Correlation of Lithium-Ion Battery Performance with Structural and Chemical Transformations

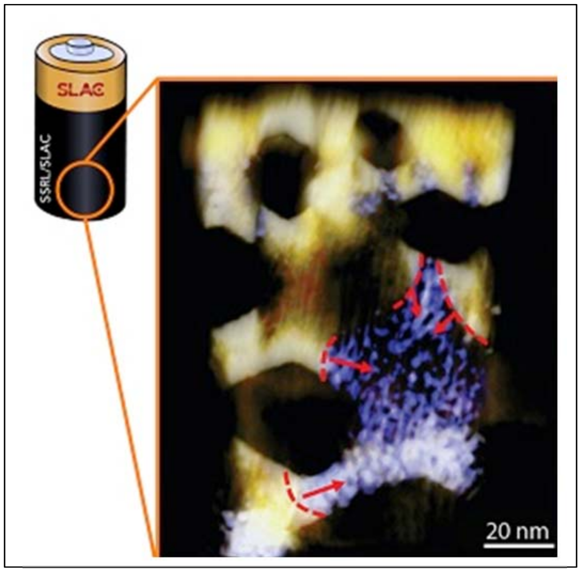
Chemical evolution and structural transformations in a material directly influence characteristics relevant to a wide range of prominent applications including rechargeable batteries for energy storage. Structural and/or chemical rearrangements at surfaces determine the way a material interacts with its environment, thus controlling the functionalities of the material. Specifically, the surfaces of lithium-ion battery electrodes evolve simultaneously with charge-discharge cycling. Moreover, the phase distribution in the bulk of electrode particles determines the pathway and efficiency of lithium intercalation and deintercalation, strongly impacting the cyclability of lithium-ion batteries. Therefore, resolving the spatial dependence of structural and chemical evolution could enlighten our mechanistic understanding, elucidate the origins of material properties, and enable the rational design of battery and other materials.

The present work, published in two separate articles in *Nature Communications*, sets a refined example for the study of structural and chemical transformations in battery materials using combined diagnostic tools at complementary length scales. The published articles resulted from collaborative efforts between Dennis Nordlund and Tsu-Chien Weng of SSRL, Marca Doeff, Feng Lin, Isaac Markus and Mark Asta of the Lawrence Berkeley National Laboratory (LBNL), Huolin Xin of Brookhaven National Laboratory (BNL), Chunmei Ban of the National Renewable Energy Laboratory (NREL), Ryan Richards of the Colorado School of Mines, and Ye Zhu of Monash University in Australia.

The storage of energy is of paramount importance for many of the technologies we use in our daily lives. In particular, lithium-ion batteries find ubiquitous use in personal electronics and are promising candidates for applications in transportation. In a typical lithium-ion battery, charged lithium ions migrate through a chemical solution – the electrolyte – into the anode when the battery is charging and into the opposite electrode, called the cathode, when the battery is discharging.

In the published studies, the scientists separated cathode and anode from a typical lithium-ion battery and assembled each of them in coin cells using pure lithium metal as counter electrodes. The scientists designed a high-throughput methodology to achieve a full panorama for battery materials. These studies were enabled by a series of diagnostic tools including state-of-the-art high-throughput soft x-ray absorption spectroscopy at SSRL's Beam Line 10-1 and advanced electron microscopy at LBNL's National Center for Electron Microscopy and BNL's Center for Functional Nanomaterials. LBNL's Batteries for Advanced Transportation Technologies (BATT) Program supported this work.

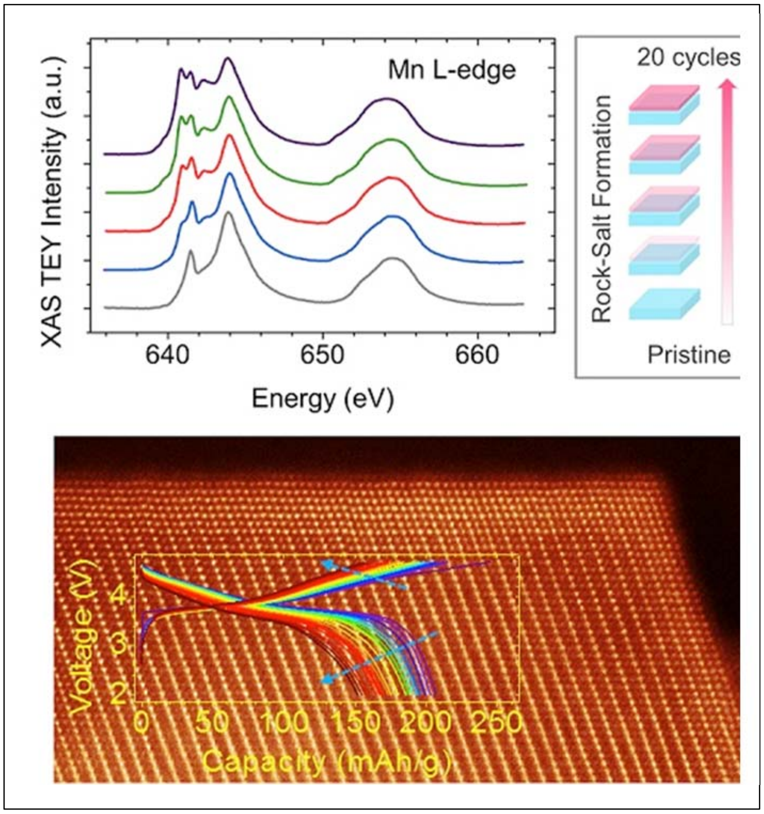
Anode Material *Nickel Oxide* (NiO)



The team discovered and reconstructed the three-dimensional nanostructures that evolve during the charging of lithium-ion batteries using nickel oxide (NiO) as anode material. They found that the initiation of the reaction fronts is spatially distant, even within the same slab of material. This is in contrast to what was previously conjectured, namely that the reactions started uniformly from the surface of the material.

Using electron microscopy in combination with synchrotron soft x-ray techniques, the dynamic changes to both the electrode surface structure and its interaction with the liquid electrolyte were characterized, giving a comprehensive understanding of the evolving structure. In addition, the combination of x-ray and fast electron spectroscopy described in the present work presents a new paradigm for correlated characterization of the evolution of chemistry in battery electrodes at complementary length scales.

Cathode Material *Lithium Nickel Manganese Cobalt Oxide* (NMC)



The team correlated cycling performance with the observation of structural reconstruction and chemical evolution at the surface of the cathode material lithium nickel manganese cobalt oxide (NMC) using statistically viable high-throughput ensemble-averaged x-ray absorption spectroscopy (XAS), as well as spatially resolved electron energy loss spectroscopy (EELS) and atomically resolved annular dark-field scanning transmission electron microscopy (ADF-STEM) imaging. The findings show that the challenge of achieving stable high-voltage cycling of NMC electrodes lies with structural and chemical metastability at the surfaces. Upon cycling and/or electrolyte exposure, the surfaces of NMC particles undergo progressive reconstruction from a layered structure to a rocksalt structure in addition to the buildup of a complex surface reaction layer. These newly formed layers passivate the battery particles and inhibit lithium in-and-out transport.

Summary

In summary, the team discovered that changes at the surface and/or in the bulk of cathode/anode particles could directly impact the performance of lithium-ion batteries. With this newly obtained knowledge, the team is now moving forward with a better design concept for cathodes and anodes in lithium-ion batteries.

Primary Citations

F. Lin, I. M. Markus, D. Nordlund, T.-C. Weng, M. D. Asta, H. L. Xin and M. M. Doeff, "Surface Reconstruction and Chemical Evolution of Stoichiometric Layered Cathode Materials for Lithium-Ion Batteries", *Nat. Commun.* **5**, 3529 (2014), DOI: 10.1038/ncomms4529

F. Lin, D. Nordlund, T.-C. Weng, Y. Zhu, C. Ban, R. M. Richards and H. L. Xin, "Phase Evolution for Conversion Reaction Electrodes in Lithium-ion Batteries", *Nat. Commun.* **5**, 3358 (2014), DOI: 10.1038/ncomms4358

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