Supplementary Information

Operando single-particle imaging reveals that asymmetric ion flux contributes to capacity degradation in aged Ni-rich layered cathodes

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Methodology

Material, battery assembly and physical characterizations

Single-crystal Ni-rich NMC with composition of LiNi_{0.88}Mn_{0.05}Co_{0.07}O₂ was supplied by Umicore. Related structural and morphology characterizations can be found in our earlier publication. ¹ Selfstanding electrodes are composed of active material Ni-rich NMC cathode, Super C65 (Timcal) as conductive agent and polytetrafluoroethylene (PTFE, DuPont, Teflon 8A) as binder at a weight ratio of 60:30:10, with active material loading density around 6~8 mg/cm². We note that a low active material loading was applied to guarantee good mechanical strength and electronic conductivity after prolonged aging process for optical measurement. To prepare self-standing electrodes, 120 mg of active Ni-rich NMC cathode and 60 mg of Super C65 were first uniformly mixed using a THINKY mixer ARE300 at 2000 rpm for 30 mins. 20 mg of PTFE was then manually added to the mixture and mixed for 40 mins in an argon filled glovebox. The components were then rolled into thin films and cut into small pieces as self-standing electrodes. All selfstanding electrodes were aged in a coin cell with Li chip as counter electrode (to avoid cathode voltage variation due to voltage slippage² in full cell), glass fiber (Whatman) as separator and LP30 (EC: DMC 1:1 volume ratio) as electrolyte. The electrode films were then extracted from the coin cell, washed with DMC, folded multiple times, flattened to enable a good optical focus, and recalendared to ensure good contact between aged particles and conductive agent before being assembled into an optical cell.

Scanning electron microscopy (SEM) experiments were performed on the self-standing electrodes using a TESCAN MIRA3 FEG-SEM at 5.0 kV with In-Beam secondary electron detection. Powder X-ray diffraction (PXRD) experiments were carried out at Beamline i11 at Diamond Light Source at a wavelength of 0.827 Å.

Electrochemistry

All electrochemical measurements were conducted on a Biologic VMP300 Potentiostat at a constant temperature of 22 °C. For GITT measurements, each step in the voltage profiles corresponds to a galvanostatic charge at 10 mA/g for 15 mins followed by a 4-h relaxation step. The lithium chemical diffusion coefficient was calculated using the following equation ³:

$$D_{Li} = \frac{4}{\pi \tau} \left(\frac{m_{\rm NMC} V_{\rm m}}{M_{\rm NMC} S} \right)^2 \left(\frac{\Delta E_{\rm s}}{\Delta E_{\rm t}} \right)^2, \ \tau \ll L^2 / D \qquad [1]$$

where τ is pulse duration, $m_{\rm NMC}$ and $M_{\rm NMC}$ are the total mass and the molecular weight of NMC, respectively, $V_{\rm m}$ is the molar volume of NMC, S is the active area which can be estimated based on the BET (Brunauer, Emmett and Teller) surface area of the NMC material (0.6 m²/g), $\Delta E_{\rm s}$ is the steady-state voltage change and $\Delta E_{\rm t}$ is the transient voltage change at each step.

Optical microscopy

Optical setup

Optical scattering microscopy measurements were conducted using a home-built inverted microscope, as applied in our previous works ^{1, 4}, adapted from an interferometric scattering microscopy setup ⁵. The microscope is equipped with an oil immersion objective ($100\times$, UPLSAPO100XO, Olympus) and CMOS detector (FLIR, Grashopper3, GS3-U3-23S6M-C) with

an overall magnification of $166.7 \times$ (effective pixel size of 34.7 nm per px). Red LED (Thorlabs SOLIS) at 740 nm was used as illumination source, which is equipped with a ground glass diffuser to minimize speckle contributions and homogenize the illumination. ⁶

The optical cell was place on an XYZ nano-positioner stack (Attocube, ECSx5050/AL/RT/NUM) with an overall movement range of 25 mm in each direction. During operando optical measurement, the sample focus position was maintained via an active external focus stabilization based on a calibrated line-reflection profile of a 980 nm reference laser, as described previously.⁵ The lateral imaging resolution in our setup is diffraction-limited to 265 nm, with a nominal depth of field of ~300 nm. The high signal-to-noise ratio of the technique can afford a lateral localisation precision of sub-5 nm. ⁵ The probing depth of the optical microscope with the red LED source is estimated to be ~200 nm. ⁵

We note that this microscope setup formed a prototype for a charge photometry instrument ('illumionONE') which has subsequently been commercially developed by 'illumion'.

Data acquisition

Images were acquired with camera exposure times between 1.5 to 3.8 ms and at a constant frame rate of 10 Hz. Images were binned together in sets of 20 to 80 to increase the signal-to-noise ratio, yielding effective frame rates of 1/2 to 1/8 Hz.

Optical image processing

Drift correction and masking

Recorded images were first corrected for stage drift in the xy-plane by isolating a bright subdiffraction limited spot in the image (unrelated to the active particles and unchanging throughout the experiments) and fitting its position over time using a two-dimensional Gaussian function. The extracted center positions in x and y for each image were subsequently used to correct for stage drift. For clarity, prior to differential analysis (described below), the drift-corrected images were further masked to exclude regions not belonging to the active particle. Pixels with intensities below a defined threshold (selected according the first frame image) were treated as background, the optical intensities of which were set to 0.

Differential image analysis

To emphasize the optical intensity evolution on cycling, a differential analysis was carried out by subtracting the first frame intensity at each pixel (after drift correction) from the i^{th} frame and normalizing it by the first frame (Equation 2). The resulting differential intensity then describes that fractional intensity change with respect to the initial frame (with the scale centred around 0):

differential intensity
$$=\frac{\bar{I}_i - I_1}{I_1}$$
, [2]

where I_i is the intensity of the *i*th frame and I_1 is the intensity of the first frame.

Transmission electron microscopy

The single crystal Ni-rich NMC pristine/aged powder sample was dispersed on a 300 mesh Cubased lacey carbon film grid (Agar) for carrying out TEM studies. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired at 300 kV using a FEG mono-chromated and probe-corrected microscope, Thermo Scientific Spectra 300. The TEM data was analyzed using the Thermo Scientific Velox software and ImageJ.

Finite element modelling

The composite NMC cathode of the Li-ion cell consists of storage particles embedded inside a polymeric binder. We consider a single crystal NMC storage particle having an idealized geometry of a right-circular cylinder of height h and diameter d surrounded by the electrolyte. The particle is electrically connected through the electron conducting carbon additives and the Li⁺ conducting electrolyte. We therefore assume that the particle remains electroneutral.

The NMC crystal has a layered structure of transition metal oxides with the Li⁺ occupying the interlayer lattice sites. The layers span the crystallographic ab-plane while the crystallographic c-axis is perpendicular to these layers. In this work, we shall assume that the lattice parameters of the NMC unit cell do not change due to lithiation/delithiation. Introduce Cartesian coordinates x_i (1, 2, 3) with orthonormal base vectors e_i such that e_1 and e_2 lie in the ab-plane and e_3 is parallel to the crystallographic c-axis. Let Ω denote the domain of the cylindrical particle whose axis aligns with e_3 . We assume that bounding surfaces of the cylinder parallel to the ab-plane remain inactive to charge transfer as the layered structure does not allow diffusion of Li⁺ across the ab-plane. The lateral surface of the cylinder is active and is denoted by S.

Let the position vector of a material point be denoted by $x = x_i e_i$, where repeated indices imply summation following Einstein's notation. Let N_L denote the molar concentration of lattice sites for Li atoms and $N_{Li}(x,t)$ denote the molar concentration of Li atoms at the spatial location x at time tin an NMC crystal. Denote $F(N_{Li},T)$ as the Helmholtz free energy per unit volume of NMC with N_{Li} and at a temperature T. Upon introducing the occupancy (normalized concentration) of Li as $\theta(x,t) \equiv N_{Li}(x,t)/N_L$, the chemical potential $\mu_{Li}^c(\theta)$ of Li atoms can be written as

$$\mu_{Li}^{c}(\theta) = \frac{\partial F}{\partial N_{Li}} \Big|_{T} = \frac{1}{N_{L} \partial \theta} \Big|_{T}.$$
[3]

We are interested in the chemical potential ${}^{\mu}_{Li^+}^{c}$ of Li⁺ as the delithiation/lithiation of the cathode is governed by the flux of Li⁺ ions in the NMC lattice. The addition of an Li atom is equivalent to the addition of a Li⁺ and an electron. Upon defining ${}^{N}_{Li^+}$ and ${}^{N}_{e^-}$ as the molar concentrations of Li⁺ and electrons respectively, the chemical potentials Li⁺ and electrons can be written as ${}^{\mu}_{Li^+} = \partial F / \partial N_{Li^+}$ and ${}^{\mu}_{e^-} \equiv \partial F / \partial N_{e^-}$ respectively such that,

$$\mu_{Li}^{c} \equiv \frac{\partial F}{\partial N_{Li}} \Big|_{T} = \mu_{Li}^{c} \left(\frac{\partial N_{Li}}{\partial N_{Li}} \right) \Big|_{T} + \mu_{e}^{c} \left(\frac{\partial N_{el}}{\partial N_{Li}} \right) \Big|_{T},$$

$$[4]$$

The electroneutrality of NMC particle demands that $N_{Li^+} = N_{e^-} = N_{Li}$. Equation [4] can now be rewritten as,

$$\mu_{Li}^{\ c} = \mu_{Li}^{c} - \mu_{e}^{\ c}.$$
[5]

We shall assume that the chemical potential (Fermi level) of the electrons $\mu_{e^-}^c$ is independent of θ and proportional to the electrical potential ϕ^c of the NMC particle, i.e. $\mu_{e^-}^c = -F\phi^c$, where F is the Faraday constant. The chemical potential of Li⁺ can be written as a function of θ ,

$$\mu_{Li}^{\ c}(\theta) = \mu_{Li}^{c}(\theta) + F\phi^{c}.$$
[6]

The functional dependence of μ_{Li}^c upon θ is obtained using a GITT experiment conducted with NMC cathode and Li metal anode. The voltage between the electrodes is measured at electrochemical equilibrium at various states of charge θ of the cathode. At electrochemical equilibrium, let ϕ_{eq}^c and ϕ_{eq}^a respectively denote the electric potentials of the NMC cathode and Li metal anode respectively. Then μ_{Li}^c can be expressed as a function of the open circuit voltage $V_{oc}(\theta) = \phi_{eq}^c - \phi_{eq}^a$,

$$\mu_{Li}^c(\theta) = -FV_{oc}(\theta) + \mu_{Li}^a,$$
[7]

where μ_{Li}^a is the chemical potential (constant) of Lithium metal anode. Upon combining Eqs. [6] and [7], we write

$$\mu_{Li}^{c}(\theta) = -FV_{oc}(\theta) + \mu_{Li}^{a} + F\phi^{c}.$$
[8]

The spatial gradient in ${}^{\mu}{}_{Li}{}^{c}(\theta)$ generates the driving force f on Li⁺ in the NMC particle, i.e. $f = -\nabla \mu_{Li}{}^{c}$. We assume that the drift velocity ${}^{v}{}_{d}$ of Li⁺ is proportional to f with the mobility tensor M representing the proportionality constant. We know that the diffusivity D is related to M using the Einstein's relation D = RT M, where R is the universal gas constant. Therefore, ${}^{v}{}_{d} = -(D/RT) \cdot \nabla \mu_{Li}{}^{c}$ follows. The diffusion of Li⁺ occurs only between the layered structure of NMC with 2-dimensional isotropic diffusivity in the ab-plane. In the crystallographic coordinate system, D can be expressed in matrix form as,

$$D = \begin{bmatrix} D_{ab} & 0 & 0\\ 0 & D_{ab} & 0\\ 0 & 0 & 0 \end{bmatrix}.$$
 [9]

The flux J of Li⁺ in the NMC particle can now be written using the expression of v_d and substituting Eqs. [8] and [9] such that,

$$J = N_{Li} + v_d = \frac{N_L F}{RT} \theta D_{ab} \frac{\partial V_{oc}}{\partial \theta} \left[\frac{\partial \theta}{\partial x_1} e_1 + \frac{\partial \theta}{\partial x_2} e_2 \right].$$
 [10]

We have assumed that NMC is a good electronic conductor hence $\nabla \phi^c = 0$. We use the functional forms of occupancy-dependent $D_{ab}(\theta)$ and $V_{oc}(\theta)$ as given in Xu et al. ¹ The transport Li⁺ is governed by mass balance law which requires that,

$$\frac{\partial N_{Li}}{\partial t} = -\nabla \cdot J \tag{11}$$

$$\Rightarrow N_{L} \frac{\partial \theta}{\partial t} = -\left[\frac{\partial}{\partial x_{1}} \left(\frac{N_{L}F}{RT} \theta D_{ab} \frac{\partial V_{oc} \partial \theta}{\partial \theta \partial x_{1}}\right) + \frac{\partial}{\partial x_{2}} \left(\frac{N_{L}F}{RT} \theta D_{ab} \frac{\partial V_{oc} \partial \theta}{\partial \theta \partial x_{2}}\right)\right].$$
[12]

Observe that the 3D diffusion Eq.[11] reduces to a 2D problem Eq.[12] in the ab-plane as the diffusivity along the c-axis is zero.

Fluxes through particle-electrolyte interface in presence of rock-salt

In order to completely define the boundary value problem, we have to specify the boundary conditions at the particle-electrolyte interface and the initial conditions on θ for the particle. In this work, we will focus our attention to delithiation of NMC cathode under an applied constant current (CC). In the battery literature, the CC conditions are usually quantified with the specification of C-rate. The C-rate is *n*C if the electrode nominally delithiates in (1/n) hours. We shall assume that the single storage particle experiences the same C-rate as that applied to the cathode. A constant current of *n*C is applied on the active lateral surface *S* of the particle. The storage particles cannot be fully lithiated, i.e. $\theta = 1$ in practise. Therefore, we shall delithiate the particle from an initial state of spatially uniform occupancy $\theta(x, t = 0) = 0.95 \forall x \in \Omega$.

The modelling of boundary condition is now described in detail. The main goal of the present work is to study the spatio-temporal evolution of Li^+ distribution for an aged NMC cathode under different C-rates. By aging we mean that the cathode has been undergone several prior charge-discharge cycles. With aged NMC cathodes, there is experimental evidence that a layer of rock-salt forms on the surface of storage particles. The rock-salt layer impedes the charge transfer process by partially blocking the Li^+ flux across the particle-electrolyte interface. Rather than explicitly modelling the rock-salt layer, we will partially block the Li^+ flux on a portion of particle surface which will be assumed to represent the rock-salt layer. We shall further assume that the Li^+ flux does not vary along the height of the of the cylindrical particle. With these assumptions, the boundary conditions on the 3D cylindrical particle reduce to being applied on the 2D circular cross-section on the *ab*-plane.

We denote the arc-length on the particle surface corresponding to the rock-salt layer as Γ_{RSL} . Then the arc-length corresponding to NMC follows as $\Gamma_{NMC} = \Gamma_{ab} - \Gamma_{RSL}$, where $\Gamma_{ab} = \pi d$ is the perimeter of the circular cross-section of the particle. The constant current assumption for the particle demands that the surface electronic current densities through the rock-salt layer I_{RSL} and the NMC surface I_{NMC} satisfy the condition

$$I_{NMC}\Gamma_{NMC} + I_{RSL}\Gamma_{RSL} = nQ\rho A_{ab},$$
[13]

where $Q = 200 \ mAhg^{-1}$ is the nominal capacity of NMC, $\rho = 4.78 \ g \ cm^{-3}$ is the density of active material and $A_{ab} = \pi d^2/4$ is the *ab*-plane cross-sectional area of the cylindrical particle.

The ionic fluxes of Li⁺ through the rock-salt and NMC are related to the electronic current densities as $j_{RSL} = I_{RSL}/F$ and $j_{NMC} = I_{NMC}/F$ respectively. The Li⁺ flux j_{RSL} , which is a function of the thickness of rock salt and the diffusivity of Li⁺ through the rock-salt, is in general lower than j_{NMC} . We shall assume that $j_{RSL} = \eta j_{NMC}$, $0 \le \eta < 1$. We shall further assume that the rock-salt layer covers a fraction of the total surface of the particle, i.e. $\Gamma_{RSL} = \gamma \Gamma_{ab}$, $0 \le \gamma < 1$. Note that, the case $\gamma = 1$ is excluded. This case corresponds to the situation where the entire surface of the particle is covered by the rock-salt layer, i.e. $\Gamma_{RSL} = \Gamma_{ab}$ and $\Gamma_{NMC} = 0$. As $\eta < 1$, the assumption that all the active particles experience the same current as specified by the battery C-rate is violated when $\gamma = 1$. Returning to Eq. [13], the assumptions on j_{RSL} and Γ_{RSL} imply that

$$j_{NMC}(\eta,\gamma) = \frac{1}{(1-\gamma+\eta\gamma)} \frac{nQ_{NMC}\rho_{NMC}A_{ab}}{F\Gamma_{ab}}, j_{RSL} = \eta j_{NMC}.$$
[14]

It is worth mentioning the limiting cases in Eq. [14]:

- (i) For a fresh NMC particle with no rock-salt layer, $\Gamma_{NMC} = \Gamma_{ab}$ and $\Gamma_{RSL} = 0$. The flux through the NMC surface is equal to $j_{NMC}(\eta, \gamma = 0) = nQ_{NMC}\rho_{NMC}A_{ab}/(F\Gamma_{ab})$.
- (ii) When the rock-salt layer is present $(\gamma \neq 0)$ and if it completely blocks Li⁺ flux $(\eta = 0)$, then the flux through the NMC surface is greater than Case (i), i.e. $j_{NMC}(\eta = 0, \gamma) > j_{NMC}(\eta, \gamma = 0)$.

We complete the formulation of the boundary value problem by specifying the normal flux $J \cdot n$ on the particle-electrolyte interface with the unit normal vector n as follows:

$$J \cdot n = \begin{cases} j_{NMC} \text{ if } x \in \Gamma_{NMC} \\ \\ j_{RSL} \text{ if } x \in \Gamma_{RSL} \end{cases}.$$

$$[15]$$

The governing Eq. [12] subject to the boundary conditions Eq. [15] is solved numerically via the finite element method using COMSOL Multiphysics[®] (v5.6). A parametric study is carried out to study the effect of C-rate (*n*) for selected values rock-salt parameters η and γ .

Figure S1 | Li diffusivity as a function of Li content in fresh and aged (3 - 4.3V at 50 mA/g for 200 cycles in a half coin cell) NMC materials measured from galvanostatic intermittent titration experiments (GITT).





Figure S2 | Optical responses of several other fresh particles at the beginning of charge. Scale bars 1 μ m.



Figure S3 | Optical responses of several other aged particles (first aged over 200 cycles at 3 - 4.3V and 50 mA/g in a coin cell) at the beginning of charge. Scale bars 1 μ m.



Figure S4 | Quantification of the distances between the COM of the whole particle (inset, the same particle as shown in Figure S3a) and the COM of the 'unreacted' region (differential optical intensity smaller than 0.05) of the particle at different SOC during the optical measurements when the cell was cycled at different rates. Scale bar: $1 \mu m$.



Figure S5 | Cyclability of Ni-rich NMC under four different conditions: 3 - 4.3 V at 50 mA/g, 3 - 4.3 V at 200 mA/g, 3 - 4.3 V at 400 mA/g and 3 - 4.5 V at 200 mA/g.



Figure S6 | Rate capability of fresh and aged (after 200 cycles) Ni-rich NMC under four different conditions: 3 - 4.3 V at 50 mA/g, 3 - 4.3 V at 200 mA/g, 3 - 4.3 V at 400 mA/g and 3 - 4.5 V at 200 mA/g.





Figure S7 | Summary of particles that are optically investigated following each aging condition. All images use the same scale bar.

Site	Atom	X	У	Z	Occupancy
3а	Ni	0	0	0	0.861(1)
	Mn	0	0	0	0.05
	Со	0	0	0	0.07
	Li	0	0	0	0.019(1)
3b	Li	0	0	1/2	0.981(1)
	Ni	0	0	1/2	0.019(1)
6c	Ο	0	0	0.2587(1)	1

Table S1 | Rietveld refinement results of as-received single-crystal Ni-rich NMC cathode $LiNi_{0.88}Mn_{0.05}Co_{0.07}O_2$.

Space group: R3m

Lattice parameters: a = b = 2.87495(3) Å; c = 14.1910(2) Å

Fitting quality: $R_{wp} = 7.86\%$

Supplementary References

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