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Supplementary Information

Suppressing Detrimental Phase Transitions via Tungsten Doping of $LiNiO_2$ Cathode for Next-Generation Lithium-Ion Batteries

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Formula for chemical diffusion coefficient

The chemical diffusion coefficient can be calculated at each step, using the following formula:

$$D = \frac{4}{\pi}\left(\frac{iV_m}{z_A FS}\right)^2\left[\left(dE/d\delta\right)\Big/\left(dE/d\sqrt{t}\right)\right]^2,$$

where i is the applied current, V_m is the molar volume, z_A is the charge number of the electroactive species, F is the Faraday constant, and S is the contact area between the electrode and electrolyte. $dE/d\delta$ is the slope of the coulometric titration curve, which is determined by plotting the steady-state voltages E measured after each titration step δ; $dE/d\sqrt{t}$ is the slope of the linearized plot of the voltage E during a current pulse of duration t.

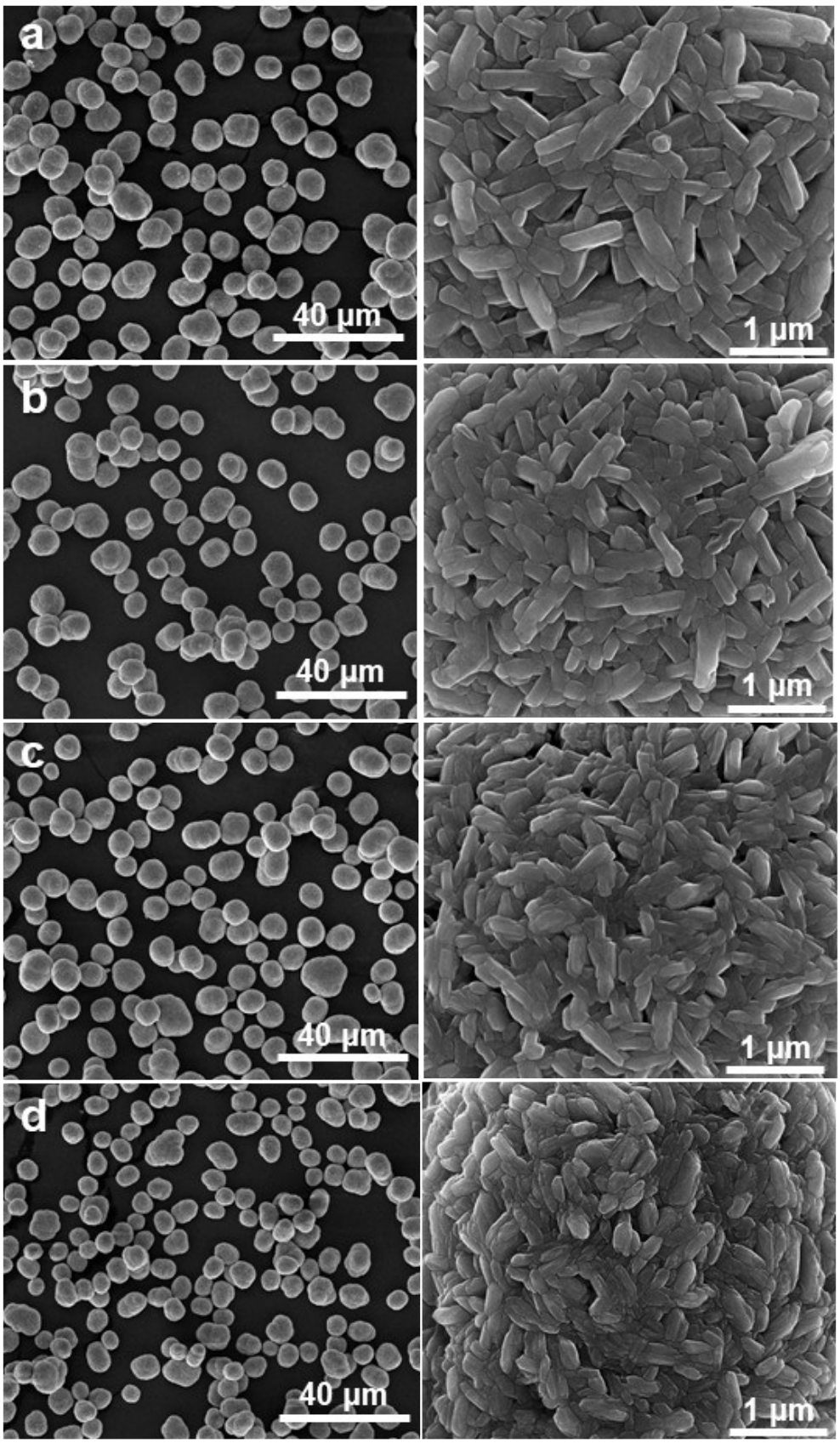

Fig. S1 SEM images of as-prepared powders: a) LNO, b) W-1 LNO, c) W-1.5 LNO, and d) W-2 LNO.

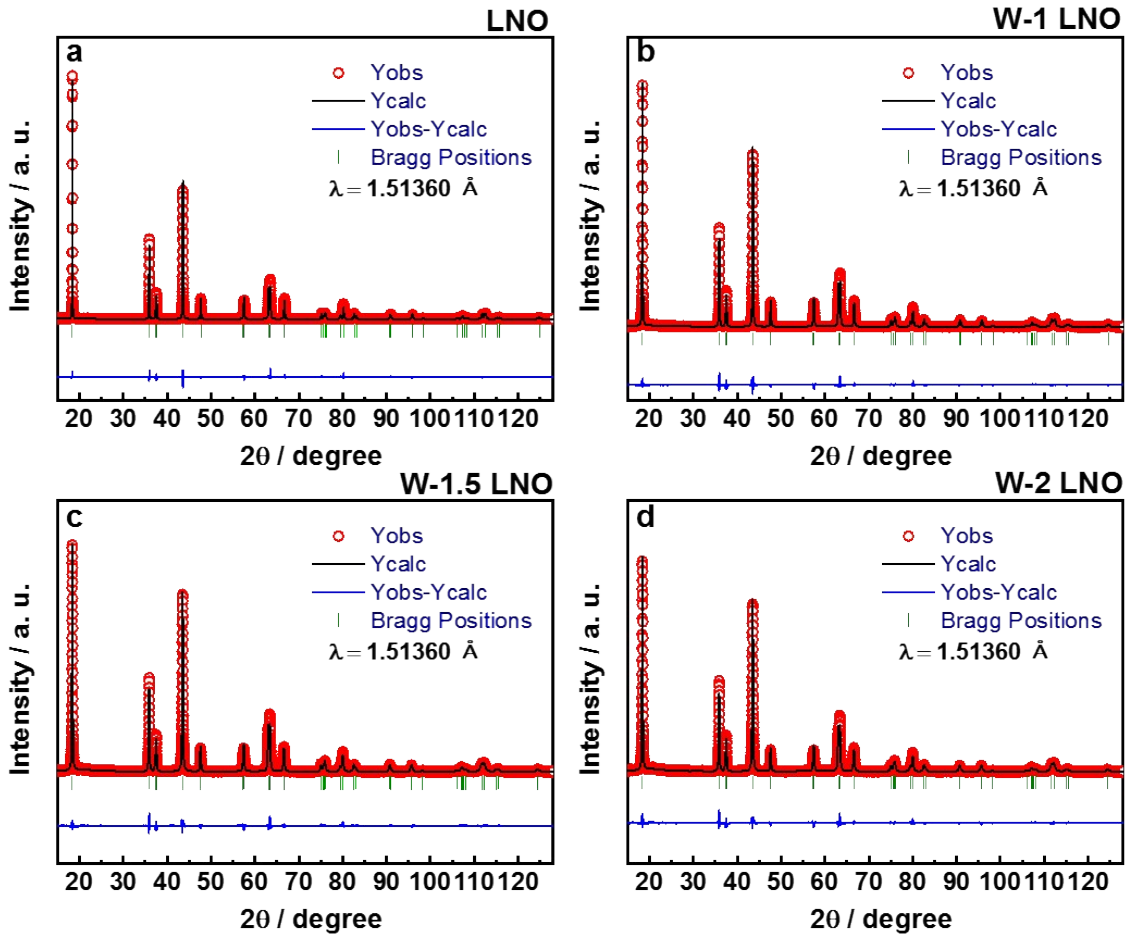

Fig. S2 Rietveld-refined synchrotron XRD patterns for a) LNO, b) W-1 LNO, c) W-1.5 LNO, and d) W-2 LNO.

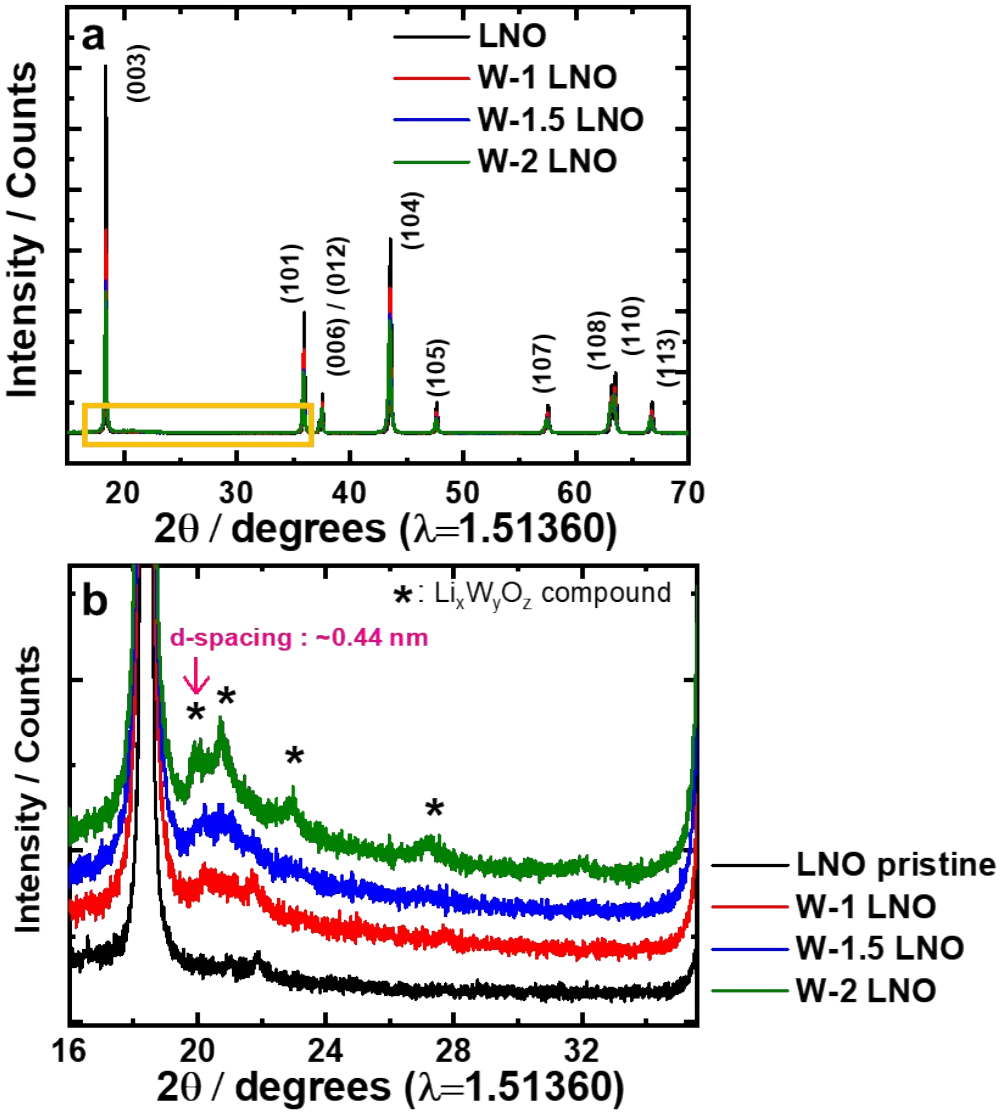

Fig. S3 Several XRD peaks of the second phase, which does not belong to the layered $R\bar{3}m$ structure.

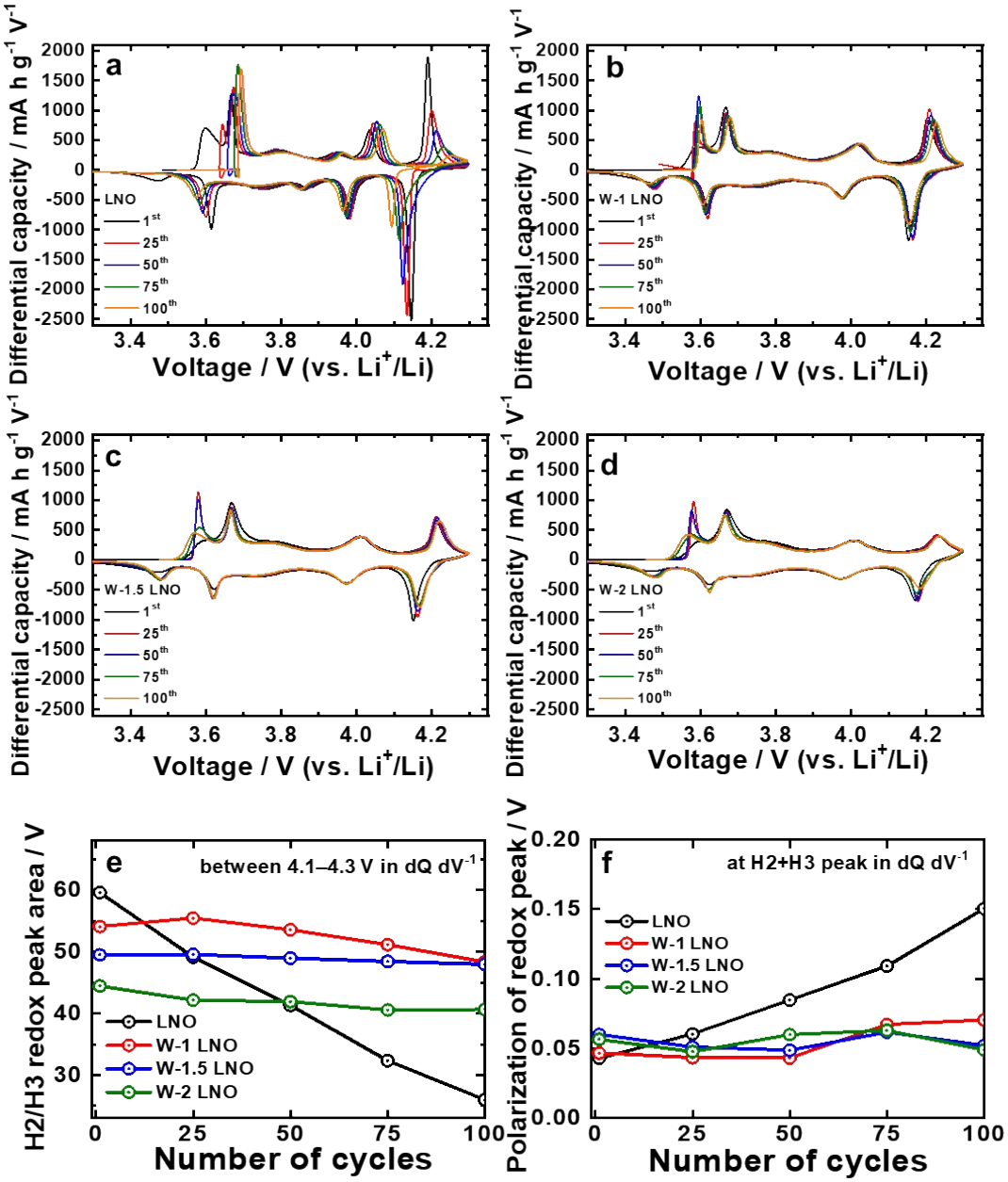

Fig. S4 Differential capacity profile (dQ dV^{-1}) as a function of the number of cycles for a) LNO, b) W-1 LNO, c) W-1.5 LNO and d) W-2 LNO. e) The integrated intensity and f) polarization for H2/H3 redox peaks with respect to the cycle number.

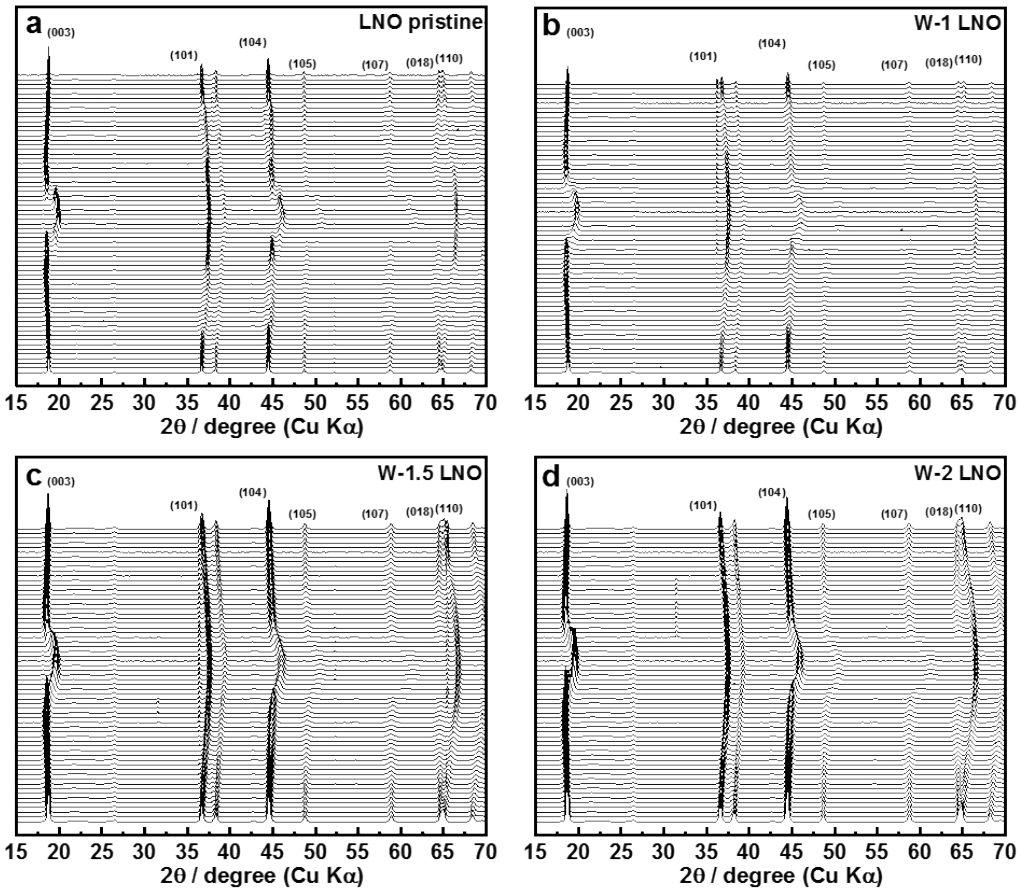

Fig. S5 Sequential diffraction patterns obtained from *in situ* XRD experiments during the 1st cycle at 0.2 C, between 2.7 and 4.5 V. For a) LNO, b) W-1 LNO, c) W-1.5 LNO, and d) W-2 LNO.

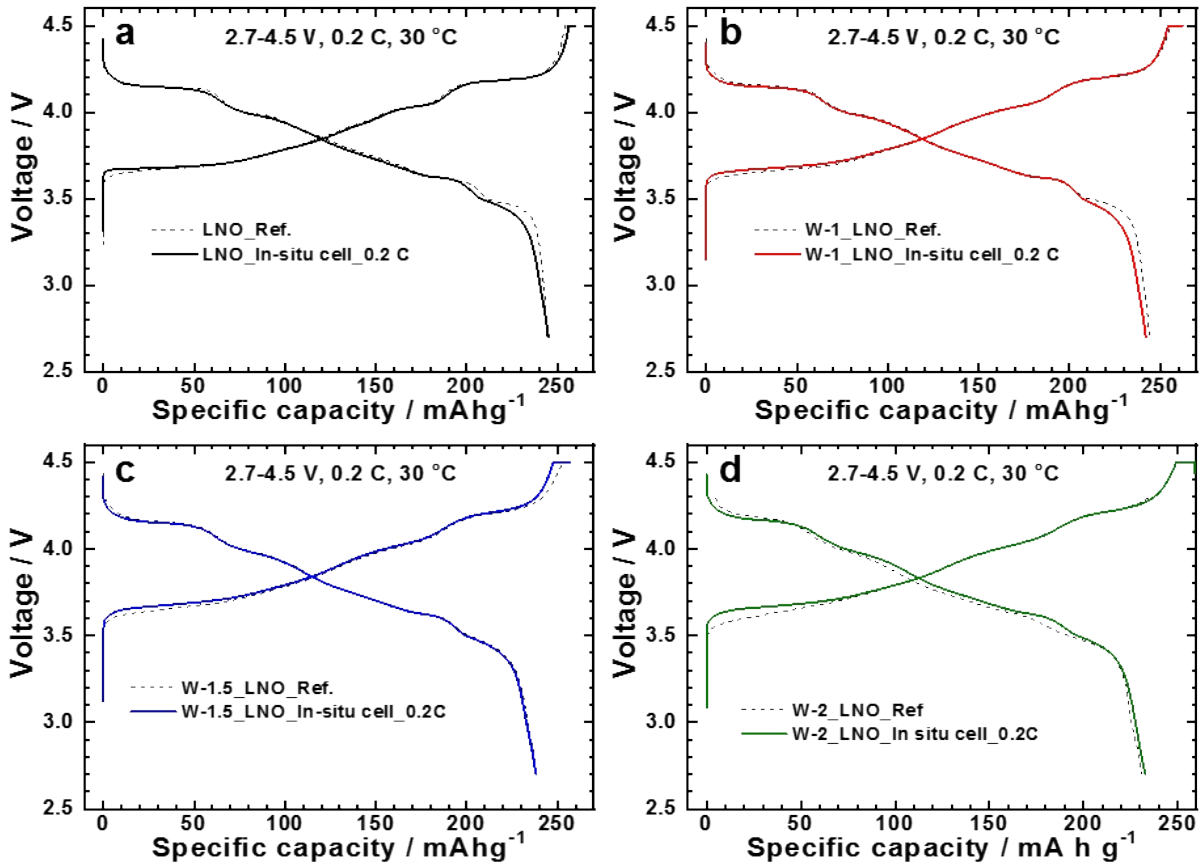

Fig. S6 Charge–discharge profiles obtained using modified 2032-type coin cells during the measurement of *in situ* XRD (solid lines), compared with the charge–discharge profiles obtained using normal 2032-type coin cells (dashed lines).

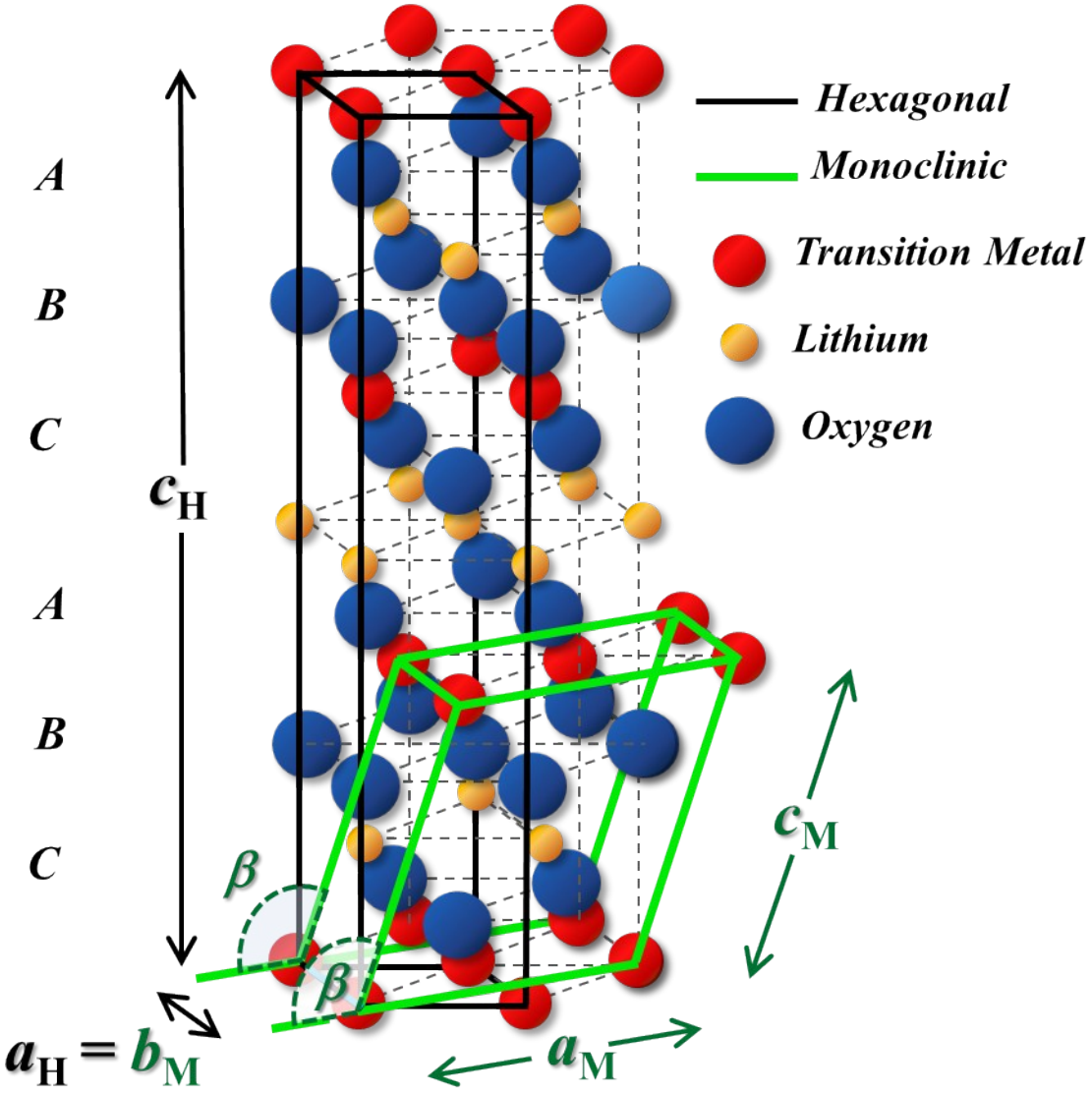

Fig. S7 Structural relationship between the hexagonal phase and the monoclinic phase.

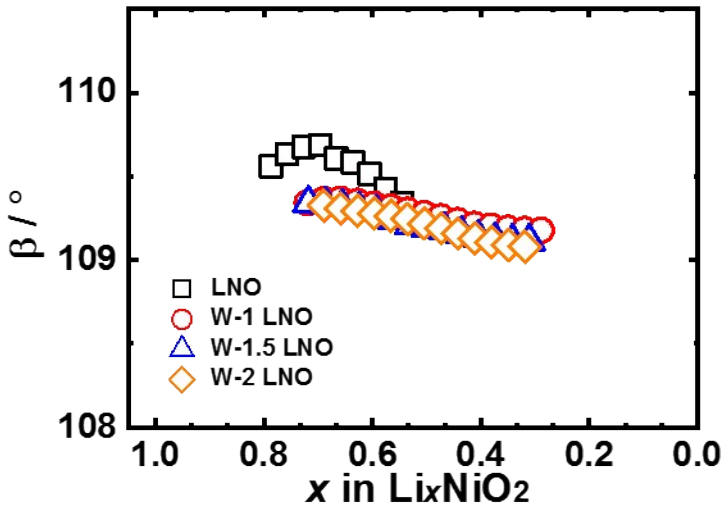

Fig. S8 Comparison of □ in the unit cell of the monoclinic phase.

Table S1 Chemical composition of the cathodes, determined via ICP analysis. Structural information obtained after Rietveld refinement.

Sample	Average composition		Structural information			
	Ni / mol%	W / mol%	*a*-axis / Å	*c*-axis / Å	Volume / Å^3	Ni^{2+} in Li layer / %
LNO	100	0	2.87594	14.1977	101.697	1.0
W-1 LNO	99.1	0.9	2.87887	14.2044	101.953	2.8
W-1.5 LNO	98.5	1.5	2.88035	14.2078	102.082	4.4
W-2 LNO	98.1	1.9	2.88159	14.2098	102.184	5.2

Table S2 Effects of Rietveld refinement on the XRD pattern of the as-prepared powder.

Formula : $LiNiO_2$		Space group : $R\bar{3}m$				
a-axis: 2.87594 (2) Å		*c*-axis: 14.1977 (1) Å		Volume: 101.697 (1) Å^3		
R_p: 7.95 %	R_{wp}: 11.2 %	R_I: 3.86 %	R_F: 2. 27%			
Atom	Wyckoff position	*x*	*y*	*z*	B_{iso}	Occupancy
Li1	3a	0	0	0	1.0	0.991
Ni2	3a	0	0	0	1.0	0.009
Ni1	3b	0	0	0.5	0.551 (9)	0.991
O1	6c	0	0	0.24144 (7)	0.641 (3)	1

Formula : $Li[Ni_{0.99}W_{0.01}]O_2$		Space group : $R\bar{3}m$				
a-axis: 2.87887 (3) Å		*c*-axis: 14.2044 (2) Å		Volume: 101.953 (2) Å^3		
R_p: 7.52 %	R_{wp}: 10.4 %	R_I: 3.97 %	R_F: 2.27 %			
Atom	Wyckoff position	*x*	*y*	*z*	B_{iso}	Occupancy
Li1	3a	0	0	0	1.0	0.972
Ni2	3a	0	0	0	1.0	0.028
W1	3b	0	0	0.5	0.555 (9)	0.010
Ni1	3b	0	0	0.5	0.555 (9)	0.990
O1	6c	0	0	0.24176 (7)	0.654 (3)	1

Formula : $Li[Ni_{0.985}W_{0.015}]O_2$		Space group : $R\bar{3}m$				
a-axis: 2.88035 (4) Å		*c*-axis: 14.2078 (2) Å		Volume: 102.082 (2) Å^3		
R_p: 7.33 %	R_{wp}: 10.4 %	R_I: 3.88 %	R_F: 2.24 %			
Atom	Wyckoff position	*x*	*y*	*z*	B_{iso}	Occupancy
Li1	3a	0	0	0	1.0	0.956
Ni2	3a	0	0	0	1.0	0.044
W1	3b	0	0	0.5	0.562 (9)	0.015
Ni1	3b	0	0	0.5	0.562 (9)	0.985
O1	6c	0	0	0.24220 (7)	0.667 (4)	1

Formula : $Li[Ni_{0.98}W_{0.02}]O_2$		Space group : $R\bar{3}m$				
a-axis: 2.88159 (4) Å		*c*-axis: 14.2098 (2) Å		Volume: 102.184 (3) Å^3		
R_p: 7.72 %	R_{wp}: 10.6 %	R_I: 4.14 %	R_F: 2.29 %			
Atom	Wyckoff position	*x*	*y*	*z*	B_{iso}	Occupancy
Li1	3a	0	0	0	1.0	0.948
Ni2	3a	0	0	0	1.0	0.052
W1	3b	0	0	0.5	0.695 (10)	0.020
Ni1	3b	0	0	0.5	0.695 (10)	0.980
O1	6c	0	0	0.24226 (7)	0.726 (5)	1

Table S3 DSC results for LNO, W-1 LNO, W-1.5 LNO, and W-2 LNO in the delithiated state at 4.3 V.

Sample	Peak temperature (℃)	Enthalpy ($J\ g^{-1}$)
LNO	**178.0**	**1827**
W-1 LNO	**191.2**	**1309**
W-1.5 LNO	**194.3**	**1235**
W-2 LNO	**196.5**	**1119**