Electronic Supplementary Material (ESI) for Energy & Environmental Science.

High-performance symmetric sodium-ion batteries using a new bipolar material O3-type $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$

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Table S1

Table S1 Lattice parameters of O3-type $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ powder samples after Rietveld refinement.

Phase		α-$NaFeO_2$
Symmetry		Rhombohedral
Space Group		R-3m
Cell parameters	a (Å)	2.96785 (2)
	b (Å)	2.96785 (2)
	c (Å)	16.27990(9)
	α (°)	90.000
	β (°)	90.000
	γ (°)	120.000
	Volume (Å³)	124.184(1)
Agreement factors	R_{wp} (%)	14.844
	R_p (%)	10.359
	S	0.8375

Table S2

Table S2 Rietveld refinement atomic coordinates for O3-type $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ based on HR-SXRD data.

Atom	Wyck position	x	y	z	Biso
Na	3b	0.000	0.000	0.500	1.99(3)
Ni	3a	0.000	0.000	0.000	0.54(1)
Ti	3a	0.000	0.000	0.000	0.54(1)
O	6c	0.000	0.000	0.26825(7)	0.66(2)

Table S3

Table S3 The comparison of the electrochemical performance between our as-prepared $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ and the reported $Na_{2/3}Ni_{1/3}Ti_{2/3}O_2$ samples[1] as bipolar materials in sodium half cells.

	Cathode performance			Anode performance			Full cells performance		
	Capacity(0.2C)	Rate(1C)	Cycles	Capacity(0.2C)	Rate(1C)	Cycles	Capacity(0.2C)	Rate(1C)	Cycles
$Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$	83mAh/g	63mAh/g	250cycles	107mAh/g	62mAh/g	250cycles	85 mAh/g	53mAh/g	150cycles
$Na_{2/3}Ni_{1/3}Ti_{2/3}O_2$ [1]	75mAh/g	35mAh/g	30cycles	78mAh/g	53mAh/g	25cycles	—	—	—

[1] R. Shanmugam, W. Lai, ECS Electrochemistry *Letters 2014, 3, A23-A25.*

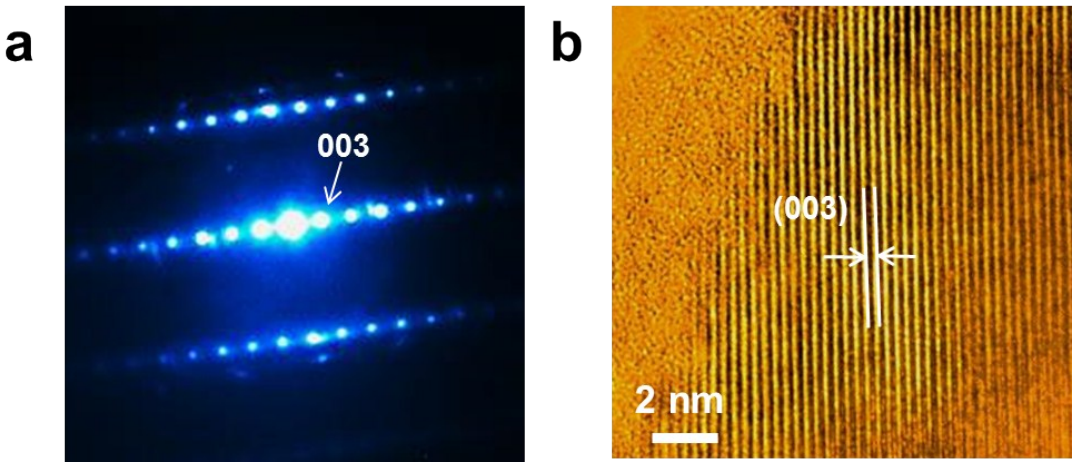

Figure S1. **(a)** The SAED patterns of $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ samples. **(b)** HR-TEM bright field images of $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ samples.

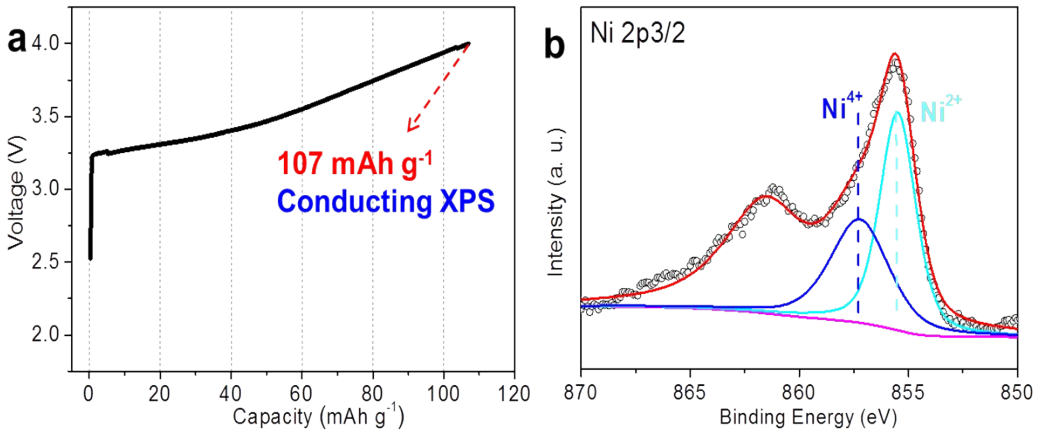

Figure S2. **(a)** The initial charge profile of $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$/Na half cells. **(b)** The XPS spectra of Ni-2p peaks of the desodiated $Na_{0.8-x}Ni_{0.4}Ti_{0.6}O_2$ after initial charge process.

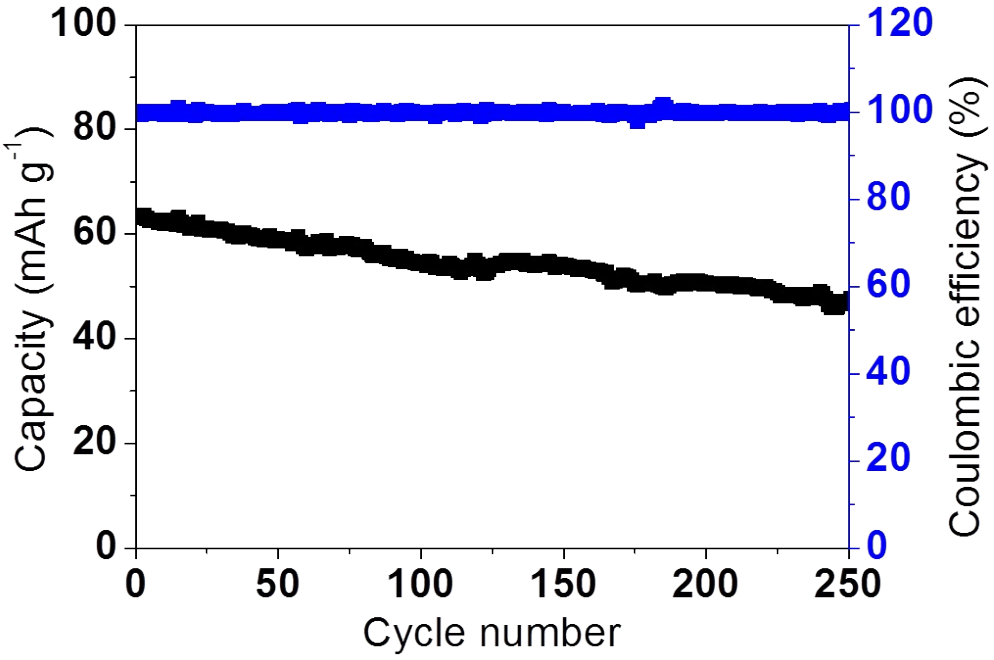

Figure S3. Cycle performance and relative coulombic efficiency of $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$//Na half cell with the voltage range of 2-4 V for 250 cycles at a 1C rate.

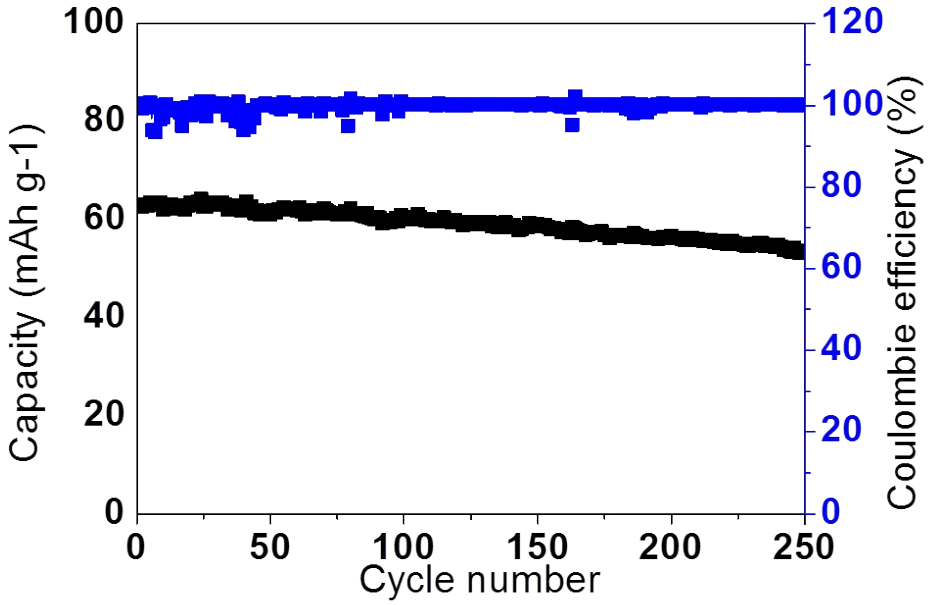

Figure S4. Cycle performance and relative coulombic efficiency of $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$//Na half cell with the voltage range of 0.01-2.5 V for 250 cycles at a 1C rate.

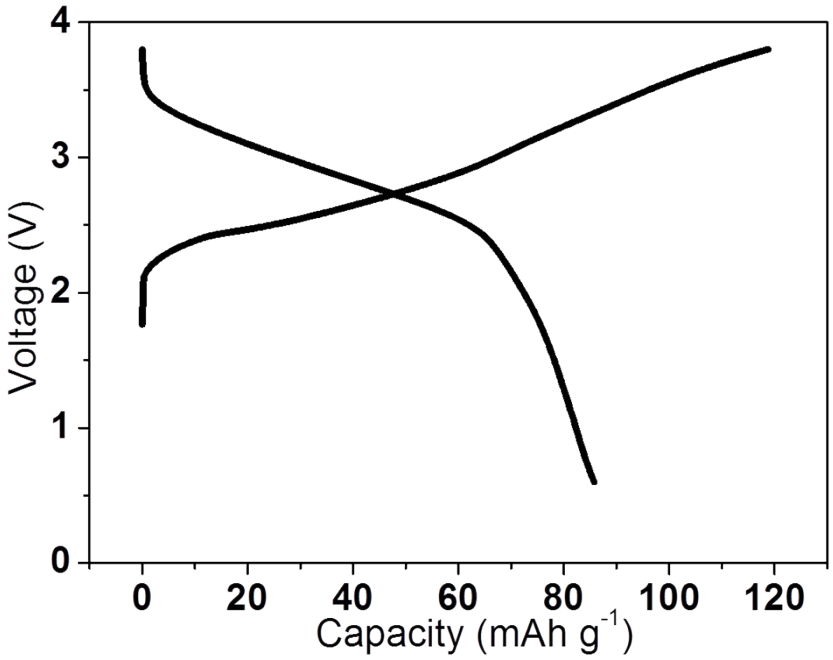

Figure S5. The first charge-discharge profile of bipolar $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$-based symmetric sodium-ion batteries.

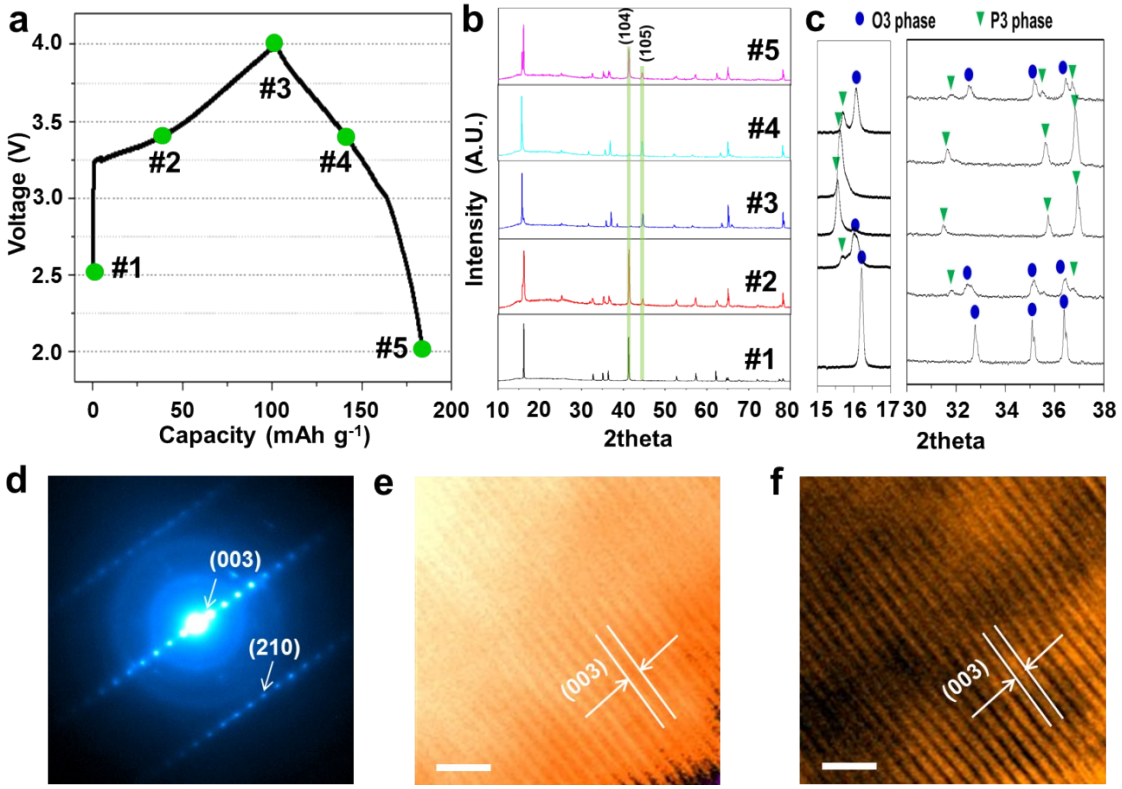

Figure S6. Structural evolution using $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ as cathode **(a)** The first charge-discharge profile of the $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$/Na half cell in a low potential area, and the green points correspond to the different charge-discharge states conducted by ex-situ XRD experiment. **(b)** The ex-situ XRD patterns of $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ at the different charge-discharge states shown in **(a)**. **(c)** The expanded view in the regions of 15-17° and 30-38° for the ex-situ XRD patterns shown in **(b)**. **(d)** The SAED patterns **(e)** HAADF-STEM image and **(f)** ABF-STEM image of the fully charged (Point 3 in **(a)**) $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ samples projected along $[1\bar{1}0]$ direction.

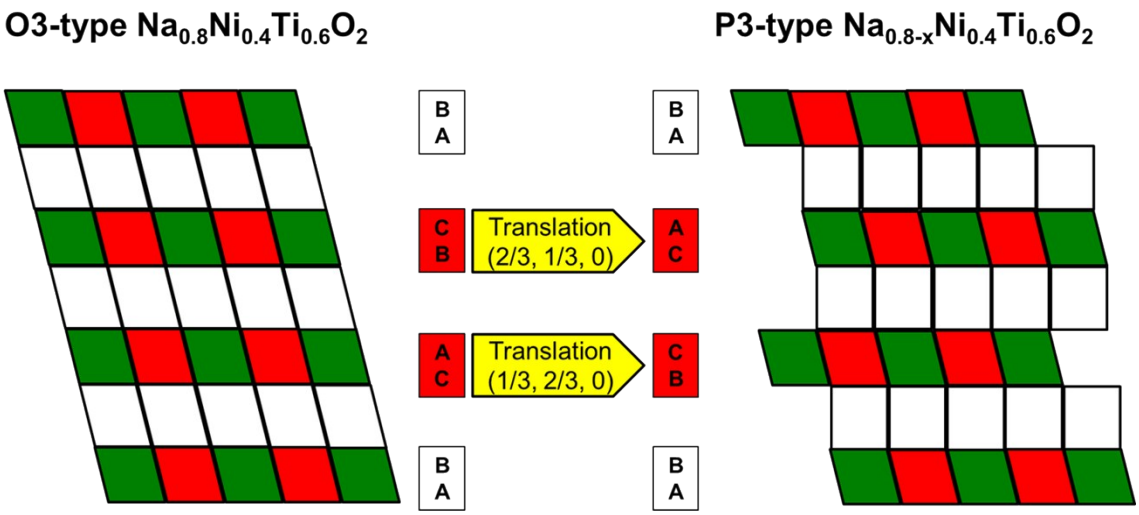

Figure S7. Schematic of the phase transition from O3-type $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ to P3-type $Na_{0.8-x}Ni_{0.4}Ti_{0.6}O_2$ in the half cell of $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$/ Na with the voltage range of 2-4 V.

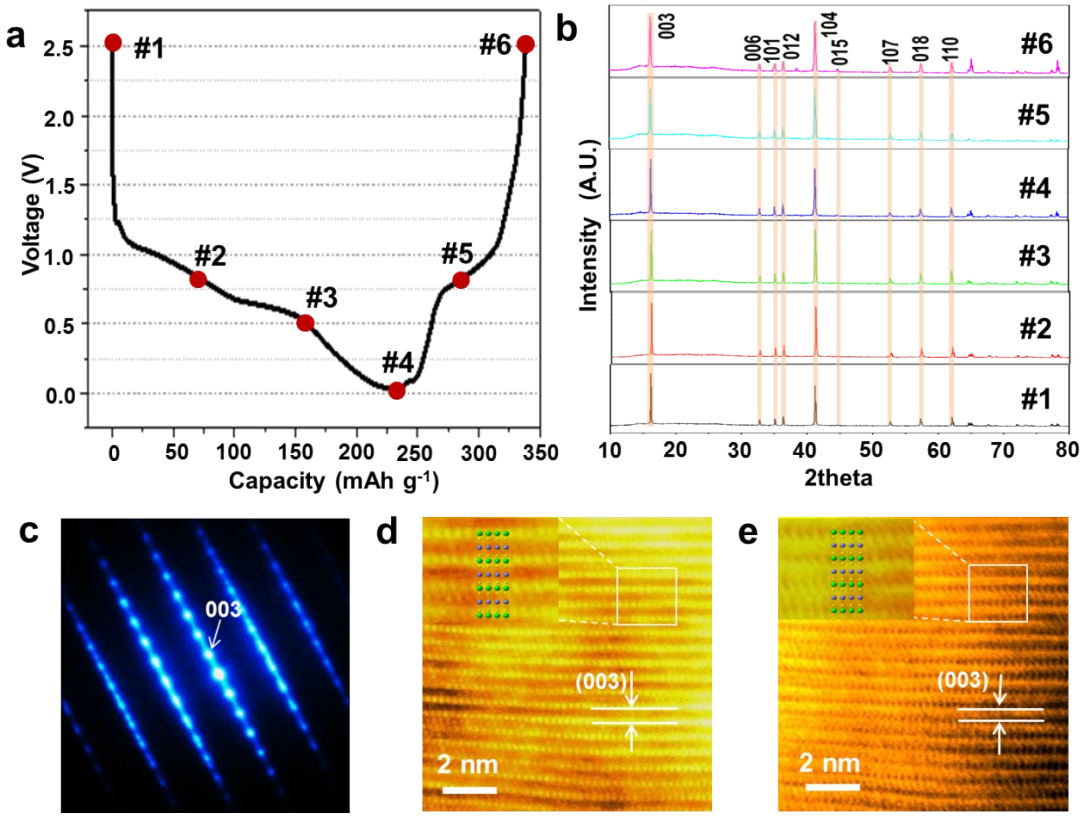

Figure S8. Structural evolution using $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ as anode **(a)** The first discharge-charge profile of the $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$/Na half cell, and the brown points correspond to the different discharge-charge states conducted by ex-situ XRD experiment. **(b)** The ex-situ XRD patterns of $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ at the different discharge-charge states shown in **(a)**. **(c)** The SAED patterns **(d)** HAADF-STEM image and **(e)** ABF-STEM image of the fully discharged (Point 4 in **(a)**) $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$ samples projected along [100] direction. The insets of **(d)** and **(e)** in top-left corners show the typical sodium (bule) and transition metal (green) occupancies in O3 layered structure.

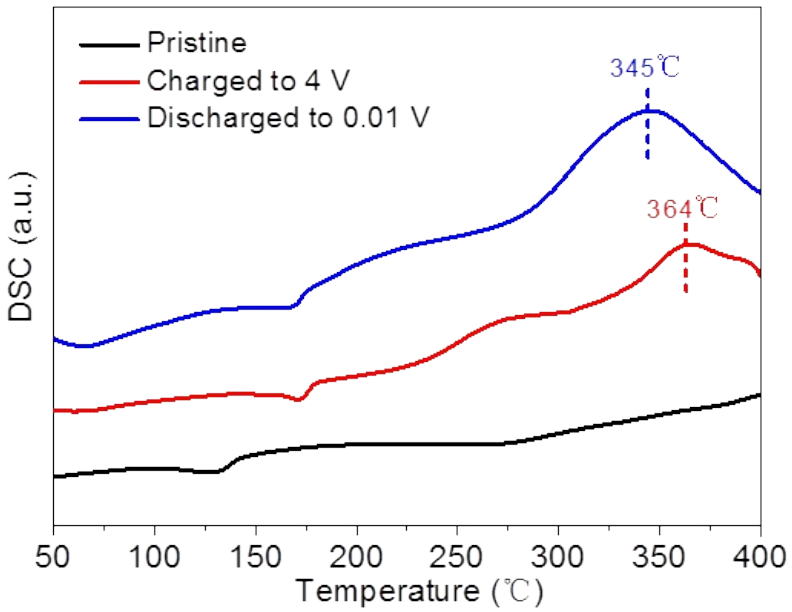

Figure S9. Differential scanning calorimetry (DSC) spectra of the pristine $Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$, desodiated $Na_{0.8-x}Ni_{0.4}Ti_{0.6}O_2$ (charging to 4 V) and sodiated $Na_{0.8+y}Ni_{0.4}Ti_{0.6}O_2$ (discharging to 0.01 V).