Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary information

Achieving structural stability and enhanced electrochemical performance through Nb-doping into Li- and Mn-rich layered cathode for lithium-ion batteries

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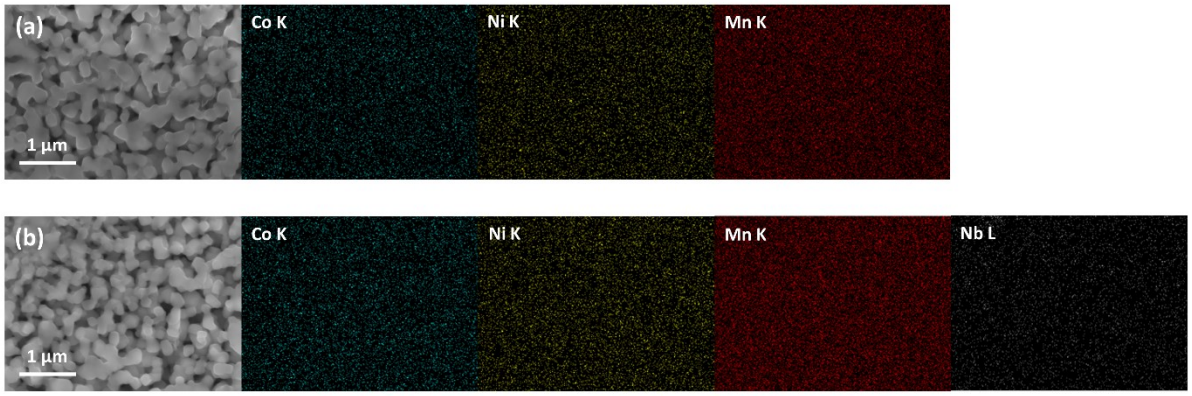

Fig. S1. Magnified cross-section SEM image of pristine (a) LNCM and (b) Nb-LNCM materials with EDS elemental mapping results of Co, Ni, Mn, and Nb.

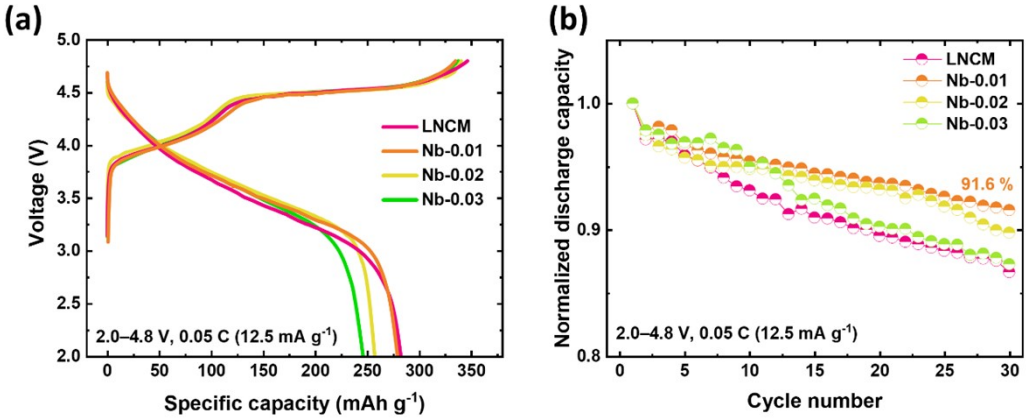

Fig. S2. (a) The voltage curves of LNCM and Nb-LNCM (0.01, 0.02, and 0.03 moles of Nb in LNCM) at a current rate of 0.05 C and in a voltage range of 2.0–4.8 V. (b) Normalized capacity retention of LNCM and Nb-LNCM (0.01, 0.02, and 0.03 moles of Nb in LNCM) at a current rate of 0.05 C and in a voltage range of 2.0–4.8 V.

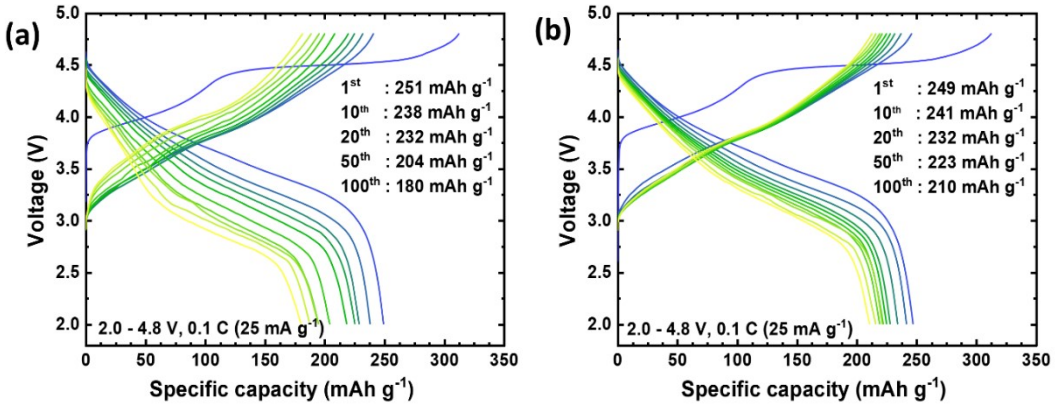

Fig. S3. Electrochemical voltage profiles of (a) LNCM and (b) Nb-LNCM at a current rate of 0.1 C in a voltage range of 2.0–4.8 V.

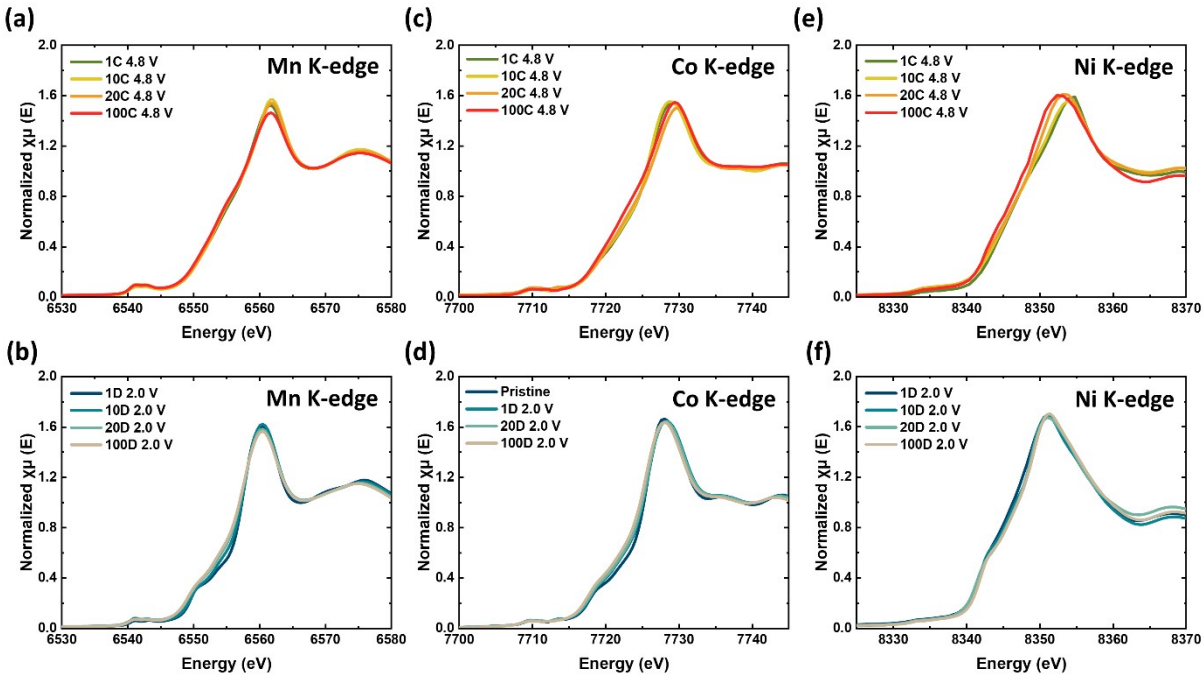

Fig. S4. Normalized Mn, Co, and Ni K-edge XANES spectra of LNCM cathode material (a, c, e) during charge and (b, d, f) discharge in the 1st, 10th, 20th, and 100th cycles.

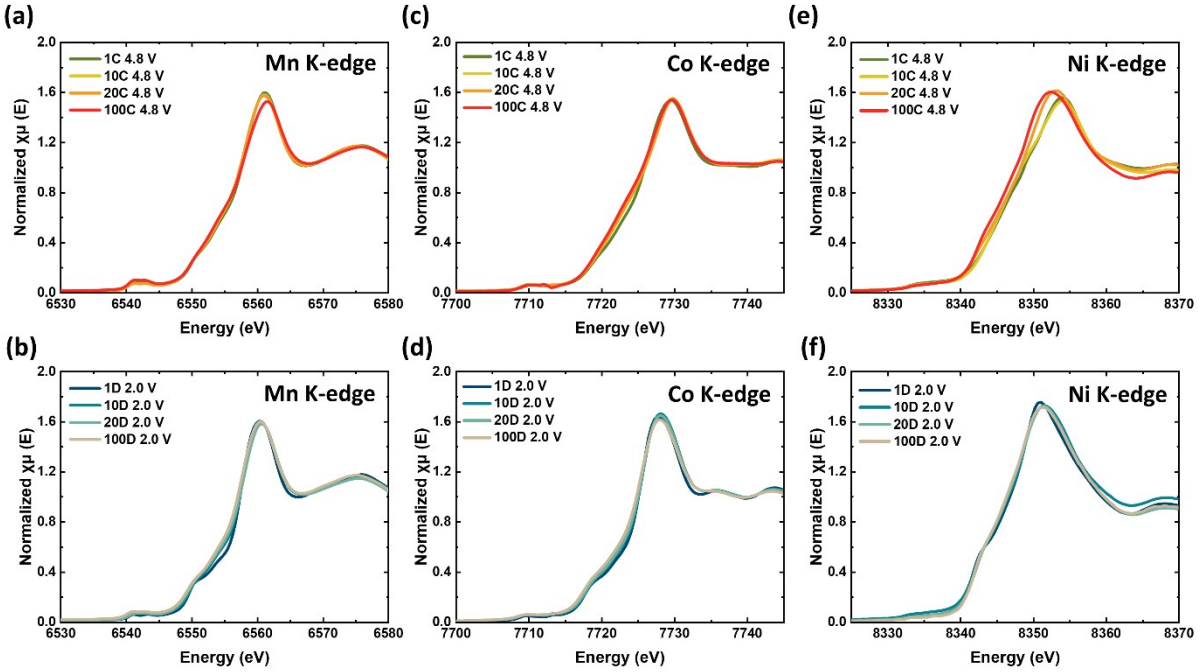

Fig. S5. Normalized Mn, Co, and Ni K-edge XANES spectra of Nb-LNCM cathode material (a, c, e) during charge and (b, d, f) discharge in the 1st, 10th, 20th, and 100th cycles.

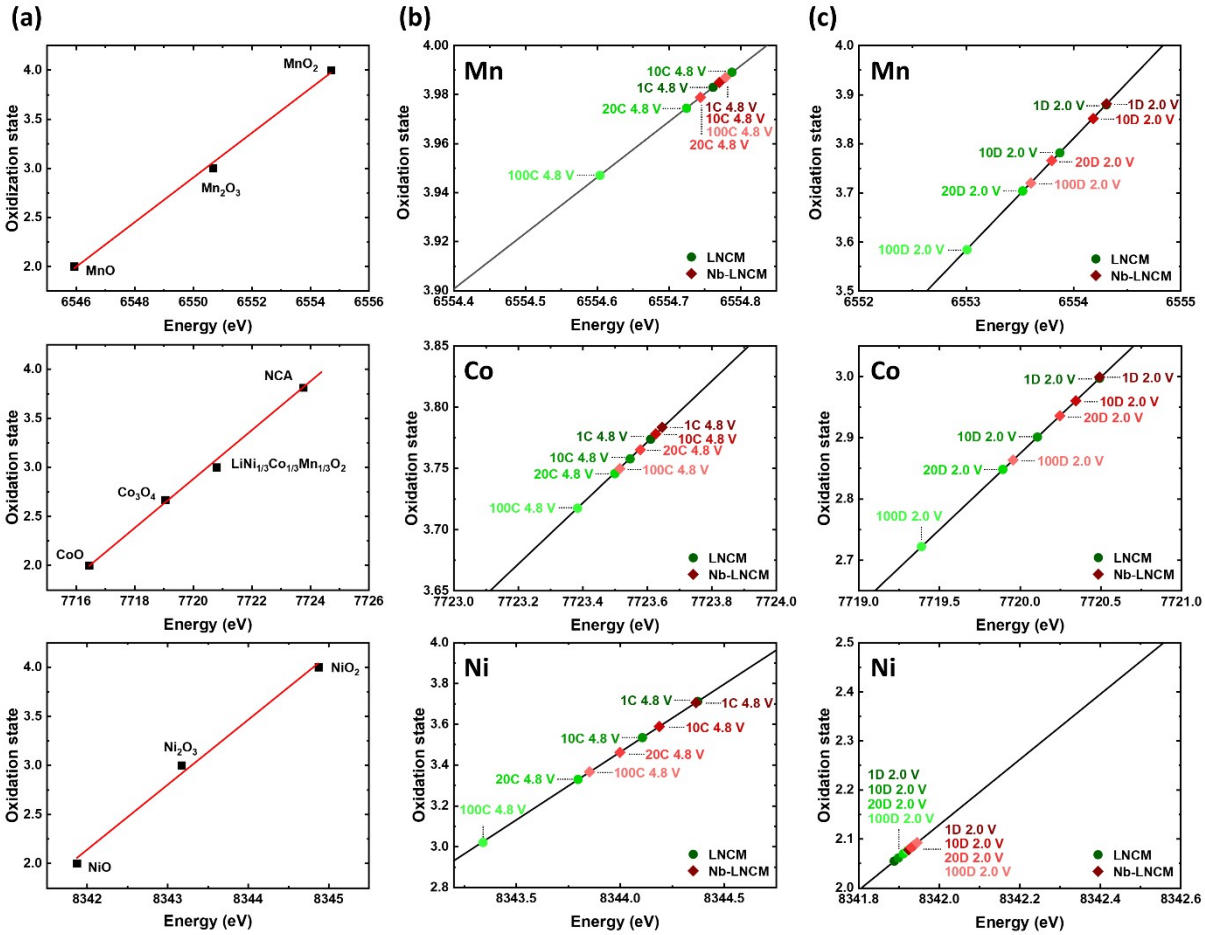

Fig. S6. (a) The relationship between the oxidation states and Mn, Co, and Ni K-edge XANES energy calculated by an integral method. Variations in the oxidation states of Mn, Co, and Ni of LNCM and Nb-LNCM between the (b) charge and (c) discharge process in the 1st, 10th, 20th, and 100th cycles, which are calculated by the integral method of XANES spectra.

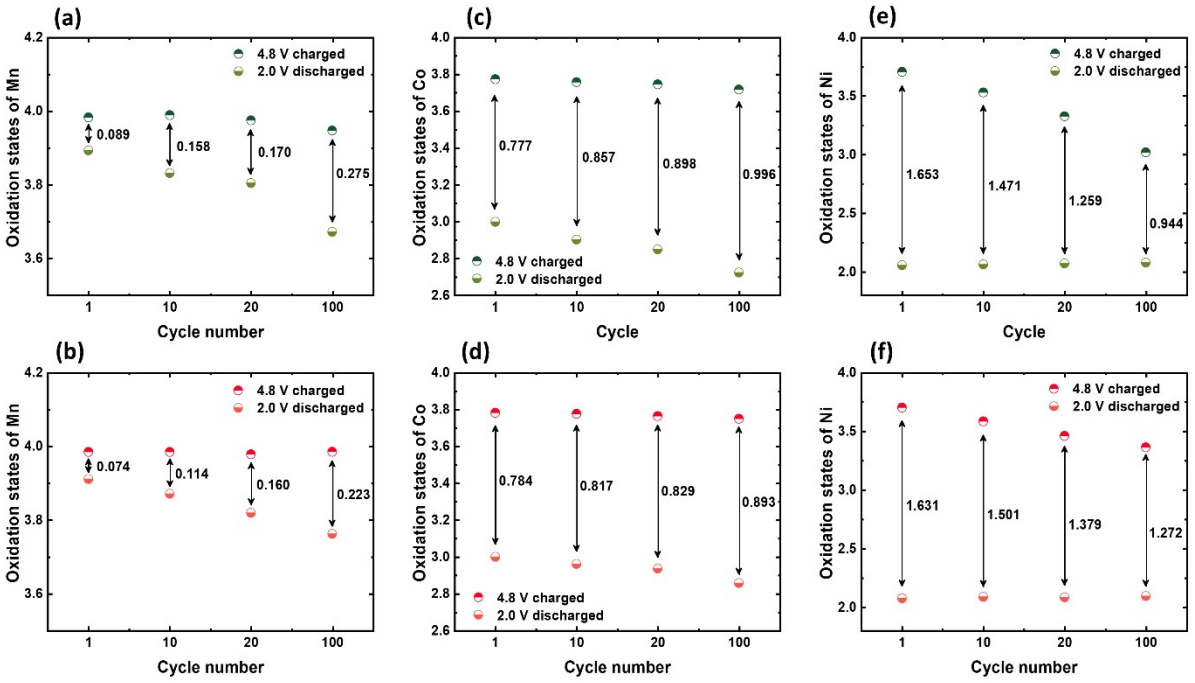

Fig. S7. Variations in the oxidation states of (a) Mn, (c) Co, and (e) Ni ions in LNCM, and (b) Mn, (d) Co, (f) Ni ions in Nb-LNCM between the charge-discharge process in the 1st, 10th, 20th, and 100th cycles, which are calculated by the integral method of XANES spectra of each transition metal.

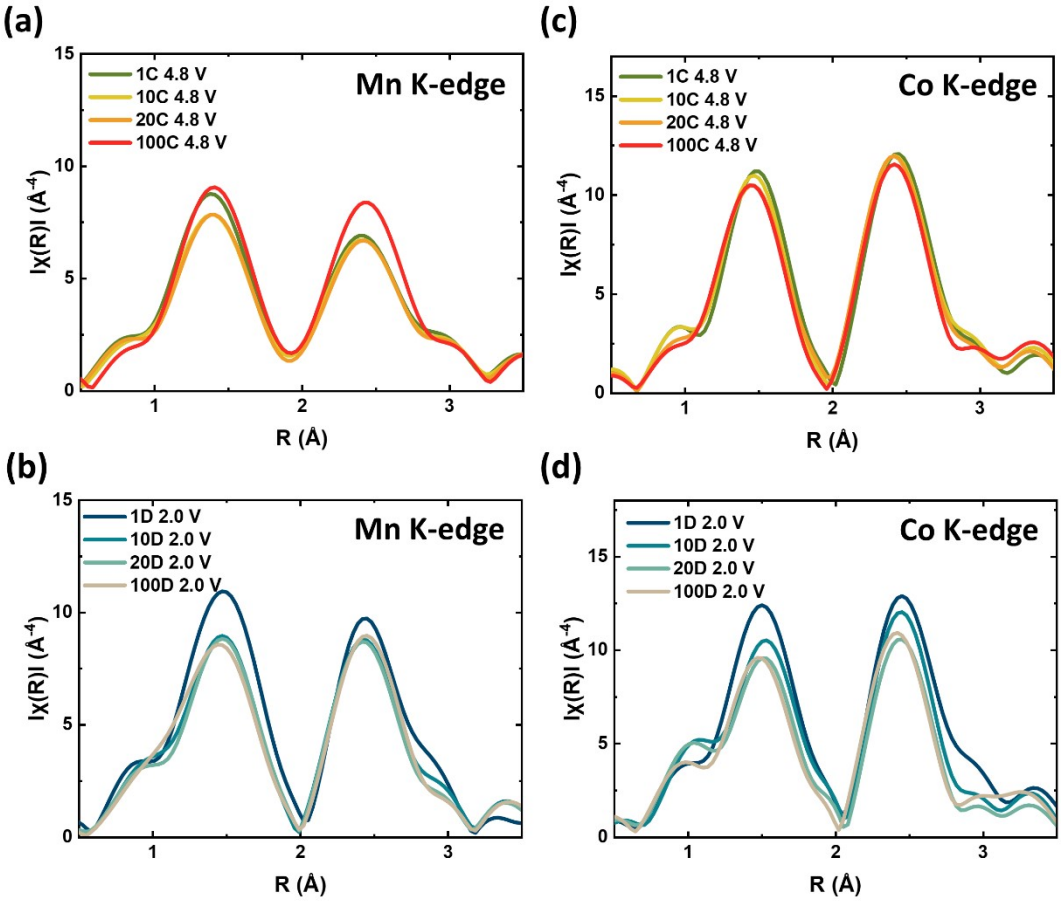

Fig. S8. k^3-weighted Mn and Co K-edge EXAFS spectra of LNCM cathode material (a, c) during charge and (b, d) discharge in the 1st, 10th, 20th, and 100th cycles.

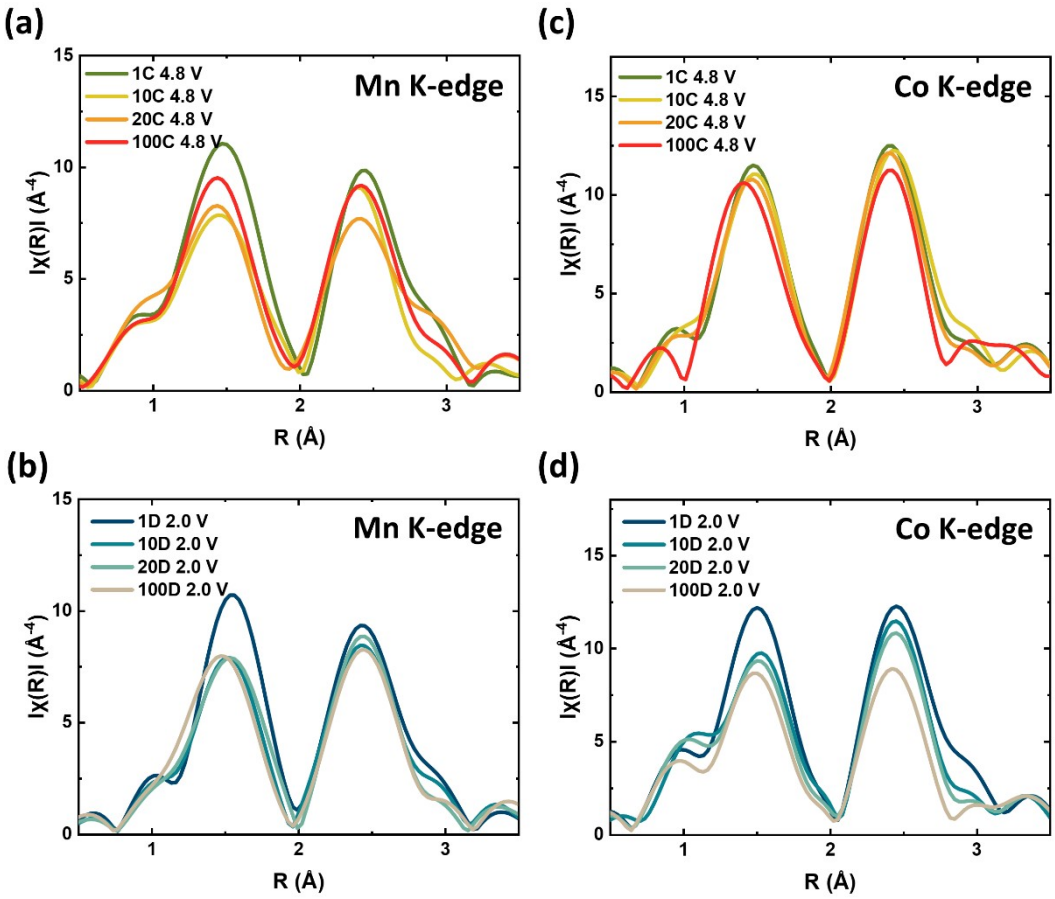

Fig. S9. k^3-weighted Mn and Co K-edge EXAFS spectra of Nb-LNCM cathode material (a, c) during charge and (b, d) discharge in the 1st, 10th, 20th, and 100th cycles.

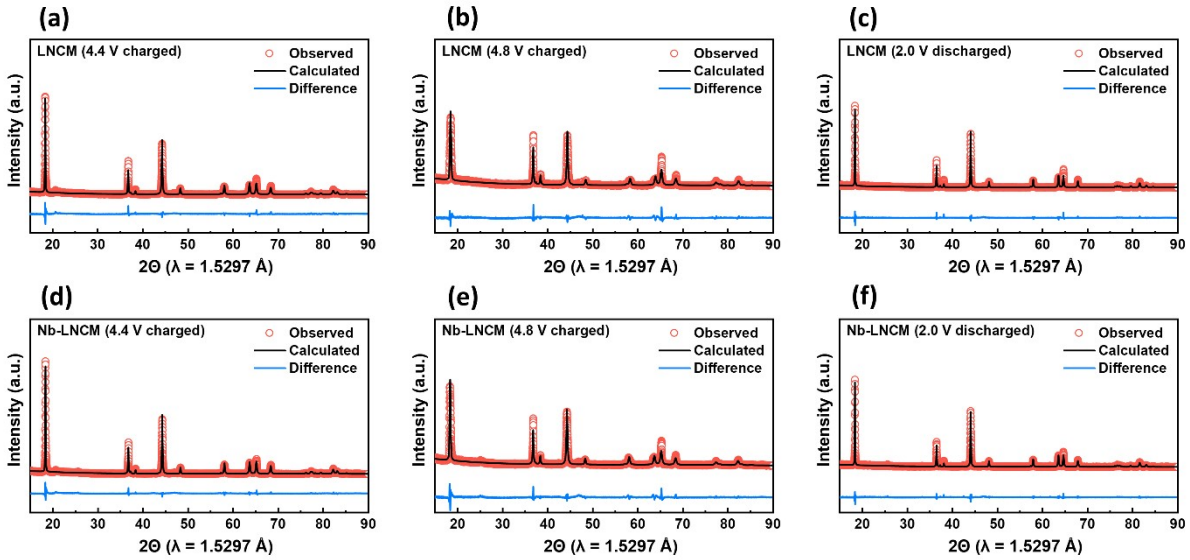

Fig. S10. HRPD patterns: observed, calculated, and difference of (a) 4.4 V charged, (b) 4.8 V charged, and (c) 2.0 V discharged states of LNCM and those of (d) 4.4 V charged, (e) 4.8 V charged, and (f) 2.0 V discharged states of Nb-LNCM.

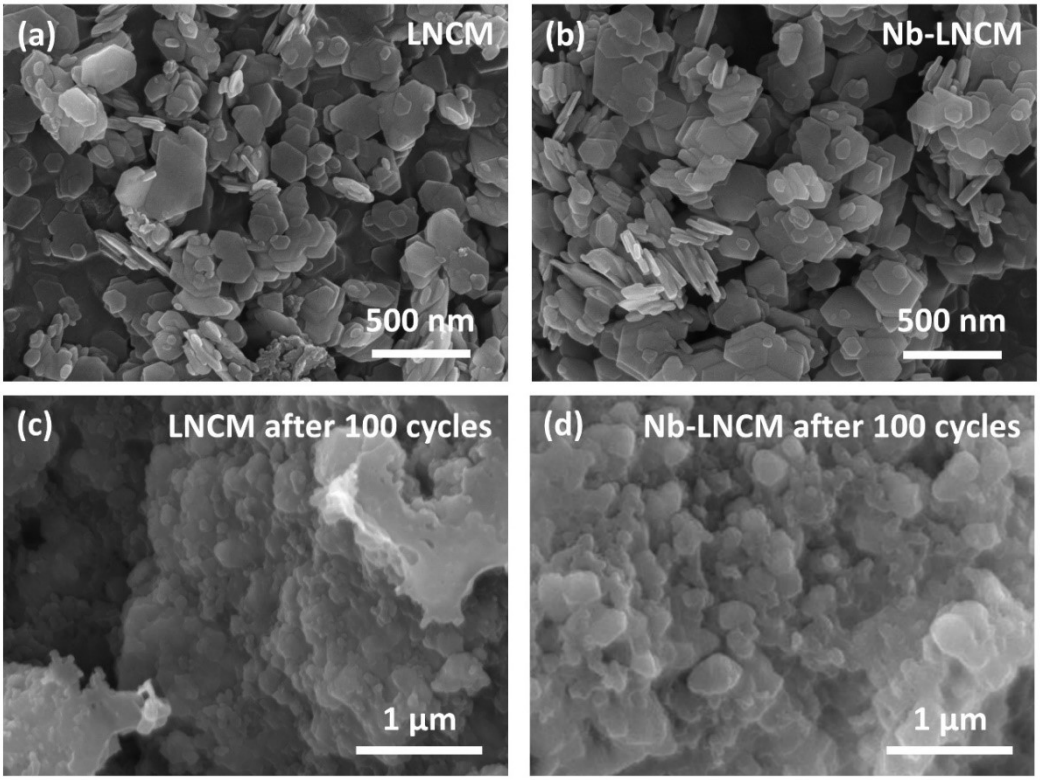

Fig. S11. SEM images of pristine (a) LNCM and (b) Nb-LNCM powders and (c) LNCM and (d) Nb-LNCM electrodes after 100 cycles.

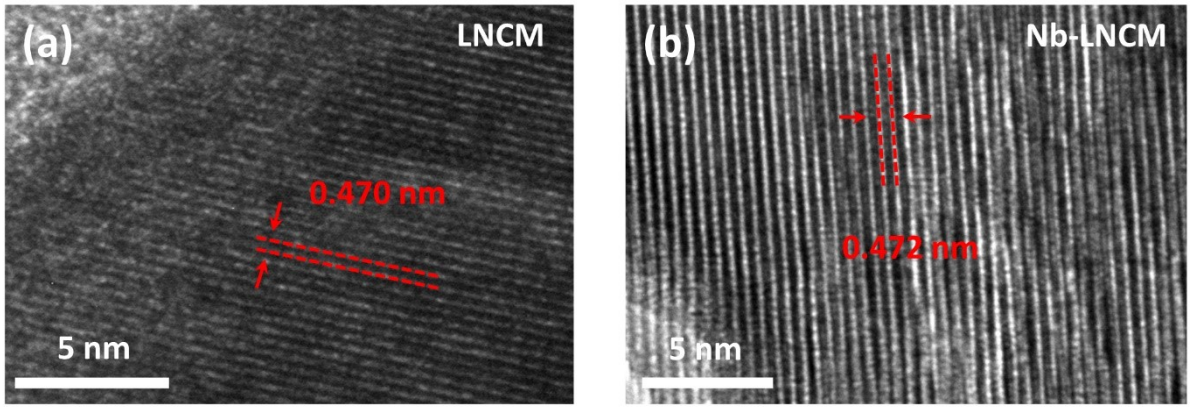

Fig. S12. HRTEM images of (a) LNCM and (b) Nb-LNCM in the pristine state.

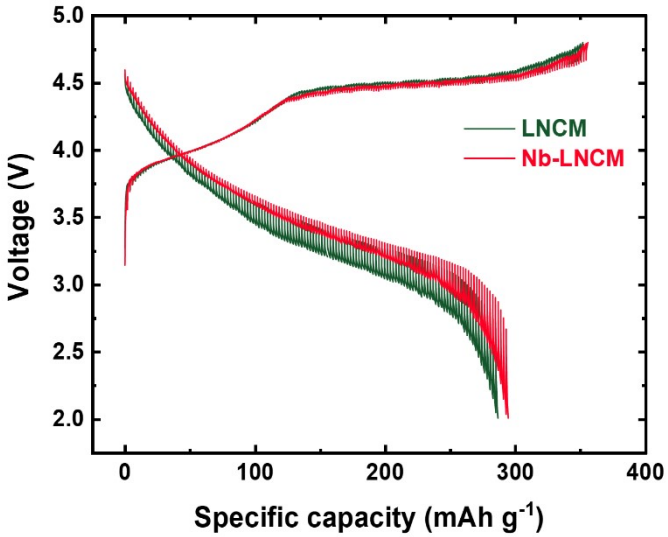

Fig. S13. GITT curves of LNCM and Nb-LNCM in the voltage range of 2.0–4.8 V at a current rate of 0.1 C during the first cycle.

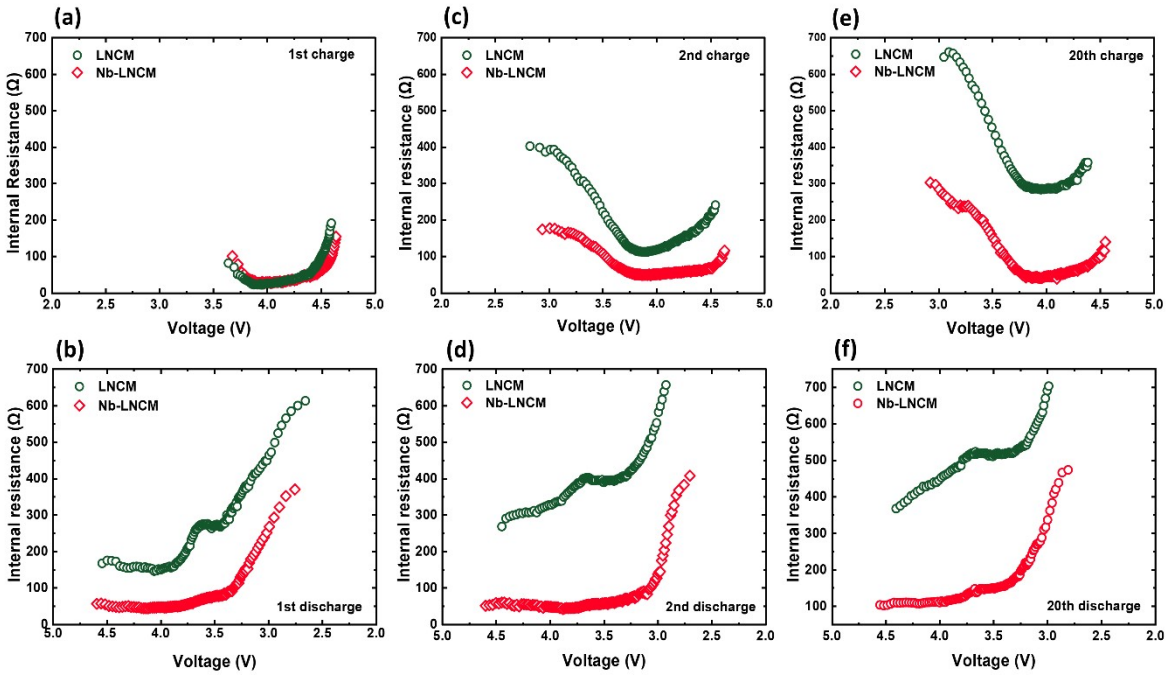

Fig. S14. Internal resistance calculated by the GITT curve of LNCM and Nb-LNCM during the 1st (a) charge and (b) discharge, 2nd (c) charge and (d) discharge, and 20th (e) charge and (f) discharge.

Table S1. The refined lattice parameters and reliability factors of Nb-LNCM when Nb^{5+} ion occupied the 3b sites (Li layer).

Concentration of Nb	a_{hex} **(Å)**	c_{hex} **(Å)**	**V (Å^3)**	**Occupancy (Nb^{5+} in 3b)**	**S (R_{wp}/R_{exp})**	**R_p**	**R_{wp}**
0.01	2.8509(2)	14.2337(2)	100.187	0	1.61	5.00	6.68

Table S2. The refined lattice parameters and reliability factors of Nb-LNCM when Nb^{5+} ion occupied the 3a sites (TM layer).

Concentration of Nb	a_{hex} **(Å)**	c_{hex} **(Å)**	**V (Å^3)**	**Occupancy (Nb^{5+} in 3a)**	**S (R_{wp}/R_{exp})**	**R_p**	**R_{wp}**
0.01	2.8509(3)	14.2337(4)	100.187	0	1.59	4.94	6.61

Table S3. Weight and atomic percentage of Mn, Co, Ni, and Nb elements in Nb-LNCM from the EDS result corresponding to **Fig. S1**.

Element	Weight %	Atomic %
Mn	63.50	65.52
Co	17.23	16.57
Ni	17.29	16.70
Nb	1.98	1.21
Totals	100.00	100.00

Table S4. Lattice parameters, atomic coordinates, and occupancies for the Rietveld refinement results of the pristine LNCM material.

Space group: *R-3m*, R_p: 4.46, R_{wp}: 6.23, S(R_{wp}/R_{exp}): 2.07						
Atom	**Wyckoff symbol**	**x**	**y**	**z**	**Occupancy**	**Lattice parameter**
Li1	3b	0	0	0.5	0.9999	
Li2	3a	0	0	0	0.2	
Ni1	3a	0	0	0	0.1329	a_{hex}= 2.8495 Å
Ni2	3b	0	0	0.5	0.0001	c_{hex}= 14.2304 Å
Mn1	3a	0	0	0	0.533	V = 100.070 Å^3
Co1	3a	0	0	0	0.133	
O1	6c	0	0	0.2618	1	

Table S5. Lattice parameters, atomic coordinates, and occupancies for the Rietveld refinement results of the pristine Nb-LNCM material.

Space group: *R-3m*, R_p: 4.94, R_{wp}: 6.61, S(R_{wp}/R_{exp}): 1.59						
Atom	**Wyckoff symbol**	**x**	**y**	**z**	**Occupancy**	**Lattice parameter**
Li1	3b	0	0	0.5	1	
Li2	3a	0	0	0	0.2	
Ni1	3a	0	0	0	0.13	
Ni2	3b	0	0	0.5	0	a_{hex}= 2.8509 Å
Mn1	3a	0	0	0	0.53	c_{hex}= 14.2339 Å
Co1	3a	0	0	0	0.13	V = 100.190 Å^3
Nb1	3a	0	0	0	0.01	
O1	6c	0	0	0.2613	1	

Table S6. Curve fitting results for the Mn K-edge EXAFS spectra of LNCM and Nb-LNCM during the 1st, 10th, 20th, and 100th discharge.

		Bond	N	Sigma^2 (Å^2)	R (Å)	S_0^2	Bond strength (10^2 N m^{-1})
LNCM	**Pristine**	Mn–O	6	0.00324	1.9228	0.73	1.2693
	1D 2.0 V	Mn–O	6	0.00488	1.9159	0.73	0.8427
	10D 2.0 V	Mn–O	6	0.00553	1.9129	0.73	0.7437
	20D 2.0 V	Mn–O	6	0.00569	1.9127	0.73	0.7227
	100D 2.0 V	Mn–O	6	0.00624	1.8951	0.73	0.6590
Nb-LNCM	**Pristine**	Mn–O	6	0.00336	1.9146	0.73	1.2239
	1D 2.0 V	Mn–O	6	0.00434	1.9174	0.73	0.9476
	10D 2.0 V	Mn–O	6	0.00526	1.9150	0.73	0.7818
	20D 2.0 V	Mn–O	6	0.00534	1.9129	0.73	0.7701
	100D 2.0 V	Mn–O	6	0.00580	1.9020	0.73	0.7090

Table S7. Curve fitting results for the Co K-edge EXAFS spectra of LNCM and Nb-LNCM during the 1st, 10th, 20th, and 100th discharge.

		Bond	N	Sigma^2 (Å^2)	R (Å)	S_0^2	Bond strength (10^2 N m^{-1})
LNCM	**Pristine**	Co–O	6	0.00322	1.9308	0.81	1.2771
	1D 2.0 V	Co–O	6	0.00516	1.9377	0.81	0.7970
	10D 2.0 V	Co–O	6	0.00563	1.9389	0.81	0.7304
	20D 2.0 V	Co–O	6	0.00571	1.9369	0.81	0.7202
	100D 2.0 V	Co–O	6	0.00688	1.9344	0.81	0.5977
Nb-LNCM	**Pristine**	Co–O	6	0.00320	1.9341	0.81	1.2851
	1D 2.0 V	Co–O	6	0.00560	1.9313	0.81	0.7344
	10D 2.0 V	Co–O	6	0.00599	1.9443	0.81	0.6865
	20D 2.0 V	Co–O	6	0.00613	1.9393	0.81	0.6709
	100D 2.0 V	Co–O	6	0.00661	1.9354	0.81	0.6221

Table S8. Lattice parameters (a_{hex} and c_{hex}), unit cell volume (V), atomic coordinate of oxygen (Z_{oxy}), and slab and interslab thickness (T_{TMO6} and T_{LiO6}) for the Rietveld refinement results of the LNCM and Nb-LNCM materials during the 1st, 10th, 20th, and 100th cycles. Interslab thickness: $T_{LiO6} = (c_{hex}/3)-T_{TMO6}$; TM slab thickness: $2(1/3-Z_{oxy})*c_{hex}$

		a_{hex} (Å)	c_{hex} (Å)	V (Å^3)	Z_{oxy}	T_{TMO6} (Å)	T_{LiO6} (Å)	S (R_{wp}/R_{exp})
LNCM	**Pristine**	2.8495(7)	14.2304(1)	100.069	0.2618(6)	2.7092	2.0341	2.07
	1C 4.4 V	2.8367(7)	14.3427(1)	99.956	0.2631(3)	2.7670	2.0138	2.64
	1C 4.8 V	2.8352(4)	14.2792(3)	99.406	0.2621(3)	2.7262	2.0334	2.16
	1D 2.0 V	2.8560(7)	14.3231(4)	101.183	0.2617(1)	2.7226	2.0517	1.53
	10D 2.0 V	2.8572(6)	14.3530(2)	101.478	0.2619(4)	2.7349	2.0494	1.93
	20D 2.0 V	2.8581(3)	14.3698(6)	101.657	0.2618(3)	2.7349	2.0549	2.00
	100D 2.0 V	2.8614(1)	14.3771(2)	101.943	0.2620(4)	2.7412	2.0511	2.16
Nb-LNCM	**Pristine**	2.8509(2)	14.2339(4)	100.187	0.2613(1)	2.6942	2.0503	1.59
	1C 4.4 V	2.8371(3)	14.3421(2)	99.977	0.2638(7)	2.7882	1.9925	2.48
	1C 4.8 V	2.8373(5)	14.3610(6)	100.125	0.2624(4)	2.7508	2.0362	2.15
	1D 2.0 V	2.8554(9)	14.3301(7)	101.191	0.2618(7)	2.7285	2.0481	1.55
	10D 2.0 V	2.8565(9)	14.3547(8)	101.442	0.2620(9)	2.7395	2.0453	1.84
	20D 2.0 V	2.8571(3)	14.3645(3)	101.550	0.2621(3)	2.7425	2.0456	1.86
	100D 2.0 V	2.8593(3)	14.3728(6)	101.765	0.2623(4)	2.7501	2.0407	1.72