

# ELECTRODE OPTIONS FOR LITHIUM-ION BATTERIES

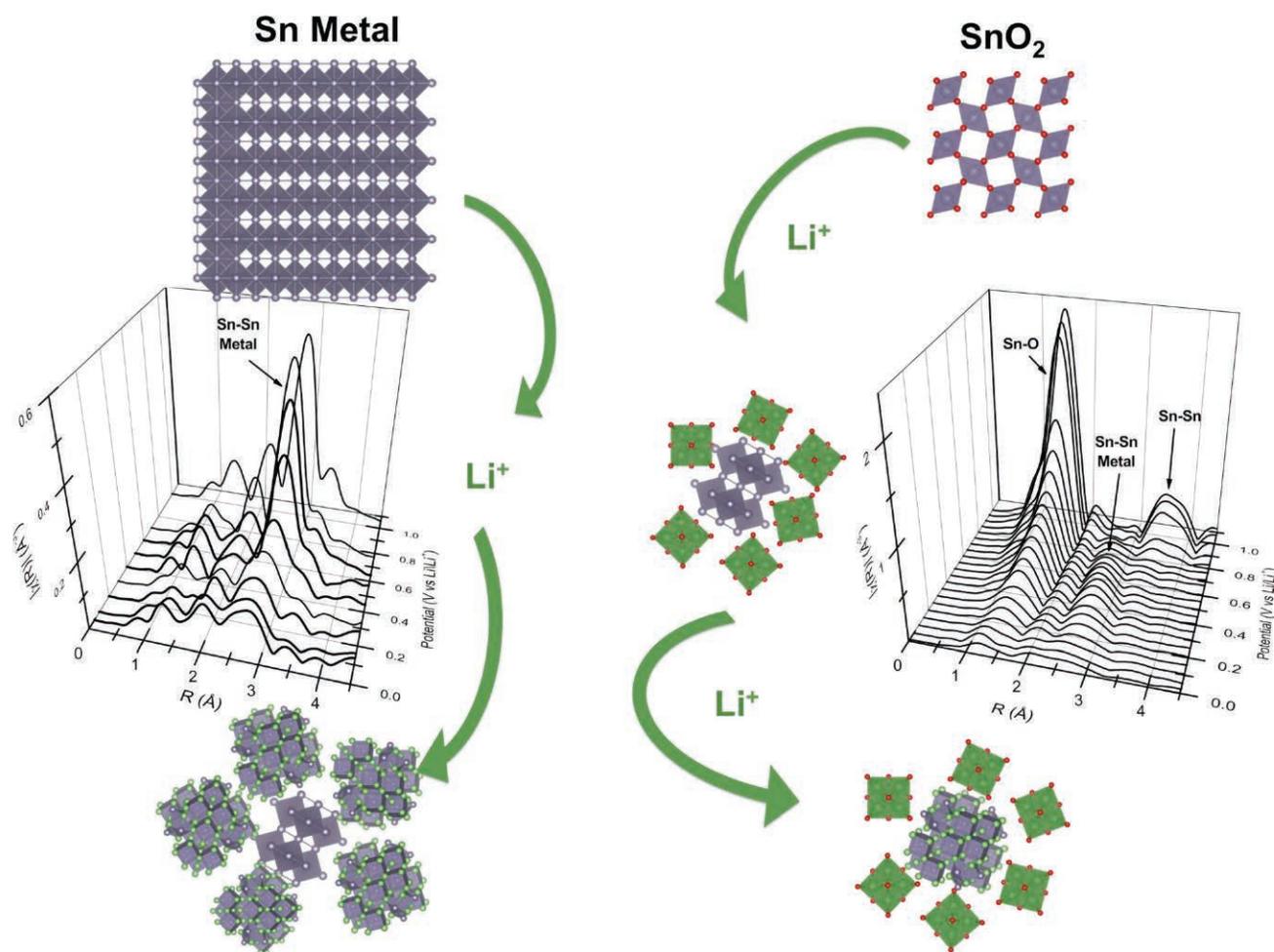


Fig. 1. Two types of battery anodes are compared. On the left, a pure tin anode is represented by a relatively large crystal nanoparticle (top). During the first lithiation, lithium ions (shown in green) begin to alloy with the tin atoms, as evidenced by a decrease in the Sn-Sn metal peak in the x-ray absorption spectrum (middle). But the peaks do not completely disappear, implying that the lithium is unable to penetrate to the core of the nanoparticle (bottom). By contrast, the right side shows a tin oxide anode. In this case, the first lithiation converts tin oxide into small tin nanoparticles, surrounded by lithium oxide. The smaller size means lithium reaches nearly all the available tin atoms. The proof of this is the near disappearance of the Sn-Sn metal peak in the x-ray absorption spectrum. Image: Christopher Pelliccione

**L**ithium-ion batteries power many of the electronic devices that we've come to depend on. But these storage devices will need an upgrade for use in electric cars, where the battery's large weight undermines the energy efficiency. One place for improvement is in the anodes (or negative electrodes) that store lithium ions during charge up. Experiments performed at the APS have investigated high-capacity, tin-based anodes using x-ray absorption spectroscopy. The observations track structural changes within tin nanostructures, revealing why these anodes often fail after multiple uses. These results provide clues to engineers trying to design a battery that can drive us into the future.

The majority of lithium-ion batteries use carbon-based materials for their anode. In the case of a cell phone or laptop, carbon can store a sufficient amount of lithium ions, but increasing capacity will require new materials. One option has been tin, which can store three times more lithium charges per mass—thus reducing the overall weight of the battery. The typical design of a tin-based anode consists of a large number of tin nanoparticles embedded in a conductive support medium. As the battery is charged, lithium ions diffuse into the tin nanoparticles. Each tin atom can bind with as many as four lithium ions. But this high capacity poses a problem as the nanoparticles swell in size. The volume expansion can cause structural damage within the anode, eventually leading to broken electronic contacts and a dead battery.

One strategy for improving tin-based anodes is to use tin oxide (SnO<sub>2</sub>) rather than pure tin (Sn metal). Tests have shown that tin oxide anodes have greater longevity, but the key to this longer life is not completely understood. Researchers from the Illinois Institute of Technology and Argonne performed experiments on tin and tin-oxide anodes at the MR-CAT 10-ID-B beamline at the APS. This beamline provides high-energy x-rays (29.2 keV) capable of exciting the K-edge of tin.

The researchers collected spectra for both x-ray absorption near-edge structure (XANES) and x-ray absorption fine structure (EXAFS) studies. The XANES data reveal the electronic state of an absorbing tin atom, whereas the EXAFS observations provide information about the surrounding atomic

structure. The team applied models to their absorption spectra, which revealed whether the tin atoms were in a metallic state (Sn-Sn bonds), an oxide state (Sn-O bonds), or in a lithium alloy phase (Sn-Li bonds). The ability to observe lithium—through its bonding to tin—was a unique feature of this study, as normally lithium is too light to give an x-ray signal.

The team began with pristine (never-before-used) anodes and observed the structural changes during the initial lithiation, when lithium ions diffuse into the anode. For the pure tin case, they found that a fraction of the tin atoms remained in the metallic state, never alloying with lithium (Fig. 1). A possible explanation is that lithium atoms collect on the outer shell of tin nanoparticles, preventing other lithium ions from reaching the core. Volume expansion causes a break between the core and shell, which reduces the electrical conductivity within the anode. An indication of this structural damage was found in a reduction in the number of lithium neighbors after multiple charging-discharging cycles.

The situation was different for the tin-oxide anode. During the first lithiation, the tin oxide transforms into metallic tin surrounded by lithium oxide. The metallic tin collects into crystalline nanoparticles, but the lithium oxide acts as a structural buffer that prevents the nanoparticles from growing too large. The team estimated that the nanoparticles in a tin-oxide anode are only a few atoms in size, as compared to 100 nanometers across in the pure-tin anode. The smaller nanoparticle size and lithium oxide barrier help prevent struc-

tural damage and electrical disconnections. This explains why the tin oxide anode showed better reversibility after multiple charges.

However, the tin oxide anode is not without its own problems. Despite its benefit to structural stability, the lithium oxide envelope has the downside of decreasing the rate of lithium diffusion. This slow diffusion explains why the researchers only recorded 8 lithium neighbors for each tin atom, when the maximum number is 14. Further work with tin-based compounds will hopefully find a compromise that affords a structural stabilizing buffer without impeding lithium ion diffusion.

— Michael Schirber

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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-65 keV • On-site • Accepting general users •