

Dual functionality of over-lithiated NMC for high energy silicon-based lithium-ion batteries

Supplementary information

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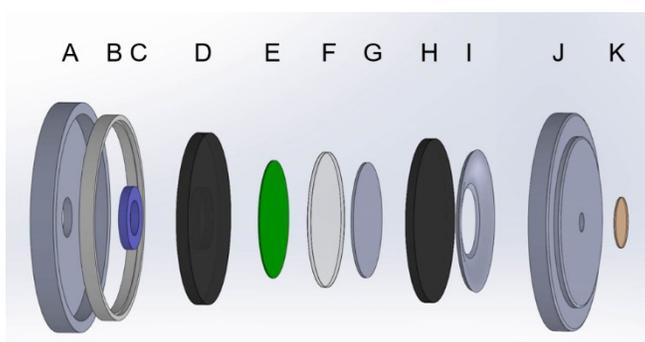


Figure S1. Schematic of the coin cell used for in situ synchrotron X-ray diffraction measurements. A. 2032 casing; B. 2032 gasket; C. fluorosilicone gasket; D. glassy carbon spacer; E. cathode laminate; F. Separator; G. Lithium anode; H. glassy carbon spacer; I. wave spring; J. 2032 casing; K. Kapton window.

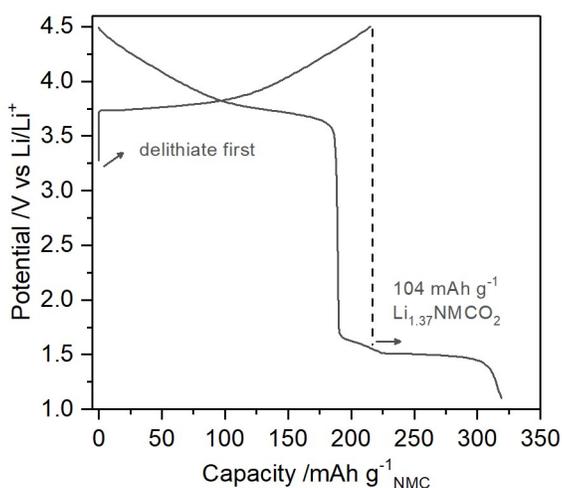


Figure S2. Illustration of the over-lithiation capability of a layered $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ cathode after a charge-discharge cycle versus lithium metal at a rate of C/10.

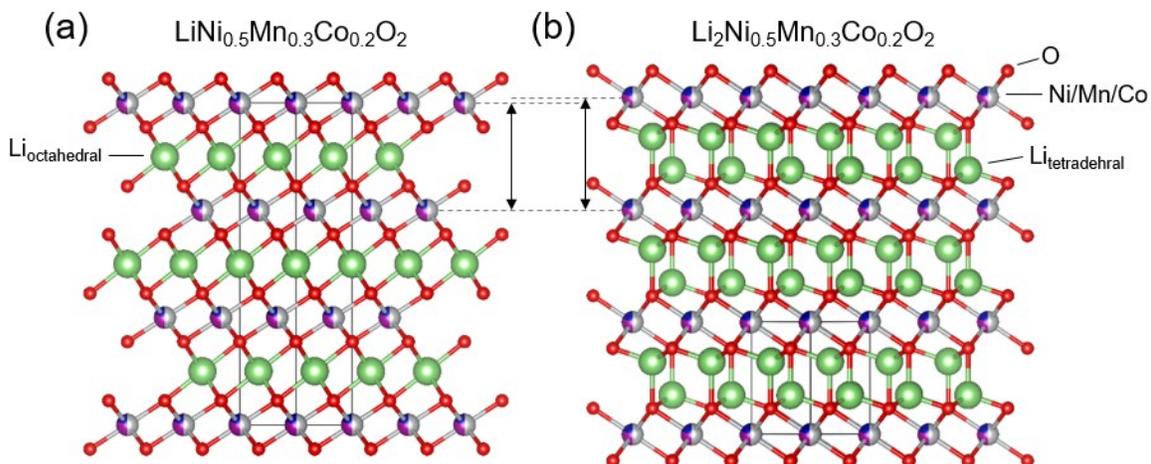


Figure S3. Schematic of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ and $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$, showing the different lithium ion coordination and the inter-layer distance.

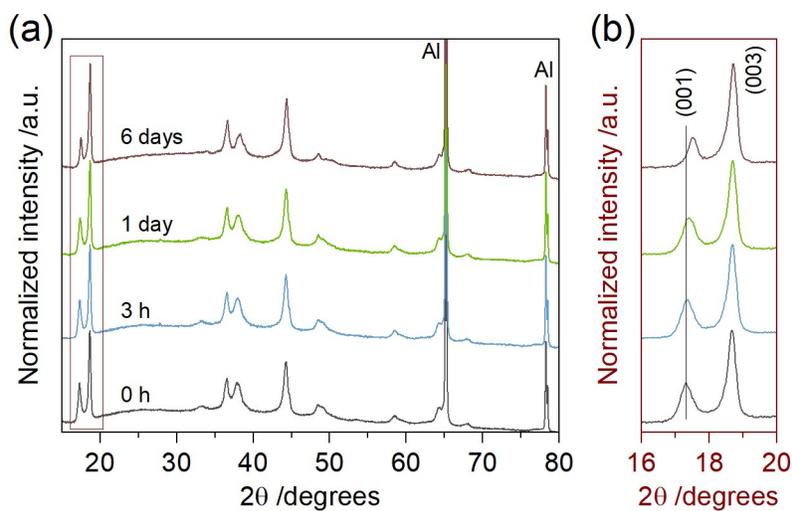


Figure S4. Ambient environment stability of an electrochemically pre-lithiated $\text{Li}_{1.46}\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ cathode after 0 h, 3 h, 1 day, and 6 days of exposure. In (a) X-ray diffraction patterns over the range $15\text{-}80^\circ$ 2θ are shown while (b) shows the zoomed in region $16\text{-}20^\circ$ 2θ focused on the evolution of the (001) reflection from $P\text{-}3m1$ $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ and the (003) reflection from $R\text{-}3m$ $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$. The shift of the (001) reflection to higher angles together with the slight decrease in intensity relative to the (003) reflection suggest a slow reaction between the $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ phase and components in the air.

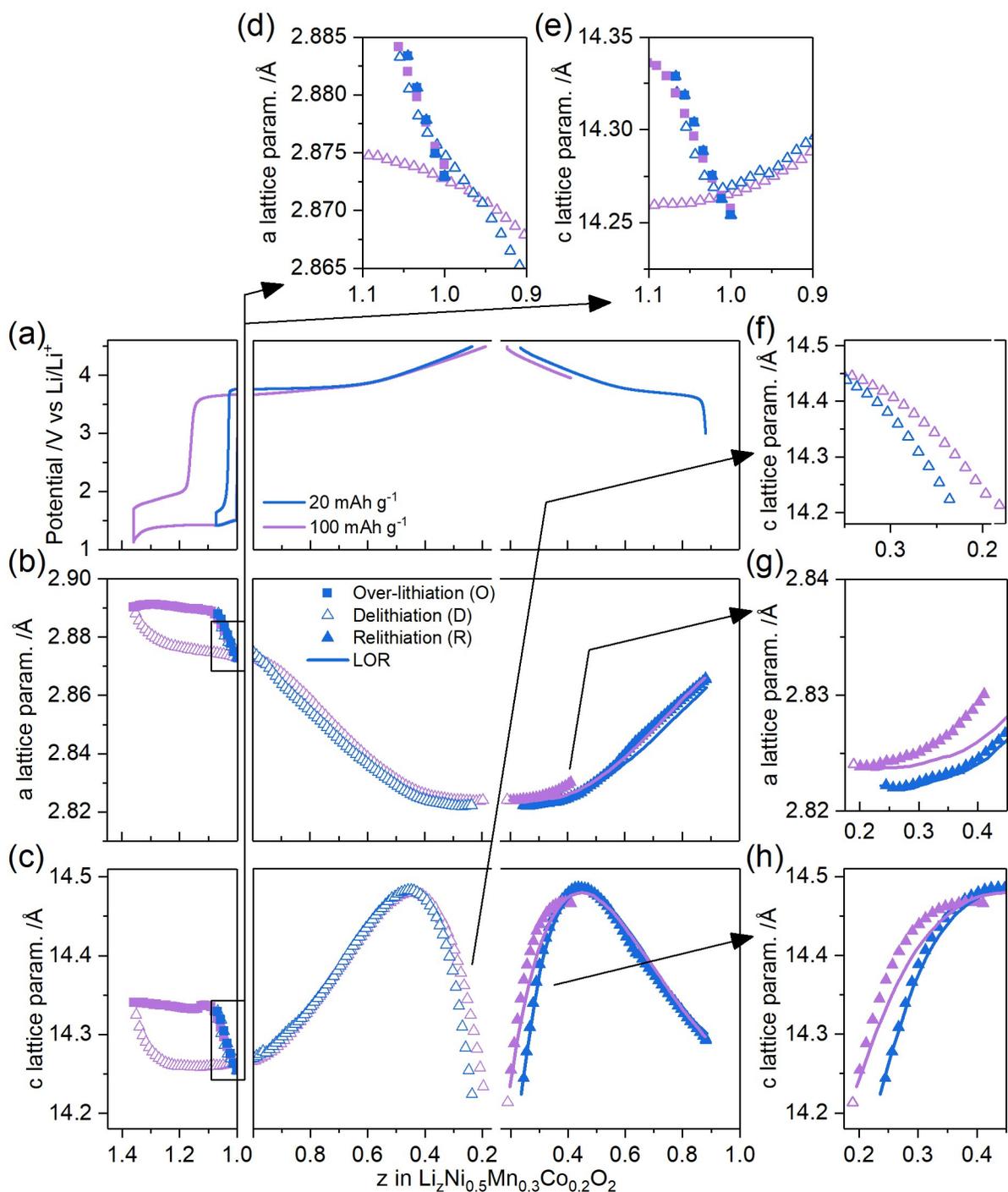


Figure S5. Potential profiles (a) and a and c lattice parameters (b) and (c), respectively, obtained from Rietveld refinements during over-lithiation (O) to 20 and 100 $\text{mAh g}^{-1}_{\text{NMC}}$, and subsequent delithiation (D) and relithiation (R). The estimated errors are within the data markers. A solid line is shown over the relithiation data showing the hypothetical pathway without structural hysteresis, labelled the line of reversibility (LOR). Critical lattice parameter differences are highlighted in (d-h); (d-e) upon return to $z=1$, (f) towards the end of delithiation, and (g-h) in the early stages of relithiation.

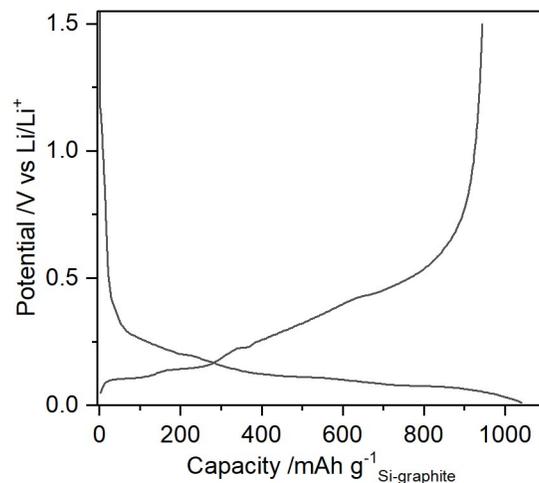


Figure S6. Representative potential profile for the Si-graphite electrode in the first cycle between 10 mV and 1.5 V versus lithium metal.

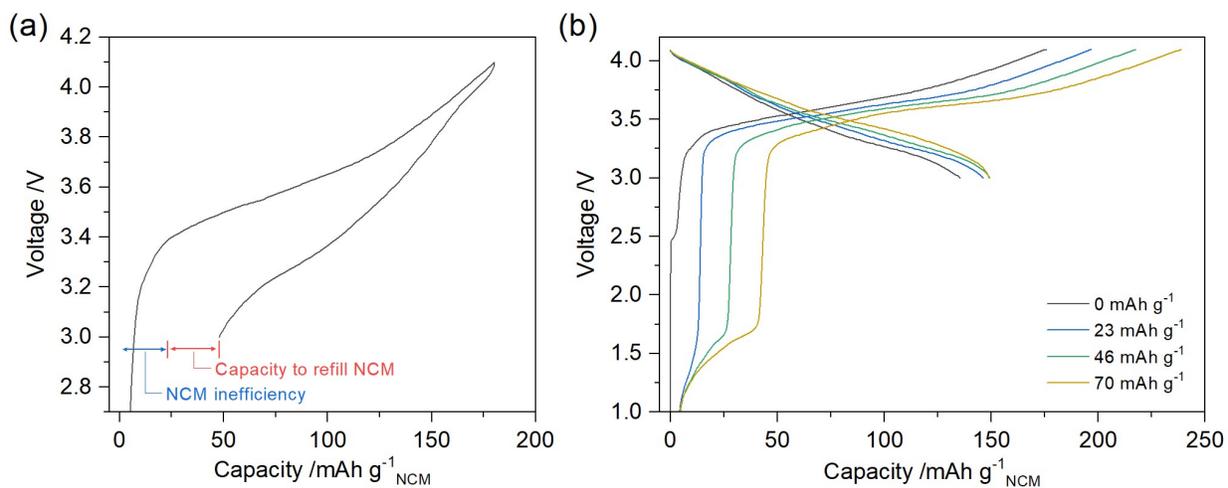


Figure S7. (a) Voltage profile of the first cycle of a $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2/\text{Si-graphite}$ full cell. The additional capacity required to refill all available lithium sites of the cathode (taking into account the coulombic efficiency of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ as measured in a half cell) is shown. (b) Voltage profiles of the first cycle of $\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2/\text{Si-graphite}$ full cells with varying degrees of electrochemical over-lithiation during cycling at C/20 between 3.0-4.1 V and at 30 °C.

Supplementary note S1. Calculation of additional capacity required to refill NMC532 cathode after the first cycle of a NMC532/Si-graphite full cell.

We have,

$$\text{NMC532/Si-graphite charge capacity} = 1.86 \text{ mAh cm}^{-2}$$

$$\text{NMC532/Si-graphite discharge capacity} = 1.39 \text{ mAh cm}^{-2}$$

$$\text{NMC532/Li metal efficiency} = 0.87$$

Therefore,

Discharge capacity to refill NMC532 cathode

$$= 1.86 \times 0.87$$

$$= 1.62 \text{ mAh cm}^{-2}$$

Difference between discharge capacity to refill NMC532 cathode and that realized in full cell

$$= 1.62 - 1.39$$

$$= 0.24 \text{ mAh cm}^{-2}$$

$$\equiv \mathbf{23.0 \text{ mAh g}^{-1}_{NMC}}$$

Supplementary note S2. Calculation of additional capacity required to completely lithiate the Si-graphite anode in the first charge of a NMC532/Si-graphite full cell.

We have,

$$\text{Target n/p ratio} = 1.1$$

$$\text{NMC532/Si-graphite charge capacity} = 1.86 \text{ mAh cm}^{-2}$$

$$\text{Si-graphite/Li metal discharge (lithiation) capacity} = 2.80 \text{ mAh cm}^{-2}$$

Therefore,

Let the additional capacity be Q_a . Then

$$n/p = 1.1$$

$$1.1 = 2.80 / (1.86 + Q_a)$$

Rearranging,

$$Q_a = 0.69 \text{ mAh cm}^{-2}$$

$$\equiv \mathbf{66.4 \text{ mAh g}^{-1}_{NMC}}$$

Q_a used in experiments = 70 mAh g⁻¹_{NMC}

n/p ratio in experiments = **1.09**

Table S1. Discharge capacity of cathodes *extracted* from Li_{1+x}NMCO₂/Si-graphite full cells after 100 or 200 cycles and *rebuilt* versus a lithium metal counter/reference electrode. Cycling was performed at a C/10 rate in the range 3.0-4.5 V. The number of cycles performed in the full cell before extraction is indicated in the first column. Capacity retention is determined by comparing the discharge capacity of the aged cathode to the discharge capacity of a fresh LiNMCO₂ cathode (i.e., 0 cycles in a full cell and 0 mAh g⁻¹_{NMC} over-lithiation) cycled versus lithium metal under the same conditions.

No. of cycles	Over-lithiation capacity mAh g ⁻¹ _{NMC}	Discharge capacity mAh g ⁻¹ _{NMC}	Capacity retention %
0	0	166.6	100
100	0	162.4	97.5
	23	157.2	94.4
200	46	152.5	91.5
	70	150.4	90.3

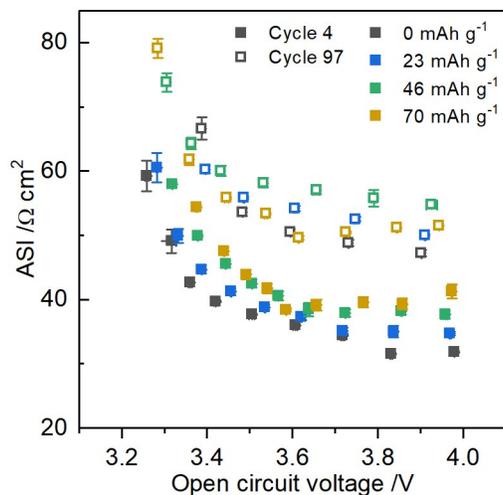


Figure S8. Area specific impedance (ASI) data as a function of the full cell voltage from the HPPC cycles. Results are averaged over two cells and the error bars (in many cases smaller than the symbols) represent the variation between the cells.

Table S2. Area specific impedance (ASI) data from HPPC cycles at ~ 3.6 V. Errors represent the variation between two cells.

Over-lithiation capacity $\text{mAh g}^{-1}_{\text{NMC}}$	ASI at ~ 3.6 V		Δ ASI $\Omega \text{ cm}^2$
	$\Omega \text{ cm}^2$		
	Cycle 4	Cycle 97	
0	36.0(2)	50.5(4)	14.5(6)
23	37.2(4)	54.2(4)	17.0(8)
46	38(1)	57.1(7)	19(2)
70	39.1(8)	49.6(3)	10(1)