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Supporting Information

Non-monotonic first cycle irreversible capacity governed by delithiation depth in Li-rich layered cathodes

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Fig. S1-14, Tables S1-2.

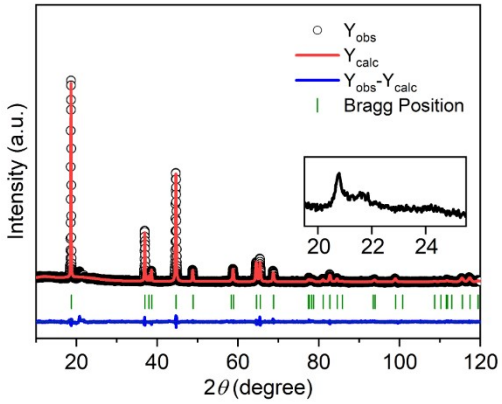

Fig. S1 XRD pattern and Rietveld refinement results of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$.

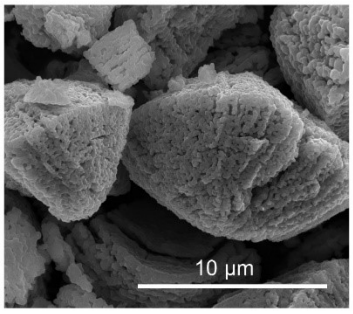

Fig. S2 SEM image of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$.

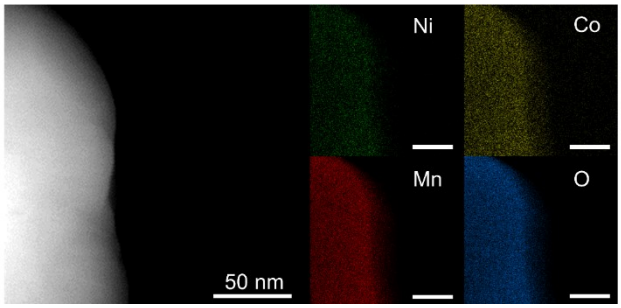

Fig. S3 EDS mapping results of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$.

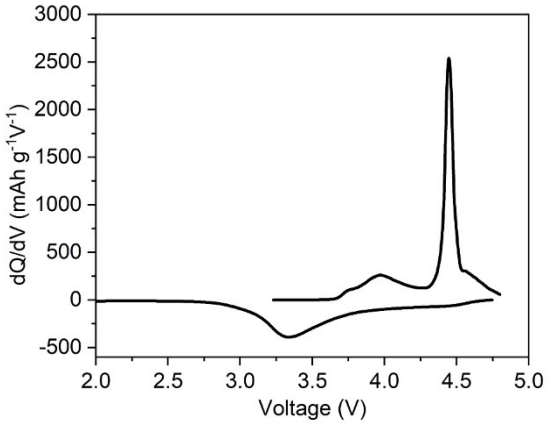

Fig. S4 dQ/dV curves of Fig. 1a.

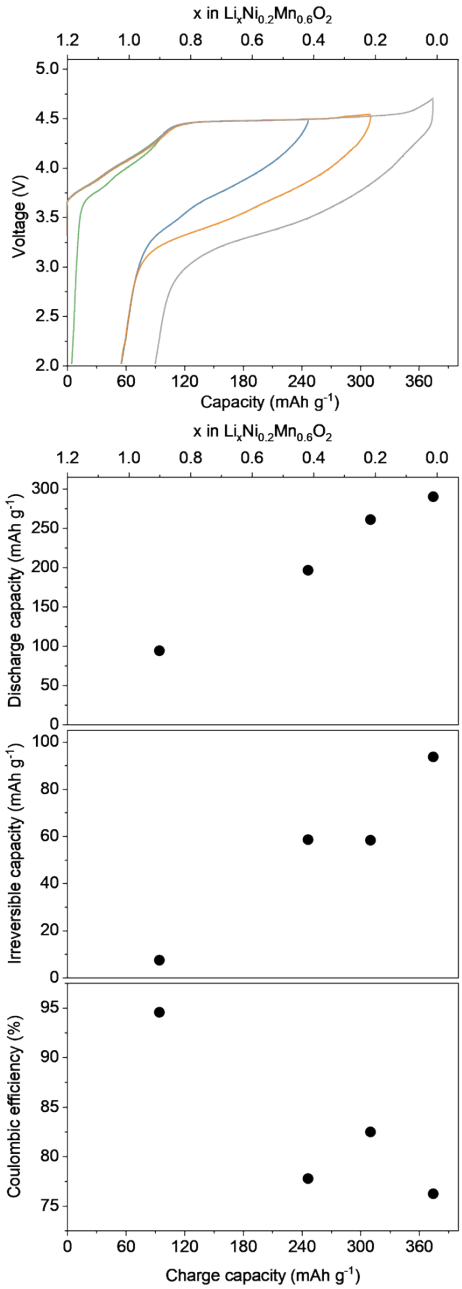

Fig. S5 (a) First-cycle electrochemical profiles with controlled charge capacity, (b) discharge capacity, irreversible capacity, and Coulombic efficiency in $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (i.e., $0.5Li_2MnO_3$-$0.5LiNi_{1/2}Mn_{1/2}O_2$).

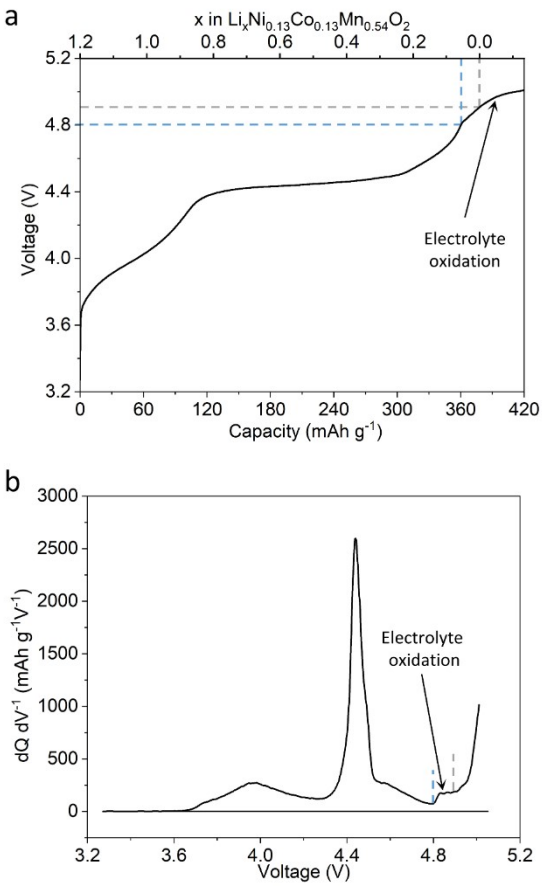

Fig. S6 (a) Charging profile for the first cycle to 420 mAh g^{-1}. (b) dQ/dV curves of (a).

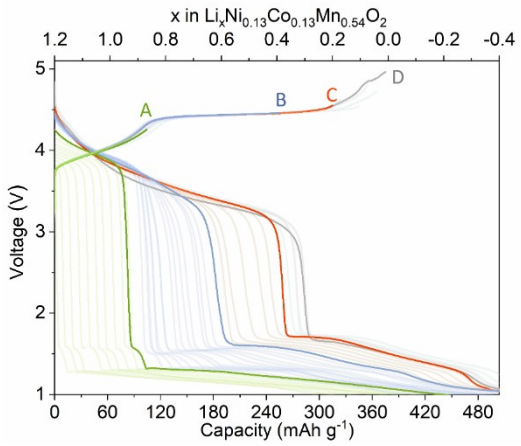

Fig. S7 First-cycle electrochemical profiles with controlled charge capacity from 5 to 395 mAg^{-1}.

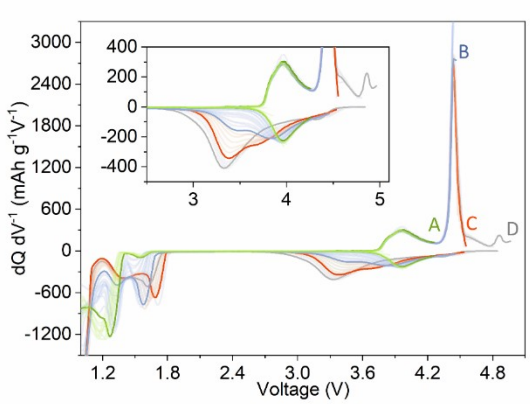

Fig. S8 dQ/dV curves of Fig. S5.

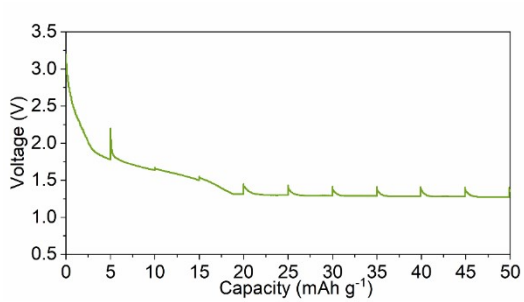

Fig. S9 GITT discharge profile of pristine material.

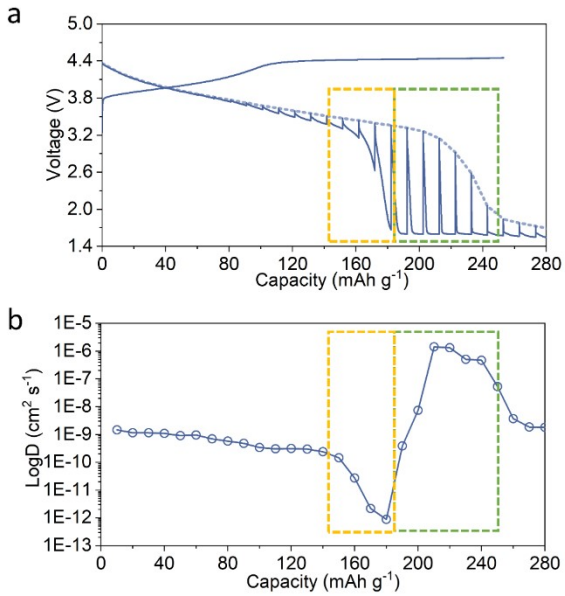

Fig. S10 (a) Capacity scaled GITT discharge profile after initial charge to 253 mAh g^{-1}. (b) Calculated lithium-ion diffusion coefficients of (a).

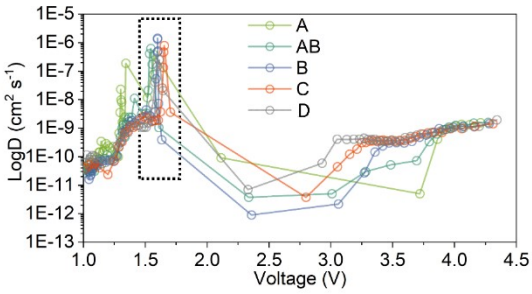

Fig. S11 Calculated lithium-ion diffusion coefficients of Fig. 2.

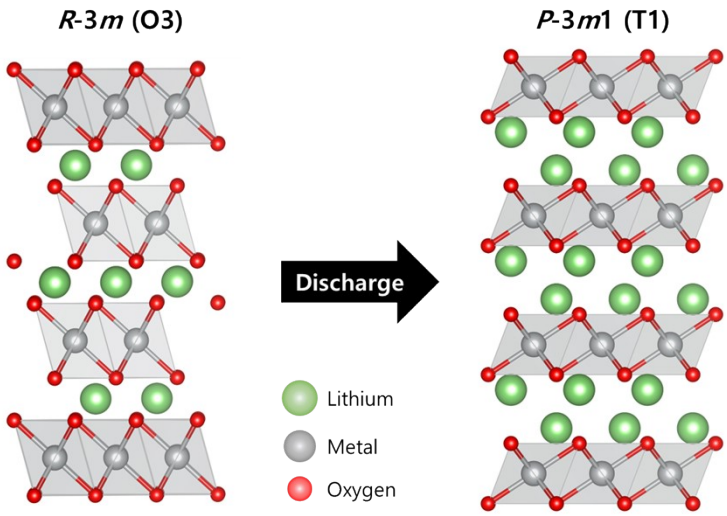

Fig. S12 Crystal structure of layered $LiMO_2$ (space group: *R-3m*) and overlithiated Li_2MO_2 (space group: *P-3m1*).

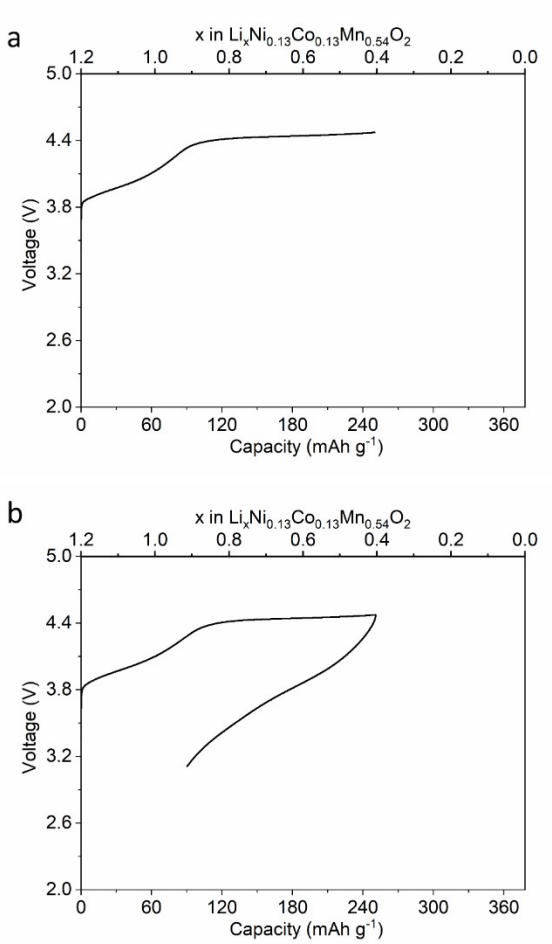

Fig. S13 The electrochemical profiles of pretreatment for operando synchrotron XRD. (a) to Fig. 3b and (b) to Fig. 3e.

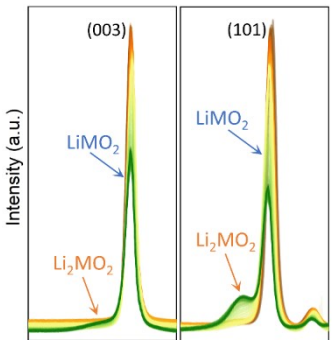

Fig. S14 The operando synchrotron XRD patterns of Fig. 3e in 1D.

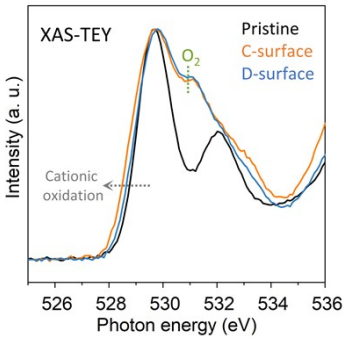

Fig. S15 O K-edge spectra measured in the TEY mode.

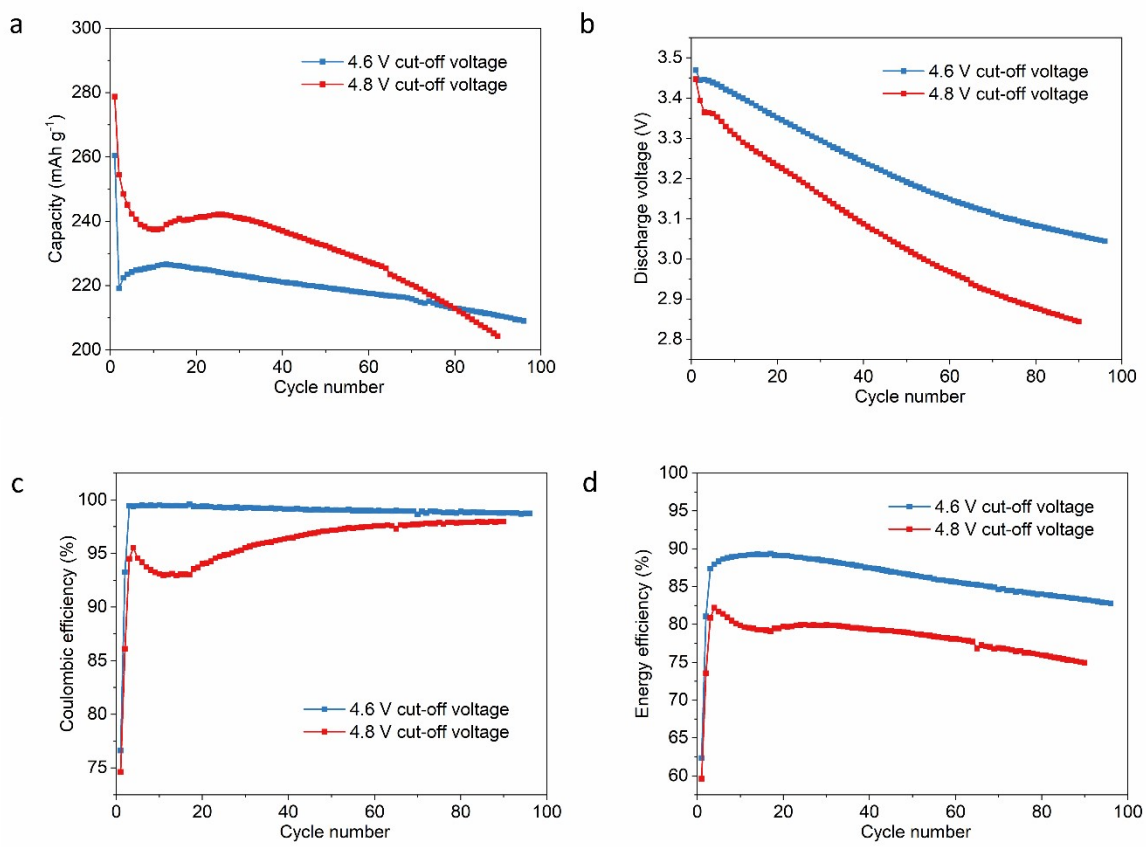

Fig. S16 (a) The capacity retention, (b) average discharge voltage, (c) coulombic efficiency, and (d) energy efficiency of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ cycled under 4.6 V and 4.8 V cut-off voltages.

Table S1 Rietveld refinement results of pristine $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$.

Crystal system		Rhombohedral				
Space group		R$\bar{3}$m (166)				
a = 2.8466(3) Å		c = 14.218(2) Å		Volume = 99.78(3)		
R_wp = 1.95%		GOF = 1.21				
Atom	Site	x	y	z	Occ	B value
Li(1)	3b	0	0	0.5	1	0.25(3)
Li(2)/Ni(1)/ Co(1)/Mn(1)	3a	0	0	0	0.2/0.13/0.13/0.54	0.25(3)
O1	6c	0	0	0.2586(1)	1	0.73(6)

theoretical chemical formula	measured atomic ratio			
	Li	Ni	Co	Mn
$Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$	1.201(1)	0.134(1)	0.133(1)	0.534(1)

Table S2 Chemical composition analysis results from Inductively coupled plasma atomic emission spectroscopy (ICP-AES).