Nano-mechanical study offers new assessment of silicon for next-gen batteries

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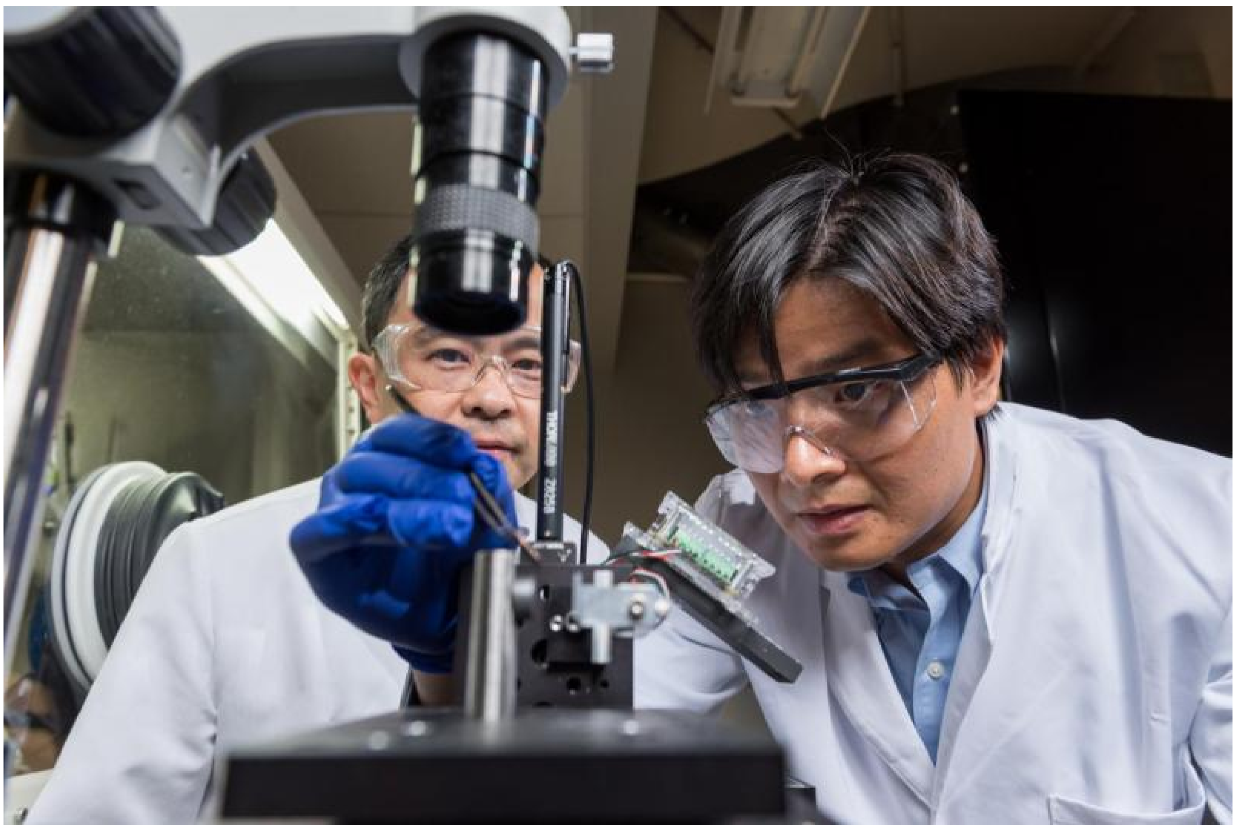


Professor Ting Zhu and Assistant Professor Suman Xia, both from Georgia Tech's Woodruff School of Mechanical Engineering, show how a thin film electrode made of amorphous silicon was tested in a custom environmental indenter. To provide proper environmental control, samples containing lithiated silicon were tested with the device inside the glove box shown in the background. Credit: Rob Felt, Georgia Tech

A detailed nano-mechanical study of mechanical degradation processes in silicon structures containing varying levels of lithium ions offers good news for researchers attempting to develop reliable next-generation rechargeable batteries using silicon-based electrodes.

Anodes - the negative electrodes - based on silicon can theoretically store up to ten times more lithium ions than conventional graphite electrodes, making the material attractive for use in high-performance lithium-ion batteries. However, the brittleness of the material has discouraged efforts to use pure silicon in battery anodes, which must withstand dramatic volume changes during charge and discharge cycles.

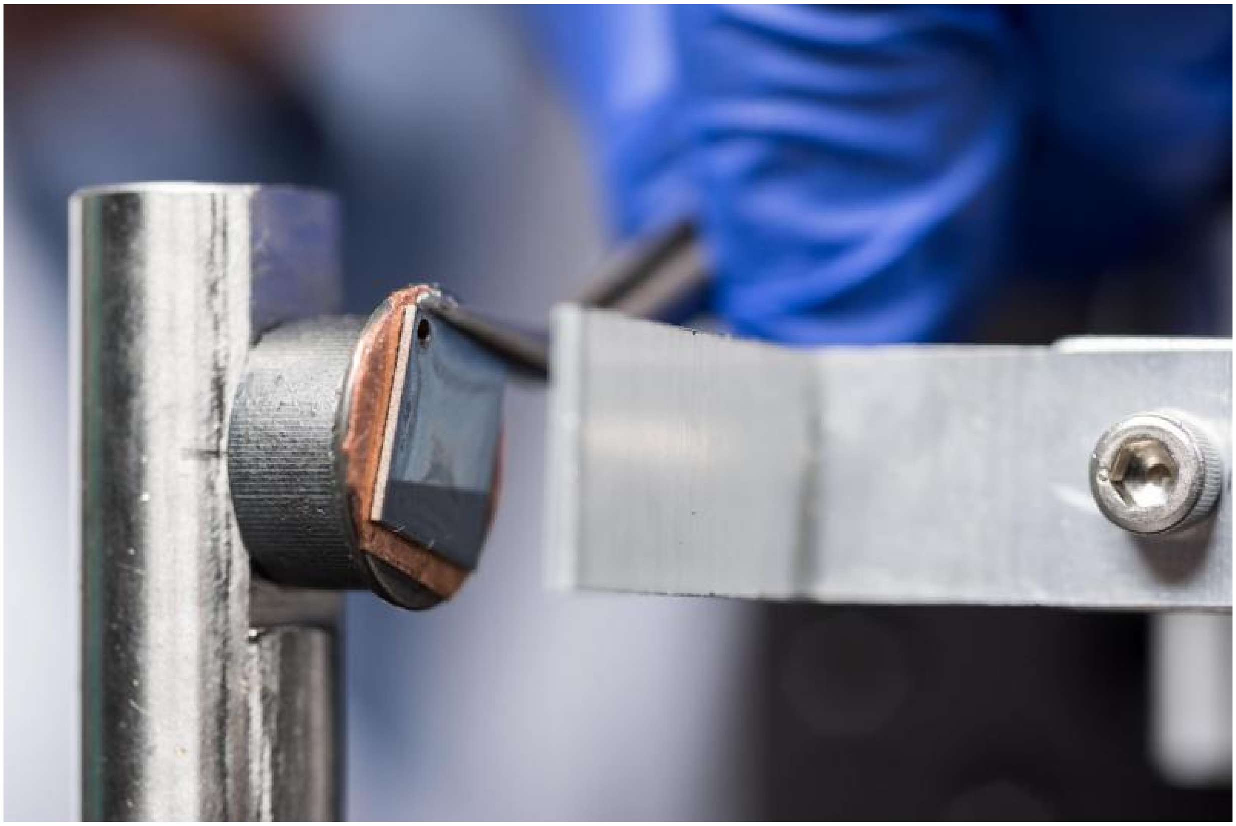
Using a combination of experimental and simulation techniques, researchers from the Georgia Institute of Technology and three other research organizations have reported surprisingly high damage tolerance in electrochemically-lithiated silicon materials. The work suggests that all-silicon anodes may be commercially viable if battery charge levels are kept high enough to maintain the material in its ductile state.

Supported by the National Science Foundation, the research is reported September 24 in the journal *Nature Communications*.

"Silicon has a very high theoretical capacity, but because of the perceived mechanical issues, people have been frustrated about using it in next-generation batteries," said Shuman Xia, an assistant professor in the George W. Woodruff School of Mechanical Engineering at Georgia Tech. "But our research shows that lithiated silicon is not as brittle as we may have thought. If we work carefully with the operational window and depth of discharge, our results suggest we can potentially design very durable silicon-based batteries."

Lithium ion batteries are used today in a wide range of applications from hand-held mobile devices up to laptop computers and electric vehicles.

A new generation of high-capacity batteries could facilitate expanded transportation applications and large-scale storage of electricity produced by renewable sources.



Shown are details of a custom environmental indenter used to test thin film electrodes made of amorphous silicon. The device was used to develop a detailed nano-mechanical study of mechanical degradation processes in silicon thin films. Credit: Rob Felt, Georgia Tech

The challenge is to get more lithium ions into the anodes and cathodes of the batteries. Today's lithium batteries use graphite anodes, but silicon has been identified as an alternative because it can store substantially more lithium ions per atom. However, storing those ions produces a volume change of up to 280 percent, causing stress that can crack anodes made from pure silicon, leading to significant performance degradation. One strategy is to use a composite of silicon particles and graphite, but that does not realize the full potential of silicon for boosting battery capacity.

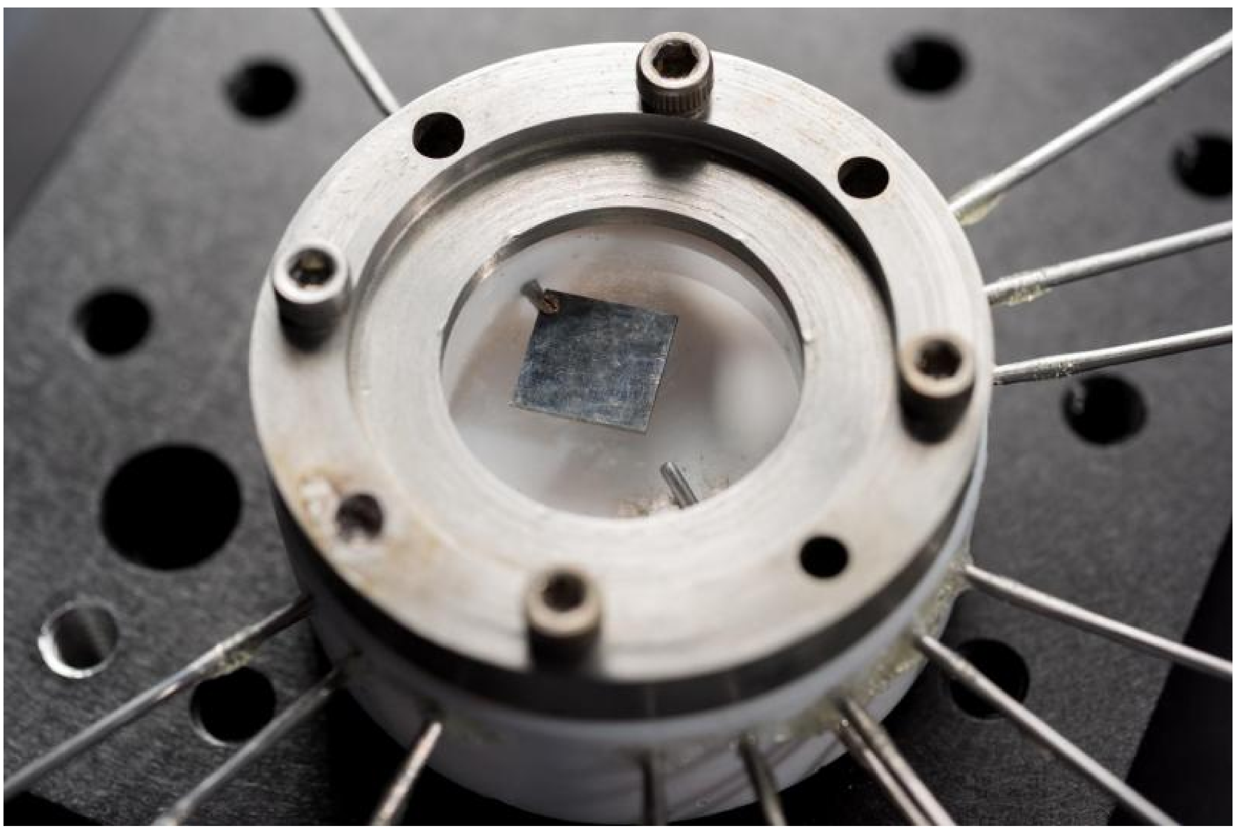
In an effort to understand what was happening with the materials, the research team used a series of systematic nano-mechanical tests, backed up by molecular dynamics simulations. To facilitate their study, they used silicon nanowires and electrochemical cells containing silicon films that were about 300 nanometers in thickness.

The researchers studied the stress produced by lithiation of the silicon thin films, and used a nanoindenter - a tiny tip used to apply pressure on the film surface - to study crack propagation in these thin films, which contained varying amounts of lithium ions. Lithium-lean silicon cracked under the indentation stress, but the researchers were surprised to find that above a certain concentration of lithium, they could no longer crack the thin film samples.

Using unique experimental equipment to assess the effects of mechanical bending on partially lithiated silcon nanotires, researchers led by Professor Scott Mao at the University of Pittsburgh studied the nanowire damage mechanisms in real-time using a transmission electron microscope (TEM). Their in-situ testing showed that the silicon cores of the nanowires remained brittle, while the outer portion of the wires became more ductile as they absorbed lithium.

"Our nanoindentation and TEM experiments were very consistent," said Xia. "Both suggest that lithiated silicon material becomes very tolerant of damage as the lithium concentration goes above a certain level - a lithium-to-silicon molar ratio of about 1.5. Beyond this level, we can't even induce cracking with very large indentation loads."

Ting Zhu, a professor in Woodruff School of Mechanical Engineering at Georgia Tech, conducted detailed molecular dynamics simulations to understand what was happening in the electrochemically-lithiated silicon. As more lithium entered the silicon structures, he found, the ductile lithium-lithium and lithium-silicon bonds overcame the brittleness of the silicon-silicon bonds, giving the resulting lithium-silicon alloy more desirable fracture strength.



Shown is a sample holder used to test samples of lithiated silicon to determine its nano-mechanical properties. The device was used to develop a detailed nano-mechanical study of mechanical degradation processes in silicon thin films. Credit: Rob Felt, Georgia Tech

"In our simulation of lithium-rich alloys, the lithium-lithium bonds dominate," Zhu said. "The formation of damage and propagation of cracking can be effectively suppressed due to the large fraction of lithium-lithium and lithium-silicon bonds. Our simulation revealed the underpinnings of the alloy's transition from a brittle state to a ductile state."

Using the results of the studies, the researchers charted the changing mechanical properties of the silicon structures as a function of their lithium content. By suggesting a range of operating conditions under which the silicon remains ductile, Xia hopes the work will cause battery engineers to take a new look at all-silicon electrodes.

"Our work has fundamental and immediate implications for the development of high-capacity lithium-based batteries, both from practical and fundamental points of view," he said. "Lithiated silicon can have a very high damage tolerance beyond a threshold value of lithium concentration. This tells us that silicon-based batteries could be made very durable if we carefully control the depth of discharge."

In future work, Xia and Zhu hope to study the mechanical properties of germanium, another potential anode material for high-rate rechargeable lithium-ion batteries. They will also look at all-solid batteries, which would operate without a liquid electrolyte to shuttle ions between the two electrodes. "We hope to find a solid electrolyte with both high lithium ion conductivity and good mechanical strength for replacing the current liquid electrolytes that are highly flammable," Zhu said.

"The research framework we have developed here is of general applicability to a very wide range of electrode materials," Xia noted. "We believe this work will stimulate a lot of new directions in battery research."

More information: Xueju Wang, et al., "High Damage Tolerance of Electrochemically Lithiated Silicon," *Nature Communications*, 2015. dx.doi.org/10.1038/ncomms9417

Provided by Georgia Institute of Technology