
Supplementary information

Origin and regulation of oxygen redox instability in high-voltage battery cathodes

In the format provided by the
authors and unedited

Supplementary Information for

Origin and regulation of oxygen redox instability in high-voltage battery cathodes

Xiang Liu^{1,10}, Gui-Liang Xu^{1,10*}, Venkata Surya Chaitanya Kolluru^{2,3}, Chen Zhao¹, Qingtian Li⁴, Xinwei Zhou², Yuzi Liu², Liang Yin⁵, Zengqing Zhuo⁴, Amine Daali¹, Jing-Jing Fan⁶, Wenjun Liu⁵, Yang Ren⁵, Wenqian Xu⁵, Junjing Deng⁵, Inhui Hwang⁵, Dongsheng Ren⁷, Xuning Feng⁷, Chengjun Sun⁵, Ling Huang⁶, Tao Zhou², Ming Du⁵, Zonghai Chen¹, Shi-Gang Sun⁶, Maria K. Y. Chan², Wanli Yang^{4*}, Minggao Ouyang^{7*}, Khalil Amine^{1,8,9*}

¹ Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA

² Centre for Nanoscale Materials, Argonne National Laboratory, Lemont, IL 60439, USA

³ Department of Materials Science and Engineering, University of Florida, 1885 Stadium Road, Gainesville, FL 32611, USA

⁴ Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

⁵ X-ray Science Division, Argonne National Laboratory, Lemont, IL 60439, USA

⁶ Department of Chemistry, Xiamen University, Xiamen 361005, China

⁷ State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing 100084, China

⁸ Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

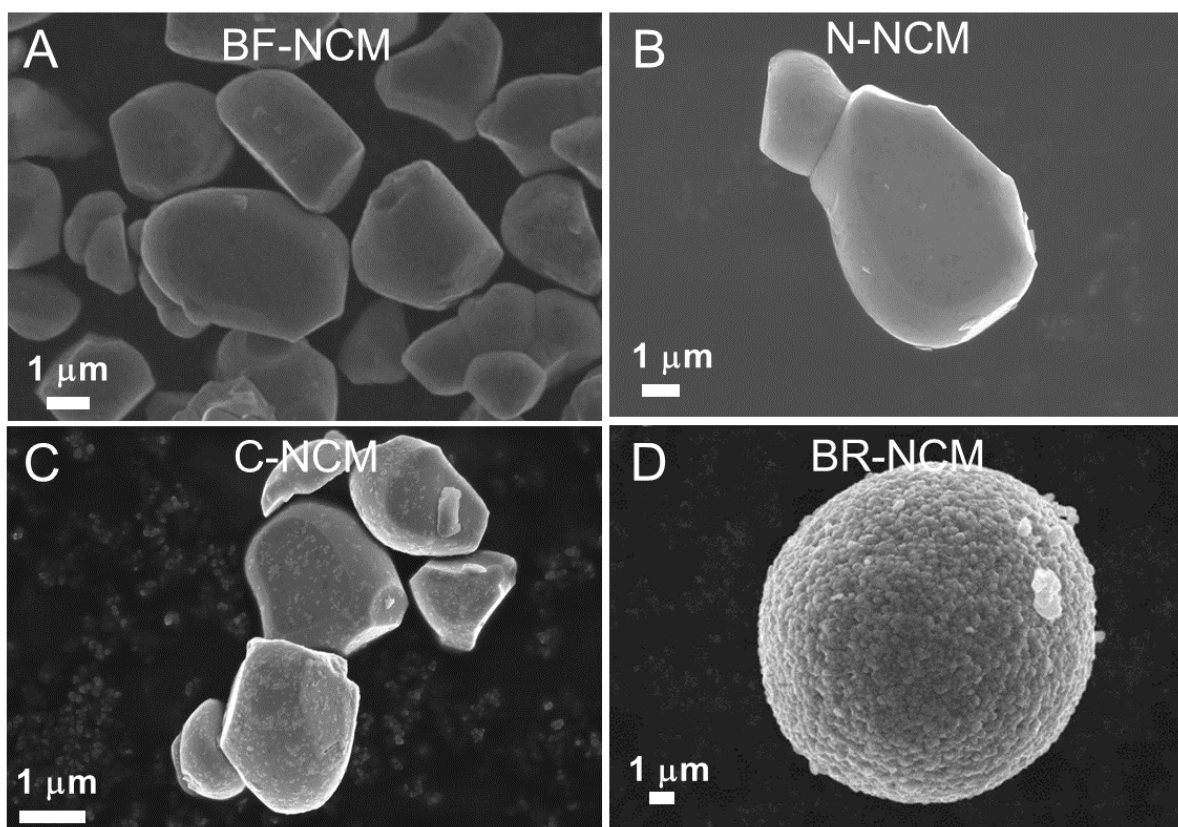
⁹ Materials Science, Energy and Nano-engineering Department, Mohammed VI Polytechnic University (UM6P), Benguerir, Morocco

¹⁰ These authors contributed equally to this work

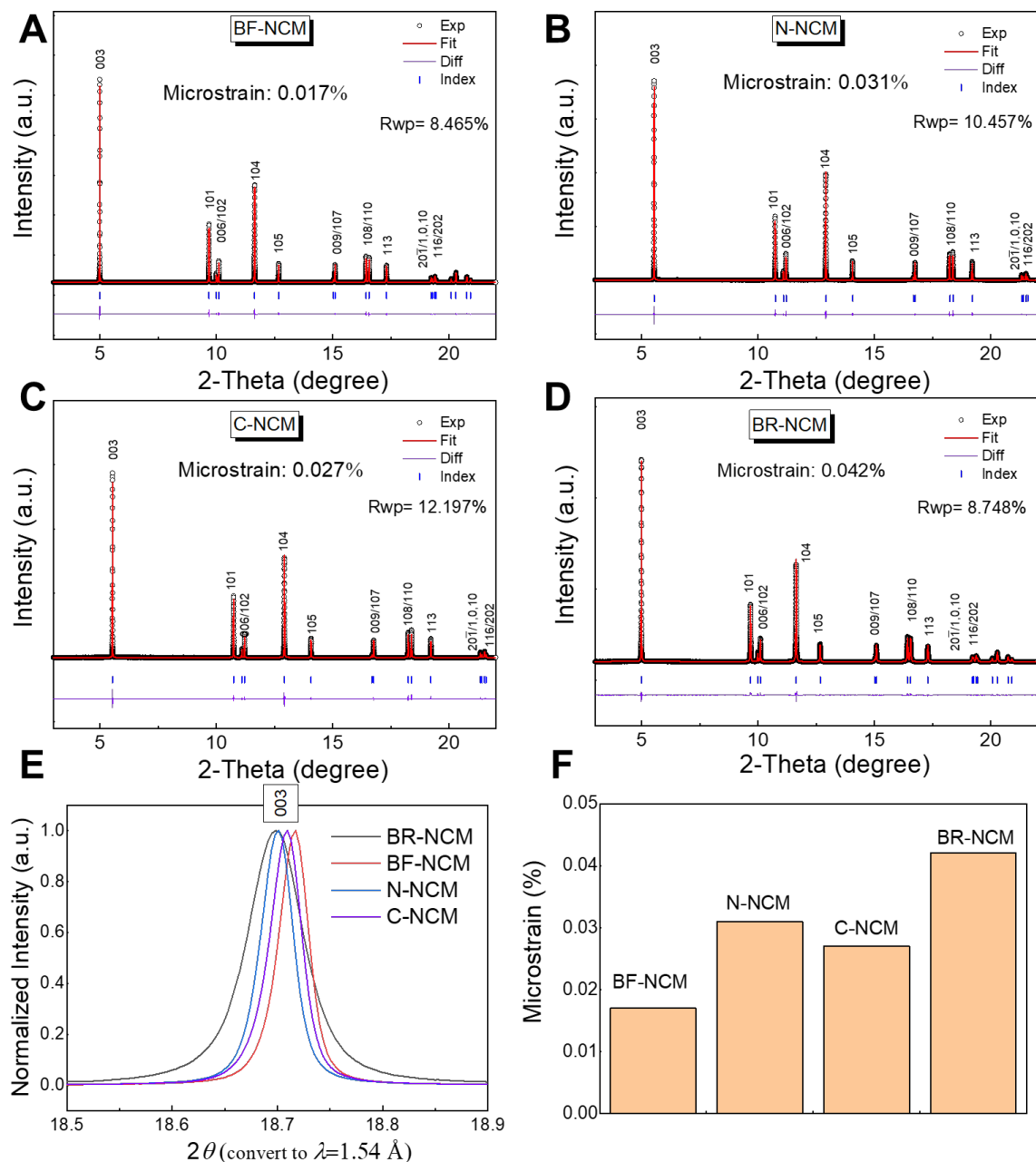
*Corresponding author. Email: xug@anl.gov; wlyang@lbl.gov; ouymg@tsinghua.edu.cn; amine@anl.gov

Inventory of Supplementary Information:

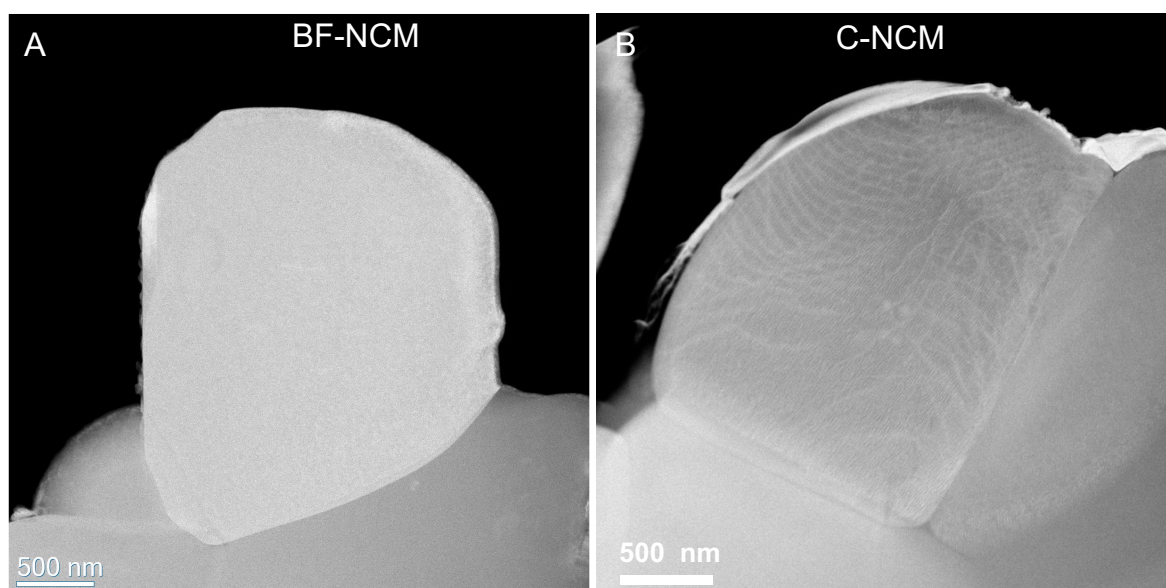
- Supplementary Figures 1-30 Page 2-31
- Supplementary Tables 1-8 Page 32-39



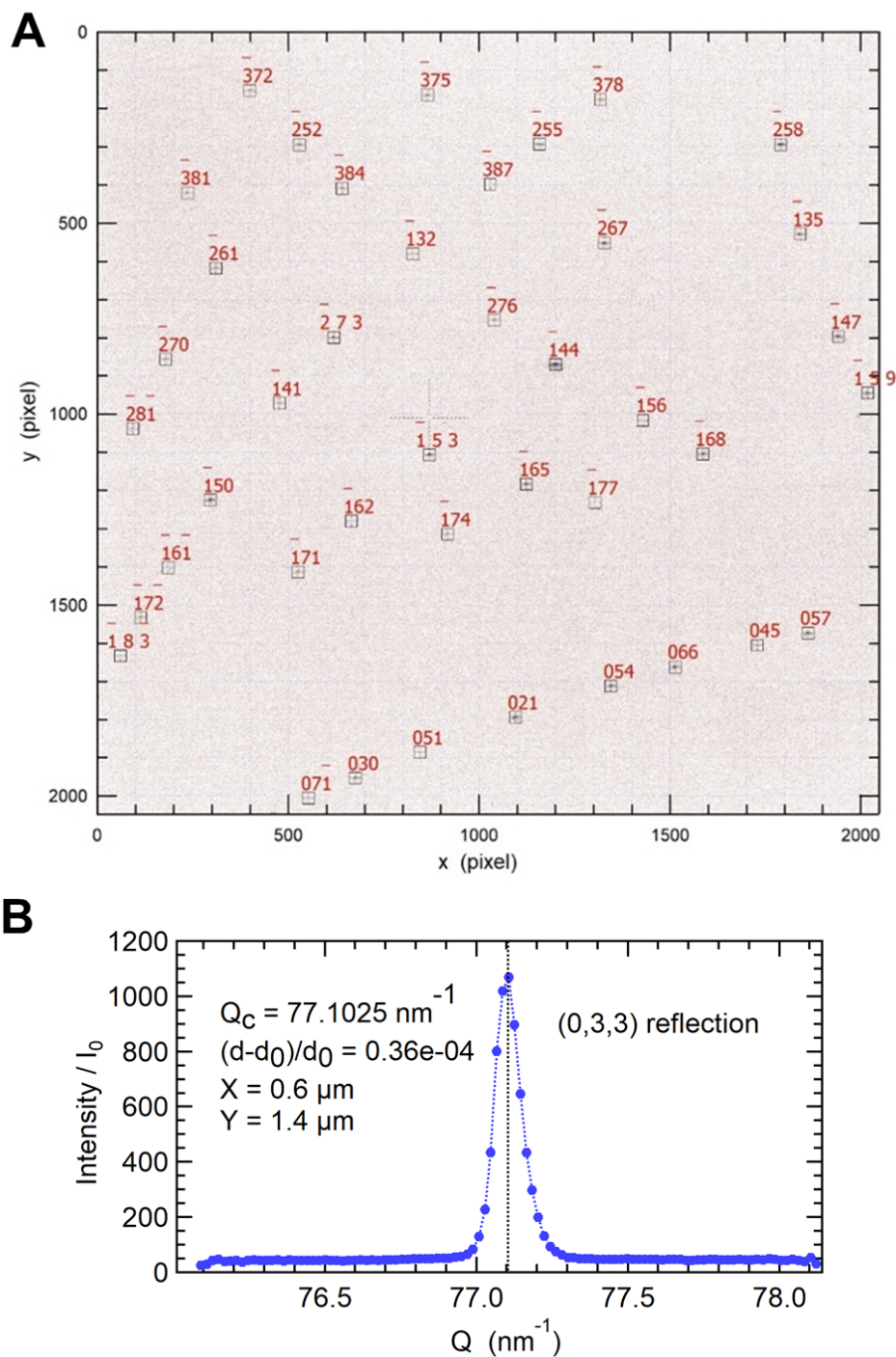
Supplementary Fig. 1. The SEM images of (A) BF-NCM, (B) N-NCM, (C) C-NCM and (D) BR-NCM cathodes.



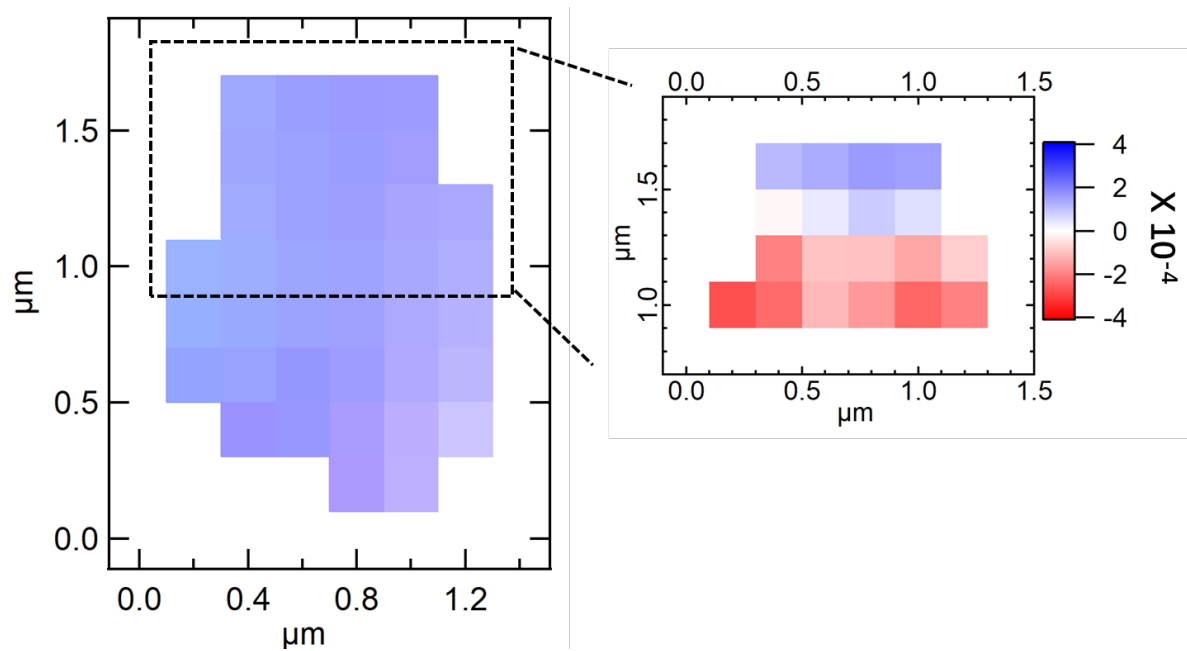
Supplementary Fig. 2. High-resolution synchrotron XRD and Rietveld refinement with lattice parameter (see **Supplementary Tables 1-4**) and microstrain (inset in figure) of pristine (A) BF-NCM, (B) N-NCM, (C) C-NCM and (D) BR-NCM cathodes. (E) The comparison of the layered (003) diffraction peak of the investigated cathodes. (F) The comparison of the lattice microstrain of investigated cathodes.



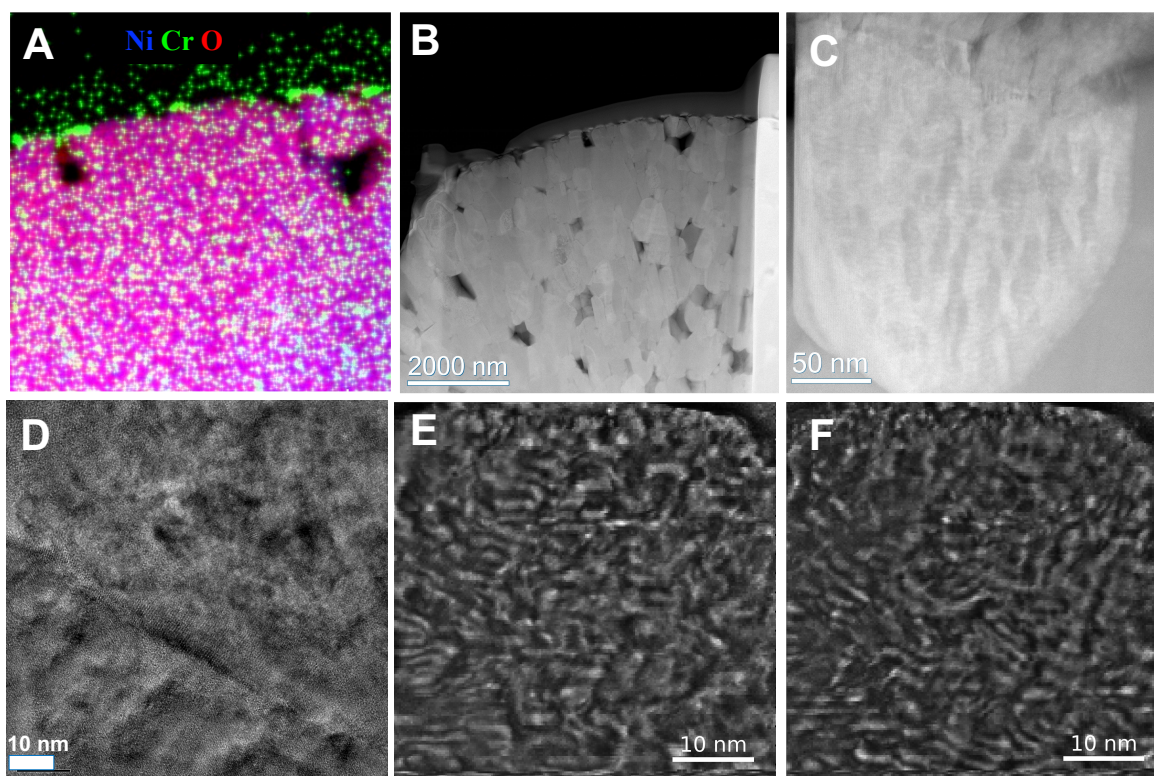
Supplementary Fig. 3. HAADF-STEM image of (A) BF-NCM and (B) C-NCM cathodes.



Supplementary Fig. 4. Synchrotron Laue diffraction microscopy characterization of BF-NCM: (A) Representative Laue diffraction pattern by polychromatic X-rays. (B) Representative diffraction line profile of $|q|$ -distribution by scanning X-ray energy. Lattice plane of (0,3,3,) was measured.

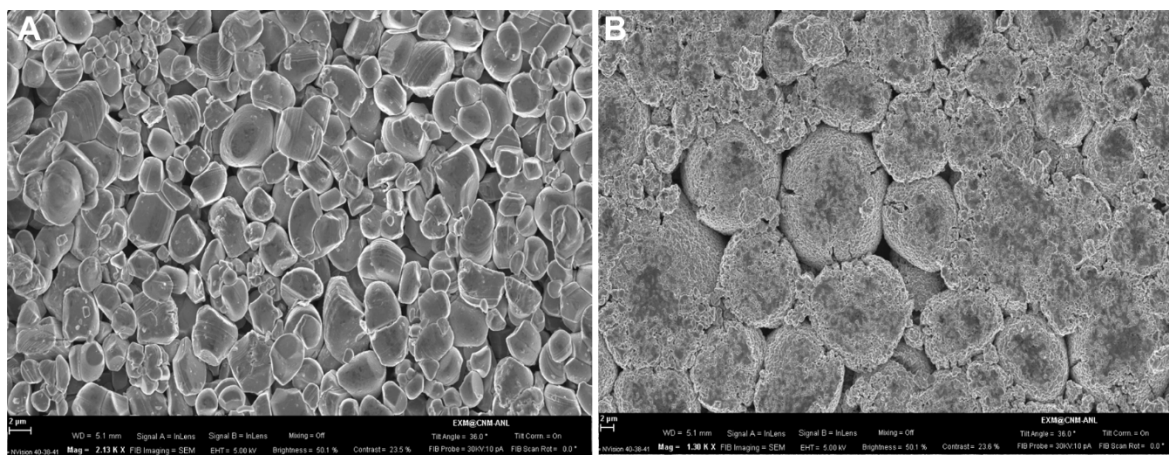


Supplementary Fig. 5. Crystal strain maps of BF-NCM measured by synchrotron Laue diffraction microscopy, showing the enlarged lattice strain scale on the right.

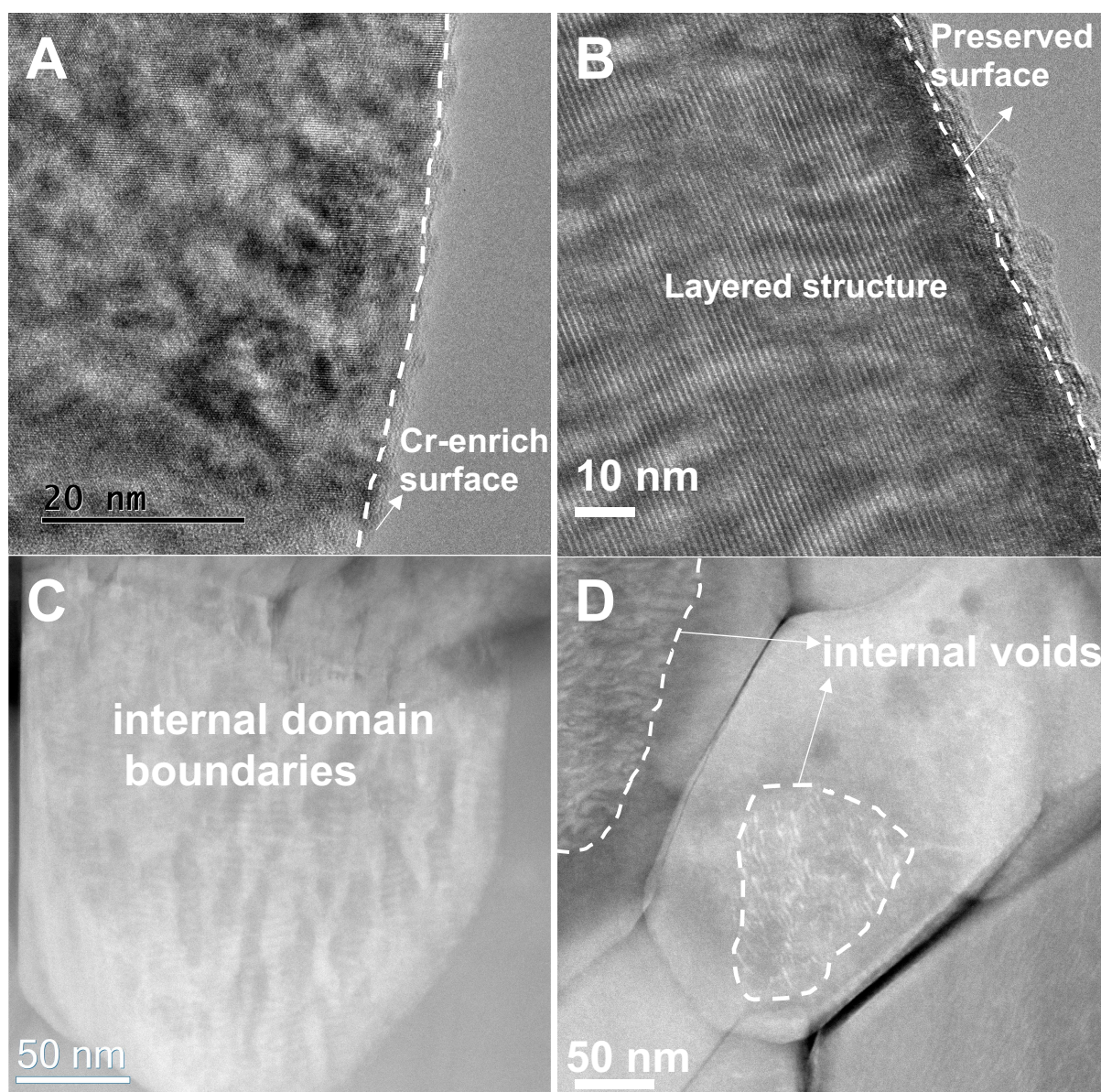


Supplementary Fig. 6. (A) Elemental mapping of BR-NCM (Co and Mn are not shown). (B) Low and (C) high magnification HAADF-STEM images of BR-NCM particles. (D) HRTEM image of BR-NCM particle. (E, F) 4D-STEM dark field images of BR-NCM showing the existence of two families of tilt domain boundaries.

As shown, BR-NCM particles exhibit abundant sub-crystallites with different orientations that lead to a high density of random DBs within the primary particles (Supplementary Figs. 6B-6D). The 4D-STEM dark field images in Supplementary Figs. 6E and 6F clearly show the presence of two families of tilt domains with elongated shape and an average width of ~ 1 nm.

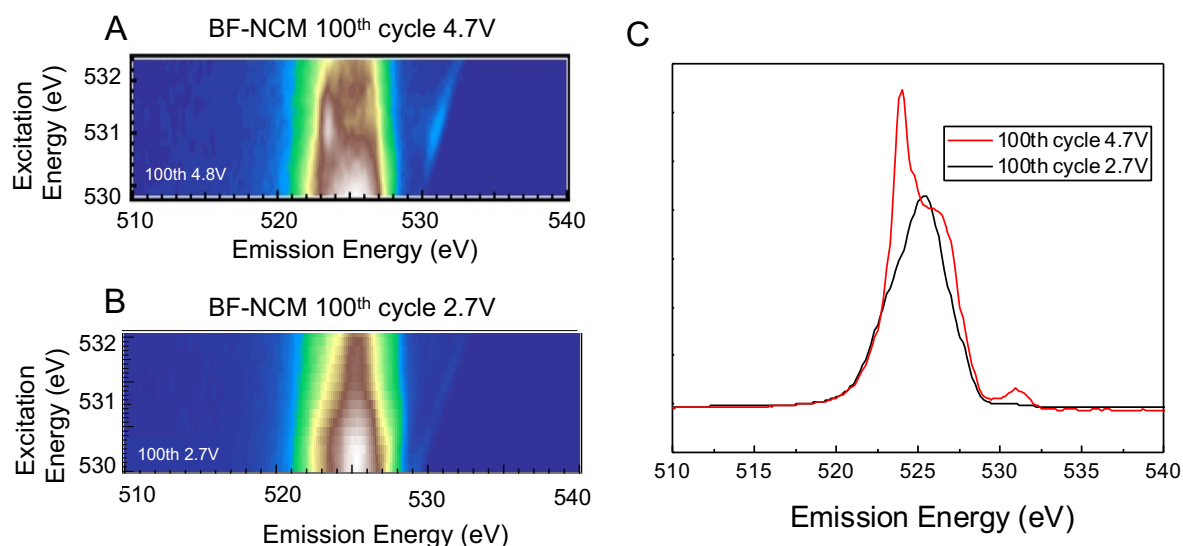


Supplementary Fig. 7. SEM image of pressed (A) BF-NCM and (B) BR-NCM under 3-ton hydraulic pressing. The size of pellet is 13mm in diameter, which is 1.33 cm² in area. Then, the normalized pressure is 22556.4 t/m², which is equal to ~220 MPa.

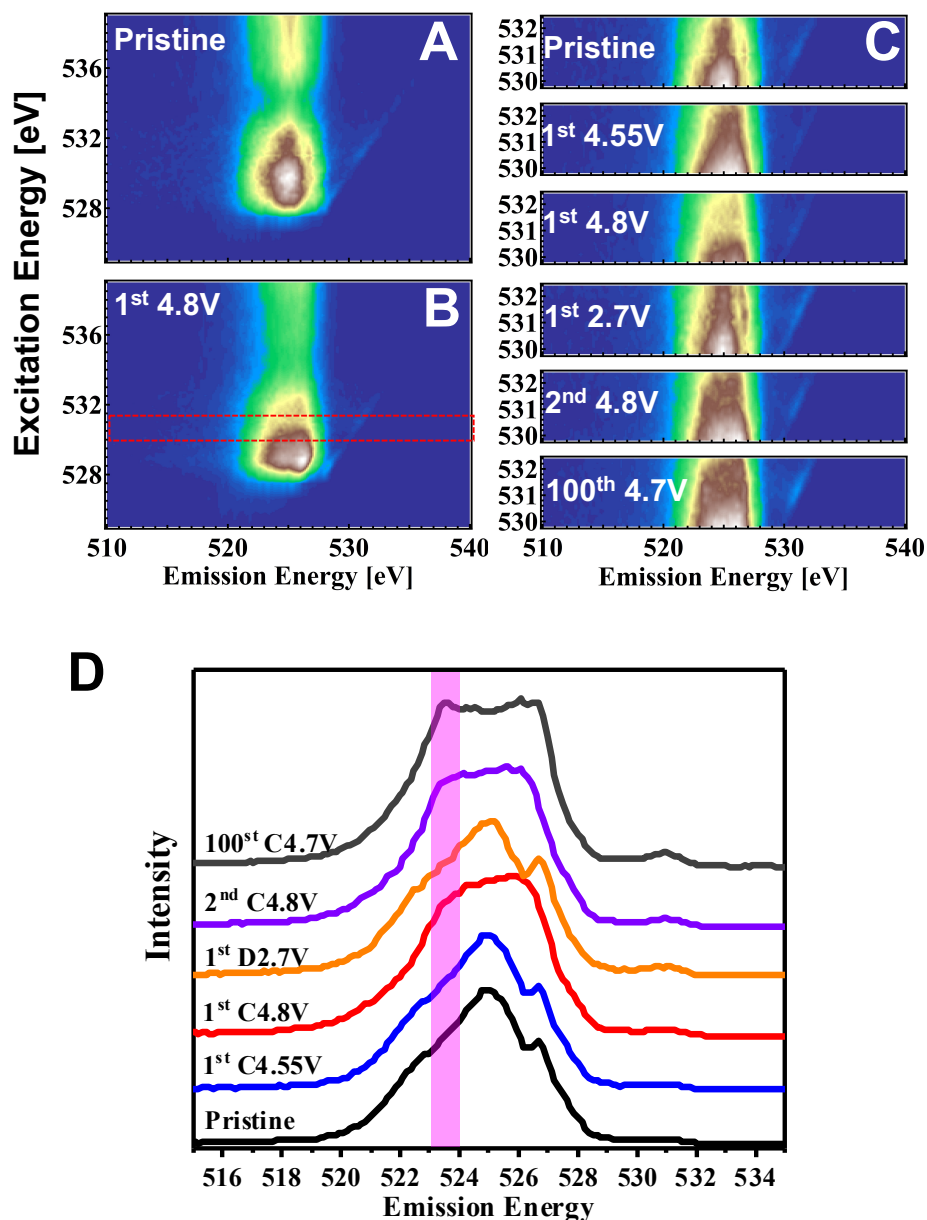


Supplementary Fig. 8. HRTEM images of surface Cr-enrichment BR-NCM (**A**) before and (**B**) after 100 cycles (3.0-4.7 V). HAADF-STEM images of surface Cr-enrichment BR-NCM (**C**) before and (**D**) after 100 cycles (3.0-4.7 V).

As shown below, the layered structure of BR-NCM at the surface was still well-maintained after cycling due to surface Cr enrichment (Supplementary Figs. 8A and 8B), while the internal particle has shown visible damage and formation of voids (Supplementary Fig. 8D) due to the existence of internal domain boundaries (Supplementary Fig. 8C).

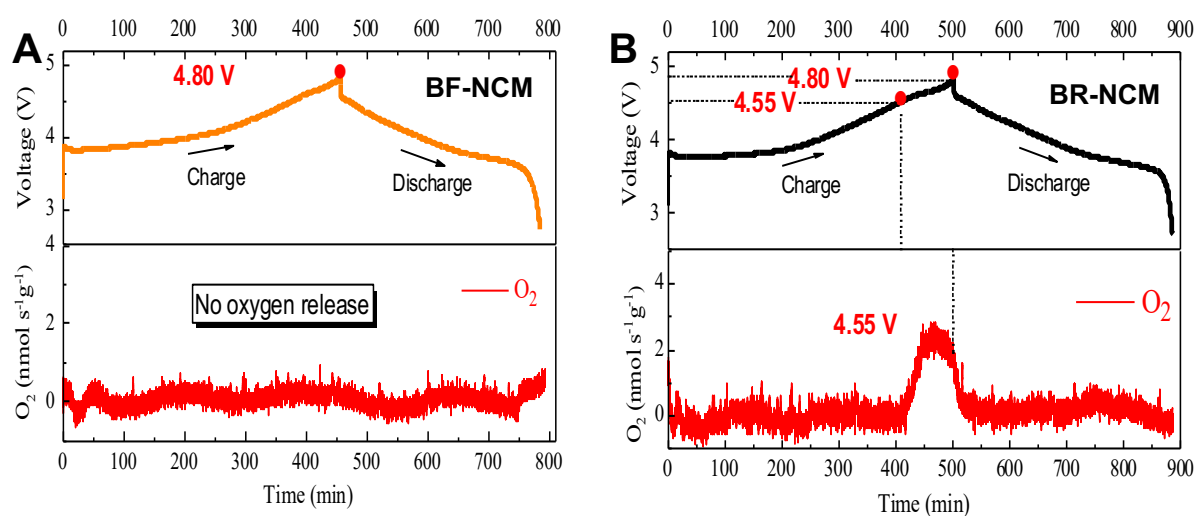


Supplementary Fig. 9. The O K-edge mRIXS map of BF-NCM cathode at 100th charge (4.7V, **A**) and discharge (2.7V, **B**) state. (**C**) Integrated RIXS intensity in the characteristic energy range, from 530.6 to 531.8 eV, of BF-NCM electrodes at the 100th charged (4.7V) and discharged (2.7V) states. The clear contrast on the strong 523.7 eV peak of the 100th cycle charged (red) and its disappearance of the discharged state (black) suggests the highly reversible OR for a hundred cycles. The colour in (**A**) and (**B**) represents the intensity, with white and blue represents high and low, respectively.

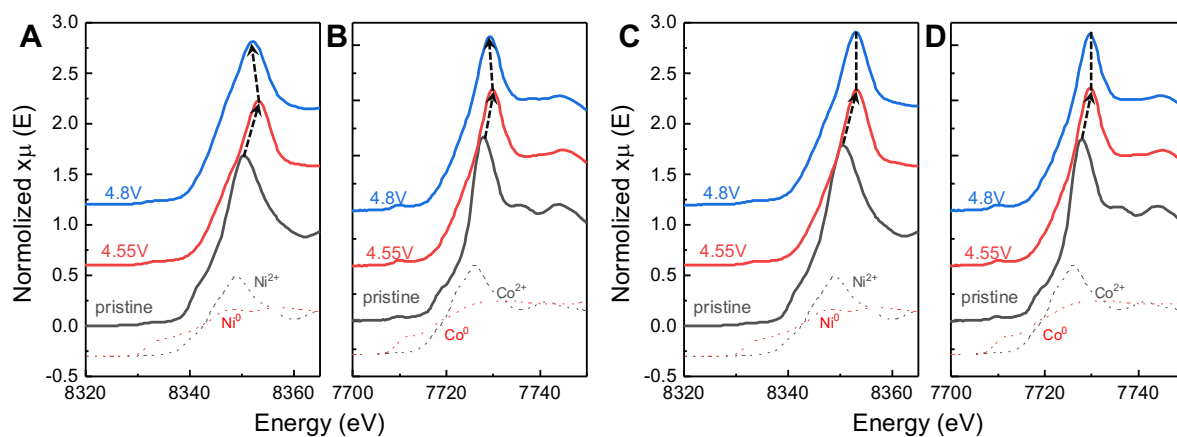


Supplementary Fig. 10. (A-C) The O K-edge mRIXS map of BR-NCM cathodes at different charge/discharge states. (D) Integrated mRIXS intensity in the characteristic energy range, from 530.6 to 531.8 eV, of OR for BR-NCM cathode at different charge/discharge states. The colour in (A-C) represents the intensity, with white and blue represents high and low, respectively.

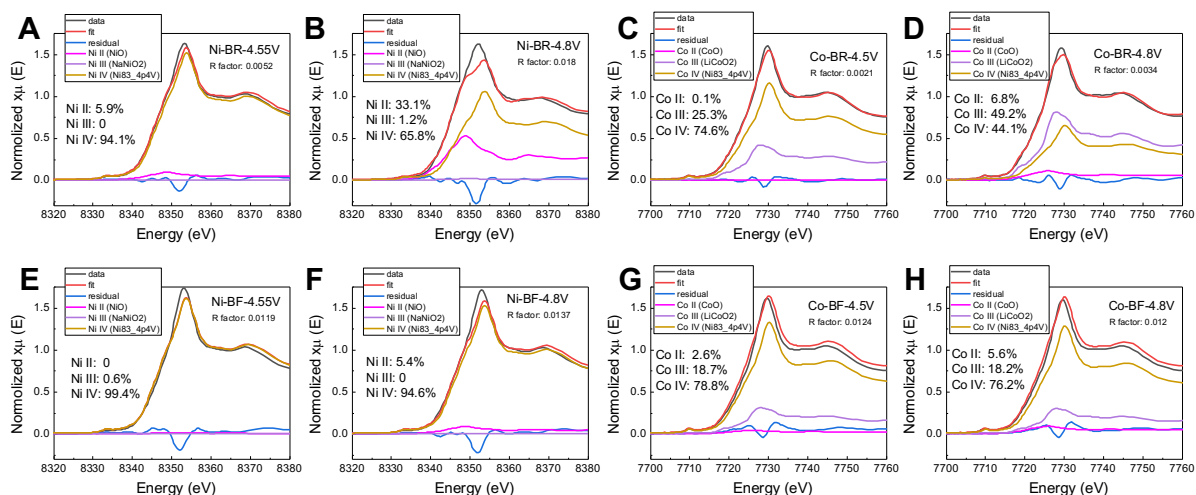
As shown, a peak at 527 eV could be observed in the RIXS spectra. there are two contributions to the features around the 527eV peak, a relatively weak feature that does emerge with oxidized oxygen and non-intrinsic feature not from the electrode material itself. Because the intrinsic part is well/better represented by the 523.7 eV feature, we thus focus on the evolution of the 523.7 eV peak to discuss the lattice oxygen activities instead.



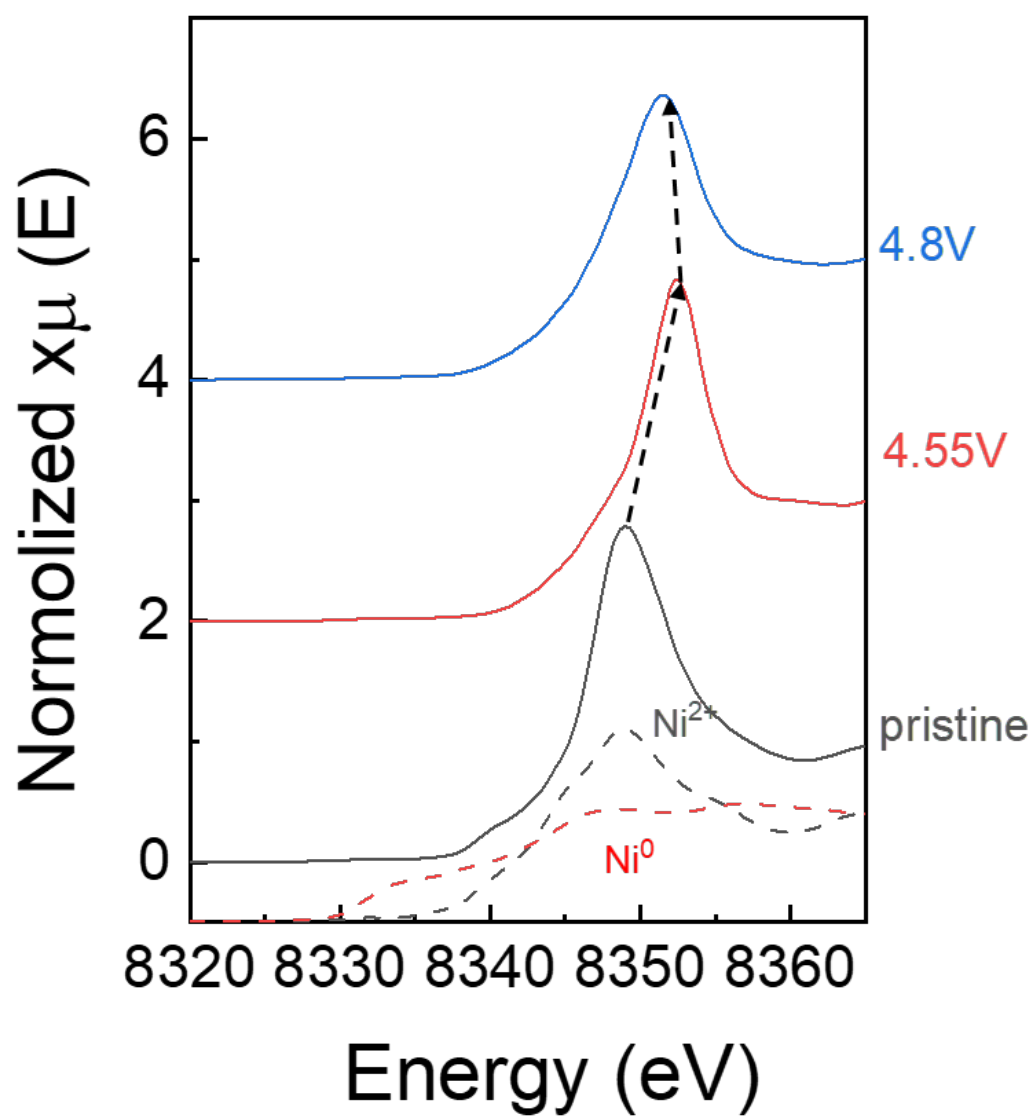
Supplementary Fig. 11. In-situ DEMS characterization of (A) BF-NCM and (B) BR-NCM cathode during charge/discharge between 2.7 and 4.8 V at 45.6 mA/g.



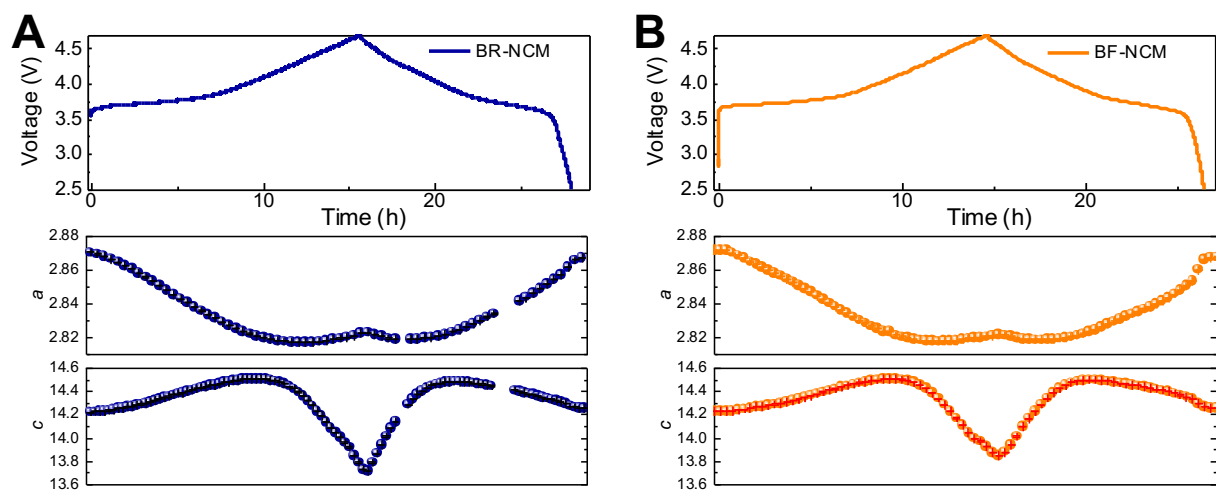
Supplementary Fig. 12. Ni K-edge XAS spectra of BR-NCM (A) and BF-NCM (C) cathodes at different charge states. Co K-edge XAS spectra of BR-NCM (B) and BF-NCM (D) cathodes at different charge states.



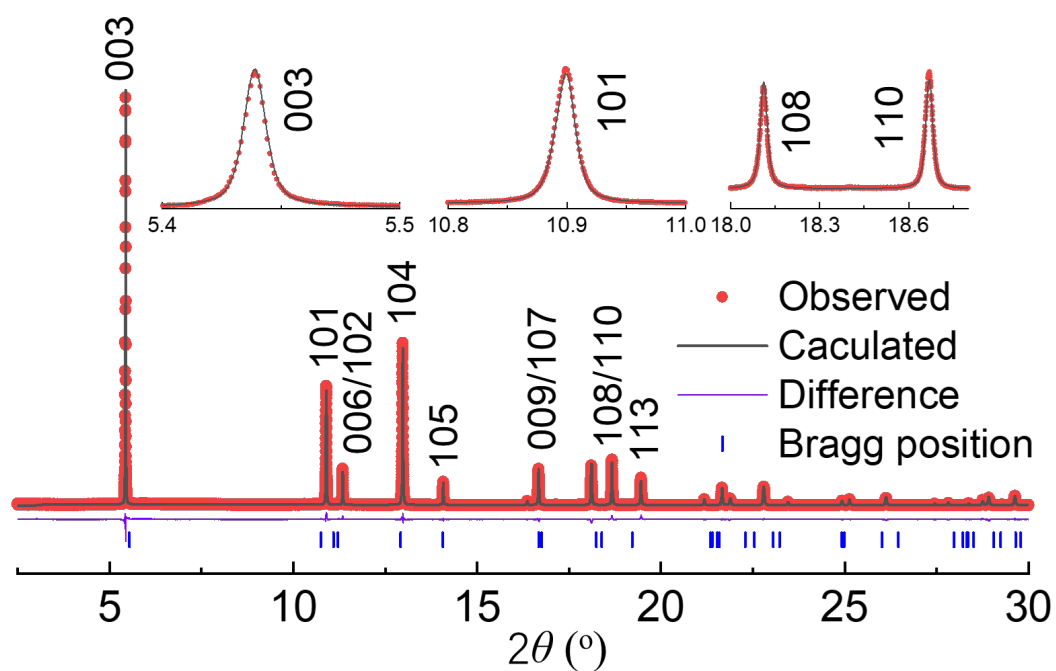
Supplementary Fig. 13. Linear combination fitting of transition metal (TM) K-edge XANES spectra of charged cathodes: Ni K-edge XANES of BR-NCM at 4.55 V (A) and 4.8 V (B); Co K-edge XANES of BR-NCM at 4.55 V (C) and 4.8 V (D). Ni K-edge XANES of BF-NCM at 4.55 V (E) and 4.8 V (F); Co K-edge XANES of BF-NCM at 4.55 V (G) and 4.8 V (H).



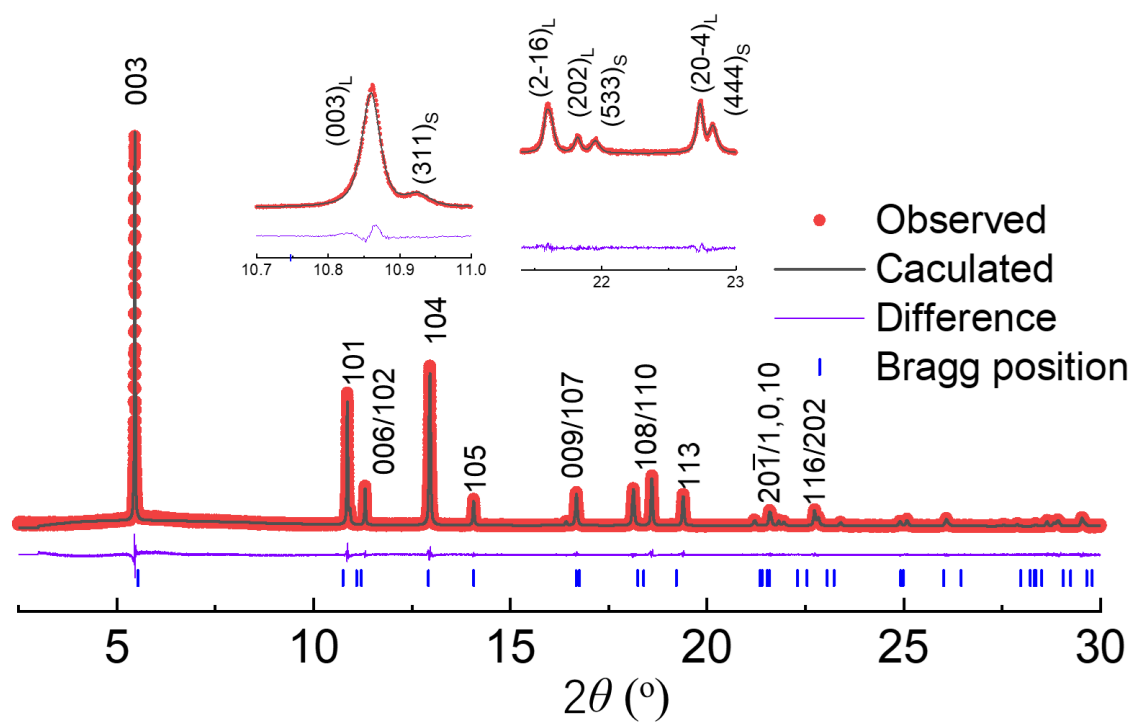
Supplementary Fig. 14. Ni K-edge XAS spectra of C-NCM cathode at different state of charge.



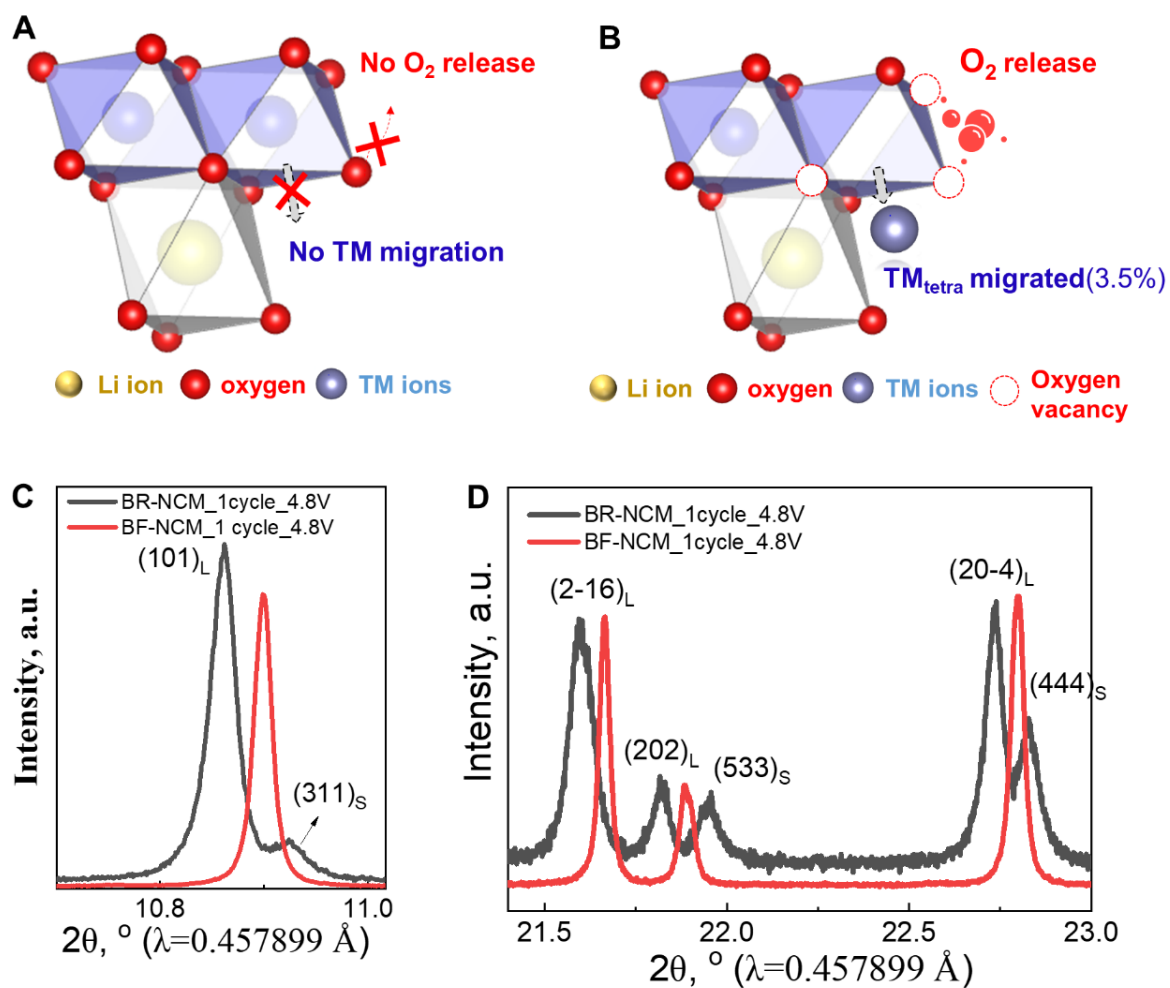
Supplementary Fig. 15. Lattice parameters change of (A) BR-NCM and (B) BF-NCM cathodes during charge/discharge within 3.0-4.7 V.



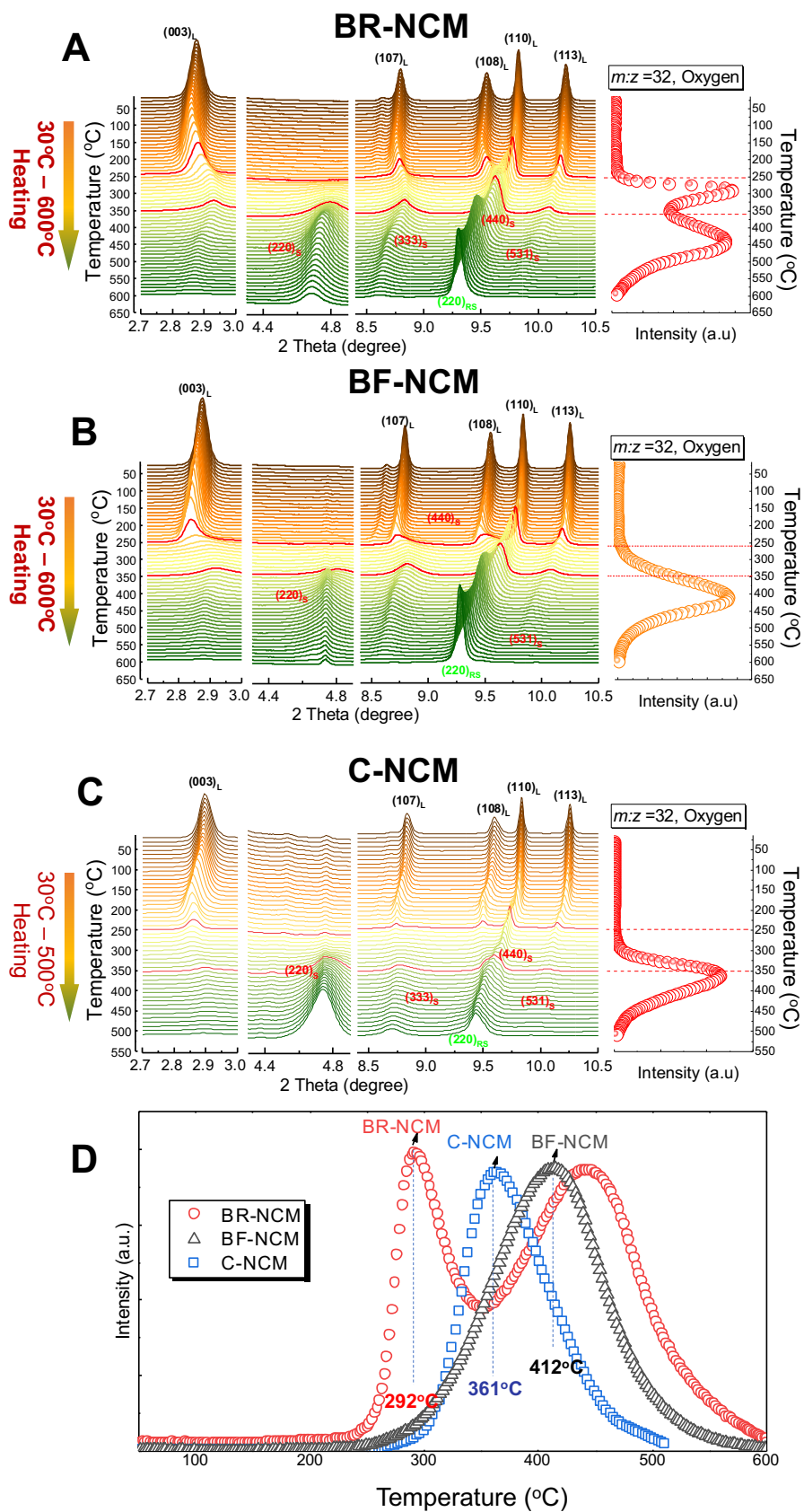
Supplementary Fig. 16. HRXRD pattern and Rietveld refinement of BF-NCM cathode after charging to 4.8V, with the enlarged figures showing the (003), (101) and (108, 110) diffraction peaks.



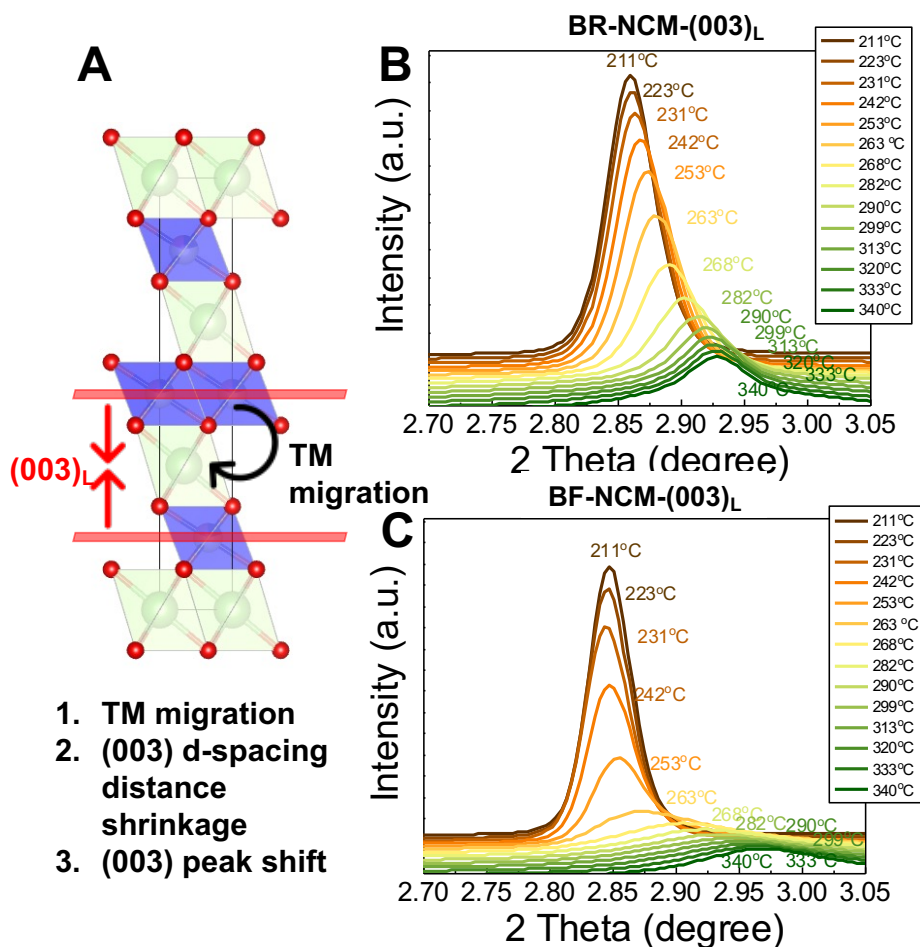
Supplementary Fig. 17. HRXRD pattern and Rietveld refinement of BR-NCM cathode after charging to 4.8 V. L and S represent layered and spinel phase respectively.



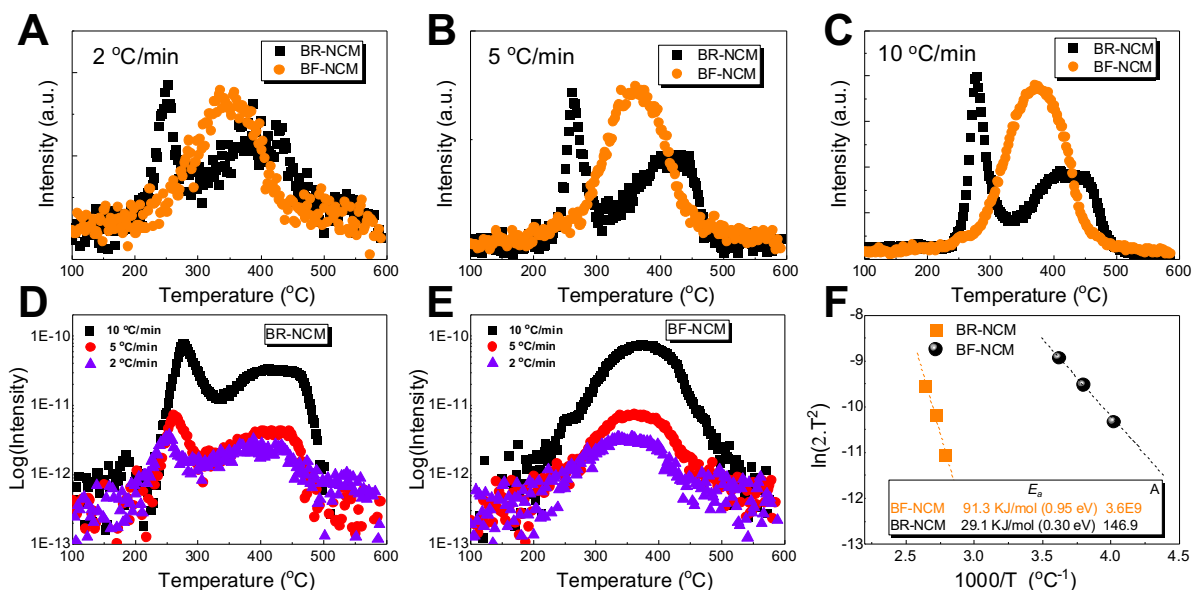
Supplementary Fig. 18. (A, B) Schematic illustration of the lattice structure of the 4.8V charged BF-NCM and BR-NCM cathodes, showing that BF-NCM preserved the layered structure without transition metal migration and lattice oxygen release, compared with lattice oxygen release and 3.5% transition metal cations migrated to the tetrahedra site for BR-NCM cathode. (C, D) The zoomed-in comparison of the HRXRD pattern of BF-NCM and BR-NCM cathode after charging to 4.8 V. L and S represent layered and spinel phase respectively.



Supplementary Fig. 19. In-situ HEXRD and oxygen evolution for charged (A) BR-NCM, (B) BF-NCM and (C) C-NCM cathode during heating. (D) Comparison on the oxygen evolution behaviours of different cathodes.

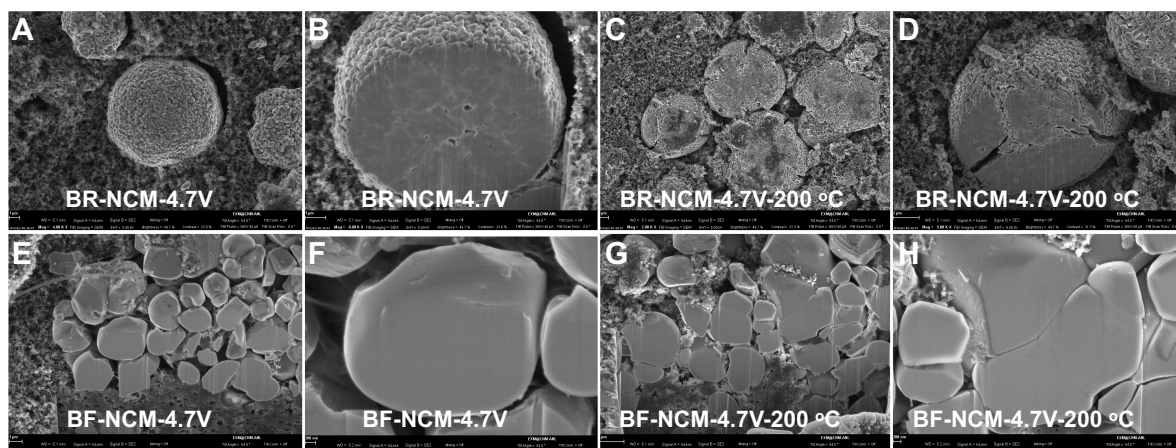


Supplementary Fig. 20. In-situ HEXRD (003) peak evolution of charged BR-NCM and BF-NCM cathodes during heating: (A) Schematic of transition metal migration and the corresponding (003) *d*-spacing shrinkage. (B) Diffraction plots of (003) peak evolution of BR-NCM cathode during heating. (C) Diffraction plots of (003) peak evolution of BF-NCM cathode during heating.

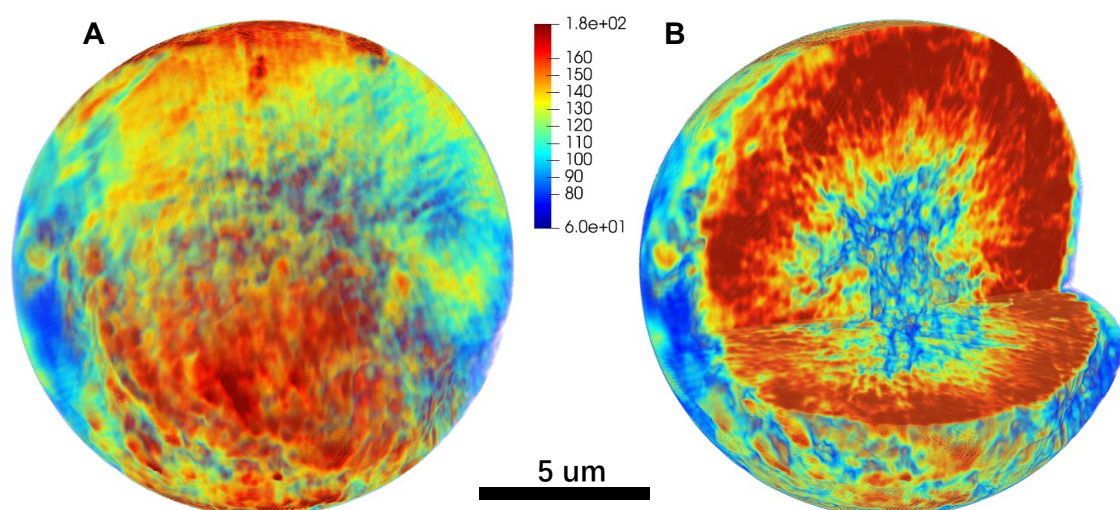


Supplementary Fig. 21. Kinetic barriers of oxygen release for charged cathodes: (A-C) DSC profiles of charged cathodes at different heating rates. (D-F) The fitting of the first oxygen release kinetics of charged BR-NCM and BF-NCM based on the Arrhenius equation.

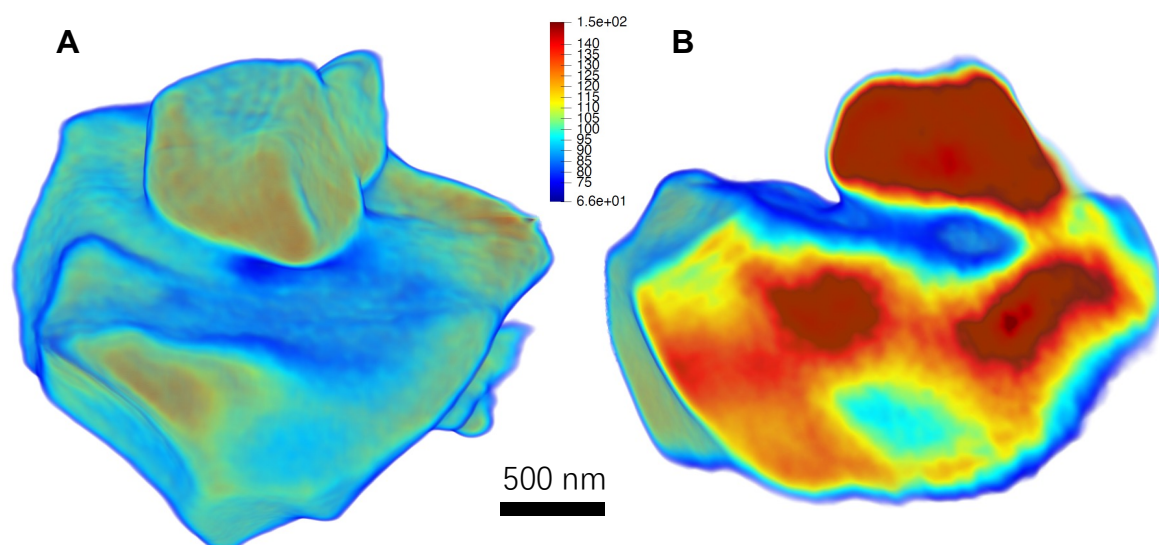
The oxygen release kinetics for charged BR-NCM and BF-NCM were calculated by the Arrhenius equation with a Netzsch thermal gravity analysis and mass spectroscopy (TGA/MS) system. The active materials are the same as described for the HEXRD measurement. Approximately 5 mg charged cathode materials was loaded in an alumina pan with a hole on the top for measurement. Ultra-high purity argon gas was used as loading gas for oxygen release analysis. Heating rates of 2 °C/min, 5 °C/min, and 10 °C/min were used to calculate the oxygen release kinetics. The first oxygen release peaks for the charged BR-NCM cathode are 250 °C, 262 °C, and 279 °C at 2 °C/min, 5 °C/min, and 10 °C/min, respectively. As shown in Supplementary Fig. 21, in the case of charged BF-NCM, the first oxygen release peaks are 360 °C, 271 °C, and 283 °C at 2 °C/min, 5 °C/min, and 10 °C/min, respectively. The calculated activation energy barrier for the first oxygen release of the 4.2-V-charged BR-NCM cathode is 0.3 eV (29.1 kJ/mol), while for the BF-NCM cathode at the same de-lithiation state, the energy barrier is 0.95 eV (91.3 kJ/mol).



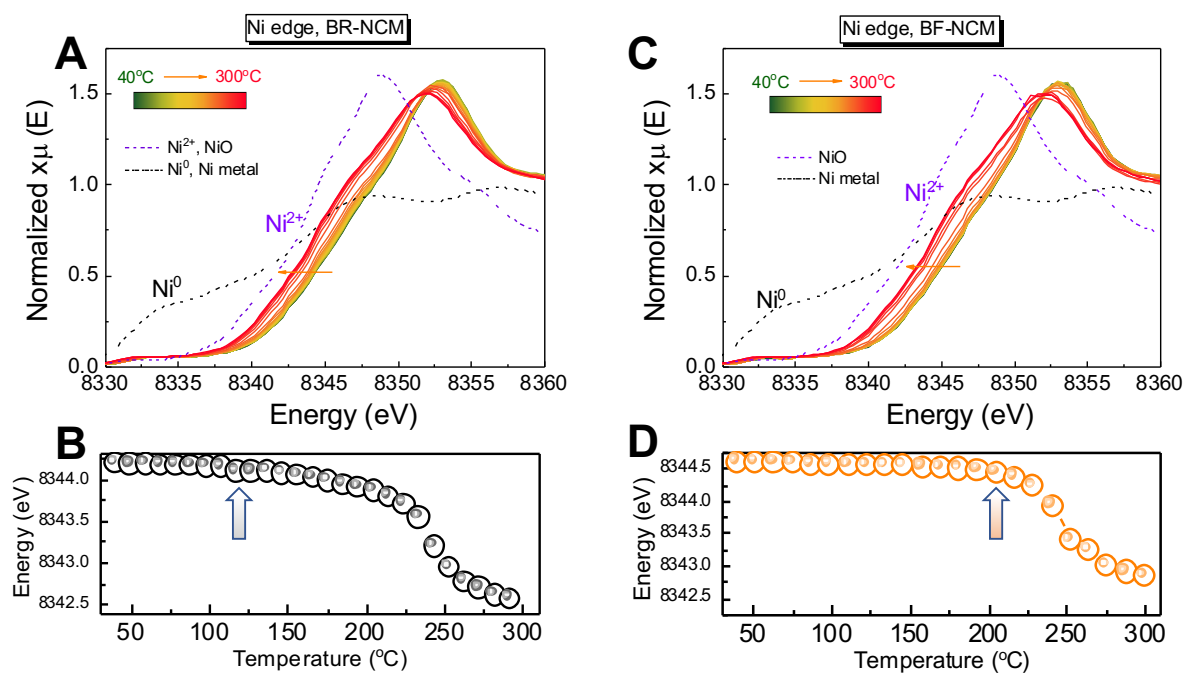
Supplementary Fig. 22. Morphology characterization of 4.7-V-charged cathodes before and after heating to 200 °C. **(A, B)** Cross-section SEM images of charged BR-NCM cathode before heating. **(C, D)** Cross-section SEM images of charged BR-NCM cathode after heating to 200 °C. **(E, F)** Cross-section SEM images of charged BF-NCM cathode before heating. **(G, H)** Cross-section SEM images of charged BF-NCM cathode after heating to 200 °C.



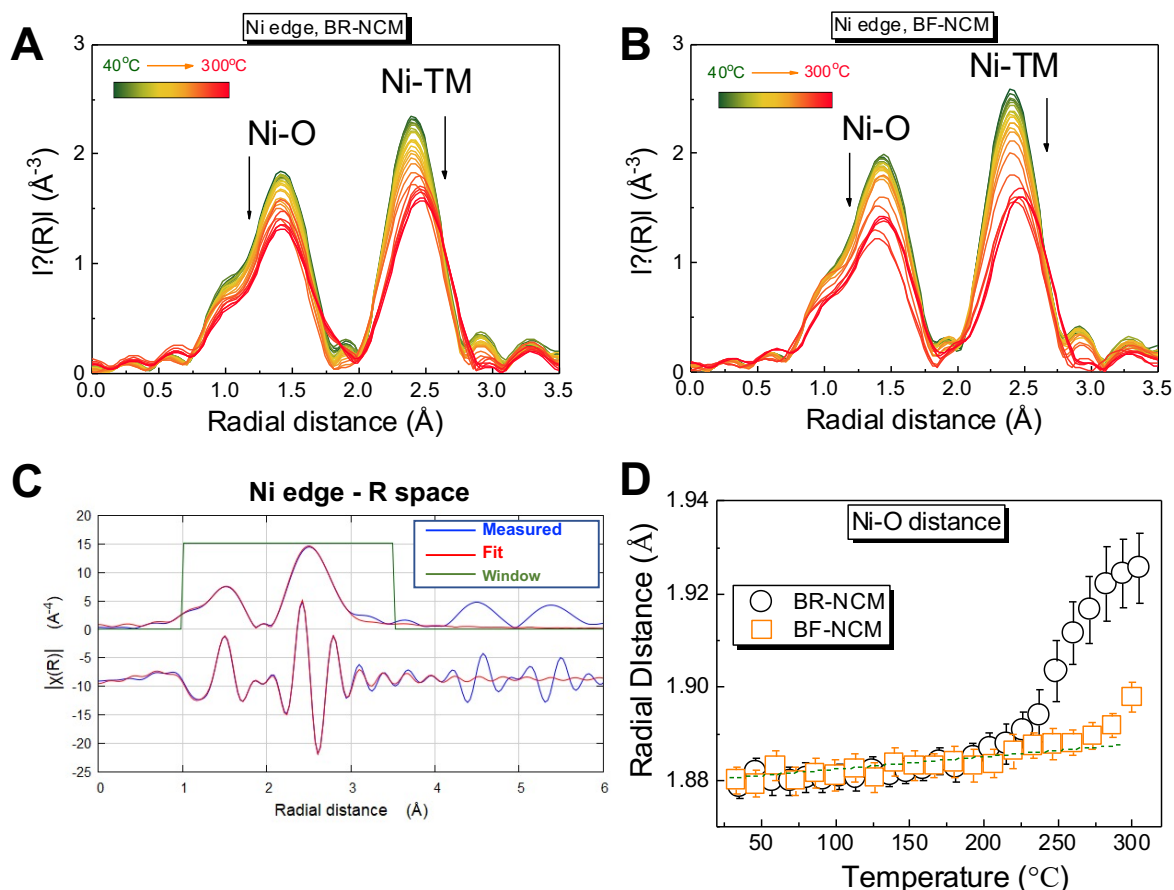
Supplementary Fig. 23. Ptychographic X-ray computed nanotomography of charged BR-NCM after heating to 210 °C: (A) The whole particle and (B) cross-section image. The results clearly show the particle cracking (low electron density map intensity, where red and blue represent highest and lowest intensity, respectively) in the central interior after heating. The colour in (A) and (B) represents the relative intensity, with red and blue represents high and low, respectively.



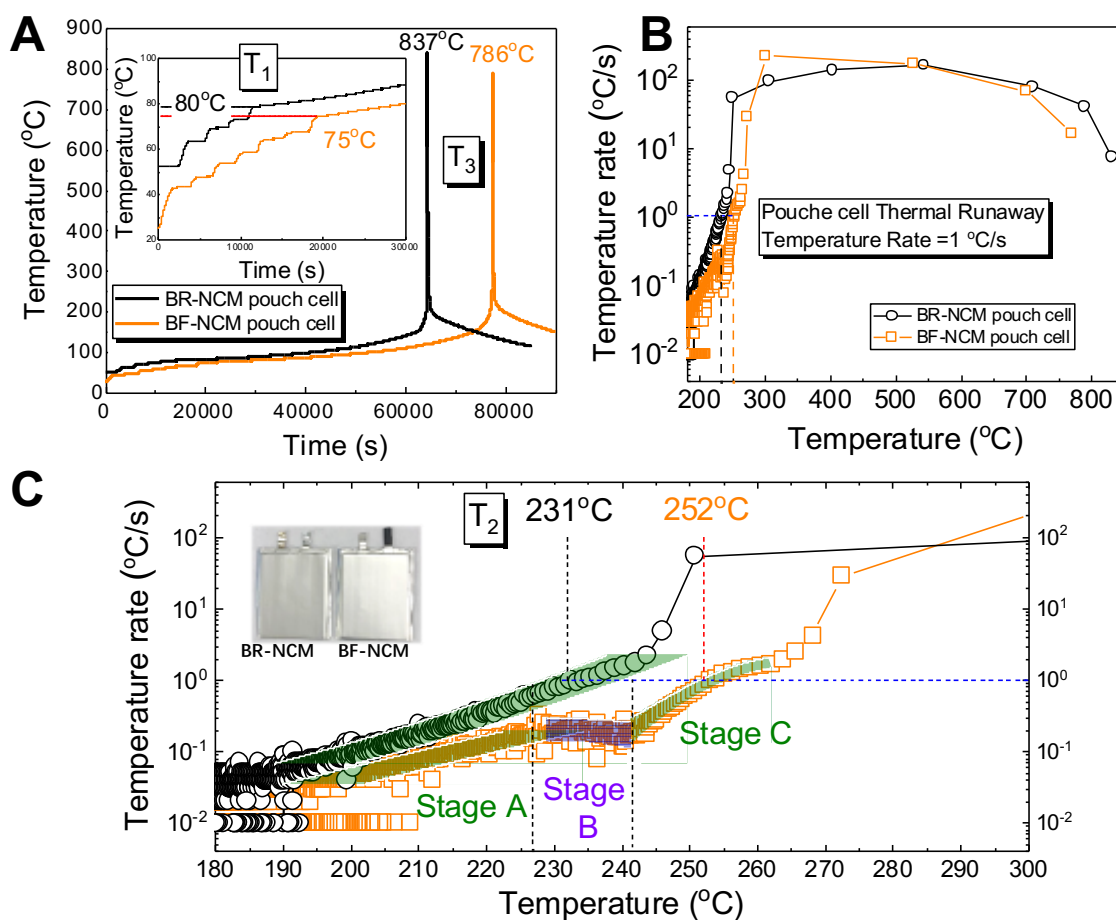
Supplementary Fig. 24. Ptychographic X-ray computed nanotomography of charged BF-NCM after heating to 210 °C: **(A)** The whole particle and **(B)** cross-section image. The results indicate no visible cracking in the BF-NCM cathode even after heating to 210 °C. The colour in **(A)** and **(B)** represents the relative intensity, with red and blue represents high and low, respectively.



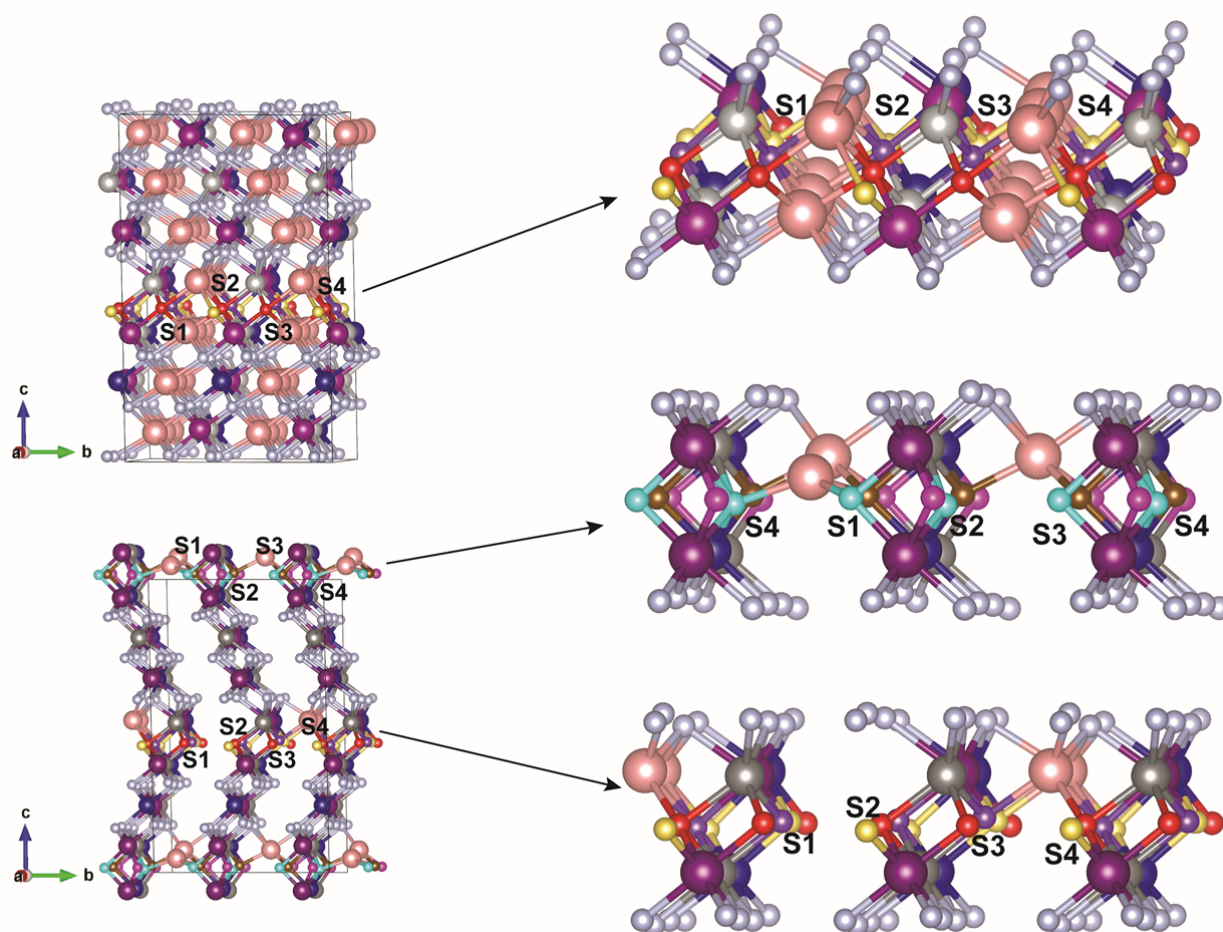
Supplementary Fig. 25. In-situ Ni K-edge XANES spectra and their corresponding intersection of absorption plots as a function of normalized energy, with $y=0.5$ for charged cathodes during heating. (A, B) charged BR-NCM and (C, D) charged BF-NCM cathodes. Upon heating, both charged cathodes showed a decrease of the Ni valence state but with faster kinetics in the charged BR-NCM cathode as indicated by the lower on-set temperature.



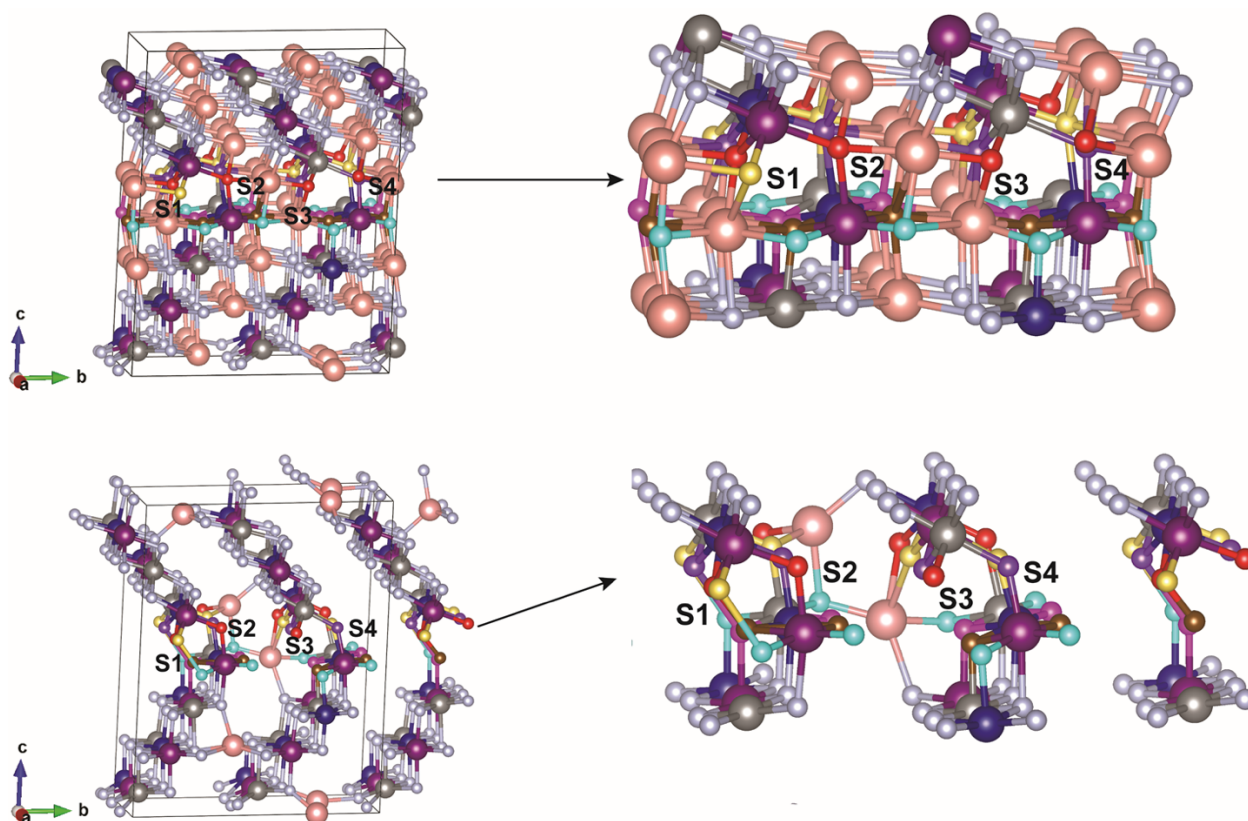
Supplementary Fig. 26. In-situ Ni K-edge EXAFS characterization of charged cathodes during heating: **(A, B)** Ni K-edge EXAFS of charged BR-NCM and BF-NCM cathodes during heating, respectively. **(C)** Example of EXAFS fitting for the first-shell Ni-O and Ni-TM bond distance. **(D)** The first-shell EXAFS fitting of the Ni-O bond distance of charged cathodes during heating. Through the first-shell EXAFS fitting, the Ni-O bonding evolution during heating was tracked. The Ni-O distance of BR-NCM increased tremendously beyond 190 $^{\circ}\text{C}$, indicating Ni^{4+} reduction and O^{2-} oxidation. Strikingly, BF-NCM shows limited increase in the Ni-O bond distance, confirming no oxygen oxidation and TM reduction taking place. The errors bars in **(D)** refer to the statistical deviation.



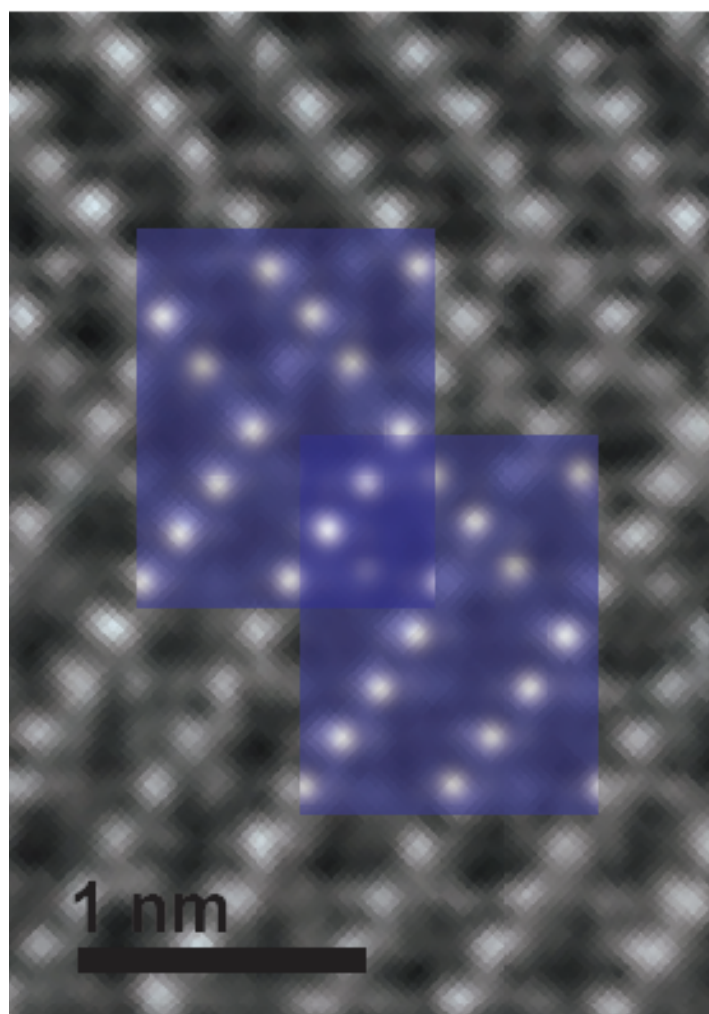
Supplementary Fig. 27. Accelerating rate calorimeter test of BR-NCM and BF-NCM pouch cells after charging to 4.2 V vs. graphite: **(A)** Overall thermal runaway temperature profile. **(B)** Increasing temperature rate curves between 200°C and 800°C. **(C)** Same curves for narrower temperature range. A characteristic self-terminated temperature rate increment for the BF-NCM cathode is reported for the first time (Stage B). Compared to the exponential temperature rise in the BR-NCM cathode, BF-NCM constrained the self-accelerated chain reactions by suppressing the irreversible oxygen release.



Supplementary Fig. 28. Simulated atomic structures of (Top) fully lithiated $\text{Li}_3\text{MnCoNiO}_6$ and (Bottom) partially lithiated $\text{Li}_{0.375}\text{NiCoMnO}_6$ with tilt boundary structure and their zoomed-in view. Larger spheres with orange, navy, purple, and grey colour represent Li, Co, Mn and Ni atoms, respectively, while oxygen atoms at DBs were labelled by smaller spheres with colour of yellow, red, purple, cyan, brown and magenta., oxygen atoms at the bulk are marked by white spheres.



Supplementary Fig. 29. Simulated atomic structures of (Top) fully lithiated $\text{Li}_3\text{MnCoNiO}_6$ and (Bottom) partially lithiated $\text{Li}_{0.357}\text{NiCoMnO}_6$ with tilt boundary structure and their zoomed-in view. Larger spheres with orange, navy, purple, and grey colour represent Li, Co, Mn and Ni atoms, respectively, while oxygen atoms at DBs were labelled by smaller spheres with colour of yellow, red, purple, cyan, brown and magenta., oxygen atoms at the bulk are marked by white spheres.



Supplementary Fig. 30. Computed HAADF-STEM image of fully lithiated $\text{Li}_3\text{MnCoNiO}_6$ after relaxation.

Supplementary Table 1. HRXRD Rietveld refinement results of pristine BF-NCM

Formula		BF-NCM particle			
Crystal system		Rhombohedral			
Space group		$R\bar{3}m$			
Atom	Site	x	y	z	Occupancy
Li	3a	0	0	$\frac{1}{2}$	0.97664(5)
Ni2	3a	0	0	$\frac{1}{2}$	0.02336(5)
Ni1	3b	0	0	0	0.6
Mn	3b	0	0	0	0.2
Co	3b	0	0	0	0.2
O	6c	0	0	0.24130 (4)	1
a -axis/ Å		2.86605(0)			
c -axis/ Å		14.20540(1)			
Volume/ Å ³		101.05356(1)			
R_{wp} / %		8.465			

Supplementary Table 2. HRXRD Rietveld refinement results of pristine N-NCM

Formula		N-NCM			
Crystal system		Rhombohedral			
Space group		$R\bar{3}m$			
Atom	Site	x	y	z	Occupancy
Li	3a	0	0	1/2	0.9653(5)
Ni2	3a	0	0	1/2	0.0347(5)
Ni1	3b	0	0	0	0.6
Mn	3b	0	0	0	0.2
Co	3b	0	0	0	0.2
O	6c	0	0	0.24141(3)	1.0
a -axis/Å		2.869266(5)			
c -axis/Å		14.21919(3)			
Volume/Å ³		101.3788(4)			
R_{wp} /%		10.457			

Supplementary Table 3. HRXRD Rietveld refinement results of pristine C-NCM

Formula		C-NCM			
Crystal system		Rhombohedral			
Space group		$R\bar{3}m$			
Atom	Site	x	y	z	Occupancy
Li	3a	0	0	$\frac{1}{2}$	0.9769(6)
Ni2	3a	0	0	$\frac{1}{2}$	0.0231(6)
Ni1	3b	0	0	0	0.6
Mn	3b	0	0	0	0.2
Co	3b	0	0	0	0.2
O	6c	0	0	0.24141(4)	1
a -axis/ Å		2.868287(4)			
c -axis/ Å		14.21299(3)			
Volume/ Å ³		101.2655(3)			
R_{wp} / %		12.839			

Supplementary Table 4. HRXRD Rietveld refinement results of pristine BR-NCM

Formula		BR-NCM			
Crystal system		Rhombohedral			
Space group		$R\bar{3}m$			
Atom	Site	x	y	z	Occupancy
Li	3a	0	0	$\frac{1}{2}$	0.96691(3)
Ni2	3a	0	0	$\frac{1}{2}$	0.03309 (3)
Ni1	3b	0	0	0	0.6
Mn	3b	0	0	0	0.2
Co	3b	0	0	0	0.2
O	6c	0	0	0.24141 (2)	1
a -axis/ Å		2.86835(0)			
c -axis/ Å		14.21987(3)			
Volume/ Å ³		101.319 (0)			
R_{wp} / %		8.748			

Supplementary Table 5. Comparison on the electrochemical performance of BF-NCM, N-NCM, C-NCM and BR-NCM with reported NCM cathodes

Cathode	Voltage window	Initial discharge capacity (mAh/g)	Capacity retention @ cycle number	Ref.
BR-NCM	3.0-4.7V	227.0	88%@100 th cycle	This work
BF-NCM	3.0-4.7V	220.8	97%@100 th cycle	This work
N-NCM	3.0-4.7V	218.3	70%@80 th cycle	This work
C-NCM	3.0-4.7V	219.1	71%@100 th cycle	This work
SC $\text{LiNi}_{0.76}\text{Mn}_{0.14}\text{Co}_{0.1}\text{O}_2$	2.7-4.3V	193.4	72%@200 th cycle	<i>Science</i> , 2020, 370, 1313.
Ta-Ni90	2.7-4.3V	227	75%@100 th cycle	<i>Nat. Commun.</i> , 2021, 12, 6552.
VG-NCM811	2.7-4.4V	200	87%@100 th cycle	<i>Nat. Commun.</i> , 2021, 12, 2350.
LiAlO_2 -coated $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$	2.7-4.3V	200	97.4%@100th cycle	<i>Nat. Commun.</i> , 2021, 12, 4564.
PEDOT-skinned $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05}\text{O}_2$	2.7-4.3V	175	91%@100 th cycle	<i>Nat. Energy.</i> , 2019, 4, 484.
$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$	2.7-4.7V	200	70%@100 th cycle	<i>Nat. Commun.</i> , 2017, 8, 14101.
SC $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$	2.8-4.2V	120	93.8%@200 th cycle	<i>Nat. Commun.</i> , 2020, 11, 3050.
SC $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$	2.8-4.3V	140	86.3%@200 th cycle	<i>Nat. Commun.</i> , 2020, 11, 3050.
SC $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$	2.8-4.7V	215	25.6%@200 th cycle	<i>Nat. Commun.</i> , 2020, 11, 3050.
$\text{Co}_x\text{B-NMC811}$	3.0-4.4V	200	82.2%@200 th cycle	<i>Nat. Energy.</i> , 2021, 6, 362.
Sulfonamide-based electrolyte NCM811	3.0-4.7V	231	88%@90 th cycle	<i>Nat. Energy.</i> , 2021, 6, 495.

Supplementary Table 6. Discharge capacity, average working voltage and energy density of NCM622 cathode at different charge cut-off voltage

	Discharge capacity (mAh/g)	Discharge mean voltage (V)	Energy density (Wh/Kg)	Energy density increasement (%)
4.3V	177.8	3.785	672.9	
4.5V	184.7	3.789	699.8	4.0
4.6V	206.7	3.822	790.0	17.4
4.7V	219.9	3.847	845.9	25.7

Supplementary Table 7. HRXRD Rietveld refinement results of 4.8 V-charged BF-NCM cathode

Formula		BF-NCM 4.8V			
Crystal system		Rhombohedral			
Space group		$R\bar{3}m$			
Atom	Site	x	y	z	Occupancy
Li	3a	0	0	$\frac{1}{2}$	0.1193(5)
Ni2	3a	0	0	$\frac{1}{2}$	0.0807(5)
Ni1	3b	0	0	0	0.6
Mn	3b	0	0	0	0.2
Co	3b	0	0	0	0.2
O	6c	0	0	0.23741(5)	1
a -axis/ Å		2.823197(6)			
c -axis/ Å		14.47868(6)			
Volume/ Å ³		99.9406(6)			
R_{wp} / %		10.4008979			

Supplementary Table 8. HRXRD Rietveld refinement results of 4.8 V-charged BR-NCM cathode

Formula		BR-NCM 4.8V			
Crystal system		Rhombohedral			
Space group		<i>R-3m</i>			
Atom	Site	x	y	z	Occupancy
Li	3a	0	0	1/2	0.1370(7)
Ni2	3a	0	0	1/2	0.0630(7)
Ni1	3b	0	0	0	0.6
Mn	3b	0	0	0	0.2
Co	3b	0	0	0	0.2
O	6c	0	0	0.24111(1)	1
TM _{tetra}	6c	0	0	0.0447(7)	0.0350(4)
<i>a</i> -axis/ Å		2.833975(15)			
<i>c</i> -axis/ Å		14.42987(16)			
<i>Volume</i> / Å ³		100.3656(15)			
<i>Rwp</i> / %		10.8871349			