Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary information

A fluorinated O3-type layered cathode for long-life sodium-ion batteries

Tae-Yeon Yu[a] and Yang-Kook Sun*[,a]

[a] Department of Energy Engineering, Hanyang University, Seoul 04763, Republic of Korea

*Corresponding author: yksun@hanyang.ac.kr

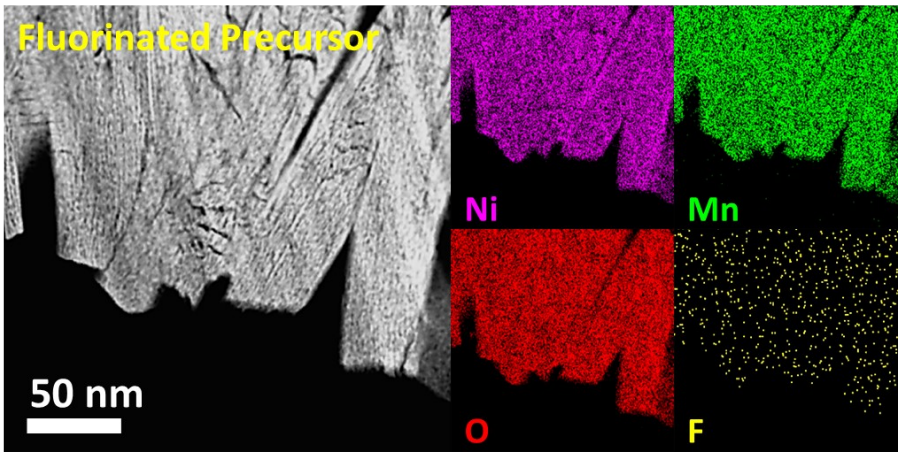

Fig. S1 TEM-EDS maps of Ni, Mn, O, and F in fluorinated $[Ni_{0.5}Mn_{0.5}](OH)_2$ (the precursor used in this study).

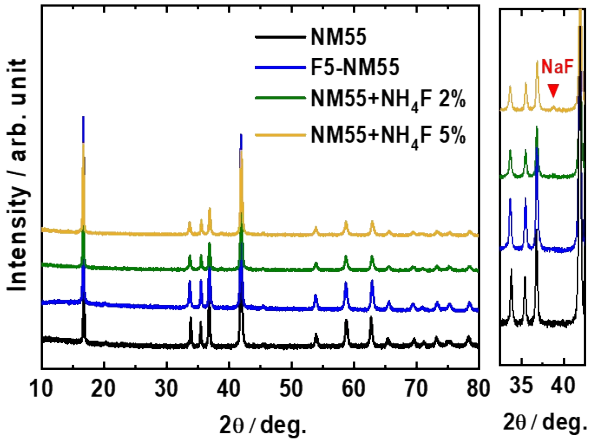

Fig. S2 Powder XRD patterns of NM55, F5-NM55, and sodiated NM55 heat treated with 2 and 5% NH_4F.

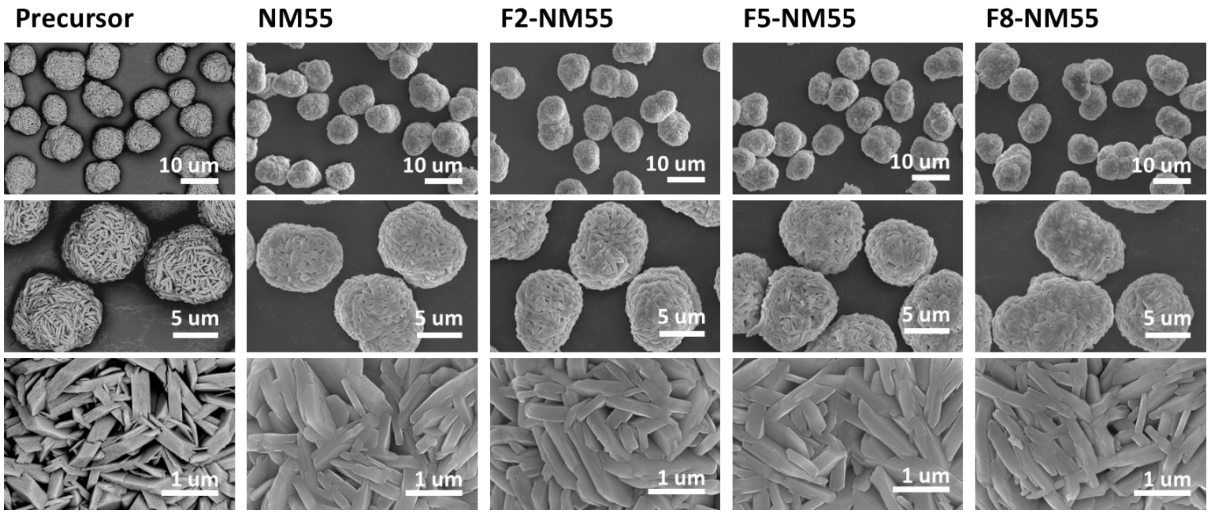

Fig. S3 SEM images of the precursor and fluorinated cathode materials.

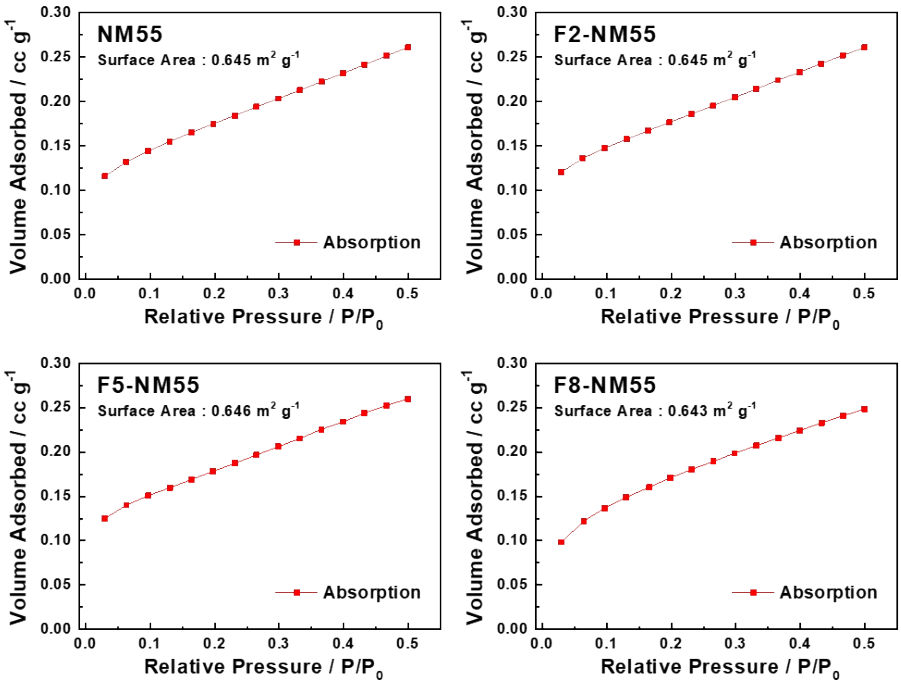

Fig. S4 Surface area of the NM55 and the fluorinated cathode materials.

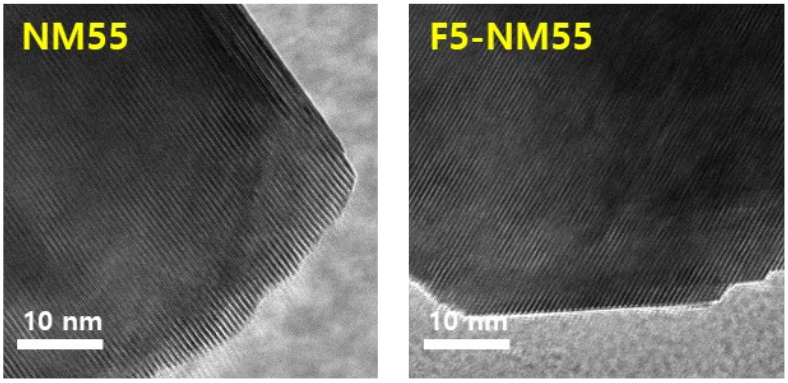

Fig. S5 TEM images at primary particle surface of NM55 and F5-NM55 cathode.

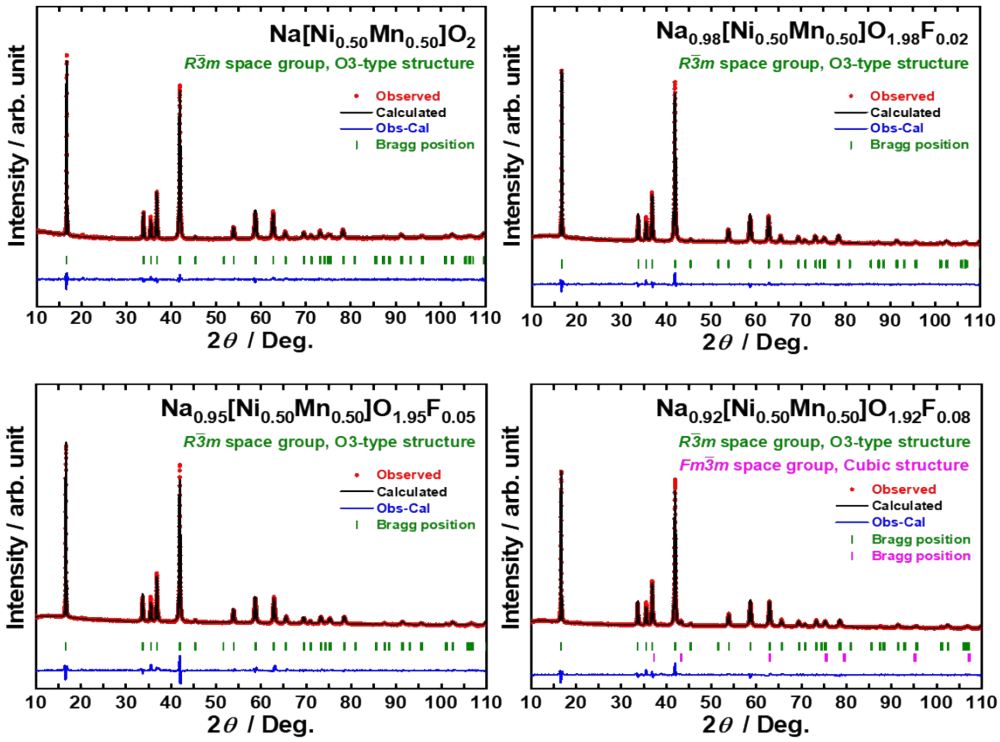

Fig. S6 Profile-matched XRD patterns of the fluorinated cathode materials.

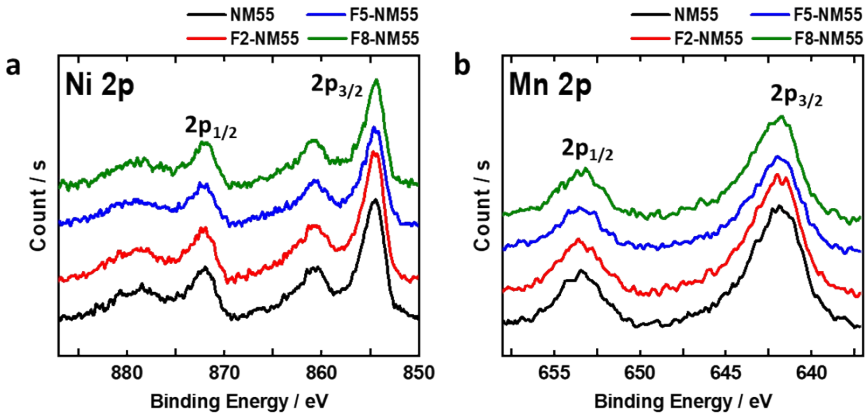

Fig. S7 (a) Ni 2p and (b) Mn 2p XPS spectra of the cathode materials.

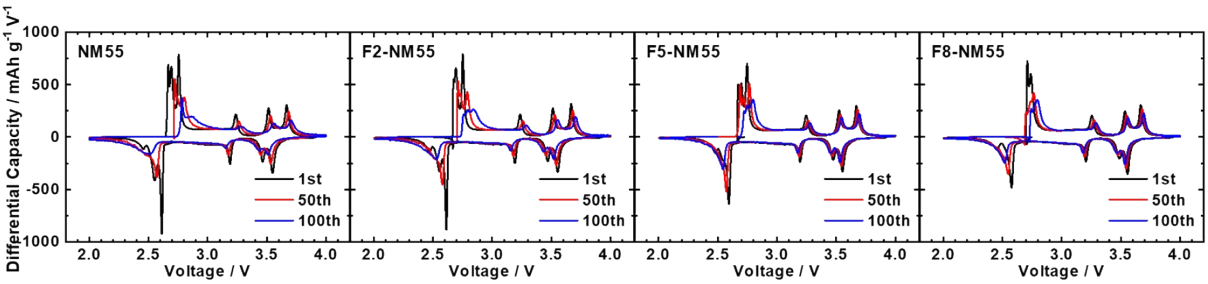

Fig. S8 Differential capacity profiles of half cells featuring the NM55, F2-NM55, F5-NM55, and F8-NM55 cathodes with respect to the 1st, 50th, and 100th cycles.

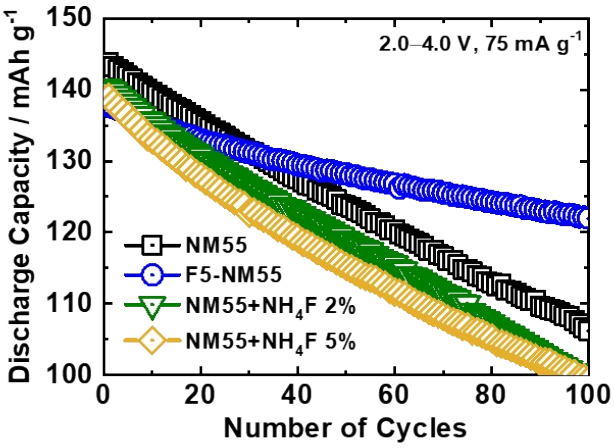

Fig. S9 Cycling stability of NM55, F5-NM55, and sodiated NM55 heat treated with 2 and 5% NH_4F in half cells cycled at 75 mA g^{-1}.

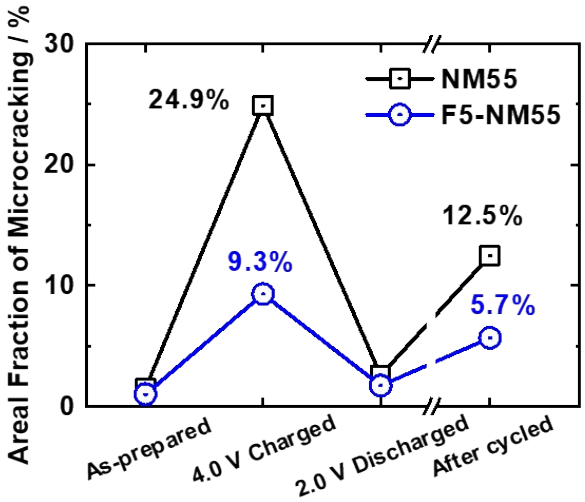

Fig. S10 Variation of the areal fraction of microcracks for the NM55 and F5-NM55 cathodes.

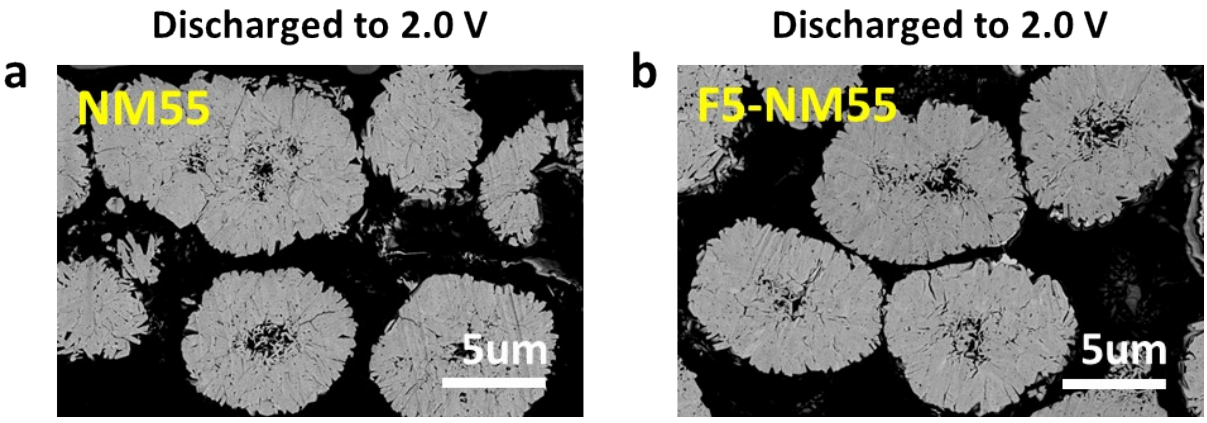

Fig. S11 Cross-sectional SEM images of the (a) NM55 and (b) F5-NM55 cathodes discharged to 2.0 V.

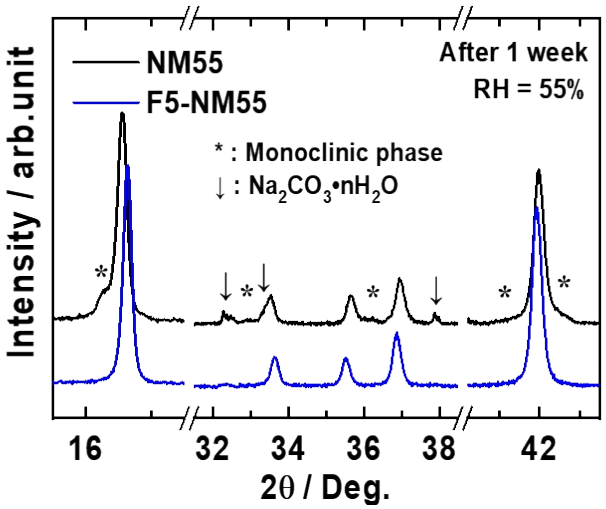

Fig. S12 Comparison of XRD patterns collected from the NM55 and the F5-NM55 cathode materials after 1 week of exposure to air with a relative humidity of ≈55%.

Table S1 IC results of the fluorinated cathode materials

Determination results by IC		
	F^-	
	mg / kg	mol%
NM55	-	-
F2-NM55	2807.93	1.64
F5-NM55	7056.01	4.11
F8-NM55	13078.03	7.59

Table S2. ICP-OES results of the fluorinated cathode materials.

Metal stoichiometry determined by ICP-OES			
	Chemical composition (at%)		
	Na	Ni	Mn
NM55	0.9951	0.4958	0.5042
F2-NM55	0.9830	0.4984	0.5016
F5-NM55	0.9448	0.4968	0.5032
F8-NM55	0.9187	0.4979	0.5021

Table S3. Lattice parameters of $Na[Ni_{0.5}Mn_{0.5}]O_2$ ($R\bar{3}m$ space group) deduced from the Rietveld refined XRD data.

$Na[Ni_{0.5}Mn_{0.5}]O_2$

Lattice parameters *a* (Å) = 2.9582 (6), *c* (Å) = 15.9192 (9)

R_{wp} = 2.86%

Atom	Site	x	y	z	B_{iso}	Occ
Na	3a	0	0	0	1.5*	1
Ni	3b	0	0	0.5	0.43 (5)	0.5
Mn	3b	0	0	0.5	0.43 (5)	0.5
O	6c	0	0	0.2319 (9)	0.33 (9)	1

* Not refined

Table S4. Lattice parameters of $Na_{0.98}[Ni_{0.5}Mn_{0.5}]O_{1.98}F_{0.02}$ ($R\bar{3}m$ space group) deduced from the Rietveld refined XRD data.

$Na_{0.98}[Ni_{0.5}Mn_{0.5}]O_{1.98}F_{0.02}$

Lattice parameters *a* (Å) = 2.9524 (7), *c* (Å) = 15.9529 (5)

R_{wp} = 2.79%

Atom	Site	x	y	z	B_{iso}	Occ
Na	3a	0	0	0	1.5*	1
Ni	3b	0	0	0.5	0.38 (9)	0.5
Mn	3b	0	0	0.5	0.38 (9)	0.5
O	6c	0	0	0.2325 (1)	0.25 (7)	0.99
F	6c	0	0	0.2325 (1)	0.25 (7)	0.01

* Not refined

Table S5. Lattice parameters of $Na_{0.95}[Ni_{0.5}Mn_{0.5}]O_{1.95}F_{0.05}$ ($R\bar{3}m$ space group) deduced from the Rietveld refined XRD data.

$Na_{0.95}[Ni_{0.5}Mn_{0.5}]O_{1.95}F_{0.05}$

Lattice parameters *a* (Å) = 2.9459 (8), *c* (Å) = 16.0081 (3)

R_{wp} = 2.94%

Atom	Site	x	y	z	B_{iso}	Occ
Na	3a	0	0	0	1.5*	0.95
Ni	3b	0	0	0.5	0.42 (0)	0.5
Mn	3b	0	0	0.5	0.42 (0)	0.5
O	6c	0	0	0.2313 (5)	0.28 (4)	0.975
F	6c	0	0	0.2313 (5)	0.28 (4)	0.025

* Not refined

Table S6. Lattice parameters of $Na_{0.92}[Ni_{0.5}Mn_{0.5}]O_{1.92}F_{0.08}$ ($R\bar{3}m$ space group) deduced from the Rietveld refined XRD data.

$Na_{0.92}[Ni_{0.5}Mn_{0.5}]O_{1.92}F_{0.08}$

Lattice parameters *a* (Å) = 2.9423 (2), *c* (Å) = 16.0430 (7)

R_{wp} = 5.59%

Atom	Site	x	y	z	B_{iso}	Occ
Na	3a	0	0	0	1.5*	0.92
Ni	3b	0	0	0.5	0.36 (8)	0.5
Mn	3b	0	0	0.5	0.36 (8)	0.5
O	6c	0	0	0.2309 (6)	0.31 (2)	0.96
F	6c	0	0	0.2309 (6)	0.31 (2)	0.04

* Not refined

Table S7. Electrochemical performance of the optimized cathode developed in this study and previously reported fluorine-doped O3-type cathodes and NM55-derived cathodes.

Cathode	Cut-off Potential	Current Density (1.0C)	Discharge Capacity	Cycling Performance	Rate Performance	Full Cell	Ref
$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_{1.99}F_{0.01}$	2.0–4.0 V	150 mA g^{-1}	122 mAh g^{-1} @ 0.2C	90% (@ 1C) after 70 cycles	62 mAh g^{-1} @ 2C 51% @ 2C/0.1C	X	[S1]
$Na_{0.82}Li_{0.05}Ni_{0.3}Fe_{0.4}Mn_{0.3}O_{1.95}F_{0.05}$	2.0–4.0 V	-	123 mAh g^{-1} @ 0.05C	88% (@ 1C) after 100 cycles	70 mAh g^{-1} @ 5C 57% @ 5C/0.05C	X	[S2]
$NaNi_{0.4}Mn_{0.25}Ti_{0.3}Co_{0.05}O_{1.92}F_{0.08}$	2.0–4.4 V	200 mA/g^{-1}	177 mAh g^{-1} @ 0.05C	65.2% (@ 0.25C) after 200 cycles	97 mAh g^{-1} @ 5C 55% @ 5C/0.05C	X	[S3]
$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_{1.99}F_{0.01}$	2.0–4.0 V	150 mA/g^{-1}	140.3 mAh g^{-1} @ 0.1C	85.3% (@ 1C) after 100 cycles	90 mAh g^{-1} @ 5C 64% @ 5C/0.1C	X	[S4]
Spherical $NaNi_{0.5}Mn_{0.5}O_2$	2.0–4.0 V	120 mA/g^{-1}	147 mAh g^{-1} @ 0.1C	84% (@ 0.5C) after 50 cycles	95 mAh g^{-1} @ 10C 65% @ 10C/0.1C	72% @ 50 cycles	[S5]
$NaNi_{0.5}Mn_{0.5}O_2$/CNT	2.0–4.0 V	240 mA/g^{-1}	141 mAh g^{-1} @ 0.05C	97% (@ 0.05C) after 100 cycles	81 mAh g^{-1} @ 2C 57% @ 2C/0.05C	X	[S6]
Bar-shaped $NaNi_{0.5}Mn_{0.5}O_2$	2.0–4.0 V	125 mA/g^{-1}	133 mAh g^{-1} @ 0.075C	77% (@ 0.15C) after 100 cycles	54 mAh g^{-1} @ 15C 40.6% @ 15C/0.075C	X	[S7]
$NaNi_{0.4}Fe_{0.2}Mn_{0.4}O_2$	2.0–4.0 V	240 mA/g^{-1}	133 mAh g^{-1} @ 0.05C	89% (@ 0.05C) after 30 cycles	86 mAh g^{-1} @ 10C 65% @ 10C/0.05C	X	[S8]
$NaNi_{0.35}Fe_{0.3}Mn_{0.35}O_2$	2.0–4.0 V	240 mA/g^{-1}	130.3 mAh g^{-1} @ 0.1C	80% (@ 1C) after 100 cycles	82.3 mAh g^{-1} @ 5C 63.2% @ 5C/0.1C	X	[S9]
$NaNi_{0.5}Mn_{0.2}Ti_{0.3}O_2$	2.0–4.0 V	240 mA/g^{-1}	135 mAh/g^{-1} @ 0.05C	85% (@ 1C) after 200 cycles	93 mAh g^{-1} @ 5C 69% @ 5C/0.05C	X	[S10]
$NaNi_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}O_2$	2.0–4.0 V	240 mA/g^{-1}	124 mAh g^{-1} @ 0.1C	70.2% (@ 1C) after 500 cycles	81 mAh g^{-1} @ 10C 65.3% @ 10C/0.1C	X	[S11]
MgO-$NaNi_{0.5}Mn_{0.5}O_2$	2.0–4.2 V	150 mA/g^{-1}	165 mAh g^{-1} @ 0.1C	75% after 100 cycles	99 mAh g^{-1} @ 10C 60% @ 10C/0.1C	70% after 200 cycles	[S12]
P2-coated $NaNi_{0.5}Mn_{0.5}O_2$	2.0–4.0 V	125 mA/g^{-1}	141.4 mAh g^{-1} @ 0.1C	85.3% (@ 1C) after 150 cycles	103.7 mAh g^{-1} @ 15C 73% @ 15C/0.1C	83% after 250 cycles	[S13]
$Na_{0.95}Ni_{0.5}Mn_{0.5}O_{1.95}F_{0.05}$	2.0–4.0 V	150 mA/g^{-1}	139 mAh g^{-1} @ 0.1C	89% (@ 0.5C) after 100 cycles	110 mAh g^{-1} @ 10C 78% @ 10C/0.1C	92% after 500 cycles	This work

References

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[S11] *J. Am. Chem. Soc.*, 2017, **139**, 8440**.**

[S12] *J. Mater. Chem. A*, 2018, **6**, 16854**.**

[S13] *Energy Storage Mater.*, 2022, **47**, 515.

Table S8 The electrochemical impedance of the NM55 and F5-NM55 cathode, charged to 4.0 V and stored in an electrolyte at 60 ℃.

Electrochemical impedance						
	Before storage		3 days		1 week	
Sample	R_{sf} (Ω)	R_{ct} (Ω)	R_{sf} (Ω)	R_{ct} (Ω)	R_{sf} (Ω)	R_{ct} (Ω)
NM55	4.7	7.1	38.4	181.3	80.0	428.1
F5-NM55	2.5	5.8	12.8	8.0	59.0	13.7