Too many electrons at the lithiation front in silicon are a problem

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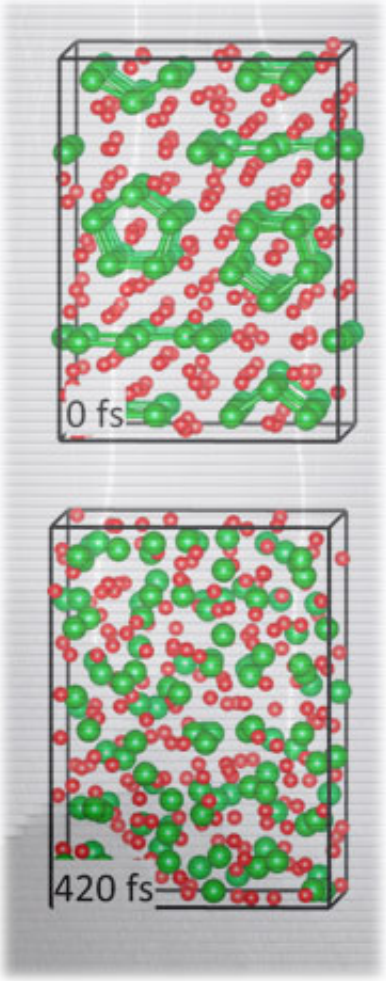

Molecular simulations and experiments show the initial structure of the lithium silicon alloy and the amorphization that occurs after 420 femtoseconds. The lithium ions are the red spheres and the silicon atoms are the green spheres.

(Phys.org) —Ubiquitous but frustrating, lithium-ion batteries fade because the materials lose their structure in response to charging and discharging. This structural change is closely related to the formation of electron-rich regions within the electrode, according to scientists at Pacific Northwest National Laboratory (PNNL), the University of Electronic Science and Technology of China, Northwestern University, and Rensselaer Polytechnic Institute. The team used experiments and molecular simulations to show that the electron-rich region causes silicon bonds to break. The bond breakage transforms crystalline silicon into an amorphous alloy of lithium and silicon.

"It was absolutely unclear what was going on, although a lot of papers described how inserting lithium ions into materials leads to amorphization," said Dr. Fei Gao, a chemical physicist and a corresponding author on the study. "We propose that local electron-rich conditions induce amorphization."

As every owner of a mobile phone knows, lithium-ion batteries fade, storing less energy each time they are charged. Over time, a battery declines to the point that it has to be replaced, at both an environmental and financial cost. This study explains what has been seen time and again in experiments: operating batteries with silicon, zinc oxide, germanium, or certain other insulating materials leads to amorphized electrodes, but aluminum or some other metals remain a crystalline alloy. This study's results could assist in designing longer lasting materials for not just cell phones, but also for electric cars.

"The ever-growing energy demands of information and transportation rely on the progress of energy storage techniques, such as lithium-ion batteries because of their relatively high energy density and design flexibility. Timely development of a better battery is the driving force for creating new materials for energy storage," said Dr. Chongmin Wang, chemical imaging expert at PNNL and investigator on this study.

When a lithium-ion battery is charged, lithium ions are inserted into the anode, a process known as lithiation. The anode's ions begin by being arranged in a well-defined lattice, but in certain cases devolve into an amorphous jumble. In this study, the scientists used phosphorous-doped silicon nanowire anodes. The nanowires were grown at DOE's Center for Integrated Nanotechnologies, at Los Alamos National Laboratory and Northwestern University, using chemical vapor deposition.

The team took the nanowires to DOE's EMSL, located at PNNL, and assembled them into a tiny battery inside an aberration-corrected transmission electron microscope and observed lithiation, at lattice resolution. They further watched the behavior of these regions with scanning transmission electron microscopy images and electron energy loss spectroscopy maps. To complement experimental observations, they studied metal-based electrodes using a large-scale density functional theory molecular dynamics method and saw crystals form. The team also examined the reactions that result in crystalline lithium silicide under electron-rich conditions.

They discovered that amorphorization always starts at interfaces between the silicon and a lithium-silicon alloy where a localized high concentration of electrons occurs. To adjust to the extra electrons and a high level of lithium ions entering the lattice, the bonds between silicon atoms in the crystalline lattice break. The broken bonds create isolated silicon atoms and lead to the disordered phases.

"Expertise on both lithium-ion batteries and chemical imaging gave us the edge," said Dr. Louis Terminello, who leads the Chemical Imaging Initiative at PNNL, the principal sponsor of this study.

The scientists are conducting computational simulations to support experiments aimed at fully understanding batteries. For example, they continue to explore graphene's behavior, a material of great interest in

the energy storage. Also, they are doing computational work with experimentalists to elucidate ions' behavior in materials for the rechargeable lithium ion battery, specifically the lithium nickel manganese oxide cathode.

More information: Wang Z, M Gu, Y Zhou, X Zu, JG Connell, J Xiao, D Perea, LJ Lauhon, J Bang, S Zhang, C Wang, and F Gao. 2013. "Electron-Rich Driven Electrochemical Solid-State Amorphization in Li-Si Alloys." *Nano Letters* 13(9):4511-4516. DOI: 10.1021/nl402429a

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