Supplementary Information

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

Hoon-Hee Ryu,^a Geon-Tae Park,^a Chong S. Yoon^{b, *} and Yang-Kook Sun^{a, *}

^aDepartment of Energy Engineering, Hanyang University, Seoul 04763, Republic of Korea ^bDepartment of Materials Science and Engineering, Hanyang University, Seoul 04763, Republic of Korea

Formula for chemical diffusion coefficient

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

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

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^{δ} is the slope of the coulometric titration curve, which is determined by plotting the steady-state voltages *E* measured after each titration step $^{\delta}$; 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.

4



Fig. S3 Several XRD peaks of the second phase, which does not belong to the layered R^3m 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 **2** in the unit cell of the monoclinic phase.

	Average composition		Structural information				
Sample	Ni / mol%	W / mol%	<i>a</i> -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 S1 Chemical composition of the cathodes, determined via ICP analysis. Structuralinformation obtained after Rietveld refinement.

i omuna .	LiNiO ₂	Space group)∶R∃m			
<i>a</i> -axis	: 2.87594 (2) Å	<i>c</i> -axis: 14.1977 (1) Å		Volume: 101.697	′(1) ų	
R _p : 7.95 %	R _{wp} : 11.2 %	<i>R</i> _I : 3.86 %	$R_{\rm F}: 2.27$	⁷ %		
Atom	Wyckoff position	x	у	z	Biso	Occupancy
Lil	3a	0	0	0	1.0	0.991
Ni2	3a	0	0	0	1.0	0.009
Nil	3b	0	0	0.5	0.551 (9)	0.991
01	6c	0	0	0.24144 (7)	0.641 (3)	1
Formula : <i>a</i> -axis	$Li[Ni_{0.99}W_{0.01}]O_2$: 2.87887 (3) Å	Space group <i>c</i> -axis: 14.2044 (2)	o∶R∃m Å	Volume: 101.953	(2) Å ³	
R _n : 7.52 %	R _{wn} : 10.4 %	R ₁ : 3.97 %	$R_{\rm F}: 2.27$	%		
Atom	Wyckoff position	x	v	Z	B	Occupancy
Lil	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
Nil	3b	0	0	0.5	0.555 (9)	0.990
01	6c	0	0	0 24176 (7)	0.654(3)	1
		0	0	0.211/0 (/)	0.001 (0)	
Formula :	Li[Ni _{0.985} W _{0.015}]O ₂	Space group	: R3m			
a-avis	· 2 88025 (4) Å	a arris: 14 2078 (2)	Å	Voluma: 102.002	(2) Å3	
u-anis	. 2.00055 (4) A	c-axis. 14.2078 (2)	A	volume. 102.082	(2) A-	
R _p : 7.33 %	R _{wp} : 10.4 %	$R_{\rm I}$: 3.88 %	R _F : 2.24	%	. (2) A ²	
R _p : 7.33 %	R_{wp} : 10.4 % Wyckoff position	$R_{\rm I}: 3.88\%$	$R_{\rm F}: 2.24$	%	B _{iso}	Occupancy
$\frac{R_{\rm p}: 7.33 \%}{\rm Atom}$	$\frac{R_{wp}: 10.4 \%}{Wyckoff position}$	$\frac{R_{\rm I}: 3.88\%}{2}$	$\frac{R_{\rm F}: 2.24}{\frac{y}{0}}$	$\frac{z}{0}$	B _{iso} 1.0	Occupancy 0.956
Atom Li1 Ni2	$\frac{R_{wp}: 10.4 \%}{R_{wp}: 10.4 \%}$ Wyckoff position 3a 3a	$ \frac{R_{\rm I}: 3.88 \%}{0} $	$\frac{R_{\rm F}: 2.24}{\frac{y}{0}}$	volume. 102.082 % 	B _{iso} 1.0 1.0	Occupancy 0.956 0.044
Atom R _p : 7.33 % Atom Li1 Ni2 W1	$\frac{R_{wp}: 10.4 \%}{R_{wp}: 10.4 \%}$ $\frac{Wyckoff \text{ position}}{3a}$ $3a$ $3b$	$ \frac{R_{\rm I}: 3.88 \%}{R_{\rm I}: 3.88 \%} $		volume: 102.082 % 2 0 0 0 0.5	$\frac{B_{iso}}{1.0}$ 0.562 (9)	Occupancy 0.956 0.044 0.015
Atom Li1 Ni2 W1 Ni1	$ \frac{R_{wp}: 10.4 \%}{R_{wp}: 10.4 \%} $ Wyckoff position 3a 3a 3b 3b 3b	$ \frac{R_{\rm I}: 3.88 \%}{R_{\rm I}: 3.88 \%} $	$ \begin{array}{c} R_{\rm F}: 2.24 \\ \hline $	volume: 102.082 % 2 0 0 0.5 0.5	$ B_{iso} 1.0 1.0 0.562 (9) 0.562 (9) $	Occupancy 0.956 0.044 0.015 0.985
Atom Li1 Ni2 W1 Ni1 O1	$ \begin{array}{r} R_{wp} : 10.4 \ \% \\ \overline{\ Wyckoff \ position} \\ 3a \\ 3a \\ 3b \\ 3b \\ 3b \\ 6c \\ \end{array} $				$ \begin{array}{r} B_{iso} \\ \hline $	Occupancy 0.956 0.044 0.015 0.985 1
Atom Li1 Ni2 W1 Ni1 O1	$ \frac{R_{wp}: 10.4 \%}{R_{wp}: 10.4 \%} $ Wyckoff position 3a 3a 3b 3b 6c		$ \begin{array}{c} R_{\rm F}: 2.24 \\ \hline $		$\frac{B_{iso}}{1.0}$ 1.0 1.0 0.562 (9) 0.562 (9) 0.667 (4)	Occupancy 0.956 0.044 0.015 0.985 1
Atom <u>Atom</u> Li1 Ni2 W1 Ni1 O1 Formula :	$ \frac{R_{wp}: 10.4 \%}{R_{wp}: 10.4 \%} $ Wyckoff position 3a 3a 3b 3b 6c Li[Ni _{0.98} W _{0.02}]O ₂	$ \begin{array}{r} R_{\rm I}: 3.88 \% \\ \hline $	$R_{\rm F}: 2.24$ $\frac{y}{0}$ 0 0 0 0 $0: R\overline{3}m$	volume: 102.082 % 2 0 0 0.5 0.5 0.5 0.24220 (7)	$\frac{B_{iso}}{1.0}$ $\frac{1.0}{0.562} (9)$ $0.562 (9)$ $0.667 (4)$	Occupancy 0.956 0.044 0.015 0.985 1
Atom Li1 Ni2 W1 Ni1 O1 Formula : <i>a</i> -axis	Rwp: 10.4 % Rwp: 10.4 % Wyckoff position 3a 3b 3b 3b 6c Li[Ni _{0.98} W _{0.02}]O ₂ : 2.88159 (4) Å	$ \begin{array}{c} R_{\rm I}: 3.88 \% \\ \hline R_{\rm I}: 3.88 \% \\ \hline \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \hline \\ 0 \\ 0 \\ 0 \\ \hline \\ Space group \\ c-axis: 14.2098 (2) \\ \end{array} $	$R_{\rm F}: 2.24$ $\frac{V}{0}$ 0 0 0 0 0 0 0 0 0 $R\overline{3}m$ A	Volume: 102.082 % 2 0 0 0.5 0.5 0.5 0.24220 (7) Volume: 102.184	$ \begin{array}{r} B_{iso} \\ \hline B_{iso} \\ 1.0 \\ 1.0 \\ 0.562 (9) \\ 0.562 (9) \\ 0.667 (4) \\ 4 (3) Å^{3} \end{array} $	Occupancy 0.956 0.044 0.015 0.985 1
$\frac{R_{p}: 7.33 \%}{A \text{ tom}}$ $\frac{A \text{ tom}}{Li1}$ $Ni2$ $W1$ $Ni1$ $O1$ Formula : $a\text{-axis}$ $R_{p}: 7.72 \%$	$R_{wp} : 10.4 \%$ $R_{wp} : 10.4 \%$ $R_{wp} : 10.4 \%$ $R_{wp} : 10.4 \%$ $R_{wp} : 10.6 \%$	$ \begin{array}{c} R_{\rm I}: 3.88 \% \\ \hline R_{\rm I}: 4.14 \% \\ \hline $	$R_{\rm F}: 2.24$ $\frac{V}{0}$ 0 0 0 0 0: R3m Å R_{\rm F}: 2.29	Volume: 102.082 % 2 0 0 0 0.5 0.5 0.24220 (7) Volume: 102.184 %	$\frac{B_{iso}}{1.0}$ $\frac{1.0}{0.562} (9)$ $0.562 (9)$ $0.667 (4)$ $4 (3) Å^{3}$	Occupancy 0.956 0.044 0.015 0.985 1
$R_p: 7.33 \%$ AtomLi1Ni2W1Ni1O1Formula : a -axis $R_p: 7.72 \%$ Atom	$ \frac{R_{wp} : 10.4 \%}{R_{wp} : 10.4 \%} $ Wyckoff position 3a 3a 3b 3b 3b 6c Li[Ni _{0.98} W _{0.02}]O ₂ : 2.88159 (4) Å $R_{wp} : 10.6 \%$ Wyckoff position	$ \begin{array}{c} R_{\rm I}: 3.88 \% \\ \hline R_{\rm I}: 4.14 \% \\ \hline R_{\rm I}: 4.14 \% \\ \hline \end{array} $	$ \begin{array}{c} R_{\rm F}: 2.24 \\ \hline \\ \\ \\ $	volume: 102.082 % 2 0 0 0 0.5 0.5 0.24220 (7) Volume: 102.184 % z	B _{iso} 1.0 1.0 0.562 (9) 0.562 (9) 0.667 (4) 4 (3) Å ³ B _{iso}	Occupancy 0.956 0.044 0.015 0.985 1
$R_{p}: 7.33 \%$ Atom Li1 Ni2 W1 Ni1 O1 Formula : a -axis $R_{p}: 7.72 \%$ Atom Li1	$R_{wp} : 10.4 \%$ $R_{wp} : 10.4 \%$ Wyckoff position 3a 3a 3b 3b 6c Li[Ni _{0.98} W _{0.02}]O ₂ : 2.88159 (4) Å $R_{wp} : 10.6 \%$ Wyckoff position 3a	$ \begin{array}{c} R_{\rm I}: 3.88 \% \\ \hline R_{\rm I}: 4.14 \% \\ $	$R_{\rm F}: 2.24$ $\frac{V}{0}$ 0 0 0 0 $R\overline{3}m$ A $R_{\rm F}: 2.29$ $\frac{V}{0}$	$\frac{z}{0} \\ 0 \\ 0 \\ 0.5 \\ 0.5 \\ 0.24220 (7) \\ 0 \\ 0 \\ 0 \\ 0.5 \\ 0.24220 (7) \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	$\frac{B_{iso}}{1.0}$ $\frac{1.0}{0.562} (9)$ $0.562 (9)$ $0.667 (4)$ $4 (3) Å^{3}$ $\frac{B_{iso}}{1.0}$	Occupancy 0.956 0.044 0.015 0.985 1 1 Occupancy 0.948
$R_p: 7.33 \%$ AtomLi1Ni2W1Ni1O1Formula : a -axis $R_p: 7.72 \%$ AtomLi1Ni2	$ \frac{R_{wp} : 10.4 \%}{R_{wp} : 10.4 \%} $ Wyckoff position 3a 3a 3b 3b 3b 6c Li[Ni _{0.98} W _{0.02}]O ₂ : 2.88159 (4) Å $R_{wp} : 10.6 \%$ Wyckoff position 3a 3a 3a 3a 3a 3a 3b 3b	$ \begin{array}{c} R_{\rm I}: 3.88 \% \\ \hline R_{\rm I}: 4.14 \% \\ \hline R_{\rm I}: 4.14 \% \\ \hline R_{\rm I}: 4.14 \% \\ \hline R_{\rm I}: 0 \\ \hline 0 \\ 0 \end{array} $	$ \begin{array}{c} R_{\rm F}: 2.24 \\ \hline \\ \\ \\ $	$\frac{z}{0}$ 0 0 0 0.5 0.5 0.24220 (7) Volume: 102.184 % $\frac{z}{0}$ 0 0 0	$\frac{B_{iso}}{1.0}$ $\frac{1.0}{0.562} (9)$ $0.562 (9)$ $0.667 (4)$ $\frac{1.0}{1.0}$ $\frac{1.0}{1.0}$	Occupancy 0.956 0.044 0.015 0.985 1 1 Occupancy 0.948 0.052
$R_{p}: 7.33 \%$ Atom Li1 Ni2 W1 Ni1 O1 Formula: a -axis $R_{p}: 7.72 \%$ Atom Li1 Ni2 W1	$R_{wp} : 10.4 \%$ $R_{wp} : 10.4 \%$ Wyckoff position 3a 3b 3b 6c Li[Ni _{0.98} W _{0.02}]O ₂ : 2.88159 (4) Å $R_{wp} : 10.6 \%$ Wyckoff position 3a 3a 3b	$ \begin{array}{c} R_{\rm I}: 3.88 \% \\ \hline R_{\rm I}: 4.14 \% \\ $	$R_{\rm F}: 2.24$ $\frac{y}{0}$ 0 0 0 0 0 R3m Å R_{\rm F}: 2.29 $\frac{y}{0}$ 0 0 0 0 0 R = 100000000000000000000000000000000000	$\frac{z}{0}$ $\frac{z}{0}$ 0 0 0.5 0.5 0.24220 (7) Volume: 102.184 % $\frac{z}{0}$ 0 0 0 0.5	$\frac{B_{iso}}{1.0}$ $\frac{1.0}{0.562} (9)$ $0.562 (9)$ $0.562 (9)$ $0.667 (4)$ $4 (3) Å^{3}$ $\frac{B_{iso}}{1.0}$ 1.0 1.0 $0.695 (10)$	Occupancy 0.956 0.044 0.015 0.985 1 1 Occupancy 0.948 0.052 0.020
$R_{p}: 7.33 \%$ Atom Li1 Ni2 W1 Ni1 O1 Formula: a-axis $R_{p}: 7.72 \%$ Atom Li1 Ni2 W1 Ni1	$ \frac{R_{wp} : 10.4 \%}{R_{wp} : 10.4 \%} $ Wyckoff position 3a 3a 3b 3b 6c Li[Ni _{0.98} W _{0.02}]O ₂ : 2.88159 (4) Å $R_{wp} : 10.6 \%$ Wyckoff position 3a 3b 3b 3b 3b 3b 3b 3b	$ \begin{array}{c} R_{\rm I}: 3.88 \% \\ \hline R_{\rm I}: 4.14 \% \\ \hline R_{\rm I}: 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$	$ \begin{array}{c} R_{\rm F}: 2.24 \\ \hline \\ \\ \\ $	$\frac{z}{0}$ 0 0 0 0.5 0.5 0.24220 (7) Volume: 102.184 % $\frac{z}{0}$ 0 0 0 0.5 0.5 0.5	$\begin{array}{c} B_{iso} \\ \hline B_{iso} \\ \hline 1.0 \\ 1.0 \\ 0.562 (9) \\ 0.562 (9) \\ 0.667 (4) \\ \hline \end{array}$	Occupancy 0.956 0.044 0.015 0.985 1 1 Occupancy 0.948 0.052 0.020 0.980

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

Table S3 DSC results for LNO, W-1 LNO, W-1.5 LNO, and W-2 LNO in the delithiated state at4.3 V.

Sample	Peak temperature (°C)	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	