Supporting Information

A High-Rate and Air-Stable Cathode Material for Sodium-Ion Batteries: Yttrium-Substituted O3-Type Ni/Fe/Mn-Based Layered Oxides

Chunyu Jiang,[a] Yingshuai Wang,[a] Yuhang Xin,[a] Qingbo Zhou,[a] Yanfei Pang,[a] Baorui Chen,[a] Ziye Wang[a] and Hongcai Gao*[abc]

[a] School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China.
[b] Yangtze Delta Region Academy of Beijing Institute of Technology, Jiaxing 314019, P.R. China.
[c] Beijing Institute of Technology Chongqing Innovation Center, Chongqing 401120, P.R. China.

Table S1: ICP-OES results of the pristine $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ (NFM) and Y-substituted $NaNi_{1/3}Fe_{1/3-x}Mn_{1/3}Y_xO_2$ (x = 0.01, 0.02) samples

Theoretical chemical formula	Measured atomic ratio				
	Na	Ni	Fe	Mn	Y
NFM	0.999	0.335	0.333	0.332	0
NFMY1	0.997	0.333	0.322	0.330	0.012
NFMY2	0.998	0.332	0.311	0.331	0.023

Table S2: Atom occupancy parameters obtained from Rietveld refinements of NFM and Y-substituted O3-NFM samples

Atom	**Site**	**Occupancy**		
		NFM	**NFMY1**	**NFMY2**
Na	**3a**	0.9999	1	0.9998
Ni	**3b**	0.3334	0.3330	0.3332
Fe	**3b**	0.3332	0.3221	0.3118
Mn	**3b**	0.3333	0.3331	0.3331
O	**6c**	1	1	1.002
Y	**3b**	0	0.0102	0.0210

Table S3: Crystallographic parameters of the pristine NFM and Y-substituted O3-NFM samples

	***a*/Å**	***c*/ Å**	***v*/ Å^3**	**R_p/%**	**R_{wp}/%**	**$d_{(003)}$/ Å**	**S_{NaO2}/ Å**	**S_{TMO2}/ Å**
NFM	2.9707	16.010	122.368	3.39	4.39	5.3368	3.1679	2.1689
NFMY1	2.9724	16.006	122.474	3.49	4.50	5.3354	3.2279	2.1074
NFMY2	2.9749	16.002	122.728	3.39	4.37	5.3341	3.2610	2.0730

Table S4: The discharge capacities (mAh g^{-1}) of pristine NFM and Y-substituted O3-NFM samples in different rates.

Samples	Current density						
	0.1C	**1C**	**2C**	**5C**	**10C**	**20C**	**0.1C**
NFM	145.5	134.8	128.4	118	104.4	75.7	136.6
NFMY1	137.4	130.5	127.3	120.6	111.8	94.3	132.6
NFMY2	133.6	126.7	124.7	117	107.1	85.7	129.4

Table S5: Comparison of rate capability under 5C between our work and published previously.

Modification methods	Standard current density(1C)/mA g^{-1}	Discharge capacity(5C)/mAh g^{-1}	Voltage range(V)	Reference
Y substitution	130	120.6	2-4V	This work
Polycrystalline preparation	150	119	2-4V	64
Al/Cu cosubstitution	130	113	2-4V	49
V doping	120	85.8	2-4V	59
Na_2SiO_3 coating	120	58	1.5-4.2V	57
$NaTi_2(PO_4)_3$ coating	130	103.1	1.5-4.2V	67
Sn substitution	150	81	2-4.1V	37
TiO_2 coating	200	62.6	1.5-4.2V	65
F substitution	130	105.1	2-4V	4
Zr substitution	130	89.1	1.5-4V	66
Zn substitution	130	100.2	2-4V	62
Al substitution	150	81.5	2-4.2V	61
Zr substitution	130	104.7	2-4V	60
Ca substitution	130	102.1	2-4V	63

Table S6: Simulated parameters from the EIS after different cycles.

Cathodes	3rd		200th	
	R_{sf}/Ω	R_{ct}/Ω	R_{sf}/Ω	R_{ct}/Ω
NFM	730.7	3749	654.2	5849
NFMY1	773.7	2204	308	2297
NFMY2	604.3	1665	302.3	2498

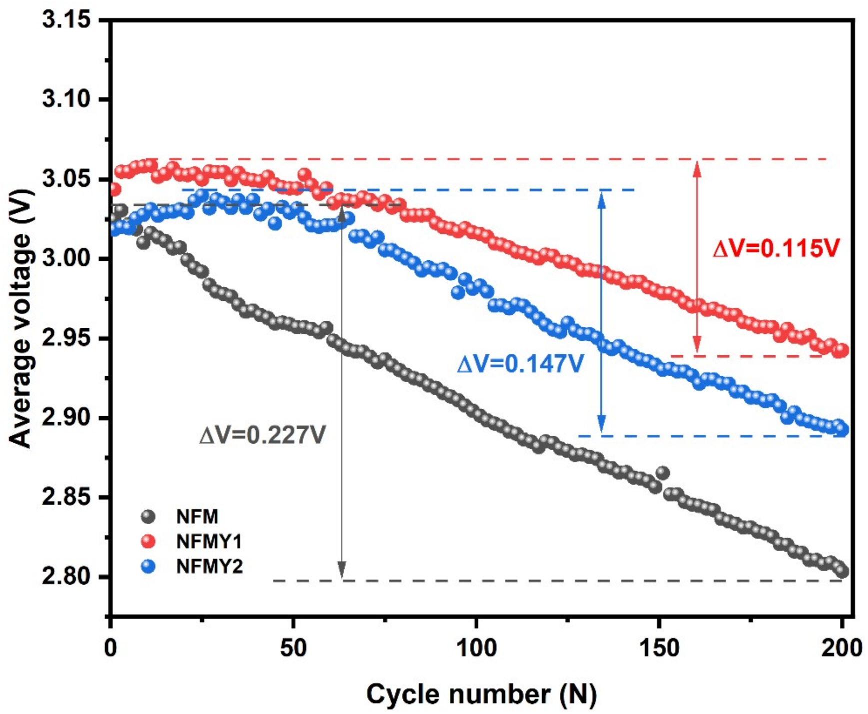

Fig. S1: Working voltage - Cycle number curves for three samples at 1C.

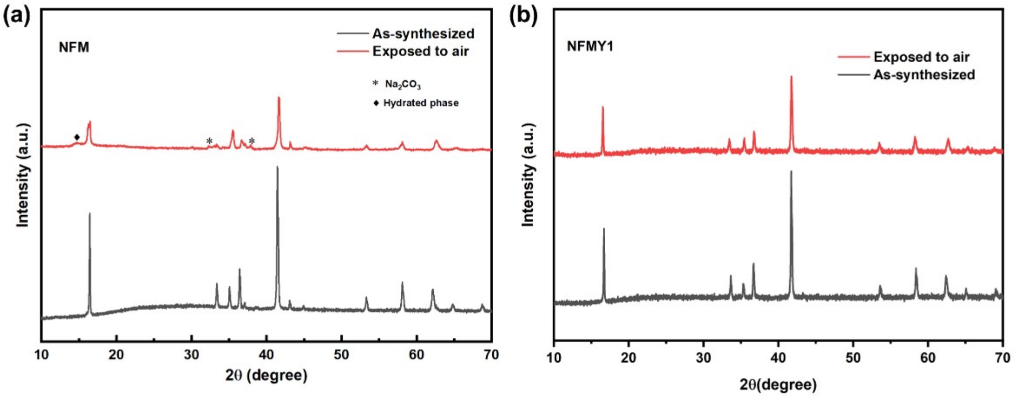

Fig. S2: The XRD patterns of (a) NFM and (b) NFMY1 samples exposed in the ambient air for 7 days.

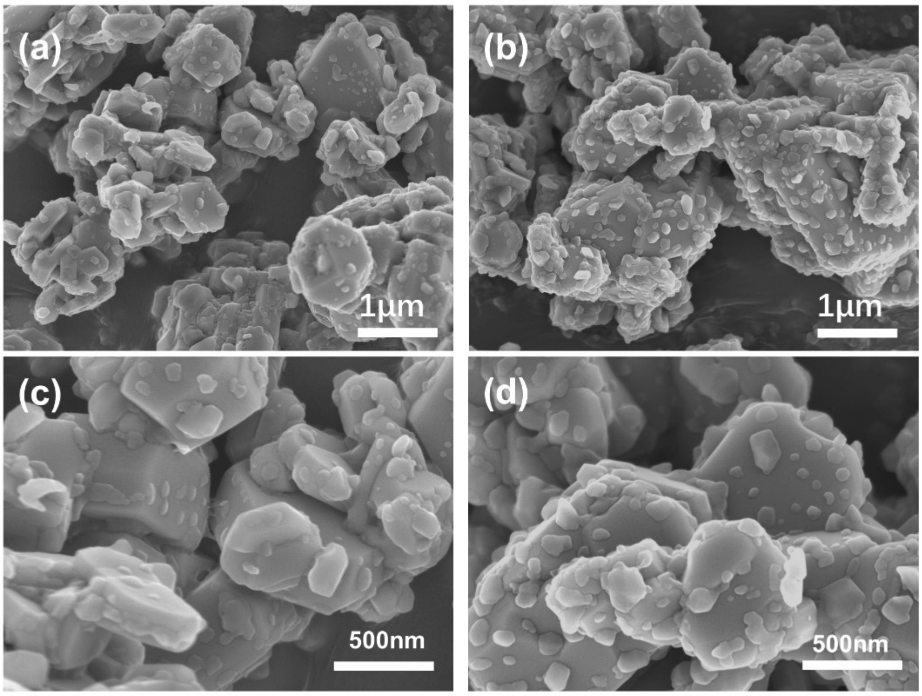

Fig. S3: SEM images of the (a, c) NFM and (b, d) NFMY1 sample after aging experiments.

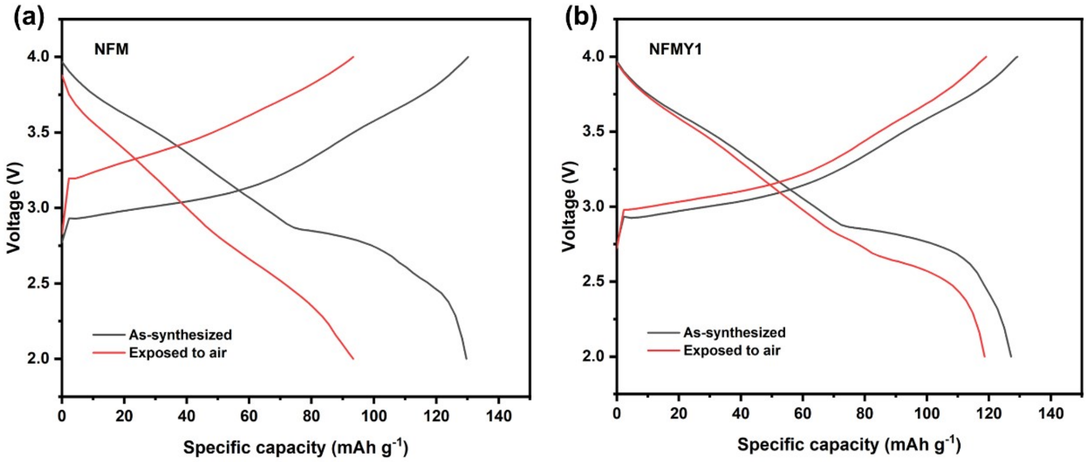

Fig. S4: The charge/discharge curves of (a) NFM and (b) NFMY1 exposed in the ambient air for 7 days.

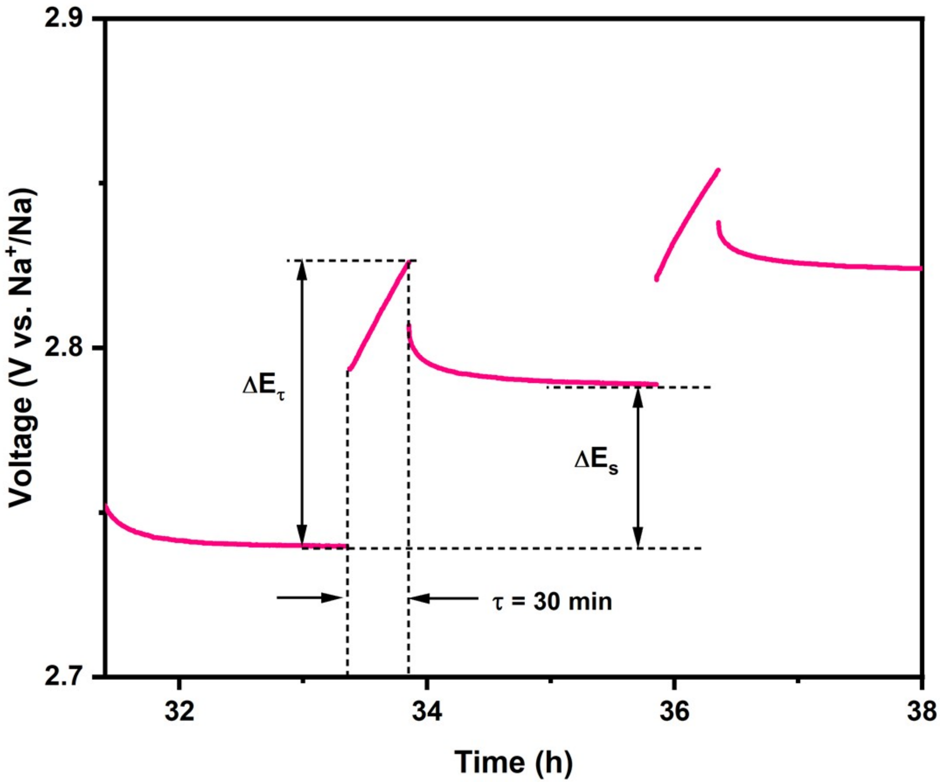

Fig. S5: Schematic illustration of selected steps of GITT test for pristine NFM and Y-substituted O3-NFM samples with a charge/discharge time of 30 min and a relaxation time of 2 h.

GITT measurements were performed by charging at a current density of 0.1 C for 30 min following a 120 min open circuit relaxation. D_{Na^+} from GITT results is calculated by the following equation:

$$D_{Na^+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \qquad (S1)$$

In the above equations, D represents the diffusion coefficient of Na^+ in the cathode, V_M (cm^3 mol^{-1}) denotes the molar volume, m_B and M_B refer to the molecular weight and relative molar weight of the cathode material. S represents the surface area of the electrode. τ represents the time duration of the applied current during galvanostatic intermittent titration. ΔE_S and ΔE_τ represent the steady voltage state and the overall variation in battery voltage E during the current pulse, respectively.