

Supporting Information

Preparation of Sodium-Ion Cathode Materials with Excellent Performance Using a Co₃O₄-Modified Conformation Strategy

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Experimental details

1. Materials Synthesis:

The required materials were synthesized using solid-state reaction method which included NaNi_{0.4}Fe_{0.2}Mn_{0.4}O₂(NFM424), Co₃O₄ and Na₂CO₃. Initially, the necessary materials namely NFM424, Co₃O₄ and Na₂CO₃ were subjected to vacuum drying at a temperature of 100°C for a duration of 10 h. Subsequently 98wt% NFM424 and 2wt% Co₃O₄ (Aladdin, 99.5% purity) were milled for a period of time. Then an appropriate amount of anhydrous Na₂CO₃ (Aladdin, 99.5% purity) was added to compensate for potential Na element volatilization losses at high temperatures. Then grinding process was performed. Finally, the mixture was placed in a muffle furnace and heated at a rate of 2°C min⁻¹ to reach a temperature of 900°C with a heating duration of 12 h. After the heating process, the resulting product was thoroughly ground to obtain the desired material NaNi_{0.4}Fe_{0.2}Mn_{0.35}Co_{0.05}O₂ (NFMC).

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2. Materials Characterizations:

The crystal morphology of the grey powder was investigated using an X-ray diffractometer (XRD, Brook-D8 Advance) in the range of 10° to 80° with a scanning rate of $10^\circ \text{ min}^{-1}$. The electronic state of the sample surface was probed using an X-ray photoelectron spectrometer (XPS, AXIS-ULTRA DLD). The high-resolution microstructure of the material was observed by scanning electron microscopy (SEM, JEOL JSM7500) to study the crystal morphology. High-resolution transmission electron microscopy (HR-TEM) images and energy-dispersive X-ray spectroscopy (EDS) mapping were obtained using a JEM-F200 microscope equipped with an acceleration voltage of 200 kV and an Oxford Instruments EDS detector. Differential scanning calorimetry (DSC) measurements were carried out with a DSC 214 Polyma (Netzsch) instrument in an argon atmosphere, with a scanning rate of 5°C min^{-1} . Thermal gravimetric analysis (TGA) data were collected under an argon atmosphere using an STA 449F3 instrument at a scanning rate of 5°C min^{-1} . Additionally, the chemical analysis of metal ion molar ratios in the sample was conducted using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

3. Electrochemical Property:

During the cathode preparation process, a slurry was formed by mixing the 70wt% active material, 20wt% carbon black and 10wt% polyvinylidene fluoride (PVDF) along with an appropriate amount of N-methyl-2-pyrrolidone (NMP). Subsequently, this slurry was uniformly coated onto Al foil and subjected to vacuum drying at 120°C for a continuous period of 12 h. Upon completion of the drying process, the Al foil was cut

into circular discs with a diameter of 14 mm and then pressed to ensure that the quality of the cathode sheets fell within the range of 7.0-8.5 mg. The sodium-ion electrolyte used consisted of a 1M NaClO₄ solution mixed with ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) in a 1:1:1 ratio with the addition of 2% FEC as an additive. Composite sodium foils (Fig. S1) were used as the anode (Al foil on one end, sodium metal on the other) and a GF/A (Whatman CAT No.1820-047) glass fiber separator was employed. Electrochemical charge/discharge experiments were conducted on battery measurement system (CT2001A Wuhan Jinuo Electronics Co. Ltd.). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed at room temperature on a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). EIS measurements were carried out in the frequency range of 100 kHz to 0.01 Hz with an amplitude of 5 mV at open-circuit voltage. CV curves were obtained with a scan rate of 0.2 mV s⁻¹ in the voltage range of 2.5-3.85 V.

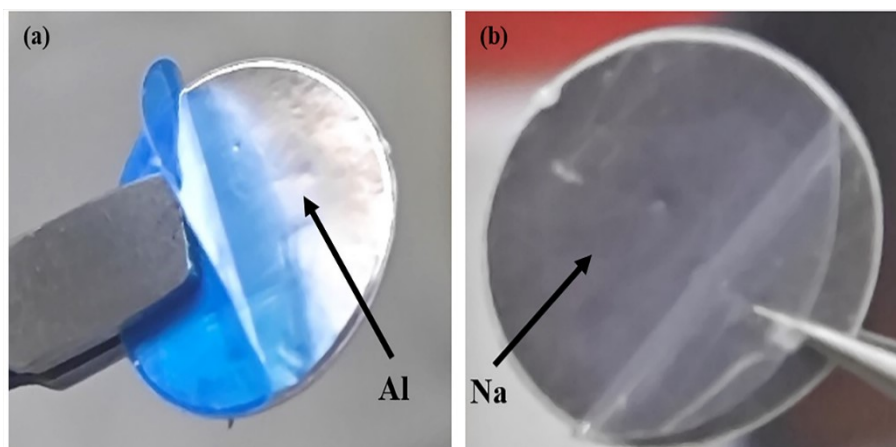


Fig. S1. Composite sodium foil.

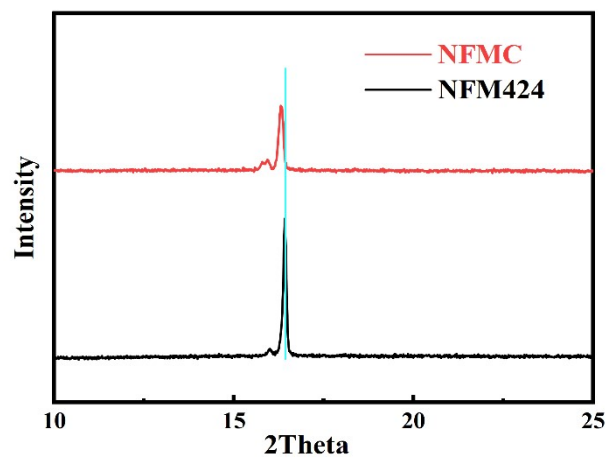


Fig.S2.XRD patterns of NFM424 and NFM424 at 10~25°.

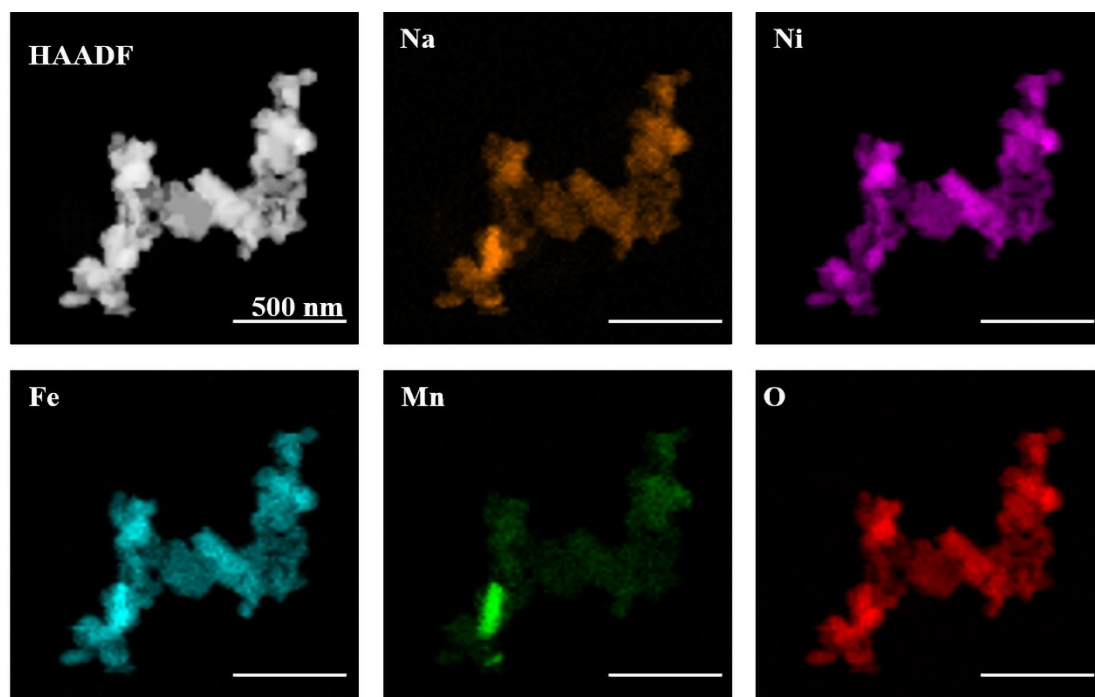


Fig. S3. HAADF-STEM image element mapping for NFM424.

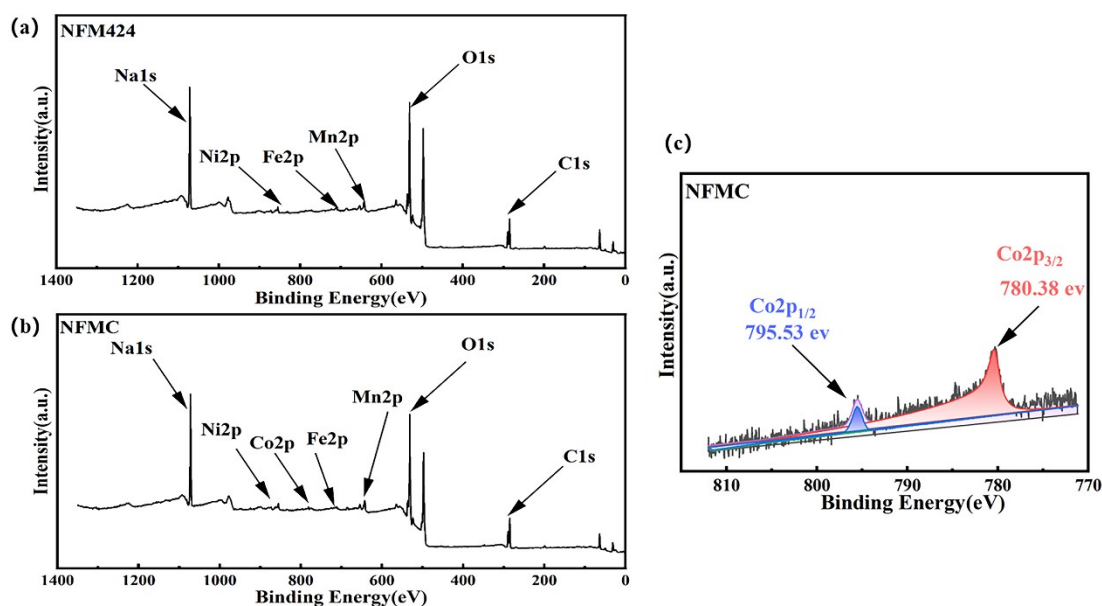


Fig. S4. XPS spectroscopy was conducted on NFM424 cathode materials: (a) measurement scan. The XPS spectra of NFMc cathode materials were also obtained: (b) measurement scans. (c) Co2p spectrogram.

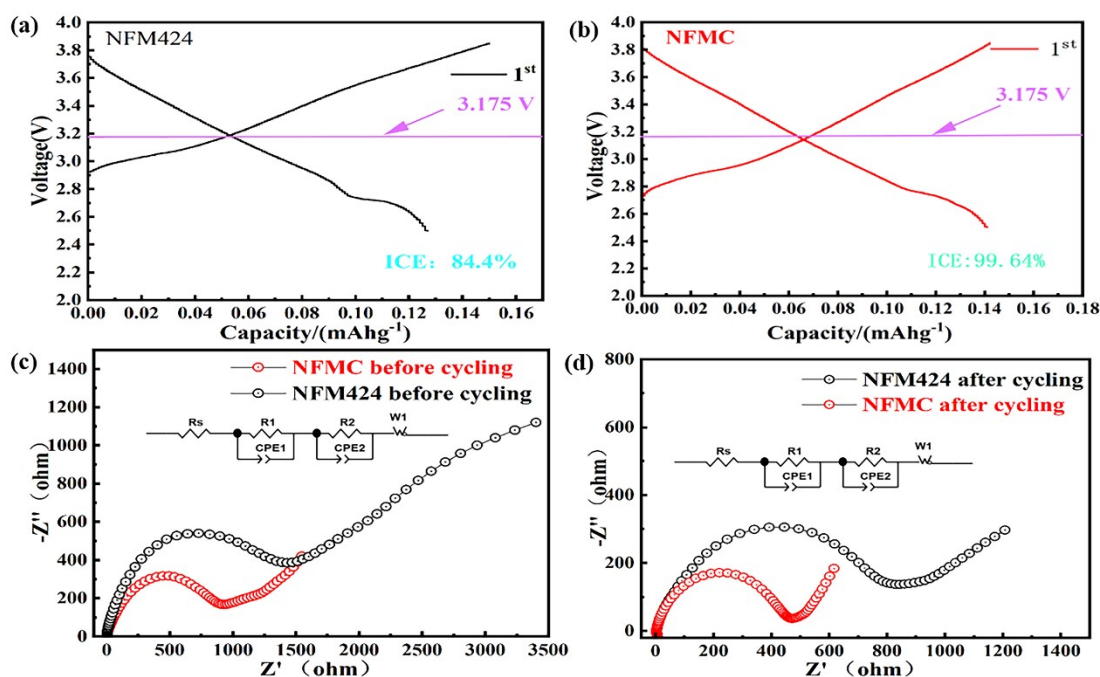


Fig. S5. Electrochemical properties of NFM424 and NFMc cathodes: (a) Opening charge-discharge curves of the NFM424 and (b) NFMc cathodes at 0.2 C during cycling between 2.5-3.85 V. Electrochemical impedance spectroscopy of both cathodes (c) before cycling and (d) after cycling.

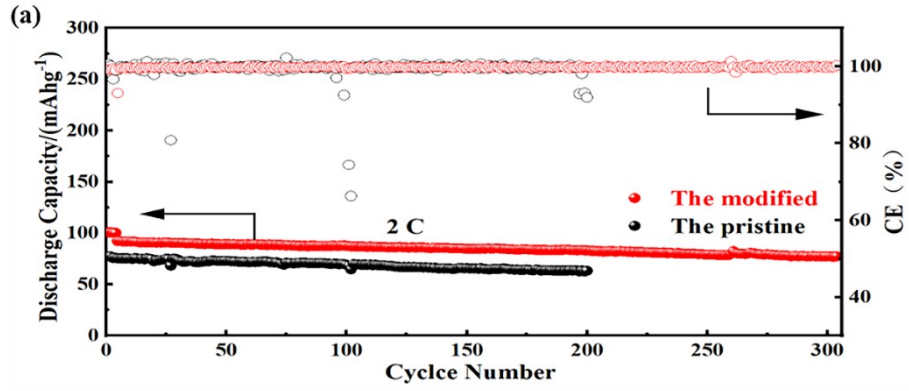


Fig. S6. Cycling performance of both cathodes at 2 C.

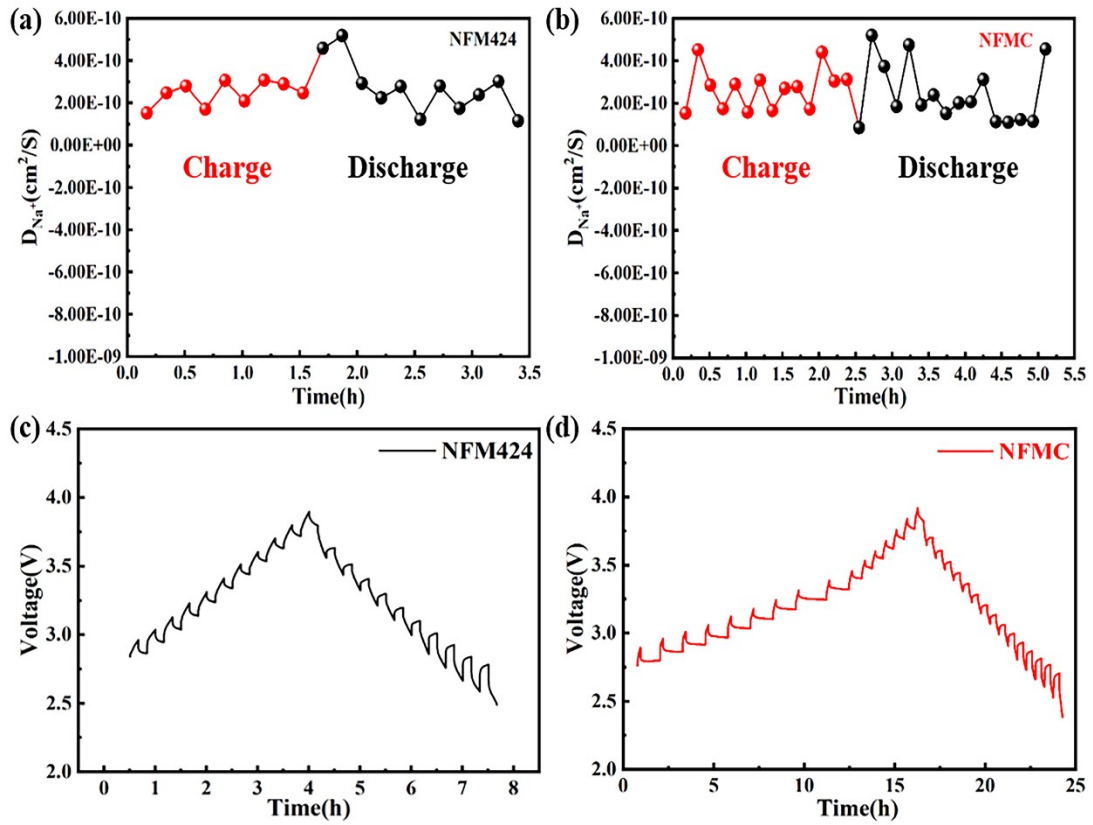


Fig. S7. Corresponding D_{Na^+} for the states of cathode materials NFM424 (a) and NFMC (b). Charge and discharge status of NFM424 (c) and NFMC (d) first cycle.

Table S1. Lattice parameters of NFM424 and NFMC cathode materials

	NFM424 D/Å	NFMC D/Å
b	2.951	2.934
c	16.211	16.267

Table S2. The chemometrics of NFMC and NFM424 compounds were analyzed using ICP-AES.

	NFM424	NFMC
Na	1.0	1.0
Ni	0.40	0.4
Fe	0.20	0.2
Mn	0.40	0.35
Co	/	0.05

Table S3. The specific results of each impedance.

	R_s/Ω	R_{int}/Ω
NFM424(before)	3.153	1577.5
NFM424 (after)	3.419	882.41
NFMC (before)	3.039	981.29
NFMC (after)	3.28	480.26

Notes: R_s : electrolyte resistance; R_{SEI} : solid electrolyte interface resistance; R_{ct} : charge transfer resistance; $R_{int} = R_{ct} + R_{SEI}$, representing interfacial resistance between the electrode and the electrolyte.