

# Persistent and Partially Mobile Oxygen Vacancies in Li-Rich Layered Oxides

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## Abstract

Increasing the energy density of layered oxide battery electrodes is challenging as accessing high states of delithiation often triggers voltage degradation and oxygen release. Here, we utilize transmission-based X-ray absorption spectromicroscopy and ptychography on mechanically cross-sectioned  $\text{Li}_{1.18-x}\text{Ni}_{0.21}\text{Mn}_{0.53}\text{Co}_{0.08}\text{O}_{2-\delta}$  electrodes to quantitatively profile the oxygen deficiency over cycling at the nanoscale. The oxygen deficiency penetrates into the bulk of individual primary particles ( $\sim 200$  nm) and is well-described by oxygen vacancy diffusion. Using an array of characterization techniques, we demonstrate that, surprisingly, bulk oxygen

36 vacancies which persist within the native layered phase are indeed responsible for the observed  
37 spectroscopic changes. We additionally show that the arrangement of primary particles within  
38 secondary particles ( $\sim 5 \mu\text{m}$ ) causes significant heterogeneity in the extent of oxygen release  
39 between primary particles. Our work merges an ensemble of length-spanning characterization  
40 methods and informs promising approaches to mitigating the deleterious effects of oxygen  
41 release in lithium-ion battery electrodes.

## 42 **Introduction**

43 Two of the primary challenges facing the commercialization of lithium- and  
44 manganese-rich (LMR) materials are the progressive fading of the discharge voltage over  
45 cycling<sup>1-7</sup> and their tendency to release oxygen at high states of delithiation. While oxygen  
46 release in layered oxides has been extensively studied on the first electrochemical cycle, less is  
47 known about the process over extended cycling. This is partly due to the fact that, in contrast to  
48 the first cycle, only small quantities of oxygen are released in each subsequent cycle such that  
49 negligible signal can be detected in electrochemical mass spectrometry studies<sup>8-10</sup>. Additionally,  
50 it remains challenging to reconcile nanoscale observations, some of which suggest significant  
51 mass loss and Li depletion coincident with a release of nearly one-fifth of the oxygen<sup>11</sup>, with  
52 cell-level observations of negligible capacity fade over 100+ cycles<sup>11,12,13</sup>. Nevertheless, oxygen  
53 release during extended cycling has recently been proposed to be the underlying cause of the  
54 voltage fade, as it activates lower-voltage redox couples<sup>12,14</sup> and is believed to inevitably cause  
55 pernicious phase transitions<sup>7,15</sup>. Therefore, in order to develop practical strategies for mitigating  
56 both oxygen release and voltage decay in LMR materials, several aspects of the oxygen release  
57 phenomenon must be clarified.

58 First, the ability of these materials to transport oxygen at room temperature is uncertain,  
59 and thus it is unclear whether the oxygen deficiency is limited to the near-surface (a few nm)  
60 region<sup>9,16,17</sup> or penetrates into the bulk of primary particles (hundreds of nm) after many cycles<sup>11</sup>.  
61 Second, due to a gap in length scales accessed by standard analytical techniques, the influence of  
62 microstructure on the heterogeneity of oxygen release has not been assessed. Third, there is  
63 significant confusion over the structural implications of oxygen release during extended cycling.  
64 The established view, supported primarily from local TEM observations<sup>7,15</sup>, is that oxygen  
65 release is invariably associated with a phase transition to a more transition-metal-rich phase (e.g.  
66 a spinel or ‘spinel-like’ phase)<sup>7,15,16,18–21</sup>. However, bulk-sensitive XRD studies often do not  
67 show the growth of new peaks indicative of a macroscopic phase transformation<sup>2,5</sup>, calling into  
68 question whether bulk phase transformations indeed govern the behavior of LMR layered oxides.  
69 Finally, it remains ambiguous whether oxygen release is simply correlated with the commonly  
70 observed bulk cation disordering (within the native layered phase)<sup>3,5</sup> or if there exists a  
71 mechanistic relationship between the two phenomena.

72 In this work, we obtain oxidation state maps spanning interfaces (~ 10 nm), primary  
73 particles (~ 200 nm), secondary particles (~ 5 μm), and the entire electrode thickness (> 40 μm)  
74 using nanoscale X-ray spectromicroscopy and ptychography on electrodes sectioned by  
75 solvent-free ultramicrotomy. These quantitative maps reveal that oxygen originating in the bulk  
76 of primary particles is eventually released over hundreds of cycles at room temperature. The  
77 oxygen deficiency profiles suggest that oxygen vacancy diffusion, as opposed to a phase  
78 transition, likely governs oxygen release in  $\text{Li}_{1.18-x}\text{Ni}_{0.21}\text{Mn}_{0.53}\text{Co}_{0.08}\text{O}_{2-\delta}$  (LMR-NMC). The  
79 existence of bulk oxygen vacancies which persist within the native layered phase is confirmed by  
80 additional chemical and structural analysis, overturning the prevailing view that oxygen release

81 is necessarily accompanied by a phase transition. This result also contradicts the suspicion that  
82 oxygen vacancies, if present, will inevitably undergo vacancy condensation and be eliminated  
83 from the lattice<sup>11</sup>. Importantly, the existence of bulk oxygen vacancies provides a plausible  
84 atomistic explanation linking progressive oxygen release to progressive single-phase cation  
85 disordering<sup>3,5</sup>, unifying two previously proposed explanations for the voltage decay. Finally, we  
86 reveal that the extent of oxygen release for an individual primary particle depends strongly on  
87 the surrounding secondary structure, with those residing in the interior of large secondary  
88 particles being more protected from oxygen release. These results together inform new chemical,  
89 structural, and morphological strategies for preventing oxygen release in layered oxide positive  
90 electrodes.

## 91 **Cation Disordering and Reduction Over Cycling**

92 Uncoated LMR-NMC electrodes were cycled in full cells against graphite (Samsung  
93 mini-18650, see Methods). Electrodes were harvested at various cycle numbers and assembled  
94 into half cells where they were cycled once more against Li metal. Figure 1a shows charging and  
95 discharging at  $\sim 4 \text{ mA g}^{-1}$  in a half cell after up to 500 full cell cycles (see Methods). With  
96 cycling, the quasi-open-circuit voltage of various redox processes decreases on both charge and  
97 discharge, implying that significant changes occur in the bulk of the material<sup>5</sup>. Despite these  
98 changes, however, the capacity fade is minimal, with the electrode retaining 96% of its initial  
99 low-rate discharge capacity (Supplementary Fig. 1). The stable low-rate discharge capacity  
100 suggests that the Li content of electrodes discharged at low rate (in a half cell) is similar  
101 regardless of cycle number, which we confirm directly through inductively coupled plasma mass  
102 spectroscopy (ICP-MS, Supplementary Fig. 2).

103 Rietveld refinement of synchrotron powder X-ray diffraction (SXR) patterns reveals  
104 that LMR-NMC remains single phase with the  $R\bar{3}m$  space group after 500 cycles with no  
105 tetrahedral occupancy of transition metals (Fig. 1b, Supplementary Fig. 3–6). The lack of  
106 secondary crystallographic phases is also supported by selected area electron diffraction  
107 (Supplementary Figure 7) and high-resolution transmission electron microscopy (Supplementary  
108 Figures 8 and 9). Interestingly, Rietveld refinement does show that the transition metal (TM)  
109 occupancy in Li layer octahedral sites increases steadily from 2 to 10 at. % with cycling (Fig.  
110 1c), consistent with previous reports<sup>5,22</sup>.

111 We additionally probed the spatially-averaged electronic structure<sup>23</sup> using  
112 transmission-based TM K-edge X-ray absorption spectroscopy (XAS) (Supplementary Figs. 10–  
113 12). With cycling, Mn and Co are progressively reduced from their initial  $Mn^{4+}$  and  $Co^{3+}$  states  
114 while Ni remains in its initial  $Ni^{2+}$  state (Fig. 1c). Given that the Li content in each sample is  
115 approximately identical and that the crystallographic phase of the material is unchanged, we infer  
116 from bulk electroneutrality that the spectroscopic changes here correspond to oxygen release<sup>12</sup>.  
117 This conclusion is also consistent with the SXR Rietveld refinements<sup>24</sup> (Supplementary Figs. 3  
118 and 13) and nanoscale oxidation state maps, which are discussed below. Interestingly, the  
119 reduction of Mn and Co over cycling can be partially reversed by conducting a low-temperature  
120 heat treatment at 150 °C in 100%  $O_2$  (Fig. 1c). We will discuss this intriguing result in detail  
121 later.

122 The TM oxidation states from XAS were used to estimate the fraction of oxygen release  
123 relative to the pristine material:  $\sim 3.3$  at. % after the first cycle (which is preceded by formation  
124 cycling) and  $\sim 6.5$  at. % after 500 cycles (Supplementary Note 1). The large first-cycle oxygen  
125 release is consistent with the findings of previous gas analysis experiments<sup>16,25,26</sup>. Our XAS

126 results, taken together with our findings from SXRD, reveal that both phenomena previously  
127 linked to voltage fade—progressive cation disordering and progressive oxygen release—occur  
128 simultaneously over extended cycling. The strong correlation observed here (Fig. 1c) suggests  
129 that the two may be mechanistically linked to one another, a point which we will return to later.

130 To map oxygen loss at the nanoscale, we utilized soft X-ray scanning transmission X-ray  
131 microscopy (STXM) and X-ray ptychography at the Advanced Light Source, the latter with  
132 greater spatial resolving power<sup>27–30</sup>. Using these two transmission-based microscopy techniques  
133 in spectro-microscopy mode, we probed the TM L<sub>3</sub> absorption edges and the oxygen K edge  
134 without self-absorption effects. With cycling, Mn and Co reduction are both observed in the  
135 averaged (Supplementary Methods) L<sub>3</sub> edge spectra, whereas no change was observed at the Ni  
136 L<sub>3</sub> edge<sup>2</sup> (Supplementary Fig. 14–17). These spectral changes, visible from the difference plots  
137 even without quantification (Fig. 1d), are in strong agreement with TM K-edge spectroscopy  
138 results, providing unambiguous evidence that the *d* electron count increases with cycling.

### 139 **Oxidation State Heterogeneity within Primary Particles**

140 As in most layered oxides, primary particles in LMR-NMC exist in secondary particle  
141 agglomerates (~ 5 μm) rather than as isolated particles. To preserve the secondary structure  
142 while also making the sample sufficiently transparent to soft X-rays, thin cross-sectional  
143 lamellae were prepared by dry mechanical ultramicrotomy (Supplementary Fig. 18, Methods).  
144 We first discuss the oxidation state heterogeneity within individual primary particles using X-ray  
145 spectro-ptychography at the Mn L<sub>3</sub> edge, which has a resolution of ~ 5–20 nm (Fig. 2a–c,  
146 Supplementary Fig. 19). As expected, the Mn reduction after a single cycle is concentrated near  
147 the particle edges, indicating that oxygen release initiates at the surface of particles (Fig. 2d,

148 Supplementary Figs. 20 and 21). This observation spatially decouples first-cycle oxygen release,  
149 which is concentrated at surfaces, from oxidized lattice oxygen<sup>31</sup>, which charge compensates the  
150 majority of the capacity in the first-cycle voltage plateau and exists throughout the particle bulk  
151 even on the initial cycle<sup>2</sup>. Additionally, there is significant heterogeneity in the extent of oxygen  
152 release between primary particles (Fig. 2b), which we will return to later. Finally, oxygen  
153 deficiency that begins on the particle surface progressively enters (> 100 nm) into the bulk  
154 material over many electrochemical cycles (Fig. 2d). This observation is consistent with previous  
155 electron<sup>13</sup> and X-ray<sup>32</sup> microscopy studies showing TM reduction beyond the surface of LMR  
156 particles.

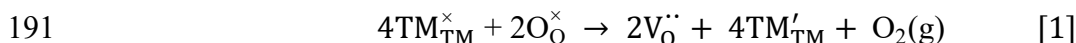
157         The quantitative nature of the oxidation state maps of primary particles allows us to  
158 directly evaluate two mechanistic possibilities. The first is single-phase oxygen ambipolar  
159 diffusion from the bulk to the particle surface. The second is a two-phase (core-shell)  
160 reaction<sup>21,33,34</sup>, in which a new phase with a more reduced Mn oxidation state grows inwards  
161 from the surface. Figure 2e,g shows three independent fittings to the Mn<sup>3+</sup> concentration profiles  
162 of individual particles for each of the two models (Supplementary Note 2). The fits utilizing a  
163 two-phase reaction are poor, as a depth-averaged core-shell model predicts a constant Mn<sup>3+</sup>  
164 concentration in the shell which is not observed experimentally. Conversely, the individual  
165 particle fits utilizing the vacancy diffusion model describe the data reasonably well  
166 (Supplementary Figure 22), suggesting that oxygen chemical diffusion governs bulk oxygen  
167 release in LMR-NMC.

168         Quantitatively, the fitting (Supplementary Note 2) gives room-temperature oxygen  
169 chemical diffusivities ( $D_O$ ) within an order of magnitude of  $10^{-17}$  cm<sup>2</sup> s<sup>-1</sup> in the delithiated state,  
170 where oxygen is known to be most mobile<sup>35,36</sup>. This room-temperature oxygen chemical

171 diffusion coefficient, although large enough to cause bulk oxygen depletion over extended  
172 cycling, is six to seven orders of magnitude lower than those of some fast oxygen-ion-conducting  
173 perovskite oxides<sup>39-42</sup>. Several factors may contribute to oxygen transport in LMR-NMC. Since  
174 LMR-NMC is known to have oxidized oxygen species at high extents of delithiation (such as  
175 molecular O<sub>2</sub>, O<sub>2</sub><sup>2-</sup>, or O<sup>-</sup>)<sup>2,43</sup>, the diffusing species may in fact be a less ionized oxygen which  
176 could be more mobile<sup>44,45</sup> than O<sup>2-</sup>. Extended defects such as dislocations may also  
177 contribute<sup>46,47</sup>. We note that although fitting with a constant oxygen chemical diffusivity gives  
178 good fits to the data, the true chemical diffusivity is likely not constant during cycling due to  
179 progressive changes in the material structure. For completeness, we also performed STXM  
180 imaging on dispersed<sup>2</sup> (rather than cross-sectioned) samples, which are consistent with the  
181 conclusion of bulk oxygen release (Supplementary Figs. 16 and 17).

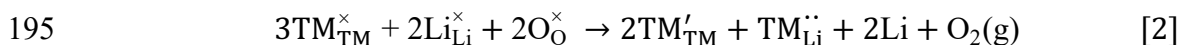
## 182 **The Existence of Bulk Oxygen Vacancies**

183 Although the spatial analysis of Mn<sup>3+</sup> concentration suggests oxygen vacancies may be  
184 present in the bulk material, proof of this remains lacking because neither XAS nor SXRD can  
185 directly resolve the anion sublattice. Given that LMR-NMC remains single phase over cycling,  
186 we consider two structural models<sup>24,48</sup> for the electrode after 500 cycles (Fig. 3a). The first  
187 involves an anion sublattice with vacancies that persist over many cycles, which we refer to as  
188 the oxygen vacancy structure ([Li<sub>1.18</sub>TM<sub>0.82</sub>] [O<sub>1.87</sub>□<sub>0.13</sub>], where the first and second brackets  
189 define the cation and anion sublattice, respectively). Here, the point defect reaction governing the  
190 changes over cycling in the lithiated material can be written in Kröger-Vink notation as:





192 The second structural model involves a fully occupied anion sublattice referred to as the  
193 densified structure ( $[\text{Li}_{1.06}\text{TM}_{0.94}][\text{O}_2]$ ), whereby the evolved oxygen causes TMs at the surface  
194 to back diffuse into the bulk<sup>19,21,49-51</sup>. The analogous point defect reaction can be written as:



196 These two structure models are indistinguishable using XAS, as both models can explain a  
197 reduction in the average TM oxidation state (Fig. 3a). They are also nearly indistinguishable with  
198 neutron diffraction (Supplementary Fig. 23) or SXRD<sup>24,48</sup> (Supplementary Fig. 24).

199 Crucially, the predominant difference between the two structure models is that the  
200 densified structure has a considerably lower Li to TM elemental ratio (Li:TM) of 1.12 while the  
201 oxygen vacancy structure has a Li:TM of 1.44 (Supplementary Note 3). Figure 3b shows that,  
202 consistent with the meager capacity fade observed both here and elsewhere<sup>11,12,13</sup>, the Li:TM of  
203 electrodes discharged to and held at 2.5 V vs.  $\text{Li}/\text{Li}^+$  is nearly constant with cycling, indicating  
204 that bulk densification is only a minor contributor ( $\sim 15\%$  if the entire decrease in Li:TM and  
205 electrochemical capacity is due to densification) to the structure of the cycled material. We note  
206 that while the cathode electrolyte interphase (CEI) may contribute to the ICP-MS signal, the CEI  
207 would have to contain 22.5% of the Li content of LMR-NMC (after 500 cycles, discharged in a  
208 half cell) and no TMs to explain the ICP-MS results with the densified structure. As a recent  
209 cryo-EM study has shown that CEI on Li-rich materials is essentially non-existent<sup>52</sup>, we  
210 therefore conclude that contrary to earlier reports<sup>7,48,49</sup>, the bulk oxygen vacancy structure is far  
211 more likely to explain both the nearly constant Li:TM over extended cycling as well as the stable  
212 electrochemical capacity (Supplementary Note 4).

213 The material density also contrasts significantly between the two structural models, with  
214 the predicted densities differing by nearly 10% after 500 cycles (Supplementary Note 5).  
215 Therefore, we utilized helium gas pycnometry, which has been used previously to measure  
216 cation vacancy concentrations in layered oxides<sup>53</sup>, to determine the density of LMR-NMC with  
217 cycling. The experimental results agree reasonably well with the density changes predicted by  
218 the oxygen vacancy structure model, providing more support for the existence of oxygen  
219 vacancies (Fig. 3b). We note that the presence of closed pores may complicate the interpretation  
220 of the pycnometry measurement, a point which is discussed thoroughly in Supplementary Note 6  
221 (also see Supplementary Figures 25–27).

222 As a final piece of evidence, we return to the oxidation of TMs upon annealing the cycled  
223 material (Fig. 1c, Supplementary Figure 28), a similar experiment to those conducted in several  
224 recent works<sup>47,54</sup> (see Supplementary Note 7). In addition to TM K edge XAS, evidence for TM  
225 oxidation includes TM K edge extended X-ray absorption fine structure (EXAFS) data, Rietveld  
226 refinement, and electrochemical analysis (Supplementary Figures 3, 29–31). The TM oxidation  
227 during annealing could come from a change in either the Li or O stoichiometry. If the densified  
228 structure were operative *before* the annealing process, an increase in the oxygen stoichiometry  
229 would have to proceed via the insertion of oxygen interstitials:

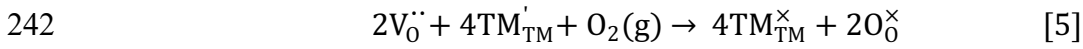


231 In addition to being intuitively unlikely, the insertion of oxygen interstitials almost certainly  
232 would expand the lattice rather than resulting in the contraction that is experimentally observed.  
233 Alternatively, Li could be removed from the structure during annealing via the following  
234 reaction, where Li on the product side is some Li containing compound (e.g. Li<sub>2</sub>O):

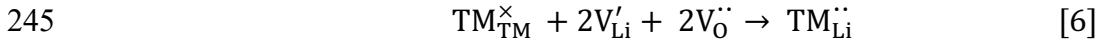


236 This process, representing lithium loss of a slightly less Li-rich (than the pristine material) oxide  
 237 in the absence of electrolyte at 150° C, is also extremely unlikely. We can therefore conclude  
 238 that the densified structure is a poor explanation for the structure of the material *prior* to  
 239 annealing.

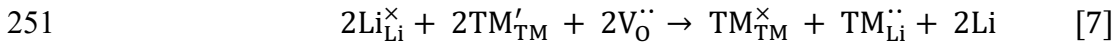
240 Conversely, if the oxygen vacancy structure were operative, an increase in the oxygen  
 241 stoichiometry could proceed via the refilling of previously formed oxygen vacancies:



243 Additionally, a decrease in Li stoichiometry may be possible, as oxygen vacancies present *before*  
 244 the annealing process could combine with Li vacancies formed via eqn. (4):



246 Eqn. 6, while potentially being kinetically inhibited at room temperature, should be  
 247 thermodynamically favorable, as the elimination of oxygen vacancies would restore  
 248 undercoordinated transition metals to their full coordination<sup>20</sup>. Combining eqn. (4) and eqn. (6)  
 249 results in a net defect reaction which could cause TM oxidation if oxygen vacancies are present  
 250 *before* annealing, where Li on the product side is some Li containing compound (e.g. Li<sub>2</sub>O):



252 Because of the thermodynamic favorability of eqn. (6), eqn. (7) is much more plausible  
 253 alternative to eqn. (4). Thus, regardless of whether a change in the Li or O stoichiometry governs  
 254 the TM oxidation, the oxygen vacancy structure is far more likely to explain the material *before*  
 255 annealing.

256 We emphasize that in the above discussion (summarized in Supplementary Table 1) we  
257 were concerned with the structural changes occurring in the bulk of the material rather than in  
258 the near-surface region (a few nm), as many works have reported a densified surface layer that  
259 does not significantly change in thickness during cycling<sup>7,19,37,38</sup>.

## 260 **Oxygen Vacancies and the Cation Sublattice**

261 The existence of bulk oxygen vacancies confirms that single-phase vacancy diffusion is  
262 responsible for the Mn<sup>3+</sup> concentration profiles within primary particles (Fig. 2). This overturns  
263 the accepted view that bulk oxygen release kinetics in LMR-NMC are necessarily governed by  
264 phase transitions<sup>12</sup>. Furthermore, bulk oxygen vacancies provide an atomistic link between  
265 single-phase cation disordering and oxygen release, both of which occur progressively with  
266 cycling and have been independently proposed as the reason for the voltage decay<sup>5,12</sup>. Namely,  
267 an oxygen vacancy will cause neighboring TMs to become undercoordinated and therefore more  
268 likely to move to alternative lattice sites. We note that this explanation was previously suggested  
269 to be responsible for the observed surface densification process<sup>13,17,19,58</sup>. Cation disordering may  
270 also promote oxygen vacancy formation, allowing the lattice to more easily accommodate and/or  
271 transport an oxygen vacancy. This coupling suggests that the strategic prevention of either of  
272 these phenomena may enhance electrochemical performance in part due to the coupling between  
273 them. Indeed, surface modifications designed to prevent oxygen release mitigate both voltage  
274 decay and cation disordering<sup>14,15,59,60</sup>. Likewise, modified stacking sequences or large interlayer  
275 spacings which restrict TM mobility mitigate both voltage decay<sup>55,61,62</sup> and oxygen release<sup>62,63</sup>.

276 As a final point of interest, EXAFS data (Fig. 3c) show a decrease in the scattering  
277 intensity of the first coordination shell with cycling for both Mn and Co, but not Ni. This

278 decrease in intensity can originate from the formation of both  $V_O^{\cdot\cdot}$  and  $TM_{Li}^{\cdot\cdot}$  (Fig. 3d,  
279 Supplementary Fig. 32), although a disorder in the first shell M–O bond distances due to the loss  
280 of in-plane ordering or the fractional average oxidation states of Mn and Co may also contribute.  
281 However, the Ni first shell scattering intensity remains higher than would be predicted based on  
282 a random distribution of both  $V_O^{\cdot\cdot}$  and  $TM_{Li}^{\cdot\cdot}$ . Therefore, we hypothesize that the oxygen vacancies  
283 may preferentially form around Mn and Co, the same atoms which undergo TM reduction  
284 (Supplementary Note 8). The EXAFS data additionally suggest that if Ni atoms migrate during  
285 delithiation, as has been suggested from previous EXAFS data<sup>2</sup>, these migrations may be more  
286 reversible than those of Mn and Co. We speculate that this may be due to the large change in  
287 ionic radius Ni experiences during cycling, as the sites  $Ni^{4+}$  migrates into on delithiation may not  
288 be suitable for the  $Ni^{2+}$  which forms on lithiation.

### 289 **Importance of Secondary Particle Microstructure**

290 Although cross-sectioning the electrode into nominally 80 nm-thick lamellae cuts through  
291 secondary particles, some information about the location of a given primary particle within the  
292 secondary structure can be inferred. Specifically, large agglomerates in the lamella represent  
293 cross-sections that went through the center of large secondary particles. Smaller agglomerates  
294 could either represent a cross-section closer to the secondary particle edge or through the center  
295 of a smaller secondary particle (Supplementary Fig. 18).

296 Mn oxidation state maps after one cycle were obtained via STXM at the electrode level  
297 ( $\sim 50 \times 50 \mu\text{m}$ , Fig. 4a) as well as that of a single large agglomerate with finer resolution ( $\sim 5 \times 5$   
298  $\mu\text{m}$ , Fig. 4b). Figure 4b reveals that the primary particles inside of the large agglomerate are  
299 significantly more oxidized, and thus release less oxygen, than those outside of the agglomerate.

300 Figure 4c quantitatively demonstrates that this trend is preserved even when controlling for the  
301 pixel-wise thickness of the primary particle being examined (Supplementary Fig. 33). This  
302 implies that even primary particles of identical size will exhibit a degree of oxygen release that is  
303 heavily dependent on their location within the secondary structure. Additionally, Fig. 4b shows  
304 that within the large agglomerate, primary particles near the exterior are more reduced than those  
305 on the interior (Fig. 4b,d , Supplementary Fig. 34). Taken together, these findings reveal that  
306 primary particles originating from the interior of large secondary particles release comparably  
307 less oxygen. Conversely, primary particles originating from either the exterior of large secondary  
308 particles or from small secondary particles release a relatively large quantity of oxygen. Both of  
309 these observations are quantitatively supported by investigation of an ensemble of large  
310 agglomerates (Fig. 4a,d , Supplementary Figs. 35–37).

311         Interestingly, the fact that the  $\text{Mn}^{3+}$  distribution in each individual primary particle (Fig.  
312 2a–c) is nearly radial indicates that each primary particle releases oxygen from its surface.  
313 Therefore, the observed heterogeneity cannot be explained by differences in the effective oxygen  
314 diffusion length among primary particles, as would occur if oxygen release occurred entirely  
315 from the secondary particle surface (Supplementary Fig. 38). Although the fundamental reason  
316 for the heterogeneity is still under investigation, one possibility is that stress buildup in large  
317 secondary particles<sup>64</sup> could modify the local oxygen chemical potential and/or diffusivity.  
318 Diminished electrolyte-induced oxygen release for interior primary particles is also possible,  
319 although electrolyte penetration into the secondary particle interior may also occur<sup>65,66</sup>.

320         Regardless of the underlying cause, the observed heterogeneity shows that many primary  
321 particles must be examined to arrive at robust conclusions (Supplementary Fig. 39). The results  
322 additionally suggest that larger secondary particles, with the primary particle size held constant,

323 are expected to exhibit less oxygen release and possibly greater voltage retention. While this  
324 improvement may come at the expense of usable capacity and/or rate capability,  
325 spectromicroscopy analysis of delithiated samples suggests that large secondary particles may  
326 achieve Li contents comparable to those of smaller secondary particles (Supplementary Fig. 40).  
327 Previous work also suggests that the primary particle size may be a more important factor in  
328 determining the achievable capacity<sup>65,67</sup>. The possibility of cycling a similar quantity of Li while  
329 simultaneously mitigating oxygen release advocates for the exploration of larger LMR-NMC  
330 secondary particles.

### 331 **Spectroscopic Analysis of the Delithiated State**

332 While the Mn L<sub>3</sub>-edge XAS shows progressive reduction with cycling in the discharged  
333 state, all LMR-NMC electrodes charged to 4.6 V exhibited a uniform Mn<sup>4+</sup> oxidation state, even  
334 after 500 cycles (Supplementary Fig. 41). This finding verifies the emergence of a reversible  
335 Mn<sup>3/4+</sup> redox couple upon cycling<sup>12,16</sup> and further confirms that the bulk Mn reduction observed  
336 in the discharged state cannot be due to an electrochemically-inactive second phase.

337 Conversely, oxidation state maps at the Ni L<sub>3</sub> edge show the opposite behavior. While the  
338 Ni oxidation state remains uniform in the discharged electrodes with cycling (Supplementary  
339 Fig. 42 and 43), it is heterogeneous in the charged electrodes (Fig. 5). Specifically, Figure 5d  
340 shows that thicker regions reach a higher oxidation state than thinner regions<sup>2</sup>. This  
341 heterogeneity is not likely due to sluggish Li<sup>+</sup> transport both because of the long constant voltage  
342 hold and the fact that thicker regions would be expected to be less oxidized if transport were  
343 limiting. Instead, the lower oxidation state of thinner regions may be due to the fact that thinner  
344 are expected to have more reduced Mn in the discharged state (Fig. 2d, 4c). This allows Mn to

345 compensate more charge during delithiation, requiring less charge compensation from Ni.  
346 Additionally it is known that the atomic structure at the surface of the particle (~ 5 nm)  
347 reconstructs significantly due to interactions with the electrolyte<sup>38</sup>. This modified surface  
348 structure may not cycle as much Li and is generally more reduced than the bulk material<sup>38</sup>, which  
349 may also contribute to the observed thickness dependence.

350 Interestingly, the O K-edge spectra, like the Ni L<sub>3</sub>-edge spectra, are uniform in the  
351 discharged state (Supplementary. Figs. 42 and 44) but exhibit heterogeneity at 4.6 V (Fig. 5c).  
352 As shown in Fig. 5d, the O and Ni oxidation state exhibit a similar dependence on particle  
353 thickness, likely for the same reasons described earlier. The significant amounts of Ni and O  
354 oxidation observed<sup>68</sup>, particularly for thicker regions where the LMR-NMC bulk is responsible  
355 for the majority of the signal, indicate that the existence of bulk oxygen vacancies does not  
356 inhibit the redox of either of these elements. This observation is consistent with the negligible  
357 capacity fade after 500 cycles.

### 358 **Implications for Oxygen Release Mitigation**

359 Substantial effort has been devoted to the mitigation of oxygen release in layered oxide  
360 positive electrodes. By a large margin, the most common approach to resolving this issue is to  
361 apply surface treatments to the electrodes<sup>14,15,59,60,69,70</sup>. However, additional approaches should  
362 also be considered, particularly because they could work synergistically with an appropriate  
363 surface coating. Our results, obtained from an industrially-relevant LMR-NMC material, suggest  
364 several additional strategies which have not been adequately examined. First, chemical or  
365 structural modifications which can decrease the oxygen chemical diffusivity, a property which is  
366 crucial but hardly understood<sup>51</sup> in Li-ion layered oxides, should be explored. Second, the



367 prevention of cation disordering, which is inhibited in many Na-ion materials due to their large  
368 interlayer spacing and unique stacking order<sup>71</sup>, is another important strategy which may inhibit  
369 the structural changes necessary to accommodate an oxygen vacancy. This route has been shown  
370 to successfully mitigate oxygen release in Na-ion materials even when they undergo a phase  
371 transition involving layer sliding<sup>62,63</sup>. Finally, our results suggest that morphological control is a  
372 potential chemistry-agnostic method to achieve stability against oxygen release. For LMR oxides  
373 specifically, larger secondary particles, with the primary particle size held constant, may mitigate  
374 the oxygen release problem while preserving electrochemical capacity<sup>65</sup>.

## 375 **Conclusions**

376 Using X-ray spectromicroscopy and ptychography, we showed that bulk lattice oxygen is  
377 released in significant quantities during extended cycling. The extent of oxygen release for an  
378 individual primary particle was found to be highly dependent on its location within the secondary  
379 structure, offering opportunities for morphological mitigation of the oxygen release  
380 phenomenon. While oxygen release is typically associated with a phase transition between two  
381 or more phases each containing a full anion sublattice, we demonstrate here that only a small  
382 amount ( $\sim 15\%$ ) of material densification occurs, likely at the very surfaces of primary particles.  
383 Instead, surprisingly, the majority of oxygen release over cycling creates bulk oxygen vacancies  
384 which form and persist within the native layered phase. These vacancies, created at the primary  
385 particle surface, enter into the bulk over extended cycling with a fitted oxygen chemical  
386 diffusivity of  $\sim 10^{-17} \text{ cm}^2 \text{ s}^{-1}$  in the delithiated state. Our observations unify previous  
387 observations of TM reduction and single-phase cation disordering and imply that  
388 cycling-induced oxygen release can be mitigated via chemical or structural modifications which  
389 inhibit the formation and/or transport of oxygen vacancies within the bulk material.

## 390 **Methods**

391 **Materials.** The  $\text{Li}_{1.18}\text{Mn}_{0.53}\text{Ni}_{0.21}\text{Co}_{0.08}\text{O}_2$  materials were synthesized as previously  
392 reported<sup>2</sup>. In short,  $\text{Mn}_{0.53}\text{Ni}_{0.21}\text{Co}_{0.08}(\text{OH})_2$  precursor powder was synthesized by coprecipitation  
393 of stoichiometric quantities of  $\text{NiSO}_4$ ,  $\text{CoSO}_4$ , and  $\text{MnSO}_4$ . The precursor was then mixed with  
394 the appropriate amount of  $\text{Li}_2\text{CO}_3$  and calcined at 900 °C for 10 h to obtain powder of the target  
395 composition,  $\text{Li}_{1.18}\text{Mn}_{0.53}\text{Ni}_{0.21}\text{Co}_{0.08}\text{O}_2$ . We used this target composition for all calculations in  
396 the text.

397 **Electrochemical measurements.** All samples that are not labeled as “Pre-Formation”  
398 were first subject to electrochemical cycling inside mini-18650 cells (Samsung) containing a  
399 92% LMR-NMC, 4% carbon, and 4% binder composite by mass as the positive electrode and  
400 graphite as the negative electrode. The cells used a 1.3 M  $\text{LiPF}_6$  in 3:8:9 (vol/vol/vol)  
401 fluoroethylene carbonate (FEC)/ hydrofluoro ether (HFE)/dimethyl carbonate (DMC) electrolyte  
402 with some proprietary additives. This cycling included a four cycle formation cycling procedure  
403 (see Supplementary Methods) followed by cycling at 25°C for the number of cycles specified in  
404 the text at a 1C/2C charge/discharge rate between 2.5 – 4.55 V with a ~ 45 min constant voltage  
405 hold at 4.55 V until C/20 current was reached. Note that each of these cycles also included a 10  
406 min rest after both charging and discharging. C-rates were calculated based on a capacity of 215  
407 mAh  $\text{g}^{-1}$ . After the appropriate number of cycles was performed, the cells were then dismantled  
408 in a dry room. The electrodes harvested from these cells were then subject to further  
409 electrochemical testing, as detailed below.

410 All electrochemical tests shown in the text, other than the full cell tests shown in  
411 Supplementary Fig. 1, were performed in 2032-type coin cells. A microbalance with  $\mu\text{g}$  level

412 accuracy (XPR2, Mettler Toledo) was used to mass the electrodes. They were assembled in an  
413 argon filled glove box using lithium counter electrodes and 1M LiPF<sub>6</sub> in EC:DEC (1:1 by  
414 weight) electrolyte (LP40, Gotion). They were electrochemically cycled using on a BCS-805  
415 (Bio-logic) potentiostat at the current specified in the text. In Fig. 1a, the cycle numbers given  
416 are one higher than the number of cycles conducted in the mini-18650 cell (e.g. the trace labeled  
417 cycle 46 underwent formation cycling, 45 normal charge-discharge cycles in the mini-18650, and  
418 then 1 more cycle at low rate in a coin cell, which is shown). Note that in Fig. 1a, all samples  
419 were cycled between 2.5 and 4.6 V other than the 2<sup>nd</sup> and 46<sup>th</sup> cycle, which were charged from 2  
420 V, a negligible change given that less than 0.5 mAh g<sup>-1</sup> of capacity was observed between 2 and  
421 2.5 V. The sample labeled “Pre-Formation” in Supplementary Fig. 1 was directly fabricated into  
422 a 2032-type half cell with no prior formation cycling and included a hold at 4.6 V for 9 mAh g<sup>-1</sup>  
423 of capacity to facilitate the ‘activation’ process. This sample was an 80% LMR-NMC, 10%  
424 carbon, and 10% binder composite by mass. The 2<sup>nd</sup> cycle data had a negligible hold of 3 mAh g<sup>-1</sup>  
425 <sup>1</sup> at 4.6 V which was excluded from the dQ/dV plot. We note that for the tests shown in  
426 Supplementary Figure 54, a different cycling protocol was followed than is listed above. The  
427 protocol is explained in detail in that Figure.

428 **X-ray diffraction.** X-ray diffraction was performed at beamline 2-1 at the Stanford  
429 Synchrotron Radiation Lightsource (SSRL) at 17 keV beam energy. A LaB<sub>6</sub> standard reference  
430 material was used to calibrate the energy. The capillaries were 0.5 mm special glass capillaries  
431 (Charles Supper) and were loaded inside an argon filled glovebox. The samples were rotated  
432 continuously throughout the measurement to avoid preferential orientation effects. The beam was  
433 0.5 mm in width and 1 mm in height. Raw data was recorded using a Pilatus100K detector at a  
434 700 mm distance from the capillary sample.

435           **X-ray absorption.** X-ray absorption was conducted in transmission mode on electrodes  
436 sealed under a pouch under argon at beamline 2-2 at SSRL. A Si (220)  $\phi = 90^\circ$  monochromator  
437 was used and was detuned to 50-60% of maximum intensity to eliminate higher order harmonics.  
438 The spectra of Ni, Co, and Mn reference foils were used to calibrate the photon energy by setting  
439 the first crossing of zero of the second derivative of the absorbance spectrum to be 8333 eV,  
440 7709 eV, and 6539 eV, respectively. Three ion chambers were used in series to simultaneously  
441 measure  $I_0$ ,  $I_{\text{sample}}$ , and  $I_{\text{ref}}$ . Spectrum normalization and alignment was performed using the  
442 Athena software package<sup>72</sup>. The samples measured for Supplementary Fig. 51 were measured at  
443 beamline 11-2 at SSRL with a similar setup. EXAFS analysis and simulation was performed  
444 using the Artemis software package (see Supplementary Methods)<sup>72</sup>. All EXAFS data and  
445 simulations presented are based upon  $k^2$ -weighted EXAFS spectra [ $k^2\chi(k)$ ].

446           **Ultramicrotomy sample preparation.** Electrode-sized thin sections were prepared by  
447 removing the positive electrode from the coin cell assembly using a coin cell disassembling tool  
448 (Hohsen). Once removed, the positive electrode was dipped three times into a vial of DMC to  
449 remove any electrolyte or precipitated Li salts and allowed to dry for approximately 10 minutes.  
450 The dried electrodes were then cut into smaller pieces, typically into circular sectors. The cut  
451 electrodes were placed into a BEEM embedding capsules (size 0) with pointed end down.  
452 Subsequently, EpoFix, which is a low viscosity epoxy was poured into the capsule and all  
453 remaining gas bubbles were removed from the capsule to ensure a uniform embedding of the  
454 sample and adequate penetration of the electrode pores. The epoxy was allowed to set for 24 hours  
455 until hardened. Once hardened the embedded samples were trimmed using a Leica Ultramicrotome  
456 UC7 equipped with a diamond trimming block (Diatome). The lateral size of the resulting  
457 blockface was typically 150-200  $\mu\text{m}$  square or rectangle. Once the block was shaped, sections were

458 created using the Leica Ultramicrotome UC7 and a custom diamond knife (Diatome). The custom  
459 diamond knife was created specifically for dry-sectioning of the embedded electrode sample thus  
460 removing the need for traditional water-based sample collection. The section thickness was  
461 normally set to a nominal thickness of 80 nm, although for preparing the samples shown in  
462 Supplementary Figs. 7, 25, and 26, the nominal thickness was set to 60 nm. During sectioning, a  
463 constant AC pulse was provided using a CRION antistatic device, in order to ensure sections did  
464 not stick to the surface of the knife away from the edge. Sequential sections were collected using  
465 a gold coated eyelash controlled using a micromanipulator, which utilized a static DC charge pulse,  
466 using the anti-static device, to attract the sections on to the eyelash. Once contacted, the eyelash  
467 was used to create a large ribbon consisting sequential sections by keeping the ribbon taut while  
468 new sections were cut. Once a sufficiently long ribbon was created, a second micromanipulator  
469 holding a TEM sample grid was brought into contact with the sample ribbon and then an DC pulse  
470 was used to detach the sample from the eyelash and attach it to the grid. From there, mesh grid  
471 samples were stored in a grid box inside of a glovebox until the X-ray microscopy measurements  
472 were performed. The reasonable agreement of the spatially-averaged Mn oxidation state in the  
473 sectioned samples ( $\text{Mn}^{3.80+}$  in Fig. 4a) with Mn oxidation states found from both K- and  $L_3$ -edge  
474 spectroscopy of non-sectioned samples (Fig. 1a and Supplementary Fig. 16) indicates that  
475 sectioning does not significantly alter the chemical state of the discharged electrodes. Likewise,  
476 the significant presence of oxidized oxygen (Fig. 5c) in the sectioned charged samples<sup>2,68,73</sup>  
477 suggests that sectioning is unlikely to significantly alter the chemical state of the charged samples.  
478 Based on the qualitative similarities in, for example, Supplementary Figs. 26 and 27, it is likely  
479 that many primary particles remain intact after the ultramicrotomy process. Still, the cutting of  
480 some primary particles may occur and cannot be excluded. This sample preparation method was

481 used for all images of the material shown in the main text with the sole exception of the pristine  
482 particles in Fig. 2a.

483 **Dispersed sample preparation.** Samples prepared via sonication and dispersion were  
484 removed from coin cells as above and then prepared as reported previously<sup>2</sup>. These samples  
485 account for the spectra in Fig. 1d (which are taken from the images shown in Supplementary  
486 Figure 16) as well as the image of the pristine sample in Fig. 2a and all samples in  
487 Supplementary Figures 16,17,39,41,43,44,50 (pristine and Mn<sub>2</sub>O<sub>3</sub>), and 52.

488 **Scanning transmission x-ray microscopy.** Sectioned and dispersed samples were  
489 loaded onto 3 mm Si<sub>3</sub>N<sub>4</sub> TEM grids (Norcada), with some measurements being taken on 3 mm  
490 copper TEM grids with a formvar film coated with a layer of carbon (Ted Pella, mesh 100). The  
491 samples were transported sealed under argon to the Advanced Light Source (ALS) at Lawrence  
492 Berkeley National Laboratory. STXM measurements were performed at beamlines 11.0.2.2 and  
493 7.0.1.2 using a zone plate with outer zone width of 45 nm. Images at different X-ray energies  
494 were aligned using the aXis2000 software package when possible and a custom Python script  
495 when necessary. The energy of the beam was calibrated at each edge using a reference sample,  
496 generally the pristine LMR material. Analysis was performed using custom MATLAB software.

497 **X-ray Ptychography.** Ptychography measurements were performed at beamline 7.0.1.2  
498 at the ALS and were taken almost exclusively in double exposure mode to allow for maximum  
499 spatial resolution while avoiding detector saturation. The scan step size was set to ~ 40 nm, with  
500 a reconstructed image pixel size of ~ 5 nm. Supplementary Fig. 52 and 53 show that the samples'  
501 chemical states are not significantly altered by the high X-ray dose of ptychography  
502 measurements.

503           **Scanning electron microscopy (SEM).** Samples for scanning electron microscopy were  
504 prepared by light sonication (~ 2 min) in isopropanol followed by being dropcast on small  
505 sections of aluminum foil. Scanning electron micrographs were recorded on a Sirion SEM (FEI)  
506 at Stanford Nano Shared Facilities (SNSF).

507           **Inductively coupled plasma mass spectrometry (ICP-MS).** ICP-MS was performed on  
508 a Thermo Scientific XSERIES 2 ICP-MS at Stanford's Environmental Measurements Facility.  
509 Samples were prepared by washing with anhydrous dimethyl carbonate after cell disassembly,  
510 and then by dissolving the sample in 2% HNO<sub>3</sub> in the presence of ~ 1% H<sub>2</sub>O<sub>2</sub>. Although the  
511 carbon did not dissolve, the elemental composition found from an electrode was nearly identical  
512 to that found of the pristine material, confirming the robustness of the preparation method. The  
513 quantity of each element present was found using a calibration curve generated by preparing  
514 seven standard solutions of known concentrations. Stock solutions of Li, Ni, Mn, and Co  
515 dissolved in 2% HNO<sub>3</sub> (Inorganic Ventures) were used to prepare the standard solutions.

516           **Pycnometry.** Density measurements were conducted using a 1 cm<sup>3</sup> AccuPyc II 1340  
517 automatic gas pycnometer (Micromeritics) using a 0.1 cm<sup>3</sup> insert and 99.9999% pure He gas  
518 (Praxair). The volume of the insert and the expansion chamber were calibrated using a 0.718541  
519 cm<sup>3</sup> standard ball bearing (Micromeritics). Ten or more repeat measurements with cap  
520 removal/replacement were made of each sample, with the average and standard error reported in  
521 Fig. 3b.

522           **Neutron diffraction.** ~ 500 mg of pristine material was loaded in a 3 mm vanadium can,  
523 sealed under argon, and transported the POWGEN beamline at Oak Ridge National Laboratory.

524 The diffraction pattern was then collected at room temperature in high resolution mode using a  
525 beam of neutrons with a center wavelength of 1.5 Å.

526 **Annealing of Cycled Electrodes.** The annealing of cycled electrodes was conducted by  
527 heating the cycled electrode, which was first discharged to and held at 2.5 V vs. Li/Li<sup>+</sup> for ~ 6  
528 hrs, at 150 °C for 18 hr in a 100% O<sub>2</sub> gas environment. The electrode did not delaminate during  
529 this process, and therefore the electrochemical test shown in Supplementary Fig. 31 was  
530 conducted simply by reassembling a coin cell with the electrode following heat treatment.

531 **Transmission Electron Microscopy.** Scanning TEM Annular Dark Field (STEM-ADF)  
532 images were taken using a FEI Titan Environment TEM operating at 300 kV with an image  
533 corrector. The probe size was 0.5 nm and the convergence and collection semi-angles were 9.3  
534 mrad and 19 – 25 mrad, respectively. Selected area diffraction patterns (SADP) were collected  
535 using the same TEM. High resolution transmission electron microscopy (HRTEM) images  
536 (Supplementary Figures 8 and 9) were taken on a different TEM (FEI Tecnai G2 F20 X-TWIN),  
537 which was operated at an accelerating voltage of 200 kV.

538 **Focused Ion Beam (FIB) Sectioning.** For the FIB-SEM-prepared TEM lamella, the  
539 work was done on the FEI Helios 600i DualBeam Focused Ion Beam/Scanning Electron  
540 Microscope at the Stanford Nano Shared Facilities. Electron-beam and then ion-beam platinum  
541 deposition was performed sequentially to planarize the region to be extracted, at approximately  
542 300nm and 500nm thicknesses, each. Trench cuts were milled in front of and behind the  
543 protected region to expose the cross-section to be extracted. The lamella was polished down to  
544 about 1 micron thickness for extraction while at 30 kV and with the sample orthogonal to the ion  
545 beam. Re-orienting the sample normal to the electron beam, an “U”-cut was made cleanly



546 through to define the edges of the lamella, leaving two tabs at either top edge. An Omniprobe  
547 AutoProbe 200 standard tungsten tip was inserted and welded to one top corner using ion-beam  
548 deposited platinum. The lamella was then severed from the substrate and subsequently attached  
549 cantilever-style to the edge of a copper Omniprobe lift-out grid post, also using ion-beam  
550 deposited platinum, and the needle was severed to release. The lamella was then further polished  
551 with the ion beam, both front and back, to sub-200 nm thickness while at 30 kV and an  
552 additional  $\pm 1.5^\circ$  tilt off-normal to strive for parallel sidewalls. Final polishing was done at 5 kV  
553 and  $\pm 3^\circ$  off-normal tilt to minimize amorphization damage and achieve electron-transparency.  
554 This sample preparation method was used to create the images shown in Supplementary Figures  
555 8 and 9.

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### 773 **Author Contributions**

774 P.M.C., S.S.K., W.E.G., D.A.S., M.F.T., and W.C.C. conceived the study. S.S.K. and E.K.  
775 performed the ultramicrotomy sectioning. P.M.C., S.S.K., W.E.G., Y.-S.Y. and D.A.S. collected  
776 ex situ STXM and ptychography images and analyzed the data. P.M.C., K.L., and K.H.S.  
777 collected SXRD data. P.M.C. collected ND data. P.M.C., K.L., K.H.S., and M.F.T. analyzed the  
778 diffraction data. S.-J.A. synthesized the material and cycled the mini-18650 cells. P.M.C.  
779 performed the ICP-MS, SEM, and pycnometry experiments. P.M.C. collected transition metal  
780 K-edge spectra and K.L., W.E.G., and M.F.T. contributed to the interpretation. P.M.C and  
781 W.C.C. developed the diffusion and two-phase core-shell models used. Y. L. and X.X. collected  
782 TEM images. Y.L., X.X., P.M.C., A.F.M., R.S., and W.C.C. analyzed the TEM data. P.M.C,  
783 W.C.C., and M.F.T. wrote the manuscript and all authors revised the manuscript.

### 784 **Competing Interests**

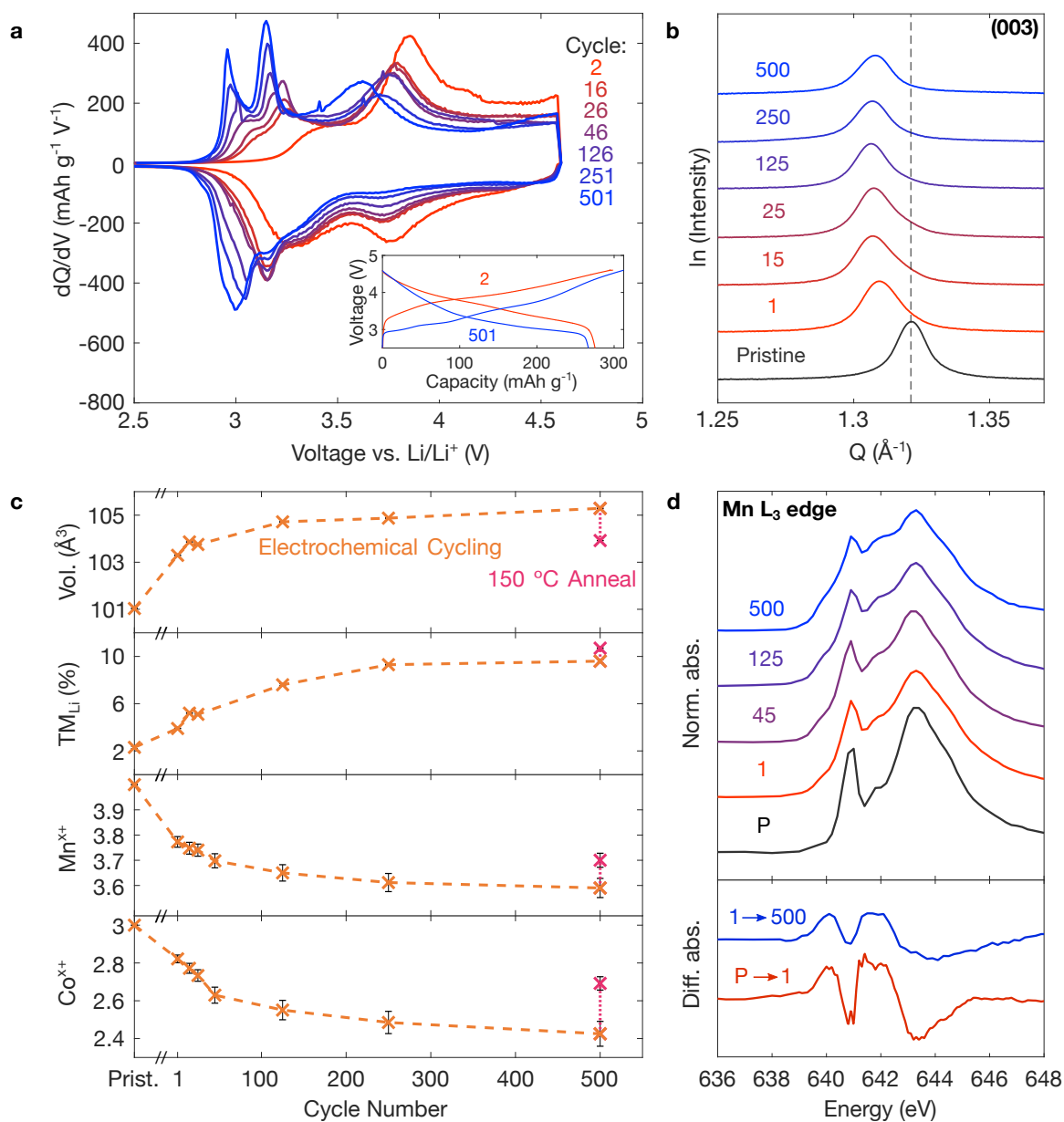
785 The authors declare no competing interests.

### 786 **Data Availability**

787 Data supporting all main text figures can be found at <https://doi.org/10.5281/zenodo.4697951>.

788 Data supporting all supplementary information figures can be found at

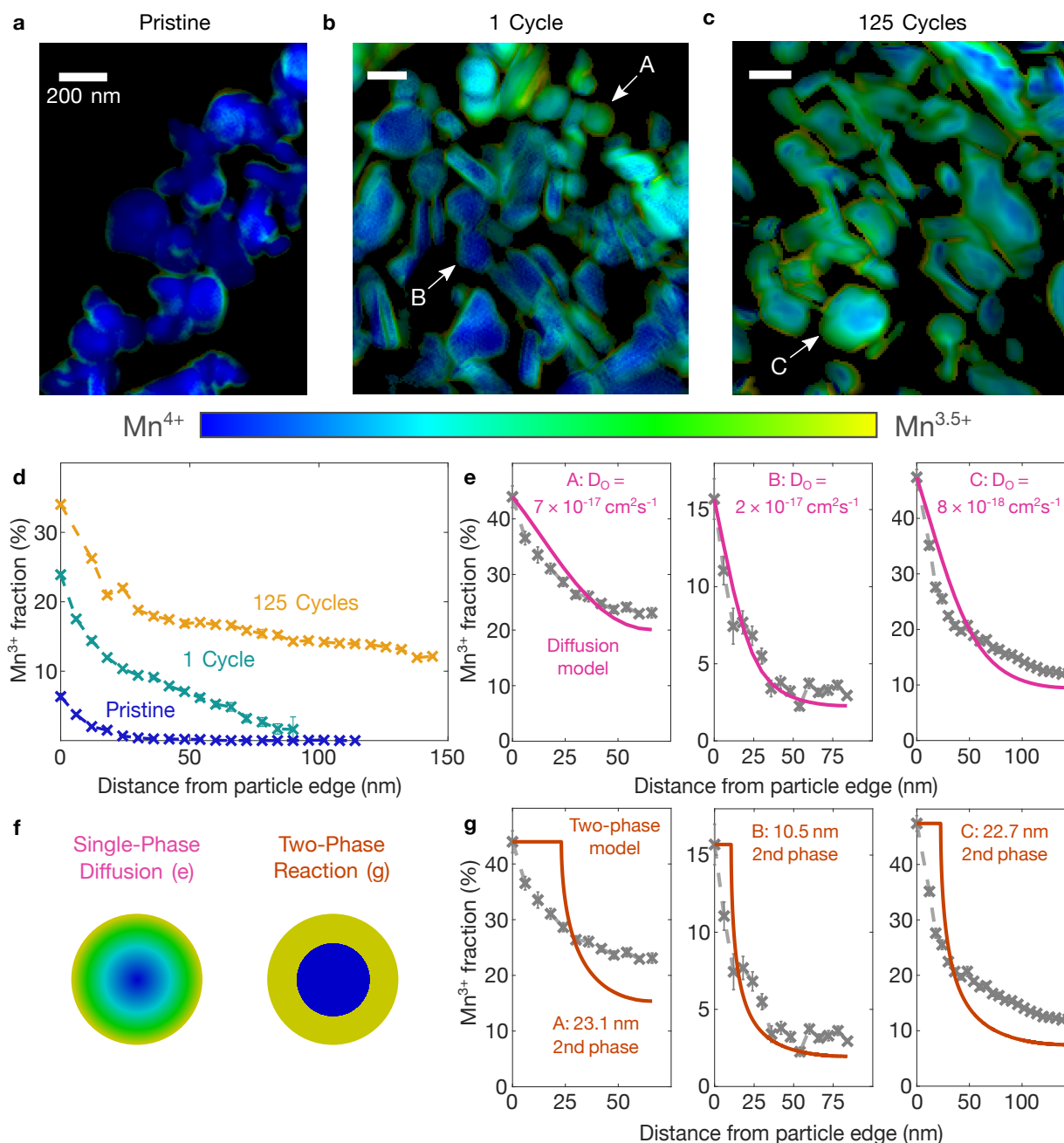
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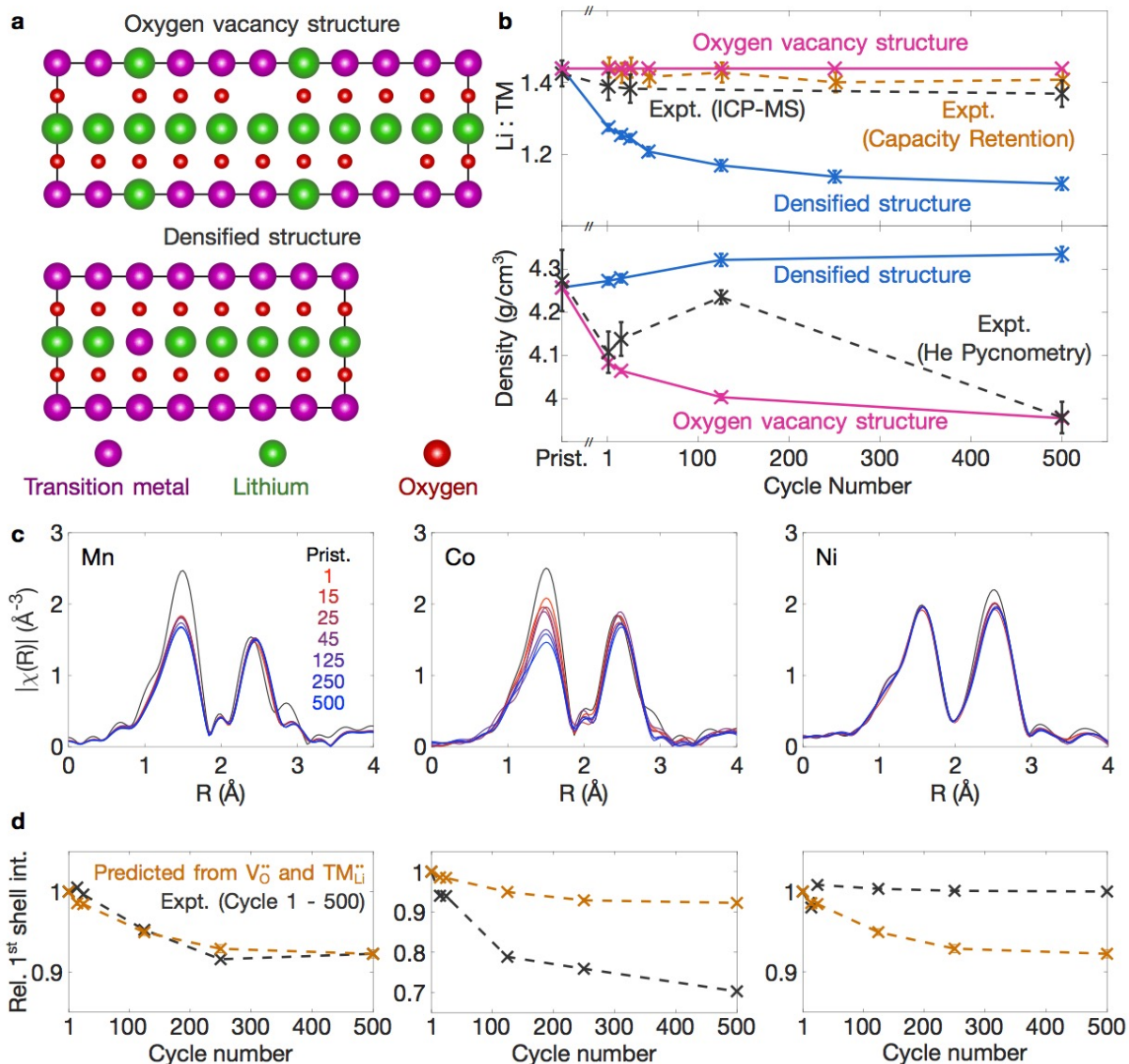
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791 **Figure 1. Electrochemical voltage depression linked to cation disordering and TM reduction.** **a**  
 792 Electrochemical differential capacity plots taken at  $\sim 4 \text{ mA g}^{-1}$ . The inset shows that the discharge  
 793 capacity remains at  $\sim 96\%$  of its initial value even after 500 cycles. **b** (003) peak plotted on a logarithmic  
 794 scale after varying numbers of cycles with an absence of secondary peaks, indicating that the bulk  
 795 material remains a single phase upon cycling. **c** The voltage depression upon cycling is correlated with an  
 796 increase in the unit cell volume (Vol.), an increase in the TM occupancy in the Li layer ( $\text{TM}_{\text{Li}}$ ), and the  
 797 reduction of the average TM oxidation state ( $\text{Co}^{\text{x}+}$  and  $\text{Mn}^{\text{x}+}$ ). Error bars are from Rietveld refinement  
 798 (Supplementary Fig. 3) and the uncertainty in the edge position vs. oxidation state slope (Supplementary  
 799 Fig. 11). The TM reduction and lattice volume expansion which occur over cycling can be partially  
 800 reversed by annealing the cycled electrode at  $150 \text{ }^\circ\text{C}$ . **d** Transmission-based Mn  $\text{L}_3$ -edge spectra obtained  
 801 through STXM showing significant changes over 500 cycles. The differential spectra reveal that a similar  
 802 change takes place between the 1<sup>st</sup> and 500<sup>th</sup> cycle as that which occurs between the pristine material and  
 803 1<sup>st</sup> cycle. Raw data for this figure is available (see Data Availability).





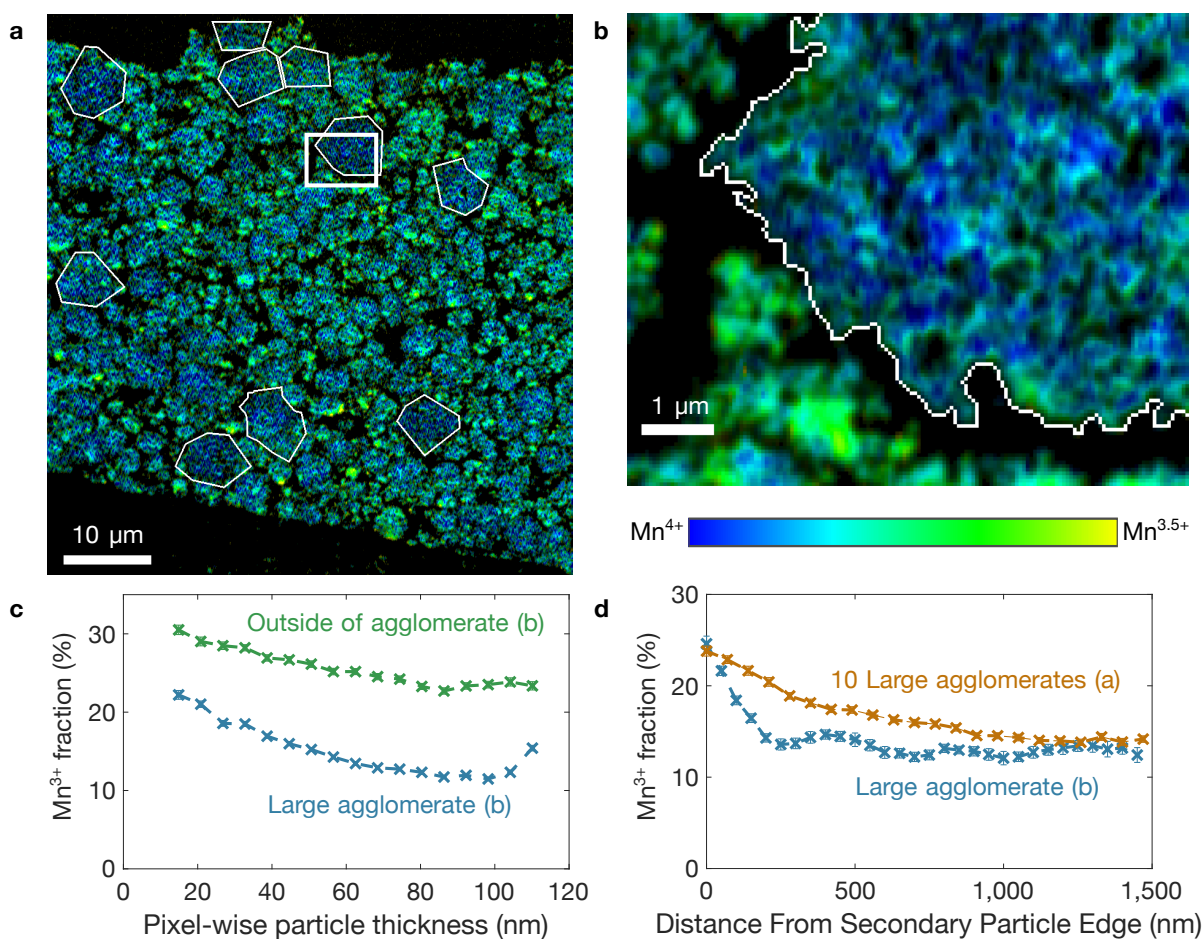
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805 **Figure 2. Spatial dependence of the Mn oxidation state within primary particles.** X-ray ptychography  
806 images of the **a** pristine material and material after **b** 1 cycle and **c** 125 cycles are shown. The scale bar in  
807 each image is 200 nm. **d** The Mn<sup>3+</sup> content as a function of distance from the particle edge. **e** The Mn<sup>3+</sup>  
808 spatial distribution in selected particles (with minimal particle overlap) fit with a diffusion profile and  
809 individual chemical diffusion coefficient. The results suggest an overall oxygen chemical diffusion  
810 coefficient of  $\sim 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ . **f** Schematic illustration of two possible mechanisms which can give rise to a  
811 Mn<sup>3+</sup> concentration which is lower in the bulk than on the surface. **g** The Mn<sup>3+</sup> spatial distribution in  
812 individual particles fit with a two-phase core-shell model. The fits using this model are qualitatively and  
813 quantitatively poor. Error bars are based on the weighted standard error of the Mn<sup>3+</sup> concentration of the  
814 pixels contributing to each data point. Raw data for this figure is available (see Data Availability).  
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 817 **Figure 3. Structural Consequences of Oxygen Release.** **a** Graphical depiction of the two possible  
 818 structures after 500 cycles discussed in the text. The initial structure in this illustration (not shown) is  
 819 identical to the vacancy structure but with a full oxygen sublattice. Both structures depicted here would  
 820 have an identical average TM oxidation state of 2.75+. **b** ICP-MS, capacity retention, and helium  
 821 pycnometry density measurements with the pink and blue lines representing the expected measurement  
 822 values if all of the oxygen release were accompanied by the formation of oxygen vacancies or  
 823 densification, respectively. All three measurements indicate that the majority of the oxygen release causes  
 824 the formation of oxygen vacancies. ICP-MS and pycnometry error bars are based on the standard error of  
 825 repeat measurements. Capacity retention error bars are based on an estimated 5 mAh g<sup>-1</sup> uncertainty in  
 826 discharge capacity. Error bars for the structure models are propagated from the uncertainty in the edge  
 827 position vs. oxidation state slope (Supplementary Fig. 11) **c** EXAFS data at the TM K edge as a function  
 828 of cycle number showing a decrease in the first shell scattering intensity with cycling for Mn and Co, but  
 829 not Ni. **d** A quantitative comparison of the relative changes in first shell scattering intensity  
 830 (approximated by the maximum value of  $|\chi(R)|$ ) at the Mn, Co, and Ni K edge with that which would be  
 831 predicted from the presence of both  $V_O^{\bullet\bullet}$  and  $TM_{Li}^{\bullet\bullet}$  defects alone. Error bars in the predicted values are

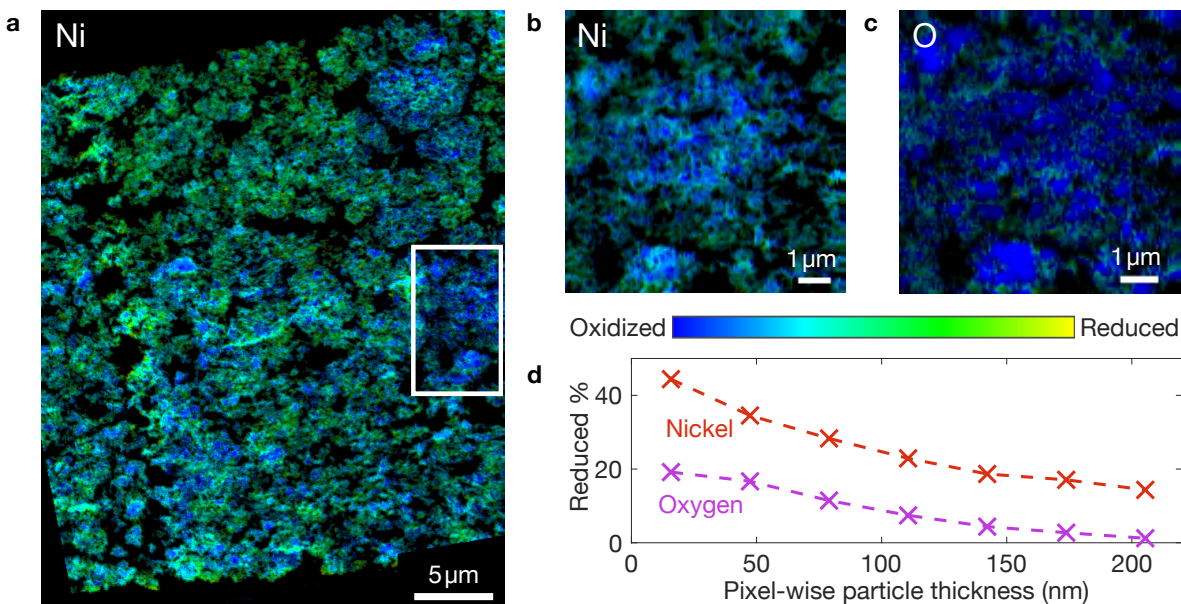
832 propagated from uncertainty in the  $V_O^{\ddot{}}$  and  $TM_{Li}^{\ddot{}}$  concentrations. Raw data for this figure is available  
833 (see Data Availability).

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 859 **Figure 4. Oxidation state heterogeneity on the secondary particle scale.** All samples in this figure are  
 860 taken after 1 cycle followed by discharging to 2.5 V vs. Li/Li<sup>+</sup> and holding for ~ 6 h. **a** Image with the  
 861 field of view covering the entire electrode thickness (~ 40 μm). Ten large agglomerates are outlined in  
 862 white. **b** A single large agglomerate (top right of image, outlined in white) that is significantly more  
 863 oxidized than the surrounding areas. This image, taken at finer resolution than Fig. 4a, corresponds to the  
 864 region in the thick white rectangle in Fig. 4a. **c** The trend of a relatively more oxidized large agglomerate  
 865 is maintained even at a fixed particle thickness, implying that a primary particle of identical size and  
 866 shape will be more oxidized within the large agglomerate than outside of it. **d** The primary particles at the  
 867 exterior of large agglomerates are more reduced than the primary particles in interior. Error bars are based  
 868 on the weighted standard error of the Mn<sup>3+</sup> concentration of the pixels contributing to each data point.  
 869 Raw data for this figure is available (see Data Availability).

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 876 **Figure 5. Oxidation State Heterogeneity in the Charged State.** All samples in this figure are taken  
 877 after 125 cycles following by charging to 4.6 V vs. Li/Li<sup>+</sup> and holding for ~ 6 h. **a** Distribution of the Ni  
 878 oxidation state with the field of view covering the entire electrode thickness. The area in the white boxed  
 879 region was imaged a second time with finer energy resolution, which is shown in Fig. 5b,c. **b** Distribution  
 880 of the Ni oxidation state in a large secondary particle. **c** Distribution of the O oxidation state in a large  
 881 secondary particle. **d** Fraction of the reduced component (see Supplementary Fig. 42) present as a  
 882 function of particle thickness for Fig. 5b,c. The results indicate that the surface of the material is not able  
 883 to achieve as high of an oxidation state as the bulk. Error bars are based on the weighted standard error of  
 884 the Mn<sup>3+</sup> concentration of the pixels contributing to each data point. Raw data for this figure is available  
 885 (see Data Availability).  
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