

ADVANCED ENERGY MATERIALS

Supporting Information

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Origin of Rapid Delithiation In Secondary Particles Of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and $\text{LiNi}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ 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 $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 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 $50 \times 50 \times 50 \mu\text{m}^3$.

Within the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ particles, the mass transport is calculated as [8, 13]

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

where c_p is the Li concentration in the electrode particles, t is time, r is the radial distance, D_p is the Li diffusivity in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. The subscript k represents the particle number from hereon.

The boundary conditions for Equation 1 are as follows [8, 13]

$$-D_p \frac{\partial c_{p,k}}{\partial r} \Big|_{r=R_{p,k}} = J_k, \quad (2a)$$

$$-D_p \frac{\partial c_{p,k}}{\partial r} \Big|_{r=0} = 0, \quad (2b)$$

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

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

$$J_k = \frac{i_0}{F} \times \left(\exp \left(\frac{0.5F}{RT} \eta_k \right) - \exp \left(\frac{-0.5F}{RT} \eta_k \right) \right), \quad (3a)$$

$$\eta_k = \phi_{p,k} - \phi_e - U_k^0, \quad (3b)$$

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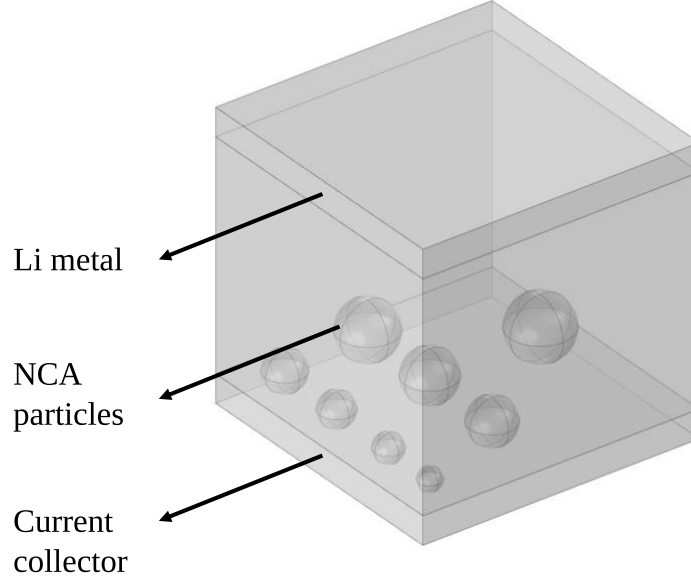


Figure S1: The 8-particle simulation setup in COMSOL.

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

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

$$-\sigma_p \nabla \phi_{p,k} = i_{p,k}, \quad (4)$$

where σ_p is the electronic conductivity of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 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]

$$J_{\text{Li}} = \frac{i'_0}{F} \times \left(\exp \left(\frac{0.5F}{RT} \eta_{\text{Li}} \right) - \exp \left(\frac{-0.5F}{RT} \eta_{\text{Li}} \right) \right), \quad (5a)$$

$$\eta_{\text{Li}} = \phi_{\text{Li}} - \phi_e - U_{\text{Li}}^0, \quad (5b)$$

where J_{Li} , i'_0 , and η_{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 ϕ_{Li} and U_{Li}^0 , respectively. Furthermore, ϕ_{Li} is obtained as [8, 13]

$$-\sigma_{\text{Li}} \nabla \phi_{\text{Li}} = i_{\text{app}}, \quad (6)$$

where σ_{Li} is the electronic conductivity of Li metal and i_{app} is the applied current density to the cell. It should be noted that $\sum_k 4\pi R_{p,k}^2 i_{p,k} = i_{\text{app}} A$, where A is the cross-sectional area of both the current collector (in contact with the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 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]

$$\frac{\partial c_e}{\partial t} = \nabla \cdot (D_e \nabla c_e) - \frac{i_e \cdot \nabla t_+^0}{F}, \quad (7)$$

where c_e and D_e represent the electrolyte concentration and diffusivity, respectively. The term i_e represents the electrolyte current density and t_+^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]

$$i_e = -\sigma_e \nabla \phi_e + \frac{2RT}{F} \sigma_e \left(1 + \frac{\partial \ln(f_{\pm})}{\partial \ln(c_e)} \right) (1 - t_+^0) \nabla \ln c_e, \quad (8)$$

where σ_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 $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ /electrolyte interface (Equations 3a and 3b). We do not solve for the electrostatic potentials in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 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 3a to a form suitable for the smoothed boundary method [29, 14]. The reformulated form is written as [14]

$$\frac{\partial c_{p,k}}{\partial t} = \frac{1}{\psi_k} \nabla \cdot \psi_k D_p \nabla c_{p,k} + \frac{|\nabla \psi_k|}{\psi_k} J_k, \quad (9)$$

where ψ_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 $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ particles were set to 6.5×10^{-7} and 1×10^{-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 1×10^{-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 grid spacing of $0.1 \mu\text{m}$. We set the time-stepping as 0.02 s and the relative tolerance for the applied current during each time step is 1×10^{-4} .

3 Configuration of Particles in the 30-Particle Ensemble

The particle sizes of the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders are D10: $3.7 \mu\text{m}$, D50: $6.5 \mu\text{m}$, and D90: $9.8 \mu\text{m}$. We assume a log-normal distribution to describe the particle size distribution:

$$f(y) = \frac{1}{\sqrt{2\pi}\sigma y} \exp\left(-\frac{(\ln y - \mu)^2}{2\sigma^2}\right), \quad (10a)$$

$$F(y) = \frac{1}{2} \text{erfc}\left(-\frac{\ln y - \mu}{\sqrt{2}\sigma}\right), \quad (10b)$$

where y is the random variable satisfying a log-normal distribution, $f(y)$ is the probability density function of y , σ is the standard deviation of y , μ is the mean of y , $F(y)$ is the cumulative density function of y , and 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, ψ_k :

$$\psi_k = \frac{1}{2} + \frac{1}{2} \tanh\left(\frac{r-d}{\delta}\right), \quad (11)$$

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

Figure S2 shows the particle size distributions obtained by stratified sampling [19] and the computational domain for the 30-particle simulations.

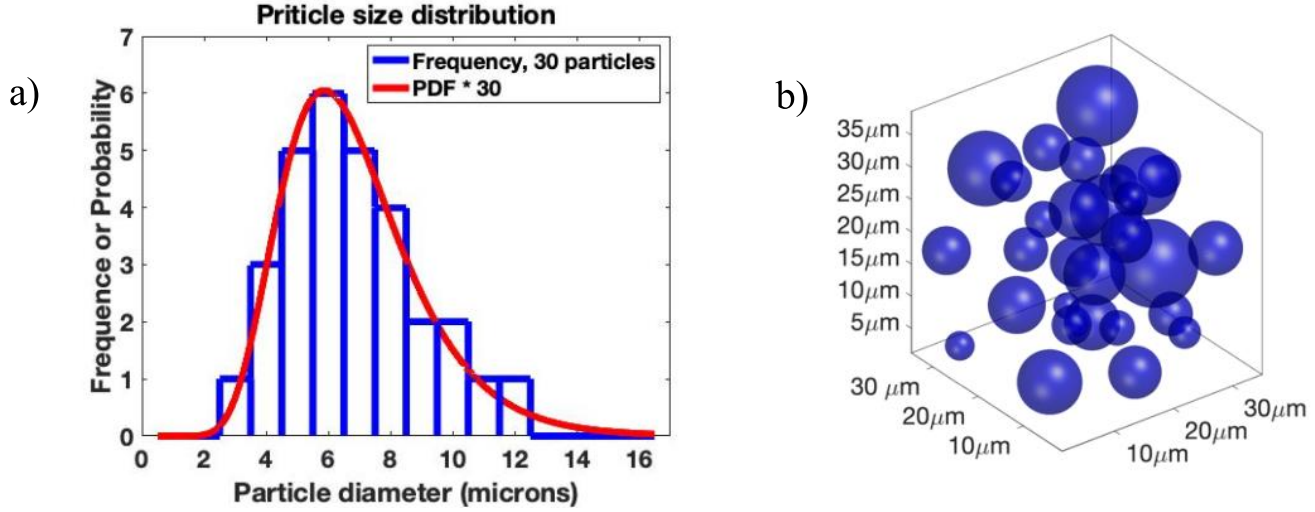


Figure S2: (a) The size distribution in the 30-particle system. (b) The computational domain for the 30-particle system. The domain has a size of $36 \times 36 \times 40 \mu\text{m}^3$ ($360 \times 360 \times 400$ grid points).

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 [15].

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

$$OCV = a \ln \left(\frac{x}{1-x} \right) + b(x-1)^2 + cx^2 + d, \quad (12)$$

where $a = -0.06809 \text{ V}$, $b = 0.9009 \text{ V}$, $c = 0.2749 \text{ V}$, $d = 3.544 \text{ V}$, and x represents the lithium fraction (in the main text, x_{Li} is used to denote this quantity).

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. [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.

4.3 Electrolyte Parameters

As in our previous works [5, 6], all the electrolyte parameters, namely σ_e , D_e , $\frac{\partial \ln(f_{\pm})}{\partial \ln(c_e)}$, and t_+^0 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 the Form of Exchange Current Density (i_0)

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

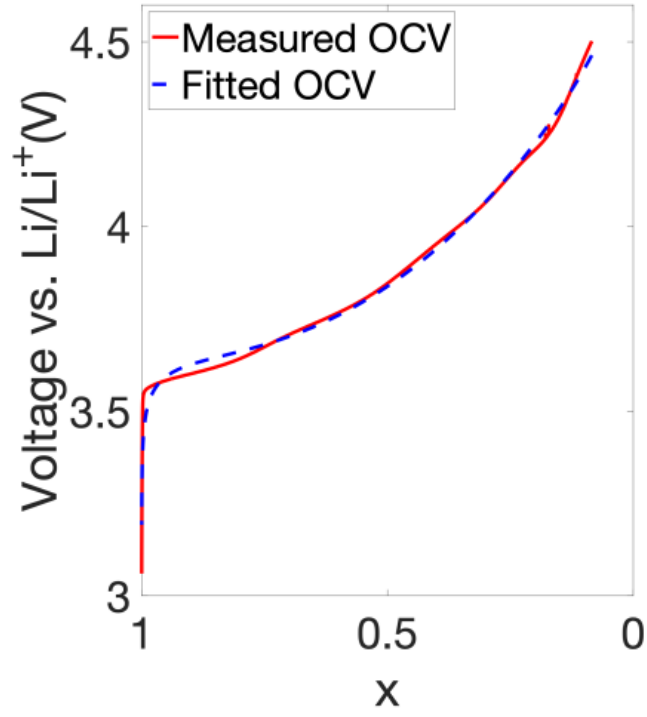


Figure S3: Measured and fitted OCV curves. Red line denotes the measured OCV curve, the blue line denotes the fitted OCV curve.

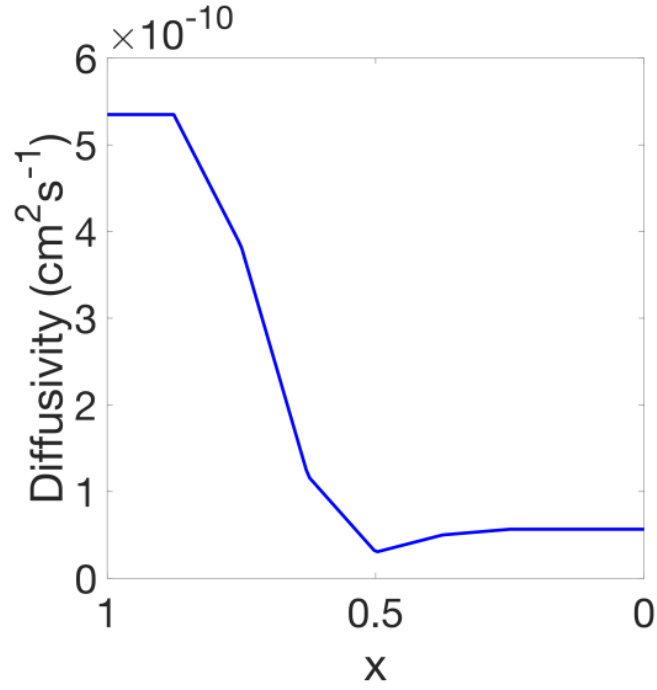


Figure S4: D_s as a function of the Li site fraction, x , for $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ [3].

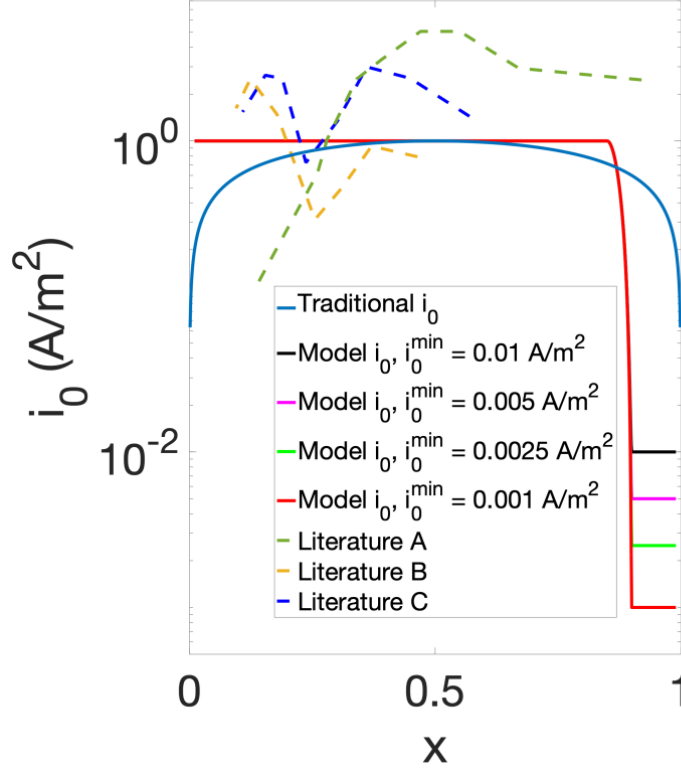


Figure S5: Log scale comparison of different i_0 functions used in the sensitivity analyses. The literature-reported functions are shown in dashed lines. The plot labeled as “Literature A” is obtained from Ref. [1], whereas the plots labeled as “Literature B” and “Literature C” are obtained from Ref. [25].

5.1 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 $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ [18] and $\text{LiNi}_y\text{Mn}_z\text{Co}_{1-y-z}\text{O}_2$ [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.

Table S1: Additional parameters used in physics modeling.

Parameters	Values	Units	Source
Electronic conductivity of NCA + carbon additive, σ_p	9.1×10^1	S m^{-1}	Literature [4]
Electronic conductivity of Li, σ_{Li}	1×10^5	S m^{-1}	—
Exchange current density of Li, i_0^{Li}	9.65×10^1	A m^{-2}	Literature [16]
OCV of Li metal, U_{Li}^0	0	V	—
Maximum Li concentration in NCA, c_p^{max}	4.8×10^4	mol m^{-3}	Estimated based on literature [12, 23, 24]
Initial Li concentration in NCA, c_p^0	$0.99 \times c_p^{\text{max}}$	mol m^{-3}	Assumed
Initial electrolyte salt concentration, c_e	1×10^3	mol m^{-3}	Experiment
Temperature	2.98×10^2	K	Experiment
1C current density	1.164	A m^{-2}	Experiment

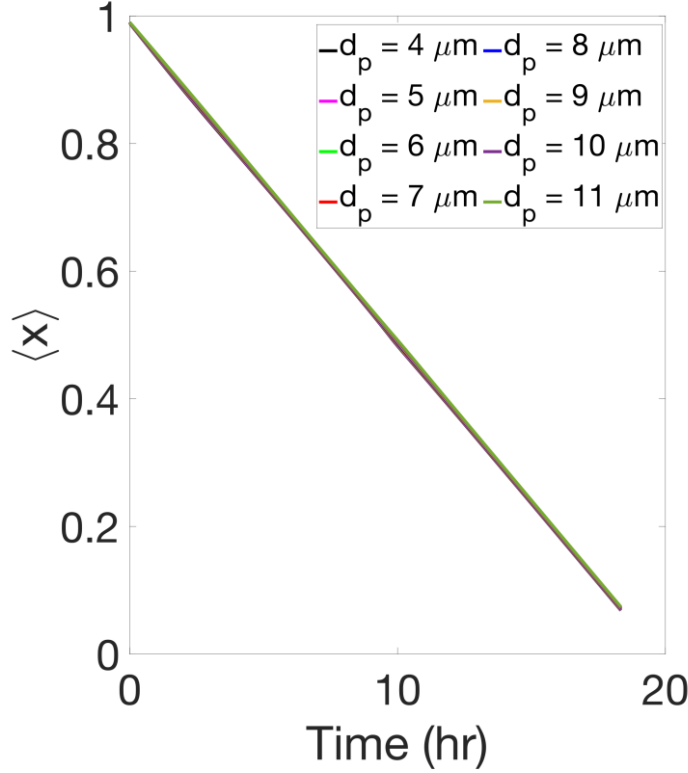


Figure S6: Evolution of $\langle x \rangle$ for the 8-particle system obtained using the traditional function of i_0 . All the particles delithiate at the same rate.

The traditional form only has the max value of i_0 , $i_0^{\max}$, as a tunable parameter, whereas the model form has four parameters: $i_0^{\min}$, the minimum value of i_0 ; $i_0^{\max}$; x^* , the value of x where the transition begins from $i_0^{\min}$ to $i_0^{\max}$; and Δx , the width of the compositional 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 $i_0^{\max}$ reported in the literature [25, 1] do not vary widely, we selected an intermediate value, $i_0^{\max} = 1 \text{ A m}^{-2}$. The comparison of the literature values with the traditional and model functions of i_0 is provided in Figure S5.

5.2 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 h^{-1} ($\text{C}/20$) 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 $i_0^{\min}$, x^* , and Δx .

5.3 Sensitivity Analyses with Respect to $i_0^{\min}$

We chose four different values of $i_0^{\min}$ ranging from 0.001 A m^{-2} to 0.01 A m^{-2} , while setting the value of other parameters as $i_0^{\max} = 1 \text{ A m}^{-2}$, $x^* = 0.9$, and $\Delta x = 0.05$. The comparison of different i_0 functions that differ in terms of $i_0^{\min}$ 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 $i_0^{\min}$. Furthermore, as $i_0^{\min}$ is decreased, the $\langle x \rangle$ value at which the accelerated delithiation of each particle halts also decreases, which will hereafter be denoted as $\langle x \rangle^\dagger$. Since the $i_0^{\min}$ value of 0.001 A m^{-2} resulted in a similar value of $\langle x \rangle^\dagger$ as the experiments, we selected this $i_0^{\min}$ value as the nominal value. As explained in the main text, the oscillations in $\langle x \rangle$ in a few cases originate because of the large difference between $i_0^{\min}$ and $i_0^{\max}$.

5.4 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 $i_0^{\max} = 1 \text{ A m}^{-2}$, $i_0^{\min} = 1 \times 10^{-3} \text{ A m}^{-2}$, and $\Delta x = 0.05$. Figure S8 shows the comparison of different x^* values. The onset of the accelerated

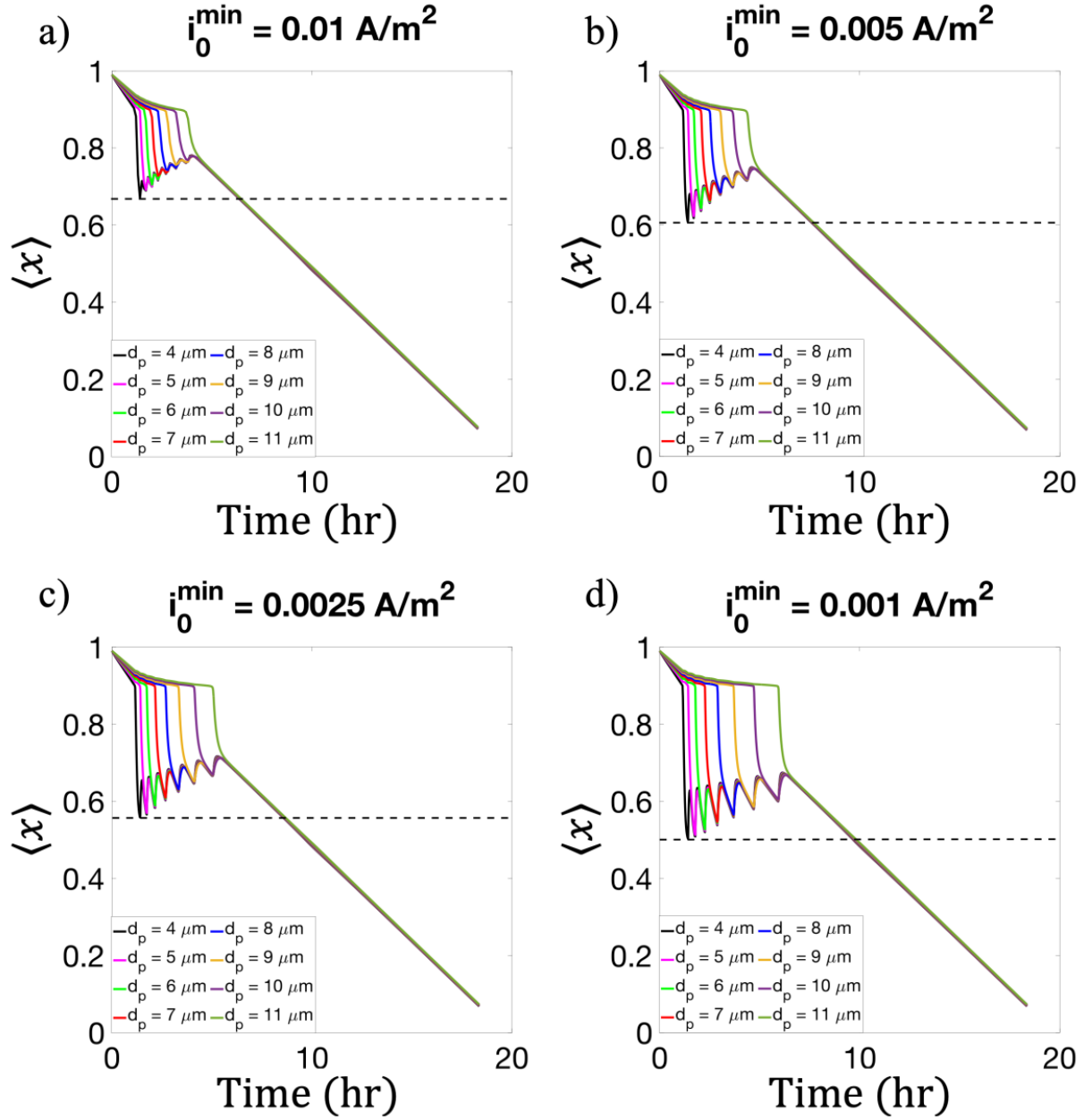


Figure S7: Evolution of $\langle x \rangle$ for the 8-particle system obtained using the model form of i_0 with four different values of $i_0^{\min}$: a) 0.01 A m^{-2} , b) 0.005 A m^{-2} , c) 0.0025 A m^{-2} , and d) 0.001 A m^{-2} . The black dashed line in each plot represents $\langle x \rangle^\dagger$ for the smallest particle in the ensemble; $\langle x \rangle^\dagger$ decreases with a decrease in $i_0^{\min}$.

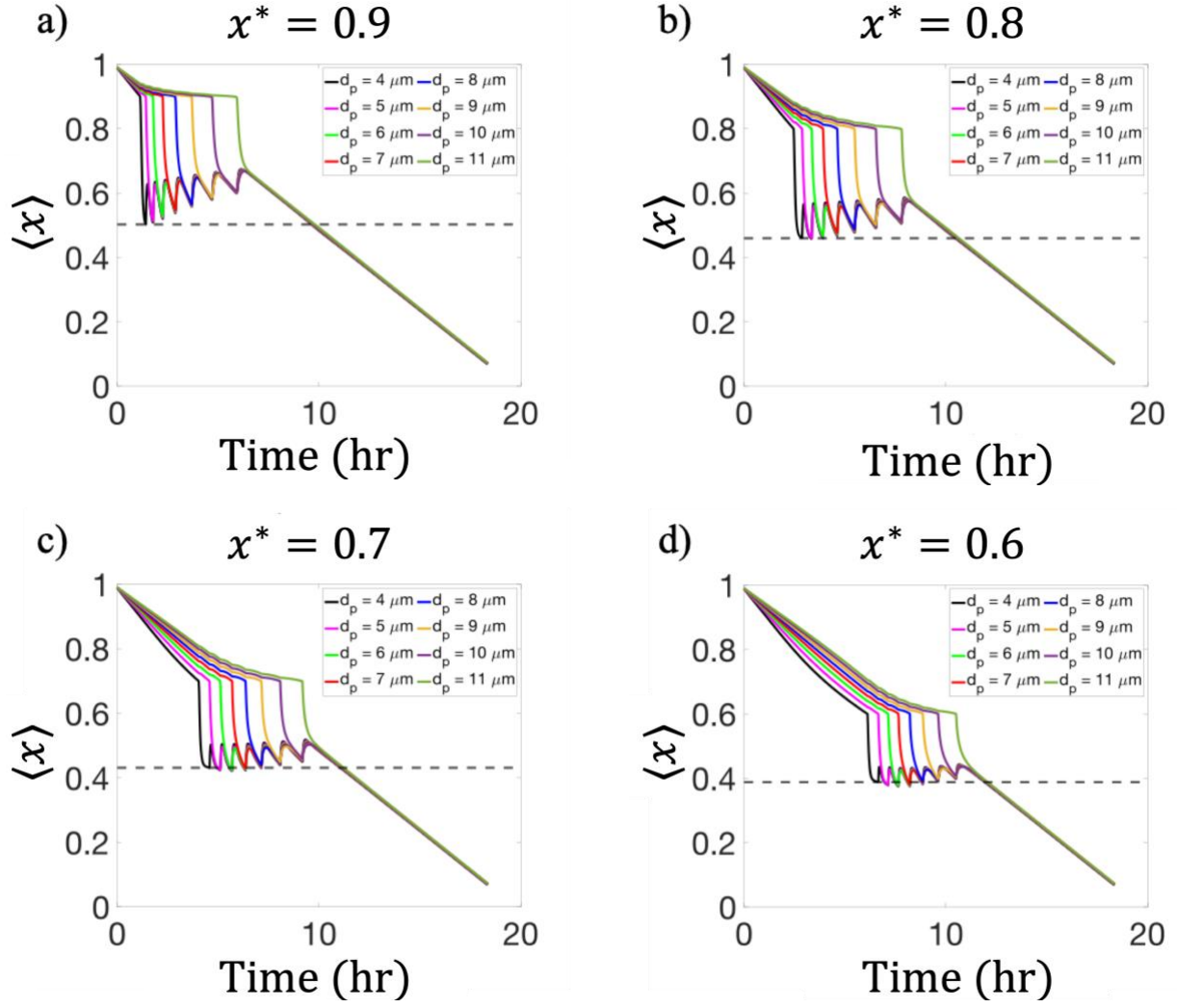


Figure S8: Evolution of $\langle x \rangle$ for the 8-particle system obtained using the model form of i_0 with four different values of x^* : a) 0.9, b) 0.8, c) 0.7, and d) 0.6. The black dashed line in each plot represents $\langle x \rangle^\dagger$ for the smallest particle in the ensemble. Note that $\langle x \rangle^\dagger$ decreases with a decrease in x^* .

delithiation is determined by the x^* value and $\langle x \rangle^\dagger$ decreases with a decrease in x^* .

5.5 Sensitivity Analyses with Respect to Δx

We choose four different values of the width of the compositional transition zone, Δx , ranging from 0.05 to 0.8, and we set other parameters as $i_0^{\max} = 1 \text{ A m}^{-2}$, $i_0^{\min} = 1 \times 10^{-3} \text{ A m}^{-2}$, and $x^* = 0.9$. Figure S9 shows the comparison of different Δx values. Both the amplitudes of the oscillations and the rate of accelerated delithiation are reduced as Δx is increased.

6 Additional Figures and Data

Table S2: Reported energies of Ni K-edge whiteline. In-situ XAS of $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (Ref. [7]) and ex-situ XAS $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (Ref. [22]). Data extracted from published figures using WebPlotDigitizer [21]. Relative shifts in whiteline energy (Δ) calculated as difference from fully lithiated state ($x = 1$).

$\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$			$\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$		
x	Whiteline /eV	Δ /eV	x	Whiteline /eV	Δ /eV
0.945	8353.98	0.21	1.00	8348.84	0.00
0.751	8354.72	0.94	0.80	8349.61	0.78
0.570	8355.45	1.68	0.60	8350.14	1.30
0.386	8356.12	2.35	0.25	8350.78	1.95
0.257	8356.43	2.66	0.00	8351.16	2.32

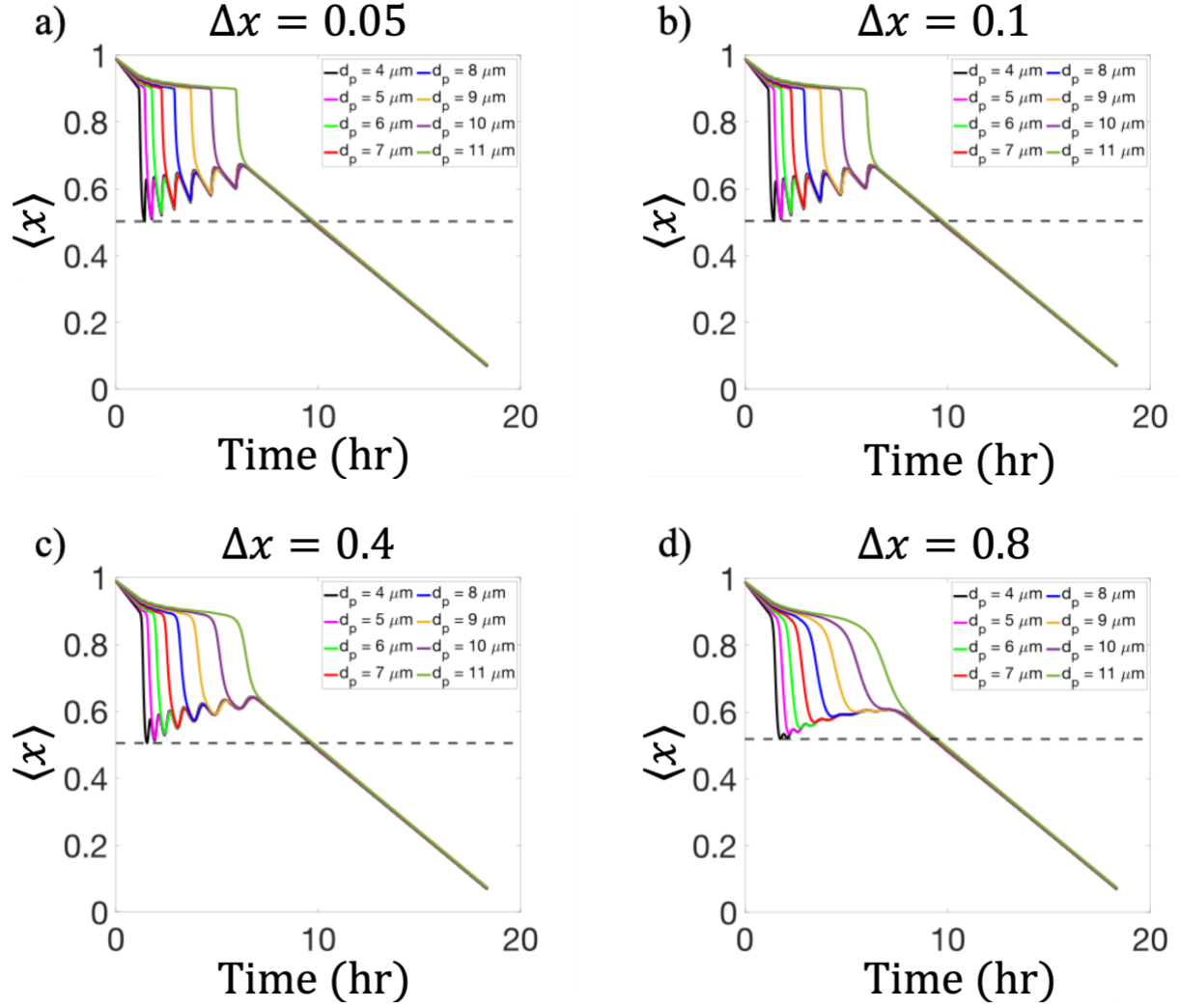


Figure S9: Evolution of $\langle x \rangle$ for the 8-particle system obtained using the model form of i_0 with four different values of Δx : a) 0.05, b) 0.1, c) 0.4, and d) 0.8. The black dashed line in each plot represents $\langle x \rangle^\dagger$ for the smallest particle in the ensemble. The rapid delithiation rate and the amplitude of the oscillations decrease as Δx increases.

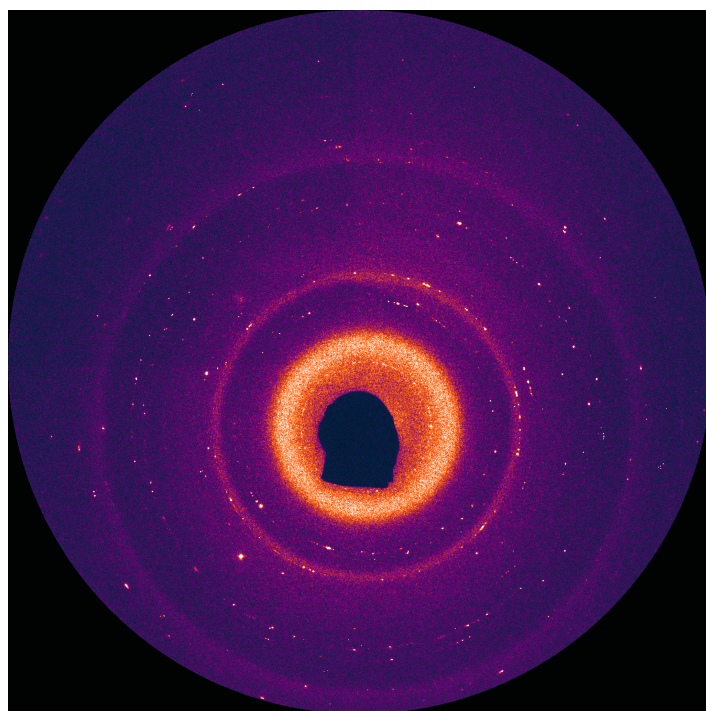


Figure S10: Exemplar 2D diffraction pattern for a single position during charging.

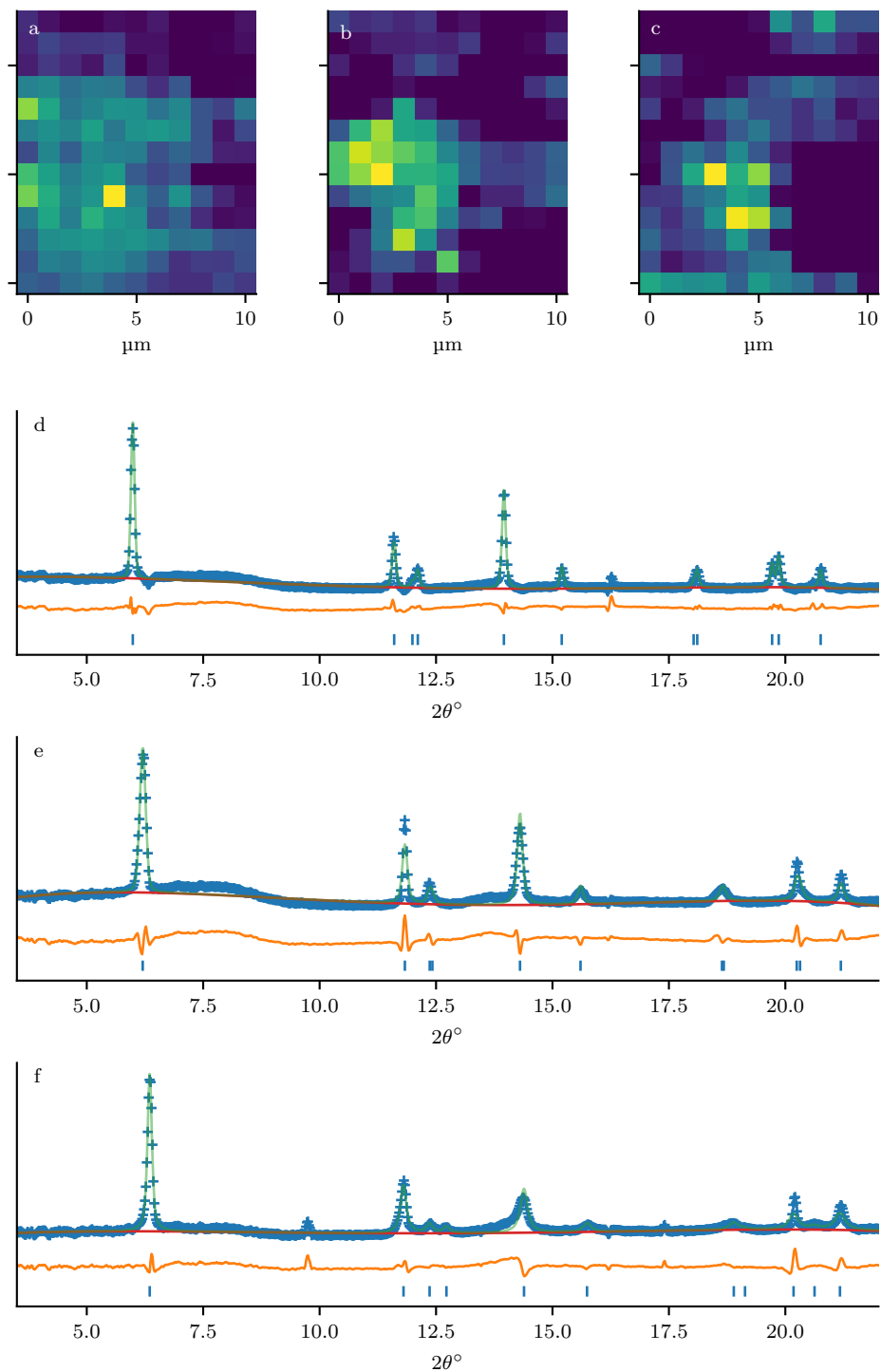


Figure S11: $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ μ -XRD. (a-c) Maps of summed diffraction intensity for particles 1, 2, and 3 respectively. (d-f) Whole-pattern LeBail refinements for summed diffraction intensities of particle 1 (d) in the pristine state, (e) during first charge, and (f) at the end of first charge. Ticks show expected positions for reflections of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ with $R\bar{3}m$ space group.

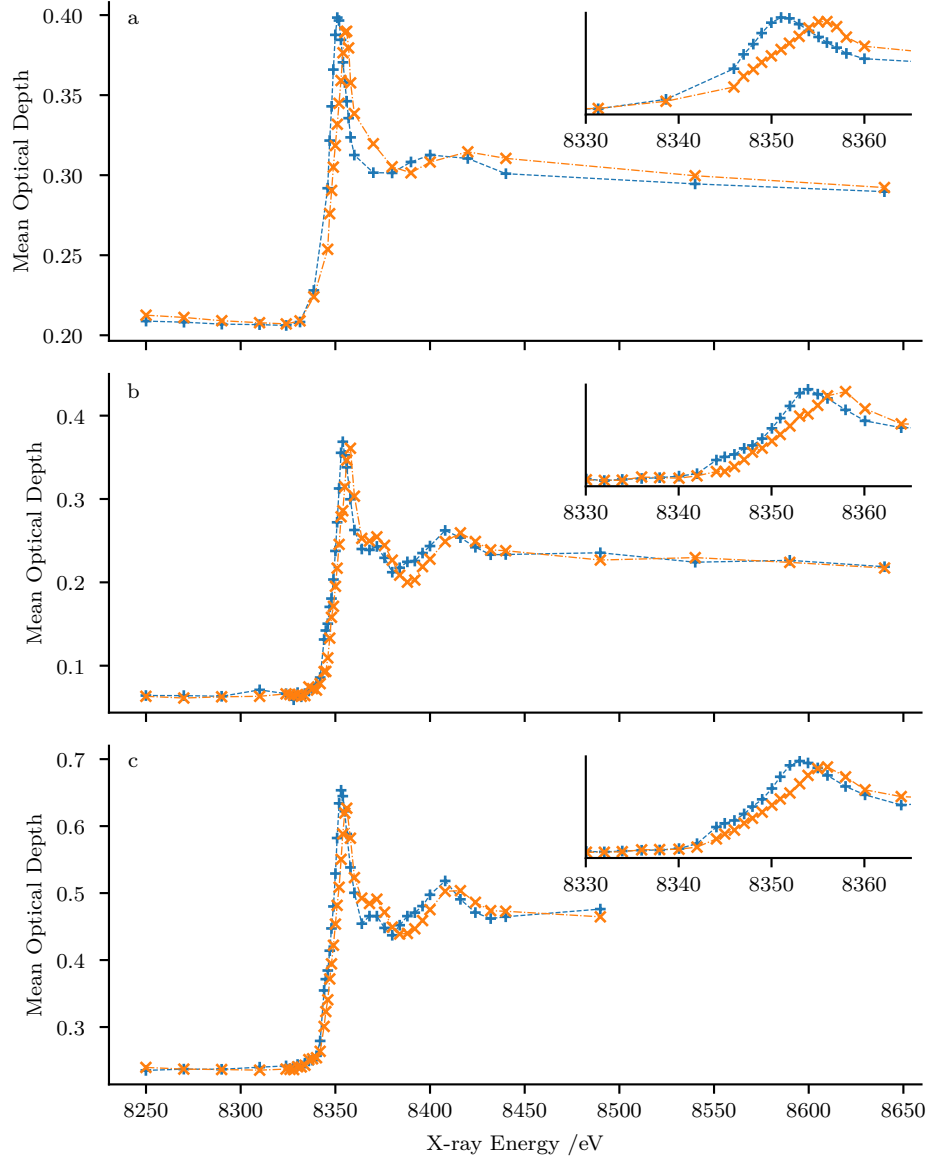


Figure S12: Ni K-edge absorption spectra for TXM fields of view. Mean optical depth of pixels after edge filter for (-+ -) most reduced and (-x -) most oxidized time-steps for (a) $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, (b) $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, and (c) $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$.

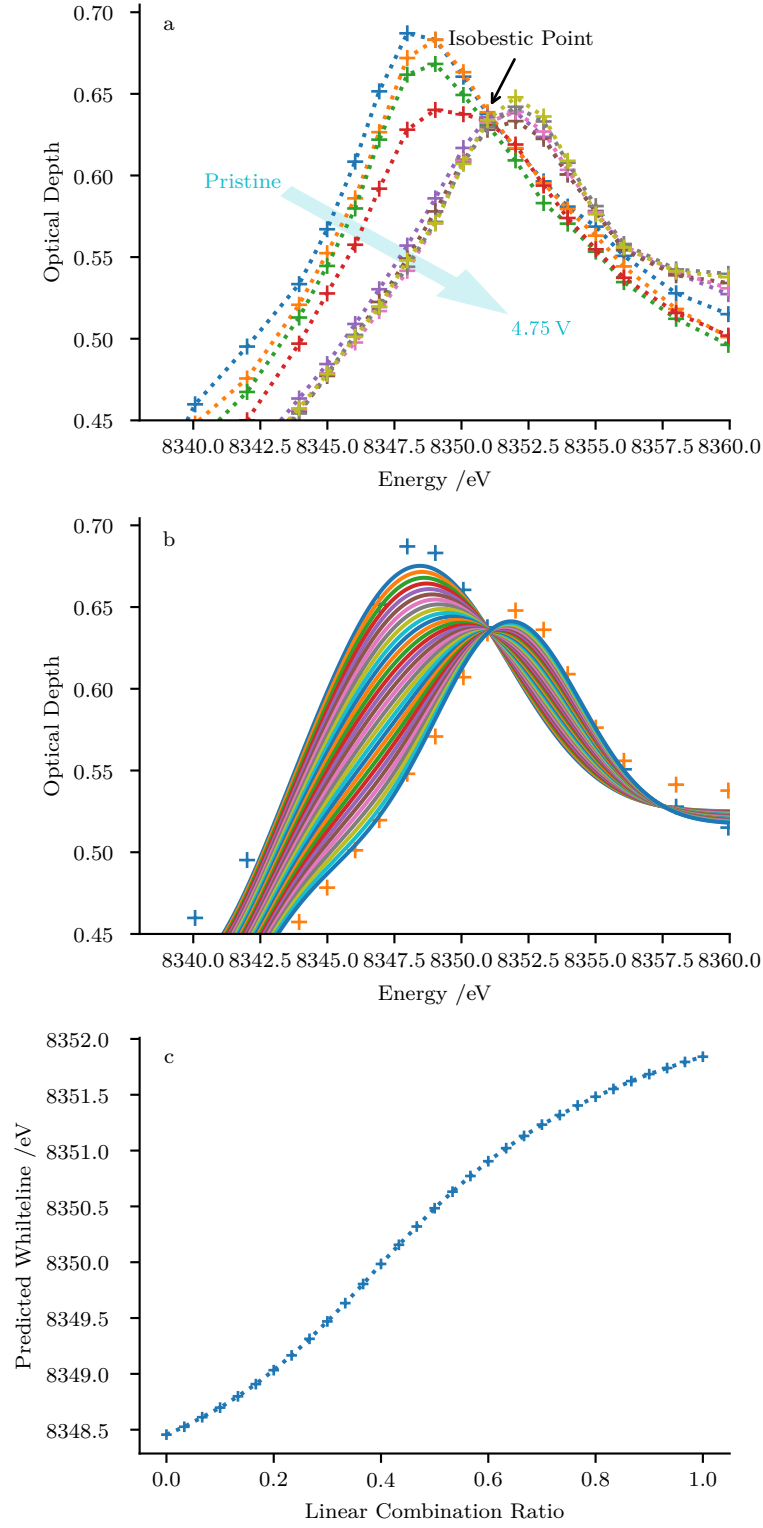


Figure S13: Demonstration of isobestic point for $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Ni K-edge. (a) Observed mean optical depth spectra for TXM frames during operando oxidation, with dashed lines added as visual guides. (b) Results of mathematical linear combinations of fit spectra (—) for observed spectral end-members for the most reduced (+) and oxidized (+) points in the $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ frames in (a). (c) Effect of linear combination ratio of spectral end-members in b on resultant whiteline energy.

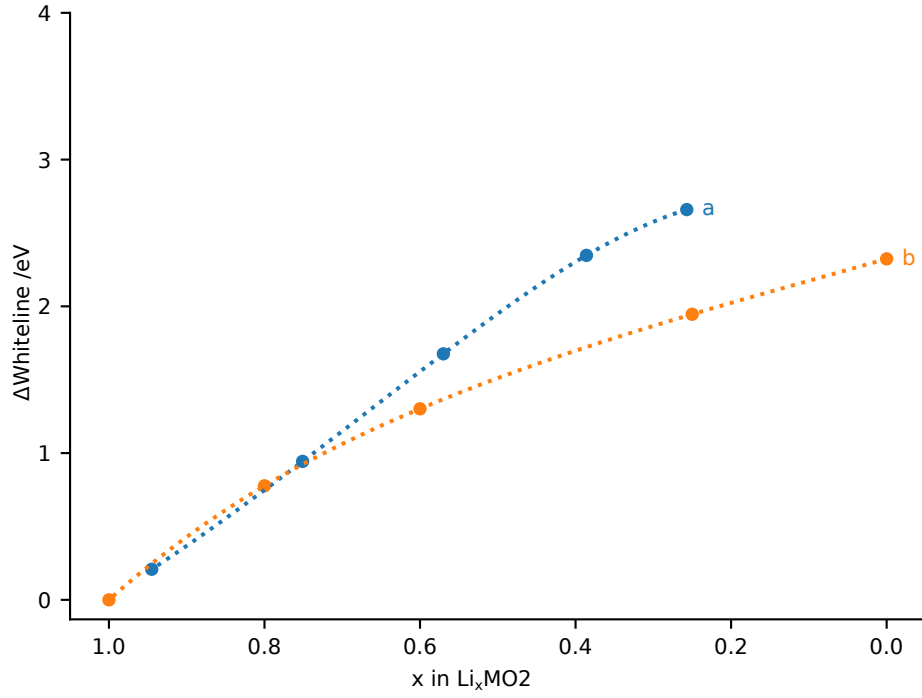


Figure S14: Reported changes of Ni K-edge whiteline energy. (a) In-situ XAS of $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and (b) ex-situ XAS of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. Data extracted from published figures as described in Table S2.

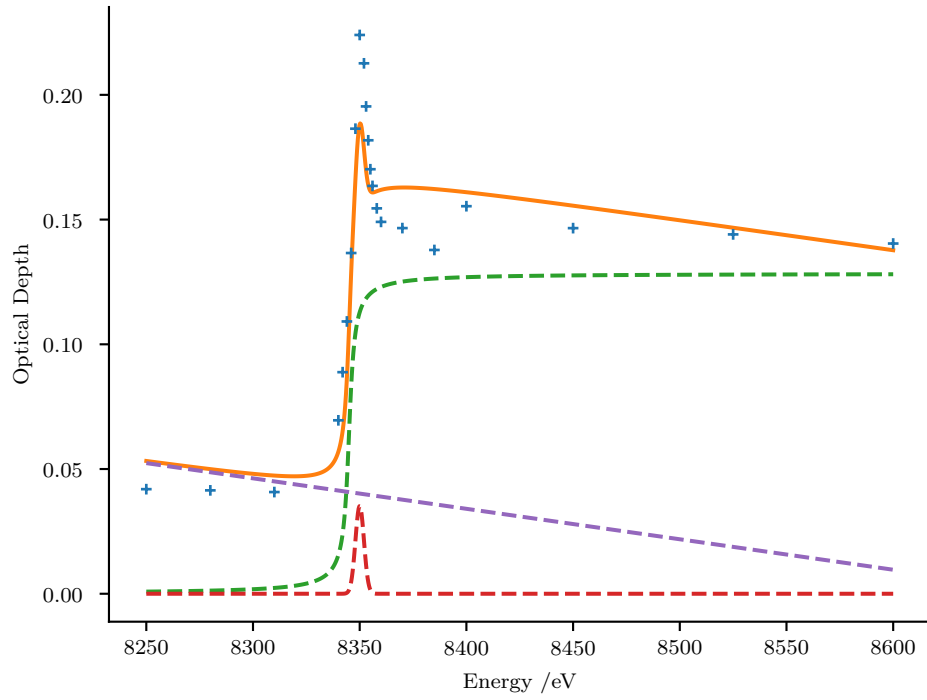


Figure S15: Sample decomposition of Ni K-edge fitting. Spectrum of mean optical depth of a frame of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ particles as (+) observed optical depth; (—) overall least squares fit; and (---) arctangent, (---) Gaussian and (---) background components of least squares fit.

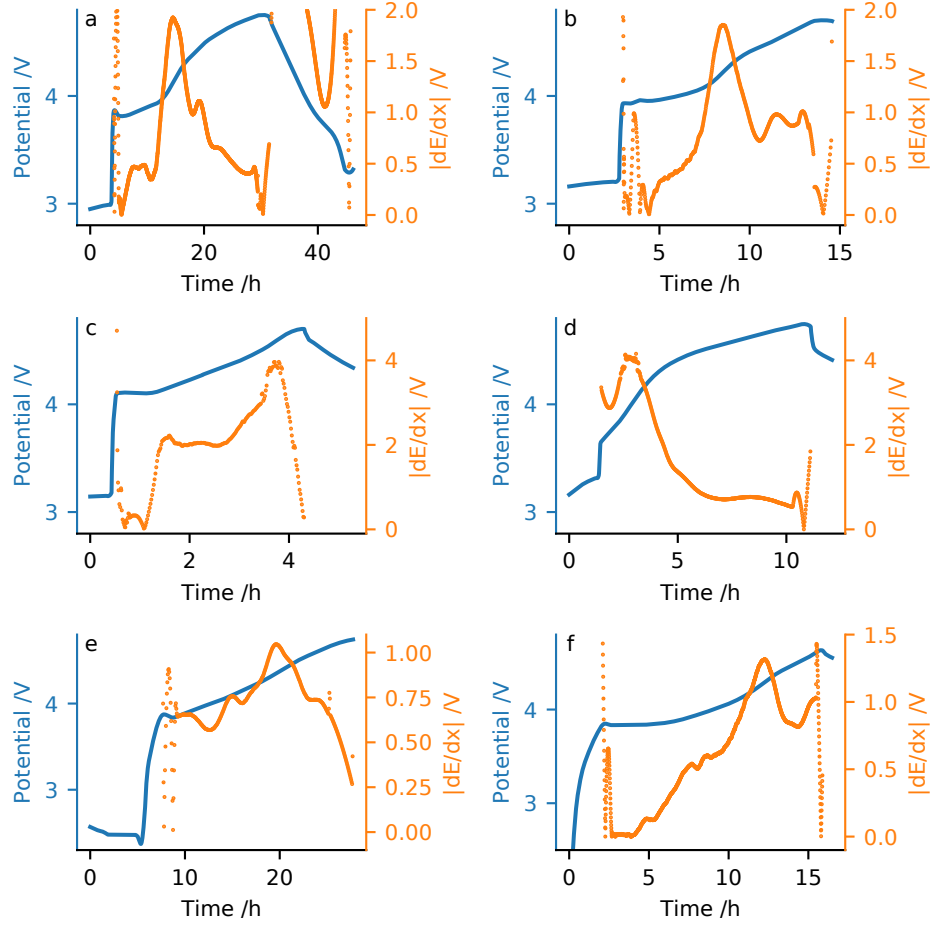


Figure S16: Cell potential (—) and derivative of potential with respect to x in Li_xMO_2 (···) during galvanostatic charge/discharge. (a,b) $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode in modified coin-cell during first charge, (c) $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode in pouch-cell during first charge, (d) $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode in pouch-cell during second charge, (e) $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode charged in modified coin-cell, and (f) $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ cathode charged in modified coin-cell. All galvanostatic profiles treated with third-order Savitzky-Golay filter with 101-point window prior to calculating derivative.

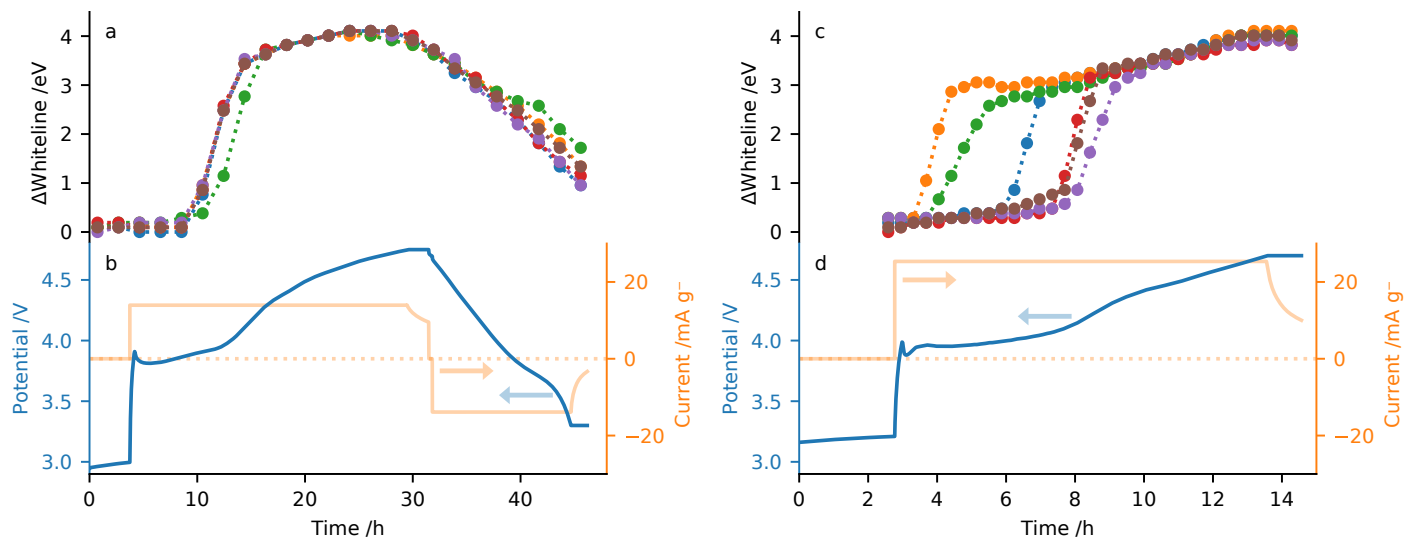


Figure S17: Particle-level oxidation during first charge and discharge of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. (a) Changes in mean whiteline energies relative to 8351.69 eV for secondary particles during first charge and discharge. (c) Changes in mean whiteline energies relative 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 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ samples in modified coin-cells.

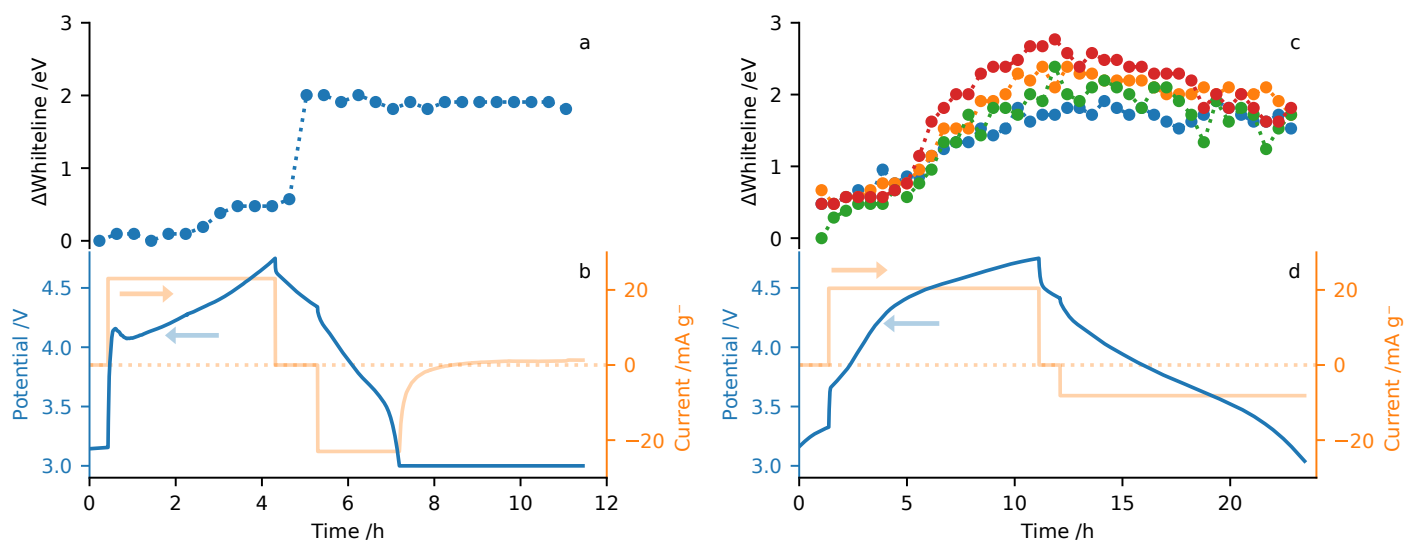


Figure S18: Particle-level oxidation during first and second discharge of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ samples in pouch cells. (a) Changes in mean whiteline energies relative to 8350.92 eV for secondary particle during first charge/discharge cycle. (c) Changes in mean 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.

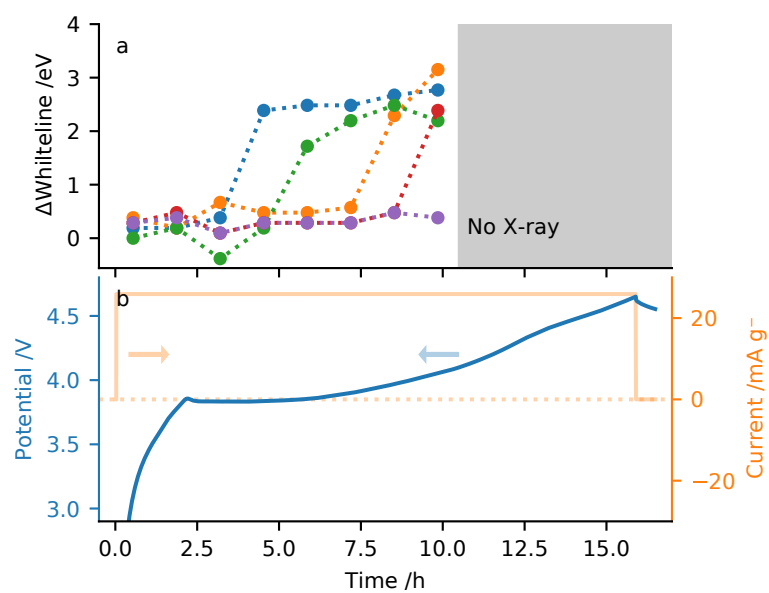


Figure S19: Particle-level oxidation during first charge and discharge of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$. (a) Mean whiteline energies of secondary particles during charge/discharge. (b) Operando potential (—) and current (—) for galvanostatic cycling for $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ samples in modified coin-cells. X-rays unavailable after 10 h due to maintenance.

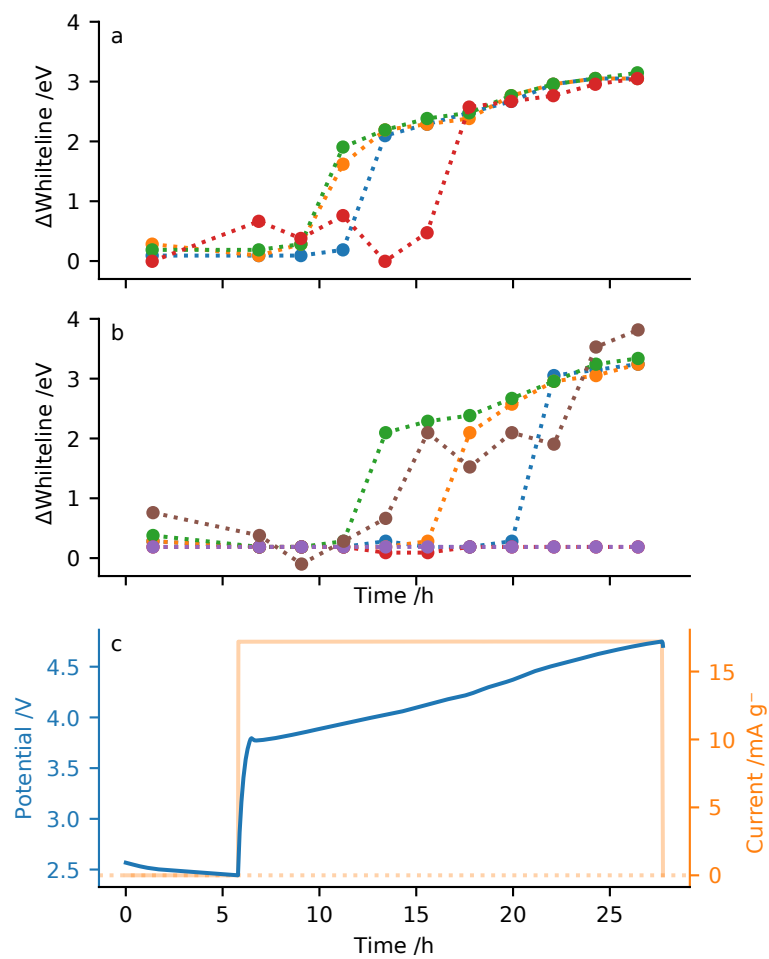


Figure S20: Operando TXM of secondary $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ particles during first charge. Mean changes in whiteline energies relative to 8354.18 eV for secondary particles (a) without static X-ray exposure, and (b) with a 3 h static X-ray exposure prior to operando imaging. (c) Galvanostatic charging profile for modified coin-cell with $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode.

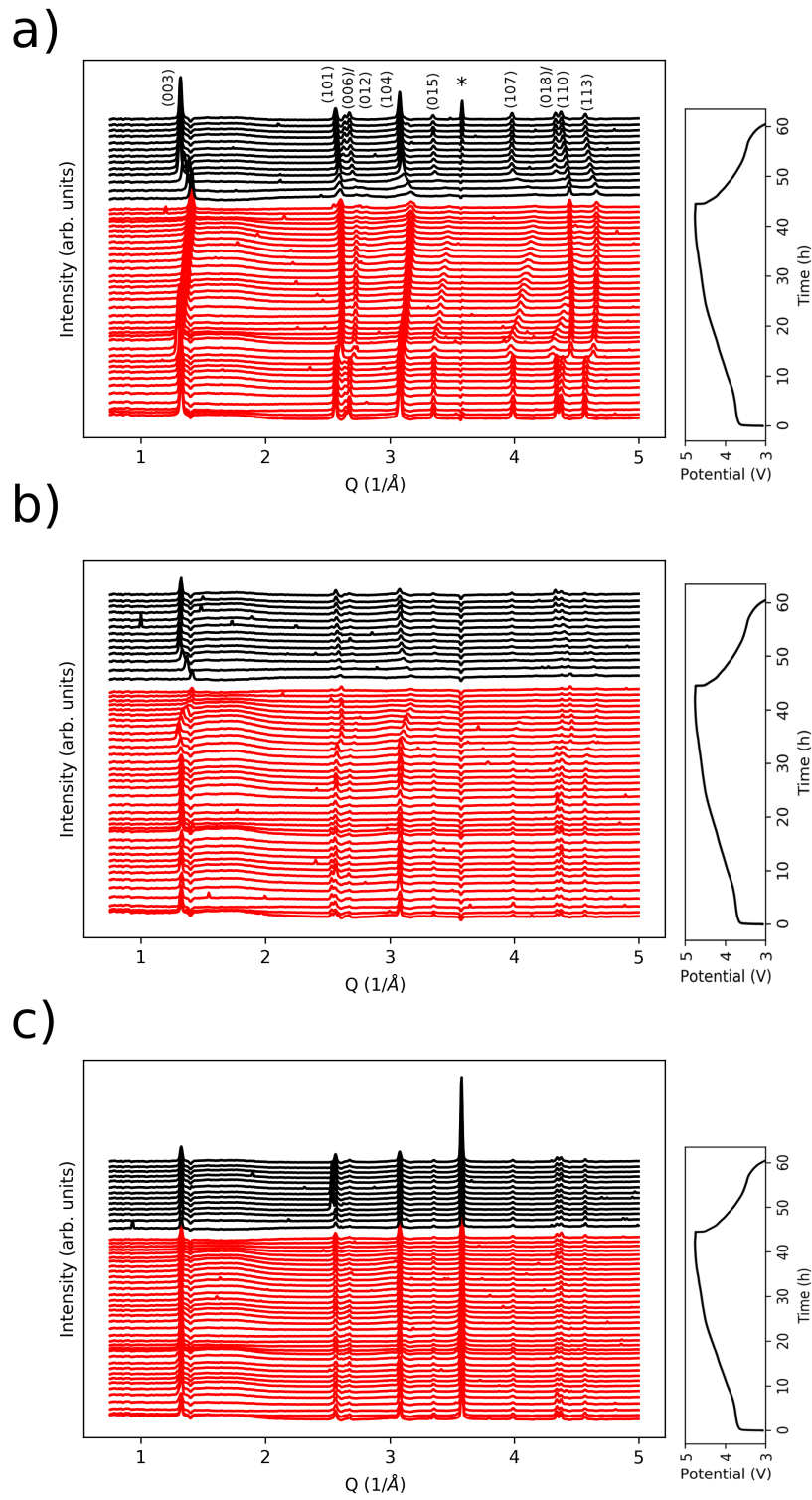


Figure S21: Diffraction patterns for $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ through charge (red) and discharge (black) for a) P1, b) P2, and c) P3. Feature due to Li is denoted with a *.

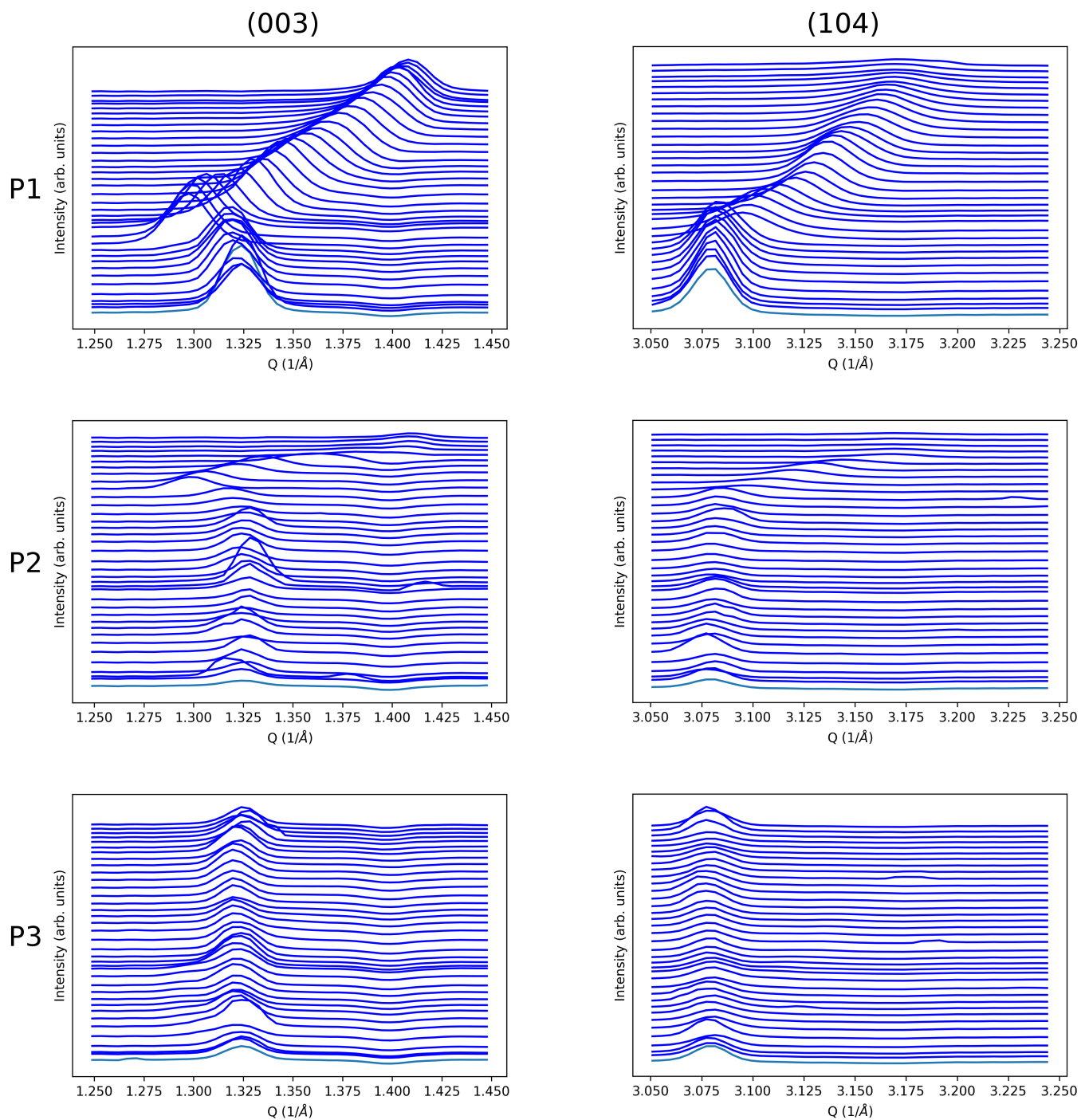


Figure S22: (003) (left) and (104) (right) reflections of P1, P2, and P3 (top to bottom) during the first charge.

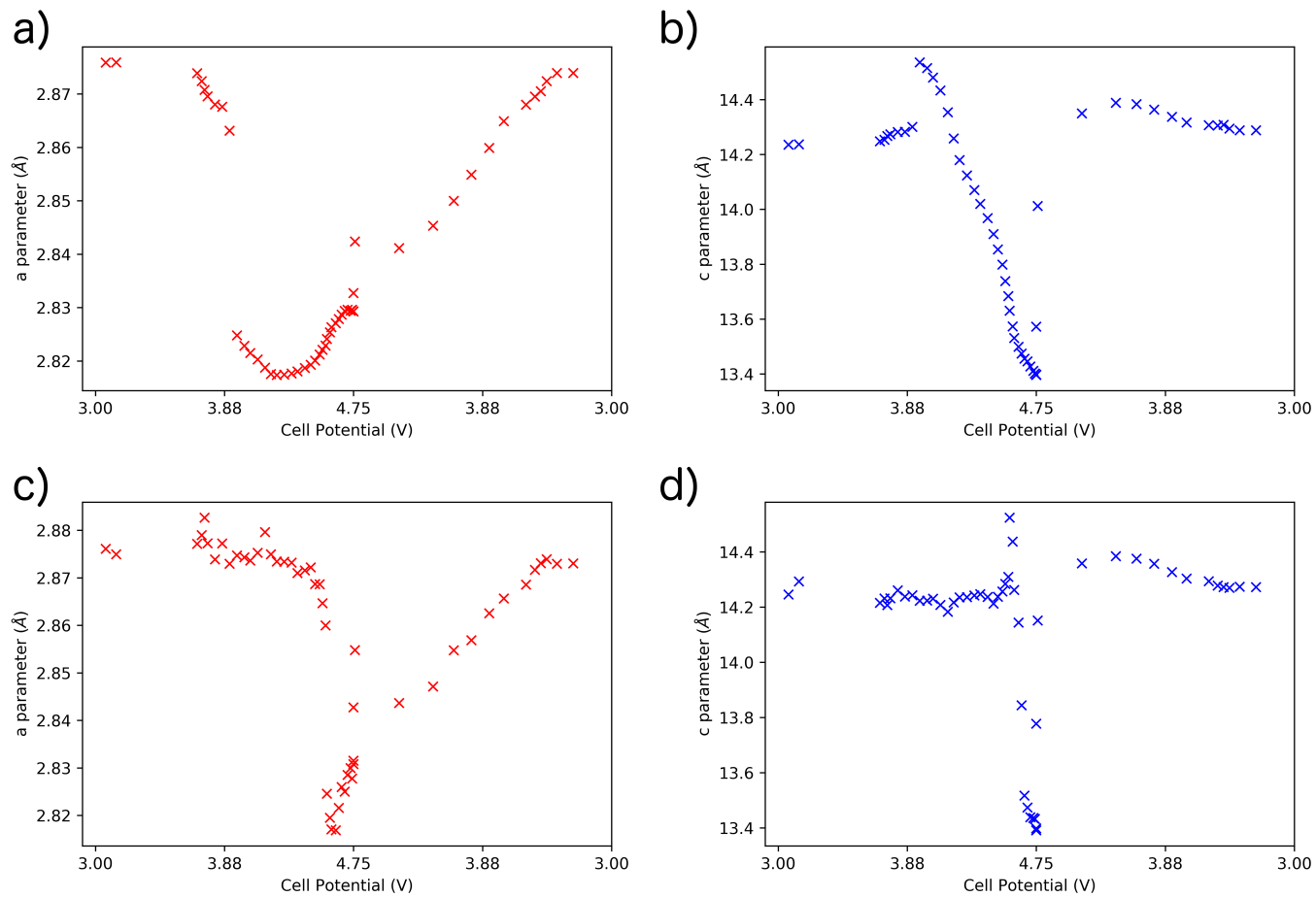


Figure S23: Unit cell parameters as a function of cell potential for a) P1 a parameter b) P1 c parameter c) P2 a parameter and d) P2 c parameter

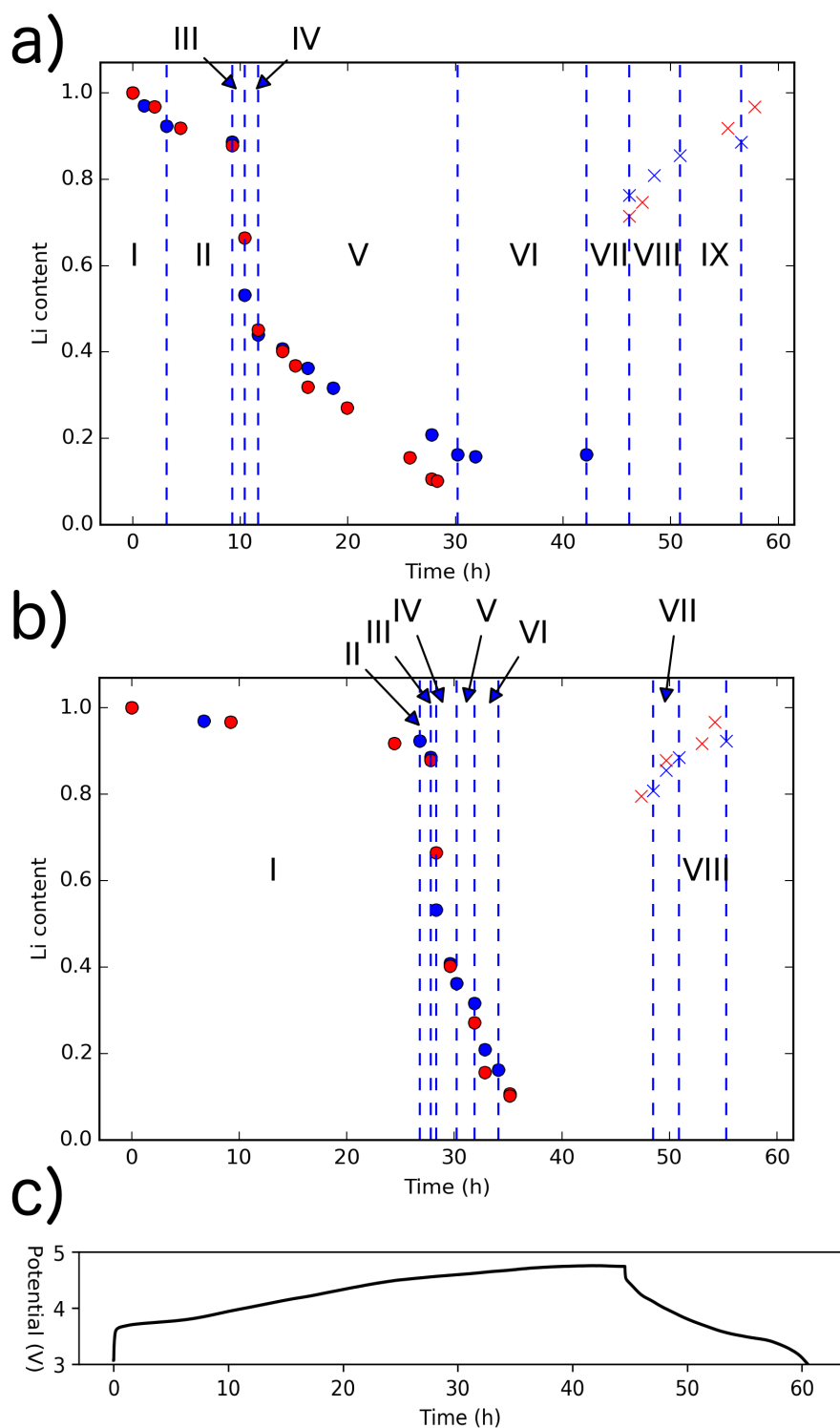


Figure S24: Li content (x in $\text{Li}_x\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) as a function of time during the first cycle for P1 (a) and P2 (b). The charge-discharge curve is shown below (c). Li values were correlated with equivalent values in Ref. [20], for the a unit cell parameter (red) and c unit cell parameter (blue). Charge is represented by circles while discharge is represented by x markers.

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