



# Mechanical stresses and crystallization of lithium phosphorous oxynitride-coated germanium electrodes during lithiation and delithiation



Ahmed Al-Obeidi <sup>a</sup>, Dominik Kramer <sup>b, c</sup>, Reiner Mönig <sup>b, c, \*\*</sup>, Carl V. Thompson <sup>a, \*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

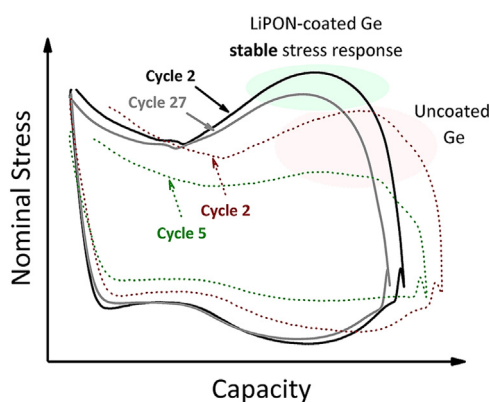
<sup>b</sup> Institute for Applied Materials, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

<sup>c</sup> Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstraße 11, 89081 Ulm, Germany

## HIGHLIGHTS

- Mechanical measurements are used to probe electrochemical processes in germanium.
- Mechanically rigid Li<sup>+</sup>-conductive coatings can suppress morphological evolution.
- Rate experiments indicate that lithium transport is limited by diffusion.
- Formation of crystalline Li<sub>15</sub>Ge<sub>4</sub> appears as a small tensile feature in stress.
- Amorphization of crystalline Li<sub>15</sub>Ge<sub>4</sub> reduces the energy efficiency of the cell.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The evolution of mechanical stresses during the cycling of lithium phosphorous oxynitride (LiPON) coated germanium thin film electrodes was monitored using substrate curvature measurements. By coating germanium thin films with LiPON, morphology evolution, e.g. crack and island formation, can be strongly suppressed. LiPON-coated germanium thin film electrodes can retain their planar form during cycling, resulting in a clear and reproducible stress response originating primarily from the electrochemical processes occurring during lithiation and delithiation. Together with the electrochemical data, stress measurements were used to infer mechanisms underlying the alloying of lithium with germanium. The stress signatures associated with individual phases, crystallization, and amorphization of lithium-germanium alloys are reported and discussed.

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\* Corresponding author. Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA.

\*\* Corresponding author. Institute for Applied Materials, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

E-mail addresses: [alobeidi@mit.edu](mailto:alobeidi@mit.edu) (A. Al-Obeidi), [dominik.kramer@kit.edu](mailto:dominik.kramer@kit.edu) (D. Kramer), [reiner.moening@kit.edu](mailto:reiner.moening@kit.edu) (R. Mönig), [cthomp@mit.edu](mailto:cthomp@mit.edu) (C.V. Thompson).

## 1. Introduction

The need to store more energy in lighter and smaller batteries has driven efforts to develop new high capacity materials that exceed graphite's limited capacity of  $372 \text{ A h kg}^{-1}$ . Previous work has shown that lithium has the attractive capability of alloying with group IV elements to result in room temperature capacities as high as  $3579 \text{ A h kg}^{-1}$  ( $\text{Li}_{15}\text{Si}_4$ ) and  $1385 \text{ A h kg}^{-1}$  ( $\text{Li}_{15}\text{Ge}_4$ ) [1]. The lithium-germanium ( $\text{Li}_x\text{Ge}$ ) system is particularly interesting for microbattery applications since its rate capabilities are superior to silicon while offering volumetric capacities ( $7366 \text{ A h l}^{-1}$ ) competitive to silicon ( $8334 \text{ A h l}^{-1}$ ). Moreover, germanium does not readily form a native oxide, whereas silicon can spontaneously form a native oxide that further reacts to form a lithium oxide [2]. This process leads to an irreversible capacity loss during the first cycle and can be a notable issue when using high-surface area nanostructured electrodes [3–5]. Germanium is an ideal candidate for exploring alloying type materials since its chemical similarity to silicon may provide insight relevant to both materials. In situ XRD studies on amorphous germanium thin film electrodes indicated that lithiation proceeds through a series of amorphous  $\text{a-Li}_x\text{Ge}$  intermediates to ultimately form  $\text{c-Li}_{15}\text{Ge}_4$  [6], while another study indicated crystalline phases, namely  $\text{c-LiGe}$ ,  $\text{c-Li}_7\text{Ge}_2$ , and  $\text{c-Li}_{15}\text{Ge}_4$ , with other additional phases also forming in small quantities [7]. In a recent in situ nuclear magnetic resonance (NMR) study, lithiation of micron particles of crystalline Ge resulted in a mixture of amorphous  $\text{Li}_x\text{Ge}$  ( $\text{a-Li}_x\text{Ge}$ ) and  $\text{c-Li}_7\text{Ge}_2$ , followed by a series of disordered phases that led to a phase with a local structure similar to  $\text{c-Li}_7\text{Ge}_2$ . Nearing the end of lithiation,  $\text{c-Li}_{15}\text{Ge}_4$  formed and was then over-lithiated to give rise to the solid solution  $\text{Li}_{15+\delta}\text{Ge}_4$  [8]. These conflicting results indicate that there is no complete picture of the lithiation process yet. Although the detailed reaction pathway is not clear, knowledge of the fully lithiated crystalline phase exists. The formation of  $\text{c-Li}_{15}\text{Ge}_4$  has been studied using in situ XRD [6] and by nuclear magnetic resonance [8] which detect  $\text{c-Li}_{15}\text{Ge}_4$  at voltages below about 100 mV. Electrochemically, formation of  $\text{c-Li}_{15}\text{Ge}_4$  appears as a small CV peak at 50 mV, while delithiation of  $\text{c-Li}_{15}\text{Ge}_4$  results in a sharp CV peak around 0.5 V corresponding to the transition back to the amorphous  $\text{a-Li}_x\text{Ge}$  state [6]. In this work, simultaneous measurements of both electrochemical and mechanical data were used to study the fundamental processes associated with the lithiation and delithiation of germanium thin films. Such studies are complicated by the fact that electrode degradation processes can overlap with the electrochemical processes of interest.

One major form of electrode degradation is stress-induced damage due to large volume changes in alloying-type electrodes like germanium. For example, silicon film electrodes can crack and delaminate from the substrate when cycled extensively [9–11]. For germanium thin film electrodes [12], film evolution was also found to occur but without significant film delamination. Deformation of ductile  $\text{Li}_x\text{Ge}$  alloys during cycling resulted in electrode morphologies with reduced overall mechanical stresses [12]. While understanding how these changes in the mechanical response occur is necessary for designing reliable, high performance electrodes, these changes can complicate the measured data and make the investigation of fundamental electrochemical processes difficult. In addition to mechanical degradation, chemical degradation is also a source of concern. At low electrode potentials, the electrolyte is thermodynamically unstable and partially reduces to form a surface layer on the electrode, commonly known as the solid electrolyte interphase (SEI) [13,14]. The SEI is permeable to  $\text{Li}^+$  ions but is electronically insulating. This layer prevents further electrolyte decomposition and ideally self-limits after the first few

cycles [13,15]. However, in the case of materials with large volume changes, cycling causes the SEI to crack repeatedly, thereby exposing fresh surface to the electrolyte, which results in continuous SEI formation [16]. This mechanism leads to capacity loss due to lithium being trapped in the SEI. In addition, the mechanically-induced damage weakens the ability of the SEI to protect the electrode, allowing side reactions that can consume the electrode material [17,18]. For some electrode materials, these effects can be suppressed using coated electrodes. For these materials (but so far not germanium), it has been shown that coatings lead to improved cyclability by improving electrical conductivity [19], accommodating or limiting volume changes [19–21], preventing electrode fragmentation and agglomeration [22,23], and modifying the surface to stabilize the SEI [5]. For example, thin coatings of  $\text{Al}_2\text{O}_3$  have been used to improve the performance of silicon electrodes [24–26], where in situ formation of a  $\text{Li-Al-O}$  glass film during the first cycle acts as a solid electrolyte that is more resistant to cracking [21]. For thin film batteries, lithium phosphorus oxynitride (LiPON) has been used as a solid electrolyte. LiPON has a room temperature ionic conductivity of about  $2 \times 10^{-6} \text{ S cm}^{-1}$ , a wide electrochemical stability range, and the ability to serve as an artificial SEI that is resistant to mechanical damage [27–29]. While LiPON's room temperature conductivity is three orders of magnitude lower than liquid electrolytes such as LP30 (1 M  $\text{LiPF}_6$  in 1:1 ethylene carbonate: dimethyl carbonate by weight), LiPON does not readily react with the electrode during cycling like liquid electrolytes. In the case of silicon thin film electrodes, LiPON coatings result in anodes capable of cycling hundreds of times without an appreciable loss in capacity [30]. In this study, we applied LiPON coatings to germanium thin films and measured the mechanical stress evolution of the electrodes during cycling. By comparing the stresses of coated and uncoated films, the effects that LiPON coatings have on both stress and electrochemistry were investigated. The retention of the planar electrode morphology enabled by the LiPON coating and the resulting fidelity of the mechanical stress response allowed for the investigation of mechanisms governing the lithiation and delithiation of germanium electrodes.

## 2. Experimental procedures

Cantilevers were fabricated using double-side polished aluminum oxide (99.6%  $\text{Al}_2\text{O}_3$ , 254  $\mu\text{m}$  thick, Coorstek). The aluminum oxide was cut into 16 mm by 5 mm pieces and cleaned using a 5:1:1 mixture of deionized water, ammonium hydroxide, and hydrogen peroxide at 85 °C for 30 min. Samples were rinsed with deionized water and dried by nitrogen. A thin, 100 nm thick tungsten film was deposited by direct current magnetron sputtering (CMS 18, Kurt Lesker) using an argon pressure of 3 mTorr and a power of 50 W. A shadow mask exposing only 10 mm by 5 mm of the cantilever area was then used to deposit germanium by radio frequency magnetron sputtering using argon at a pressure of 2.5 mTorr and a power of 90 W. The film thickness was about 170 nm and was verified using spectral reflectance (Filmetric F20) and cross-sectional SEM. XRD and Raman spectroscopy indicated that the as-deposited films were amorphous. On some samples, lithium phosphorous oxynitride (LiPON) was deposited by reactively sputtering a  $\text{Li}_3\text{PO}_4$  target using nitrogen at a pressure of 9.8 mTorr and a power of 100 W RF to a thickness of about 850 nm. To measure the ionic conductivity of LiPON, electrochemical impedance spectroscopy (EIS) was used on a stack consisting of 100 nm platinum, 850 nm LiPON and 100 nm of platinum. Samples were dried under vacuum at 80 °C for 12 h before cell assembly. The liquid electrolyte was prepared by mixing bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, Sigma

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