Supplementary Information

In-situ forming NaTi₂(PO₄)₃ coating layer to enhance the high-temperature performance of NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ cathode material

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Experimental section

Materials synthesis

Synthesis of sodium titanium phosphate (NTP) precursor: With 0.02 mol sodium titanium phosphate as the target, nano-titanium dioxide (99.8%, Aladdin), ammonium dihydrogen phosphate (99.99%, Macklin), and sodium carbonate (99.5%, Aladdin) were added into a stainless-steel ball-milling tank in accordance with the molar stoichiometric ratio. An appropriate amount of anhydrous ethanol was added as the dispersant. The mixture was then ball-milled at 600 rpm for 120 minutes to obtain a homogeneous paste. This paste was blast dried at 80 °C overnight, resulting in a brown-yellow precursor powder.

Preparation of the coating samples: The as-prepared precursor powder was dispersed in anhydrous ethanol, with the amount determined by the target coating content. The dispersion was magnetically stirred for 5 hours until a homogeneous suspension was formed. Subsequently, the cathode matrix material, NFM powder, was added to the suspension and stirred at 80 °C to form the composites. The resulting mixture was further mixed using a mortar and pestle, and then sintered in a tube-type furnace filled with oxygen at 450 °C for 4 hours, followed by 750 °C for 6 hours, with a heating rate of 5 °C min⁻¹. Finally, the samples were labeled as NFM-Blank and NFM@NTP-x (x=1,2,3,5) based on the coating content of 0, 1, 2, 3, and 5 wt.%, respectively. The coating content was calculated based on the total mass of raw materials, i.e., x wt.% refers to the total mass of nano-TiO₂, NH₄H₂PO₄, and Na₂CO₃ is x percent to the matrix material's mass.

Materials characterization

Powder X-ray diffraction (XRD, Ultima IV, Cu-Kα) was utilized to determine the phase structure and lattice parameters of the as-synthesized samples with a 2θ range of 10 to 80° and a step rate of 5 ° min⁻¹. The analysis of morphology, particle size, and element distribution of material samples was performed by field-emission scanning electron microscopy (FE-SEM, SM-IT700HR) coupled with an energy dispersive spectrometer (EDS, Xplore 30) using mapping mode. Transmission electron microscopic (TEM, TitanG2 60-300) was employed to observe the internal microstructure, surface texture, and lattice fringe of samples. The X-ray photoelectron

spectroscopy (XPS, PHI VersaProbe4) was utilized to detect the element type and bonding information on the surface of samples.

Electrochemical measurement

The electrochemical performance of NFM@NTP-x (x=0,1,2,3,5) samples were evaluated using CR2032 coin-type cells. A uniform slurry was formed by dispersing the as-prepared materials, polyvinylidene fluoride (PVDF), and Super-P (90:5:5 in weight ratio) in N-methyl-2-pyrrolidone (NMP). Then, the slurry was pasted onto aluminum foil and dried under vacuum at 90 °C for 10 hours. The cathode electrodes were punched into round disks with a 12 mm diameter, and the mass loading of electroactive material was 4.5-5 mg cm⁻². For hard carbon (HC) anode, mixing HC, carboxymethyl cellulose (CMC), Styrene, 1,3-butadiene polymer (SBR), and Super-P (95:1.5:2.5:1) in weight ratio) in deionized water to a uniform slurry. Then, the slurry was pasted onto aluminum foil and dried at 120 °C for 10 hours. The anode electrodes were punched into round disks with a 14 mm diameter, and the mass loading of electroactive material of electroactive material was 2-3 mg cm⁻². Sodium metals were served as the reference and counter electrode. The electrolyte consisted of a 1 M NaPF₆ salt dissolved in ethylene carbonate (EC): propylene carbonate (PC)=3:2 (in volume ratio) solution, supplemented with 3 wt.% fluoroethylene carbonate (FEC) and 1 wt.% 1,3-propane sultone (PS) as additives. Glass fiber (Whatman, GF/D) was used as the separator.

To collect galvanostatic charge and discharge data, the NEWARE battery testing system (Shenzhen, China) was employed within the voltage range of 2.0 to 4.0 V (vs. Na⁺/Na), and the standard current density of 1C equivalent to 130 mA g⁻¹. Likewise, the full batteries were activated in a voltage range of 1.0 to 4.0 V and then cycled in the voltage scope of 1.5-3.95 V. Galvanostatic intermittent titration technique (GITT) measurements were performed at 0.05C, using a pulse time of 0.5 hour and a relaxation time of 1 hour within the voltage range 2.0 to 4.0 V. Cyclic voltammetry (CV) profiles were recorded with an electrochemical workstation (CHI 7000, Chenhua), spanning from 2.0 to 4.0 V at a scan rate of 0.1 mV s⁻¹. For the electrochemical impedance spectroscopy (EIS) test, the cells were charged to 3.5 V at 0.1C and measurements were performed on an electrochemical workstation (INTERFACE5000E, Gamry) in the frequency range of 10 mHz-100 kHz, employing an AC signal amplitude of 5 mV.



Fig.S1 Characterizations for NTP precursor: (a) XRD patterns; (b-d) SEM images and corresponding EDS-mapping results



Fig. S2 XRD patterns of the NTP and NFM@NTP-20 obtained through increasing the coating content to 20 wt.% and 100 wt.% under the same sintering condition



Fig. S3 SEM images for (a, b) NFM-Blank, (c, d) NFM@NTP-1, (e, f) NFM@NTP-2, (g, h) NFM@NTP-3, (i, j) NFM@NTP-5 and (k) corresponding EDS-mapping results for NFM@NTP-2. The scalebar of inserted images is 2 µm.



Fig. S4 XPS results for NFM-Blank (top) and NFM@NTP-2 (bottom): (a) survey spectrum and high-resolution spectra for (b) Ni 2p, (c) Fe 2p, (d) Mn 2p



Fig. S5 Micro-structure features of samples: (a) HAADF image and corresponding EDS-mapping results for NFM-Blank; (b-e) FFT patterns of rectangular regions I, II, III, and IV depicted in Fig. 2a, respectively; (f, g) FFT patterns of rectangular regions V and VI depicted in Fig. 2b



Fig.S6 Representative charge-discharge profiles at 0.5C for the 1st, 10th, 20th, 50th, and 100th cycles for (a) NFM-Blank and (b) NFM@NTP-2



Fig.S7 SEM images and corresponding EDS-mapping results of P and Ti elements for (a) NFM@NTP-1, (b) NFM@NTP-2, (c) NFM@NTP-3, and (d) NFM@NTP-5



Fig.S8 Contrast of the cycle performance for samples: (a) coated by the identical amount of nano-TiO₂ (NFM@TiO₂), NH₄H₂PO₄-Na₂CO₃ (NFM@Na₃PO₄), NTP precursor pre-sintered at 450 °C for 4 h (NFM/Pre-NTP) and pure NTP sintered at 450 °C for 4 h and 750 °C for 6 h (NFM/Pure-NTP), respectively; (b) comparison of the capacity retention rate



Fig.S9 Electrochemical properties of full batteries. (a) initial charging-discharging profile of hard carbon anode at 0.1C, 25 °C; (b) schematic of full cells' configuration and working principle; the first three activation curves for (c) NFM-Blank/HC and (d) NFM@NTP-2/HC at 0.1C, 25 °C and in the voltage range of 1 to 4 V; (e) long-term cyclic stability for NFM-Blank/HC and NFM@NTP-2/HC at 0.5C, 45 °C and in the voltage range of 1.5 to 3.95 V



Fig.S10 XRD patterns of samples: (a) comparison for samples with different NTP coating content and Rietveld refinements of XRD pattern for (b) NFM@NTP-1, (c) NFM@NTP-3, (d) NFM@NTP-5, and (e) NFM@NTP-TiO₂, respectively



Fig.S11 Schematic diagram of thickness change in Na interslab and TM interslab after partial Ti doping

The spacing of the Na interslab $(S(NaO_2))$ and the TM interslab $(S(MO_2))$ can be calculated by the following equation according to the stacking law of layered oxides:

$3 \times S(MO_2) + 3 \times S(NaO_2) = c$	(eq. S1)
$S(MO_2) + 0.5 \times S(NaO_2) = c \times Z_{ox}$	(eq. S2)

Herein, The Z_{ox} means the oxygen position at 6c, which is 0.2296 and 0.2283 for NFM-Blank and NFM@NTP-2 according to XRD refinements, respectively.



Fig.S12 Ex-situ XRD patterns for (a) NFM-Blank and (b) NFM@NTP-2 in the initial charge-discharge process at 0.1C under 45 °C



Fig.S13 XRD refinements for (a) NFM-Blank-100th and (b) NFM@NTP-2-100th. Kinetic properties of cycled samples: (c) Graphic illustration for each symbol in the eq. S3 in a single titration, (d) GITT curves and (e) Na⁺ diffusivity derived from the GITT measurement during charge-discharge process for NFM-Blank-100th and NFM@NTP-2-100th

The Na^+ values were calculated according to the following equation^{1, 2}:

$$D = \frac{4}{\pi \tau} \left(\frac{n_m V_m}{S} \right)^2 \cdot \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$
(eq. S3)

Where, τ is the duration of the current pulse (s); n_m is the number of moles (mol); V_m is the molar volume of the electrode (cm³ mol⁻¹); *S* is the contact area between the electrode and the electrolyte (cm²); ΔE_s and ΔE_{τ} are the voltage change in charge/discharge process and the single titration process, respectively.



Fig.S14 The EIS results for NFM-Blank, NFM-Blank-100th, NFM@NTP-2, and NFM@NTP-2-100th: (a) Nyquist plots; (b) Individual Nyquist plots for individual electrode, where the origin, green and purple color refer to the impedance of the battery, sodium anode and NFM@NTP-2 cathode, respectively; (c) the linear fitting of Z' versus $\omega^{-1/2}$ derived from (a). The dot and line represent the raw data and fitting results, respectively

A three-electrode configuration was assembled to investigate the impedance characteristics of individual electrodes, as shown in Fig. S14b. The Nyquist plots for the battery (Z_{we-Ce}) and the sodium anode (Z_{Ce}) exhibit a three semi-circle feature, whereas the NFM@NTP-2 cathode (Z_{we}) displays two semi circles, suggesting the additional semi-circle largely attributed to the sodium foil.

Additionally, the corresponding values of Na^+ derived from the EIS results can be calculated by the following equation^{3, 4}:

$$D_{Na^{+}} = \frac{R^{2}T^{2}}{2A^{2}n^{4}F^{4}C^{2}\sigma^{2}}$$
 (eq. S4)
Z' = R_s + R_{ct} + $\sigma\omega^{1/2}$ (eq. S5)

Herein, *R* is the gas constant (J mol⁻¹ K⁻¹). *T* is the absolute temperature (K), *A* is the surface area of the cathode (cm²). *n* is the number of electron transport per molecule in the redox process. *F* is the Faraday constant (C mol⁻¹). *C* is the molar density of sodium ion in electrode material (mol cm⁻³). *Z*' is the real part of Warburg resistance (Ω). ^R_s and ^R_{ct} represents the ohmic resistance and charge-transfer resistance. σ is the Warburg factor related to *Z*' and angular frequency. ω is the angular frequency.

Supplementary Figure S15



Fig.S15 DCR results for NFM-Blank, NFM-Blank-100th, NFM@NTP-2, and NFM@NTP-2-100th. The inserted image reflects the change in DCR value for samples before and after cycling at high temperature.

The testing program of the direct current internal resistance (DCR) is set as following:

Stage 1: charging batteries to fully charge state (100 SOC) at a current density of 0.1C, then discharging at a current density of 1C for 10 s, followed by relaxation for 5 min.

Stage 2: discharging batteries to next SOC at a current density of 0.5C and relaxing for 30 min. And then repeating **stage 1** and **stage 2** until the SOC reaching 0.

The DCR in each 1C-discharging period can be calculated by the Ohm's law:

$$R = \frac{\Delta E}{I}$$
 (eq. S6)

Samples	NaOH (wt.%)	Na ₂ CO ₃ (wt.%)	Residual sodium (wt.%)
NFM-Blank	0.152	2.104	1.001
NFM@TP-2	0.040	1.655	0.741
NFM@NTP-2	0.109	1.689	0.796

Table S1 The titration results of residual sodium for NFM-Blank, NFM@TP-2 and NFM@NTP-2

Remark: the NFM@TP-2 refers to the matrix merely coated by the mixture of nano-TiO₂ and NH₄H₂PO₄

Titration of residual sodium: the materials were dispersed in the deionized water and magnetically stirred at 300 rpm for 3 minutes, and then filtered the suspension to obtain the filtrate. Then, the filtrate was titrated by an automatic potentiometric titrator (ZDJ-4B, INESA) using a concentration of 0.1mol L⁻¹ hydrochloric acid as the titrant. The titration destinations were labeled as V₁, V₂ and V₃, which represents the volume consumption of hydrochloric acid of the OH⁻, $HCO_3^{-}-CO_3^{2-}$ and the CO_3^{-2} , respectively.

	Initial	Initial	Initial	Capacity	Dischargo
	discharge	Coulombic	discharge	retention at	
Samples	capacity at	efficiency (25	capacity at	0.5C after	
	0.1C (25 °C,	°C %)	0.5C (45 °C,	100 cycles	$2C(25^{-1}C)$
	mAh g⁻¹)	C, 78j	mAh g⁻¹)	(45 °C, %)	mang)
NFM-Blank	136.2	91.8	135.4	83.0	94.4
NFM@NTP-1	133.4	92.5	129.1	76.2	102.0
NFM@NTP-2	133.0	93.8	131.5	90.3	104.5
NFM@NTP-3	130.1	93.3	129.5	84.0	97.7
NFM@NTP-5	125.5	95.4	122.7	85.7	97.0

Table S2 The specific electrochemical properties data of all NFM@NTP-x samples

Samples	Initial discharge capacity at 0.1C (25 °C, mAh g ⁻¹)	Initial Coulombic efficiency (25 °C, %)	Initial discharge capacity at 0.5C (45 °C, mAh g ⁻¹)	Capacity retention at 0.5C after 100 cycles (45 °C, %)
NFM-Blank	136.2	91.8	135.4	83.0
NFM@NTP-2	133.0	93.8	131.5	90.3
NFM@TiO ₂	135.9	93.8	133.9	79.9
NFM@Na ₃ PO ₄	132.0	92.1	131.0	86.7
NFM/Pre-NTP	128.8	93.9	128.2	81.8
NFM/Pure-NTP	130.1	93.5	126.6	82.4

Table S3 The specific electrochemical properties data of all samples with different modifications

Samples	Initial discharge capacity at 0.1C (25 °C, mAh g ⁻¹)	Initial Coulombic efficiency (25 °C, %)	Initial discharge capacity at 0.5C (45 °C, mAh g ⁻¹)	Capacity retention at 0.5C after 100 cycles (45 °C, %)
HC/Na	336.3 (sodiation)	91.6		
NFM-Blank/HC	128.0	88.2	<mark>113.9</mark>	<mark>84.0</mark>
NFM@NTP-2/HC	127.5	90.4	<mark>107.0</mark>	<mark>76.9</mark>

 Table S4 The specific electrochemical properties data of NFM-Blank/HC and NFM@NTP-2/HC

Samples	a (Å)	c (Å)	V (ų)	R _w (%)	NiO (wt.%)
NFM-Blank	2.9857	15.9939	123.471	3.73	1.39
NFM@NTP-1	2.9834	16.0087	123.395	2.32	2.52
NFM@NTP-2	2.9811	16.0169	123.268	1.47	2.25
NFM@NTP-3	2.9822	16.0175	123.363	1.46	2.12
NFM@NTP-5	2.9788	16.0471	123.309	1.47	3.69
NFM@TiO ₂	2.9702	16.1191	123.149	4.48	2.19

 Table S5 The XRD refinements data and lattice parameters of all samples

Samples	atom	x	Y	Z
	Na	0.0000	0.0000	0.0000
	Ni	0.0000	0.0000	0.5000
NFM-Blank	Fe	0.0000	0.0000	0.5000
	Mn	0.0000	0.0000	0.5000
	0	0.0000	0.0000	0.2296
	Na	0.0000	0.0000	0.0000
	Ni	0.0000	0.0000	0.5000
	Fe	0.0000	0.0000	0.5000
NFINI@NTP-1	Mn	0.0000	0.0000	0.5000
	Ti	0.0000	0.0000	0.5000
	0	0.0000	0.0000	0.2305
	Na	0.0000	0.0000	0.0000
	Ni	0.0000	0.0000	0.5000
	Fe	0.0000	0.0000	0.5000
NFM@NTP-2	Mn	0.0000	0.0000	0.5000
	Ti	0.0000	0.0000	0.5000
	0	0.0000	0.0000	0.2283
	Na	0.0000	0.0000	0.0000
	Ni	0.0000	0.0000	0.5000
	Fe	0.0000	0.0000	0.5000
NFIVI@NTP-5	Mn	0.0000	0.0000	0.5000
	Ti	0.0000	0.0000	0.5000
	0	0.0000	0.0000	0. 2289
	Na	0.0000	0.0000	0.0000
	Ni	0.0000	0.0000	0.5000
	Fe	0.0000	0.0000	0.5000
NFIVI@NTP-5	Mn	0.0000	0.0000	0.5000
	Ti	0.0000	0.0000	0.5000
	0	0.0000	0.0000	0.2283
	Na	0.0000	0.0000	0.0000
	Ni	0.0000	0.0000	0.5000
	Fe	0.0000	0.0000	0.5000
	Mn	0.0000	0.0000	0.5000
	Ti	0.0000	0.0000	0.5000
	0	0.0000	0.0000	0.2288

Table S6 The information about atomic site occupation of all samples

Samples	a (Å)	c (Å)	V (ų)	R _w (%)	Chi ²		
NFM-Blank-100th	2.9762	16.0202	122.15	5.94	2.20		
NFM@NTP-2-100th	2.9705	16.0435	122.596	4.13	5.49		

 Table S7
 The XRD refinements results of NFM-Blank-100th and NFM@NTP-2-100th

Samples	atom	Х	Y	Z
	Na	0.0000	0.0000	0.0000
	Ni	0.0000	0.0000	0.5000
NFM-Blank-100th	Fe	0.0000	0.0000	0.5000
	Mn	0.0000	0.0000	0.5000
	0	0.0000	0.0000	0.2382
	Na	0.0000	0.0000	0.0000
	Ni	0.0000	0.0000	0.5000
NFM@NTP-2-100th	Fe	0.0000	0.0000	0.5000
	Mn	0.0000	0.0000	0.5000
	Ti	0.0000	0.0000	0.5000
	0	0.0000	0.0000	0.2355

 Table S8 The information about atomic site occupation of cycled NFM-Blank and NFM@NTP-2

Samples	R _e (Ω)	R _c (Ω)	$R_{f}(\Omega)$	R _{ct} (Ω)	σ_{ω}	D ^{Na +} (cm² s ⁻¹)
NFM-Blank	3.707	8.66	45.94	38.91	4.846	9.02×10 ⁻¹³
NFM@NTP-2	4.030	13.54	32.08	24.46	2.599	3.14×10 ⁻¹²
NFM-Blank-100th	6.264	30.65	112.80	473.3	31.734	2.11×10 ⁻¹⁴
NFM@NTP-2-100th	6.489	66.70	63.44	245.50	13.250	1.21×10 ⁻¹³

 Table S9 The fitting data of the EIS for NFM-Blank and NFM@NTP-2 before and after cycling

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