

Supporting Information for

Impact of Transition Metal Layer Vacancy on the Structure and Performance of P2 Type Layered Sodium Cathode Material

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Supplementary Tables and Figures

Table S1 ICP-AES results comparison of pristine NRM and V-NRM powders

Theoretical chemical formula	Na	Ni	Mn	Ru
$\text{Na}_{0.604}[\text{Ni}_{0.303}\text{Ru}_{0.297}\text{Mn}_{0.400}]\text{O}_2$	0.604	0.303	0.400	0.297
$\text{Na}_{0.702}[\text{Ni}_{0.202}\text{V}_{\text{Ni}0.1}\text{Ru}_{0.298}\text{Mn}_{0.400}]\text{O}_2$	0.702	0.202	0.400	0.298

Table S2 Rietveld refinement results of the XRD data for $\text{Na}_{0.604}[\text{Ni}_{0.303}\text{Ru}_{0.297}\text{Mn}_{0.400}]\text{O}_2$ (NRM)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>g</i>	<i>B</i> _{iso} /Å ²	Site
Na _e	0.66667	0.33333	0.25	0.362(1)	3.3	2 <i>d</i>
Na _f	0	0	0.25	0.23(6)	3.0	2 <i>b</i>
O	0.33333	0.66667	0.0882(1)	1.0	0.1	4 <i>f</i>
Ni	0	0	0	0.303(2)	0.5	2 <i>a</i>
Mn	0	0	0	0.4(2)	0.5	2 <i>a</i>
Ru	0	0	0	0.297(2)	0.5	2 <i>a</i>

Hexagonal/Space group: *P6₃/mmc*

Cell parameter: *a*=*b*=2.9128(4)Å, *c*=11.2554(1)Å, *V*=82.57(6)Å³, *α*=*β*=90°, *γ*=120°

*R*_{wp}% = 5.02%

Table S3 Rietveld refinement results of the XRD data for $\text{Na}_{0.702}[\text{Ni}_{0.202}\text{V}_{\text{Ni}0.1}\text{Ru}_{0.298}\text{Mn}_{0.400}]\text{O}_2$ (V-NRM)

Atom	x	y	z	g	$B_{\text{iso}}/\text{\AA}^2$	Site
Na_e	0.66667	0.33333	0.25	0.462(3)	3.3	$2d$
Na_f	0	0	0.25	0.24(2)	3.0	$2b$
O	0.33333	0.66667	0.0957(5)	1.0	0.9	$4f$
Ni	0	0	0	0.202(1)	0.5	$2a$
Mn	0	0	0	0.4(1)	0.5	$2a$
Ru	0	0	0	0.298(1)	0.5	$2a$

Hexagonal / Space group: $P6_3/mmc$

Cell parameter: $a=b=2.9105(9)\text{\AA}$, $c=11.2075(8)\text{\AA}$, $V=82.35(2)\text{\AA}^3$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$

$R_{\text{wp}}\% = 4.12\%$

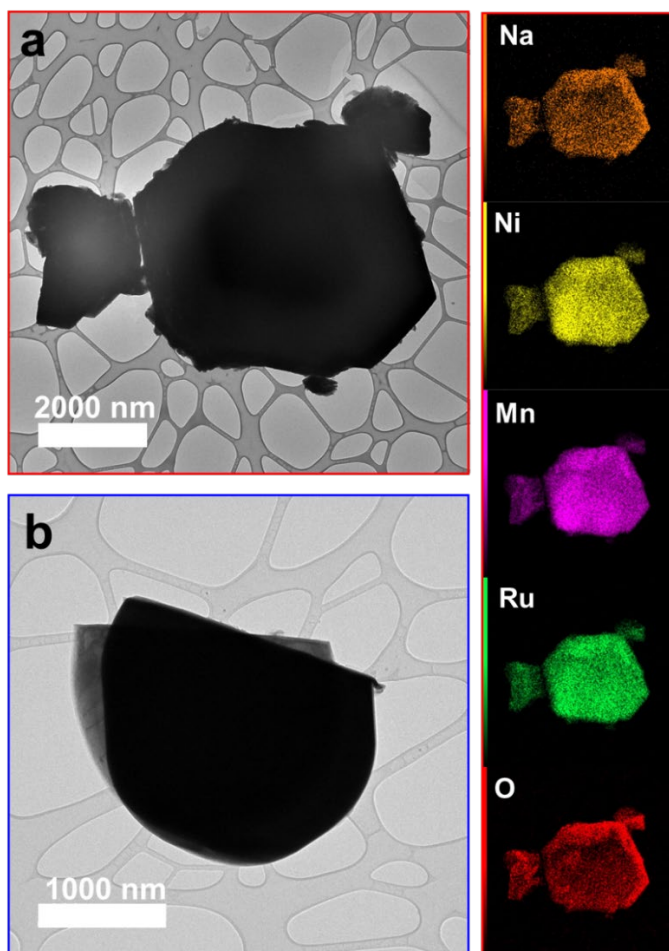


Fig. S1 TEM image and TEM-EDS elemental mapping of pristine **a)** NRM and **b)** V-NRM particles

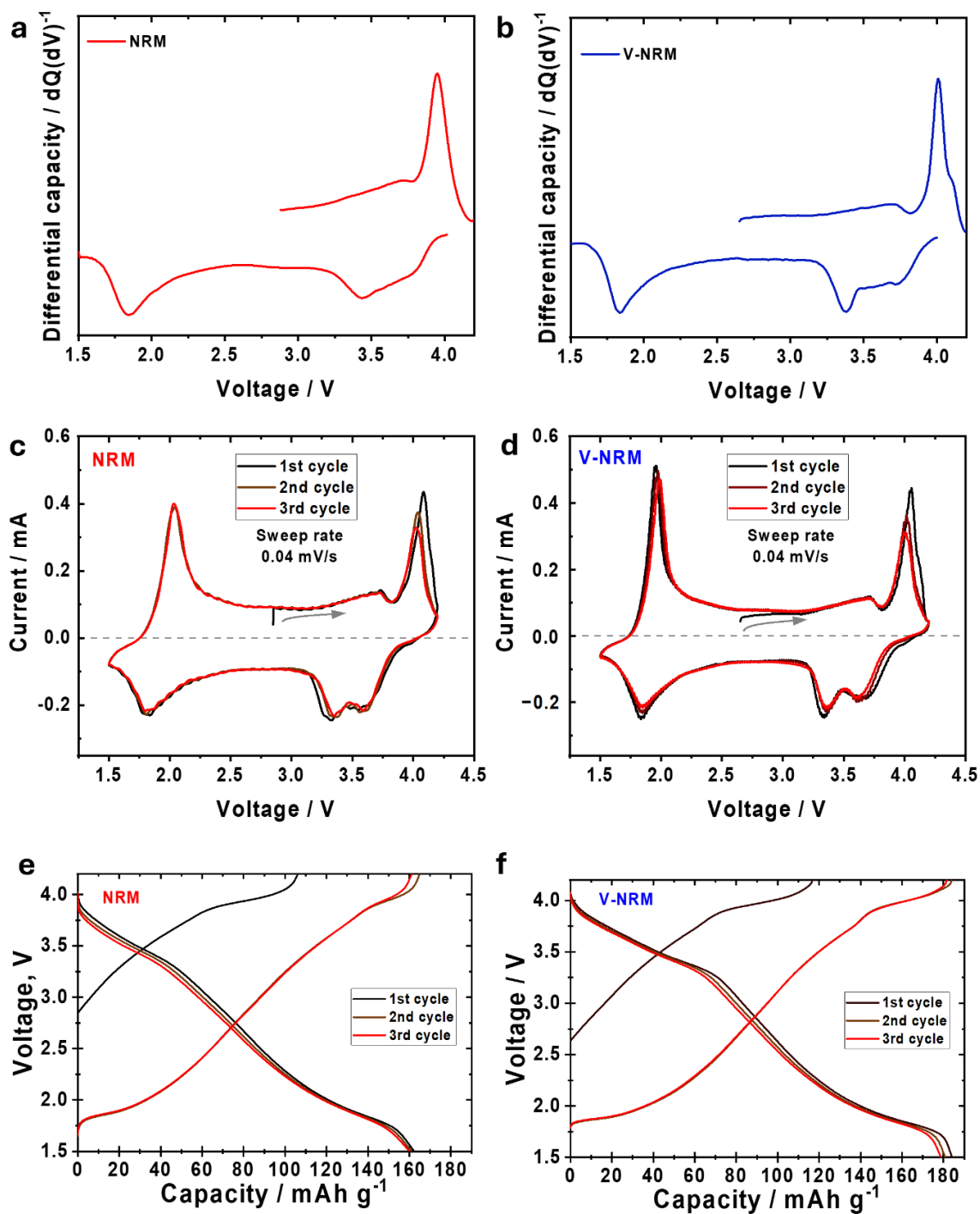


Fig. S2 Comparison of differential capacity (dQ/dV) curves of initial cycles of **a)** NRM and **b)** V-NRM half-cells at 0.05C. Cyclic voltammetry (CV) results of **c)** NRM and **d)** V-NRM half-cells at 0.04 mV/s. Voltage profile results of **e)** NRM and **f)** V-NRM half-cells at 0.1C

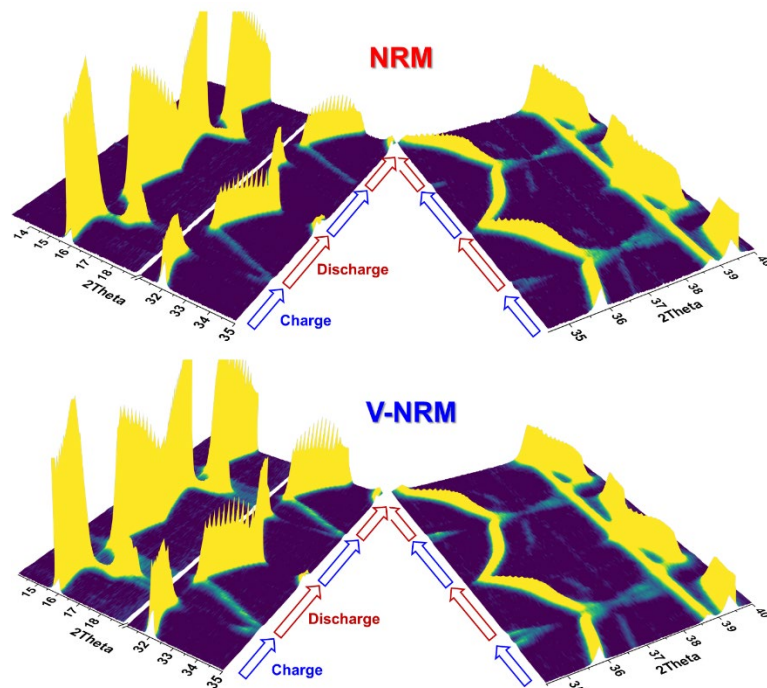


Fig. S3 NRM and V-NRM half-cells comparing operando XRD results from **Fig. 4** remapped in 3D format

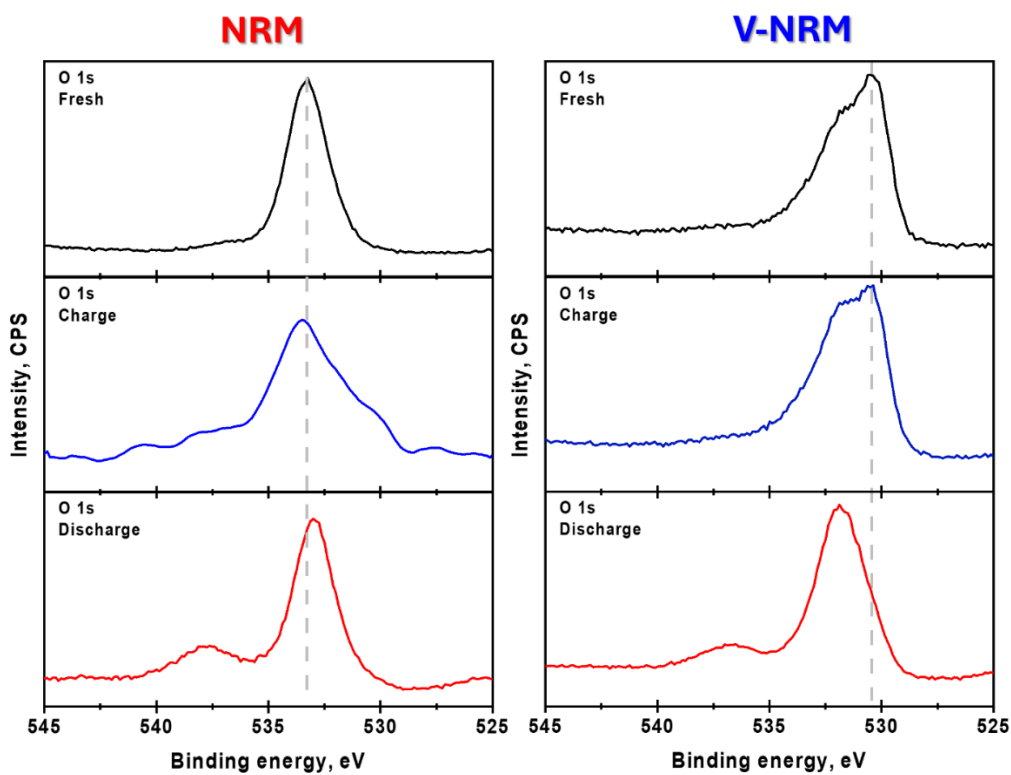


Fig. S4 Comparison of XPS spectra of O 1s of NRM and V-NRM at pristine, charge and discharge states

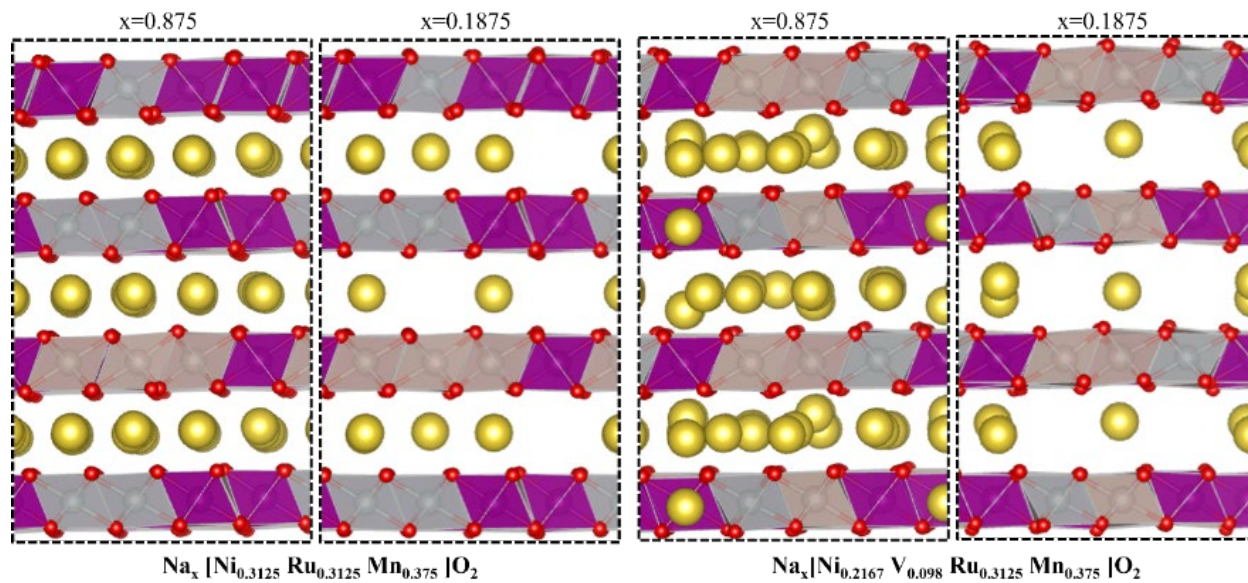


Fig. S5 Computed atomistic structures of $\text{Na}_x[\text{Ni}_{0.3125}\text{Ru}_{0.3125}\text{Mn}_{0.375}]\text{O}_2$ and $\text{Na}_x[\text{Ni}_{0.2167}\text{V}_{0.098}\text{Ru}_{0.3125}\text{Mn}_{0.375}]\text{O}_2$ at discharged ($x=0.875$) and charged ($x=0.1875$) states