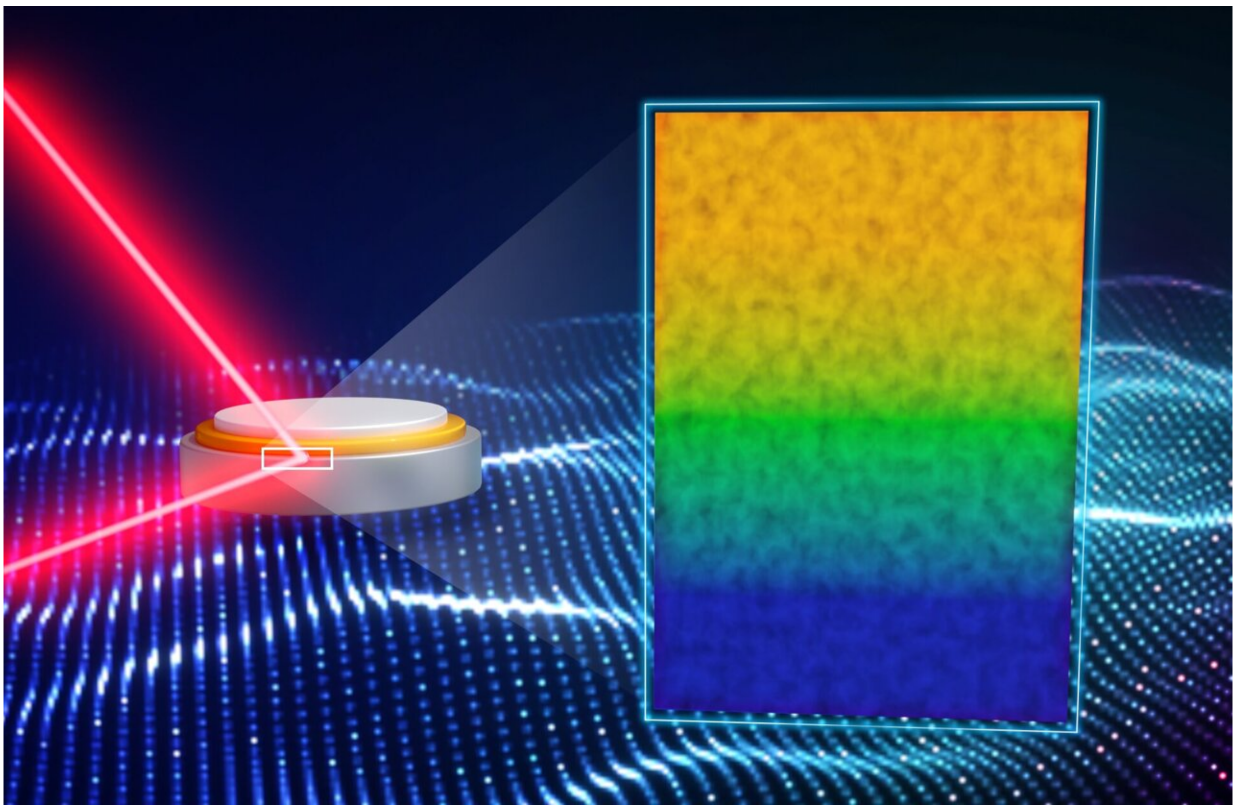
Using neutron reflectometry to look inside working solid-state battery and discover its key to success

June 28 2023, by Dawn Levy



In a solid-state battery, reactive lithium metal (blue) can coexist stably with a solid electrolyte called LiPON (yellow) when an interphase (green), about 70 atoms thick, forms. Credit: Jill Hemman/ORNL, U.S. Dept. of Energy

Researchers at the Department of Energy's Oak Ridge National Laboratory were the first to use neutron reflectometry to peer inside a working solid-state battery and monitor its electrochemistry. They discovered that its excellent performance results from an extremely thin layer, across which charged lithium atoms quickly flow as they move from anode to cathode and blend into a solid electrolyte.

"We want better batteries," said ORNL's Andrew Westover, who co-led a study published in *ACS Energy Letters* with James Browning at the lab's Spallation Neutron Source. "That means more energy density, lower cost, faster and safer battery charging and longer life."

Rechargeable batteries rely on lithium, a small metal atom that packs tightly into the negatively charged anode to maximize energy density. However, lithium is unstable with most electrolytes—a factor in flammability of smartphone, laptop and electric vehicle batteries that use liquid electrolytes.

"To fix the flammability issue, we want to switch to solid electrolytes," Westover said.

Enter lithium phosphorus oxynitride, or LiPON, a solid electrolyte invented at ORNL nearly 30 years ago. "It's never been understood why it works really well," Westover said. "We want to make what works with LiPON work on a much larger scale. But we have to understand it first."

Prior work showed the solid electrolyte interphase, or SEI—a layer that forms to protect and stabilize the solid-state battery—is key to its ability to charge and discharge repeatedly. In this case, the interphase is a chemical gradient consisting of a lithium-rich layer whose lithium content decreases as it blends into pure LiPON.

"In a normal battery, an interphase forms between the electrolyte and the working electrode," Browning said. "Over time as you cycle a battery—charge and discharge it—that material can change in composition and thickness."

"If you have a good SEI, your battery works. If you have a bad SEI, it doesn't," Westover said. "The reason that the capacity of your cell phone battery slowly decreases year after year is because your SEI is expanding and consuming your electrolyte in the liquid-based battery."

In a LiPON-based solid-state battery, however, a thin SEI layer forms to passivate lithium, making it unreactive, and does not grow like the SEI in a traditional battery.

Scientists coupled neutron reflectometry with electrochemistry to measure this stable interphase between LiPON and lithium for the first time. It was as thin as 7 nanometers. "We discovered with this study that the layer formed is about 70 atoms thick," Westover said. "This work shows it is possible to make interfaces in solid-state batteries that are thin and provide excellent performance."

That small scale plus the solid state of the materials drove the researchers to use neutrons to look inside the battery. "Prior to the discovery of X-rays, you couldn't look under skin to see bones inside a body. You had to cut the skin open," Westover said. "Until now, that's basically been the approach that most people have used to look at interphases in batteries. In this case the scale is too small to cut anything open. We needed a tool that would allow us to go through the material, to probe it nondestructively at that scale and understand what's happening at the interphase. That's where neutron reflectometry came in."

Browning added, "We're interested in how a battery is performing, so we need a way of looking inside while it's doing its thing, operating on a length scale that's important to the functioning of the device, to explore stability, long-term cyclability, etc. Because neutrons are weakly interacting, we can get them to the point we want to probe without any interference and then, more importantly, get them back out so we can determine what happened at the place of interest—the interphase in this case."

Coupling neutron reflectometry with electrochemistry accelerated understanding of the interphase between lithium metal and solid electrolytes in solid-state batteries.

"This combination of techniques opens the door for us to look at the entire spectrum of solid-state electrolyte materials and determine which ones will enable your fast-charging, high-energy batteries," Westover said. "We've already started version 2.0, where we're looking at a different type of solid electrolytes and starting to understand what they look like."

He added, "New materials need to be invented that have this stability." Design of future high-performance batteries will depend on it.

More information: Katie L. Browning et al, In Situ Measurement of Buried Electrolyte–Electrode Interfaces for Solid State Batteries with Nanometer Level Precision, *ACS Energy Letters* (2023). DOI: 10.1021/acsenergylett.3c00488

Provided by Oak Ridge National Laboratory