

Mapping Lattice Distortions in LiNi_{0.5}Mn_{1.5}O₄ Cathode Materials

Stephanie L. Spence, Anyang Hu, Meng Jiang, Zhengrui Xu, Zhijie Yang, Muhammad Mominur Rahman, Luxi Li, Yong S. Chu, Xianghui Xiao, Xiaojing Huang,* and Feng Lin*



variations, which may indicate differences in phase distributions. Bragg coherent diffraction is also used to observe phase heterogeneities in single grains. Lattice distortions and structural defects could shut down or open up local diffusion pathways for lithium ions, making lithium ion diffusion more complicated and potentially more tortuous than that in a perfect LNMO lattice.

espite the prevalence of lithium-ion batteries, continued improvements in electrochemical performance, safety, and lifetime are required to expand applications to larger scales, including electric vehicles and grid energy storage.¹ Spinel LiNi_{0.5}Mn_{1.5}O₄ (LNMO) is a promising high-voltage cathode material for lithium-ion batteries because of its high energy and high power. LNMO has a working potential of 4.7–4.9 V vs Li/Li⁺, a theoretical capacity of 148 mAh/g, and a theoretical energy density of 650 Wh/kg at the materials level.^{2–4} Three-dimensional lithium-ion pathways present in the spinel framework allow for facile ion transport and can potentially enable high rate performance.⁵

 \sim 22% of Mn³⁺, respectively. Differences in properties between the two particles give rise to different distributions of lattice

LNMO can adopt two crystallographic structures: an ordered primitive simple cubic structure with the $P4_332$ space group where Mn and Ni ions occupy 12b and 4a octahedral sites, respectively, and a disordered face-centered cubic structure with the $Fd\overline{3}m$ space group where Mn and Ni ions are randomly arranged on the 16d octahedral sites.⁶ The formation of the disordered spinel phase requires higher synthesis temperatures than the ordered phase and is often associated with the loss of oxygen from the material lattice, as well as the reduction of a small amount of Mn⁴⁺ to Mn³⁺ for charge compensation.^{6–8} Rock-salt Li_xNi_{1-x}O-type impurity formation, Jahn–Teller distortion, and transition-metal dis-

solution suggest the presence of Mn^{3+} is disadvantageous to the application of LNMO.⁹ However, a small amount of Mn^{3+} has been reported to be beneficial to performance.^{10,11} An additional voltage plateau is observed in the charge/discharge curve of disordered LNMO at ~4.0 V due to the Mn^{3+}/Mn^{4+} redox, whereas Ni is the only redox-active transition metal in the fully ordered material.⁶

1 µm

The relationship between structural disordering and Mn³⁺ content is not straightforward; therefore, much effort in LNMO research has attempted to gain further understanding between the two.^{10,12} Thus far, a quantitative relationship is still not available. Efforts have been undertaken to control the global structural ordering of LNMO and correlate properties to electrochemical performance.^{10,12–16} Careful synthesis can be used to control the formation of LNMO with either ordered or disordered structures or to minimize impurity phases. Practically, it is difficult to obtain pure disordered or ordered phase LNMO. In reality, varying degrees of cation ordering are likely

Received: December 17, 2021 Accepted: January 13, 2022 Published: January 18, 2022







Figure 1. Bragg coherent diffraction patterns of octahedral LNMO crystals at the (111) Bragg position illustrating the coexistence of two phases. The color bar represents the diffraction intensity (white, highest intensity; black, lowest intensity).

present throughout local regions of individual particles in the synthesized materials.^{17,18} Factors such as particle size and facet orientation may influence how cation ordered regimes distribute in single-particle samples. The presence of phase and chemical heterogeneities can exacerbate the degradation of Lion cathode materials upon cycling; therefore, understanding such heterogeneities is vital for improving stability and performance.¹⁹⁻²¹

We hypothesize that the distribution of Mn^{3+} in disordered LNMO materials may be heterogeneous and that the extent of structural ordering varies between samples, depending on the synthesis conditions. The larger ionic radius of Mn^{3+} compared to Mn^{4+} can increase lattice spacing and internal strain within particles.¹² Changes in lattice spacing have been used to identify phase heterogeneity in $LiMn_2O_4$ during lithiation.²² We, therefore, propose significant phase heterogeneity exists within the particles of LMNO prepared under different synthesis conditions and containing different quantities of Mn^{3+} .

Herein, we investigate structural defects and lattice distortion at the individual particle scale for octahedral and plate-like LNMO samples using high-spatial-resolution nanodiffraction mapping techniques to demonstrate that lattice distortion can provide significant insights into understanding phase heterogeneity in single-crystal LNMO. Combining techniques such as powder X-ray diffraction, X-ray absorption near-edge structure (XANES) analysis, Bragg coherent X-ray diffraction, and nanodiffraction, we observe differences in electronic states and structural heterogeneities between two LNMO samples. Continued exploration of the structural characteristics of LNMO samples of various morphologies and Mn oxidation states can provide valuable insights into the relationship between several materials' properties, as well as the influence on the resultant electrochemical performance.

The octahedral LNMO sample was prepared at 650 °C using eutectic LiCl:KCl as a molten salt flux, while the plate sample was prepared at 750 °C in pure LiCl flux (see the Supporting Information for experimental details).^{23,24} Samples were thoroughly characterized through ensemble-averaged techniques, which revealed that a mixture of ordered and disordered spinel phases was present in both samples (see the Supporting Information, Figures S1–S3 for a detailed discussion). The Mn³⁺ content was estimated for each sample from the electrochemical discharge profiles and calculated to be 5.7% and 22.0% for the octahedral and plate samples, respectively. Ensemble-averaged characterization techniques cannot distinguish local structural variations and, therefore,

cannot provide a full picture of the materials' properties; highspatial-resolution diffraction is necessary to identify the distribution of the different phase regions within the particles.

Investigating Structure through Bragg Coherent Xray Diffraction. Bragg coherent X-ray diffraction relies on coherent X-ray interference and can be used to study defects and strain in single-crystal materials.²⁵ Bragg coherent diffraction imaging has been used to study dislocation evolution in LNMO under operating conditions.²⁶ Bragg coherent X-ray diffraction is used to measure the 2D diffraction patterns of the pristine LNMO material. Particles with twophase coexistence are observed as in Figure 1. The two bright Bragg peaks appear at different diffraction angles, indicating that there are two phases. The fringes about the Bragg center show the sharp surface structure in these local domains (or primary particles). The interference between the two Bragg spots indicates that the diffraction from two phases comes from the same particle. This behavior was also observed previously by Singer et al. during the two-phase transformation of LNMO spinel material during the charging process.²⁷ This observation illustrates that large structural heterogeneities exist within individual particles of LNMO. Analysis of this Bragg diffraction pattern suggests the complexity of the LNMO system. To determine the origin of such complexity, we next utilize nanodiffraction techniques.

Investigating Lattice Distortion Heterogeneity through Nanodiffraction. Both Mn^{3+} and cation disorder have been found to increase with increased synthesis temperatures above 700 °C.^{24,28} The presence of both Mn^{4+} and Mn^{3+} unevenly distributed can lead to strain and lattice parameter distortion within particles due to the differences in ionic radii of Mn, where more Mn^{3+} will lead to increased lattice spacing. Operando X-ray diffraction computed tomography (XRD-CT) has been used to spatially quantify inter- and intraparticle crystallographic heterogeneities in $Li_xMn_2O_4$ through tracking lattice parameter variation.²² Through highspatial-resolution nanodiffraction, we can observe the heterogeneity and distribution of lattice distortions in individual LNMO particles.

For the octahedral sample, the shape of the target particle for nanodiffraction was reconstructed by three-dimensional X-ray fluorescence tomography (Figure S4a and Movie S1). While our material is primarily single-crystal, the target particle selected contains multiple intergrown crystals. The unique features of the selected particle can provide additional insight into the structural parameters near the domain boundaries within the particles. X-ray fluorescence mapping shows the elemental distribution of Ni and Mn in the particle, which are relatively homogeneous (Figure S4b and Movie S2).

The nanodiffraction technique with a scanning hard X-ray beam was used to examine lattice defects in the LNMO samples. A schematic of the experimental setup of the hard Xray nanoprobe (HXN) is illustrated in Figure 2a. In the setup,



Figure 2. (a) Schematic illustration of hard X-ray nanoprobe experimental setup. Inset: SEM images of octahedral and plate target particles for HXN measurements. (b) 2D raster mapping of the octahedral sample particle as the particle is rocked over θ . The pixel size for the diffraction images is 50 × 50 nm². (c) Diffraction geometry and lattice distortions of *d*-spacing, lattice bending in the *z*-axis, and lattice twisting in the *y*-axis extracted from data.

the sample was illuminated with X-rays focused to a ~30 nm spot size, the crystal orientation was adjusted to excite a Bragg diffraction, and a pixel-array detector was oriented to record the diffracted pattern from each scan position allowing for spatially resolved diffraction measurements.²⁹ The sample is rocked over a two-degree range in the vicinity of the selected Bragg peak while a 2D raster scan with 50 nm step size is conducted at each rocking angle, resulting in the mapping shown in Figure 2b for the octahedral sample. The final image resolution is a convolution between the beam profile and the image pixel size $(50 \times 50 \text{ nm}^2)$. Rocking curves at each Bragg position are shown in Movies S3-S8. Scanning probe measurements were conducted in the on-the-fly scan mode to mitigate unnecessary radiation to the sample. For each peak, lattice distortions can be extracted by tracking the location of the Bragg diffraction peak over the rocking angular range at each scanned position.²⁹ The rocking-curve nanodiffraction measurement collects the 3D Bragg diffraction pattern at each scanned point. The position of the 3D diffraction pattern can be decomposed into three orthogonal directions, which

include two components on the plane defined by the corresponding Debye–Scherrer ring (perpendicular and tangential to the ring direction) and one component perpendicular to that plane. As shown in Figure 2*c*, these three components represent the *d*-spacing, lattice bending in the *z*-axis, and lattice twisting in the *y*-axis, respectively.

The increase in lattice variation for $\Delta d/d$ in the measured peaks can be attributed to changing *d*-spacing in the spinel phases and/or internal strain, while changes in bending *y*-axis and twisting *z*-axis arise from out-of-plane distortions as the crystals are not completely flat. The results of the nanodiffraction mapping for the octahedral sample at (311), (331), and (333) Bragg locations are shown in Figure 3. Visually,



Figure 3. Lattice distortion mapping of octahedral LNMO at (311), (331), and (333) Bragg positions. Red arrows indicate direction of radial increase in distortion intensity.

there are obvious heterogeneities in each map, which show the relative distribution of the total distortions present for each measurement. The change in *d*-spacing is significant near the particle surfaces for the (311) and (333) peaks (Figure S5). An increase in disorder near the particle surfaces can be rationalized by the surface oxygen loss and/or Ni-rich impurity formation which occurs primarily on the surface and can accompany the reduction of Mn.³⁰ At each measured peak, both bending y-axis and twisting z-axis maps show abrupt changes at a boundary within the particle, suggesting different domains with different crystal orientations or rotations. The radial-like change in distortion intensity indicates the likely presence of a screw dislocation (see arrows in Figure 3). We observe components of the dislocation in both the y and zdirections, with a larger contribution from the z-axis. From the strain map, we see these domains have similar *d*-spacing but are rotated.

The plate sample was measured at the (111), (311), and (222) Bragg positions, and the nanodiffraction mapping is summarized in Figure 4. The differences in the shape of the maps for the (111) and (311) compared to the (222) positions of the plate sample indicate there are two distinct grains or crystal domains within the particle with slightly different orientations. Overlaying the images results in the full shape of the target particle (Figure S6). Similar to the octahedral sample, a large-scale heterogeneity for rotation was observed in the *y*- and *z*-axes. All distortions are more prominent toward the boundary of the two large particle grains (Figure S6 and



Figure 4. Lattice distortion mapping of plate LNMO at (111), (311), and (222) Bragg positions.

S7). The plate sample also contains several, small local domains with abrupt changes in the distortion intensities.

For each map, a pixel intensity analysis was performed, resulting in histograms illustrating the relative distribution of the distortions (Figure 5). For each plot, a larger variation (or standard deviation) corresponds to a larger overall distortion. The distortion variation appears facet-dependent. Figure S8 shows schematics of the atomic arrangements at each crystal plane. When the measurements at the (311) plane for the octahedral and plate samples are compared, the plate samples show a slightly wider distribution in the variations with a larger skewing toward increased *d*-spacing, bending *y*-axis, and twisting *z*-axis values. The (333) plane of the octahedral and the (111) plane of the plate show distribution behavior similar to their corresponding (311) planes. Finally, the (331) plane of the octahedral sample and (222) plane of the plate sample show the smallest relative distortions.

The average *d*-spacings for the (311) plane of the octahedral and the plate samples were calculated as 0.2469 and 0.2548 nm, respectively. This is consistent with the expectation that the plate sample containing more overall Mn^{3+} (with increased ionic radius) would contain larger *d*-spacing. We speculate that the areas with increased relative *d*-spacing in the distortion maps correlate with regions that contain more Mn^{3+} . There is a slightly wider degree of *y*-bending and *z*-twisting variation for the plate sample, which may be due to more Mn^{3+} or the presence of multiple domains with slightly different orientations. Ultimately, we observe inherent distortions in the two samples prepared under different synthesis conditions with octahedral and plate-like morphologies. The significant lattice distortion heterogeneity in both samples is indicative of phase heterogeneity which may be induced by an uneven distribution of Mn^{3+} .

In conclusion, lattice distortions were investigated in LNMO cathode materials with octahedral and plate-like morphologies. A mixed Mn oxidation state was present in pristine materials synthesized via a molten salt synthesis route. The total Mn^{3+} contents were estimated through electrochemical testing to be ~6% and ~22% for octahedral and plate materials, respectively. Nanodiffraction analysis illustrated large heterogeneities for lattice distortions in single particles, with greater distortions at particle surfaces; a screw dislocation defect in the octahedral particle; and multiple, small crystal domains in the plate particle. Large structural and phase heterogeneities are therefore likely present in the samples.

This preliminary study serves as a proof of concept for analyzing the variations in lattice distortion as a proxy for understanding phase heterogeneity in spinel LNMO. The high power density of LNMO make it an attractive cathode material, but its commercialization is hindered in part by its complex phase transition behavior. Lattice distortions and structural defects could shut down or open up local diffusion pathways for lithium ions, making the lithium ion diffusion more complicated and potentially more tortuous than that in a perfect LNMO lattice. Understanding the inherent structural and defect properties in the material under various synthesis conditions can help inform synthetic efforts to mitigate large heterogeneities, as well as provide a rational for performance degradation. Future studies expanding on this work can be undertaken to fully relate the distribution of lattice distortion to samples with various materials properties and at different states of charge. Such studies can begin to elucidate the relationship between physical properties in cathode materials that can then be used to help design and optimize materials for high-performance lithium-ion batteries.



Figure 5. Lattice variation histograms based on pixel intensity analysis for the (a) octahedral and (b) plate particle samples.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c02759.

Experimental method; ensemble-averaged characterization results and discussion; Raman spectra of LNMO; lattice variation depth profile for octahedral particle; overlay of nanodiffraction maps for plate particle; lattice variation depth profile for plate particle; schematic of atomic arrangements at different surface orientations (PDF)

Movie S1: octahedral target particle 3D tomography reconstruction (AVI)

Movie S2: octahedral target particle X-ray fluorescence mapping slices (AVI)

Movie S3: HXN 2D raster mapping of the octahedral particle as a function of θ at (311) Bragg position (AVI) Movie S4: HXN 2D raster mapping of the octahedral particle as a function of θ at (333) Bragg position (AVI) Movie S5: HXN 2D raster mapping of the octahedral particle as a function of θ at (331) Bragg position (AVI) Movie S6: HXN 2D raster mapping of the plate particle as a function of θ at (111) Bragg position (AVI) Movie S7: HXN 2D raster mapping of the plate particle as a function of θ at (111) Bragg position (AVI)

as a function of θ at (311) Bragg position (AVI) Movie S8: HXN 2D raster mapping of the plate particle as a function of θ at (222) Bragg position (AVI)

AUTHOR INFORMATION

Corresponding Authors

- Xiaojing Huang National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, United States; Email: xjhuang@bnl.gov
- Feng Lin Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States; orcid.org/ 0000-0002-3729-3148; Email: fenglin@vt.edu

Authors

- Stephanie L. Spence Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States; orcid.org/0000-0002-7039-3554
- Anyang Hu Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States; Occid.org/ 0000-0003-0669-9126
- Meng Jiang Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States
- Zhengrui Xu Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States; Occid.org/ 0000-0002-6549-4713
- Zhijie Yang Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States
- Muhammad Mominur Rahman Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, United States; orcid.org/0000-0001-6814-456X

Luxi Li – Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois 60439, United States

- Yong S. Chu National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, United States
- Xianghui Xiao National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsenergylett.1c02759

Author Contributions

F.L. conceived and led the study. S.L.S. and F.L. designed the experiments. S.L.S. performed materials synthesis, electrochemical measurements, and Raman measurements. Z.X. and Z.Y. collected synchrotron XAS measurements. M.M.R. performed SEM and synchrotron XRD measurements. L.L., S.L.S., and A.H. performed BCDI measurements. S.L.S., M.J., Y.S.C., and X.H. performed HXN measurements and assisted with data analysis. X.X. participated in scientific discussion and assisted with data analysis. S.L.S. and F.L. wrote the manuscript with feedback from all coauthors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by the National Science Foundation under Grant No. DMR-1832613. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. This research used 3-ID of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. The authors acknowledge Dr. Chunguang Kuai for assistance with synchrotron XRD measurements and Dr. Chengjun Sun for assistance with XANES measurements.

REFERENCES

(1) Armand, M.; Tarascon, J. M. Building Better Batteries. *Nature* **2008**, 451 (7179), 652–657.

(2) Patoux, S.; Daniel, L.; Bourbon, C.; Lignier, H.; Pagano, C.; Le Cras, F.; Jouanneau, S.; Martinet, S. High Voltage Spinel Oxides for Li-Ion Batteries: From the Material Research to the Application. *J. Power Sources* **2009**, *189* (1), 344–352.

(3) Santhanam, R.; Rambabu, B. Research Progress in High Voltage Spinel LiNi0.5Mn1.5O4Material. *J. Power Sources* **2010**, *195* (17), 5442–5451.

(4) Zhong, Q.; et al. Synthesis and Electrochemistry of LiNi_xMn_{2-x}O₄. J. Electrochem. Soc. **1997**, 144 (1), 205.

(5) Huang, Y.; Dong, Y.; Li, S.; Lee, J.; Wang, C.; Zhu, Z.; Xue, W.; Li, Y.; Li, J. Lithium Manganese Spinel Cathodes for Lithium-Ion Batteries. *Adv. Energy Mater.* **2021**, *11*, 2000997.

(6) Kim, J. H.; Myung, S. T.; Yoon, C. S.; Kang, S. G.; Sun, Y. K. Comparative Study of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathodes Having Two Crystallographic Structures: Fd3m and P4332. *Chem. Mater.* **2004**, *16* (5), 906–914.

(7) Kunduraci, M.; Al-Sharab, J. F.; Amatucci, G. G. High-Power Nanostructured $\text{LiMn}_{2-x}\text{Ni}_xO_4$ High-Voltage Lithium-Ion Battery Electrode Materials: Electrochemical Impact of Electronic Conductivity and Morphology. *Chem. Mater.* **2006**, *18* (15), 3585–3592. (8) Kim, S.; Hegde, V. I.; Yao, Z.; Lu, Z.; Amsler, M.; He, J.; Hao, S.; Croy, J. R.; Lee, E.; Thackeray, M. M.; Wolverton, C. First-Principles Study of Lithium Cobalt Spinel Oxides: Correlating Structure and Electrochemistry. *ACS Appl. Mater. Interfaces* **2018**, *10* (16), 13479–13490.

(9) Liu, G. Q.; Wen, L.; Wang, X.; Ma, B. Y. Effect of the Impurity $Li_xNi_{1-x}O$ on the Electrochemical Properties of 5 v Cathode Material LiNi0.5Mn 1.5O4. *J. Alloys Compd.* **2011**, 509 (38), 9377–9381.

(10) Duncan, H.; Hai, B.; Leskes, M.; Grey, C. P.; Chen, G. Relationships between Mn^{3+} Content, Structural Ordering, Phase Transformation, and Kinetic Properties in LiNi_x $Mn_{2-x}O_4$ Cathode Materials. *Chem. Mater.* **2014**, *26* (18), 5374–5382.

(11) Moorhead-Rosenberg, Z.; Huq, A.; Goodenough, J. B.; Manthiram, A. Electronic and Electrochemical Properties of $Li_{1-x}Mn_{1.S}Ni_{0.5}O_4$ Spinel Cathodes As a Function of Lithium Content and Cation Ordering. *Chem. Mater.* **2015**, *27* (20), 6934–6945.

(12) Xiao, J.; Chen, X.; Sushko, P. V.; Sushko, M. L.; Kovarik, L.; Feng, J.; Deng, Z.; Zheng, J.; Graff, G. L.; Nie, Z.; Choi, D.; Liu, J.; Zhang, J.-G.; Whittingham, M. S. High-Performance LiNi_{0.5}Mn_{1.5}O₄ Spinel Controlled by Mn ³⁺ Concentration and Site Disorder. *Adv. Mater.* **2012**, *24* (16), 2109–2116.

(13) Cabana, J.; Casas-Cabanas, M.; Omenya, F. O.; Chernova, N. A.; Zeng, D.; Whittingham, M. S.; Grey, C. P. Composition-Structure Relationships in the Li-Ion Battery Electrode Material LiNi_{0.5}Mn_{1.5}O₄. *Chem. Mater.* **2012**, *24* (15), 2952–2964.

(14) Liu, H.; Zhang, X.; He, X.; Senyshyn, A.; Wilken, A.; Zhou, D.; Fromm, O.; Niehoff, P.; Yan, B.; Li, J.; Muehlbauer, M.; Wang, J.; Schumacher, G.; Paillard, E.; Winter, M.; Li, J. Truncated Octahedral High-Voltage Spinel LiNi_{0.5}Mn_{1.5}O₄ Cathode Materials for Lithium Ion Batteries: Positive Influences of Ni/Mn Disordering and Oxygen Vacancies. J. Electrochem. Soc. **2018**, 165 (9), A1886–A1896.

(15) Casas-Cabanas, M.; Kim, C.; Rodríguez-Carvajal, J.; Cabana, J. Atomic Defects during Ordering Transitions in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and Their Relationship with Electrochemical Properties. *J. Mater. Chem. A* **2016**, *4* (21), 8255–8262.

(16) Hong, S. K.; Mho, S. II; Yeo, I. H.; Kang, Y.; Kim, D. W. Structural and Electrochemical Characteristics of Morphology-Controlled Li[Ni_{0.5} $Mn_{1.5}$]O₄ Cathodes. *Electrochim. Acta* **2015**, *156*, 29–37.

(17) Aktekin, B.; Valvo, M.; Smith, R. I.; Sørby, M. H.; Lodi Marzano, F.; Zipprich, W.; Brandell, D.; Edström, K.; Brant, W. R. Cation Ordering and Oxygen Release in $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}O_{4-y}$ (LNMO): In Situ Neutron Diffraction and Performance in Li Ion Full Cells. *ACS Appl. Energy Mater.* **2019**, *2* (5), 3323–3335.

(18) Kim, J. H.; Huq, A.; Chi, M.; Pieczonka, N. P. W.; Lee, E.; Bridges, C. A.; Tessema, M. M.; Manthiram, A.; Persson, K. A.; Powell, B. R. Integrated Nano-Domains of Disordered and Ordered Spinel Phases in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for Li-Ion Batteries. *Chem. Mater.* **2014**, 26 (15), 4377–4386.

(19) Tian, C.; Xu, Y.; Nordlund, D.; Lin, F.; Liu, J.; Sun, Z.; Liu, Y.; Doeff, M. Charge Heterogeneity and Surface Chemistry in Polycrystalline Cathode. *Materials. Joule* **2018**, *2* (3), 464–477.

(20) Kuppan, S.; Xu, Y.; Liu, Y.; Chen, G. Phase Transformation Mechanism in Lithium Manganese Nickel Oxide Revealed by Single-Crystal Hard X-Ray Microscopy. *Nat. Commun.* **201**7, *8*, 14309.

(21) Xu, Y.; Hu, E.; Zhang, K.; Wang, X.; Borzenets, V.; Sun, Z.; Pianetta, P.; Yu, X.; Liu, Y.; Yang, X. Q.; Li, H. In Situ Visualization of State-of-Charge Heterogeneity within a $LiCoO_2$ Particle That Evolves upon Cycling at Different Rates. *ACS Energy Lett.* **2017**, *2* (5), 1240–1245.

(22) Finegan, D. P.; Vamvakeros, A.; Tan, C.; Heenan, T. M. M.; Daemi, S. R.; Seitzman, N.; Di Michiel, M.; Jacques, S.; Beale, A. M.; Brett, D. J. L.; Shearing, P. R.; Smith, K. Spatial Quantification of Dynamic Inter and Intra Particle Crystallographic Heterogeneities within Lithium Ion Electrodes. *Nat. Commun.* **2020**, *11* (1), 631.

(23) Hai, B.; Shukla, A. K.; Duncan, H.; Chen, G. The Effect of Particle Surface Facets on the Kinetic Properties of $LiMn_{1.5}Ni_{0.5}O_4$ Cathode Materials. J. Mater. Chem. A 2013, 1 (3), 759–769.

(24) Spence, S. L.; Xu, Z.; Sainio, S.; Nordlund, D.; Lin, F. Tuning the Morphology and Electronic Properties of Single-Crystal $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$: Exploring the Influence of LiCl–KCl Molten Salt Flux Composition and Synthesis Temperature. *Inorg. Chem.* **2020**, *59*, 10591–10603. (25) Li, L.; Xie, Y.; Maxey, E.; Harder, R. Methods for Operando Coherent X-Ray Diffraction of Battery Materials at the Advanced Photon Source. *J. Synchrotron Radiat.* **2019**, *26* (1), 220–229.

(26) Ulvestad, U.; Singer, A.; Clark, J. N.; Cho, H. M.; Kim, J. W.; Harder, R.; Maser, J.; Meng, Y. S.; Shpyrko, O. G. Topological Defect Dynamics in Operando Battery Nanoparticles. *Science* (80-.) **2015**, 348 (6241), 1344–1347.

(27) Singer, A.; Ulvestad, A.; Cho, H. M.; Kim, J. W.; Maser, J.; Harder, R.; Meng, Y. S.; Shpyrko, O. G. Nonequilibrium Structural Dynamics of Nanoparticles in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ cathode under Operando Conditions. *Nano Lett.* **2014**, *14* (9), 5295–5300.

(28) Song, J.; Shin, D. W.; Lu, Y.; Amos, C. D.; Manthiram, A.; Goodenough, J. B. Role of Oxygen Vacancies on the Performance of $\text{Li}[\text{Ni}_{0.5-x}\text{Mn}_{1.5+x}]O_4$ (x = 0, 0.05, and 0.08) Spinel Cathodes for Lithium-Ion Batteries. *Chem. Mater.* **2012**, *24* (15), 3101–3109.

(29) Hong, Y. S.; Huang, X.; Wei, C.; Wang, J.; Zhang, J. N.; Yan, H.; Chu, Y. S.; Pianetta, P.; Xiao, R.; Yu, X.; Liu, Y.; Li, H. Hierarchical Defect Engineering for $LiCoO_2$ through Low-Solubility Trace Element Doping. *Chem.* **2020**, *6* (10), 2759–2769.

(30) Chen, Y.; Sun, Y.; Huang, X. Origin of the Ni/Mn Ordering in High-Voltage Spinel LiNi_{0.5}Mn_{1.5}O₄: The Role of Oxygen Vacancies and Cation Doping. *Comput. Mater. Sci.* **2016**, *115*, 109–116.

Recommended by ACS

Reversible and Irreversible Redox Processes in Li-Rich Layered Oxides

Michael Merz, Karin Kleiner, *et al.* DECEMBER 09, 2021 CHEMISTRY OF MATERIALS

READ 🗹

Highly Oriented {010} Crystal Plane Induced by Boron in Cobalt-Free Li- and Mn-Rich Layered Oxide

Daqiang Wang, Xiaodong Guo, et al.

JANOART 03, 2022	
ACS APPLIED MATERIALS & INTERFACES	READ 🗹

Kinetic Rejuvenation of Li-Rich Li-Ion Battery Cathodes upon Oxygen Redox

Jinhyuk Lee, Ju Li, *et al.* JULY 24, 2020

ACS APPLIED ENERGY MATERIALS READ

Phase Compatible NiFe₂O₄ Coating Tunes Oxygen Redox in Li-Rich Layered Oxide

Jiming Peng, Zaiping Guo, et al. JUNE 24, 2021 ACS NANO

READ 🗹

Get More Suggestions >