

**Novel Ti(III)/Ti(IV) mixed-valence doping for enhancing both the
structural stability and specific capacity of P2 layered
Na_{0.67}Ni_{0.2}Mn_{0.8}O₂ cathode for sodium-ion batteries**

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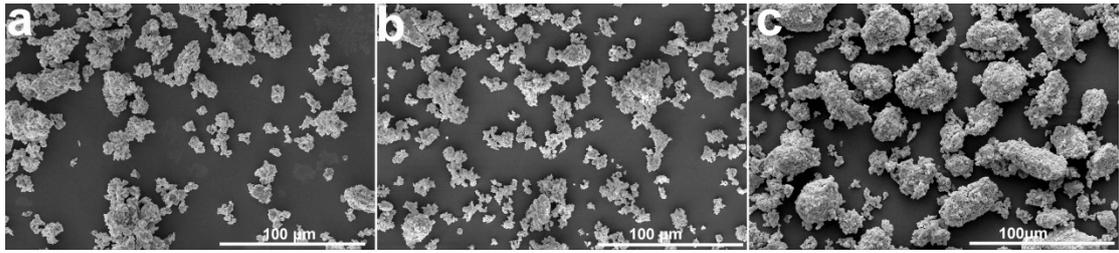


Figure S1. SEM images of (a) NNM-OA, (b) NNTM0.125-OA, and (c) NNTM0.125-NOA samples.

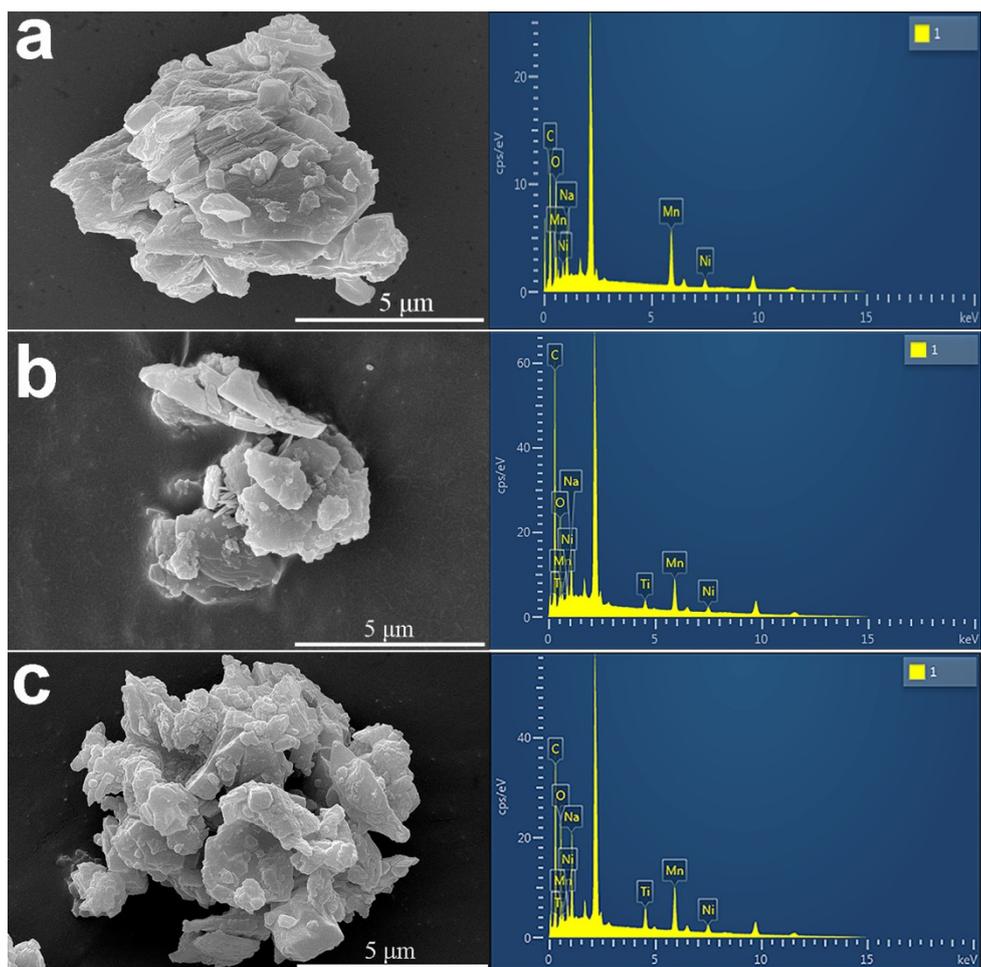


Figure S2. EDS results of (a) NNM-OA, (b) NNTM0.125-OA, and (c) NNTM0.125-NOA samples.

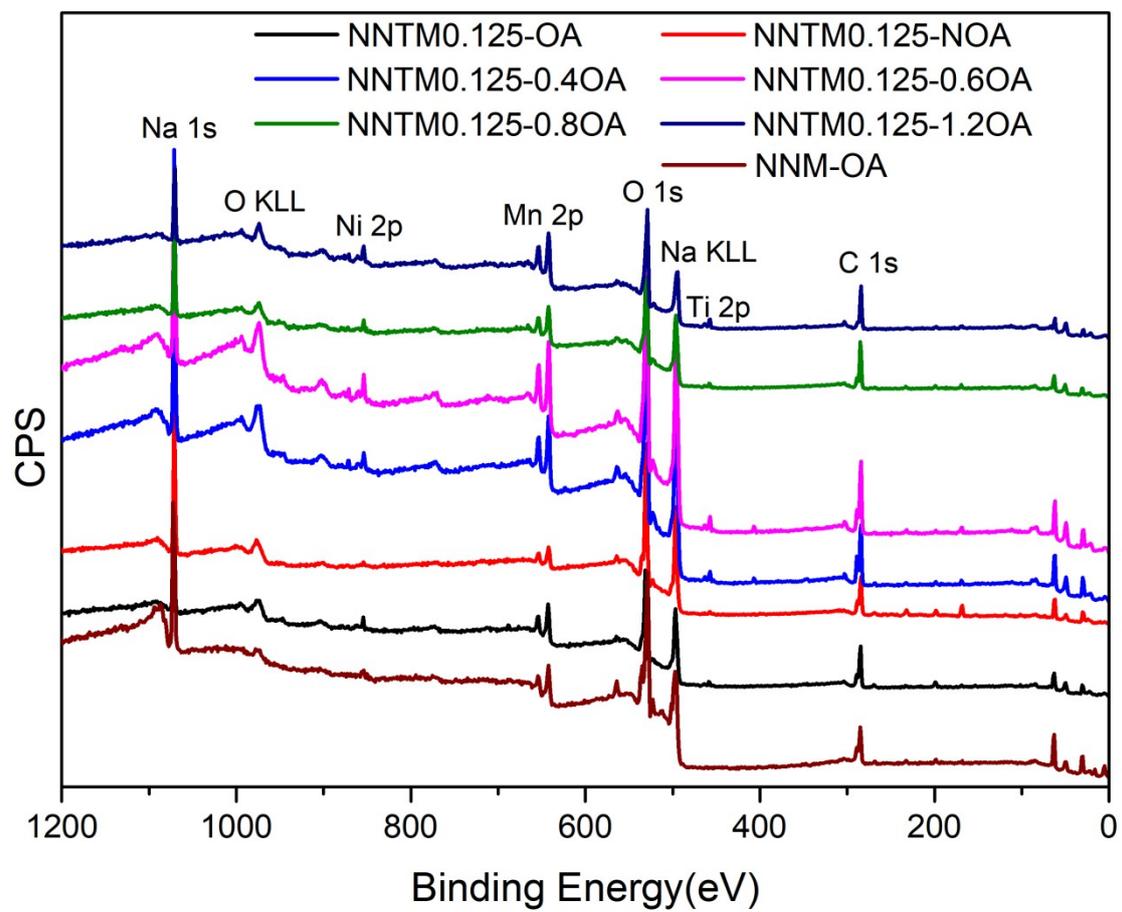


Figure S3. XPS survey spectra of NNM-OA and NNTM0.125-OA to NNTM0.125-1.2OA samples.

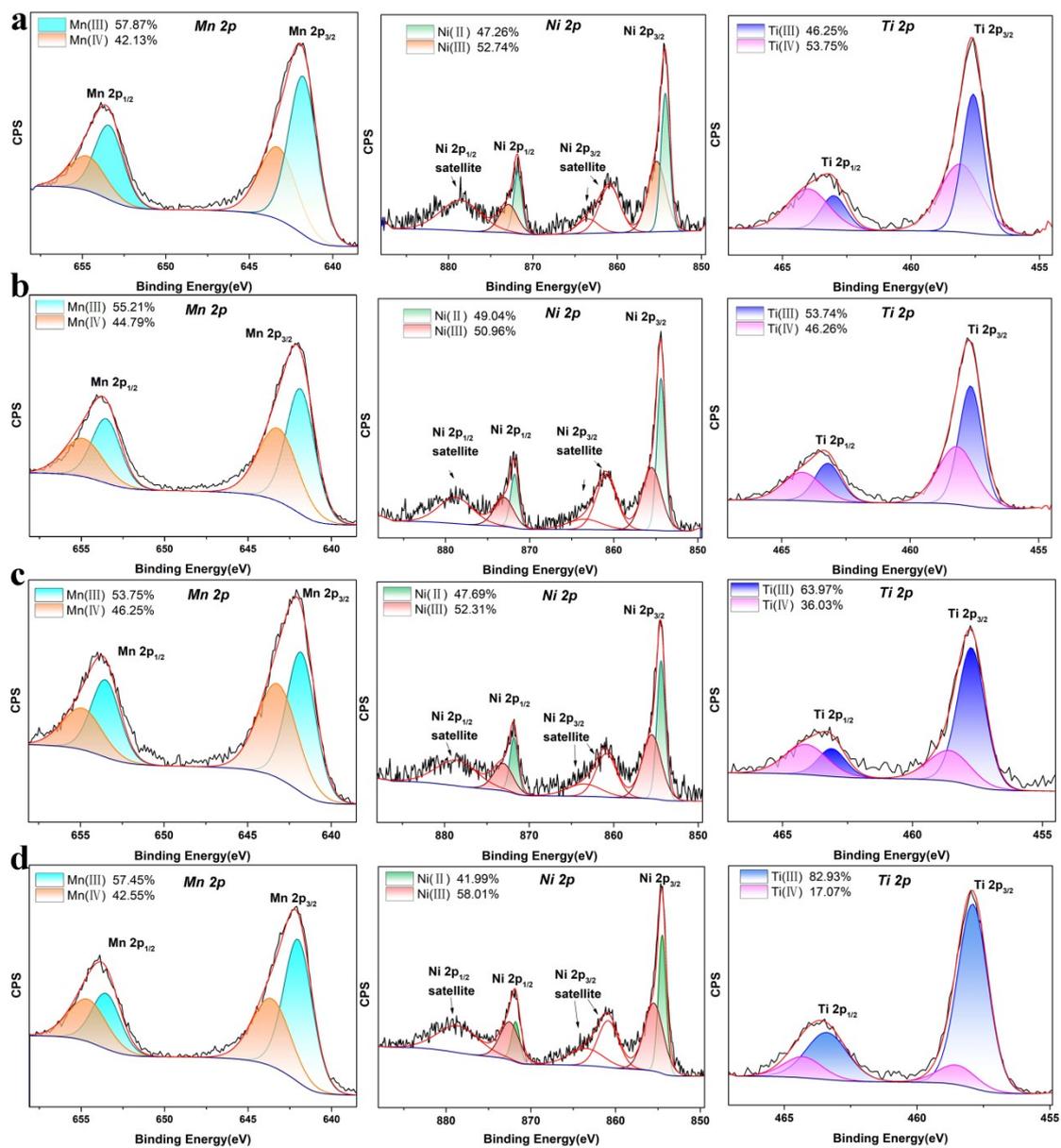


Figure S4. The Mn 2p, Ni 2p and Ti 2p XPS spectra of (a) NNTM0.125-0.4OA, (b) NNTM0.125-0.6OA, (c) NNTM0.125-0.8OA, (d) NNTM0.125-1.2OA.

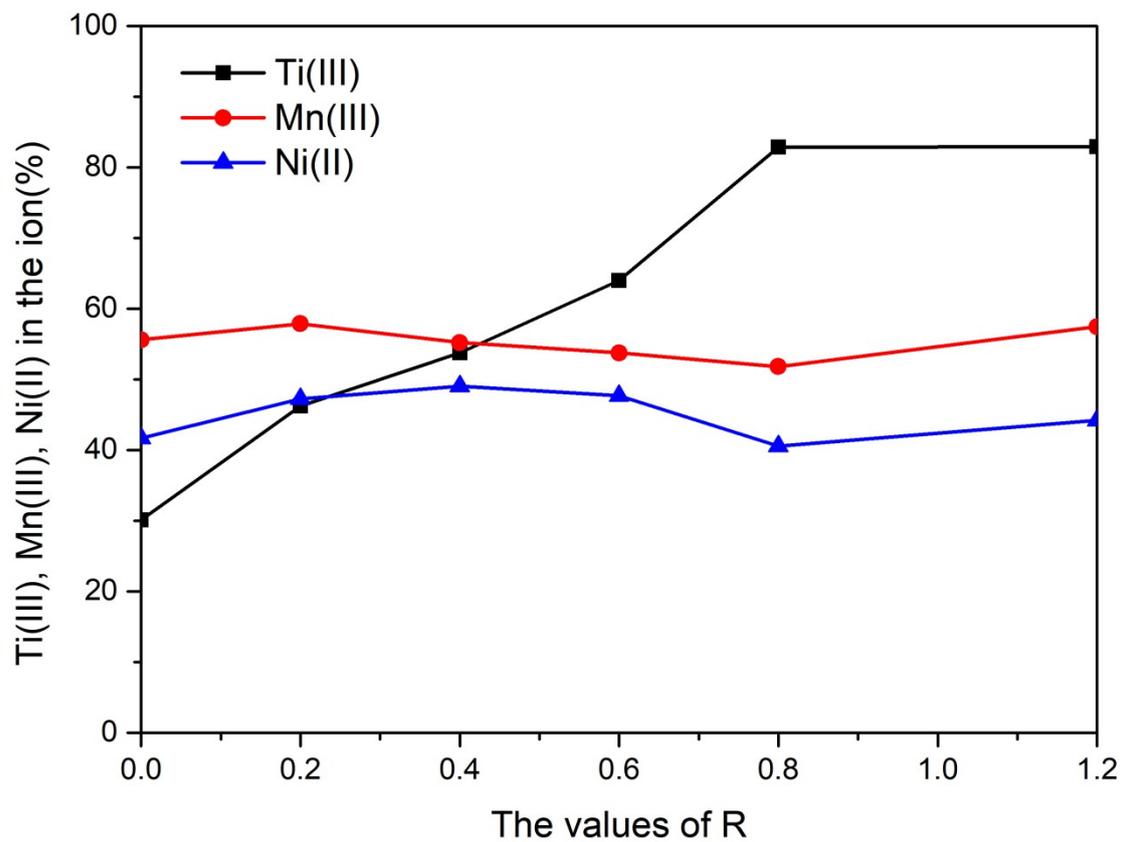


Figure S5. The relationship between the percentage of Ti(III), Mn(III), Ni(II) and R values.

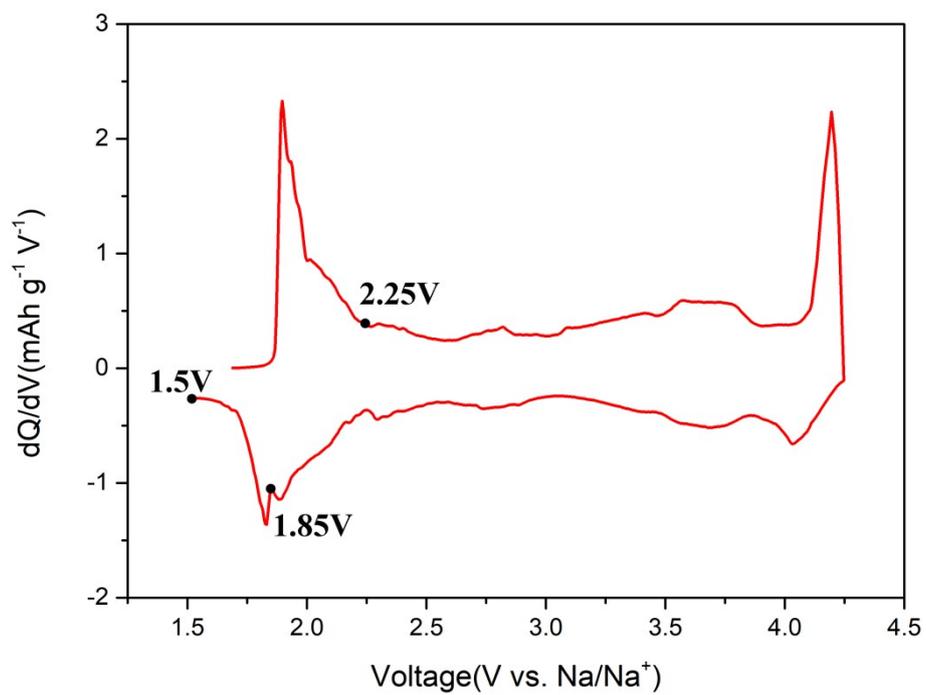


Figure S6. The selected voltage levels for ex-situ XPS characterization.

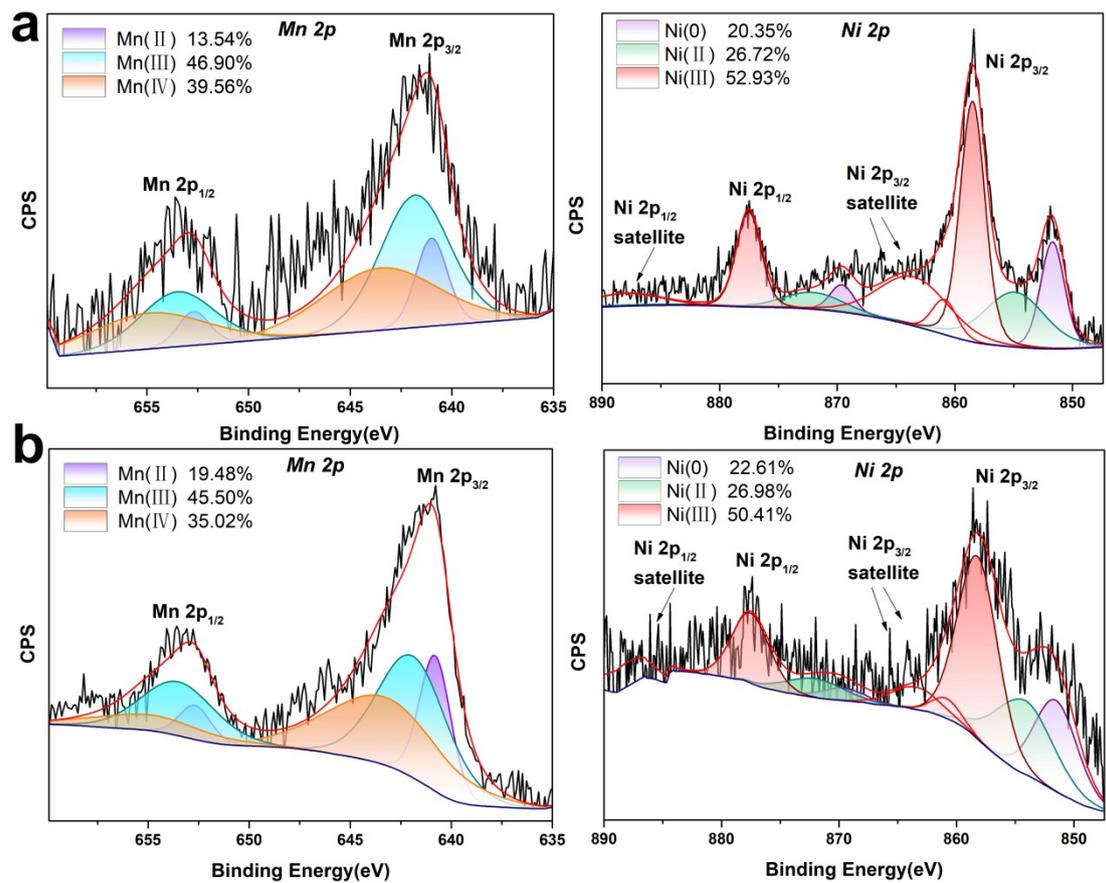


Figure S7. Ex-situ XPS spectra of Mn 2p, Ni 2p for NNM-OA cycled to different potentials: (a) discharged to 1.85 V, and (b) discharged to 1.50 V

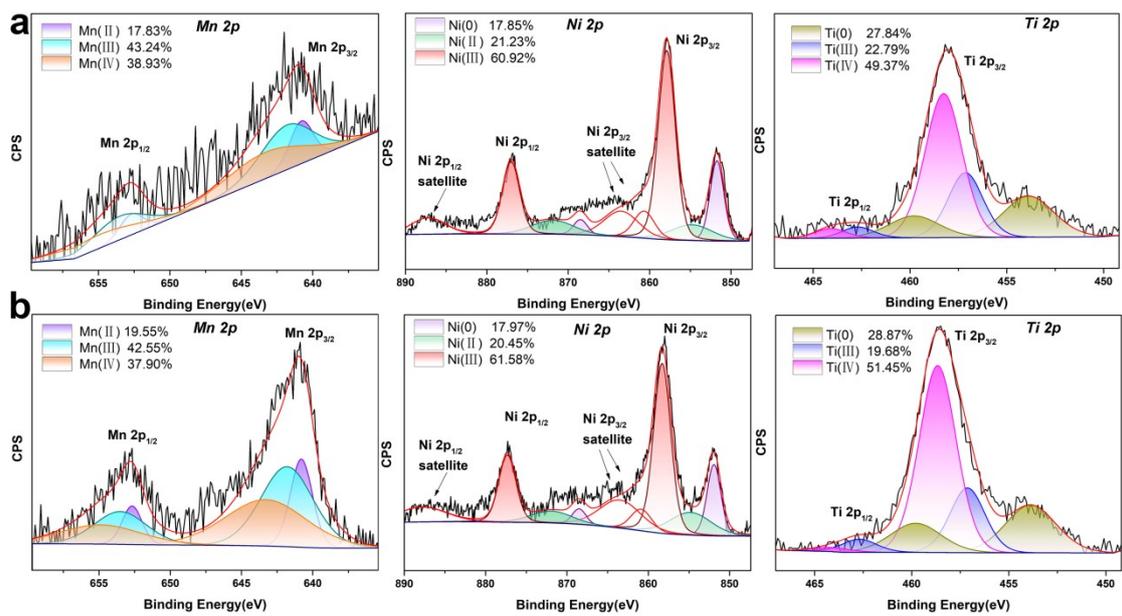


Figure S8. Ex-situ XPS spectra of Mn 2p, Ni 2p and Ti 2p for NNTM0.125-NOA cycled to different potentials: (a) discharged to 1.85 V, and (b) discharged to 1.50 V.

Table S1. Crystallographic parameters of NNM-OA, NNTM0.125-OA and NNTM0.125-NOA samples by the Rietveld method

Samples	a (Å)	c (Å)	V (Å ³)	R _{wp} (%)	R _p (%)
NNM-OA	2.86868	11.12404	79.279	3.64	2.45
NNTM0.125-OA	2.90229	11.21938	81.843	3.88	2.74
NNTM0.125-NOA	2.88428	11.12828	80.174	3.71	2.62

Table S2. The EDS analysis results of NNM-OA, NNTM0.125-OA, and NNTM0.125-NOA samples

Samples	Na	Ni	Ti	Mn
NNM-OA (theoretical)	0.670	0.200	0	0.800
NNTM0.125-OA (theoretical)	0.670	0.200	0.125	0.675
NNM-OA (measured)	0.726	0.198	0	0.800
NNTM0.125-OA (measured)	0.722	0.208	0.117	0.675
NNTM0.125-NOA (measured)	0.734	0.219	0.127	0.675

Table S3. The elemental content (theoretical and measured) of the prepared cathode materials calculated by XPS results

Samples	Na	Ni	Ti	Mn
NNM-OA (theoretical)	0.670	0.200	0	0.800
NNTM0.125-OA (theoretical)	0.670	0.200	0.125	0.675
NNM-OA (measured)	1.263	0.190	0	0.800
NNTM0.125-OA (measured)	1.338	0.186	0.108	0.675
NNTM0.125-NOA (measured)	1.312	0.191	0.116	0.675
NNTM0.125-0.4OA (measured)	1.357	0.190	0.109	0.675
NNTM0.125-0.6OA (measured)	1.249	0.184	0.116	0.675
NNTM0.125-0.8OA (measured)	1.310	0.181	0.112	0.675
NNTM0.125-1.2OA (measured)	1.213	0.175	0.111	0.675

Table S4. Cycling performance of cathodes with inactive ions doping in publications

Pristine material	Modified materials	Initial capacity of pristine material (mAh g ⁻¹)	Initial capacity of modified materials (mAh g ⁻¹)	Capacity changes (%)	Capacity retention (%)	References
Na _{0.66} Ni _{1/3} Mn _{2/3} O ₂	Na _{0.66} La _{0.01} [Ni _{1/3} Mn _{1/2} Ti _{1/6}]O ₂	145	121	-16.56 (0.1 C)	80 (50 cycles)	23
Na _{0.67} Ni _{0.33} Mn _{0.67} O ₂	Na _{0.78} Al _{0.05} Ni _{0.33} Mn _{0.60} O ₂	148	131	-11.28 (0.1 C)	84 (50 cycles)	30
Na _{2/3} Ni _{1/3} Mn _{2/3} O ₂	Na _{2/3} [Ni _{1/3} Mn _{1/2} Ti _{1/6}]O ₂	160	120	-25 (13 mA g ⁻¹)	84 (40 cycles)	32
Na _{2/3} Fe _{1/3} Mn _{2/3} O ₂	Na _{2/3} Fe _{1/3} Mn _{0.5} Ti _{0.1} O ₂	173	156	-9.82 (0.2 C)	76 (50 cycles)	34
Na _{0.67} Mn _{0.5} F _e _{0.5} O ₂	Na _{0.67} Mn _{0.47} Al _{0.03} Fe _{0.5} O ₂	157	151	-3.95 (0.1 C)	75 (50 cycles)	53
Na _{0.67} Mn _{0.5} F _e _{0.5} O ₂	Na _{0.67} Fe _{0.50} Mn _{0.45} Ti _{0.05} O ₂	133	130	-2.25 (0.5 C)	42 (45 cycles)	54
Na _{0.67} Ni _{0.2} Mn _{0.8} O ₂	Na _{0.67} Ni _{0.2} Ti _{0.1} Mn _{0.675} O ₂	139	154	10.79 (0.2 C)	82 (50 cycles)	This work