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# Main manuscript

**Introduction**

The rapidly boosting market for consumer electronics and electric vehicles (EVs) has motivated the tremendous ongoing efforts in researching lithium ion battery materials and chemistry, aiming to improve energy and power density, enhance safety, prolong lifetime, and reduce cost. An important aspect of the battery research is to identify the fading pathways of battery particles and electrodes at multiple length/time scales in response to the real-world operating conditions1 . The hierarchical architecture of the lithium-ion batteries2 is vital to the desired functionality of on-demand energy storage and release. Independent efforts have been devoted to the study of different battery components (e.g., cathode, anode, electrolyte, binder, etc.). In practice, however, it is the synergy among all of the battery components that determines the ultimate battery performance. In lithium ion batteries, the cathode materials still present a bottleneck for further improving the energy density of lithium ion batteries3 . It is, therefore, of fundamental interest and importance to systematically investigate the cathode materials’ morphological, chemical, and mechanical properties, which intertwine at different time and length scales [ref].

Nickel-rich layered materials LiNi1-x-yMnxCoyO2 (NMC) are promising cathode candidate for high energy density lithium ion batteries4,5,6. They, however, suffer from the capacity fade, especially, when charged to a high cut-off voltage, which is a necessary procedure to unleash the high energy density potential of this material7 . In the current landscape of the NMC research, we are seeing a growing emphasis on the compounds with even higher Ni and lower Co/Mn content. Such a trend further accentuates the need to understand and, subsequently, to enhance the structural and chemical stability of the nickel-rich NMC cathode. This is because, while the increment in Ni content offers more redox active cations for the charge compensation during energy storage/release and, thus, favors high energy density, the reduction in Co and Mn content could harm the morphological integrity6, thermal robustness8, and lattice structural stability9,10.The electro-chemo-mechanical interplay in nickel-rich NMC cathode is an active research topic that has attracted a great amount of attention 11. The development of morphological defects, i.e. micro-cracks, is not only dependent on the global cathode composition7, but also can be largely influenced by the difference in the externally applied reaction driving forces including the cycling rate12,13, the cycling voltage window14[**Yuwei Joule**; ], and the environmental temperature15,16,17,18,19. Advanced imaging methods, e.g. synchrotron-based x-ray probes20,21,22,23,24,25,26, scanning/transmission electron microscopy27,28,29, and atomic force microscopy30 have been employed for in-depth investigations in this field. Among all these diagnostic tools, the x-ray probes with sufficient spatial resolution and compositional/chemical sensitivity show advantages for correlating the morphological and chemical features of the material. Particularly, when coupled with advanced computing methods for quantification31,32,33 and modeling34,24 of the data, the x-ray imaging methods have been demonstrated to be non-invasive, effective and informative.  Nevertheless, there has not been a study for the electrode-level to offer insights into many-particle electro-chemo-mechanical analysis with nanometer spatial resolution that could resolve the structural and chemical details within every individual particle. Such a study would open an avenue for probing the spatially resolved charge distribution and chemomechanical response for an entire battery composite electrode.

In this work, we combined hard x-ray phase contrast nano-tomography, transmission x-ray microscopy, nanoscale hard x-ray spectro-microscopy, soft x-ray absorption spectroscopy and transmission electron microscopy to systematically investigate the morphological and chemical degradation in LiNi0.6Mn0.2Co0.2O2 (NMC622) electrode under fast charging conditions (5C). At the atomic scale, we observed the local phase transition, which is associated with and is likely responsible for the initiation of the micro-cracks. Such a process propagates to the secondary particle level (i.e. at the mesoscale), where we elucidated two stages of the particle cracking, which entail different chemical responses on the crack surface: 1) the host material’s local lattice structural transition and 2) liquid electrolyte infiltration that forms new diffusion pathway for lithium ions. We further quantified the x-ray phase contrast nano-tomography data of the whole cathode electrode and reported the depth-dependent particle fracturing profile at the electrode level, which has depth-dependent chemical consequences as confirmed by the soft x-ray absorption spectroscopic measurements. The lateral heterogeneity in the electrode-level cracking profile suggests that the degree of local electrode usage evolves as a function of location and time. The heterogeneity in the degree of particle cracking across the electrode is attributed to the local morphological damage and the mismatch between local electric and ionic conductivity. Finite element modeling (FEM) is used to gain further insights into the electrode level strain distribution and propagation. Our results offer valuable insights that could inform the rational design of next-generation battery material with superior electro-chemo-mechanical robustness.

**Results**

**Local phase transition and lattice defects formation.**The lattice structure of the cathode material is vital to the transportation of lithium-ion in the solid phase. The successful and/or promising choices of cathode materials for lithium-ion batteries can be grouped into three categories, which are of 1D (e.g. LiFePO435,36,37,38 with olivine structure), 2D (e.g. LiCoO233,39, LiNixMnyCozO2 (NMC)40,41, and Li- and Mn- rich NMC material42,43 with layered structure), and 3D (e.g. Li1.211Mo0.467Cr0.3O244 and Li1.3Nb0.3Mn0.4O234 with disordered rocksalt structure, and LiMn1.5Ni0.5O429 with spinel structure) lithium diffusion channels, respectively. The layered transition metal oxides, which is the focus of this work, are currently a key player on the market thanks to its excellent performance that is superior in many different aspects. The layered lattice structure offers 2D open space between the layers that hosts the lithium-ions in the process of intercalation and de-intercalation. It has been reported that upon prolonged cycling45,46 or under thermal abuse conditions15,16,17,18 the surface of the material could undergo undesired structural transitions, forming a mixture of spinel and rocksalt structure that hinders the fast lithium-ion diffusion. The participation of liquid electrolyte is found to play a key role and to accelerate such a side reaction47. Under fast charging and/or deep charging conditions, the redox reaction of transition metals cations43,48 and the oxygen anions49,50,51,52 could cause migration of the lattice atoms and, subsequently, trigger the formation of local lattice defects and local structural transition.

To systematically investigate the degradation mechanism of the NMC622 cathode material under fast charging conditions, we start at the atomic scale and show, in Figure 1, a transmission electron microscopy (TEM) image of a cracked area on the extensively cycled NMC622 cathode. While different atomic structures (see highlighted regions of interest, (e) and (h)) can already be visualized, the (inverse) fast Fourier transform analysis **[ref]** of the selected areas (Figures 1d to 1h) and the whole image (Figures 1b and 1c) provides strong evidences, showing the intimate co-presence of layered and rocksalt phases over the localized region. The observed local lattice defect formation and phase transition can serve as nucleation points for further developments of micro-cracks that could propagate throughout the cathode particles.

Figure 1. NMC electrode’s morphological defects at nano and meso scales. Panel (a) shows a transmission electron microscopy image that reveals the mixed rocksalt and layered structure along the region of local defects in NMC cathode material. Panels (b) and (c) are the fast Fourier transform (FFT) and inversed FFT (IFFT) of the entire high-resolution image (a), showing the intimate co-presence of layered and rocksalt phases.  Panels (d) to (h) are the localized FFT ((d) and (f)) and IFFT ((e) and (h)), showing the presence of layered and rocksalt phases, respectively. Panels (i) to (l) show the mesoscale structural and chemical degradation in a charged secondary NMC particle. Panel (i) shows the 3D rendering of the particle morphology with a few xz slices through a number of different positions displayed in the center. Panel (j) is an xy slice through the center of the particle. Two different types of cracks, e.g. the wide open cracks (black; red arrows in (j)) and fine cracks (gray pattern with lower contrast; green arrows in (j)), can be observed. Panel (k) is the false-colored map (colormap shown in the inset) of local Ni K-edge energy over the same xy slice in (j). The local edge energy over the fine cracks was segmented and displayed in panel (l). The scale bar in (a) is 10 nm, the ones in (i) and (j) are both 5 μm.

Mesoscale morphological defects and the crack surface chemistry. While the unwanted lattice defects formation and the local phase transition are often considered as the root causes of the cathode degradation, the structural and chemical heterogeneity at the mesoscale adds further complexity to the system26. At the mesoscale, the secondary particles of the NMC622 cathode are populated with grain boundaries and micro-porosity, which not only critically influence the electric and ionic transportation in the system, but also govern the propagation of the reaction fronts when a reaction driving force is applied externally16.

We employed nano-resolution x-ray spectro-microscopy53 to visualize the mesoscale morphological defects (i.e. micro-cracks) and the corresponding chemical responses in a charged NMC622 particle after it was cycled extensively (50 cycles with a rate of 5C). As shown in the three-dimensional (3D) rendering of the particle morphology in Figure 1i, a severe disintegration of the particle can be clearly observed. The electrochemical cycling induced disintegration of NMC secondary particle can be attributed to the repeated lattice breathing **[ref]** and SoC heterogeneity47. There are a number of factors, e.g. the cycling rate, the cycling voltage window, the environmental temperature, and the particle size and shape, which could influence the degree of the particle cracking. We refer to our recent paper for a more detailed discussion of the causes and consequences of the mesoscale cracks12.

The chemical sensitivity provided by the nano-resolution x-ray spectro-microscopy offers the opportunity to investigate the correlation between the mesoscale morphological defects and the local chemical responses. We show in Figure 1j an xy slice through the center of the particle with the corresponding edge energy map (over the Ni K-edge) displayed in Figure 1k. A close look at Figure 1j suggests that there are two types of micro-cracks co-existing in the imaged NMC622 particle. Some of the cracks are well-developed and appear to be of excellent image contrast (red arrows); while the other cracks are less visible (green arrows), likely due to the fact that they are in the early stage of the crack development and there is a significant amount of sub-pixel-level porosity caused by fine micro-cracks over the corresponding regions. These fine micro-cracks are often beyond the x-ray spectro-microscopy’s spatial resolution limit at ~30 nm . It is anticipated that these two different types of cracks could have different local chemical responses, which can be further elucidated by detailed analysis of the XANES mapping data.

The redox of Ni cation is the major charge compensation mechanism for lithium intercalation/deintercalation. As a result, the Ni K-edge energy is often used as a proxy for the local SoC. The surface of the particle and the well-developed cracks appear to be more oxidized in Figure 1k as indicated by the red contour. This is likely caused by the delithiation process, which extracts the lithium-ions from the hosting material through the reaction-active solid electrolyte interphase (SEI). The well-developed cracks facilitate the infiltration of the liquid electrolyte, activating the lithium-ion exchange at the crack surface. On the other hand, the change in the spectroscopic fingerprint over the newly developed cracks is less obvious. We extracted the cracks with weaker visibility based on the grayscales in Figure 1j and segmented the Ni valence map accordingly. As shown in Figure 1l, the newly developed cracks are scattered throughout the particle. There isn’t an obvious contrast (in terms of the Ni oxidation state) between the bulk and the cracks at their early stage of development. This is likely due to the lack of liquid electrolyte wetting at these locations.

The wetting effect of liquid electrolyte is a topic of great interest to both industry and academia54. The wettability can be influenced by the properties of the liquid electrolyte (e.g. the viscosity and surface tension) and the micro-texture of the solid electrode (e.g. the local surface curvature etc.). At the early stage of the micro-crack development, the formation of local lattice defects and phase transition could act as physical barriers that cause detouring of the lithium-ions. When the cracks are further developed, infiltration of the liquid electrolyte takes place, affecting the local lithium diffusion kinetics, and the redox events can then be initiated over the wetted crack surface.

Reaction heterogeneity at the electrode scale. The mesoscale structural and chemical complexity can be further amplified at the electrode level. In a real-life battery cathode electrode, secondary particles are embedded in the porous carbon matrix with a rather high mass loading of ~10 mg/cm2 or greater **[ref]**. Close packing of active materials is essential to ensure the desired volumetric density. In addition to accommodating the active particles, the porous carbon matrix is also responsible for providing the electric contact throughout the electrode. The liquid electrolyte soaks the porous matrix and provides an interconnected tortuous diffusion network for the lithium ions. The mismatch in the local electric and ionic conductivity, both of which could change as a function of time and position, can lead to reaction heterogeneity at the electrode scale, which is closely relevant to the real-life cell aging and even failure.

We show in Figure 2 the rendering of the x-ray phase contrast tomographic results of the NMC622 electrode that was cycled for 10 times at a rate of 5C. For penetrating the thick electrode, the x-ray imaging experiment was carried out at high energy (17 keV), which, unfortunately, sacrifices the absorption contrast and, thus, accentuates the need for the sensitivity improvement with phase contrast methodology5556. Figure 2a is an overview of the electrode (phase contrast micro tomography data), with a magnified region of interest (ROI) shown in Figure 2b and a selected slice through the center of the ROI shown in Figure 2c (70 nm pixel size). Three of the representative particles are highlighted in red (severely damaged), green (mildly damaged), and blue (least damaged). The corresponding central slices of these particles are shown in Figures 2d-2f. Further comparison of the electrode with different cycling history (10 cycles vs. 50 cycles) is shown in Figure 2g, suggesting that the particle cracking continues to develop upon electrochemical cycling.

Figure 2. Multiple length scale x-ray tomography of NMC622 electrode. Panel (a) is microtomography (0.65 μm pixel size) data of a piece of NMC electrode. Panel (b) is the 3D rendering of the nano-tomography data (100 nm pixel size) of an arbitrarily selected region of interest over the electrode, with its central slice in the lateral direction shown in panel (c). Three of the representative particles are highlighted in red (panel (d)), green (panel (e)), and blue (panel (f)). They are labeled as severely damaged, mildly damaged, and least damaged particles, respectively. The relative frequency of these three kinds of particles, which changes as a function of the cycling history, are summarized in the radar chart in panel (g). The scale bar in panel (a), (b) and (c), (d) are 150 μm, 20 μm, and 3 μm, respectively.

The x-ray phase contrast tomography data covers over a thousand active particles with spatial resolution down to ~50 nm. Such unprecedented amount of morphological details can facilitate a more detailed quantification. We show in Figures 3a-3d two lateral virtual slices (xy plane) at different z position. Figure 3a represents the slice near the top surface of the electrode (close to separator), while Figure 3b is the data near bottom surface (near the aluminum current collector). Figures 3c and 3d are the same slices with color-coding to the degree of particle fracturing. The corresponding relative probability distribution are shown in the insets in Figures 3c and 3d, respectively. It is evident in our observation that a depth-dependent particle fracturing pattern has been developed in this electrode.

To understand the chemical implications of the different degrees of morphological degradation at the top and the bottom of the electrode, we carried out surface sensitive soft x-ray absorption spectroscopic (soft XAS) measurements of the top and the bottom of the electrode. The total electron yield (TEY, probing depth at ~10 nm) and total fluorescence yield (TFY, probing depth at ~100 nm) signals are acquired over the absorption L-edges of Ni (Figures 3e and 3f), Mn, Co, and the K-edge of O (Supplementary Figures S1), respectively. In Ni rich NMC cathode, Ni’s redox reaction is the major mechanism for the charge compensation during repeated lithium (de)intercalation. We, therefore, present the Ni L-edge data in Figures 3e and 3f for in-depth discussions and leave the rest of the spectroscopic data, whose implications are less significant, in the Supplementary Information. In the TEY mode, Ni2+ component is clearly observed on both the top and bottom of the electrode (Figure 3e), suggesting that notable surface reconstruction57 happens throughout the entire electrode under fast charging conditions. The difference shown in Figure 3e indicates that the top of the electrode experiences more severe undesired local phase transition from the layered structure to a mixture of spinel and rocksalt structure. On the other hand, the bulk sensitive TFY signal shows only little difference between the top and the bottom of the electrode. This observation suggest that, at the electrode level, we do not observe significant depth heterogeneity in the SoC. While the mesoscale SoC heterogeneity could persist after long term relaxation41, it doesn’t seem to be the case at the electrode level as the charge transfer among the active particles could be relatively easy through the interconnected liquid electrolyte and conductive carbon network.

Figure 3. The heterogeneous fracturing pattern in the NMC electrode that has gone through fast cycles at a rate of 5C. Panels (a) and (c) are the same lateral slice over the particle layer that is close to the 10-cycles electrode surface (furthest from the aluminum current collector). Panels (b) and (d) are the same lateral slices over the first layer of particles close to the aluminum current collector (10-cycles electrode). The relative ratios over these two slices is shown in the corresponding pie charts. Panels (e) and (f) are the surface sensitive soft x-ray spectroscopic results over the front (red) and the back (blue) of the 10-cycles electrode in TEY and TFY modes, respectively. The comparison of the fracturing profiles of the 10-cycles (panels (g), (i), and (k)) and 50-cycles (panels (h), (j), and (l)) electrodes. Panels (g) and (h) are the depth dependence of the fracturing profile. Panels (i) and (j) are the 3D representation of the severely fractured network, with their top views shown in panels (k) and (l), respectively.

The single-voxel-thick slices shown in Figures 3a-3d cut through the particles at different depth due to the random arrangement of the particles in the electrode. For a more precise quantification of the cracking profile, here we develop a more advanced approach. As a first step, we apply mild median filtering to the 3D image for improve the signal to noise ratio before conducting the particle edge detection (Supplementary Figure S2) based on Canny edge detection algorithm58 using the FeatureJ plugin59 in ImageJ60 software. The image filtering trades the image resolution, which is less important for the purpose of automatic particle detection and segmentation, for the reduction of the noise. The detected particle boundary is then used to automatically isolate individual particles from the 3D representation of the whole electrode. We then sum the 3D volume in any given 10-microns-thick depth window in the Z direction. The projected image (Supplementary Figure S2) is then used for identification and labeling of particles based on their degree of fracturing (Supplementary Figure S3). This procedure is repeated for the data sub-volume in different Z windows. The cracking patterns’ depth profiles of a 10-cycles and a 50-cycles electrode are summarized in Supplementary Tables S1 and S2, with the plots shown in Figures 3g and 3h, respectively. The 10-cycles electrode demonstrates a clear depth dependence in its fracturing profile, in a good agreement with the soft XAS data shown in Figures 3e and 3f. The 50-cycles electrode, on the other hand, shows more severe morphological damage and, thus, breaks down the depth dependence. Generally speaking, the degree of particle fracturing is positively correlated with the degree of active material utilization. Our data in Figure 3g and 4h suggests that the electrode’s active materials at different depth contributes to the cell level chemistry differently in both time and location. In the early cycles, particles near the separator accounts for more of the charge compensation, possibly, due to their favorable lithium diffusion rates. The higher degree of reaction near the separator causes severe local degradation, which could partially deactivate the particles in this region by detaching the particles from the conductive carbon network (see Supplementary Figure S4). Similar effect is also observed in conversion type of Si anode electrode24. Subsequently, the particles that are located deeper in the electrode take over the electrochemical activities in the later cycles, making the depth dependent fracturing profile less apparent as suggested by Figure 3h.

In addition to the depth dependent fracturing profile, which is a 1D representation of the inhomogeneous degree of active material utilization at the electrode level, our imaging data could also offer valuable insights into the lateral and, more importantly, the 3D complexity. With the extraction of the 3D centroid coordinates of all the severely damaged particles, here we develop a method to extract the network that connects all these particles based on their spatial distribution. For every severely damaged particle, our method searches for three of its nearest particles of the same kind and uses color coded bounds to connect them (see Figures 3i to 3l and the relative color map in the inset of Figure 3k). As the degree of particle cracking is positively correlated to the degree of active particle usage, we conjecture that the extracted network represents the 3D distribution of the local current density. The perspective and the top views of the networks for 10-cycles and 50-cycles electrodes are shown in Figures 3i, 3j and 3k, 3l, respectively. After the first 10 cycles, the heavily used particles are sparsely scattered throughout the 3D volume of the electrode. This is likely due to their favorable and balanced electric and ionic conductivity. After 50 cycles, this network becomes denser because the activation of more particles upon prolonged battery operation. The particle to particle distance clearly becomes smaller as it can be seen in the topological representations in Figures 3j and 3l.

**Discussion**

It is generally appreciated that the electro-chemo-mechanical processes in lithium ion batteries are ubiquitous across a wide range of length scales. While the transformation in the lattice structure at the atomic scale is often regarded as the root causes of a range of degradation phenomenon, the complexity is further amplified at the mesoscale (within the secondary particles) and the macroscale (at the electrode level). To truly understand the intertwined, heterogeneous and multiscale electro-chemo-mechanical coupling effects in composite battery electrodes, imaging techniques that can resolve features at different length scales are often combined. More specifically, it is very desirable to conduct electrode scale imaging with nanometric resolution. Such dataset could offer unprecedented amount of structural information, which could facilitated sophisticated and valuable statistical analysis.

In this work, we started at the atomic scale and used TEM to visualize the coexisting layered and rocksalt lattice structures over a cracked area. The local lattice deformation can serve as nucleation points for further development of the structural defects. Coupled with nanoscale x-ray spectro-microscopy and electron microscopy, we then reconstruct the mesoscale morphological and chemical transformations in the NMC622 secondary particles under fast charging conditions. We quantify the electrode and particle morphology and, subsequently, elucidate two stages of the chemomechanical transformation at the secondary particle level: 1) the host material’s local lattice structural transition and 2) liquid electrolyte infiltration that forms new diffusion pathway for lithium ions. Finally, we conducted hard x-ray phase contrast nano-tomography of the cathode electrode with nanometric spatial resolution. We extracted the complicated morphological degradation profile across the complete electrode slab and presented the depth dependent trend of particle fracturing as well as its lateral complexity. We developed a method to reconstruct the 3D topological representation of the local current density distribution. Our results suggest that the  electrode’s active materials contributes to the cell level chemistry differently in time and location. The presented findings and their implications offer insights into designing chemomechanically robust battery particles and formulating fast charge capable electrodes.

# Title.

Hierarchically Heterogeneous Electro-Chemo-Mechanical Coupling Effects in Composite Battery Electrodes

# Authors.

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# Abstract.

Multiscale electro-chemo-mechanical interplay governs the local structural and chemical evolution, which is fundamental to the global electrochemical properties in batteries. Cycling batteries under kinetically limited conditions induces state of charge (SoC) heterogeneity, builds up mechanical stress, and provokes morphological breakdown. These processes prevail in most battery electrodes and ultimately determine the device-level battery performance. Understanding these processes at many length scales can inform designing materials and electrodes that allow for large areal capacity, fast charging, and effective utilization of active compounds. In this study, we investigated the electro-chemo-mechanical interplay in layered oxide cathodes using hard x-ray phase contrast tomography that simultaneously covers over a thousand active particles with nanometric spatial resolution, enabling an unprecedented statistical analysis that reveals the electrode-level SoC analysis. Coupled with nanoscale x-ray spectro-microscopy and electron microscopy, we reconstruct the morphological and chemical transformations in the layered oxide cathode under fast charging conditions and, subsequently, elucidate two stages of the chemomechanical transformation at the single particle level: 1) the host material’s local lattice structural transition and 2) liquid electrolyte infiltration that forms new diffusion pathway for lithium ions. Resulted from the evolving mismatch between the local electrical and ionic conductivity, there is a depth-dependent chemomechanical response at the electrode level. The particles in the vicinity of the separator undergo more severe fracturing than those close to the current collector. We also report the lateral reaction heterogeneity at the electrode level, suggesting that the degree of local electrode utilization develops as a function of position and time. Our results offer insights into designing chemomechanically robust battery particles and formulating fast charge capable electrodes.

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# Methods.

**Transmission electron microscopy.** The TEM study was performed using a JOEL-2100 S/TEM microscope operated at 200 kV. The FFT and IFFT images were carried out using Gatan DigitalMicrograph software.

**Nano-resolution x-ray spectro-microscopy.**We conducted x-ray spectro-microscopic scan of the charged Li0.5Ni0.6Mn0.2Co0.2O2 particles using the transmission x-ray microscopy (TXM) at beamline 6-2C of Stanford Synchrotron Radiation Lightsource of the SLAC National Accelerator Laboratory. The powder sample was loaded into a quartz capillary (100 microns in diameter and 10 microns in wall thickness) for imaging under the inert gas environment (slow and steady helium flow). The typical exposure time for single images is 0.5 second. The nominal spatial resolution of this instrument is ~30 nm. More details of the synchrotron beamline configuration and the concept of x-ray spectro-microscopy and spectro-tomography can be found elsewhere53,61. In the 3D spectro-microscopic scan, the energy of the incident x-rays is scanned from 8200 eV to 8630 eV to cover the absorption K-edges of Ni, in which the tomography was performed at 68 different energy points. In the near edge region (8330 eV to 8355 eV), we chose the energy step at 1 eV to ensure sufficient energy resolution. The pre-edge and post-edge regions were scanned with larger energy steps of 10 eV to cover a relatively wide energy window for normalization of the spectra. The TXM data processing was performed using an in-house developed software package known as TXM-Wizard62. The segmentation and visualization of the 3D data were carried out using a commercial software package known as Avizo.

**Soft x-ray absorption spectroscopy (XAS).** The soft XAS measurements were carried out at the elliptically polarizing undulator (EPU) beamline 13-3 of the Stanford Synchrotron Radiation Lightsource (SSRL). The charged NMC622 electrodes were mounted in a ultra-high vacuum (UHV) chamber for the measurement. For comparison of the top and bottom of the electrode, the aluminum current collector was carefully peeled off and two pieces of the electrode were mounted facing up and down, respectively. The samples were handled in a Argon-filled glove box to minimize the air exposure. The vertically polarized x-ray (sigma-polarization) was used. The incident beam was monochromatized by a 1100-lines/mm spherical grating monochromator (SGM), and its angle was set at 30 degrees from the sample surface. Both fluorescence yield (FY) and total electron yield (TEY) signals were acquired simultaneously to probe the depth-dependent spectroscopic fingerprints. All the XAS spectra were normalized by the intensity of the incoming x-ray beam that was concurrently measured as a drain current on an electrically isolated gold-coated mesh. A linear background, which was determined by the intensity of the pre-edge region, was subtracted from the data.

**X-ray phase contrast tomography.**For the morphological study of the micro-scale structures of the Li battery cathode, synchrotron hard x-ray tomography based on phase contrast with high spatial resolution becomes our method of choice. Holotomography measurements of the samples were conducted at the ID16A-NI nano-imaging beamline63 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. This beamline offers a unique combination of nanofocus (~20nm) and a very high photon flux (up to 1012 photons/s at ΔE/E~1%). Two pairs of multilayer coated Kirkpatrick-Baez (KB) optics are used to focus the x-rays at 17 keV and 33.6 keV respectively. This experiment were performed at 17 keV. Besides the benefits of the ability to perform nano-tomography with a high energy, the magnifying geometry of the cone beam also allows large field of view (FOV) with 100 nm and 70 nm voxel size. Due to free space propagation of the x-ray beam, the contrast in the images is dominated by phase contrast, related to the real part of the complex refractive index, which is determined by the electron density of the material. By measuring the Fresnel diffraction patterns at different effective propagation distances, the phase maps of the sample can be retrieved via holographic reconstruction, the so called phase retrieval procedure64 implemented using GNU Octave software. In our measurements, the sample was placed downstream of the KB focus and magnified radiographs were recorded onto an x-ray detector using a FReLoN charged-coupled device (CCD) with a 2048x2048 binned pixels array. For every tomography scan, 1500 projections were acquired with 0.2s exposure time at 100 nm, or 70nm pixel size. Tomographies at four different focus to sample distances were acquired to complete one holotomography scan, which were subsequently used for phase retrieval. The 2D phase maps retrieved from the angular projections were then used as input for a tomographic reconstruction based on the filtered back projection (FBP) algorithm method (ESRF PyHST software package)65. The reconstructed 3D volumes are proportional to the changes in electron density of the sample.

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# References.

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## Figures

High-resolution image files are not required at initial submission, but please ensure that images are of sufficient resolution for referees to properly assess the data.

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