## Resolving Charge Distribution for Compositionally Heterogeneous Battery Cathode Materials

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impose a clear effect on the Ni oxidation. The resulting material delivers excellent reversible capacity, rate capability, and cycle life at high operating voltages. Engineering Ni/Mn/Co distribution in NMC particles may provide a path toward controlling the charge distribution and thus chemomechanical properties of polycrystalline battery particles.

**KEYWORDS:** Polycrystalline, NMC cathode, heterogeneity, charge distribution, local stoichiometry

#### INTRODUCTION

Understanding charge mechanisms represents one of the most critical research directions in developing battery materials, as electrochemically driven redox reactions fundamentally govern the energy, power, cycle life, and safety of a battery. The investigation of layered oxides has taken an unparalleled position in pursuing high-energy Li-ion batteries.<sup>1</sup> As the global battery market continues to evolve, there has been growing interest in LiNi<sub>1-x-v</sub>Mn<sub>x</sub>Co<sub>v</sub>O<sub>2</sub> (NMC) layered materials. These NMCs are derived from the R3m space group and isostructural to LiCoO<sub>2</sub>. As the Ni/Mn/Co stoichiometry moves across the compositional space, the charge compensation mechanism also gradually evolves due to the changing transition metal (TM) 3d orbital energy levels. Since these elements have different reaction kinetics, tailoring Ni/Mn/Co stoichiometry has become effective to fine tune battery performance. For example, increasing Ni content to improve battery energy density has become a field of its own in recent years, that is, nickel-rich cathode development. Researchers have found that spatially controlling the distribution of different TMs on the single-particle level can offer an efficient, low-cost path toward stabilizing cathode materials, including nickel-rich NMC materials.<sup>2-4</sup> Because of the compositional versatility and isostructural nature of LiTMO<sub>2</sub> materials, the ensemble-averaged characterization,

such as X-ray diffraction (XRD), usually fails to capture the compositional heterogeneity in NMC materials. Researchers have mostly applied compositionally homogeneous lattice models to refine and analyze XRD data. In our previous study, we found that NMCs with a highly heterogeneous TM distribution still exhibited a globally layered structure.<sup>2</sup> Recent studies on doping chemistry for Ni-rich layered cathodes also suggest that manipulating dopant distribution, which is often heterogeneous, can positively impact battery performance.<sup>5,6</sup> Therefore, there is no direct correlation between compositional homogeneity and battery performance for NMC materials, largely due to the isostructural nature of LiTMO<sub>2</sub> materials.

NMCs undergo lattice parameter changes during charge and discharge, which can create local stress.<sup>7–9</sup> Previous studies have shown that a heterogeneous state-of-charge distribution (i.e., charge distribution) can result in local stress hotspots and exacerbate the chemomechanical breakdown of NMC

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**Figure 1.** Morphology, crystal structure, and electronic properties of the pristine heterogeneous  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  material. (a) Threedimensional (3D) compositional heterogeneity of a randomly selected NMC particle characterized by transmission X-ray microscopy. The relative concentration variations of Ni, Mn, and Co over a virtual slice are shown in the top row with their corresponding zoom-in views for the blacksquare-annotated region demonstrated in the bottom row. The hot spots of Ni, Mn, and Co exhibit clear inconsistency confirming the compositional heterogeneity throughout the particle; The overall transition metal ratio is close to the  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  stoichiometry. (b) X-ray diffraction pattern of the material, where the inserted scheme shows the atomic configuration of the O3-type layered oxide. (c) Soft XAS spectra of Mn, Co, Ni  $L_3$ -edge in the TEY (red) and FY (green) modes, where the arrow on Ni *L*-edge spectra shows the change in the shoulder intensity of Ni  $L_3$ -edge, caused by the surface Ni reduction. The TEY mode and FY mode of soft X-ray spectroscopy (soft XAS) measure the electronic properties for the surface layer (up to 10 nm) and the subsurface volume (up to 100 nm) of secondary particles, respectively.

particles.<sup>10–14</sup> When the compositional heterogeneity prevails in individual NMC particles, charge distribution likely exhibits a heterogeneous pattern due to distinct redox reactions in domains with different Ni/Mn/Co stoichiometries. Thus, we believe that understanding the interplay between compositional heterogeneity and its impact on charge distribution may provide insights into engineering compositional heterogeneity to achieve desired charge distribution. With spatially resolved spectroscopic imaging capabilities, one can potentially establish the relationship between charge distribution and local compositional heterogeneity at the single-particle level. Furthermore, when the Ni/Mn/Co stoichiometry has a broad distribution in different domains of the same NMC particle, one can potentially study the electrochemical and structural properties of NMC materials with different Ni/Mn/ Co stoichiometries on the same particle.

In this study, we use a heterogeneous NMC material as the platform to investigate the charge distribution with singleparticle spectroscopic imaging measurements. Depending on the Ni/Mn/Co stoichiometry, each local domain performs redox reactions differently and provides a unique local state of charge, resulting in a heterogeneous charge distribution resembling the heterogeneous stoichiometry. We then show that the NMC material with highly heterogeneous stoichiometries can deliver at least the same or higher-level performance than those with more homogeneous stoichiometries. In summary, our study not only demonstrates that the NMC performance does not correlate with the compositional homogeneity but also suggests that tailoring the Ni/Mn/Co distribution at the single-particle level may shed light on controlling charge distribution for individual NMC particles.

#### RESULTS AND DISCUSSION

**Ensemble-Averaged and Single-Particle Characterization.** We develop a two-step method to synthesize heterogeneous LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> materials (Figure S1 and Experimental Method). The transmission X-ray microscopy (TXM) and energy-dispersive X-ray spectroscopy (EDS) results demonstrate the compositionally heterogeneous nature of this material (Figure 1a and Table S1). These materials exhibit the same global structure with a space group of  $R\overline{3}m$ (Figures 1b and S2). The global TM oxidation states are Ni<sup>2+/3+</sup>, Mn<sup>4+</sup>, and Co<sup>3+</sup> according to the soft X-ray Absorption Spectroscopy (XAS) (Figure 1c).<sup>15,16</sup> Here, we also observe



**Figure 2.** Global charge compensation mechanism of the heterogeneous NMC upon electrochemical charging and discharging. (a,b) Soft XAS spectra in the FY mode for Ni and Co *L*-edge at different states of charge. (c,d) Hard XAS spectra of Ni and Co *K*-edge at different states of charge. The corresponding voltages were 3.8 V (33% charged), 4.2 V (66% charged), 4.6 V (100% charged), and 2.5 V (fully discharged).

that Ni on the surface is slightly reduced compared to that in the subsurface, indicated by the decreased intensity of the high-energy shoulder of the  $L_3$  edge in the total electron yield (TEY) mode in comparison with fluorescence yield (FY) mode (labeled by the arrow in Figure 1c). The oxidation states of Mn and Co remain mostly constant at Mn<sup>4+</sup> and Co<sup>3+</sup> independent of the probing depth. The TM reduction at the surface is indicative of phase transformation and cation mixing.<sup>16</sup> The reduction of Ni at the surface in our material is consistent with the literature reported Ni-rich NMCs, where Ni shows the tendency to be reduced to Ni<sup>2+,17</sup> The surface carbonate species (e.g., Li<sub>2</sub>CO<sub>3</sub>) originate from the reaction between the ambient CO<sub>2</sub> and the basic NMC surfaces (Figure S3).<sup>18</sup> As the probing depth increases, there is an increase in the pre-edge intensity of the O K-edge, which is attributable to a stronger TM3d-O2p hybridization and a higher Ni oxidation state in the subsurface. Overall, the heterogeneous NMC exhibits similar characteristics to the reported NMC materials based on the ensemble-averaged characterization (XRD and XAS). On the particle level, this material displays a high degree of compositional heterogeneity, which allows us to investigate the relationship between charge distribution and local compositional heterogeneity.

**Global Charge Compensation Mechanism.** The compositional heterogeneity can create local domains that are enriched with one or two of the TMs. The distinct charge compensation in local domains may impact the global charge compensation mechanism. Here, we employ synchrotron soft XAS ( $L_{2,3}$ -edges) and hard XAS (*K*-edge) to investigate the charge compensation mechanism from the surface to the bulk of the heterogeneous NMC. Upon charging, the Ni  $L_3$ -edge soft XAS spectra in the FY mode show a continuous change in the intensities of two peaks, reflecting a constant increase in

the Ni oxidation state (Figure 2a). Meanwhile, the change in the Co  $L_3$ -edge soft XAS is subtle, but a gradual shift of soft XAS Co  $L_3$ -edge to higher energy upon charging is visible and the shift starts early at 4.2 V, indicating that cobalt oxidation takes place at the low voltage range for the heterogeneous NMC. A new absorption peak is observed at around 785 eV in Co  $L_3$ -edge (labeled with \* in Figure 2b). The origin of this peak could be attributable to the cobalt cations that are bonded to organic functional groups.<sup>19</sup> The Ni and Co *K*-edge (Figures 2c,d) reveal that the Ni<sup>2+/3+/4+</sup> and the Co<sup>3+/4+</sup> redox couples are mainly responsible for the charge compensation in the bulk NMC material, demonstrated by the continuous shift of near-edge toward higher energy upon charging. It was reported that Co is redox inactive at lower voltage in NMC materials.<sup>20</sup> In addition, Co redox activity is sensitive to the chemical compositions of LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>1-x-y</sub>O<sub>2</sub> and dopants.<sup>21–26</sup>  $Mn^{4+}$  is found to be redox inactive (Figure S4). The heterogeneous NMC material consists of Co-rich nanodomains that electrochemically behave similarly to LiCoO<sub>2</sub> thus allowing for the Co redox activity at low voltages. Our results suggest that the compositional heterogeneity has influenced the charge compensation, which is further investigated using spatially resolved single-particle TXM spectroscopic measurements.

Spatially Resolved Charge Distribution and Quantification. To understand the electrochemical consequences of the compositional heterogeneity at the particle level, we have performed nanoresolution ( $30 \text{ nm} \times 30 \text{ nm} \times 30 \text{ nm}$ ) X-ray spectrotomography, which offers sensitivity to the local composition and charge distribution in a correlative manner. We first conduct tomographic scans for two randomly selected particles (cycled 1 and 10 times stopped at the charged state of 4.6 V, respectively) at six different X-ray energies above and



Figure 3. Morphology, compositional heterogeneity, and redox heterogeneity in the heterogeneous  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$  cathode particles. (a,b) Two randomly selected particles that are cycled for 1 and 10 times (samples collected in the charged state at 4.6 V vs  $Li/Li^+$ ), respectively. The 3D renderings are shown on the left and right, the virtual slices are presented in the middle featuring the complexities in morphology, Ni concentration distribution, and electrochemically induced Ni oxidation. (c) Ternary plots for all the voxels within the reconstructed volumes of the two particles, featuring a broad distribution of Ni/Mn/Co stoichiometries.

below the K-edges of Mn, Co, and Ni. This measurement not only reveals the porous particle morphology (see renderings and slices on the left of Figure 3a,b) but also resolves the 3D spatial distribution of the transition metal elements, confirming the local compositional heterogeneity within individual secondary particles of our heterogeneous NMC material. We further visualize the degrees of compositional heterogeneity by presenting ternary plots for all the voxels within the reconstructed volumes of the two particles. As shown in Figure 3c, a broad Ni/Mn/Co stoichiometry is observed in both cases, while the averaged compositions do not exhibit any noticeable difference. The same instrument was then used to conduct 3D hard XAS imaging over the Ni K-edge to fingerprint the local oxidation states of Ni cations, which is the main redox-active element. It is important to note that, depending on the local composition, the nickel state is different at its fully discharged state. Therefore, a compositiondependent "background" (Figure S5) needs to be subtracted from the directly measured Ni oxidation map in order to quantitatively retrieve the electrochemically induced variation in Ni oxidation state in the charged state. In our approach, thanks to the correlative nature of the measurements of the local composition and Ni oxidation state, the above-described process can be carried out with good fidelity and the recovered 3D maps of electrochemically induced Ni redox heterogeneity are shown on the right side of Figure 3a,b for the respective particles.

Although a direct visual assessment of Figure 3 could already demonstrate the particle-level complexities in morphology, compositional heterogeneity, and redox heterogeneity, a more systematic quantification could potentially offer deeper insights into the interplay between compositional heterogeneity and charge distribution. Thus, we quantitatively analyze nanoresolution X-ray spectrotomography through two different strategies: (1) by evaluating the changes in electrochemically induced Ni oxidation as a function of the local composition and (2) by looking into the difference in the local composition over domains that show different electrochemically induced Ni oxidation. As shown in Figure 4a-d (for the two particles cycled once and 10 times at the charged 4.6 V, respectively), the electrochemically induced Ni oxidation clearly shows a composition dependence. For better visualizing the 3D-ternary diagram of Figures 4c,d, we project all of the data points to 2D plots shown on the right. It appears that the Mn and Ni concentrations are positively and negatively correlated with the electrochemically induced Ni oxidation, respectively, while the Co concentration does not demonstrate a clear effect on the Ni oxidation (with Pearson correlation coefficient at a low absolute value). This observation holds for both particles with a slight increase in the Ni-concentration-dependence observed in the particle that was cycled 10 times, as indicated by the higher Pearson correlation coefficient for Ni in Figure 4d compared to that in Figure 4c. We then conduct an unsupervised classification of all the data points into four groups based on their respective electrochemically induced Ni



**Figure 4.** Quantification of the interplay between local compositional heterogeneity and electrochemically induced Ni oxidation state change. (a-d) Amount of electrochemically induced Ni oxidation as a function of the local composition. The 2D plots in (c,d) are projections of the corresponding 3D-ternary diagrams in (a,b). (e-h) The local domains with different amounts of electrochemically induced Ni oxidation state change exhibit different Ni contents (with increasing Ni oxidation state change from cluster #1 to cluster #4). The Ni content appears to be negatively correlated with the electrochemical charge induced Ni oxidation state change.

oxidation. As shown in Figure 4e-h, the high-Ni-oxidation cluster (cluster #4, red) has a reduced Ni concentration, while the low-Ni-oxidation cluster (cluster #1, cyan) shows an increased Ni content. The low-Ni domains have lower Ni oxidation states prior to the charging, which is similar to low-Ni NMCs that have lower nickel oxidation states than high-Ni NMCs in their pristine state. Ni is the main redox active element in the electrochemical process. Therefore, upon charging nickel cations in these low-Ni domains can have a higher degree of Ni oxidation state change, leading to what has been observed in Figure 4.

To this point, we have shown the charge compensation mechanism of the heterogeneous NMC material through both ensemble-averaged and single-particle measurements. In summary, our single-particle spectroscopic imaging measurements have clearly shown the interplay between local stoichiometry and charge compensation mechanism and that the charge distribution is influenced by the local compositional heterogeneity.

**Battery Performance.** The heterogeneous NMC cathode, cycled to high cutoff voltages  $(4.5-4.6 \text{ V vs Li}^+/\text{Li})$ , shows good performance compared to many reported NMC622 materials.<sup>27-31</sup> The voltage profiles of the heterogeneous



**Figure 5.** The electrochemical performance of Li metal cells containing the heterogeneous NMC cathode material. (a) Charge–discharge profiles of cells containing the heterogeneous NMC material at C/10 within 2.5–4.6 V for 50 cycles. (b) Specific capacity and Coulombic efficiency at C/10 of the same coin cell as in (a) for 100 cycles. (c) Discharge capacity and Coulombic efficiency (averaged from three individual coin cells) at 1C within 2.5–4.5 V for 300 cycles. (d) Discharge capacity and Coulombic efficiency at 2C within 2.5–4.5 V for 500 cycles. (e) Discharge middle voltage as a function of cycle number at C/10, 1C, and 2C. (f) Rate capability within 2.5–4.6 V at C/10, C/5, C/2, 1C, 2C, and 5C for five cycles at each current rate. Here, the mass loading was ~7 mg/cm<sup>2</sup> (~1.5 mAh/cm<sup>2</sup>). Half and full cells with a higher mass loading (~2.8 mAh/cm<sup>2</sup>) also show good performance (see Supporting Information). Battery measurements were conducted at 23 °C.

NMC resemble those of the conventional stoichiometric NMC cathodes. The cells containing this material deliver an initial reversible discharge capacity of 216 mAh/g at C/10 in the voltage range of 2.5-4.6 V (Figure 5a,b). In the first 100 cycles, the charge-discharge profiles overlap well, indicating minimal growth of internal resistance. The capacity retention is 89% after 100 cycles after the 4.6 V high-voltage cycling. Because of the interfacial degradation (electrolyte decomposition, cathode surface reconstruction) at high voltages,<sup>16</sup> the initial Coulombic efficiency is lower than 95%. Nevertheless, it quickly rises to over 99.8% after 15 cycles and levels off in the subsequent cycles. The initial reversible capacities are 186 and 166 mAh/g at 1C and 2C (Figure 5c,d), respectively. The capacity retention at 1C achieves 85% after 300 cycles and the value at 2C is 81.5% even after 500 cycles. The initial discharge middle voltage for the C/10, 1C, and 2C voltage profiles are 3.80, 3.73, and 3.61 V, respectively. After the longterm cycling, the voltage retentions of 99.3%, 98.9% and 98.1% are achieved at C/10, 1C, and 2C, respectively (Figure 5e). Furthermore, the specific energy based on the active material is ~800 and ~700 Wh/kg at C/10 and 2C, respectively (Figure S6), which is comparable to many higher Ni NMC cathodes. Figure 5f displays the rate capability of the cell containing the heterogeneous material, where the cell is cycled at C/10, C/5, C/2, 1C, 2C, and 5C for five cycles at each current rate. Subsequently, we increased the active mass loading to 13 mg/  $cm^2$  and evaluated the battery performance (Figure S7). The initial reversible discharge capacity at C/10 is 217 mAh/g and

the capacity retention is 91% after 20 cycles at 2.5-4.6 V. Furthermore, an initial discharge capacity of 190 mAh/g and a capacity retention of 78% after 100 cycles are achieved at 1C and at a high upper cutoff voltage.

We also assembled full cells using the heterogeneous NMC material as the cathode and graphite as the anode (Figure S8a,b). For the full cell cycled at C/10 (20 mA/g), the reversible capacity reached 217 mAh/g (based on the cathode loading) and the initial Coulombic efficiency is 88.5% (Figure S8b). After being activated at C/10, the full cells could obtain 191 and 169 mAh/g at 1C and 2C, respectively (Figure S8c,d). The capacity retention of 86% at 1C after 100 cycles, and 83% at 2C after 100 cycles is obtained at high cutoff voltages (Figure S8c,d). Meanwhile, the stability of the middle voltages at 1C (3.57 V) and 2C (3.42 V) is good upon long-term cycling (Figure S8e). A good rate capability is also observed in full cells with initial reversible specific discharge capacities of 210, 196, 182, and 163 mAh/g at C/5, C/2, 1C, and 2C, respectively (Figures S8f). Therefore, our half-cell and full-cell results have shown the battery performance with the heterogeneous NMC is on par with those homogeneous NMCs (Table S2). It is important to note that the full cell data presented here have not fully exploited the performance of the cathode material, and we believe that there is still a large space for the performance improvement with more efforts on electrolyte regulation and cathode-anode optimization.

#### CONCLUSION

Multielement TM layered oxides represent an important family of cathode materials. Because of their strong capability of accommodating different metals in the lattice, many layered oxides can form globally pure layered phases even if they are heavily doped or substituted with different metal cations. In some cases, researchers have made use of such compositional flexibility to design cathode materials with many metal elements, such as high-entropy and compositionally complex cathodes.<sup>32-34</sup> However, ensemble-averaged characterization techniques cannot capture the local compositional heterogeneity. In this study, we used a compositionally heterogeneous NMC622 material as a platform to investigate how compositional heterogeneity influences global structural and electrochemical properties. The compositional heterogeneity in individual particles does not seem to impact battery performance. The spatially resolved characterization, based on TXM, reveals the interplay between chemical composition and charge compensation mechanisms in local domains within individual battery particles. The electrochemical chargeinduced Ni oxidation exhibits a negative correlation with the Ni concentration in local domains. Controlling charge distribution in individual particles has received remarkable attention because charge distribution can not only impact chemomechanical stability of materials but also dictate the fraction of the particle that contributes to delivering capacity.<sup>10,11</sup> While compositional heterogeneity has not been widely investigated to tailor charge distribution, our study suggests that engineering local compositional distribution can be a path toward modulating local charge distributions. The present study also echoes with other studies on the compositional heterogeneity of battery materials. For example, there have been studies reporting the heterogeneous distribution of dopants in layered oxides.<sup>5,35,36</sup> Combining the perspectives of the literature and our current results, we come to the conclusion that battery performance of a single-phase layered oxide does not seem to be directly related to how homogeneously different elements distribute in individual particles. Nevertheless, it should be noted that the isostructural nature of LiTMO<sub>2</sub> (O3-type) is a prerequisite for obtaining compositionally heterogeneous materials without compromising the ensemble-averaged pure layered structure. In other alkali ion-layered cathodes such as Na-layered cathode materials, the local compositional heterogeneity may result in secondary phases,<sup>37–39</sup> which is attributed to the fact that Nalayered oxides have many more possible crystal structures.40 The local compositional heterogeneity can originate from the precursor synthesis step, as shown in this study, or can result from the thermal calcination step due to the diffusion of different elements.<sup>6</sup> One can control one of these steps to design compositional heterogeneity and thus charge distribution at the single-particle level.

#### ASSOCIATED CONTENT

#### **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c04464.

Materials synthesis, materials characterization, and electrochemical characterization; figures for XRD, soft XAS, Mn K-edge XANES, TXM, and battery performance; table to show the local metal concentration variations; table to compare the performance with different NMC cathodes (PDF)

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#### **Author Contributions**

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#### **Author Contributions**

F.L. and Y.L. led the project. L.M., F.L., and Y.L. designed the experiments. L.M. performed synthesis, XRD, SEM, hard XAS, and electrochemical measurements. J.Z., Y.X., C.W., and Y.L. conducted the TXM measurement. F.L., Y.L., L.M., and J.Z. developed the TXM data analysis approaches. Y.L. and J.Z. analyzed the TXM data. M.M.R. and D.N. conducted soft XAS measurements. F.L., Y.L., and L.M. wrote the manuscript. All the authors contributed to the science of the manuscript.

#### Notes

The authors declare no competing financial interest.

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