Supplementary Information (SI) for Energy & Environmental Science.
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Supporting Information

for

Mitigating chemo-mechanical heterogeneity of Ni-rich layered cathodes through the regulated medium-range order by doping

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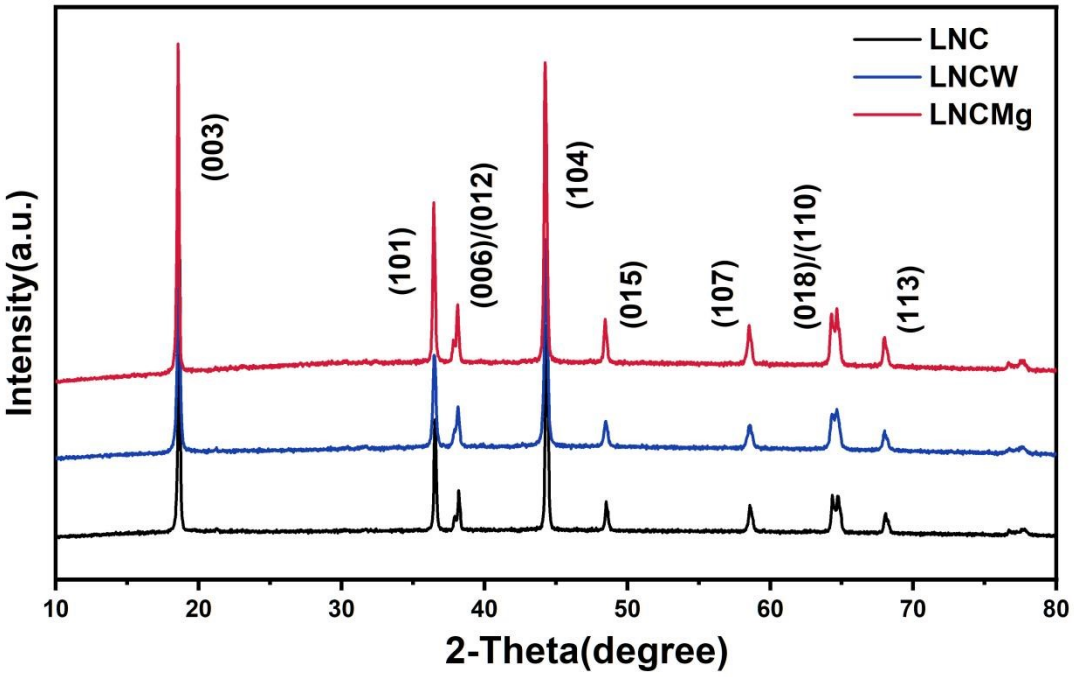

Figure S1. Laboratory XRD data of the samples.

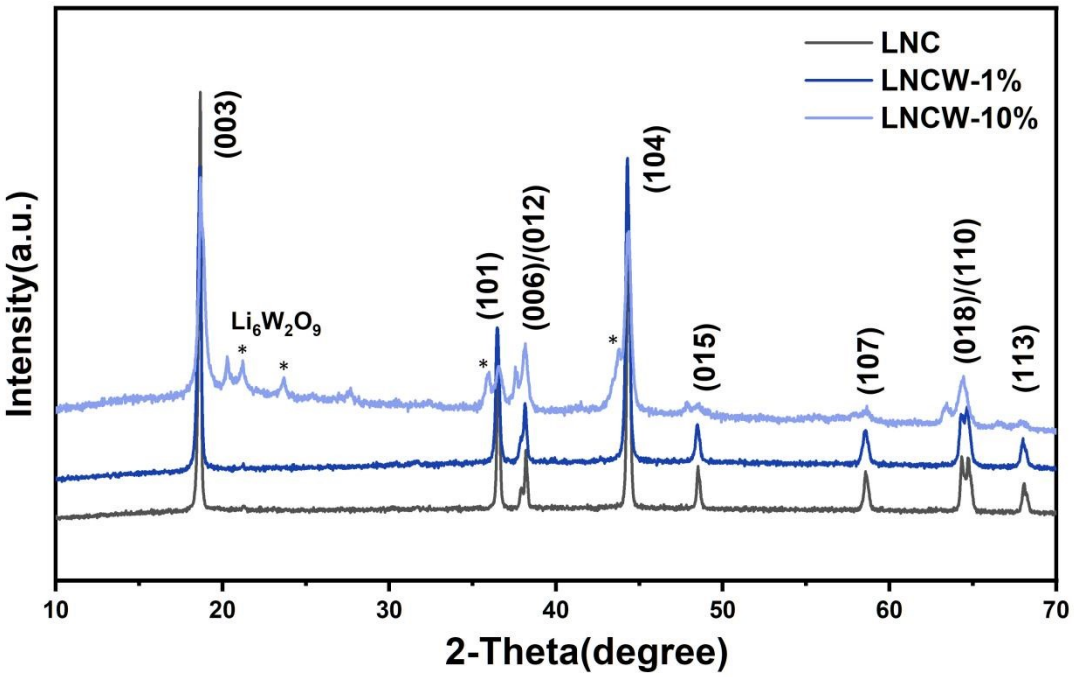

Figure S2. Laboratory XRD data for W-doped samples with different concentrations.

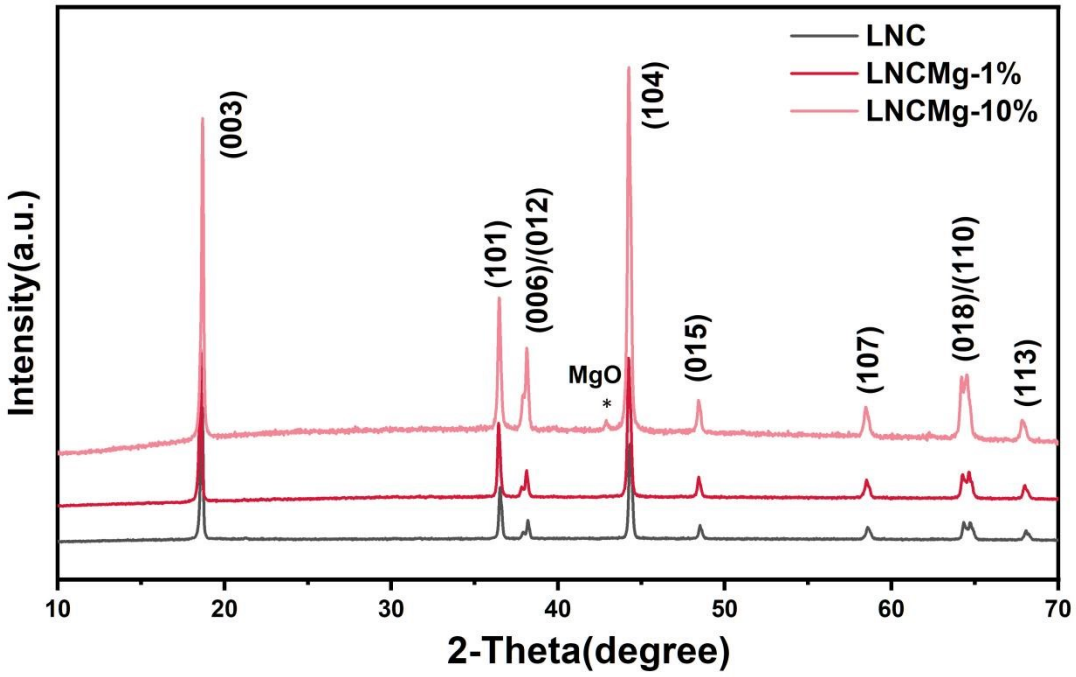

Figure S3. Laboratory XRD data for Mg-doped samples with different concentrations.

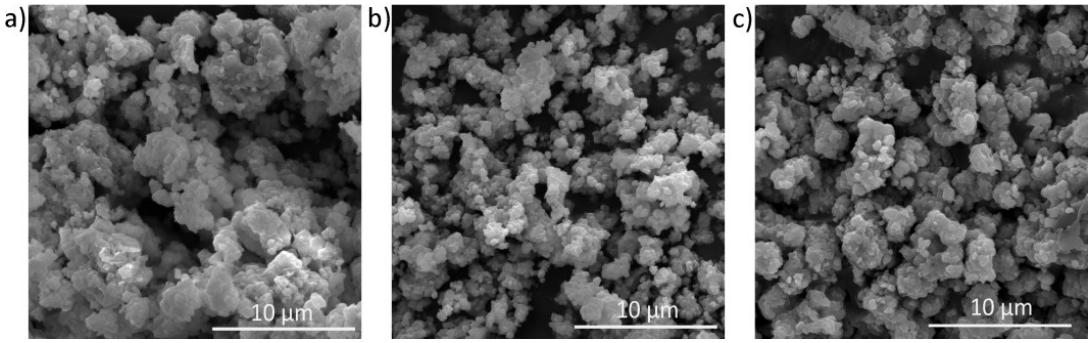

Figure S4. SEM of different samples: (a) LNC; (b) LNCW and (c) LNCMg.

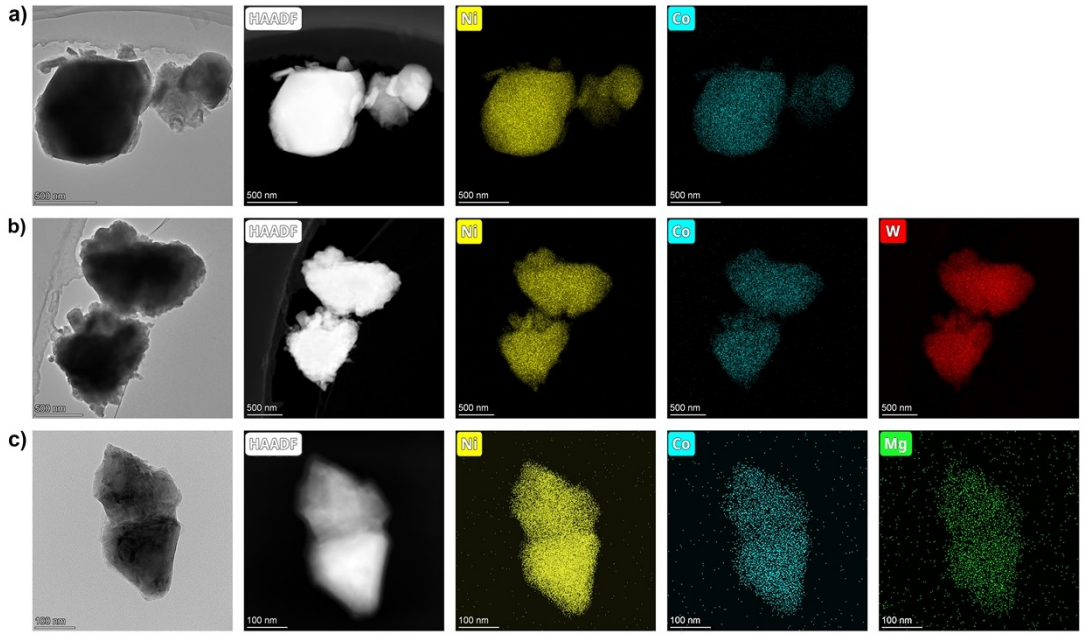

Figure S5. TEM and EDS mapping of different samples: (a) LNC; (b) LNCW and (c) LNCMg.

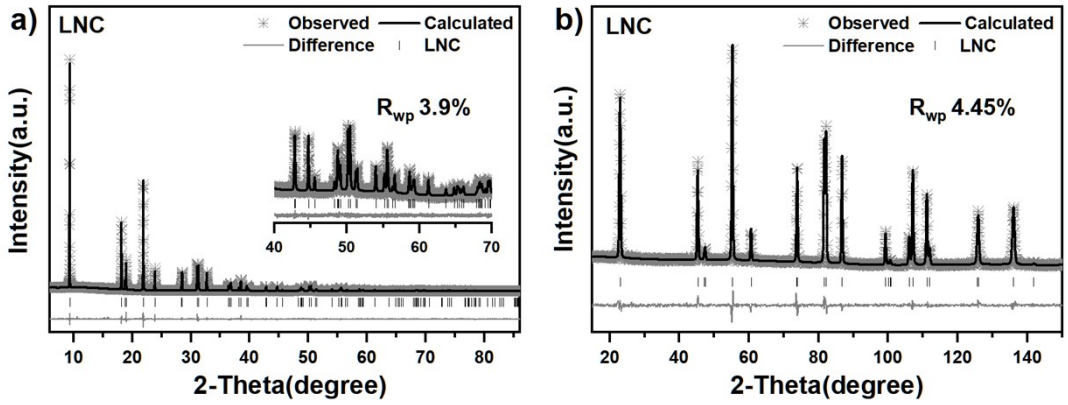

Figure S6. Synchrotron XRD results of LNC(a) and Neutron powder diffraction results of LNC(b).

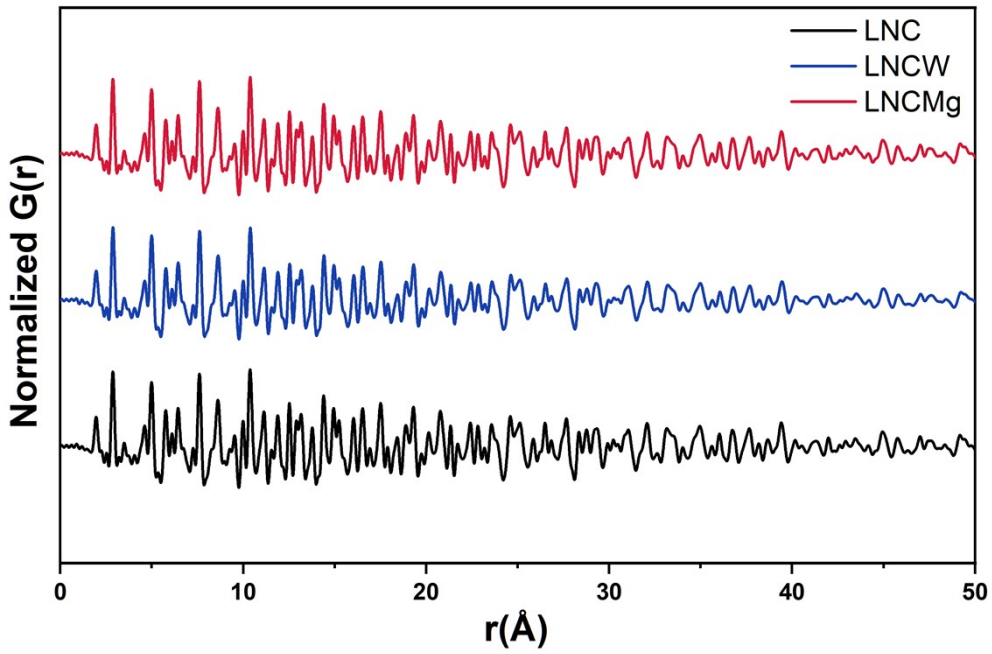

Figure S7. PDF results for the three samples upon the long-range of 2-50 Å.

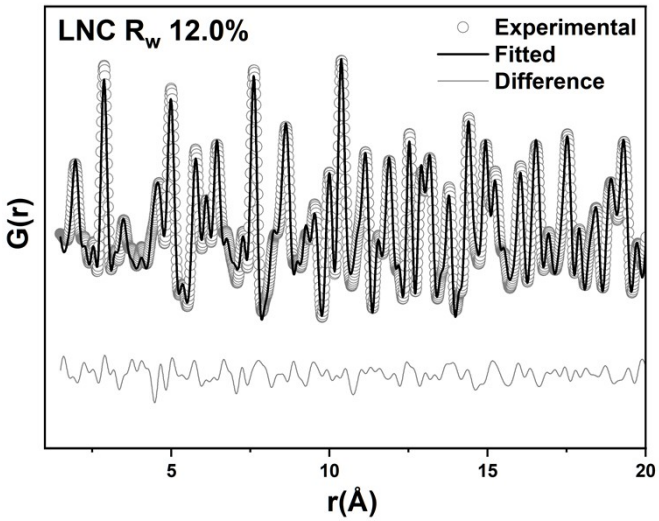

Figure S8. The fitted results of the PDF results for LNC.

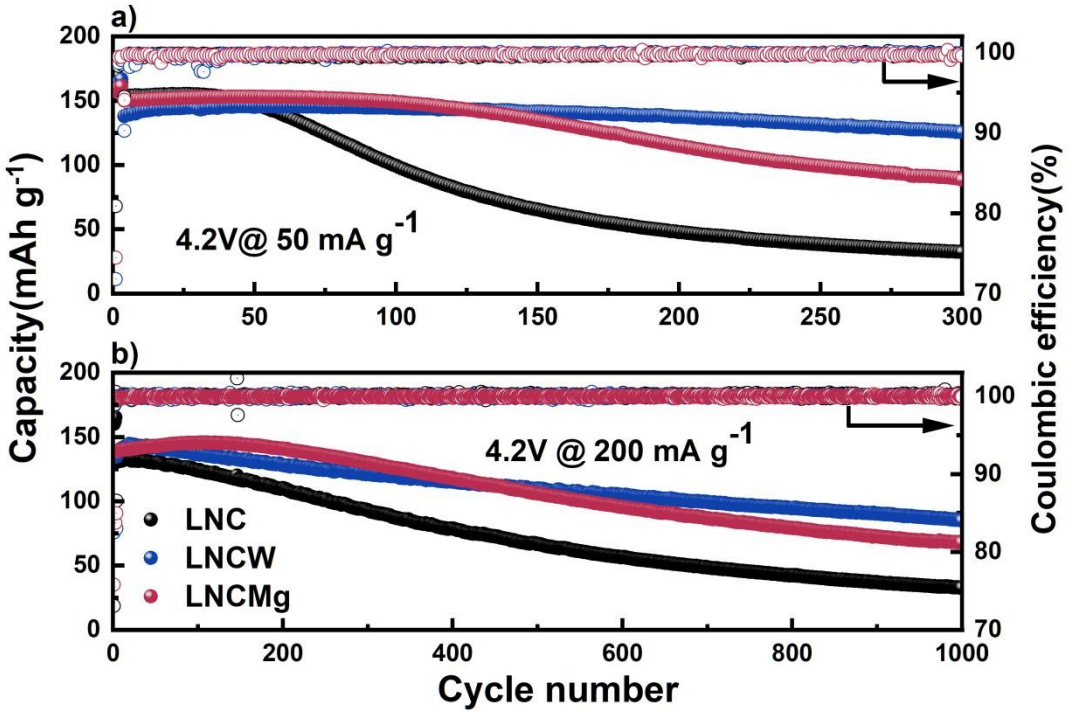

Figure S9. Long-term cycling properties and the corresponding Coulombic Efficiencies upon cycling within a potential range of 2.8 - 4.2 V at 50 mA g^{-1}(a) and 200 mA g^{-1}(b).

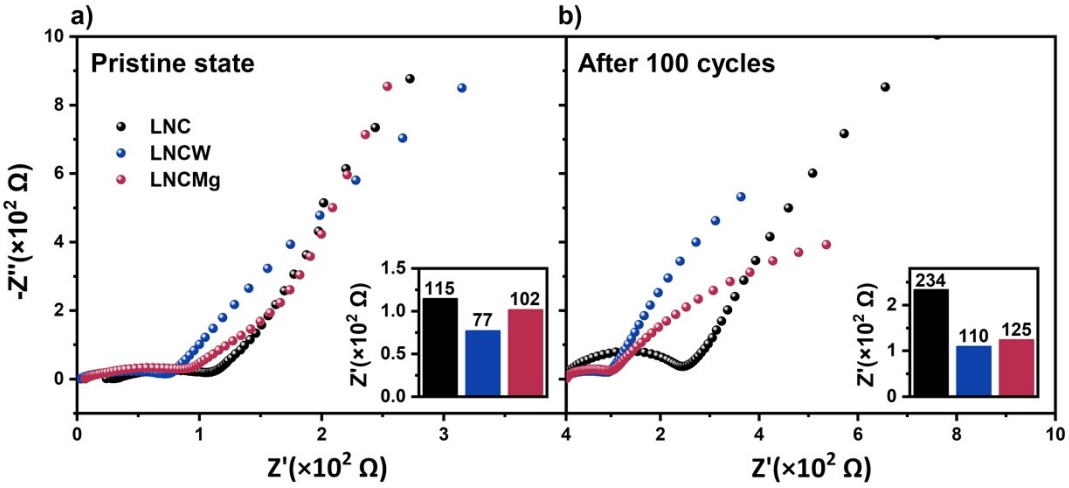

Figure S10. Resistance spectra of the cathodes collected under (a) pristine state and (b) after 100 cycling.

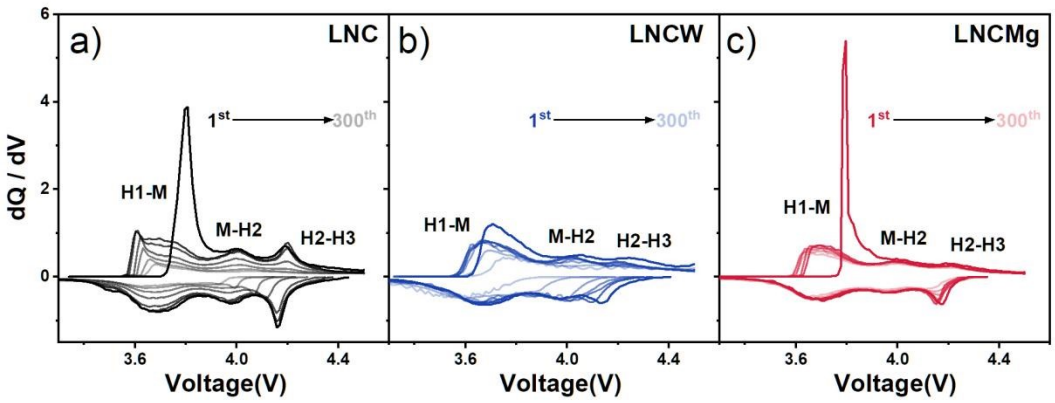

Figure S11. The dQ/dV curves for the different cycle of LNC(a), LNCW(b) and LNCMg(c).

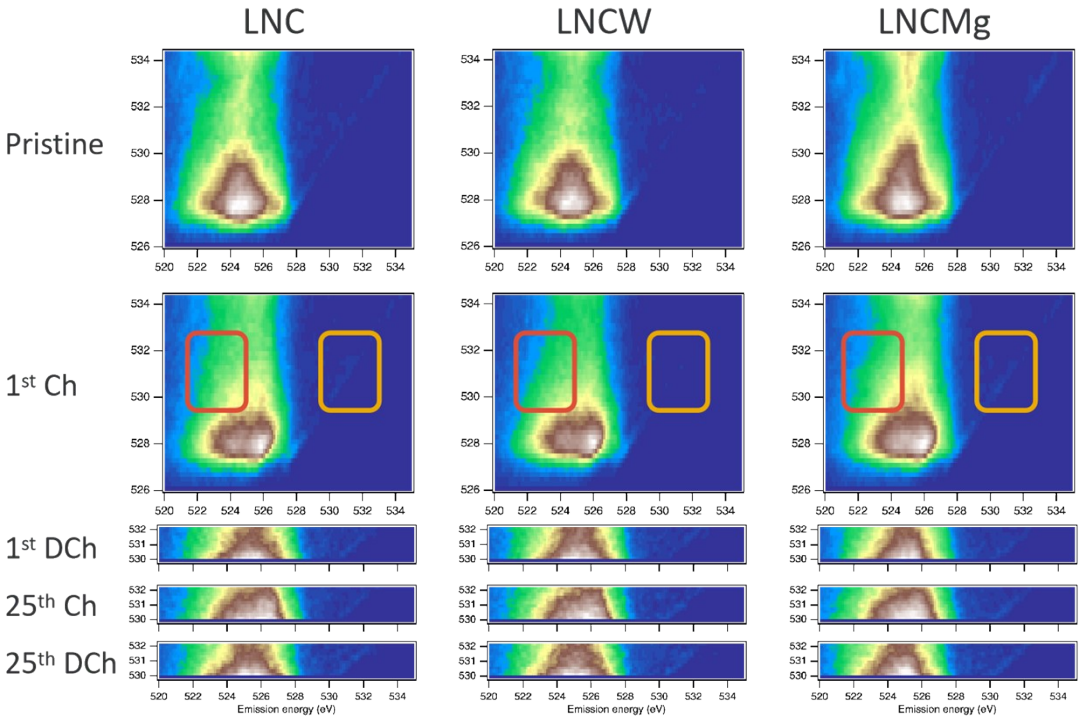

Figure S12. The RIXS results for LNC, LNCW, LNCMg under different states, Pristine means before charge/discharge, 1st Ch means charged to 4.5 V at the first time, 1st DCh donates discharged to 2.8 V after charging to 4.5 V, while 25th Ch and 25th DCh represent the samples charged to 4.5 V and 2.8 V after 25 cycles, respectively.

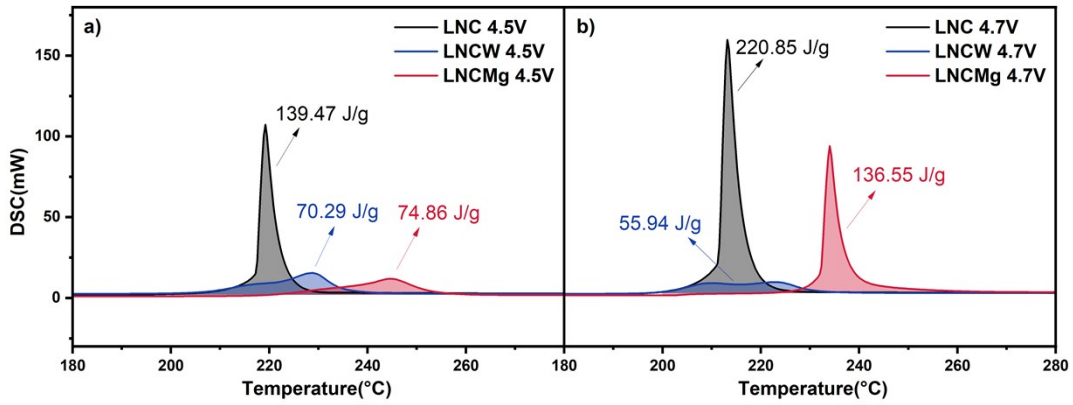

Figure S13. Heat flow of the cathodes at different delithiated states of 4.5 V and 4.7 V, the cathodes were precharged with a current density of 20 mA g^{-1} to the set voltage and held until the current density reached 10 mA g^{-1}.

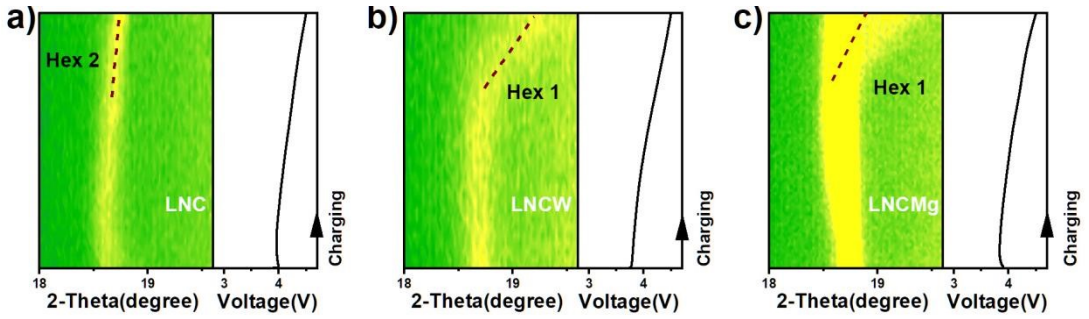

Figure S14. The (003) reflection in the operando XRD upon the 100th delithiation process for (**a**) LNC, (**b**) LNCW and (**c**) LNCMg.

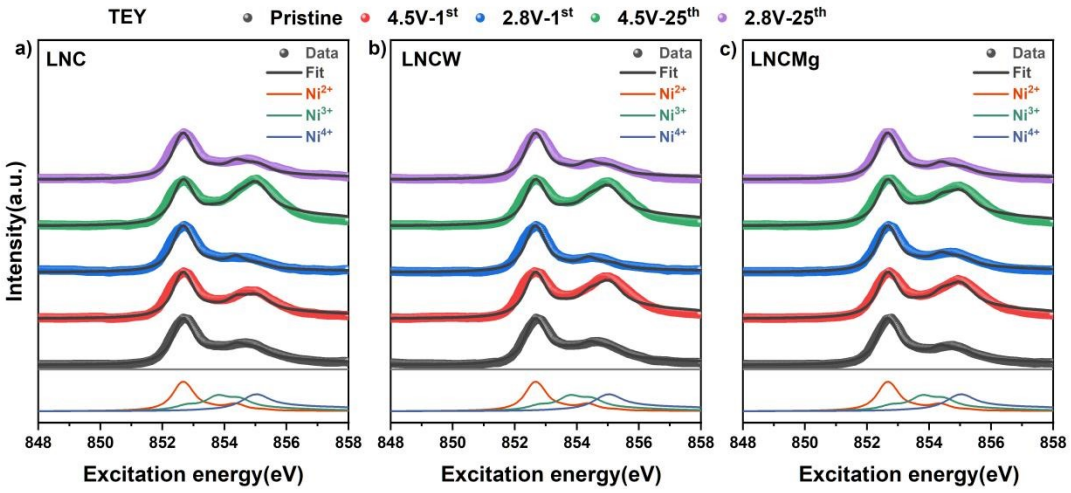

Figure S15. The semi-quantitative fitting results of the Ni-L_3 TEY sXAS spectra for the samples under different states.

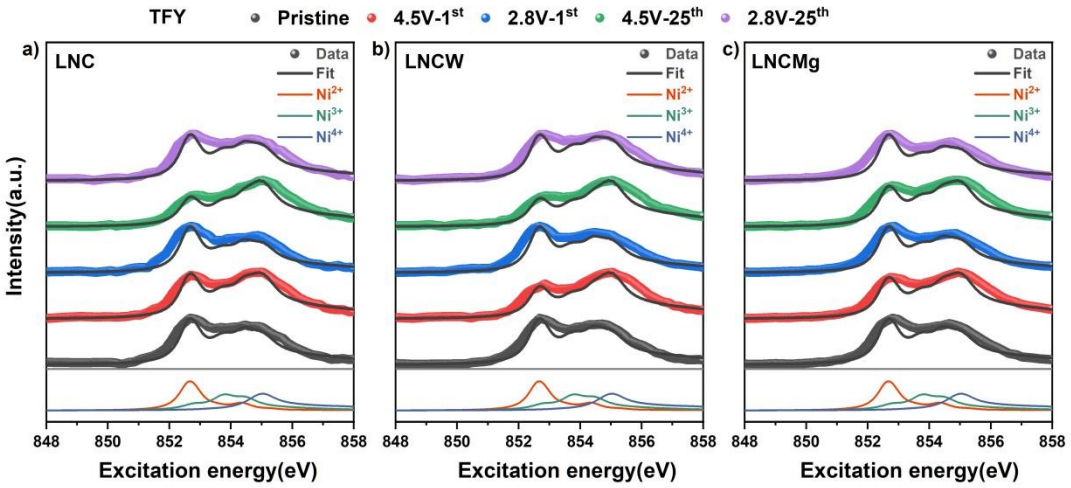

Figure S16. The semi-quantitative fitting results of the Ni-L_3 TFY sXAS spectra for the samples under different states.

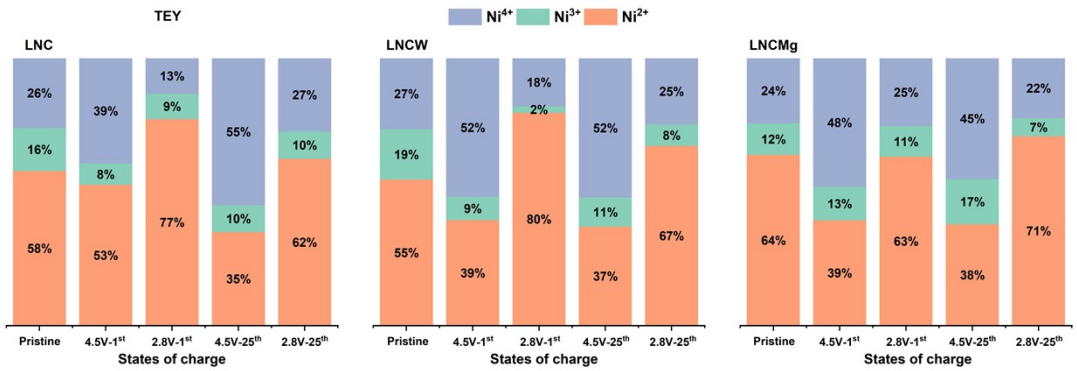

Figure S17. The Ni valence distribution from Ni-L_3 TEY sXAS spectra fitting for the samples under different states.

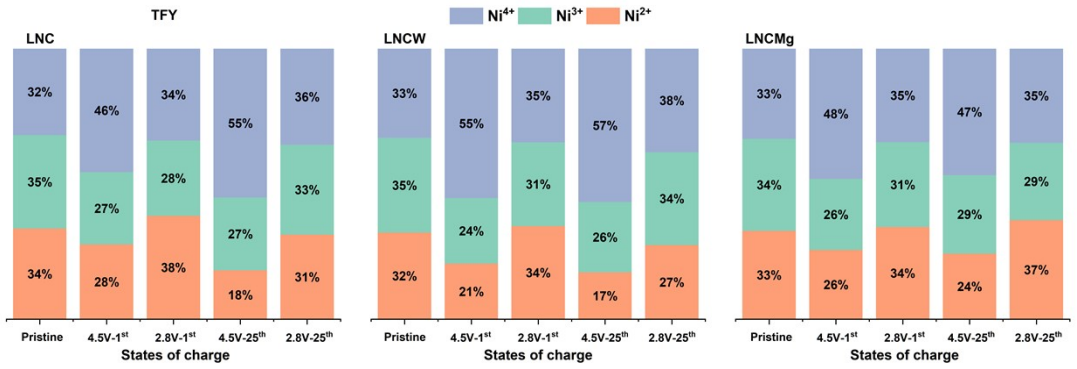

Figure S18. The Ni valence distribution from Ni-L_3 TFY sXAS spectra fitting for the samples under different states.

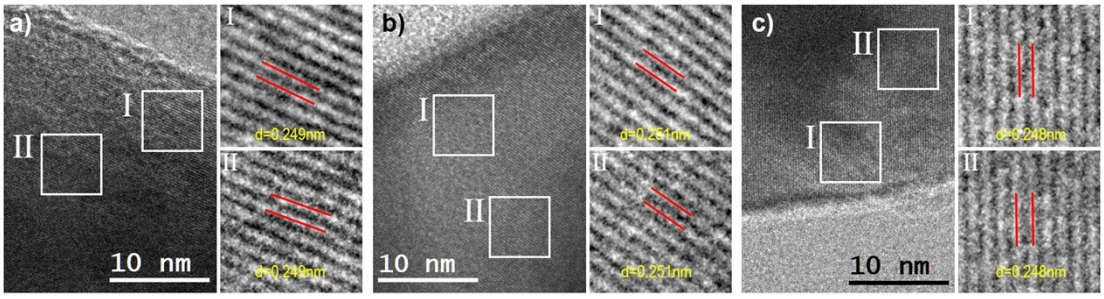

Figure S19. The HR-TEM results of pristine materials for (a) LNC, (b) LNCW, (c) LNCMg

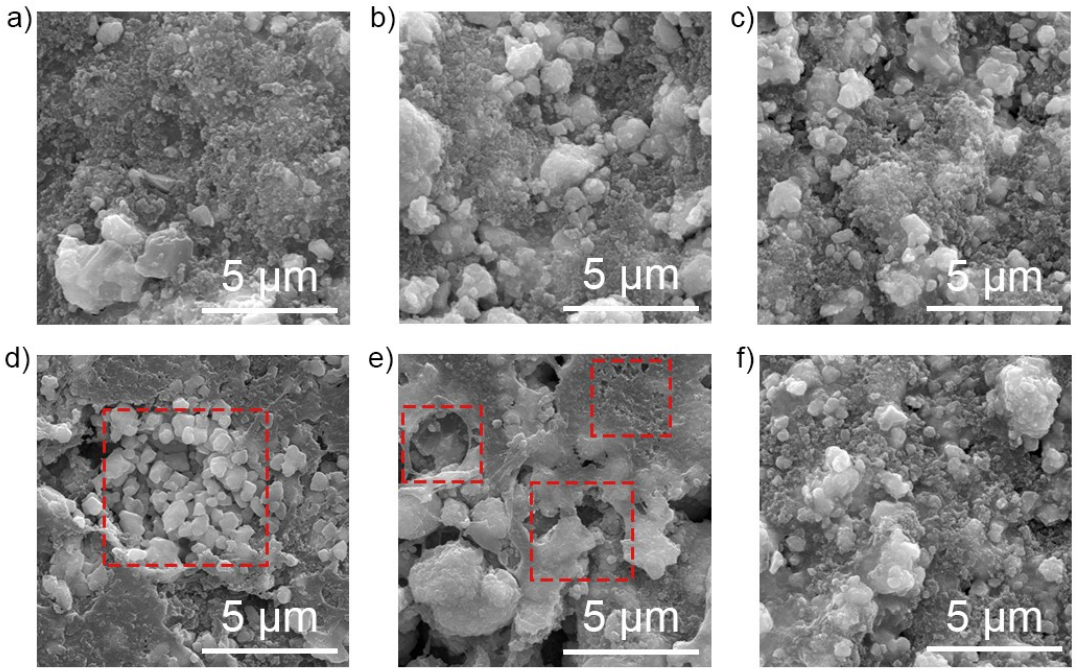

Figure S20. The SEM of pristine materials for (a) LNC, (b) LNCW, (c) LNCMg, and materials after 100 cycles for (d) LNC, (e) LNCW and (f) LNCMg.

Table S1. The atomic parameters obtained from XRD Rietveld refinement result

Selected crystallographic parameters						
Atom	**site**	***x***	***y***	***z***	**occupancy**	**B_{ios}(Å)**
LNC (space group: R-3m, No. 166): a=b=2.87313(2) Å, c=14.20816(16) Å, V=101.5732(19)Å^3						
Ni	3a	0	0	0	0.898(4)	**0.250(8)**
Co	3a	0	0	0	0.096(4)	**0.250(8)**
Li	3a	0	0	0	0.006(5)	**0.250(8)**
Li	3b	0	0	1/2	0.975(2)	**0.57(10)**
Ni	3b	0	0	1/2	0.025(2)	**0.57(10)**
O	6c	0	0	0.25901(12)	1	**0.80(3)**
LNCW (space group: R-3m, No. 166): a=b=2.87508(3) Å, c=14.2250(3) Å, V=101.832(3)Å^3						
Ni	3a	0	0	0	0.857(2)	**0.438(10)**
Co	3a	0	0	0	0.097(2)	**0.438(10)**
Li	3a	0	0	0	0.0087(7)	**0.438(10)**
W	3a	0	0	0	0.037(3)	**0.438(10)**
Li	3b	0	0	1/2	0.9552(5)	**0.53(9)**
Ni	3b	0	0	1/2	0.0440(4)	**0.53(9)**
O	6c	0	0	0.25917(12)	1	**1.05(4)**
LNCMg (space group: R-3m, No. 166): a=b=2.87493(3) Å, c=14.2035(3) Å, V=101.667(3)Å^3						
Ni	3a	0	0	0	0.840(4)	**0.215(8)**
Co	3a	0	0	0	0.093(4)	**0.215(8)**
Li	3a	0	0	0	0.068(5)	**0.215(8)**

Li	3b	0	0	1/2	0.955(6)	**0.78(11)**
Ni	3b	0	0	1/2	0.034(5)	**0.78(11)**
Mg	3b	0	0	1/2	0.012(7)	**0.78(11)**
O	6c	0	0	0.25881(16)	1	**0.95(3)**

Table S2. The atomic parameters obtained from NPD Rietveld refinement result

Selected crystallographic parameters						
Atom	**site**	***x***	***y***	***z***	**occupancy**	**B_{ios}(Å)**
LNC (space group: R-3m, No. 166): a=b=2.87451(3) Å, c=14.1904(3) Å, V=101.543(3)Å^3						
Ni	3a	0	0	0	0.900(6)	**0**
Co	3a	0	0	0	0.100(2)	**0**
Li	3a	0	0	0	0.002(2)	**0**
Li	3b	0	0	1/2	0.998(4)	**0**
Ni	3b	0	0	1/2	0.002(4)	**0**
O	6c	0	0	0.25873(15)	1	**0**
LNCW (space group: R-3m, No. 166): a=b=2.87582(5) Å, c=14.1907(4) Å, V=101.639(5)Å^3						
Ni	3a	0	0	0	0.849(3)	**0**
Co	3a	0	0	0	0.098(2)	**0**
Li	3a	0	0	0	0.023(5)	**0**
W	3a	0	0	0	0.028(3)	**0**
Li	3b	0	0	1/2	0.973(3)	**0**
Ni	3b	0	0	1/2	0.027(3)	**0**

O	6c	0	0	0.25915(13)	1	**0**
LNCMg (space group: R-3m, No. 166): a=b=2.87629(12) Å, c=14.2029(6) Å, V=101.759(10)Å^3						
Ni	3a	0	0	0	0.9063(14)	**0**
Co	3a	0	0	0	0.0995(5)	**0**
Li	3a	0	0	0	0.0622(15)	**0**
Li	3b	0	0	1/2	0.981(7)	**0**
Mg	3b	0	0	1/2	0.019(7)	**0**
O	6c	0	0	0.25919(13)	1	**0**

Table S3. The fitted atomic parameters obtained from PDF result

Selected crystallographic parameters				
Atom	***x***	***y***	***z***	occupancy
LNC (space group: R-3m, No. 166): a=b=2.87018 Å, c=14.1877 Å				
O	0	0	0.240019	1
O	0	0	0.759981	1
O	0.666667	0.333333	0.573352	1
O	0.666667	0.333333	0.093315	1
O	0.333333	0.666667	0.906685	1
O	0.333333	0.666667	0.426648	1
LNCW (space group: R-3m, No. 166): a=b=2.87305 Å, c=14.2085 Å				
O	0	0	0.241103	1
O	0	0	0.758897	1

O	0.666667	0.333333	0.574436	1
O	0.666667	0.333333	0.092231	1
O	0.333333	0.666667	0.907769	1
O	0.333333	0.666667	0.425564	1
LNCMg (space group: R-3m, No. 166): a=b=2.87085 Å, c=14.1948 Å				
O	0	0	0.240595	1
O	0	0	0.759405	1
O	0.666667	0.333333	0.573929	1
O	0.666667	0.333333	0.092738	1
O	0.333333	0.666667	0.907262	1
O	0.333333	0.666667	0.426071	1