads for the lithiated Ge electrodes. The inserts show the SEM images of indents on a pristine Ge film electrode with (a) no cracking, (b) radial cracking, and (c) massive cracking. The scale bars are 1 μ m in (a) and (b) and 2 μ m in (c).

to cause the formation of micro- and nano-cracks, as confirmed by post-mortem SEM observation.

After the electrochemical testing and film-stress measurement, the lithiated Ge electrodes were fracture tested by nanoindentation. The generated crack patterns under various levels of indentation loads can be divided into three categories: no cracking, radial cracking, and massive cracking. Figure 4 shows the two critical load curves separating the three crack-pattern regimes. The three inserts in the figure represent the SEM images of three indents made on a pristine Ge electrode at various levels of indentation loads. Under a small load of 4.13 mN, the indentation causes plastic deformation in both the film and substrate without introducing visible cracking (insert a). As the load increases to 8 mN, three radial cracks emerge from the sharp corners of the indent (insert b). When the load is further increased to 19.6 mN, massive cracking around the indent is observed (insert c). The two critical load curves in Fig. 4 are seen to vary significantly with the Li content in the Ge electrodes. Furthermore, beyond a Li/Ge molar ratio of 0.83, no cracks are observed for indentation loads up to 93 mN, suggesting an extremely ductile deformation behavior at high lithium concentrations.

Figure 5 shows the measured fracture toughness of the Li_x Ge thin films at various levels of lithiation. At each degree of lithiation, indents with radial cracks were chosen for the fracture toughness evaluation using the Morris Model. The fracture toughness of unlithiated Ge is measured to be 0.218 MPa \sqrt{m} , comparable in magnitude to that of typical brittle materials. As the degree of lithiation increases, the fracture toughness of lithiated Ge increases steadily, reaching 0.81 MPa \sqrt{m} for Li_{0.72}Ge. The fracture energy of lithiated Ge is calculated using the relationship $G_C = K_{IC}^2 / E$ and plotted in Fig. 5. The Young's modulus of lithiated Ge needed for the calculation is obtained by a linear rule of mixture $E = (xE_{Li} + E_{Ge})/(1 + x)$. Qi et al. has recently performed first principles density functional theory (DFT) calculations to investigate the dependency of the elastic properties on Li concentration for a large set of anode and cathode materials.³ The authors found that, for alloy-forming electrode materials, such as Si, β -Sn and Al, the Young's moduli of lithiated compounds follow the linear rule of mixture. Although the elastic properties of Li_xGe were not specifically investigated in this work, it is reasonable to assume that the rule of mixture is applicable to lithiated Ge since it also has an alloying reaction mechanism. The obtained fracture energy curve of lithiated Ge in Fig. 5 is seen to increase monotonically with the increase of lithium concentration. The increasing trend in



Figure 5. Fracture toughness and fracture energy of lithiated Ge electrodes as a function of lithium concentration.

fracture resistance indicates that Li_xGe undergoes a sharp brittle-toductile transition as lithiation proceeds. This transition as well as the extremely high ductility of Li_xGe thin films at high lithium concentrations (beyond x = 0.83) suggests that $Li_{2.1}Ge$ possesses a much larger fracture resistance than $Li_{0.5}Ge$. Due to this high fracture resistance, $Li_{2.1}Ge$ is more resistant to fracture and can prevent cracking induced by tensile film stress at the initial delithiation of the Ge electrode, as shown in image b of Fig. 2. However, as delithiation proceeds, the fracture resistance of the Li_xGe thin films decreases, leading to crack formation at the end of delithiation during the first cycle (image c of Fig. 2). Therefore, a cutoff voltage below the threshold voltage for crack formation during delithiation can potentially prevent fracture of the electrode. Such findings provide significant guidelines for the design and operation of Ge-based LIBs.

Figure 6 shows a direct comparison between the fracture energy of lithiated Ge obtained in this work and the previously measured fracture energy of lithiated Si.²² The fracture energy of pristine Si is 3 J/m^2 which is slightly higher than that of unlithiated Ge of 2.33 J/m^2 However, the fracture energy of lithiated Si decreases in the early stage of lithiation, which causes Si to crack more easily during charging



Figure 6. Comparison between the fracture energy of lithiated Ge electrodes and that of their Si counterparts as a function of lithium concentration. Beyond an *x* value of 0.83 for Li_x Ge and 1.56 for Li_x Si, the lithiated products do not show signs of indentation cracking due to the substantial toughening effects of lithiation.

and discharging if the concentration of Li is low. At higher levels of Li, the fracture energy of lithiated Si increases with the Li content, indicating that Si undergoes a brittle-to-ductile transition as lithiation proceeds. In our previous work, we also combined in situ TEM study and reactive-force field molecular dynamics (MD) simulations with nanoindentation testing to gain mechanistic insights into the fracture mechanisms of lithiated Si.²² All of the three different techniques have consistently shown that lithium-rich Si is more damage tolerant than lithium-lean Si. The interested reader is referred to there for more details.

Ge, on the other-hand, does not exhibit the lithiation-induced embrittlement and shows a brittle-to-ductile transition through which the fracture energy and fracture toughness steadily increase as lithiation progresses. As shown in Fig. 6, after a small amount of lithiation $(x = \sim 0.03)$, the fracture energy of Li_xGe exceeds that of Li_xSi. The fracture energy difference between the two lithiation products at a given degree of lithiation also increases as lithiation proceeds. This trend indicates that lithiated Ge is mechanically tougher than lithiated Si except at very low lithium concentrations. Furthermore, for both Li_xGe and Li_xSi, there is a critical lithium concentration, beyond which no electrode cracking is observed up to the maximum indentation load (93 mN) of the nanoindentation setup. The critical values are approximately 1.56 for Si (Li_{1.56}Si) and 0.83 for Ge (Li_{0.83}Ge), which are also a clear indication of considerably higher fracture resistance of lithiated Ge. These quantitative results explain the robust behavior of Ge nanoparticles and pillars observed in previous works.^{18,20} Lithiated Ge is clearly seen to be intrinsically more resistant to crack initiation and propagation than lithiated Si. This attribute of Ge offers substantial potential for the development of durable, high-capacity, and high-rate anodes for advanced lithium-ion batteries.

In the works reported by Lee et al.,^{20,21} the lithiation behaviors of Si and Ge micropillars were investigated and compared. When these micropillars are lithiated, a compressive hoop stress first develops at the surface and then turns into a tensile stress state which promotes the initiation of surface cracks. The unlithiated core, though inherently brittle, remains under a compressive stress state and therefore does not allow crack initiation. The authors showed that both the Si and Ge pillars display a size effect for mechanical fracture, with smaller pillars less prone to cracking. The tested Ge pillars have a critical diameter of $\sim 1.2 \,\mu$ m, below which no surface cracking occurs.²⁰ This critical value is much larger than the critical dimension of ~ 300 nm for fracture of Si pillars.²¹ The authors have attributed this difference to the more isotropic expansion of Ge pillars which results in lower tensile stress concentrations at the surface.²⁰ The experimental results from our work suggest that the higher intrinsic fracture resistance of lithiated Ge may be another possible reason for their larger critical dimension for fracture.

Recent in situ TEM studies have revealed the formation of reversible nanopores in Ge after cyclic lithiation-delithiation.³⁷ The porous Ge network structure can facilitate the relaxation of mechanical stress during lithiation/delithiation cycling, and therefore retard fracture and pulverization processes. However, the formation of nanopores is observed to occur only under deep delithiation states, as a result of the effective local aggregation of free volumes created during Li extraction. Since the LixGe electrodes used in our experiments were prepared via lithiation of Ge thin films followed by very slight delithiation, the formation of nanopores in these electrodes is very unlikely. We believe that the dominant toughening mechanism in Li_x Ge is due to the increased fraction of ductile Li-Li and Li-Ge bonds, which can help overcome the brittleness of Ge-Ge bonds and suppress the formation and propagation of cracks. We will conduct MD simulations to further elucidate the atomistic mechanism underpinning the brittle-to-ductile transition in Li_xGe, and the results will be reported elsewhere.

Conclusions

The development of advanced Li-ion batteries has been hindered by a lack of full understanding of the fracture behaviors of highperformance electrode materials. In this study, we investigated the fracture toughness and fracture energy of lithiated Ge as a viable LIB anode material and found that they increased monotonically as lithiation proceeds, indicating a sharp brittle-to-ductile transition due to lithium insertion. We also compared the fracture energy of lithiated Ge with that of lithiated Si and showed that, despite a slightly lower fracture energy of Ge than that of Si in the unlithiated state, Ge possessed much higher fracture resistance than Si in the lithiated state. This superior characteristic of Ge makes it an outstanding anode material for durable, higher-performance Li-ion batteries. The experimental findings here provide an important input for the multiphysics modeling and design of Ge-based Li-ion batteries. The experimental technique developed in this research also has general applicability to studies of other high-performance LIB anode and cathode materials.

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