Electronic Supplementary Information for:

Two-step hydrothermal synthesis of submicron $Li_{1+x}Ni_{0.5}Mn_{1.5}O_{4-\delta}$ for lithium-ion battery cathodes (x = 0.02, δ = 0.12)

Xiaoguang Hao, Mark H. Austin and Bart M. Bartlett

University of Michigan Department of Chemistry
930 N. University Avenue
Ann Arbor, MI 48109-1055 USA
Tele: +1 (734) 615-9279

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Table S1. Refinement parameters for LNMO synthesized in air. (The experimental XRD pattern is shown as Fig. 1 in the text).

Space Group	$Fd\,\bar{3}m$
Scale	5.460×10^{-4}
Lattice parameter, a (Å)	8.183
Unit Cell Mass (g•mol^{-1})	1450.260
Unit Cell Volume (Å^3)	548.141
Crystallite Size, Lorentzian (nm)	120.8
Crystal Density (g•cm^3), calculated	4.393
Crystal Linear Absorption Coefficient (cm^{-1})	592.397
Wt%-Rietveld	86.398
R_{exp}/ R_{exp}' $^{(a)}$	0.93/1.69
R_{wp}/ R_{wp}'	1.85/3.34
R_p/ R_p'	1.23/2.40
R_{Bragg}	3.607
GoF	1.98
DW_d	0.76

(*a*)-Primed parameters are background corrected.

Table S2. Atomic coordinates and isotropic thermal parameters for LNMO synthesized in air.

Atom	Wyckoff Site	*x*	*y*	*z*	SOF	B_{eq}
Li	8*a*	0	0	0	1	2.924
Mn	16*d*	0.6250	0.6250	0.6250	0.75	1.758
Ni	16*d*	0.6250	0.6250	0.6250	0.25	0.9867
O	32*e*	0.38723	0.38723	0.38723	1	-0.06318

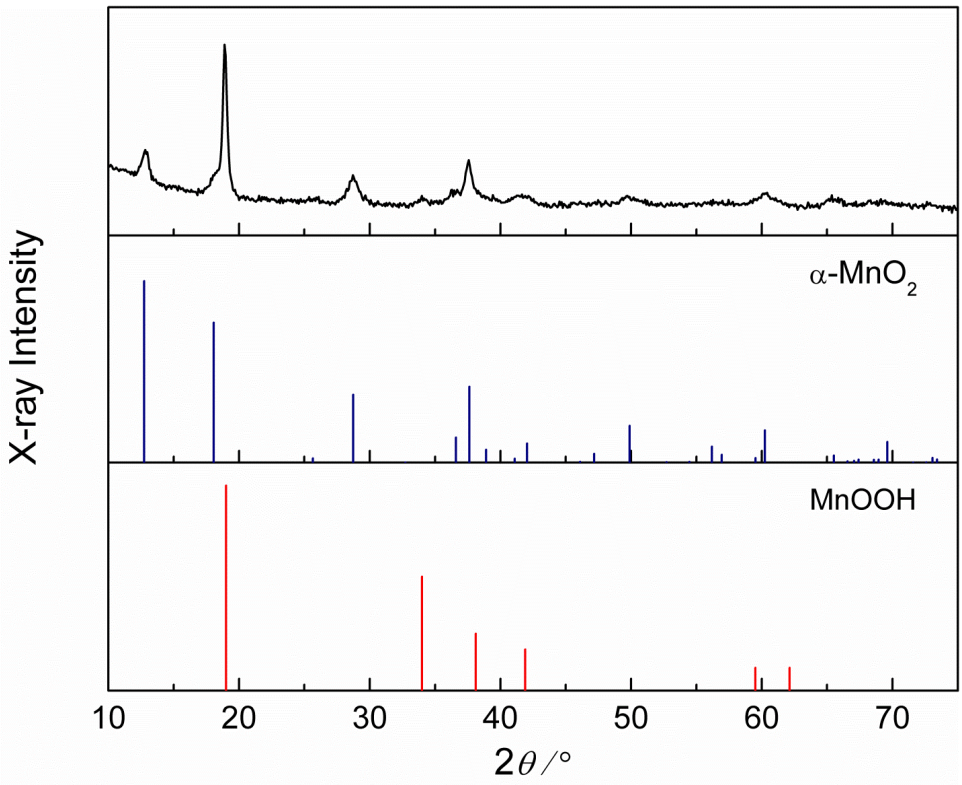

Fig. S1. Indexed XRD pattern of the NMO intermediate ($H_{0.4}K_{0.08}Ni_{0.5}Mn_{1.5}O_{3.305}$)

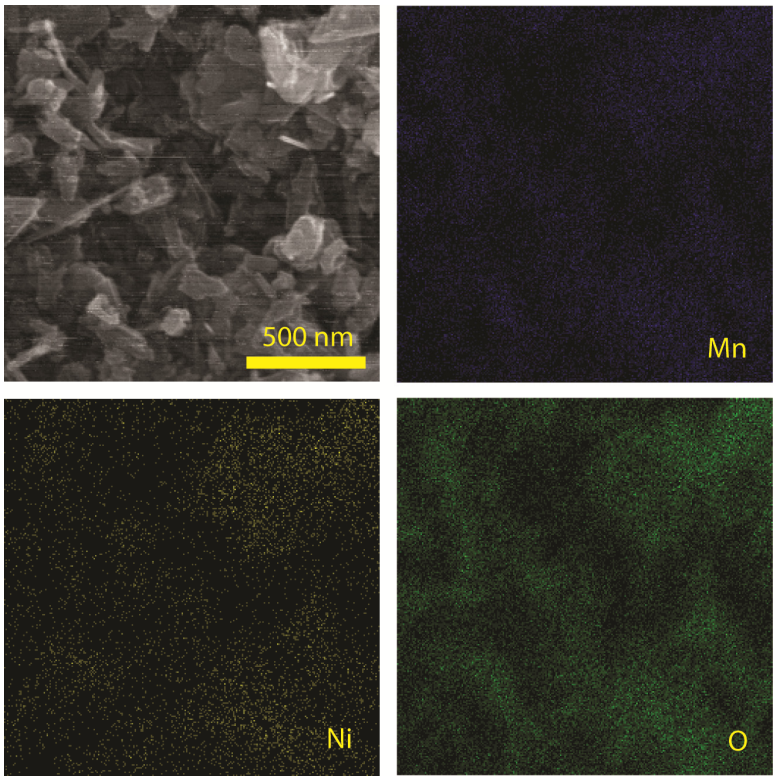

Fig. S2 EDX elemental map of the NMO intermediate

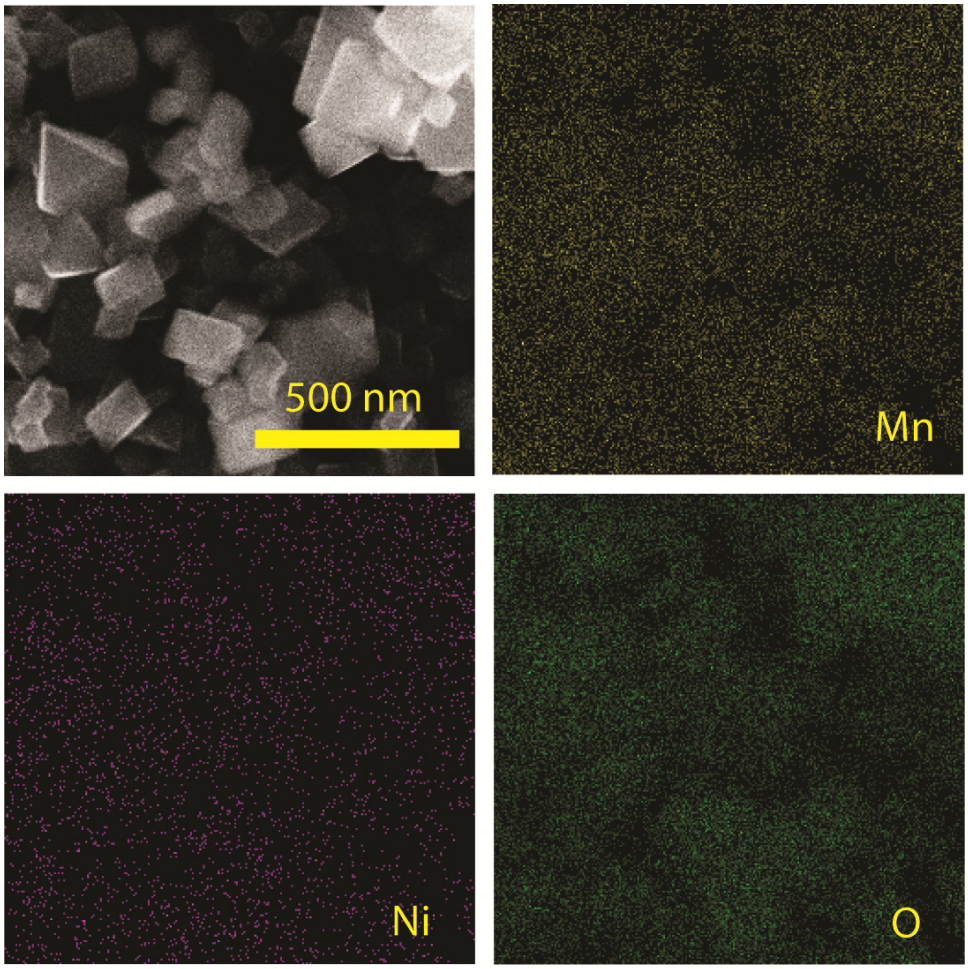

Fig. S3.EDX elemental map of the LNMO product

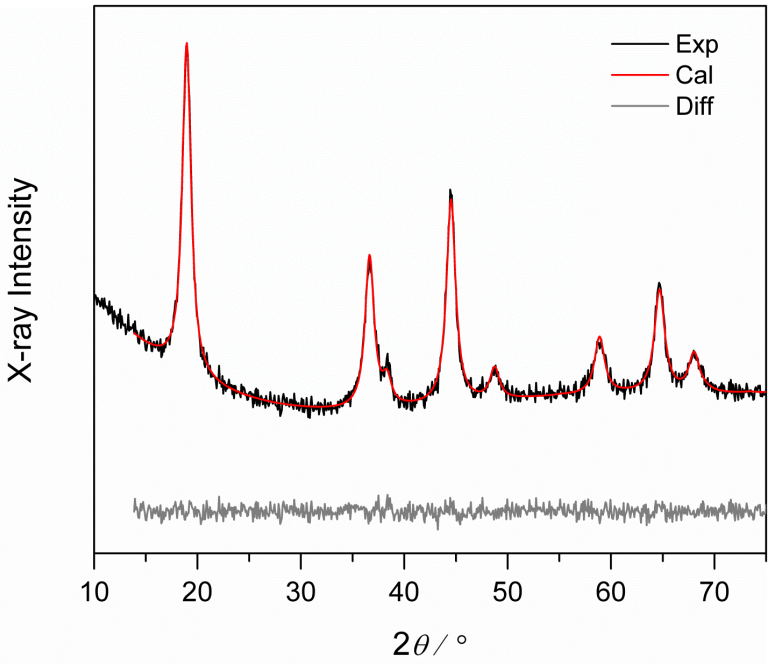

Fig. S4. XRD pattern of the one-pot synthesis LNMO product.

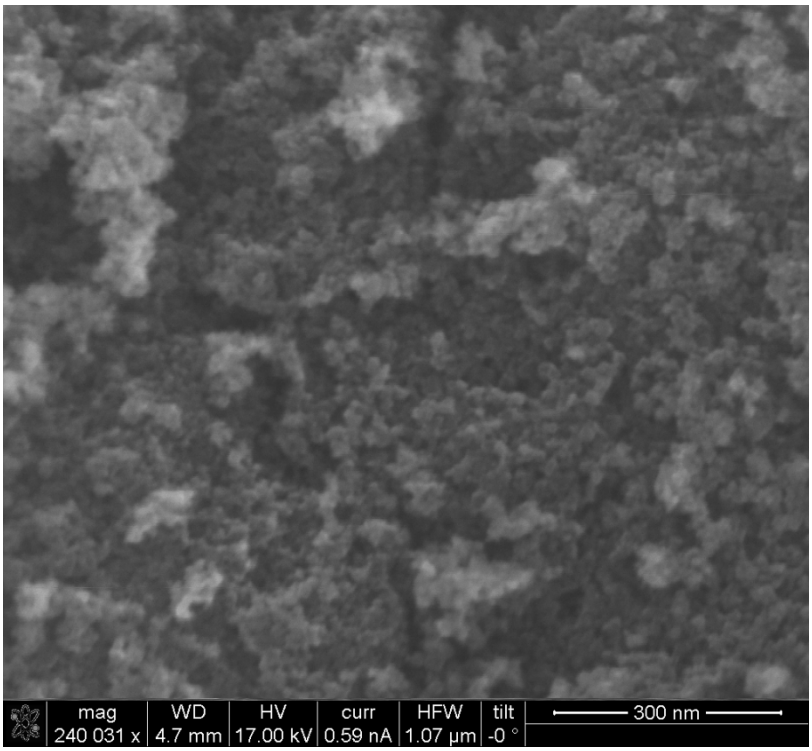

Fig. S5. SEM image of the one-pot synthesis LNMO product.

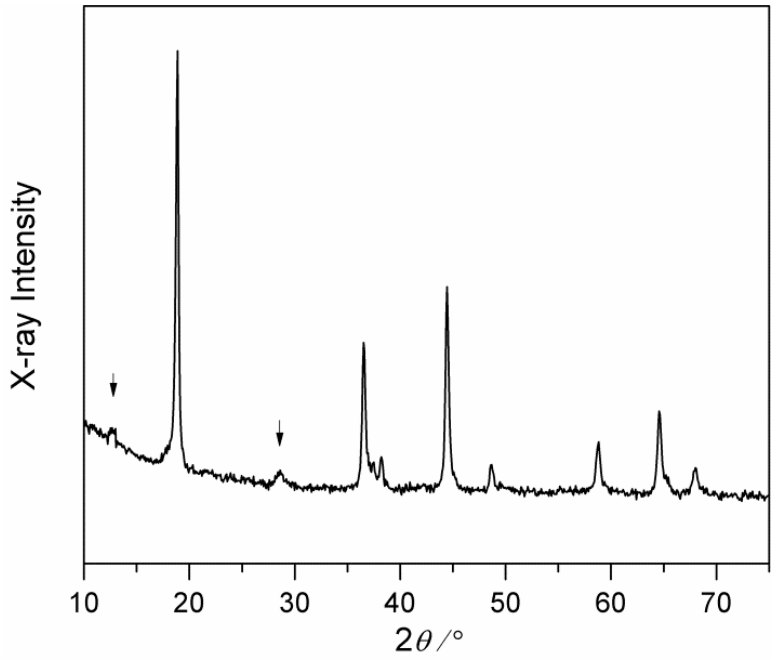

Fig. S6. XRD pattern of the products of the LNMO reaction performed under O_2. The arrows point out reflections for the α-MnO_2 impurity phase. Since the reaction product is not phase-pure, no Rietveld refinement was carried out.

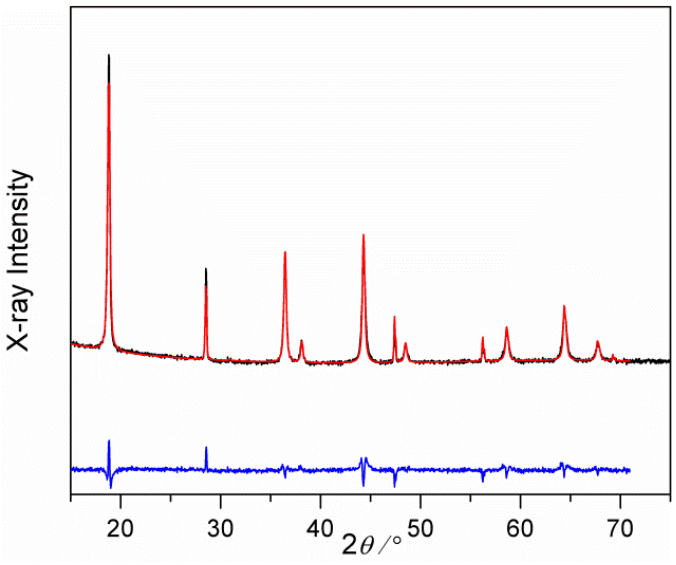

Fig. S7. XRD data (black), calculated Rietveld refinement (red), and difference pattern (blue) for LNMO with second step prepared in N_2.

Table S3. Refinement parameters for LNMO synthesized under N_2

Space Group	$Fd\bar{3}m$
Scale	5.328×10^{-4}
Lattice parameter, a (Å)	8.196
Unit Cell Mass (g•mol^{-1})	1450.260
Unit Cell Volume (Å^3)	549.649
Crystallite Size, Lorentzian (nm)	111.9
Crystal Density (g•cm^3), calculated	4.381
Crystal Linear Absorption Coefficient (cm^{-1})	590.771
Wt%-Rietveld	86.675
R_{exp}/ R_{exp}' $^{(a)}$	0.91/3.04
R_{wp}/ R_{wp}'	1.94/6.49
R_p/ R_p'	1.26/4.70
R_{Bragg}	0.413
GoF	2.14
DW_d	0.69

(a)-Primed parameters are background corrected.

Table S4. Atomic coordinates and isotropic thermal parameters for LNMO synthesized under N_2

Atom	Wyckoff Site	x	y	z	SOF	B_{eq}
Li	8a	0	0	0	1	2.916
Mn	16d	0.6250	0.6250	0.6250	0.75	1.962
Ni	16d	0.6250	0.6250	0.6250	0.25	0.9938
O	32e	0. 38749	0. 38749	0. 38749	1	-5.697×10^{-5}

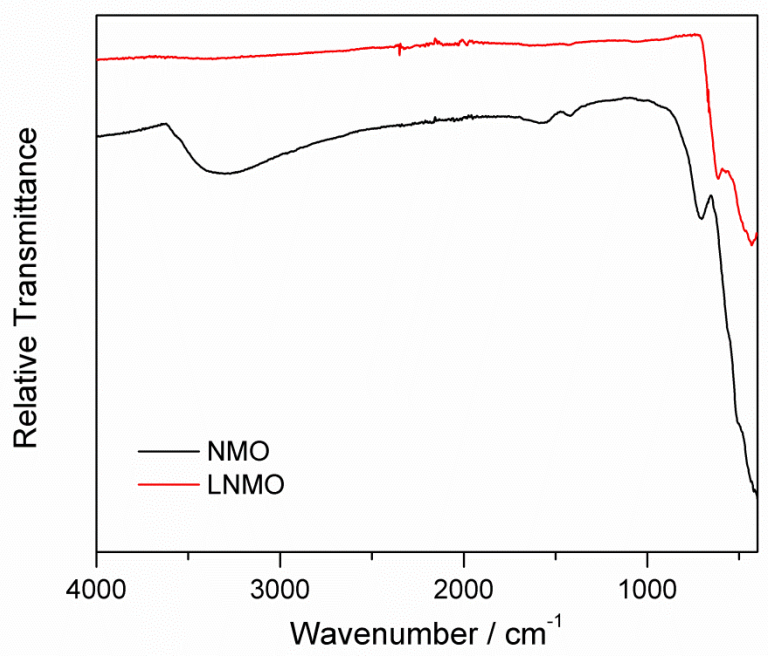

Fig. S8. FTIR spectra of the NMO intermediate and LNMO product.

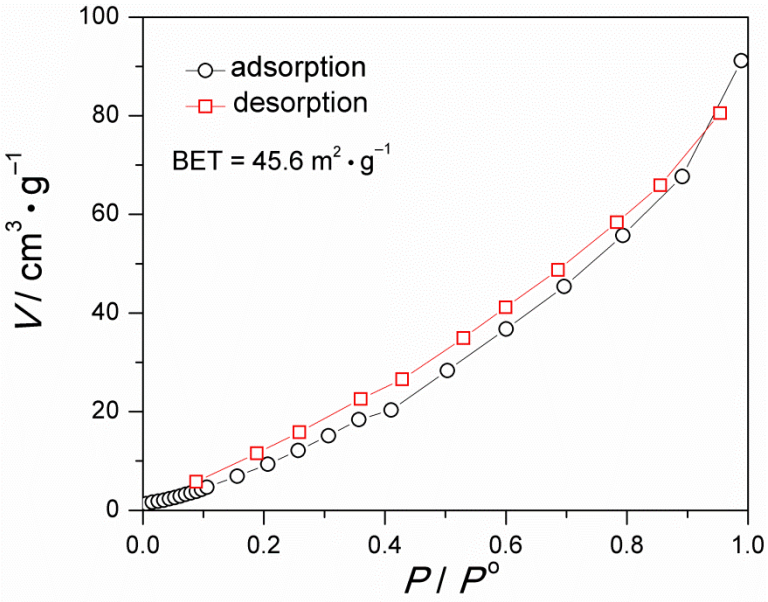

Fig. S9. N_2 sorption isotherm for the final LNMO product synthesized in the two-step hydrothermal method in air.

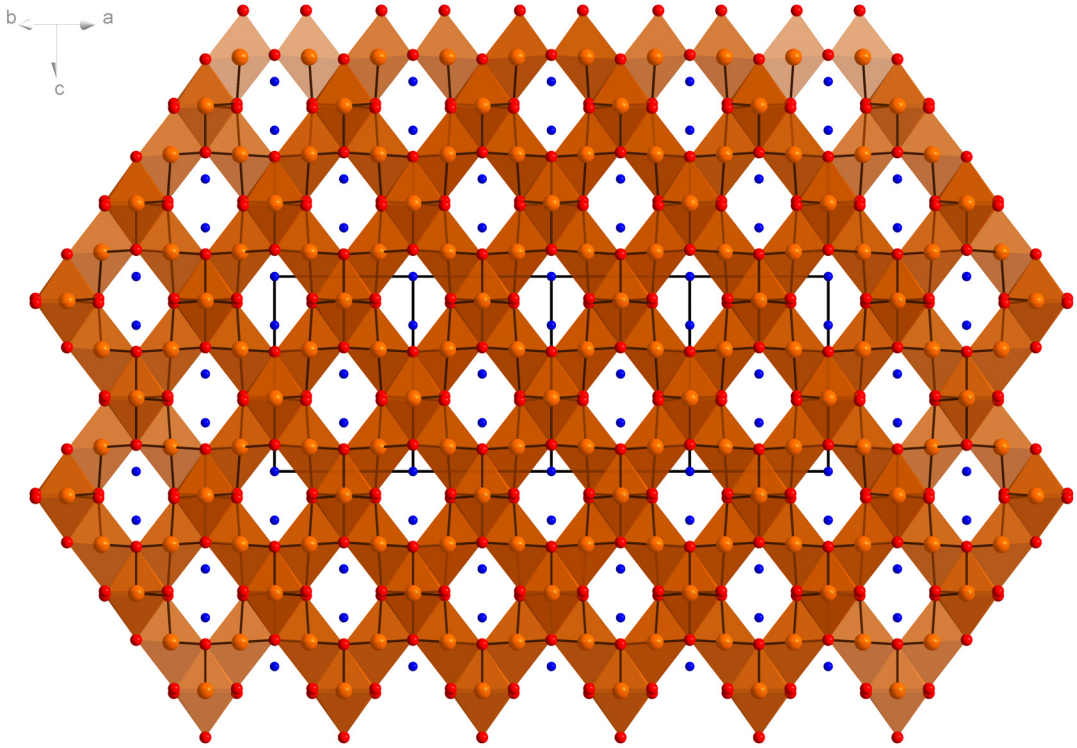

Fig. S10. View of the spinel crystal structure along the [1 1 0] direction. Blue, orange, and red spheres represent lithium, manganese/nickel, and oxygen atoms respectively.

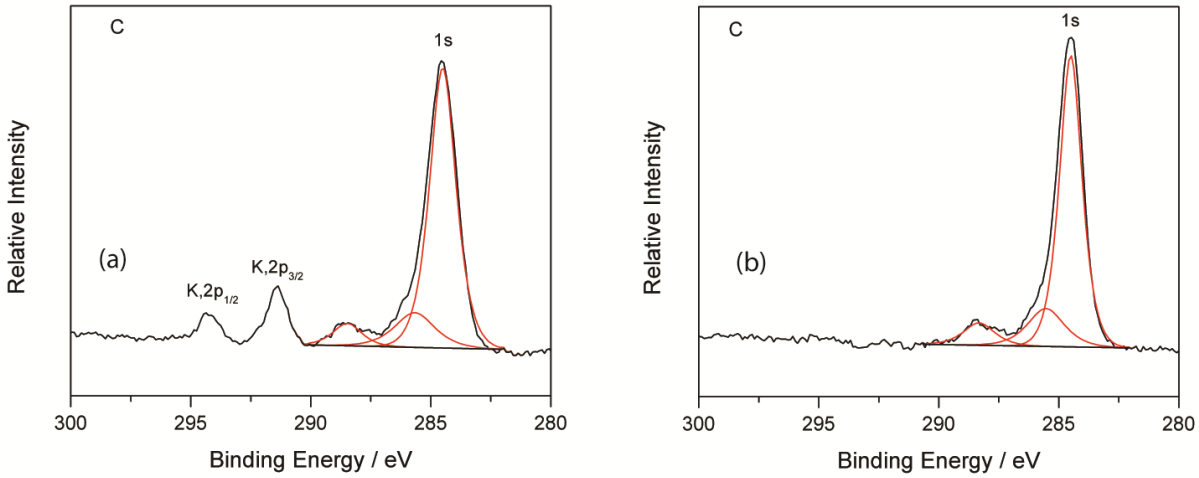

Fig. S11. C(1s) XP spectra for NMO (a) and LNMO (b). NMO also shows K(2p) features.

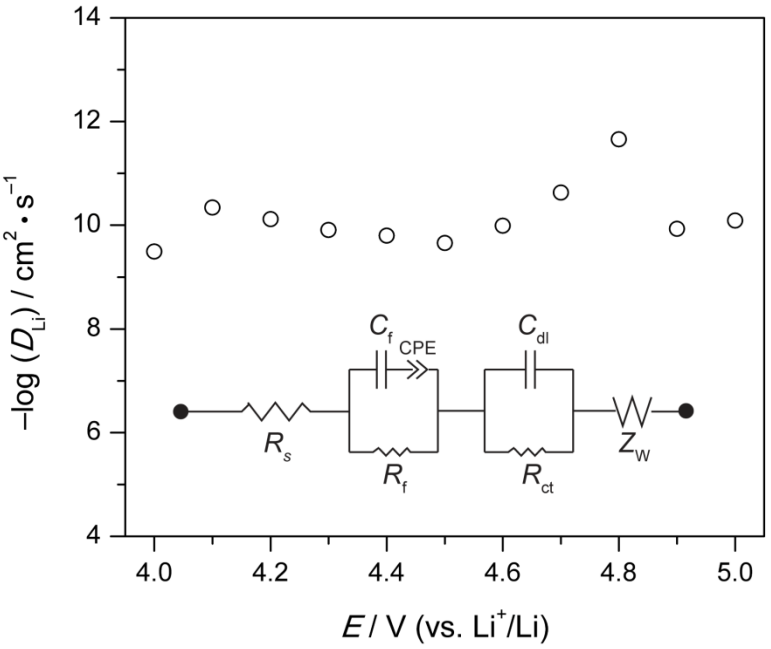

Fig. S12 Voltage-dependence of the Li^+ diffusion constant (D_{Li}) determined from electrochemical impedance spectroscopy. The data are fit to the equivalent circuit illustrated in the inset.

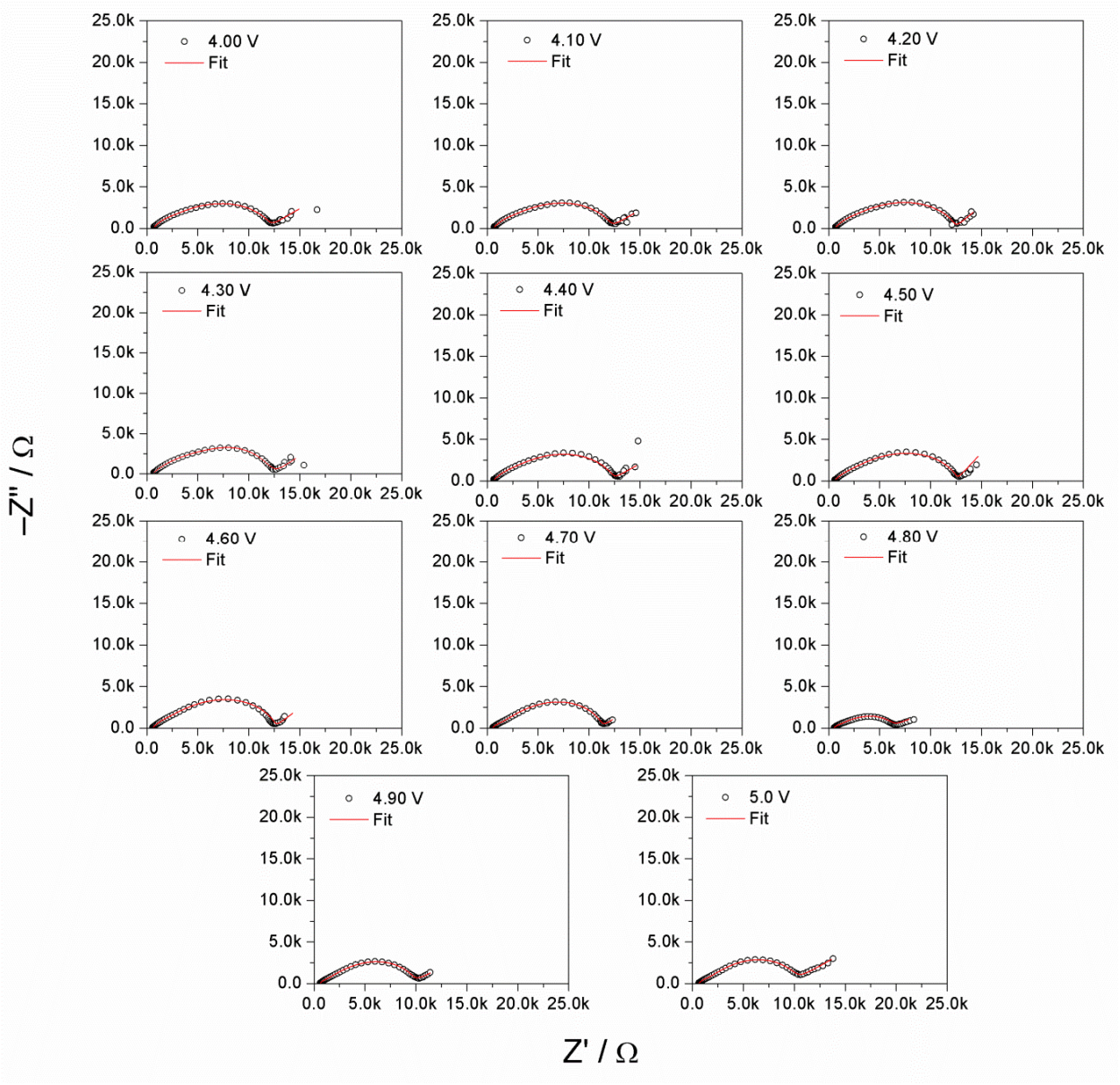

Fig S13. Nyquist plots for determining D_{Li} of LNMO as a function of potential.

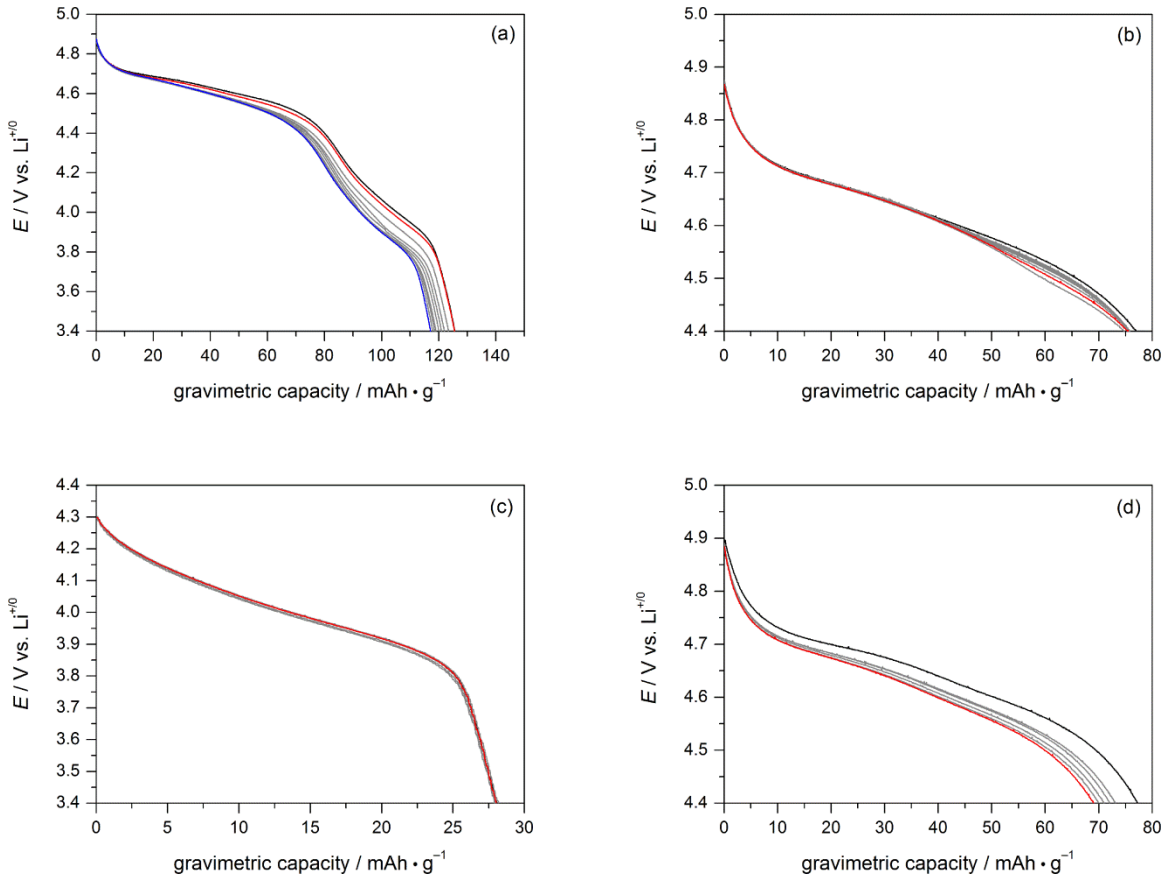

Fig. S14. Voltage profiles for the 1000 cycle LNMO cell. a) Cycles 1 – 10 performed between the voltage limits 3.4 – 5.0 V. Black, red, and blue represent cycles one, two, and ten respectively. Others are shown in gray. b) Cycles 11 – 121 performed between the voltage limits 4.4 – 5.0 V. Black and red represent cycles 11 and 121 respectively. Every 10^{th} cycle in between is shown in gray. c) Cycles 122 – 622 performed between the voltage limits 3.4 – 4.4 V. Black and red present cycles 122 and 622 respectively with every 100^{th} cycle in between shown in gray. d) Cycles 623 – 1123 performed between the voltage limits 4.4 – 5.0 V. Black and red represent cycles 623 and 1123 respectively with every 100^{th} cycle in between shown in gray.

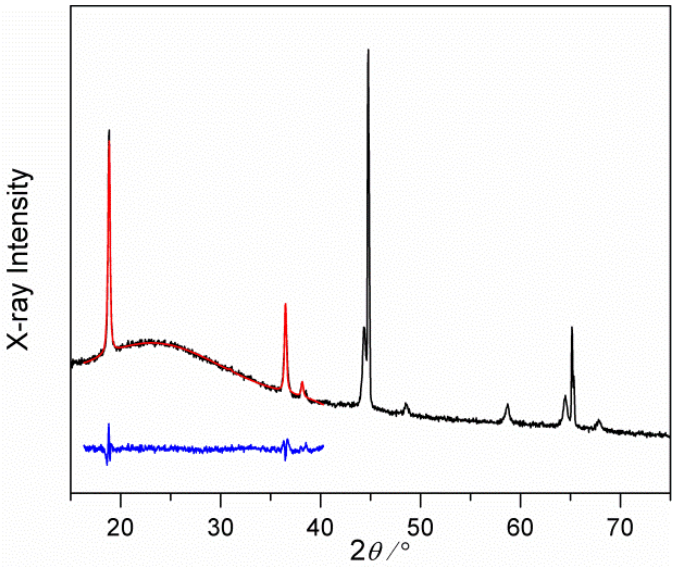

Fig. S15. XRD data (black), calculated Rietveld refinement (red), and difference pattern (blue) for a freshly prepared LNMO electrode.

Table S5. Refinement parameters for a freshly prepared LNMO electrode.

Space Group	$Fd\bar{3}m$
Scale	4.603×10^{-5}
Lattice parameter, *a* (Å)	8.185
Unit Cell Mass (g•mol^{-1})	1450.260
Unit Cell Volume (Å^3)	548.485
Crystallite Size, Lorentzian (nm)	68.8
Crystal Density (g•cm^3), calculated	4.391
Crystal Linear Absorption Coefficient (cm^{-1})	592.025
Wt%-Rietveld	100
R_{exp}/ R_{exp}' $^{(a)}$	1.28/2.50
R_{wp}/ R_{wp}'	1.93/3.78
R_p/ R_p'	1.39/2.79
R_{Bragg}	0.166
GoF	1.51
DW_d	1.01

(*a*)-Primed parameters are background corrected.

Table S6. Atomic coordinates and isotropic thermal parameters for a freshly prepared LNMO electrode.

Atom	Wyckoff Site	*x*	*y*	*z*	SOF	B_{eq}
Li	8*a*	0	0	0	1	-3.857
Mn	16*d*	0.6250	0.6250	0.6250	0.75	16.04
Ni	16*d*	0.6250	0.6250	0.6250	0.25	6.058
O	32*e*	0. 37415	0. 37415	0. 37415	1	13.79

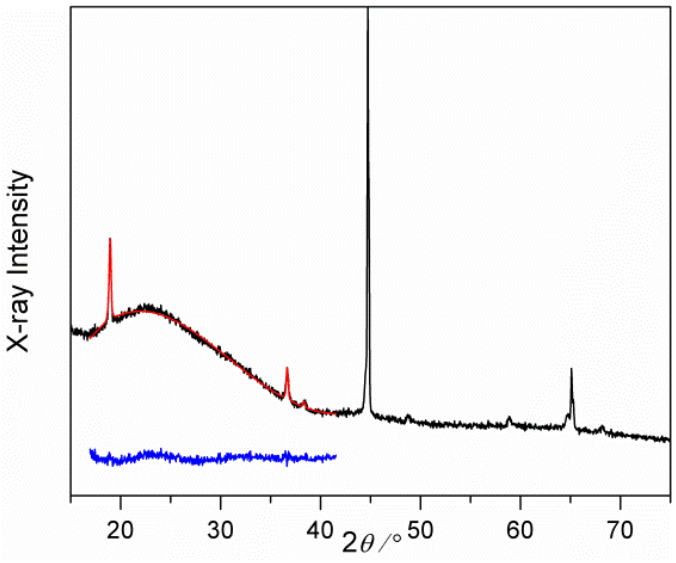

Fig. S16. XRD data (black), calculated Rietveld refinement (red), and difference pattern (blue) for an LNMO electrode after 60 cycles between 3.4 – 5.0 V.

Table S7. Refinement parameters an LNMO electrode after 60 cycles between 3.4 – 5.0 V.

Space Group	$Fd\bar{3}m$
Scale	1.187×10^{-4}
Lattice parameter, a (Å)	8.157
Unit Cell Mass (g•mol^{-1})	1450.260
Unit Cell Volume (Å^3)	542.886
Crystallite Size, Lorentzian (nm)	102.6
Crystal Density (g•cm^3), calculated	4.436
Crystal Linear Absorption Coefficient (cm^{-1})	598.131
Wt%-Rietveld	100
R_{exp}/ R_{exp}' $^{(a)}$	1.60/3.15
R_{wp}/ R_{wp}'	2.02/3.97
R_p/ R_p'	1.62/3.22
R_{Bragg}	0.058
GoF	1.26
DW_d	1.31

(a)-Primed parameters are background corrected.

Table S8. Atomic coordinates and isotropic thermal parameters for an LNMO electrode after 60 cycles between 3.4 – 5.0 V.

Atom	Wyckoff Site	x	y	z	SOF	B_{eq}
Li	8a	0	0	0	1	7.31
Mn	16d	0.6250	0.6250	0.6250	0.75	18.71
Ni	16d	0.6250	0.6250	0.6250	0.25	17.79
O	32e	0.36358	0. 36358	0. 36358	1	20

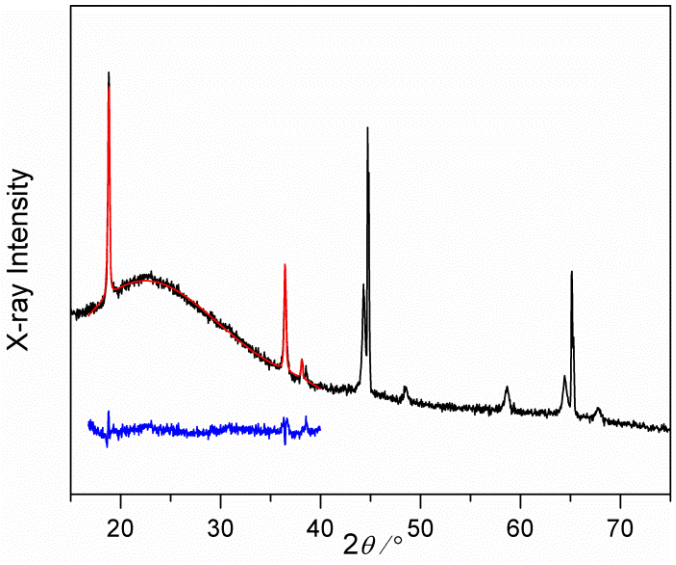

Fig. S17. XRD data (black), calculated Rietveld refinement (red), and difference pattern (blue) for an LNMO electrode after 10 cycles 3.4 – 5.0 V and 50 cycles 3.4 - 4.4 V charge/discharge.

Table S9. Refinement parameters for LNMO after 10 cycles 3.4 – 5.0 V and 50 cycles 3.4 - 4.4 V charge/discharge.

Space Group	$Fd\,\bar{3}m$
Scale	2.687×10^{-4}
Lattice parameter, a (Å)	8.194
Unit Cell Mass (g•mol^{-1})	1450.260
Unit Cell Volume (Å^3)	550.261
Crystallite Size, Lorentzian (nm)	110.0
Crystal Density (g•cm^3), calculated	4.376
Crystal Linear Absorption Coefficient (cm^{-1})	590.114
Wt%-Rietveld	100
R_{exp}/ R_{exp}' $^{(a)}$	1.45/2.85
R_{wp}/ R_{wp}'	2.01/3.95
R_p/ R_p'	1.55/3.10
R_{Bragg}	1.459
GoF	1.38
DW_d	1.21

(*a*)-Primed parameters are background corrected.

Table S10. Atomic coordinates and isotropic thermal parameters for LNMO after 10 cycles 3.4 – 5.0 V and 50 cycles 3.4 - 4.4 V charge/discharge.

Atom	Wyckoff Site	*x*	*y*	*z*	SOF	B_{eq}
Li	8*a*	0	0	0	1	13.38
Mn	16*d*	0.6250	0.6250	0.6250	0.75	19.53
Ni	16*d*	0.6250	0.6250	0.6250	0.25	1
O	32*e*	0. 36880	0. 36880	0. 36880	1	-7.117

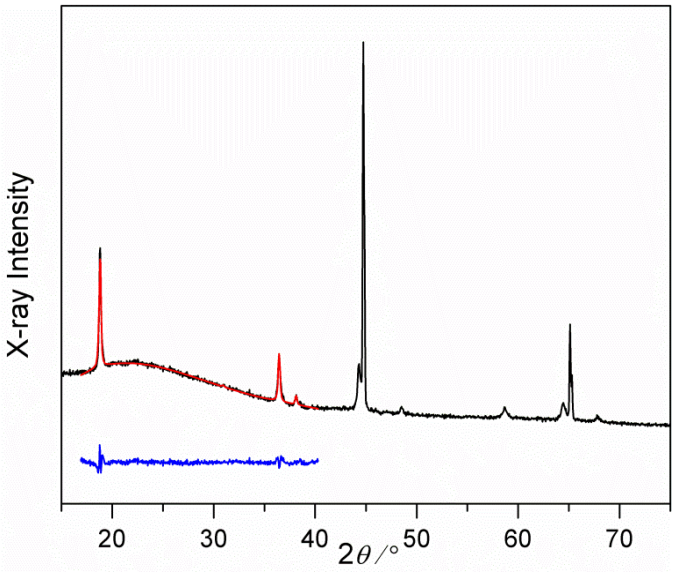

Fig. S18. XRD data (black), calculated Rietveld refinement (red), and difference pattern (blue) for an LNMO electrode after 10 cycles 3.4 - 5 V and 50 cycles 4.4 - 5 V charge/discharge.

Table S11. Refinement parameters for an LNMO electrode after 10 cycles 3.4 - 5 V and 50 cycles 4.4 - 5 V charge/discharge.

Space Group	$Fd\bar{3}m$
Scale	3.976×10^{-4}
Lattice parameter, a (Å)	8.189
Unit Cell Mass (g•mol^{-1})	1450.260
Unit Cell Volume (Å^3)	549.322
Crystallite Size, Lorentzian (nm)	83.3
Crystal Density (g•cm^3), calculated	4.384
Crystal Linear Absorption Coefficient (cm^{-1})	591.123
Wt%-Rietveld	100
R_{exp}/ R_{exp}' $^{(a)}$	1.39/2.70
R_{wp}/ R_{wp}'	2.25/4.36
R_p/ R_p'	1.64/3.21
R_{Bragg}	0.529
GoF	1.62
DW_d	1.06

(a)-Primed parameters are background corrected.

Table S12. Atomic coordinates and isotropic thermal parameters for an LNMO electrode after 10 cycles 3.4 - 5 V and 50 cycles 4.4 - 5 V charge/discharge.

Atom	Wyckoff Site	x	y	z	SOF	B_{eq}
Li	8a	0	0	0	1	-9.146
Mn	16d	0.6250	0.6250	0.6250	0.75	16.04
Ni	16d	0.6250	0.6250	0.6250	0.25	19.59
O	32e	0. 37019	0. 37019	0. 37019	1	19.93

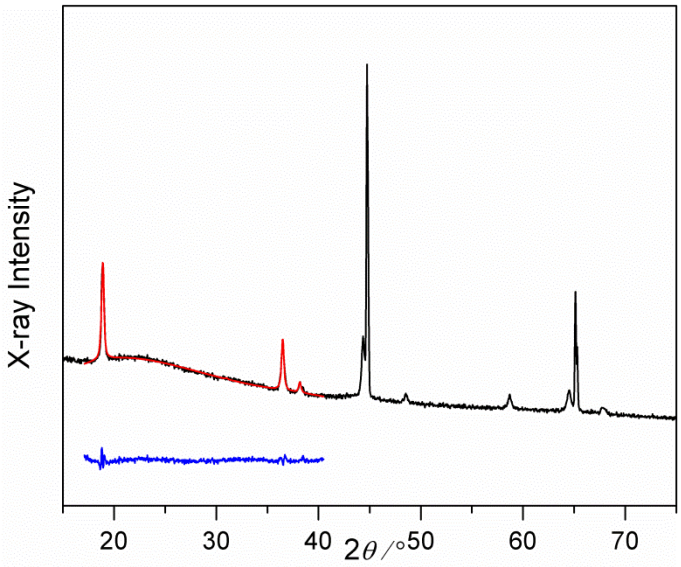

Fig. S19. XRD data (black), calculated Rietveld refinement (red), and difference pattern (blue) for an LNMO electrode after 1000 cycles with different electrochemical windows.

Table S13. Refinement parameters for an LNMO electrode after 1000 cycles with different electrochemical windows.

Space Group	$Fd\bar{3}m$
Scale	1.281×10^{-4}
Lattice parameter, a (Å)	8.209
Unit Cell Mass (g•mol^{-1})	2347.295
Unit Cell Volume (Å^3)	553.229
Crystallite Size, Lorentzian (nm)	92.5
Crystal Density (g•cm^3), calculated	4.396
Crystal Linear Absorption Coefficient (cm^{-1})	680.508
Wt%-Rietveld	100
R_{exp}/ R_{exp}' $^{(a)}$	1.41/2.71
R_{wp}/ R_{wp}'	1.98/3.80
R_p/ R_p'	1.51/2.95
R_{Bragg}	1.158
GoF	1.40
DW_d	1.06

(a)-Primed parameters are background corrected.

Table S14. Atomic coordinates and isotropic thermal parameters for an LNMO electrode after 1000 cycles with different electrochemical windows.

Atom	Wyckoff Site	x	y	z	SOF	B_{eq}
Li	8a	0	0	0	1	19.92
Mn	16d	0.6250	0.6250	0.6250	0.75	19.68
Ni	16d	0.6250	0.6250	0.6250	0.25	12.18
O	32e	0.34704	0.34704	0.34704	1	-0.8975