Supplementary Materials

Manipulating of P2/O3 Composite Sodium Layered Oxide Cathode through Ti Substitution and Synthesis Temperature

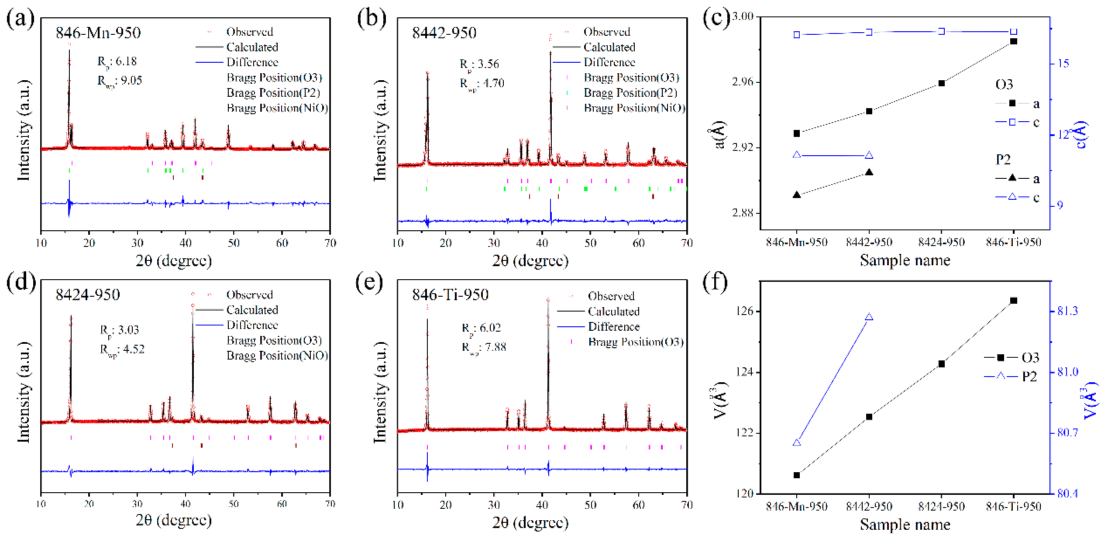

Figure S1. XRD patterns and refinement results of (a) $Na_{0.8}Ni_{0.4}Mn_{0.6}O_2$-950, (b) $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-950, (d) $Na_{0.8}Ni_{0.4}Mn_{0.2}Ti_{0.4}O_2$-950, and (e) $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$-950. (c) and (f) the evolution of cell parameters *a*, *c*, and unit cell volume *V* of O3 and P2 structures with the increase of Ti-substitution.

Table S1. Structural parameters, atomic coordinates and occupancies of the $Na_{0.8}Ni_{0.4}Mn_{0.6}O_2$-950 obtained by refining XRD pattern (*R*-factors: *R*p=6.18%, *R*wp=9.05%)

Phase content	Atom	Site	*x*	*y*	*z*	g	Lattice parameters
O3 (28.5 wt%)	Na	*3b*	0	0	0.5	0.860(9)	Space group: R-3m *a*=2.9260(7)Å *c*=16.2274(7) Å
	Ni/Mn	*3a*	0	0	0	0.4/0.6	
	O	*6c*	0	0	0.2665(12)	1	
P2 (67.8 wt%)	Na1	*2b*	0	0	0.25	0.374(10)	Space group: $P6_3/mmc$ *a*=2.8896(6)Å *c*=11.1361(2)Å
	Na2	*2d*	0.6667	0.3333	0.25	0.358(11)	
	Ni/Mn	*2a*	0	0	0	0.4/0.6	
	O	*4f*	0.6667	0.3333	0.0816(8)	1	

Table S2. Structural parameters, atomic coordinates and occupancies of the $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-950 obtained by refining XRD pattern (*R*-factors: *R*p=3.56%, *R*wp=4.70%)

Phase content	Atom	Site	*x*	*y*	*z*	g	Lattice parameters
O3 (74.9 wt%)	Na	*3b*	0	0	0.5	0.809(18)	Space group: R-3m *a*=2.9417(3)Å *c*=16.3478(3)Å
	Ni/Mn/Ti	*3a*	0	0	0	0.4/0.4/0.2	
	O	*6c*	0	0	0.2629(3)	1	
P2 (20.8 wt%)	Na1	*2b*	0	0	0.25	0.242(13)	Space group: $P6_3/mmc$ *a*= 2.9050(1)Å *c*=11.1151(5)Å
	Na2	*2d*	0.6667	0.3333	0.25	0.439(16)	
	Ni/Mn/Ti	*2a*	0	0	0	0.4/0.4/0.2	
	O	*4f*	0.6667	0.3333	0.0913(11)	1	

Table S3. Structural parameters, atomic coordinates and occupancies of the $Na_{0.8}Ni_{0.4}Mn_{0.2}Ti_{0.4}O_2$-950 obtained by refining XRD pattern

O3 phase

Atom	Site	*x*	*y*	*z*	g
Na	*3b*	0	0	0.5	0.773(18)
Ni/Mn/Ti	*3a*	0	0	0	0.4/0.2/0.4
O	*6c*	0	0	0.2666(3)	1

Space group: R-3m, *a*= 2.9594(3)Å, *c*= 16.3852(3) Å, phase fraction 96.8 wt%
R-factors: *R*p=3.03%, *R*wp=4.52%

Table S4. Structural parameters, atomic coordinates and occupancies of the $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$-950 obtained by refining XRD pattern

O3 phase

Atom	Site	*x*	*y*	*z*	g
Na	*3b*	0	0	0.5	0.809(15)
Ni/Ti	*3a*	0	0	0	0.4/0.6
O	*6c*	0	0	0.2679(3)	1

Space group: R-3m, *a*= 2.9849(19) Å, *c*= 16.3748(2) Å, phase fraction 100 wt%
R-factors: *R*p=6.02%, *R*wp=7.88%

Table S5. The designed chemical compositions of $Na_{0.8}Ni_{0.4}Mn_{0.6-x}Ti_xO_2$-950 and calculated results obtained by refining XRD patterns

Sample name	**designed composition**	**Temperature (℃)**	**Phase Weight Frac. (%)**	
846-Mn-950	$Na_{0.8}Ni_{0.4}Mn_{0.6}O_2$	950	O3-$Na_{0.86}Ni_{0.4}Mn_{0.6}O_2$	28.5
			P2-$Na_{0.73}Ni_{0.4}Mn_{0.6}O_2$	67.8
			NiO	3.7
8442-950	$Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	950	O3-$Na_{0.81}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	74.9
			P2-$Na_{0.68}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	20.8
			NiO	4.3
8424-950	$Na_{0.8}Ni_{0.4}Mn_{0.2}Ti_{0.4}O_2$	950	O3-$Na_{0.77}Ni_{0.4}Mn_{0.2}Ti_{0.4}O_2$	96.8
			NiO	3.2
846-Ti-950	$Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$	950	$Na_{0.81}Ni_{0.4}Ti_{0.6}O_2$	100

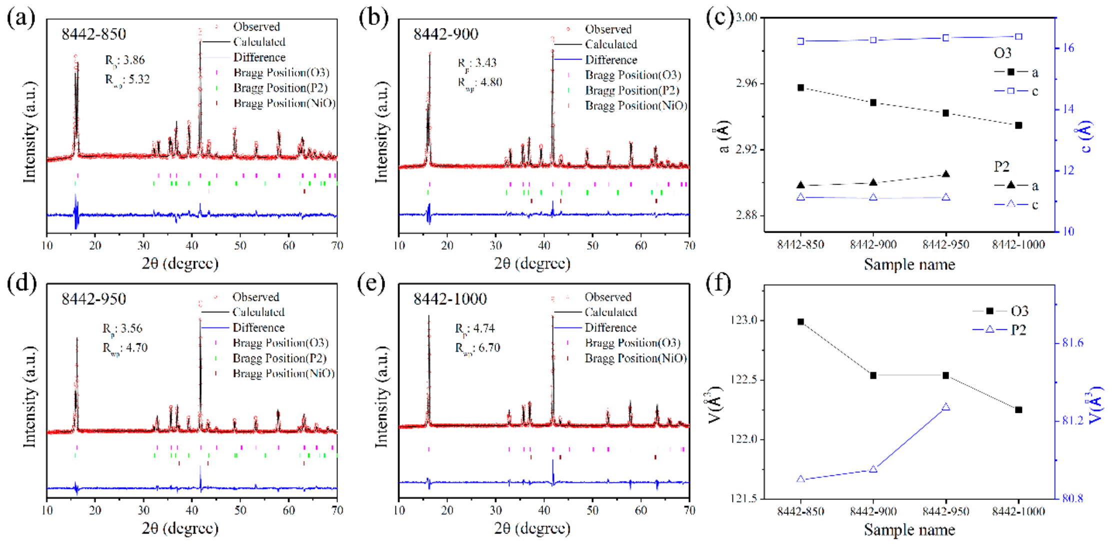

Figure S2. XRD patterns and refinement results of (a) $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-850, (b) $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-900, (d) $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-950, and (e) $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-1000. (c) and (f) the evolution of cell parameters *a*, *c*, and unit cell volume *V* of O3 and P2 structures with the increase of synthesis temperature.

Table S6. Structural parameters and atomic coordinates and occupancies of the $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-850 obtained by refining XRD pattern (*R*-factors: *R*p=3.86%, *R*wp=5.32%)

Phase content	Atom	Site	*x*	*y*	*z*	g	Lattice parameters
O3 (59.0 wt%)	Na	*3b*	0	0	0.5	0.858(10)	Space group: R-3m *a*=2.9579(5)Å, *c*=16.2345(5)Å
	Ni/Mn/Ti	*3a*	0	0	0	0.4/0.4/0.2	
	O	*6c*	0	0	0.2608(4)	1	
P2 (37.1 wt%)	Na1	*2b*	0	0	0.25	0.274(12)	Space group: $P6_3/mmc$, *a*=2.8980(9)Å *c*=11.1272(4)Å
	Na2	*2d*	0.6667	0.3333	0.25	0.389(17)	
	Ni/Mn/Ti	*2a*	0	0	0	0.4/0.4/0.2	
	4f	0.6667	0.3333	0.0983(9)	1	*4f*	

Table S7. Structural parameters and atomic coordinates and occupancies of the $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-900 obtained by refining XRD pattern (*R*-factors: *R*p=3.43%, *R*wp=4.80%)

Phase content	Atom	Site	*x*	*y*	*z*	g	Lattice parameters
O3 (67.8 wt%)	Na	*3b*	0	0	0.5	0.827(18)	Space group: R-3m *a*=2.9489(3)Å *c*=16.2762(3)Å
	Ni/Mn/Ti	*3a*	0	0	0	0.4/0.4/0.2	
	O	*6c*	0	0	0.2646(3)	1	
P2 (28.8 wt%)	Na1	*2b*	0	0	0.25	0.289(11)	Space group: $P6_3$/mmc, *a*= 2.9000(1)Å *c*=11.1191(4)Å
	Na2	*2d*	0.6667	0.3333	0.25	0.358(14)	
	Ni/Mn/Ti	*2a*	0	0	0	0.4/0.4/0.2	
	O	*4f*	0.6667	0.3333	0.0935(10)	1	

Table S8. Structural parameters and atomic coordinates and occupancies of the $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-1000 obtained by refining XRD pattern

O3 phase

Atom	Site	*x*	*y*	*z*	g
Na	*3b*	0	0	0.5	0.778(21)
Ni/Mn/Ti	*3a*	0	0	0	0.4/0.4/0.2
O	*6c*	0	0	0.2653(3)	1

Space group: R-3m, *a*= 2.93434(3) Å, *c*= 16.3860(3) Å, phase fraction 96.0 wt% *R*-factors: *R*p=4.74%, *R*wp=6.70%

Table S9. The designed chemical compositions of $Na_{0.8}Ni_{0.4}Mn_{0.6-x}Ti_xO_2$-950 and calculated results obtained by refining XRD patterns

Sample name	Designed composition	Temperature (℃)	Phase	Weight Frac. (%)
8442-850	$Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	850	O3-$Na_{0.86}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	59.0
			P2-$Na_{0.66}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	37.1
			NiO	3.9
8442-900	$Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	900	O3-$Na_{0.83}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	67.8
			P2-$Na_{0.65}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	28.8
			NiO	3.4
8442-950	$Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	950	O3-$Na_{0.81}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	74.9
			P2-$Na_{0.68}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	20.8
			NiO	4.3
8442-1000	$Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	1000	O3-$Na_{0.78}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$	96.0
			NiO	4

Table S10. Stoichiometry of $Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-T (T=850, 900, 950, 1000 ℃, denoted as 8442-T) samples determined by ICP-AES.

Sample name	Na	Ni	Mn	Ti
8442-850	0.794	0.404	0.410	0.186
8442-900	0.782	0.403	0.406	0.191
8442-950	0.773	0.406	0.406	0.188
8442-1000	0.768	0.409	0.404	0.187

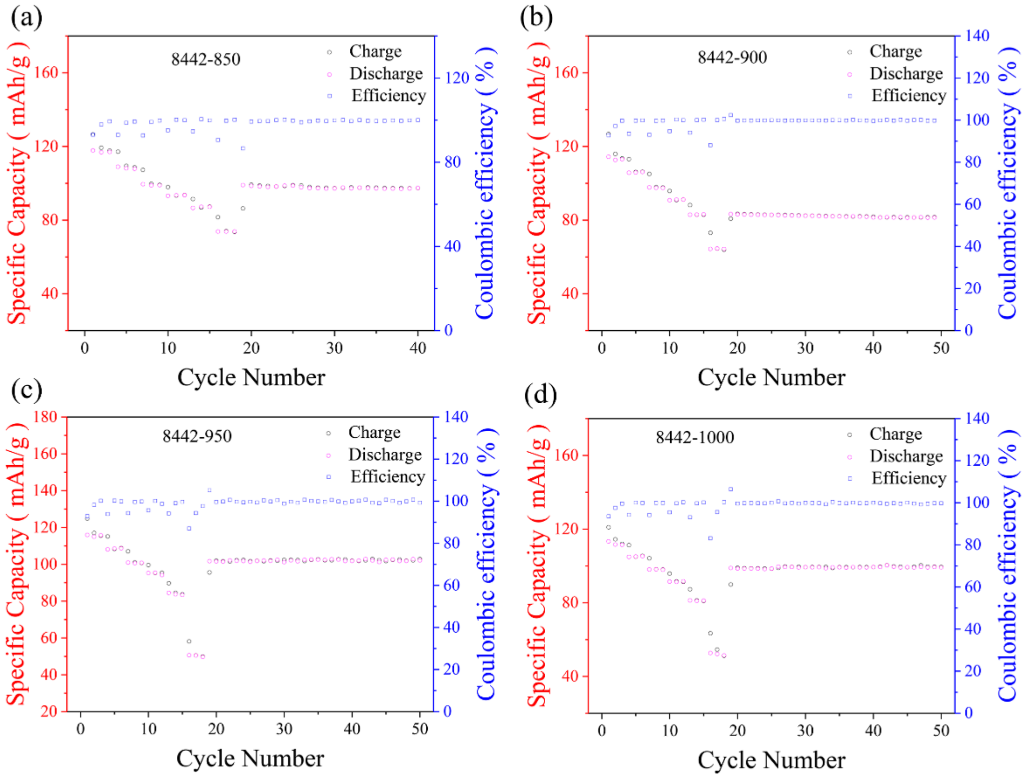

Figure S3. The cycling performance of (a) 8442-850, (b) 8442-900, (c) 8442-950, (d) 8442-1000 electrode, respectively.

Table S11. The electrochemical performance comparison of P2/O3 biphasic layered oxide cathodes.

Materials	Voltage range (V)	Capacity (0.1C, mAh/g)	Rate	Cycling
$Na_{0.67}Ni_{0.33}Mn_{0.57}Sn_{0.1}O_2$ [1]	2-4.3	155.2	66%, 150mA/g	64%, 30cycle, 0.1C
$Na_{0.67}Fe_{0.425}Mn_{0.425}Mg_{0.15}O_2$ [2]	1.5-4.2	146.1	40%, 2C	95.7%, 50cycle, 1C
$Na_{0.67}Fe_{0.5}Mn_{0.46}Mg_{0.04}O_2$ [3]	1.5-4.2	182(0.2C)	61%, 1C	63.9%, 70cycle,1C
$Li_{0.2}Na_{0.8}Ni_{0.33}Mn_{0.67}O_2$ [4]	2-4.3	127.8	53%, 20C	61.5%, 200cycle, 0.1C
P2-$Na_{2/3}MnO_2$-coated O3-$NaNi_{0.5}Mn_{0.5}O_2$ [5]	2-4	141	73%, 15C	85.3%, 150cycle, 1C
$Na_{0.85}Ni_{0.34}Mn_{0.33}Ti_{0.33}O_2$ [6]	2.2-4.4	126.6	65%, 10C	80.6, 200cycle, 1C
$Na_{0.7}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$ [7]	2-4.3	193	52%, 5C	80.04%, 300cycle, 5C
$Na_{0.766}Ni_{0.33}Mn_{0.5}Fe_{0.1}Ti_{0.07}O_2$ [8]	2.2-4.3	144(0.2C)	64%, 10C	75.4%, 500cycle, 5C
$Na_{7/9}Ni_{2/9}Mn_{4/9}Fe_{1/9}Mg_{1/9}Li_{1/9}O_2$ [9]	2-4.4	170.5	62%, 10C	71.8%, 500cycle, 5C
$Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-950	2-4.2	120	54%, 5C	84%, 700cycle, 3C
$Na_{0.8}Ni_{0.4}Mn_{0.4}Ti_{0.2}O_2$-850 (this work)	2-4.2	120	65%, 5C	74%, 700cycle, 3C

References

1. Li, R.; Liu, Y.; Wang, Z.; Li, J. A P2/O3 biphasic cathode material with highly reversibility synthesized by Sn-substitution for Na-ion batteries. *Electrochim. Acta* **2019**, *318*, 14-22. https://doi.org/10.1016/j.electacta.2019.06.020.
2. Zhou, D.; Huang, W.; Lv, X.; Zhao, F. A novel P2/O3 biphase $Na_{0.67}Fe_{0.425}Mn_{0.425}Mg_{0.15}O_2$ as cathode for high-performance sodium-ion batteries. *J. Power Sources* **2019**, *421*, 147-155. https://doi.org/10.1016/j.jpowsour.2019.02.061.
3. Zhou, D.; Zeng, C.; Ling, D.; Wang, T.; Gao, Z.; Li, J.; Tian, L.; Wang, Y.; Huang, W. Sustainable alternative cathodes of sodium-ion batteries using hybrid P2/O3 phase $Na_{0.67}Fe_{0.5}Mn_{0.5-x}Mg_xO_2$. *J. Alloys Compd.* **2023**, *931*, 167567. https://doi.org/10.1016/j.jallcom.2022.167567.
4. Feng, J.; Luo, S.-h.; Cong, J.; Li, K.; Yan, S.; Wang, Q.; Zhang, Y.; Liu, X.; Lei, X.; Hou, P.-q. Synthesis and electrochemical properties of Co-free P2/O3 biphasic $Na_{1-x}Li_xNi_{0.33}Mn_{0.67}O_2$ cathode material for sodium-ion batteries. *J. Electroanal. Chem.* **2022**, *916*, 116378. https://doi.org/10.1016/j.jelechem.2022.116378.
5. Liang, X.; Yu, T.-Y.; Ryu, H.-H.; Sun, Y.-K. Hierarchical O3/P2 heterostructured cathode materials for advanced sodium-ion batteries. *Energy Storage Mate.* **2022**, *47*, 515-525. https://doi.org/10.1016/j.ensm.2022.02.043.
6. Yu, L.; Cheng, Z.; Xu, K.; Chang, Y.-X.; Feng, Y.-H.; Si, D.; Liu, M.; Wang, P.-F.; Xu, S. Interlocking biphasic chemistry for high-voltage P2/O3 sodium layered oxide cathode. *Energy Storage Mater.* **2022**, *50*, 730-739. https://doi.org/10.1016/j.ensm.2022.06.012.
7. Zhai, J.; Ji, H.; Ji, W.; Wang, R.; Huang, Z.; Yang, T.; Wang, C.; Zhang, T.; Chen, Z.; Zhao, W.; et al. Suppressing the irreversible phase transition from P2 to O2 in sodium-layered cathode via integrating P2- and O3-type structures. *Mater. Today Energy* **2022**, *29*, 101106. https://doi.org/10.1016/j.mtener.2022.101106.
8. Cheng, Z.; Fan, X.Y.; Yu, L.; Hua, W.; Guo, Y.J.; Feng, Y.H.; Ji, F.D.; Liu, M.; Yin, Y.X.; Han, X.; et al. A rational biphasic tailoring strategy enabling high-performance layered cathodes for sodium-ion batteries. *Angew. Chem.* **2022**, *134*, e202117728. https://doi.org/10.1002/ange.202117728.
9. Liang, X.; Sun, Y.K. A novel pentanary metal oxide cathode with P2/O3 biphasic structure for high-performance sodium-ion batteries. *Adv. Funct. Mater.* **2022**, *32*, 2206154. https://doi.org/10.1002/adfm.202206154.