

Supporting Information

Boron doping modulates the electrostatic interaction of Na-O bond for inducing P2/O3 biphasic structure in layered oxide cathode

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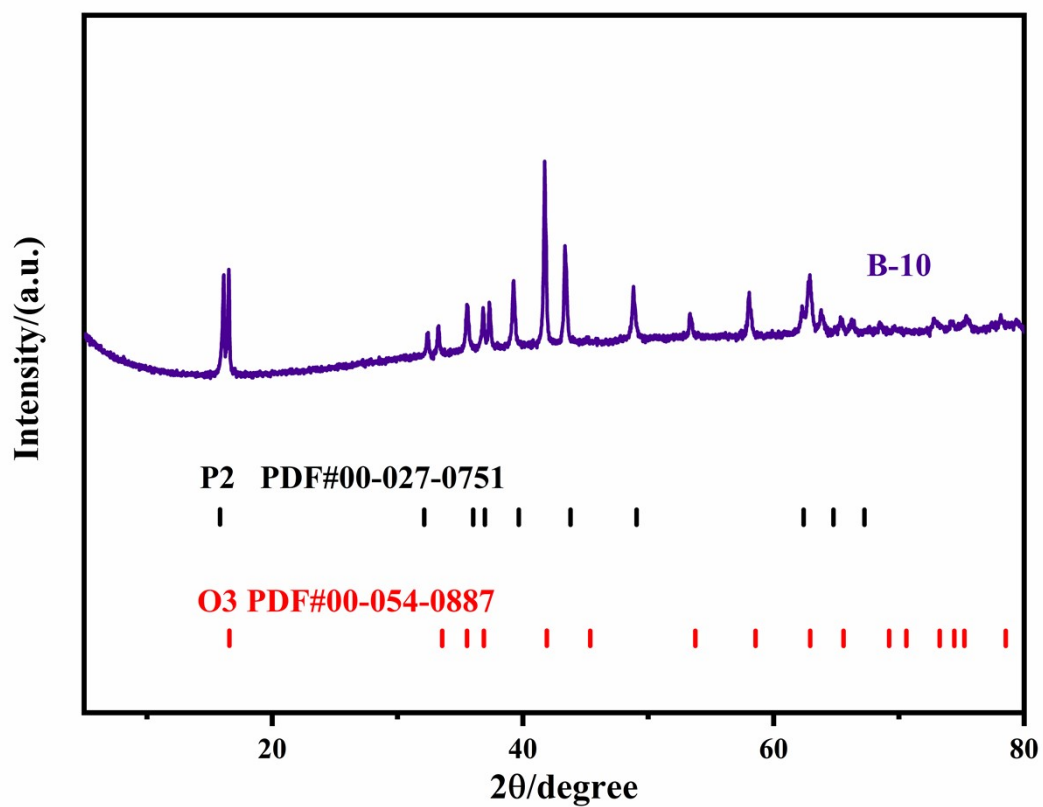


Figure S1. The XRD pattern of the B-10 ($\text{Na}_{0.8}\text{Fe}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{B}_{0.10}\text{O}_2$)

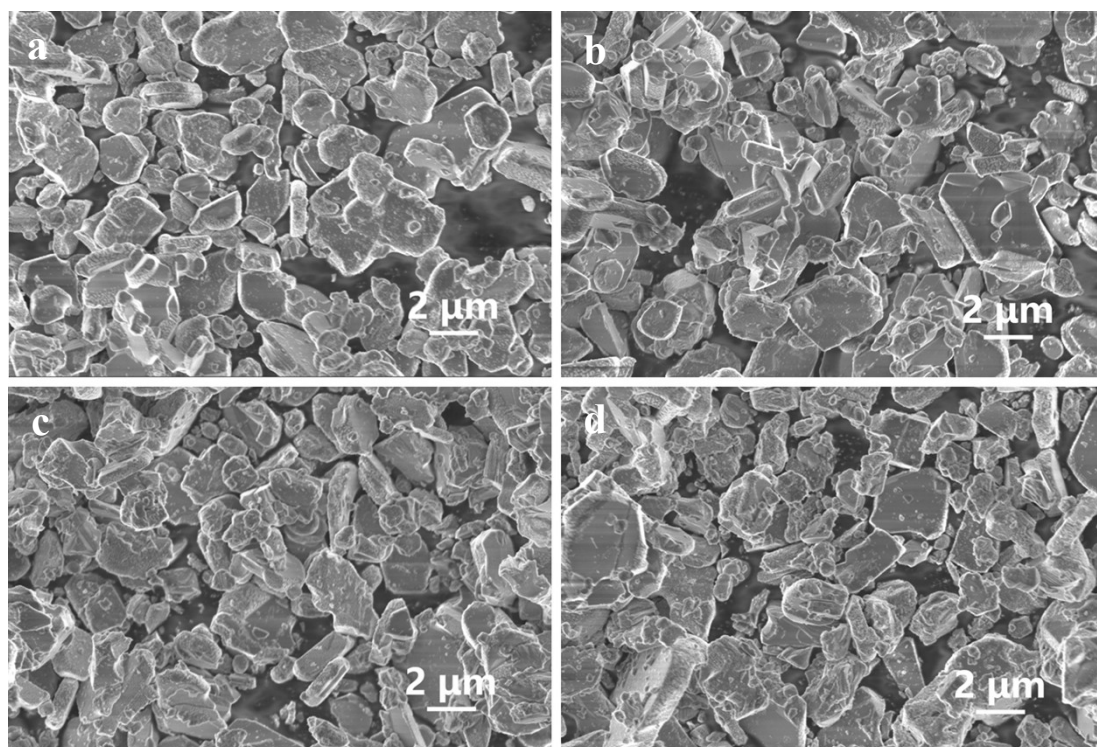


Figure S2. SEM images of a) B-1 , b) B-2, c) B-3 and d) B-4 powders

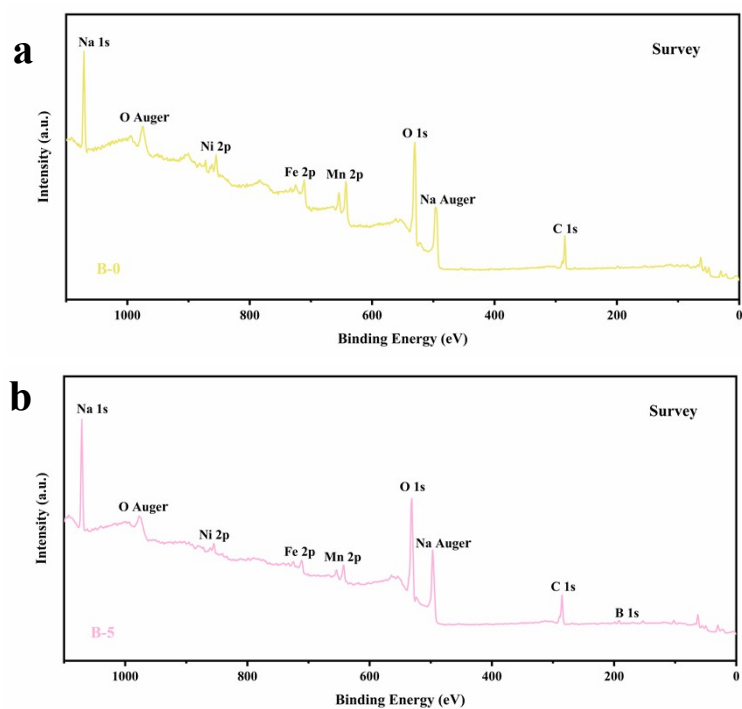


Figure S3. The XPS Survey spectrum: a) B-0, B) B-5

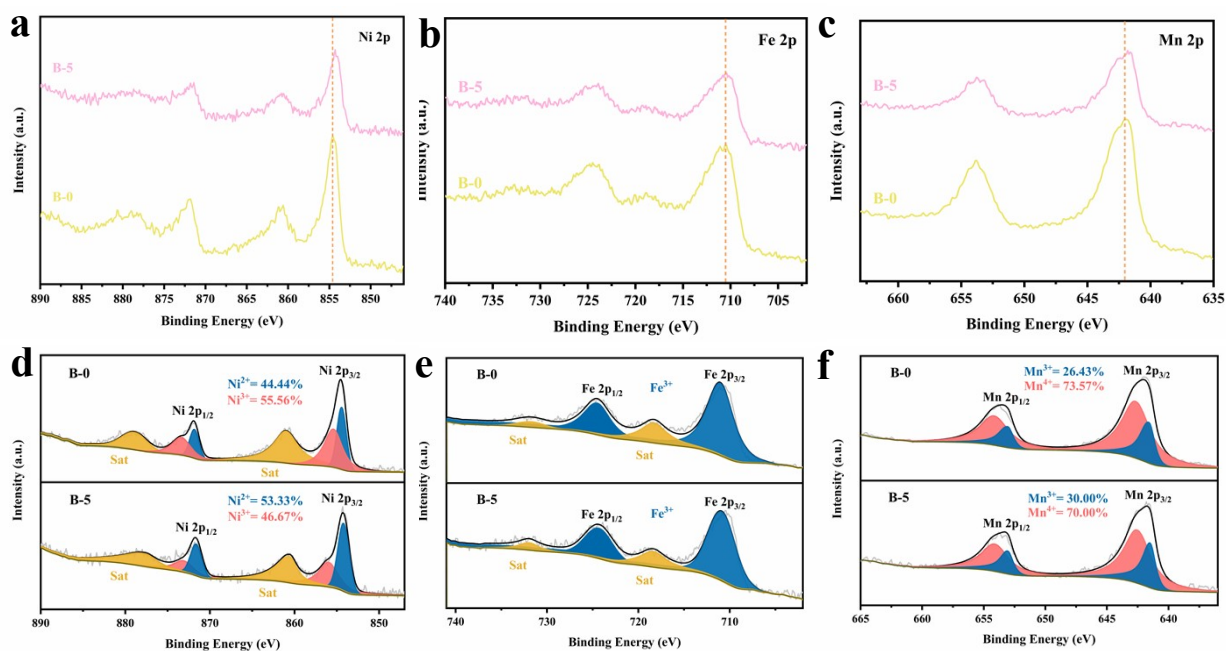


Figure S4. The XPS spectra of a,d) Ni 2p, b,e) Fe 2p and c,f) Mn 2p in B-0 and B-5

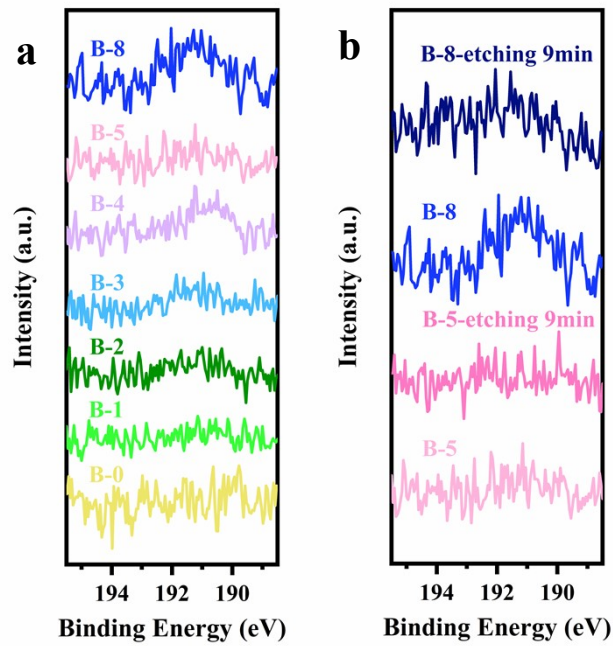


Figure S5. a) XPS spectra of B-x (x=0, 1, 2, 3, 4, 5, 8) for B1s. b) XPS spectra Comparison of B-x (x=5, 8) for B1s after etching

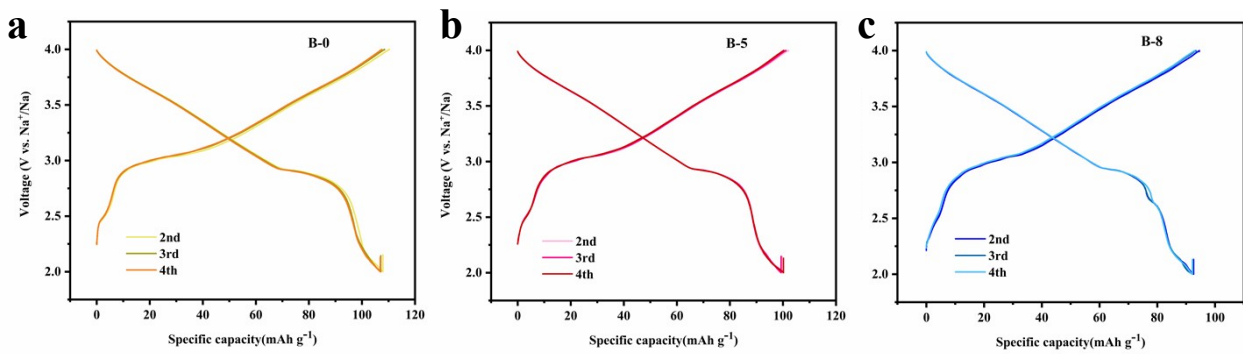


Figure S6. Galvanostatic charge-discharge curves at 0.1C of a) B-0 , b) B-5 and c) B-8 cathode

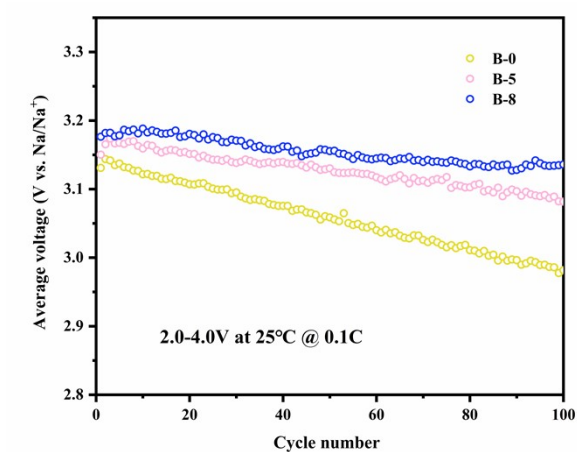


Figure S7. Average voltage over 100 cycles at 0.1C

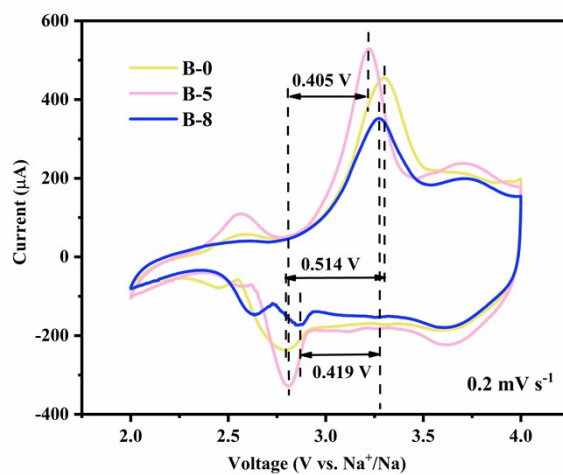


Figure S8. CV curves at 0.2 mV s^{-1} of both cathodes

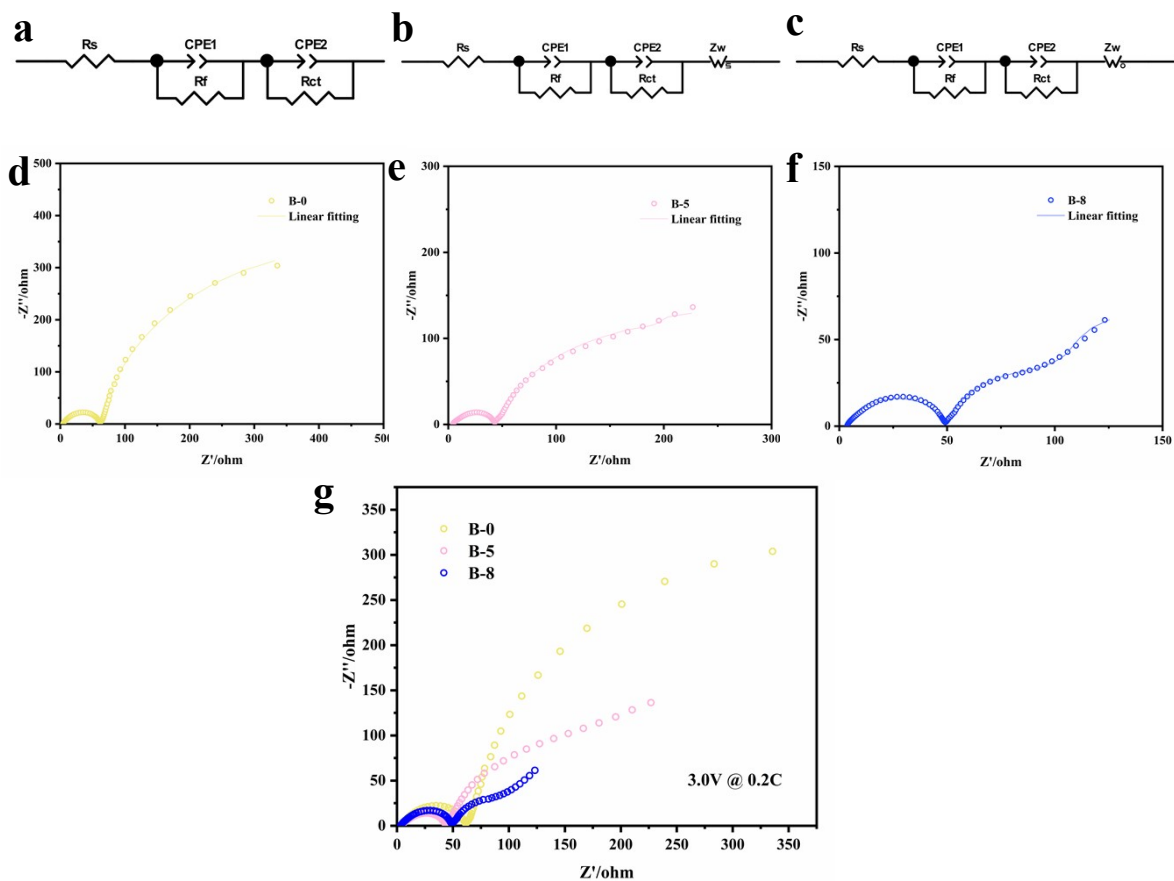


Figure S9. Equivalent circuit employed to match the electrochemical impedance spectroscopy of a)B-0, b)B-5, c)B-8. EIS measurements of d)B-0, e)B-5, f)B-8 and g)Summary at 3.0V after 12 cycles at a low current density of 0.2 C

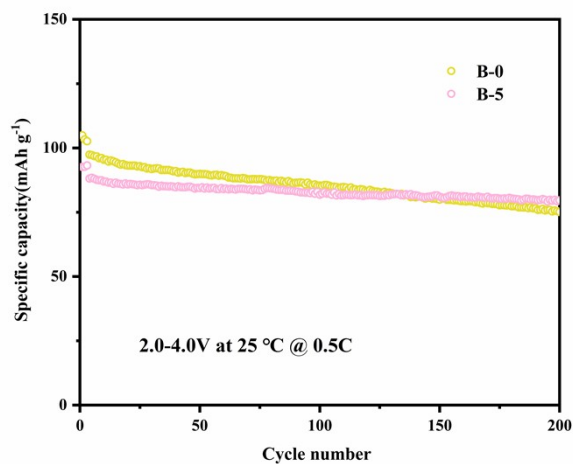


Figure S10. Long-term cycling performance at 25 °C at 0.5 C

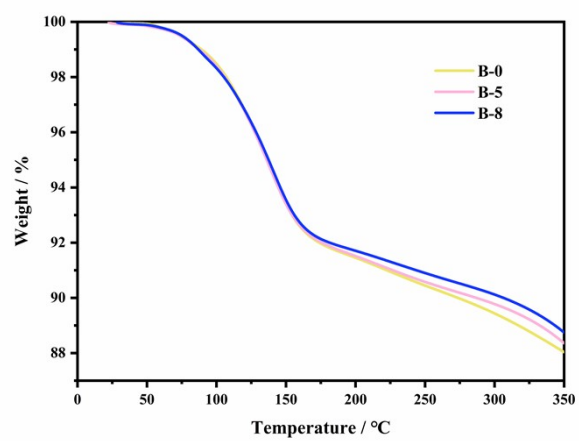


Figure S11. TG curves of B-0, B-5 and B-8

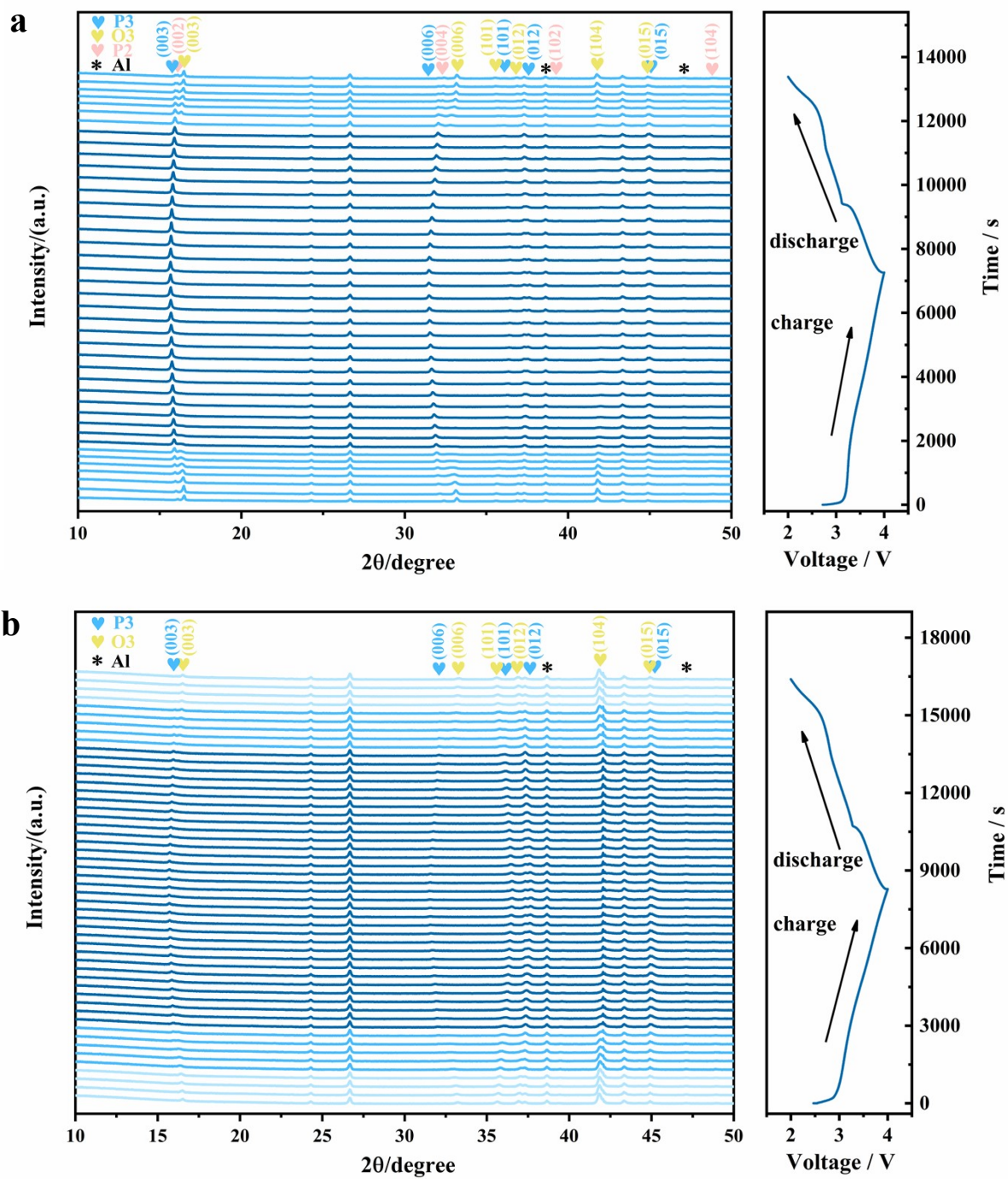


Figure S12. In situ XRD pattern of a)B-5 and b)B-0 cathode during the first charge/discharge curve at 48 mA g^{-1} between 2.0 and 4.0 V

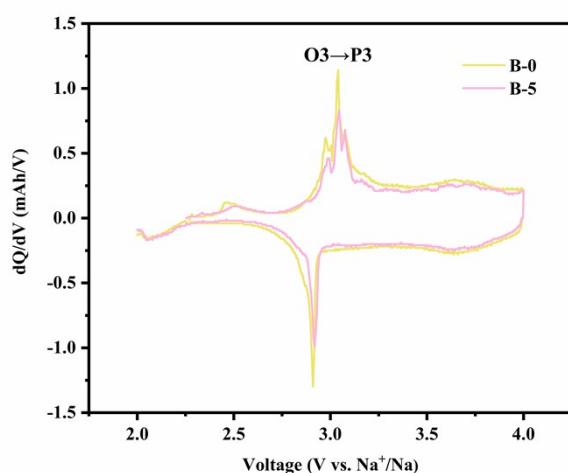


Figure S13. The dQ/dV curves of B-0 and B-5 at 0.1 C denoting the phase transition process

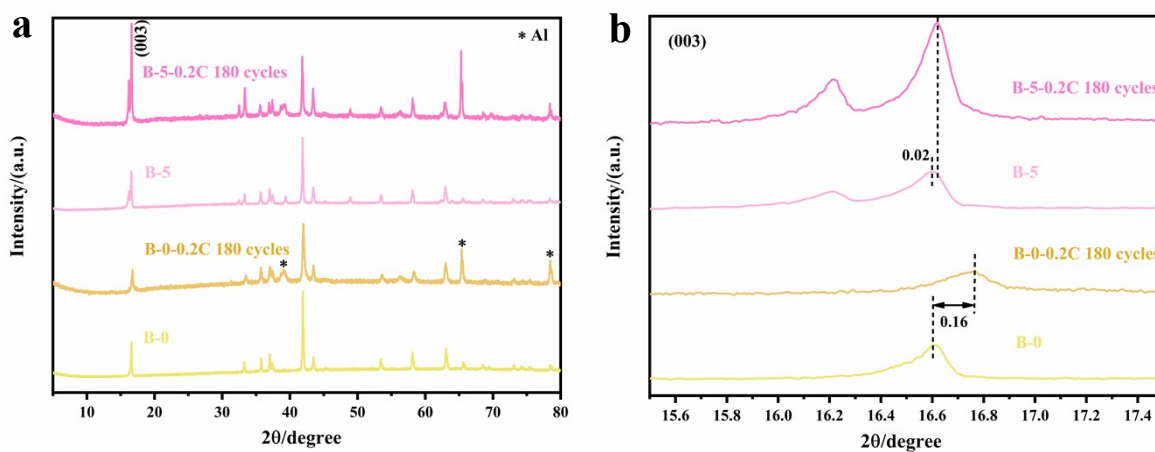


Figure S14. a)XRD patterns of B-0 and B-5 before and after 180 cycles at 0.2 C, and b)corresponding magnified view of (003) peaks.

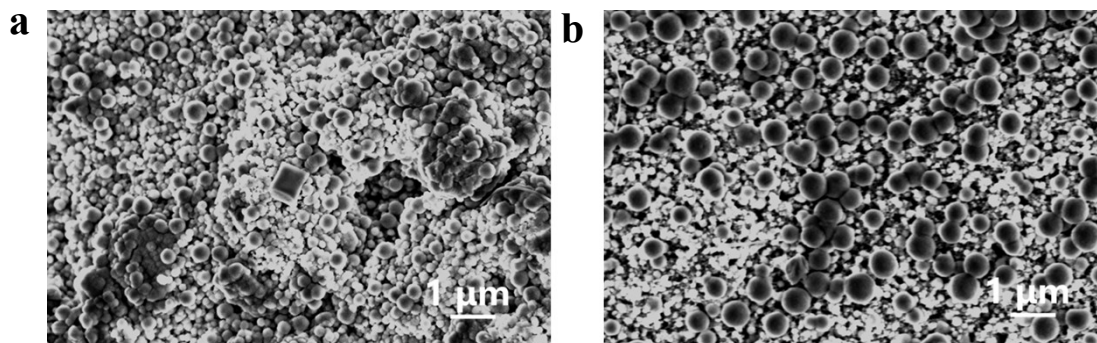


Figure S15. SEM images of a) B-0 , b) B-5 cathode after 180 cycles at 0.2 C

Table S1. Chemical composition of B-x (x=0, 1, 2, 3, 4, 5, 8) determined by ICP-OES measurements. (Atomic Ratio)

Samplpes	Na	Ni	Fe	Mn	B
B-0	0.76	0.32	0.35	0.33	0.0000
B-1	0.78	0.30	0.35	0.35	0.0044
B-2	0.76	0.31	0.34	0.35	0.0099
B-3	0.72	0.31	0.35	0.34	0.0178
B-4	0.72	0.31	0.35	0.34	0.0231
B-5	0.77	0.30	0.35	0.35	0.0291
B-8	0.76	0.31	0.35	0.34	0.0695

Table S2 Crystallographic data and atomic occupancies of the B-0 from Rietveld refinement with the corresponding XRD data.

B-0 O3 Phase			Fraction = 100%	
R _p = 3.81%			R _{wp} = 5.996%	
a (Å) = b (Å) = 2.95315			c (Å) = 16.26710	V (Å ³) = 122.860358
atom	x	y	z	Occ
Na	0.00000	0.00000	0.50000	0.800
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333
Fe	0.00000	0.00000	0.00000	0.333
O	0.00000	0.00000	0.26820	1.000

Table S3 Crystallographic data and atomic occupancies of the B-1 from Rietveld refinement with the corresponding XRD data.

B-1 O3 Phase			Fraction = 100%	
R _p = 2.81%			R _{wp} = 5.214%	
a (Å) = b (Å) = 2.95503			c (Å) = 16.25630	V (Å ³) = 122.935161
atom	x	y	z	Occ

Na	0.00000	0.00000	0.50000	0.800
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333
Fe	0.00000	0.00000	0.00000	0.333
O	0.00000	0.00000	0.26960	1.000

Table S4 B-2 Crystallographic data and atomic occupancies of the B-2 from Rietveld refinement with the corresponding XRD data.

B-2 O3 Phase		Fraction = 100%		
$R_p = 2.97\%$		$R_{wp} = 5.321\%$		
$a (\text{Å}) = b (\text{Å}) = 2.95719$		$c (\text{Å}) = 16.24810$	$V (\text{Å}^3) = 123.052854$	
atom	x	y	z	Occ
Na	0.00000	0.00000	0.50000	0.800
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333
Fe	0.00000	0.00000	0.00000	0.333
O	0.00000	0.00000	0.26750	1.000

Table S5 B-3 Crystallographic data and atomic occupancies of the B-3 from Rietveld refinement with the corresponding XRD data.

B-3 O3 Phase		Fraction = 100%		
$R_p = 2.80\%$		$R_{wp} = 5.043\%$		
$a (\text{Å}) = b (\text{Å}) = 2.95721$		$c (\text{Å}) = 16.24900$	$V (\text{Å}^3) = 123.061339$	
atom	x	y	z	Occ
Na	0.00000	0.00000	0.50000	0.800
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333
Fe	0.00000	0.00000	0.00000	0.333

O	0.00000	0.00000	0.26660	1.000
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Table S6 Crystallographic data and atomic occupancies of the B-4 from Rietveld refinement with the corresponding XRD data.

B-4 O3 Phase		Fraction = 100%		
R _p = 2.87%		R _{wp} = 5.226%		
a (Å) = b (Å) = 2.95463		c (Å) = 16.25870	V (Å ³) = 122.920017	
atom	x	y	z	Occ
Na	0.00000	0.00000	0.50000	0.800
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333
Fe	0.00000	0.00000	0.00000	0.333
O	0.00000	0.00000	0.26780	1.000

Table S7 Crystallographic data and atomic occupancies of the B-5 from Rietveld refinement with the corresponding XRD data.

B-5 O3 Phase		Fraction = 89.70%		
R _p = 2.98%		R _{wp} = 5.401%		
a (Å) = b (Å) = 2.95758		c (Å) = 16.25050	V (Å ³) = 123.103494	
atom	x	y	z	Occ
Na	0.00000	0.00000	0.50000	0.800
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333
Fe	0.00000	0.00000	0.00000	0.333
O	0.00000	0.00000	0.26910	1.000

B-5 P2 Phase		Fraction = 10.30%		
R _p = 2.98%		R _{wp} = 5.401%		

a (Å) = b (Å) = 2.91870		c (Å) = 11.09050		V (Å ³) = 81.820224
atom	x	y	z	Occ
Na _e	0.33333	0.66667	0.25000	0.374
Na _f	0.00000	0.00000	0.25000	0.426
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333
Fe	0.00000	0.00000	0.00000	0.333
O	0.33333	0.66667	0.08900	1.000

Table S8 Crystallographic data and atomic occupancies of the B-8 from Rietveld refinement with the corresponding XRD data.

B-8 O3 Phase		Fraction = 61.95%		
R _p = 3.35%		R _{wp} = 5.698%		
a (Å) = b (Å) = 2.95910		c (Å) = 16.22650		V (Å ³) = 123.048057
atom	x	y	z	Occ
Na	0.00000	0.00000	0.50000	0.800
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333
Fe	0.00000	0.00000	0.00000	0.333
O	0.00000	0.00000	0.27110	1.000
B-8 P2 Phase		Fraction = 38.05%		
R _p = 3.35%		R _{wp} = 5.698%		
a (Å) = b (Å) = 2.91730		c (Å) = 11.08840		V (Å ³) = 81.726272
atom	x	y	z	Occ
Na _e	0.33333	0.66667	0.25000	0.375
Na _f	0.00000	0.00000	0.25000	0.425
Ni	0.00000	0.00000	0.00000	0.333
Mn	0.00000	0.00000	0.00000	0.333

Fe	0.00000	0.00000	0.00000	0.333
O	0.33333	0.66667	0.08390	1.000

Table S9 The interlayer spacing and bond lengths of the B-x (x=0, 1, 2, 3, 4, 5, 8) from Rietveld refinement with the corresponding XRD data.

Samples		B-0	B-1	B-2	B-3	B-4	B-5	B-8
Fraction	O3 Phase	100	100	100	100	100	89.70	61.95
(%)	P2 Phase	0	0	0	0	0	10.30	38.05
$d_{(O-Na-O)}$ (Å)		3.3028	3.3465	3.2766	3.2475	3.2885	3.3540	3.5013
$d_{(O-TM-O)}$ (Å)		2.1187	2.0720	2.1392	2.1686	2.1309	2.0759	1.9591
$d_{(Na-O)}$ (Å)		2.3740	2.3900	2.3660	2.3560	2.3690	2.3927	2.4418
$d_{(TM-O)}$ (Å)		2.0070	1.9960	2.0150	2.0230	2.0110	1.9957	1.9618

Table S10 Electrochemical performance of recent P2/O3 oxide materials reported in the literatures.

Materials	Voltage (V)	Operating temperature (°C)	Initial capacity for cycling (mAh g ⁻¹)	Cycling performance	Capacity loss per cycle	Reference
B-5	2.0-4.0	25	86.3 (1C)	92.24% (200 cycles)	0.03882%	This work
HE-P2/O3	2.0-4.5	25	105 (1C)	85.71% (200 cycles)	0.07145%	1
NMFCAT	2.0-4.0	25	110 (1C)	80.9% (200 cycles)	0.0955%	2
HEO	2.1-4.3	25	103.5 (1C)	70.8% (300 cycles)	0.0797%	3
Na _{0.67} Fe _{0.3} Mn _{0.5} Li _{0.1} Mg _{0.1} O ₂	1.8-4.3	25	106.25 (1C)	65.88% (200 cycles)	0.1706%	4
Na _{0.76} Ni _{0.20} Fe _{0.40} Mn _{0.40} O ₂	2.0-4.2	25	114 (0.1C)	85.53% (100 cycles)	0.1447%	5
Na _{0.55} Mn _{0.4} Ni _{0.3} Fe _{0.15} Li _{0.1} Ti _{0.05} O ₂	2.0-4.2	25	80 (5C)	74.3% (2000 cycles)	0.01285%	6
NLNMTF ₃	2.5-4.15	25	78.8 (1C)	86.5% (500 cycles)	0.027%	7
Na _{0.76} Ni _{0.33} Mn _{0.48} O ₂	2.0-4.0	25	75 (2C)	85.3% (200 cycles)	0.0735%	8

Table S11 Impedance results obtained from fitting EIS through an equivalent circuit.

Samples	R_s/Ω	R_f/Ω	R_{ct}/Ω	Z_w/Ω
B-0	4.25	58.91	769.5	—
B-5	4.147	40.58	201.1	305.8
B-8	3.605	46.67	37.97	206.3

References

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