Supplemental Information: Origin of Rapid Delithiation In Secondary Particles Of LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 and LiNi_{y}Mn_{z}Co_{1–y–z}O_2 Cathodes

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1 Model Equations

1.1 8-Particle Ensemble

The cell used in our 8-particle simulations consists of a Li metal anode and an LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode, which contains 8 particles ranging from 2 µm to 5.5 µm in radius, as shown in the Figure S1. All the particles are attached to a metallic current collector, which is also shown in Figure S1. The two electrodes are separated by a pool of electrolyte. The size of the computational domain is 50 × 50 × 50 µm^3.

Within the LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 particles, the mass transport is calculated as[8, 13]

$$\frac{\partial c_{p,k}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_{p} r^2 \frac{\partial c_{p,k}}{\partial r} \right)$$

(1)

where $c_{p}$ is the Li-site fraction ($\chi_{Li}$) in the electrode particles, $t$ is time, $r$ is the radial distance, $D_{p}$ is the Li diffusivity in LiNi_{0.8}Co_{0.15}Al_{0.05}O_2. The subscript $k$ represents the particle number from hereon.
The boundary conditions for Equation 1 are as follows[8, 13]

\[-D_p \frac{\partial c_{p,k}}{\partial r} |_{r=R_{p,k}} = J_k\]  \hspace{1cm} (2a)
\[-D_p \frac{\partial c_{p,k}}{\partial r} |_{r=0} = 0\]  \hspace{1cm} (2b)

where \(R_{p,k}\) represents the particle radius. Furthermore, all the particles are set to have an initial \(x_{Li}\) of \(c_p^0\).

The electrochemical reaction flux \(J_k\) at the LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\)/electrolyte interface for each particle is calculated using the Butler-Volmer equation as[8, 13]

\[J_k = \frac{i_0}{F} \times \left( \exp \left( \frac{0.5F}{RT} \eta_k \right) - \exp \left( \frac{-0.5F}{RT} \eta_k \right) \right)\]  \hspace{1cm} (3a)

\[\eta_k = \phi_{p,k} - \phi_e - U^0_k\]  \hspace{1cm} (3b)

where \(i_0\) is the exchange current density, \(F\) is the Faraday constant, \(R\) is the ideal gas constant, \(T\) is absolute temperature, \(\eta_k\) is overpotential on the surface of \(k^{th}\) particle. Furthermore, \(\phi_{p,k}\) is the electrostatic potential of the particle, \(\phi_e\) is the electrostatic potential of the electrolyte, and \(U^0_k\) is the open circuit voltage (OCV) of LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) vs.Li/Li\(^+\).

The electrostatic potential of LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) particles is obtained as[8, 13]

\[-\sigma_p \nabla \phi_{p,k} = i_{p,k}\]  \hspace{1cm} (4)

where \(\sigma_p\) is the electronic conductivity of LiNi\(_{0.8}\)Co\(_{0.15}\)Al\(_{0.05}\)O\(_2\) and \(i_{p,k}\) is the current density on the \(k^{th}\) particle. It should be noted that \(i_{p,k} = J_k F\).
The electrochemical reaction flux and the electrostatic potential at the Li metal anode is calculated in a similar manner as Equations 3a–4 as \[28\]

\[
J_{\text{Li}} = \frac{i'_0}{F} \times \left( \exp \left( \frac{0.5F}{RT} \eta_{\text{Li}} \right) - \exp \left( -\frac{0.5F}{RT} \eta_{\text{Li}} \right) \right)
\]

(5a)

\[
\eta_{\text{Li}} = \phi_{\text{Li}} - \phi_e - U_{\text{Li}}^0
\]

(5b)

where \(J_{\text{Li}}\), \(i'_0\), and \(\eta_{\text{Li}}\) are the reaction flux, the exchange current density, and the overpotential at the Li metal anode/electrolyte interface, respectively. The electrostatic potential and the OCV of the electrode are given by \(\phi_{\text{Li}}\) and \(U_{\text{Li}}^0\), respectively. Furthermore, \(\phi_{\text{Li}}\) is obtained as \[8, 13\]

\[-\sigma_{\text{Li}} \nabla \phi_{\text{Li}} = i_{\text{app}}\]

(6)

where \(\sigma_{\text{Li}}\) is the electronic conductivity of Li metal and \(i_{\text{app}}\) is the applied current density to the cell. It should be noted that \(\sum_k 4\pi R^2_{p,k} i_{p,k} = i_{\text{app}}A\), where \(A\) is the cross-sectional area of both the current collector (in contact with the LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 cathode) and the Li metal anode. Moreover, we set the top surface of the Li metal anode as ground.

The mass transport equation for the electrolyte is written as \[8, 13\]

\[
\frac{\partial c_e}{\partial t} = \nabla \cdot (D_e \nabla c_e) - \frac{i_e \cdot \nabla i_+^0}{F} + \frac{F}{(1 + \frac{\partial \ln(f_\pm)}{\partial \ln(c_e)}) (1 - t_+^0) \nabla \ln c_e}
\]

(7)

where \(D_e\) represents the electrolyte diffusivity, \(i_e\) represents the electrolyte current density, and \(i_+^0\) represents the transference number for Li\(^+\). The initial value of \(c_e\) is set as \(c_e^0\). Finally, \(i_e\) is calculated as \[8, 13\]

\[
i_e = -\sigma_e \nabla \phi_e + \frac{2RT}{F} \sigma_e \left(1 + \frac{\partial \ln(f_\pm)}{\partial \ln(c_e)} \right) (1 - t_+^0) \nabla \ln c_e
\]

(8)

where \(\sigma_e\) is the electrolyte conductivity and \(\frac{\partial \ln(f_\pm)}{\partial \ln(c_e)}\) accounts for the salt activity coefficient dependence on the electrolyte concentration.

### 1.2 30-Particle Ensemble

For the 30-particle system, we only solve for the diffusion of Li in NCA particles (Equations 1–2b) and the electrochemical reaction at the LiNi_{0.8}Co_{0.15}Al_{0.05}O_2/electrolyte interface (Equations 3a and 3b). We do not solve for the electrostatic potentials in LiNi_{0.8}Co_{0.15}Al_{0.05}O_2 particles (Equation 6) and the electrolyte (Equation 8) and the electrolyte concentration (Equation 7) because the applied C-rate (C/20) is too low to cause any significant spatial variations in them. Thus, we assume these potentials to be constant. Furthermore, we do not include the Li-metal anode (Equations 4, 5a–5b) because it does not offer any significant overpotential during C/20 charging.

We reformulate Equations 1 and 3b to a form suitable for the smoothed boundary method\[29, 14\]. The reformulated form is written as \[14\]
\[
\frac{\partial c_{p,k}}{\partial t} = \frac{1}{\psi_k} \nabla \cdot \psi_k \nabla c_{p,k} + \frac{|\nabla \psi_k|}{\psi_k} J_k
\]  

(9)

where \( \psi_k \) represents a continuous domain parameter that a value of 1 within the \( k \)th particle and 0 outside the particle. The particle/electrolyte interface is defined as the region where \( 0 < \psi_k < 1 \).

2 Numerical implementation of the model equations

2.1 8-Particle Ensemble

The system of coupled partial differential equations listed above was solved in COMSOL Multiphysics 5.6a using the finite element method. A custom mesh with linear tetrahedral elements was used to discretize the model geometry. The maximum and minimum element sizes within the LiNi_{0.8}Co_{0.15}Al_{0.05}O_{2} particles were set to \( 6.5 \times 10^{-7} \) and \( 1 \times 10^{-8} \), respectively. The model was solved using the multifrontal massively parallel sparse direct solver [2] and a backward differential formula solver for time-stepping with a relative tolerance of \( 1 \times 10^{-5} \).

2.2 30-Particle Ensemble

The system of coupled governing equation listed above was solved by the finite difference method. The computational domain is discretized by a 3D uniform cartesian grid with a spatial resolution of \( \Delta x = \Delta y = \Delta z = 0.1 \mu m \). We set the time-stepping as 0.02 s and the relative tolerance for the applied current during each time step is \( 1 \times 10^{-4} \).

3 Configuration of Particles in the 30-Particle Ensemble

The particle sizes of the LiNi_{0.8}Co_{0.15}Al_{0.05}O_{2} powders are D10: 3.7 \( \mu m \), D50: 6.5 \( \mu m \), and D90: 9.8 \( \mu m \). We assume a log-normal distribution to describe the particle size distribution:

\[
f(x) = \frac{1}{\sqrt{2\pi}\sigma x} \exp \left( -\frac{(\ln x - \mu)^2}{2\sigma^2} \right) \quad (10a)
\]

\[
F(x) = \frac{1}{2} \text{erfc} \left( \frac{-\ln x - \mu}{\sqrt{2}\sigma} \right) \quad (10b)
\]

where \( x \) is the random variable satisfying a log-normal distribution, \( f(x) \) is the probability density function of \( x \), \( \sigma \) is the standard deviation of \( x \), \( \mu \) is the mean of \( x \), \( F(x) \) is the cumulative density function of \( x \), and \( \text{erfc} \) is the complementary error function.

We fit these three cumulative distribution values with Equation 10b, which yields \( \mu = 1.8718 \), \( \sigma = 0.1027 \). To maintain the statistics of the real particle size distribution, we use the stratified sampling[19] with sampling particle diameter systematically within each stratum. After determining the particle size distribution, we randomly generate the centers of these particles and use a hyperbolic tangent function to generate the domain parameters for individual particle, \( \psi_k \):
The domain has a size of $36 \times 36 \times 40 \ \mu\text{m}^3$ ($360 \times 360 \times 400$ grid points).}

\[ \psi_k = \frac{1}{2} + \frac{1}{2} \tanh \left( \frac{r - d}{\delta} \right) \]  \hspace{1cm} (11)

where $r$ is the radius of this particle, $d$ is the distance to the particle center, $\delta$ determines the interfacial thickness and we used $\delta = \sqrt{2}$.

Figure S2 shows the particle size distributions obtained by stratified sampling\cite{19} and the computational domain for the 30-particle simulations.

4 Model Parameters

4.1 Open Circuit Voltage

The OCV was measured for the 1st charge of Toda $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ at 0.02 h$^{-1}$ (C/50, Figure S3). The procedure of measurements can be found in Liu et al.’s paper\cite{15}.

We fitted the experimentally measured OCV data with the following equation:

\[ \text{OCV} = a \ln \left( \frac{x}{1-x} \right) + b \left( x - 1 \right)^2 + c x^2 + d \]  \hspace{1cm} (12)

Where $a = -0.06809 \ \text{V}$, $b = 0.9009 \ \text{V}$, $c = 0.2749 \ \text{V}$, $d = 3.544 \ \text{V}$. $x$ represents the lithium fraction.

4.2 Li Diffusivity in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$

The diffusivity values are obtained from the report by Amin et al\cite{3}. We use linear interpolation to estimate the diffusivity values between data points. For the regions close to fully delithiation and fully lithiation, we set the diffusivity values the same as the closest data point.
Figure S3: Parameterized fitting of OCV response. Red line denotes the measured OCV curve, the blue line denotes the fitted OCV curve.

Figure S4: $D_x$ as a function of $x$ for the LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ material[3].
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic conductivity of NCA + carbon additive, $\sigma_p$</td>
<td>$9.1 \times 10^7$</td>
<td>S m$^{-1}$</td>
<td>Literature [4]</td>
</tr>
<tr>
<td>Electronic conductivity of Li, $\sigma_{Li}$</td>
<td>$1 \times 10^{5}$</td>
<td>S m$^{-1}$</td>
<td>–</td>
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<td>Exchange current density of Li, $i_0^e$</td>
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<td>A m$^{-2}$</td>
<td>Literature [16]</td>
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<tr>
<td>OCV of Li metal, $U_{0Li}$</td>
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<td>V</td>
<td>–</td>
</tr>
<tr>
<td>Max $x_{Li}$ in NCA, $c_{pmax}^{max}$</td>
<td>$4.8 \times 10^4$</td>
<td>mol m$^{-3}$</td>
<td>Estimated based on literature [12, 23, 24]</td>
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<tr>
<td>Initial $x_{Li}$ in NCA, $c_0^p$</td>
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<td>mol m$^{-3}$</td>
<td>Presumed</td>
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<td>Initial electrolyte salt concentration, $c_0^e$</td>
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<tr>
<td>1C current density</td>
<td>1.164</td>
<td>A m$^{-2}$</td>
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Table S1: Additional parameters used in physics modeling.

4.3 Electrolyte Parameters

Like our previous works [5, 6], all the electrolyte parameters, namely $\sigma_e$, $D_e$, $\partial \ln(f_x) / \partial \ln(c_e)$, and $t_0^e$ are obtained from the report by Nyman et al [17].

4.4 Remaining Parameters

The remaining model parameters are described in Table S1.

5 Sensitivity Analyses with Respect to Exchange current density ($i_0$)

In this section, we report the results of the sensitivity studies with respect to different forms of $i_0$. We note that we set $D_s > 5 \times 10^{-15}$ m$^2$ s$^{-1}$ (as shown in Figure S4) for all simulations in this section to avoid solid-state limitation in the simulated system.

6 Selection of $i_0$ Function

Traditionally, $i_0$ is considered to be directly proportional to $\sqrt{x(1-x)}$, where $x$ is the Li site fraction in the active material [8, 9, 10, 11]. This functional form results from the theoretical consideration that Li exists in a solid solution state in the active material. However, recent studies have shown that such a dependence is not applicable for materials like LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ [18] and LiNi$_{y}$Mn$_{z}$Co$_{1-y-z}$O$_2$ [26, 27, 25]. For example, Park et al. [18] reported an exponential dependence of $i_0$ on $x$ [18]. Other studies show that $i_0$ is a monotonically decreasing function of $x$ [26, 27, 25]. Thus, the dependence of $i_0$ on $x$ is not precisely known. Furthermore, the literature is missing the $i_0$ data for $x > 0.92$.

To work with the uncertain form of $i_0$, we ran two sets of simulations. In the first set of the simulations, we employed the traditional form of $i_0$, which is shown in Figure S5. In the second set of simulations, we used a model form of $i_0$, which is also shown in Figure S5. The model form is setup to have a smooth step function of $x$; the step in the function is described by a cubic spline.

The traditional form only has the max value of $i_0$, $i_{0\text{max}}$, as a tunable parameter, whereas the model form has four parameters: $i_{0\text{min}}$, the minimum value of $i_0$; $i_{0\text{max}}$; $x^*$, the value of $x$ where the transition begins from $i_{0\text{min}}$ to $i_{0\text{max}}$; and
Figure S5: Log scale comparison of different $i_0$ functions used in the sensitivity analyses. The literature-reported functions are shown in dashed lines. The plot labeled as “Literature A” is obtained from Reference [1], whereas the plots labeled as “Literature B” and “Literature C” are obtained from Reference [25].
Figures S6: Evolution of \( \langle x \rangle \) for the 8-particle system obtained using the traditional function of \( i_0 \). All the particles delithiate at the same rate.

\( \Delta x \), the width of the transition zone. The presence of additional parameters enables the model function of \( i_0 \) to represent most of the aforementioned-literature-reported functions. Since the values of \( i_0^{\text{max}} \) reported in the literature \cite{25, 1} do not vary widely, we selected an intermediate value, \( i_0^{\text{max}} = 1 \text{ A m}^{-2} \). The comparison of the literature values with the traditional and model functions of \( i_0 \) is provided in Figure S5.

7 Effect of \( i_0 \) on the Delithiation Dynamics

The evolution of the volume average Li-site fraction, \( \langle x \rangle \), for the first set of simulations, i.e., with the traditional form of \( i_0 \) at \( 0.05 \text{ h}^{-1} \) (C/20) are provided in Figure S6. All the particles delithiate at the same uniform rate. For the second set of simulations using the model form of \( i_0 \), the evolution results will be presented individually for the sensitivity analyses with respect to \( i_0^{\text{min}} \), \( x^* \), and \( \Delta x \).

8 Sensitivity Analyses with Respect to \( i_0^{\text{min}} \)

We chose four different values of \( i_0^{\text{min}} \) ranging from 0.001 A m\(^{-2}\) to 0.01 A m\(^{-2}\), while setting the value of other parameters as \( i_0^{\text{max}} = 1 \text{ A m}^{-2} \), \( x^* = 0.9 \), and \( \Delta x = 0.05 \). The comparison of different \( i_0 \) functions that differ in terms of \( i_0^{\text{min}} \) is provided in Figure S5. The corresponding results for the evolution of \( \langle x \rangle \) are provided in Figure S7. All particles exhibit accelerated delithiation for all values of \( i_0^{\text{min}} \). Furthermore, as \( i_0^{\text{min}} \) is decreased, the \( \langle x \rangle \) value at which the accelerated
Table S2: Reported energies of Ni K-edge whiteline. In-situ XAS of Li$_{x}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (Ref. [7]) and ex-situ XAS Li$_{x}$Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (Ref. [22]). Data extracted from published figures using WebPlotDigitizer[21]. Relative shifts in whiteline energy (Δ) calculated as difference from fully lithiated state (x = 1).

delithiation of each particle halts also decreases, which will hereafter be denoted as ⟨x⟩†. Since the $i^\text{min}_0$ value of 0.001 A m$^{-2}$ resulted in a similar value of ⟨x⟩† as the experiments, we selected this $i^\text{min}_0$ value as the nominal value. As explained in the main text, the oscillations in ⟨x⟩ in a few cases originate because of the large difference between $i^\text{min}_0$ and $i^\text{max}_0$.

9 Sensitivity analyses with respect to $x^*$

We choose four different values of $x^*$ ranging from 0.9 to 0.6, and we set the parameters as $i^\text{max}_0 = 1$ A m$^{-2}$, $i^\text{min}_0 = 1 \times 10^{-3}$ A m$^{-2}$, and $\Delta x = 0.05$. Figure S8 shows the comparison of different $x^*$ values. The onset of the accelerated delithiation is determined by the $x^*$ value and ⟨x⟩† decreases with a decrease in $x^*$.

10 Sensitivity analyses with respect to $\Delta x$

We choose four different values of $\Delta x$ ranging from 0.05 to 0.8, and we set other parameters as $i^\text{max}_0 = 1$ A m$^{-2}$, $i^\text{min}_0 = 1 \times 10^{-3}$ A m$^{-2}$, and $x^* = 0.9$. Figure S9 shows the comparison of different $\Delta x$ values. Both the amplitudes of the oscillations and the rate of accelerated delithiation are reduced as $\Delta x$ is increased.

11 Additional Figures
Figure S7: Evolution of $\langle x \rangle$ for the 8-particle system obtained using the model form of $i_0$ with four different values of $i_0^{\text{min}}$: a) 0.01 A m$^{-2}$, b) 0.005 A m$^{-2}$, c) 0.0025 A m$^{-2}$, and d) 0.001 A m$^{-2}$. The black dashed line in each plot represents $\langle x \rangle^\dagger$ for the smallest particle in the ensemble; $\langle x \rangle^\dagger$ decreases with a decrease in $i_0^{\text{min}}$. 
Figure S8: Evolution of $\langle x \rangle$ for the 8-particle system obtained using the model form of $i_0$ with four different values of $x^*$: a) 0.9, b) 0.8, c) 0.7, and d) 0.6. The black dashed line in each plot represents $\langle x \rangle^\dagger$ for the smallest particle in the ensemble. Note that $\langle x \rangle^\dagger$ decreases with a decrease in $x^*$. 
Figure S9: Evolution of $\langle x \rangle$ for the 8-particle system obtained using the model form of $i_0$ with four different values of $\Delta x$: a) 0.05, b) 0.1, c) 0.4, and d) 0.8. The black dashed line in each plot represents $\langle x \rangle^\dagger$ for the smallest particle in the ensemble. The rapid delithiation rate and the amplitude of the oscillations decrease as $\Delta x$ increases.
Figure S10: Exemplar 2D diffraction pattern for a single position during charging.
Figure S11: Ni K-edge absorption spectra for TXM fields of view. Mean optical depth of pixels after edge filter for (-•-) most reduced and (••) most oxidized time-steps for (a) LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$, (b) LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, and (c) LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$. 
Figure S12: Demonstration of isobestic point for LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ Ni K-edge. (a) Observed mean optical depth spectra for TXM frames during operando oxidation, with dashed lines added as visual guides. (b) Results of mathematical linear combinations of fit spectra (——) for observed spectral end-members for the most reduced (+) and oxidized (+) points in the LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ frames in (a). (c) Effect of linear combination ratio of spectral end-members in b on resultant whiteline energy.
Figure S13: Reported changes of Ni K-edge whiteline energy. (a) In-situ XAS of Li$_x$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and (b) ex-situ XAS of Li$_x$Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$. Data extracted from published figures as described in Table S2.

Figure S14: Sample decomposition of Ni K-edge fitting. Spectrum of mean optical depth of a frame of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ particles as (+) observed optical depth; (---) overall least squares fit; and (--) arctangent, (--) Gaussian and (--) background components of least squares fit.
Figure S15: Cell potential (—) and derivative of potential with respect to $x$ in Li$_x$MO$_2$ (…) during galvanostatic charge/discharge. (a,b) LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ cathode in modified coin-cell during first charge, (c) LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode in pouch-cell during first charge, (d) LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode in pouch-cell during second charge, (e) LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode charged in modified coin-cell, and (f) LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$ cathode charged in modified coin-cell. All galvanostatic profiles treated with third-order Sovitzky-Golay filter with 101-point window prior to calculating derivative.
Figure S16: Particle-level oxidation during first charge and discharge of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. (a) Changes in mean whiteline energies relative to 8351.69 eV for secondary particles during first charge and discharge. (c) Changes in mean whiteline energies relative to 8351.22 eV for secondary particles with higher temporal resolution. (b,d) Operando potential (→) and current (→) for galvanostatic cycling with 4.75 V potentiostatic step for LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ samples in modified coin-cells.

Figure S17: Particle-level oxidation during first and second discharge of LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ samples in pouch cells. (a) Changes in mean whiteline energies relative to 8350.92 eV for secondary particle during first charge/discharge cycle. (c) Changes in mean whiteline energies relative to 8350.45 eV for secondary particles during second charge and discharge cycle. (b) Operando potential (→) and current (→) for galvanostatic oxidation, open-circuit potential, galvanostatic reduction, and potentiostatic reduction during first cycle. (d) Operando potential (→) and current (→) for galvanostatic oxidation, potentiostatic oxidation, and galvanostatic reduction during second cycle.
Figure S18: Particle-level oxidation during first charge and discharge of LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$. (a) Mean whiteline energies of secondary particles during charge discharge. (b) Operando potential (—) and current (—) for galvanostatic cycling for LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$ samples in modified coin-cells. X-rays unavailable after 10 h due to maintenance.

Figure S19: Operando TXM of secondary LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ particles during first charge. Mean changes in whiteline energies relative to 8354.18 eV for secondary particles (a) without static X-ray exposure, and (b) with a 3 h static X-ray exposure prior to operando imaging. (c) Galvanostatic charging profile for modified coin-cell with LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ cathode.
Figure S20: Diffraction patterns for LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ through charge (red) and discharge (black) for a) P1, b) P2, and c) P3. Feature due to Li is denoted with a *.
Figure S21: (003) (left) and (104) (right) reflections of P1, P2, and P3 (top to bottom) during the first charge.
Figure S22: Unit cell parameters as a function of cell potential for a) P1 a parameter b) P1 c parameter c) P2 a parameter and d) P2 c parameter
Figure S23: Li content ($x$ in $\text{Li}_x\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) as a function of time during the first cycle for P1 (a) and P2 (b). The charge-discharge curve is shown below (c). Li values were correlated with equivalent values in ref. [20], for the $a$ unit cell parameter (red) and $c$ unit cell parameter (blue). Charge is represented by circles while discharge is represented by $x$ markers.
References


