Supporting Information

Enhancing sodium storage performance of O3-type $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ cathode through a one-step double modification strategy

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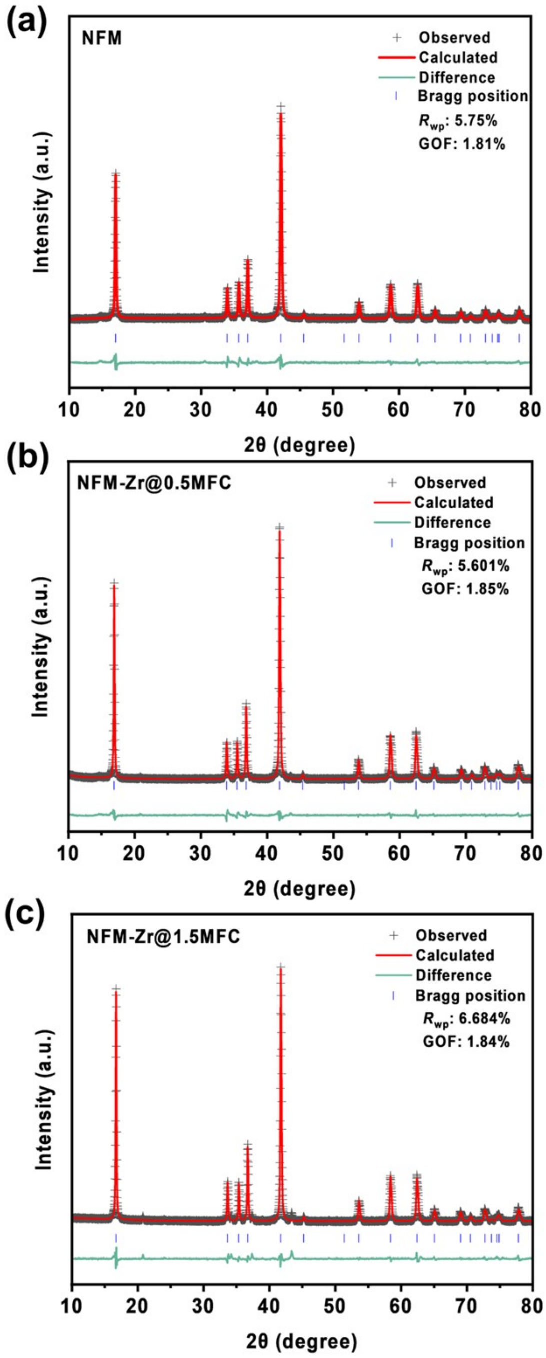

Fig. S1. XRD refinement patterns for (a) NFM, (b) NFM-Zr@0.5MFC and (c) NFM-Zr@1.5MFC

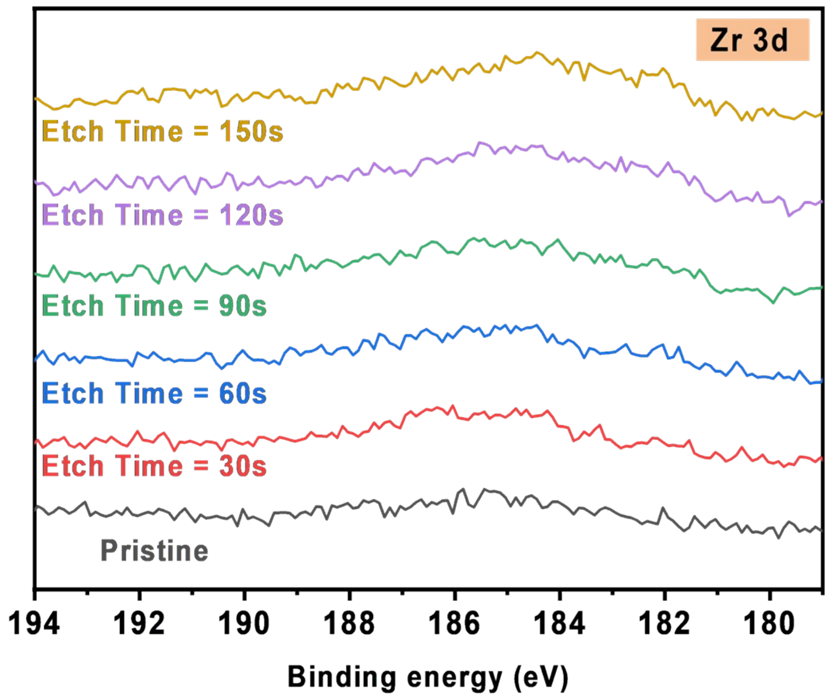

Fig. S2. Zr 3d XPS patterns at different etching depths

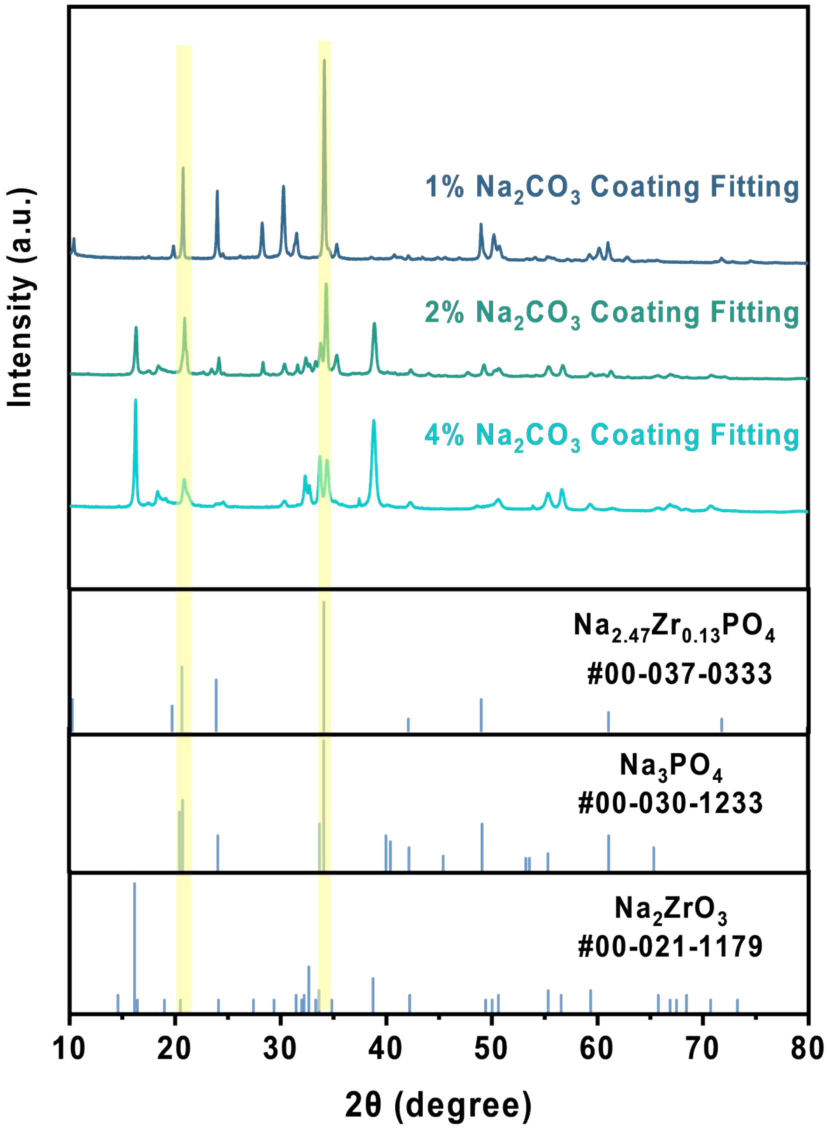

Fig. S3. XRD patterns of fitted cladding layers obtained by reacting different sodium carbonate contents (x=0.04, 0.02, 0.01 mol) with $ZrO(NO_3)_2 \cdot xH_2O$ (y=0.005 mol), $NH_4H_2PO_4$ (z=0.0075 mol) and their corresponding PDF cards. The yellow region represents the peak corresponding to the new appearance of NFM-Zr@1.0MFC.

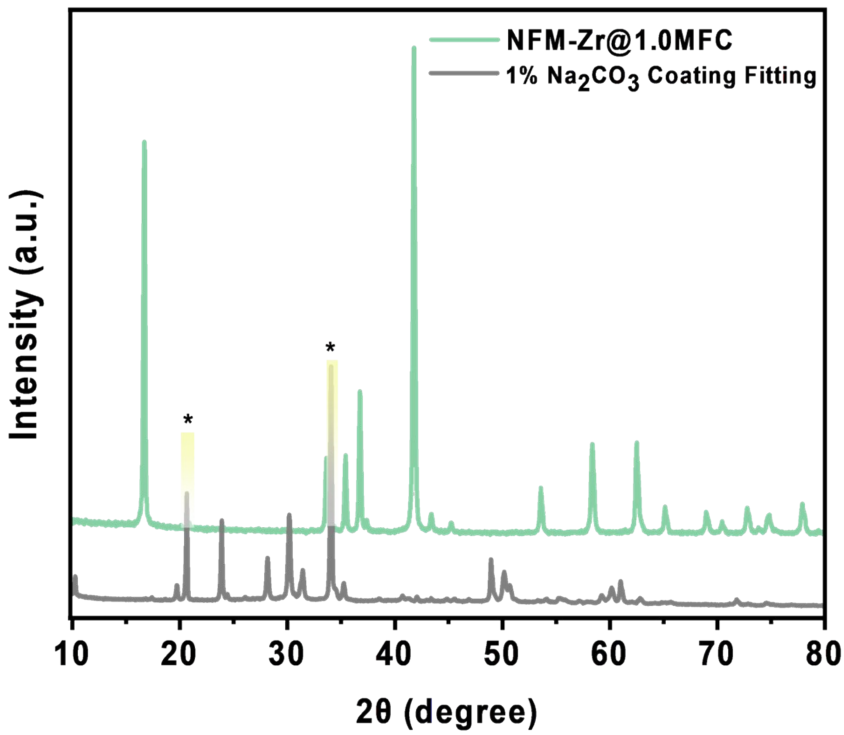

Fig. S4. MFC coating layer after 900℃/15 h heat treatment compared with NFM-Zr@1.0MFC

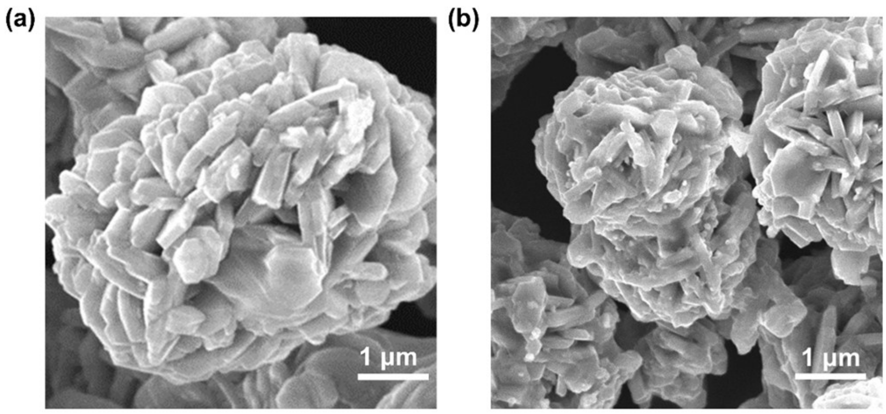

Fig. S5. SEM images of (a) NFM-Zr@0.5MFC and (b) NFM-Zr@1.5MFC.

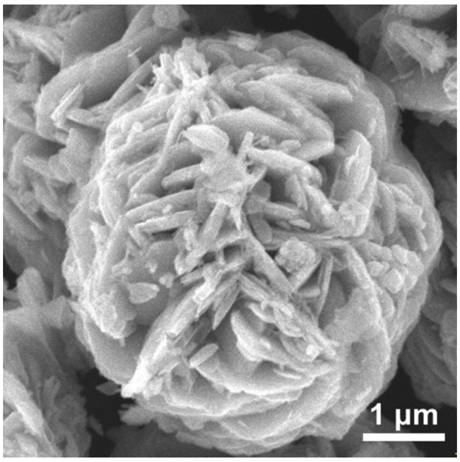

Fig. S6. SEM of $Ni_{1/3}Fe_{1/3}Mn_{1/3}(OH)_2$ precursor

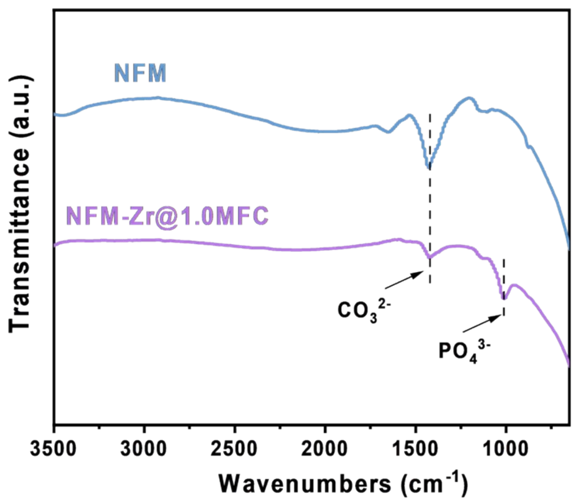

Fig. S7. Infrared spectra for NFM and NFM-Zr@1.0MFC

Surface Residual Alkali Analysis via Chemical Titration Method[1]

1. Sodium Hydroxide (NaOH) Quantification

The NFM sample (0.5 g) was initially immersed in 10 mL of ethanol under vigorous stirring for 5 minutes to dissolve surface sodium hydroxide. The resulting suspension underwent filtration through a Buchner funnel to collect the NaOH-ethanol solution. The filtrate was quantitatively transferred to a 250 mL conical flask and diluted with deionized water to a final volume of 200 mL. Methyl orange indicator was added, and the solution was titrated against standardized HCl until the endpoint transition from yellow to orange (pH 3.1-4.4). The NaOH content was calculated using the relationship (**Eq. S1**):

$$C_{NaOH} = \frac{V_{HCl} \times M_{HCl} \times M_{NaOH}}{m_{sample}} \tag{1}$$

Where V_{HCl} represents the consumed titrant volume, M_{HCl} the HCl molarity, M_{NaOH} the molecular weight of NaOH (40.00 g/mol), and m_{sample} the initial sample mass. The residual powder was collected for subsequent analysis.

2. Sodium Carbonate (Na_2CO_3) Determination

The filtered NFM powder was subsequently stirred with 10 mL of ethylene glycol in a beaker for 5 minutes to extract the surface carbonate material. After filtration, the Na_2CO_3 ethylene glycol solution was transferred to a clean conical flask and diluted to 200 mL with deionized water. Following addition of methyl orange indicator, the solution was titrated with standardized 0.1 M HCl until persistent orange coloration. The Na_2CO_3 concentration was determined using (**Eq. S2**):

$$C_{Na_2CO_3} = \frac{V_{HCl} \times M_{HCl} \times M_{Na_2CO_3}}{2 \times m_{sample}} \tag{2}$$

Where $M_{Na_2CO_3}$ denotes the molecular weight of sodium carbonate (105.99 g/mol), All titrations were performed in triplicate with temperature control at 25±0.5°C.

Fig. S8. A schematic diagram depicting color changes before and after titration

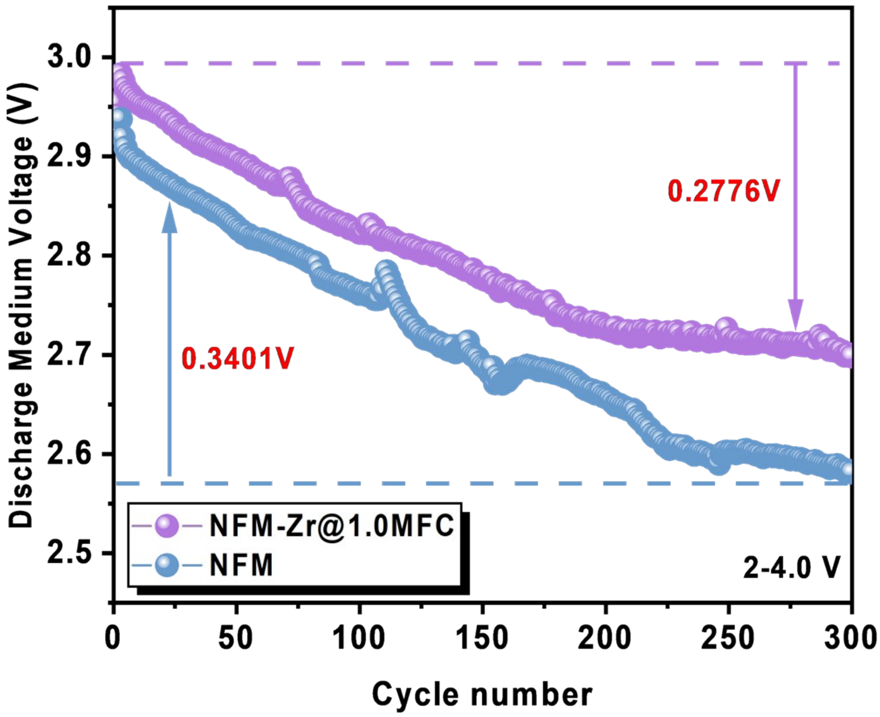

Fig. S9. Decay of discharge medium voltage of NFM and NFM-Zr@1.0MFC after 300 cycles at 1C

The fitted linear relationship indicates that the Na^+ diffusion coefficient (*D*) can be evaluated by the following Randles-Sevcik (**Eq. S3**):

$$Ip = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (3)$$

In the equation, *Ip* represents the peak current at various scan rates (A), *n* denotes the number of electrons involved in the redox reaction, *A* signifies the contact area between the two electrodes, D is the diffusion coefficient of Na^+, v represents the scan rate ($V\ s^{-1}$), and C is the concentration of Na^+ participating in the reaction.

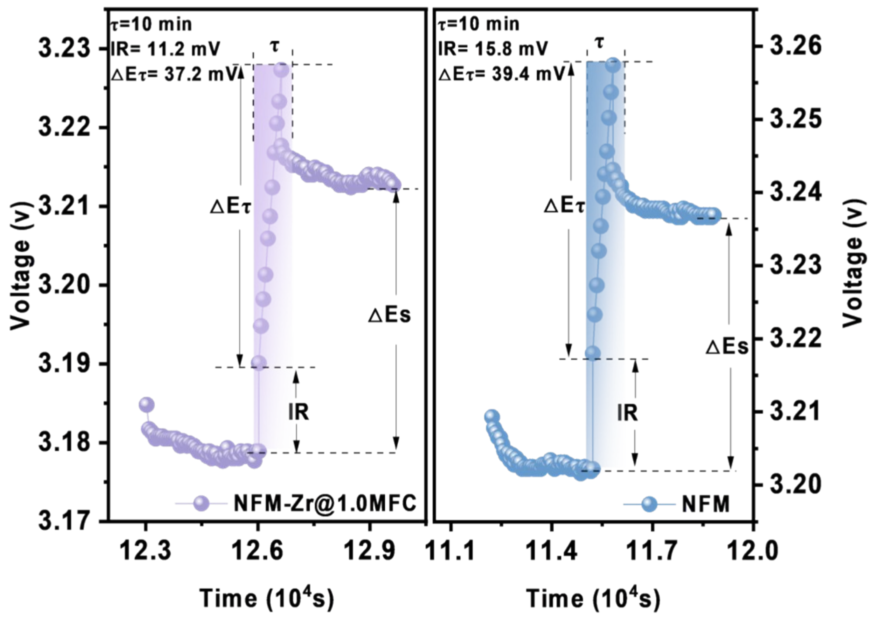

Fig. S10. An enlarged view of one GITT cycle for both NFM-Zr@1.0MFC and NFM

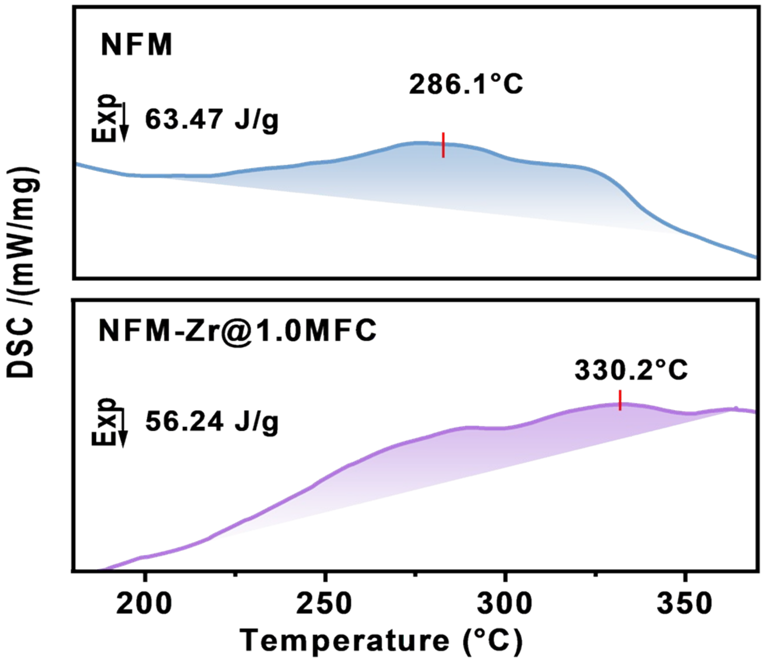

Fig. S11. DSC curves of NFM and NFM-Zr@1.0MFC in the charged state at 4.0 V.

Fig. S12. Materials for vacuum encapsulation

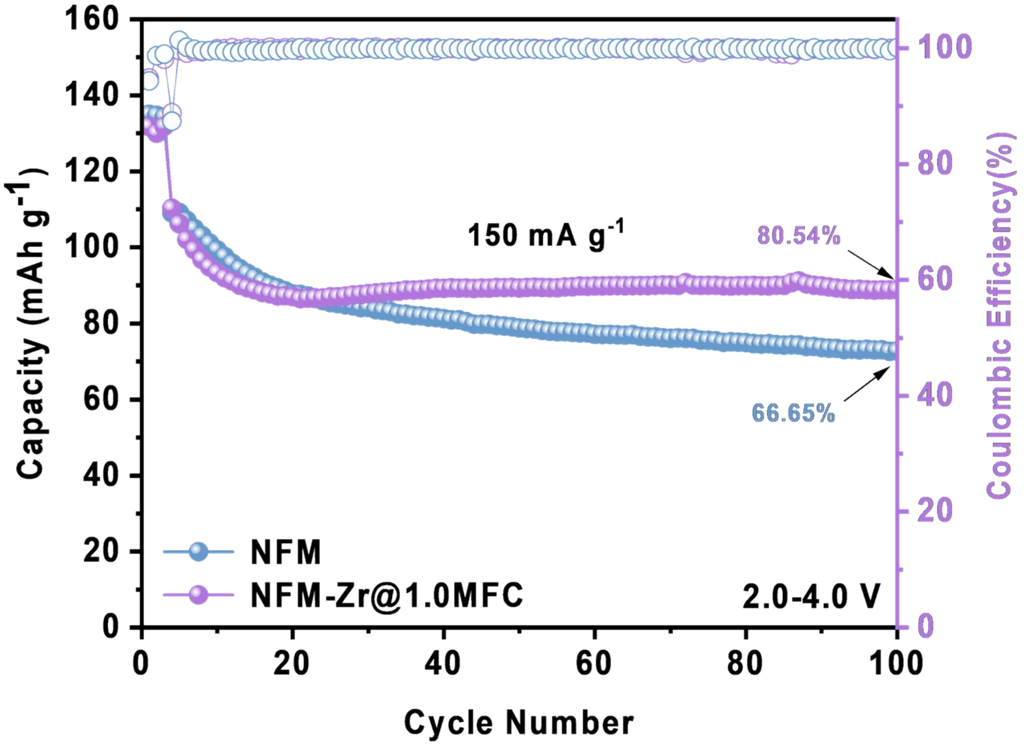

Fig. S13. The cycling performance of NFM and NFM-Zr@1.0MFC after one year of vacuum packaging.

Table S1. Crystal structure refinement of NFM, NFM-Zr@0.5MFC, NFM-Zr@1.0MFC and NFM-Zr@1.5MFC

	NFM	**NFM-Zr@0.5MFC**	**NFM-Zr@1.0MFC**	**NFM-Zr@1.5MFC**
a(Å)	2.98352	2.98179	2.9793	2.9759
c(Å)	16.00411	16.01381	16.03425	16.0406
c/a	5.36417	5.37053	5.38188	5.39016
V(Å³)	123.373	123.304	123.262	123.025
S_{MO2}(Å)	2.23753	2.21412	2.17667	2.1672
I_{NaO2}(Å)	3.10722	3.12368	3.15804	3.17967
TM-O lenth(Å)	2.05195 (3)	2.04676(4)	2.03755(3)	2.03131(5)
Na-O lenth(Å)	2.31789 (3)	2.32443(4)	2.33676(3)	2.34086(4)
Rwp(%)	5.75	5.601	6.764	6.684
GOF	1.81	1.85	2.18	1.84

Table S2. XRD refinement parameters for NFM

NFM					**Space group: $R\bar{3}m$**
Atom	Site	X	Y	Z	Occ.
Na	3a	0	0	0	1.000
Ni	3b	0	0	0.5	0.3333
Fe	3b	0	0	0.5	0.3333
Mn	3b	0	0	0.5	0.3333
O	6c	0	0	0.23467	1.000

Table S3. XRD refinement parameters for NFM-Zr@1.0MFC

NFM-Zr@1.0MFC					**Space group: $R\bar{3}m$**
Atom	Site	X	Y	Z	Occ.
Na	3a	0	0	0	1.000
Ni	3b	0	0	0.5	0.330
Fe	3b	0	0	0.5	0.332
Mn	3b	0	0	0.5	0.333
Zr	3b	0	0	0.5	0.007
O	6c	0	0	0.23644	1.000

Table S4. Stoichiometry of the six as-prepared samples determined by ICP-OES

	Na	**Ni**	**Fe**	**Mn**	**Zr**	**P**
NFM	1.025	0.330	0.338	0.331		
NFM-Zr@0.5MFC	1.016	0.334	0.334	0.324	0.468%	0.678%
NFM-Zr@1.0MFC	1.003	0.329	0.331	0.322	0.973%	1.486%
NFM-Zr@1.5MFC	0.995	0.328	0.326	0.318	1.468%	2.176%

Table S5. Residual alkali titration results of NFM and NFM-Zr@1.0MFC

	pH	Na_2CO_3	NaOH
		wt%	wt%
NFM	13.36	3.25	0.02
NFM-Zr@1.0MFC	13.03	2.36	0.01

The PH test is mainly referenced in ref 2 and the residual base titration procedure is referenced in ref 1.

Table S6. Comparison of high-voltage electrochemical performance for various sodium layered cathode materials.

Cathode materials	Voltage range [V]	Capacity retention	Ref.
$Na[Ni_{0.5}Co_{0.2}Mn_{0.3}]_{0.7}Ti_{0.3}O_2$	2.0-4.3 V	68.1%(300cycles)	3
$NaNi_{0.35}Fe_{0.2}Mn_{0.3}Ni_{0.1}Sb_{0.05}O_2$	1.9-4.1 V	76.0%(200cycles)	4
$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$	2.0-4.3 V	68.8%(200cycles)	5
$NaCaPO_4@Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$	2.5-4.3 V	74%(200cycles)	6
$Na_2Ti_6O_{13}@Na_{0.6}MnO_2$	2.0-4.1 V	78.8%(100cycles)	7
$NaPO_3@Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$	1.5-4.3 V	80%(100cycles)	8
NFM-Zr@1.0MFC	2.0-4.2 V	74.05%(300cycles)	**This work**

Table S7. The calculated ionic conductivity of potential coating compounds

Formula	Na^+ diffusion coefficient ($cm^2\ s^{-1}$)
Na_2CO_3	0.716×10^{-7}
Na_3PO_4	3.92×10^{-7}
Na_2ZrO_3	10.7×10^{-7}
$Na_{2.47}Zr_{0.13}PO_4$	5.93×10^{-5}

Table S8. Nyquist plot fitting results for NFM and NFM-Zr@1.0MFC electrodes at different temperatures

Temperatures	NFM			NFM-Zr@1.0MFC		
	$R_s(\Omega)$	$R_f(\Omega)$	$R_{ct}(\Omega)$	$R_s(\Omega)$	$R_f(\Omega)$	$R_{ct}(\Omega)$
25℃	2.378	297.01	112.64	2.275	249.73	117.47
40℃	2.275	151.69	57.06	2.208	109.27	49.66
60℃	2.127	140.75	34.64	2.106	91.04	29.4
80℃	1.847	160.18	29.92	1.62	104.92	30.24

References

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