Supporting Information

Suppressing the Phase Transition of the Layered Ni-Rich Oxide Cathode during High-Voltage Cycling by Introducing Low-Content Li₂MnO₃

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Figure S1. (a) Magnified XRD patterns of the prepared cathode materials and (b) SAED pattern of LNCMO-3070 material collected along [1-10] direction.

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Sample		<i>a</i> (Å)	C (Å)	$V(Å^3)$		
NCM-811	pristine	2.87224	14.19615	101.31952		
	cycled	2.88377	14.21073	102.34529		
LNCMO-1090	pristine	2.87088	14.20401	101.28868		
	cycled	2.88831	14.26921	103.09007		
LNCMO-3070	pristine	2.86036	14.20772	100.65332		
	cycled	2.89140	14.31484	103.64150		

Table S1. Crystal structural parameters of the pristine NCM-811, LNCMO-1090 and LNCMO-3070 and the corresponding cycled cathodes after cycling.



Figure S2. The second cyclic voltammogram curves and phase transitions of the as-prepared cathodes at a scan rate of 0.1 mV s⁻¹ between 2.0 and 4.8 V vs Li/Li⁺.

Cathodes	Charge capacity	Discharge capacity	Coulombic efficiency
	(mAh g ⁻¹)	(mAh g ⁻¹)	
NCM-811	272	232	85.3%
LNCMO-1090	277	222	80.1%
LNCMO-3070	304	214	70.4%

Table S2. Electrochemical performance of the as-prepared cathodes at a current density of 20 mA g^{-1} between 2.0 and 4.8 V vs Li/Li⁺.



Figure S3. Capacity retention of the as-prepared cathodes at a current density of 100 mA g^{-1} between 2.0 and 4.8 V vs Li/Li⁺.

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Samples		$R_{s}(\Omega)$	$\mathrm{R_{f}}\left(\Omega ight)$	$R_{ct}(\Omega)$
NCM-811	after 2 cycles	6	35	386
	after 200 cycles	11	917	6942
LNCMO-1090	after 2 cycles	5	33	116
	after 200 cycles	5	190	2147
LNCMO-3070	after 2 cycles	6	39	89
	after 200 cycles	8	186	1878

Table S3. Fitting values of the electrochemical impedance (EIS) curves of the as-prepared cathodes charged to 4.3 V after different cycle number obtained from equivalent circuit in Figure

♦ Al **⊽** PE film 003 44 46 42 104 Intensity (a.u.) 101 018 006/012 ν V 015 107 a 113 b c d e f ٠. **Spinel** (Fd-3m) 40 50 60 20 30 10 70 80 2 Theta (degree)

Figure S4. XRD patterns for the pristine NCM-811(a, black line), LNCMO-1090 (b, red line) and LNCMO-3070 (c, blue line) samples before cycling and (d, e, f) the corresponding cycled samples after cycling. The green vertical lines at the bottom of this figure are the Bragg peak positions for Li_2MnO_4 spinel phase with Fd-3m symmetry (JCPDS No. 35-0782). The diffraction signals of the Al collector (\blacklozenge) and polyethylene (PE) protective film (\bigtriangledown) are labeled with special symbols.