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Battery mystery solved: Microscopy answers longstanding questions about lithium-rich transition metal oxides

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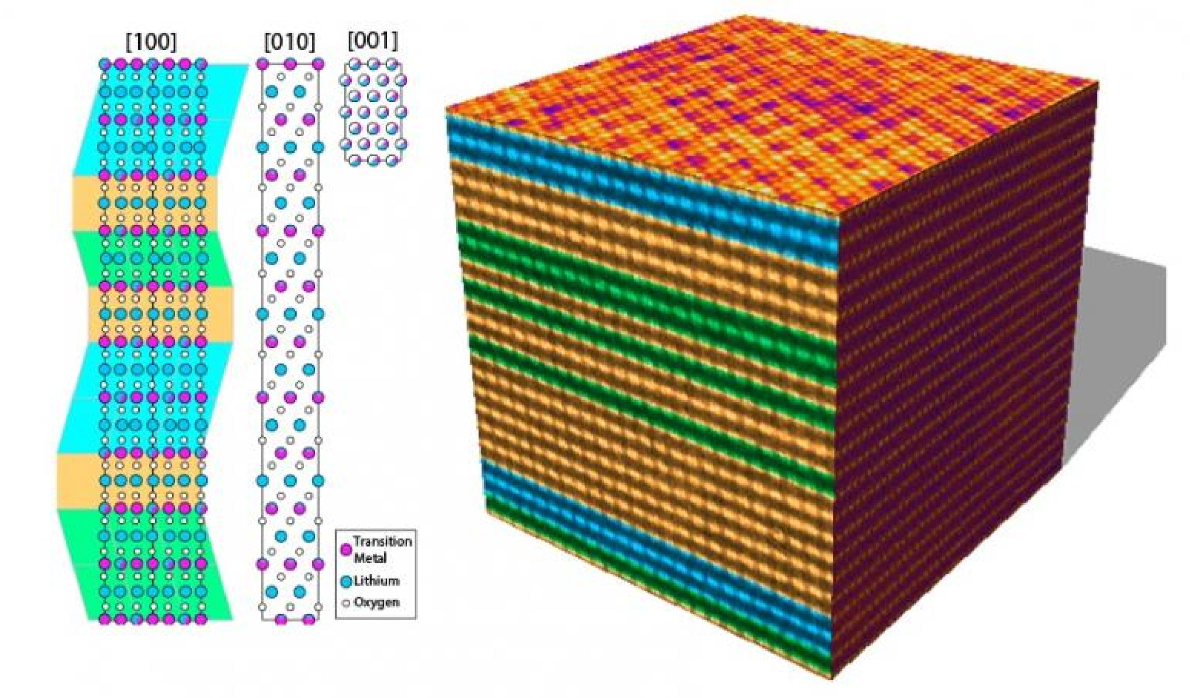


On the right the cube represents the structure of lithium- and manganese- rich transition metal oxides. The models on the left show the structure from three different directions, which correspond to the STEM images of the cube. Credit: Lawrence Berkeley National Laboratory

Using complementary microscopy and spectroscopy techniques, researchers at Lawrence Berkeley National Laboratory (Berkeley Lab) say they have solved the structure of lithium- and manganese-rich transition metal oxides, a potentially game-changing battery material and the subject of intense debate in the decade since it was discovered.

Researchers have been divided into three schools of thought on the material's structure, but a team led by Alpesh Khushalchand Shukla and Colin Ophus spent nearly four years analyzing the material and concluded that the least popular theory is in fact the correct one. Their results were published online in the journal *Nature Communications* in a paper titled, "Unraveling structural ambiguities in lithium- and manganese- rich transition metal oxides." Other co-authors were Berkeley Lab scientists Guoying Chen and Hugues Duncan and SuperSTEM scientists Quentin Ramasse and Fredrik Hage.

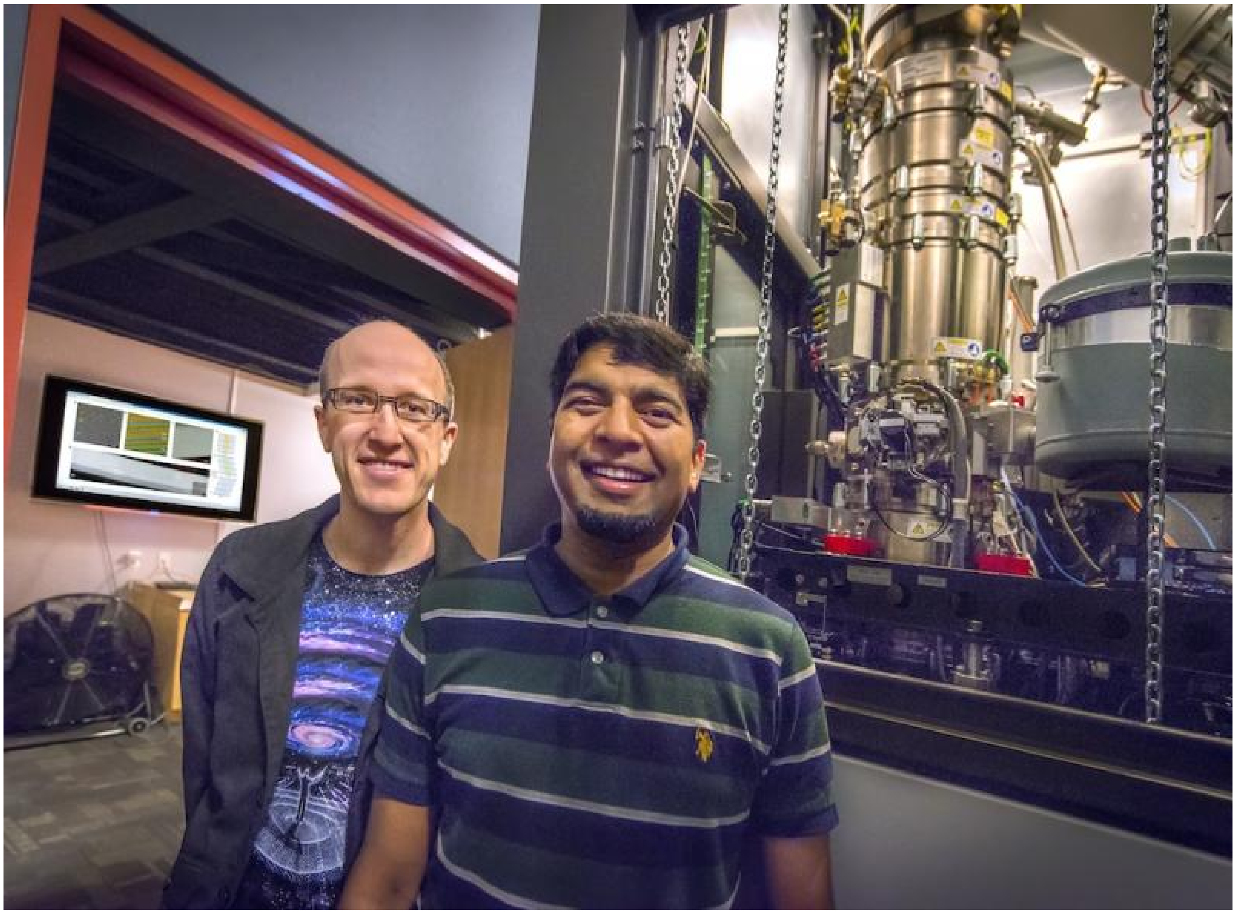
This material is important because the battery capacity can potentially be doubled compared to the most commonly used Li-ion batteries today due to the extra lithium in the structure. "However, it doesn't come without problems, such as voltage fade, capacity fade, and DC resistance rise," said Shukla. "It is immensely important that we clearly understand the bulk and surface structure of the pristine material. We can't solve the problem unless we know the problem."

A viable battery with a marked increase in storage capacity would not only shake up the cell phone and laptop markets, it would also transform the market for electric vehicles (EVs). "The problem with the current lithium-ion batteries found in laptops and EVs now is that they have been pushed almost as far as they can go," said Ophus. "If we're going to ever double capacity, we need new chemistries."

Using state-of-the-art electron microscopy techniques at the National Center for Electron Microscopy (NCEM) at Berkeley Lab's Molecular Foundry and at SuperSTEM in Daresbury, United Kingdom, the researchers imaged the material at atomic resolution. Because previous studies have been ambiguous about the structure, the researchers minimized ambiguity by looking at the material from different directions, or zone axes. "Misinterpretations from electron microscopy data are possible because individual two-dimensional projections do not give you the three-dimensional information needed to solve a structure," Shukla said. "So you need to look at the sample in as many directions as you can."

Scientists have been divided on whether the material structure is single trigonal phase, double phase, or defected single monoclinic phase. The "phase" of a material refers to the arrangement of the atoms with respect to each other; Ophus, a Project Scientist at the Molecular Foundry, explains how easy it is for researchers to reach different conclusions: "The two-phase and one-phase model are very closely related. It's not like comparing an apple to an orange—it's more like comparing an orange and a grapefruit from very far away. It's hard to tell the difference between the two."

In addition to viewing the material at atomic resolution along multiple zone axes, the researchers made another important decision, that is, to view entire particles rather than just a subsection. "Imaging with very high fields of view was also critical in solving the structure," Shukla said. "If you just look at one small part you can't say that the whole particle has that structure."



Colin Ophus (left) and Alpesh Shukla are in front of the transmission electron microscope at the Molecular Foundry. Credit: Lawrence Berkeley National Laboratory

Putting the evidence together, Shukla and Ophus are fairly convinced that the material is indeed defected single phase. "Our paper gives very strong support for the defected single-phase monoclinic model and rules out the two-phase model, at least in the range of compositions used in our study," said Ophus, whose expertise is in understanding structure using a combination of computational methods and experimental results.

Added Ramasse, director of SuperSTEM: "We need to know what goes on at the atomic scale in order to understand the macroscopic behavior of new emerging materials, and the advanced electron microscopes available at national facilities such as SuperSTEM or NCEM are essential in making sure their potential is fully realized."

In addition to solving the structure of the bulk material, which has been studied by other research groups, they also solved the surface structure, which is different from the bulk and consists of just a few layers of atoms on select crystallographic facets. "The intercalation of lithium starts at the surface, so understanding the surface of the pristine material is very important," Shukla said.

On top of the STEM (scanning transmission electron microscopy) imaging that they used for the bulk, they had to use additional techniques to solve the surface, including EELS (electron energy loss spectroscopy) and XEDS (X-ray energy dispersive spectroscopy). "We show for the first time which surface structure occurs, how thick it is, how it's oriented in relation to the bulk, and in particular on what facets the surface phase does and doesn't exist," Ophus said.

An important part of the study was the quantity and quality of the samples studied. They started with lab-made samples, prepared by Duncan, a postdoc in the lab of Chen, a chemist whose research focuses on lithium-ion batteries. They used a molten-salt method that produces high-quality discrete primary particles that are impurity-free, making them ideal candidates for performing fundamental characterization. Taking a conservative approach, the researchers also decided to procure and analyze two commercial samples from two different companies.

"We could have finished the paper a year earlier, but because there was so much controversy we wanted to make sure we didn't leave any stone unturned," said Shukla who was a scientist with Berkeley Lab's Energy Storage and Distributed Resources Division at the time he did this work but has since become a consulting scientist at Envia Systems while continuing to be affiliated with Berkeley Lab as a user of the Molecular Foundry.

In the end, it took nearly four years to complete the research. Ophus calls it a "tour de force of microscopy" because of its thoroughness.

Provided by Lawrence Berkeley National Laboratory

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