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Electronic Supplementary Information

Polymer-assisted yttrium surface-enrichment doping of O3-type

NaNi₁/₃Fe₁/₃Mn₁/₃O₂ cathodes to enhance high voltage and air stability

in sodium-ion batteries

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Fig. S1. TGA graph of the pure PVA.



Fig. S2. STEM images of the Y2@NNFM and EDS mapping of Ni, Fe, Mn, Y, and O.



Fig. S3. XPS profile of (a) Fe 2p, (b) Ni 2p, (c) Mn 2p, and (d) Y 3d. Ratio of (e) Ni²⁺ / Ni³⁺, and (f) Mn³⁺ / Mn⁴⁺, in Y0.5@NNFM and Y1@NNFM; (g) XPS depth profile of the Y 3d peak spectra in Y2@NNFM.



Fig. S4. Rate performance of the Pristine, Y0.5@NNFM, Y1@NNFM, and Y2@NNFM at 0.1, 0.2, 1, 2, 5, 10, and 0.1 C in the range 2.0 – 4.0 V (*vs.* Na/Na⁺).



Fig. S5. *Ex situ* XRD pattern of the (a) Pristine and (b) Y1@NNFM during charge/discharge at 1 C rate in the range 2.0 - 4.2 V (*vs.* Na/Na⁺), in the 20 range 10–70°.



Fig. S6. XRD pattern before cycles and after cycles of the (c) Pristine and (d) Y1@NNFM in the 2θ range $10-70^{\circ}$.



Fig. S7. Electrochemical performance of the air-stored Pristine and air-stored Y1@NNFM. (a) dQ/dV plots for 1^{st} charging, Voltage profiles of the 1^{st} formation cycle of (b) the Air-stored Pristine, and (c) the Air-stored Y1@NNFM, at 0.1 C rate in the range 2.0 - 4.2 V (*vs.* Na/Na⁺).



Fig. S8. Average charge-discharge voltage of Pristine and Y1@NNFM up to the 10th cycle in the cycle test (a) before (b) after air storage.



Fig. S9. The Nyquist plots of the air-stored Pristine and Y1@NNFM (d) before the cycle test, and (e) after 100 cycles.

Table S1.

| Pristine | Y0.5@NNFM | Y1@NNFM | Y2@NNFM |
|----------|--|---|--|
| 2.9732 | 2.9745 | 2.9751 | 2.9755 |
| 16.017 | 16.008 | 15.999 | 15.997 |
| 3.07 | 4.27 | 3.11 | 3.10 |
| 2.36 | 3.32 | 2.36 | 2.35 |
| 1.23 | 1.34 | 1.30 | 1.24 |
| | | | |
| Pristine | Y0.5@NNFM | Y1@NNFM | Y2@NNFM |
| 2.3403 | 2.3431 | 2.3448 | 2.3454 |
| 2.0274 | 2.0255 | 2.0238 | 2.0235 |
| 3.1814 | 3.1880 | 3.1925 | 3.1937 |
| 2.1576 | 2.1481 | 2.1404 | 2.1386 |
| | Pristine 2.9732 16.017 3.07 2.36 1.23 Pristine 2.3403 2.0274 3.1814 2.1576 | Pristine Y0.5@NNFM 2.9732 2.9745 16.017 16.008 3.07 4.27 2.36 3.32 1.23 1.34 Pristine Y0.5@NNFM 2.3403 2.3431 2.0274 2.0255 3.1814 3.1880 2.1576 2.1481 | PristineY0.5@NNFMY1@NNFM2.97322.97452.975116.01716.00815.9993.074.273.112.363.322.361.231.341.30PristineY0.5@NNFMY1@NNFM2.34032.34312.34482.02742.02552.02383.18143.18803.19252.15762.14812.1404 |

Lattice parameters and bond lengths of all samples from XRD Rietveld refinement.

Table S2.

| | Charge (mAh/g) | Discharge (mAh/g) | CE (%) |
|-----------|-------------------|----------------------|--------|
| Pristine | 187.2 | 160.4 | 85.7 |
| Y0.5@NNFM | 184.7 | 161.5 | 87.4 |
| Y1@NNFM | 183.9 | 162.7 | 88.5 |
| Y2@NNFM | 182.3 | 161.1 | 88.4 |

Charge/Discharge capacity and Coulombic efficiency of all samples in the 1st formation cycle at 0.1 C.

Table S3.

| | Before cycle test | | After 100 th cycles | | | |
|----------|--------------------|----------------------|--------------------------------|--------------------|----------------------|---------------------|
| | R _s (Ω) | R _{sei} (Ω) | R _{ct} (Ω) | R _s (Ω) | R _{SEI} (Ω) | R _{ct} (Ω) |
| Pristine | 4.5495 | 209.1 | 752.4 | 6.665 | 530.7 | 1656 |
| Y1@NNFM | 4.8104 | 247.3 | 625.3 | 5.238 | 403.6 | 1153 |

Fitting result of the EIS spectra for the Pristine and Y1@NNFM, before and after cycle tests.

Table S4.

Charge/Discharge capacity and Coulombic efficiency of the air-stored Pristine and Y1@NNFM in the 1st formation cycle at 0.1 C.

| | Charge (mAh/g) | Discharge (mAh/g) | CE (%) |
|------------------------|-------------------|----------------------|--------|
| Air-stored Pristine | 189.3 | 125.7 | 66.4 |
| Air-stored Y1@NNFM | 184.2 | 142.7 | 77.5 |

Table S5.

Fitting result of the EIS spectra for the air-stored Pristine and air-stored Y1@NNFM, before and after cycle tests.

| | Before cycle test | | After 100 | 0 th cycles |
|------------------------|----------------------|---------------------|----------------------|------------------------|
| | R _{SEI} (Ω) | R _{ct} (Ω) | R _{SEI} (Ω) | R _{ct} (Ω) |
| Air-stored Pristine | 510.3 | 892.5 | 910.2 | 2134 |
| Air-stored Y1@NNFM | 433.6 | 780.5 | 511.8 | 1092 |