

Final Report for 2014 Department of Energy Visiting Faculty Program

Gerald Gulley, Dominican University
Nicholas Hudak, Sandia National Laboratories
Dale Huber, Sandia National Laboratories

Abstract:

The cycling of high-capacity electrode materials for lithium-ion batteries results in significant volumetric expansion and contraction, and this leads to mechanical failure of the electrodes. To increase battery performance and reliability, there is a drive towards the use of nanostructured electrode materials and nanoscale surface coatings. As a part of the Visiting Faculty Program (VFP) last summer, we examined the ability of aluminum oxide and gold film surface coatings to improve the mechanical and cycling properties of vapor-deposited aluminum films in lithium-ion batteries. Nanoscale gold coatings resulted in significantly improved cycling behavior for the thinnest aluminum films whereas aluminum oxide coatings did not improve the cycling behavior of the aluminum films. This summer we performed a similar investigation on vapor-deposited germanium, which has an even higher theoretical capacity per unit mass than aluminum. Because the mechanism of lithium-alloying is different for each electrode material, we expected the effects of coating the germanium surface with aluminum oxide or gold to differ significantly from previous observations. Indeed, we found that gold coatings gave only small or negligible improvements in cycling behavior of germanium films, but aluminum oxide (Al_2O_3) coatings gave significant improvements in cycling over the range of film thicknesses tested.



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Improving the Cycling Life of Aluminum and Germanium Thin Films for use as Anodic Materials in Li-Ion Batteries

Introduction:

Nanostructured anode and cathode materials offer some of the best promise for dramatically increasing the performance (energy and power density) of Li-ion batteries.[1] One of the many advantages of nanostructuring is that nanostructures are able to accommodate larger volumetric changes during Li insertion and de-insertion than bulk materials.[2] This enables the use of high-capacity electrode materials that require large volume increases for full lithiation. Further research is needed to evaluate and improve the mechanical performance and reliability of nanostructured battery materials before they can be utilized in commercial battery systems.

One approach to improve cycle life is to form nanocomposite electrodes. An intriguing example of this is the use of atomic-layer deposited (ALD) aluminum oxide layers, Al_2O_3 , applied to anode and cathode phases, as described by the Dillon and George groups.[3] When these Al_2O_3 layers are extremely thin, they apparently act as a solid electrolyte, permitting ion transport while also providing mechanical support to the electrodes. Aluminum oxide is not thermodynamically stable at low potentials, so the aluminum oxide phases should convert into a stable Li-Al-O phase when polarized at potentials close to Li^0 . At the Center for Integrated Nanotechnologies (CINT), we have seen evidence for this transformation through the use of *in situ* transmission electron microscopy (TEM) of aluminum oxide layers on Al nanowires that were polarized at potentials close to Li^0 . [4] During lithiation, the aluminum oxide layer converted to a rigid Li-Al-O layer, which was at least partially responsible for the poor cycling behavior observed.

Aluminum and germanium have high theoretical capacities for electrochemically alloying with lithium: 993 mAh/g and 1680 mAh/g, respectively. However, both suffer from poor cycling. Because of this, we chose as our objective of this proposal to examine the ability of aluminum oxide and gold coatings to improve the mechanical and cycling properties of these high-capacity anode materials. As a part of the Visiting Faculty Program (VFP) last summer, we observed that a 5-nm layer of gold significantly improved the cycling behavior of aluminum films of submicron thickness, but the addition of aluminum oxide coatings did not improve the cycling properties of aluminum. This improvement was attributed to the absence of a native aluminum oxide layer, and thus the absence of the rigid Li-Al-O layer, on gold-coated aluminum. This summer, we found the reverse for our germanium samples. The addition of a 5nm layer of gold did little to enhance the cycling behavior of germanium films, but the aluminum oxide coatings significantly improved their cycling behavior.

Hypothesis and research objectives:

The cycling of Li into high capacity Li-ion battery electrode materials results in volumetric expansion and contraction that leads to mechanical failure of the electrodes and capacity loss in the battery. Our results from last summer showed promise for improving the mechanical behavior of high-capacity anode materials for Li-ion batteries. In the case of the aluminum films studied last summer, the gold coating acts as an oxygen barrier preventing the formation of an oxide layer. The dramatically improved cycling behavior can be attributed to decreased rigidity in the surface layer. Because surface characteristics are closely related to the functionality of all nanomaterials, the application of surface coatings to germanium materials are likewise expected to significantly alter their behavior in lithium-ion cells.

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The objectives of this proposal were to: 1. examine the ability of thin gold and Al_2O_3 coatings to change the mechanical and cycling properties of germanium thin-film electrodes in lithium-ion batteries; 2. Reach a better understanding of the role of surface composition in stabilizing or destabilizing the cycling of lithium-ion anodes, 3. (if time and resources allow) examine the cycling behavior of other germanium nanostructures (e.g. nanoparticles or nanowires) with or without coatings.

R&D approach:

The same experimental techniques from last year's VFP project were applied to this project. We deposited germanium thin films of various thicknesses (50 nm, 100nm, 0.25 μm , and 1.25 μm) onto copper substrate disks. The copper disks were made from copper foil obtained from Alfa Aesar (0.25 mm thick, 99.99985% purity) and were de-oxidized prior to use. The germanium films were prepared by electron-beam (E-beam) deposition onto the copper disks. Some of these germanium films were kept bare while other samples were coated further either with 5nm of gold or 5nm of Al_2O_3 . The gold layer was deposited using E-beam deposition, immediately after germanium deposition, with the sample maintained under high vacuum during and between both depositions. The Al_2O_3 layer was applied to bare germanium films using Atomic Layer Deposition (ALD).

Two-electrode electrochemical cells were made using Swagelok fixtures assembled in a glove box[5]. The germanium films on copper disks formed the working electrodes while lithium foil pressed onto steel disks formed the counter and reference electrodes. A glass microfiber separator (Whatman GF/D) soaked with lithium electrolyte is placed between the two electrodes.

The cycling behavior of germanium films was characterized by galvanostatic (constant-current) cycling techniques on PAR 263A potentiostats. In this type of cycling, the voltage is monitored as a function of time. The voltage ranges over which lithium electrochemically alloys with germanium were observed, and the capacity of the cell during subsequent charges and discharges was measured. The measured capacity is the amount of electrical charge that, in this case, the anode material can deliver. In the cycle life of a battery cell with a lithium-alloy anode, there is capacity loss over time as it is charged and discharged (cycled) due to pulverization of the anode material from volumetric expansion. Extending the capacity of electrode materials over many periods of charge and discharge is desirable and is the ultimate goal of this research.

A cycling rate of 1C was used, which corresponds to one theoretical charge or discharge of the cell in 1 hour. Cycling behavior of the bare, gold-coated, and ALD-modified germanium films was compared to observe any differences in capacity and cycling stability.

Results:

The alloying and de-alloying reaction between germanium and lithium can be observed through the voltage profile during galvanostatic cycling. Potential profiles for a 1.25- μm bare germanium sample and a 1.25- μm germanium sample with Al_2O_3 coating during galvanostatic cycling are shown in Figure 1. As shown, the alloying and de-alloying reactions occurred largely between 0.1 V and 0.6 V vs. Li/Li^+ . The general shape of the voltage curve remained the same with repeated cycling, which shows that the lithiation/de-lithiation mechanism remained the same. However, the length of time for each charge or discharge decreases with cycling, as

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the active material (germanium) pulverizes and loses electrochemical activity. Comparison between the voltage profiles in Figure 1a and Figure 1b shows that the length of time for a charge or discharge is longer over more cycles for the Al_2O_3 -coated germanium. From these figures, we can also see that all 26 cycles for the 1.25 μm bare germanium sample have been completed in 10.4 hours whereas only 11 cycles have been completed for the Al_2O_3 -coated germanium in this amount of time. This indicates that the Al_2O_3 -coated sample is retaining more of its capacity over a longer period of time.

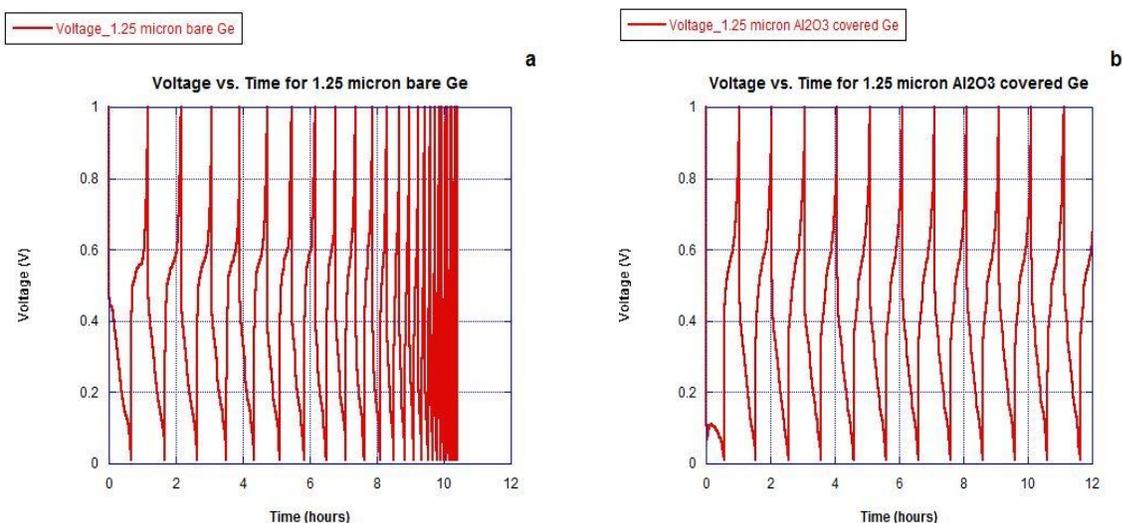


Figure 1. Voltage vs. Time for bare and Al_2O_3 -coated 1.25 μm germanium samples. The width of the charge/discharge curves are wider over a longer period of time for the Al_2O_3 -coated 1.25 μm germanium sample indicating better retention of capacity.

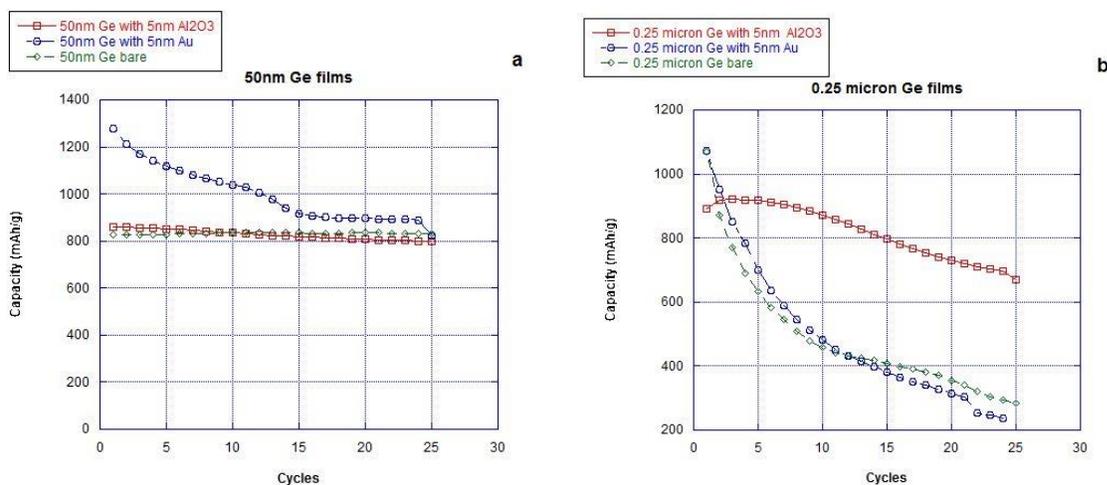


Figure 2. The delithiation capacity over 26 cycles of 50-nm and 0.25- μm germanium samples (bare, Al_2O_3 , and Au-coated) are shown. The data points are the averages of 3 experimental runs in each case.

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In Figure 2a, the capacity over 26 galvanostatic cycles is shown for the 50 nm germanium samples (bare, Au, and Al₂O₃ coated). The 5-nm Au coated germanium sample showed higher capacity over the bare germanium sample for the first 15 cycles, and the capacities of the two samples were comparable between cycles 16 and 26. The 5nm Al₂O₃ coated germanium sample exhibited comparable capacity to the bare germanium sample over all 26 cycles. Figure 2b shows that the 0.25- μ m germanium film with the Al₂O₃ coating retained 3.25 times the capacity over the bare sample of the same thickness after 26 cycles. As with the thinner sample, the gold coating did little or nothing in terms of improving the capacity retention of the 0.25- μ m germanium sample. The capacities of bare and gold-coated, 0.25- μ m germanium are comparable to each other over the 26 cycles.

For the 1.25- μ m samples, shown in Figure 3a, the Al₂O₃-coated germanium sample retained 18 times the capacity of the bare sample after 26 cycles, proving that the Al₂O₃ coating can provide a significant advantage in terms of cycling behavior. Given the excellent performance of this film, germanium films with and without Al₂O₃ coating were cycled 500 times, as shown in Figure 3b, to examine longer-term behavior. After 500 cycles, the 50-nm Al₂O₃ coated germanium sample lost only 20% of its initial cycling capacity. Furthermore, at the 500th cycle this film produced 5.8 times the capacity of the bare germanium sample of the same thickness. The 1.25- μ m Al₂O₃-coated germanium sample produced only 10% of its initial capacity after 500 cycles, which is a significant decrease in performance over the long term. However, its superior cycling behavior, in terms of capacity and stability, over the bare 1.25- μ m film is evident in both Figures 3a and 3b. Taken together, the results show conclusively that an Al₂O₃ surface is significantly beneficial to the cycling of germanium films with thicknesses in the range of 50 nm to 1.25 μ m.

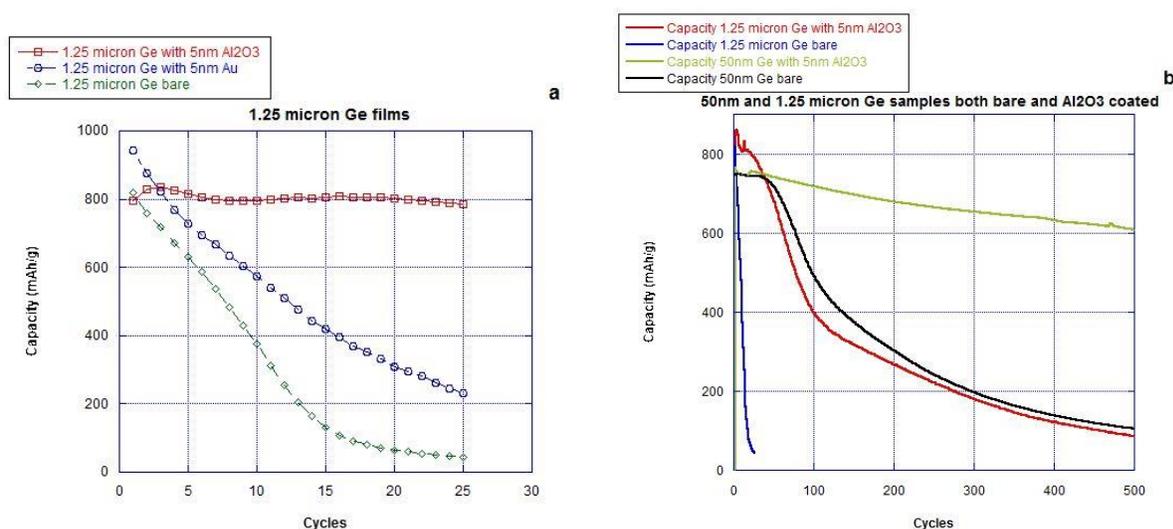


Figure 3. The delithiation capacity is shown for the 1.25 μ m germanium films over 26 cycles and 500 cycles for the 50 nm and 1.25 μ m germanium films with Al₂O₃ coatings. Note that the data points are the averages of 3 experimental runs for Figure 2a.

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Future Work:

Given the interesting observations resulting from the use of ALD and gold coatings on aluminum and germanium, we would like to investigate the effects of such coatings on nanostructured forms of germanium and aluminum such as nanoparticles and nanowires. We would also like to investigate the ability of Al₂O₃ coatings to enhance the cycling behavior of germanium films thicker than 1.25 μm.

Impact on Laboratory or National Missions:

The work proposed here has been synergistic with a Sandia Labs-funded project on the science of battery degradation along with a DOE-funded Energy Frontier Research Center (EFRC) led out of the University of Maryland. The goal of the EFRC is to understand the role of nanostructuring in influencing the performance of electrical storage systems (batteries and capacitors) and to use well-defined nanostructures and their interfaces to identify key mechanisms (defects, kinetics, etc.). Furthermore, the research presented here is well aligned with lithium-ion battery research funded by DOE's Vehicle Technologies Office.

Conclusions:

The mechanism of lithium-alloying is different for each electrode material, so we expected the effects of coating the germanium surface with aluminum oxide or gold to differ significantly from our previous aluminum results. Indeed, the 5-nm Al₂O₃ coating provided an advantage in cycling performance for the germanium films. Upon first lithiation, an Al₂O₃ surface forms a glassy Li-Al-O layer on top of the germanium and aluminum thin films. In both cases, the rigid surface layer probably keeps the active material confined close to the electrode. However, we believe the aluminum forms a strong interfacial bond with the Li-Al-O layer, whereas the germanium is not so rigidly attached to it, thus allowing for better cycling. The tendency for aluminum to remain attached to the rigid surface layer while shrinking during delithiation contributes to its increased pulverization and loss of activity, while the germanium is better able to expand and contract reversibly, without becoming discontinuous and increasingly pulverized.

References:

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Participants:

Name	Institution	Email	Role
Gerald Gulley	Dominican University	ggulley@dom.edu	Visiting Faculty Principal Investigator. Electrochemical characterization of anodic thin films.
Dale Huber	Sandia National Laboratories	Dale.Huber@sandia.gov	Co-Principal Investigator at CINT TEM and single particle electrochemistry.
Nick Hudak	Sandia National Laboratories	nhudak@sandia.gov	Co-Principal Investigator Lithium-ion cell fabrication and electrochemical characterization

Scientific Facilities:

This research was conducted at the Center for Integrated Nanotechnologies (CINT), a Dept. of Energy supported Nanoscience Research Center located at Sandia and Los Alamos National Laboratories. Specifically, this research was performed at the Core Facility located at Sandia National Labs in Albuquerque, New Mexico, and it used equipment and expertise contained within the Energy Storage Systems Lab, the Ultrathin Organic Film Lab, and the Integration Laboratory Clean Room.

Notable Outcomes:

We are currently in the process of writing a paper that includes the results from last summer and this summer. We intend to submit it for publication once we are finished.

Research Vibrancy:

I have received the VFP Program Grant 3 times, so I cannot apply for it again. However, I intend to apply for federal funding to return to CINT in the future. I would like to investigate how gold and aluminum oxide thin films affect the cycling behavior of aluminum and germanium nanowires.

Connection to Programs at Home Institution:

I plan to continue this line of research at my home institution, Dominican University. I would like to study the cycling behavior of Al₂O₃ coated germanium samples thicker than 1.25 μm.