Correlating advanced microscopies reveals atomic-scale mechanisms limiting lithium-ion battery lifetime

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The longevity of a lithium-ion battery is limited by cathode degradation. Combining atom probe tomography and scanning transmission electron microscopy reveals that the degradation results from atomic-scale irreversible structural changes once lithium leaves the cathode during charging, thereby inhibiting lithium intercalation back into the cathode as the battery discharges. This information unveils possible routes for improving the lifetime of lithium-ion batteries.

Lithium-ion batteries have received great attention due to their widespread use for applications ranging from small electronic devices, for instance mobile phones, to high-capacity energy storage, such as in electric vehicles and grid energy. A major limiting factor in renewable energy grid integration is the ability to reliably store and access electricity at a low cost. For example, solar panels are economically competitive with fossil fuels; however, solar energy is produced at nature’s will and must be stored for future distribution in the event of solar power surpluses. Lithium-ion batteries are among the best commercially viable energy storage technologies, but unfortunately, capacity degradation limits their lifetime and battery replacement is expensive. Engineering Li-ion batteries to extend their operational lifetime will decrease cost and limit the environmental footprint associated with renewable energy compared to other energy sources, facilitating widespread usage. Understanding capacity degradation mechanisms is necessary to rationally design new materials or implement operational protocols to enhance durability, but degradation mechanisms are complex and typically occur across multiple length scales, some of which are not readily accessible without using high spatial resolution characterization techniques.

Li-ion batteries consist of a cathode/electrolyte/anode heterostructure, as shown in Fig. 1. Li-ions leave the oxidized cathode host and are then inserted within or electrodeposited onto the reduced anode during charging and then collect back in the cathode via a reduction reaction as the battery discharges. High-energy density Li-ion batteries require high-voltage cathodes that are typically an oxide compound containing Li and at least one transition metal (Co, Ni, etc.). In fact, the discovery of Co-based oxides for use as Li-ion battery cathodes led to the Nobel Prize in Chemistry in 2019 to early pioneers Goodenough, Whittingham, and Yoshino.

Li-ion battery capacity degradation originates from structural defects that are created by compositional instabilities in the high-voltage cathode. Lithium removal from metal oxides at high voltage causes structural changes, which can result in defect formation including anti-site...
changes of a Li(Ni0.80Co0.15Mn0.05)O2 (NCM)-based cathode.

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STEM and APT to probe the chemical and compositional electrochemical cycling, Chae et al. combined the strengths of the other technique and therefore, a combined APT and STEM experiment can enable the correlation of atomic structure with the nanoscale Li concentrations.

To better understand the creation of the observed Li-ion concentration gradients and track the chemical evolution during electrochemical cycling, Chae et al. combined the strengths of STEM and APT to probe the chemical and compositional changes of a Li(Ni0.80Co0.15Mn0.05)O2 (NCM)-based cathode. The cathode is an agglomeration of approx. 10 µm "powder grains" that each contain several 100 nm-sized particles sintered together, such that only the surface of the 10 µm particles contact the electrolyte. Inductively coupled plasma-electron energy loss spectroscopy (ICP-AES) and electron energy loss spectroscopy (EELS). Additionally, electron diffraction can identify the crystallographic phases at the nanoscale. However, Li-containing materials are typically unstable under electron beam irradiation, and the detectability and quantification of light elements is challenging. APT is a time-of-flight mass spectrometer combined with a three-dimensional projection microscope having sub-nm spatial resolution. Aberrations in the projected ion trajectories limit the ability of APT to extract structure or elemental site occupancy, but its compositional sensitivity, in the tens of parts-per-million, extends to light elements, including Li, albeit not without challenges.

Fortunately, the shortcomings of either technique are complemented by the strengths of the other technique and therefore, a combined APT and STEM experiment can enable the correlation of atomic structure with nanoscale Li concentrations.

The cathode delithiates during charging, the TM ions move into the more energetically favorable Li sites as there is little to no repulsion from neighboring cationic species, while Li cannot readily occupy the TM vacancies on their return during discharge cycles. Significant TM ion migration into Li sites facilitates a phase change to rock salt- and spinel-like structures occurs after severe TM migration, further reducing the capacity.

What makes this work unique is the combined APT/STEM approach revealing a direct link between the amount of Li-depletion in the NCM and the degree of structural disorder. As the cathode delithiates during charging, the TM ions move into the more energetically favorable Li sites as there is little to no repulsion from neighboring cationic species, while Li cannot readily occupy the TM vacancies on their return during discharge cycles. Significant TM ion migration into Li sites facilitates a phase change to rock salt- and spinel-like structures, which inhibits subsequent Li intercalation into the cathode. As the number of available Li accommodation sites dwindles in the NCM particle near surface regions, the capacity is reduced, and full charging is prevented.
In our opinion, the study by Chae et al. is important because this article is a prime example of how using combinatorial microscopy techniques having similar length-scale resolutions but complementary strengths, can explain the behavior of complex, difficult to characterize material systems, such as phase transformations in these battery electrode materials. All microscopy techniques have strengths and shortcomings, but workflows exist that can exploit their inherent complementarity. For battery materials research, APT is a superior technique to reliably quantify Li concentrations with nanoscale resolution, albeit not without experimental challenges, while (S)TEM techniques are better suited for nano- to atomic-scale structural and local valence state identification. The combination of these techniques reveals a direct correlation of the Li loss in NCM cathodes to local structural disorder and phase transformations that limit the capacity of Li-ion batteries. What’s next? These insights demonstrate possible routes for improving the lifetime of batteries via two possible ideas: (i) adjust the material’s composition to limit the migration of TMs into anti-sites, which is related to the energetics of site-occupancy and hence may be calculable by ab initio techniques; (ii) the cores of the cathode particles remain unchanged, meaning that the Li therein is lost or rather unexploited, and as such, designing the grain architecture may help use these unused ions. We hope battery experts seize on these results and integrate them into the design of next generation batteries.

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Competing interests
The authors declare no competing interests.

Additional information
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