Supplementary Materials

Enhanced Performance of Sodium-Ion Battery Cathodes with Ti and V Co-Doped P2-Type $Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ Materials

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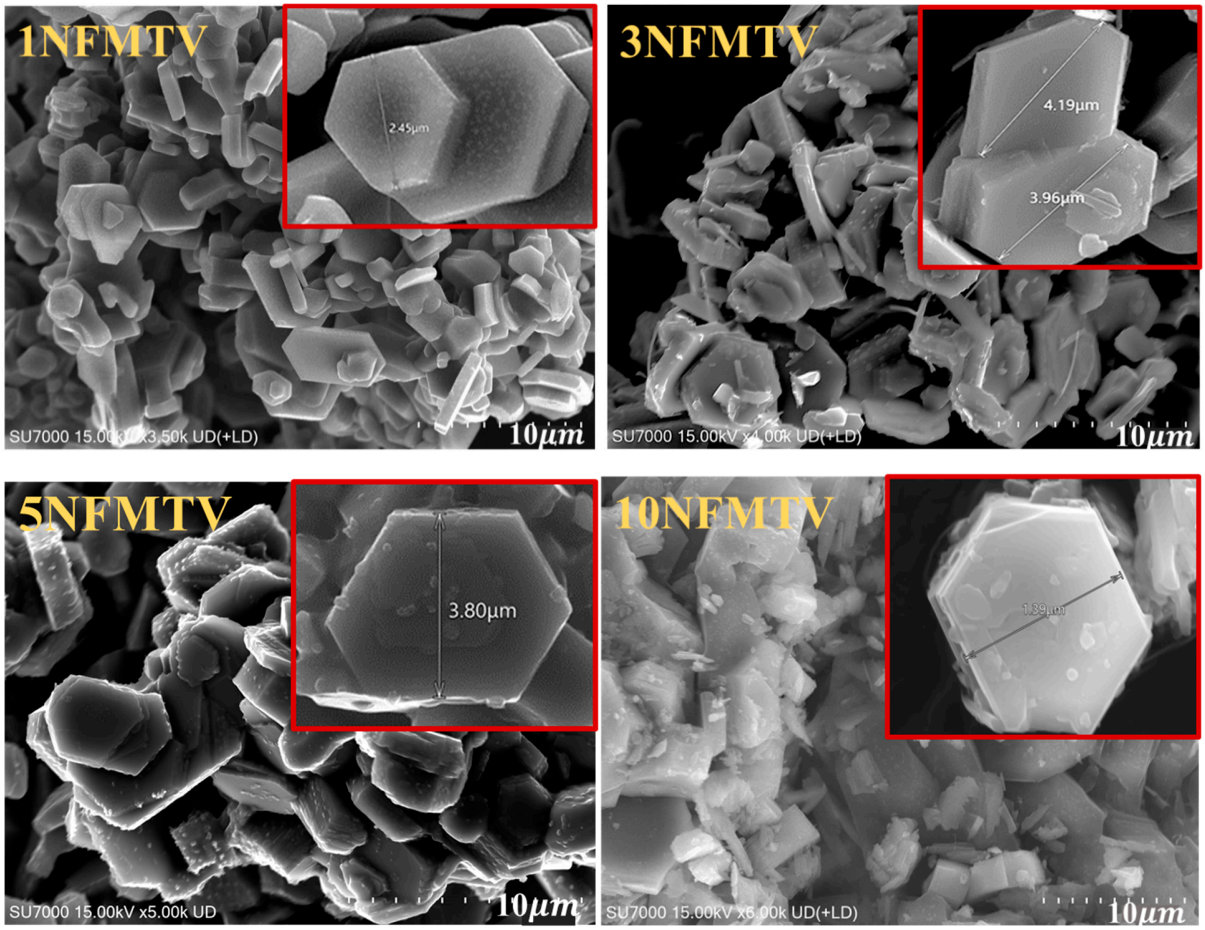


Figure S1. Scanning electron microscope images of **(a)** Pristine NFM, **(b)** 1NFMTV, **(c)** 2NFMTV, **(d)** 3NFMTV, **(e)** 5NFMTV, **(f)** 10NFMTV.

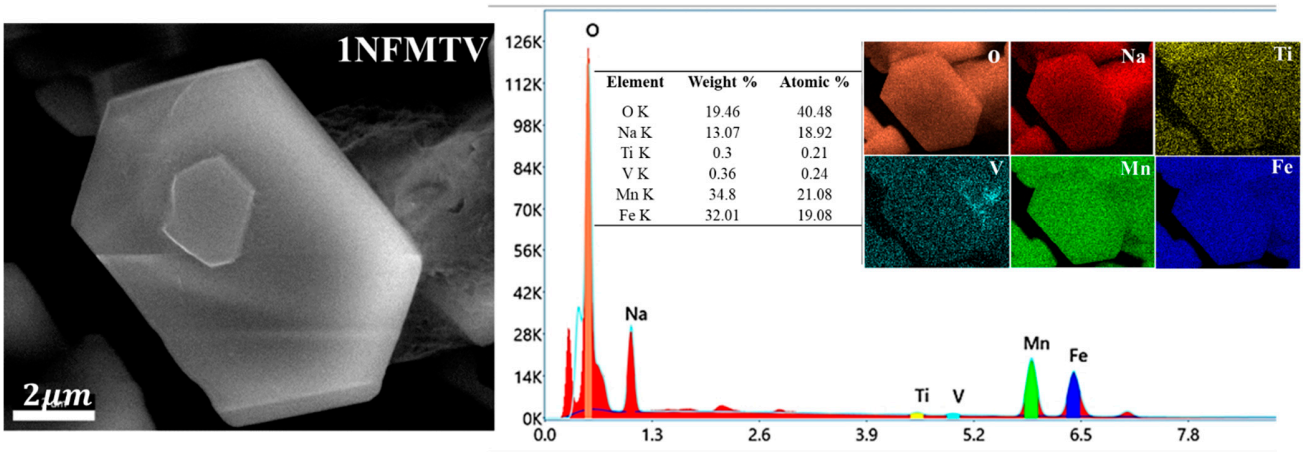


Figure S2. EDS Elemental Mapping of 1NFMTV

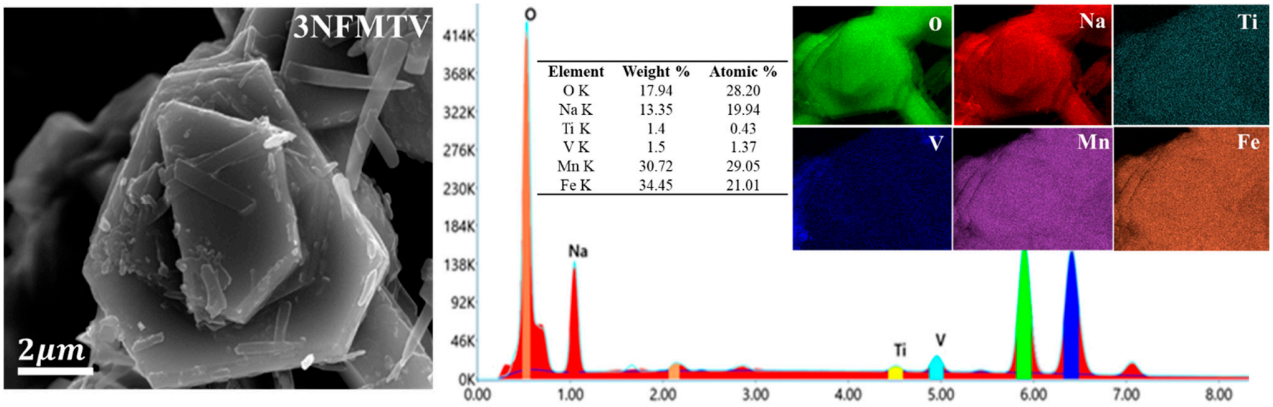


Figure S3. EDS Elemental Mapping of 3NFMTV

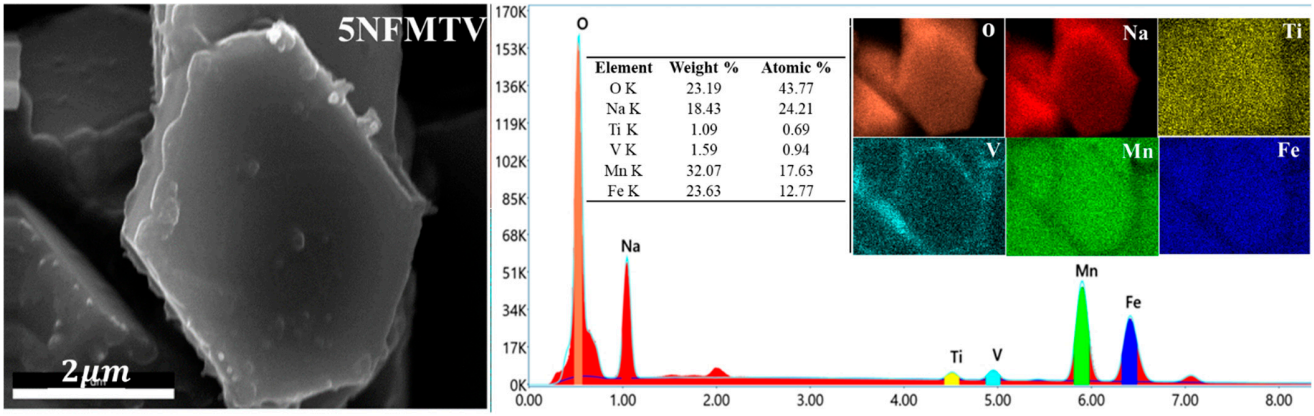


Figure S4. EDS Elemental Mapping of 5NFMTV

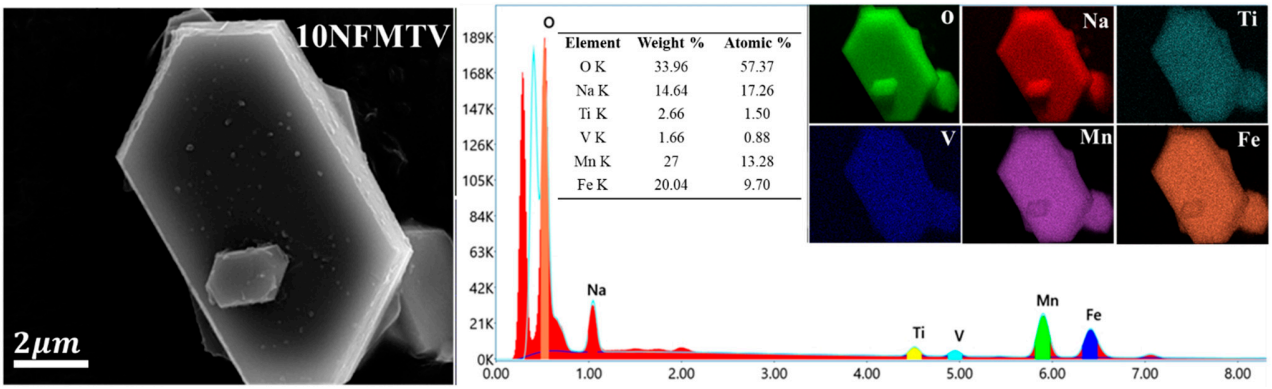


Figure S5. EDS Elemental Mapping of 10NFMTV

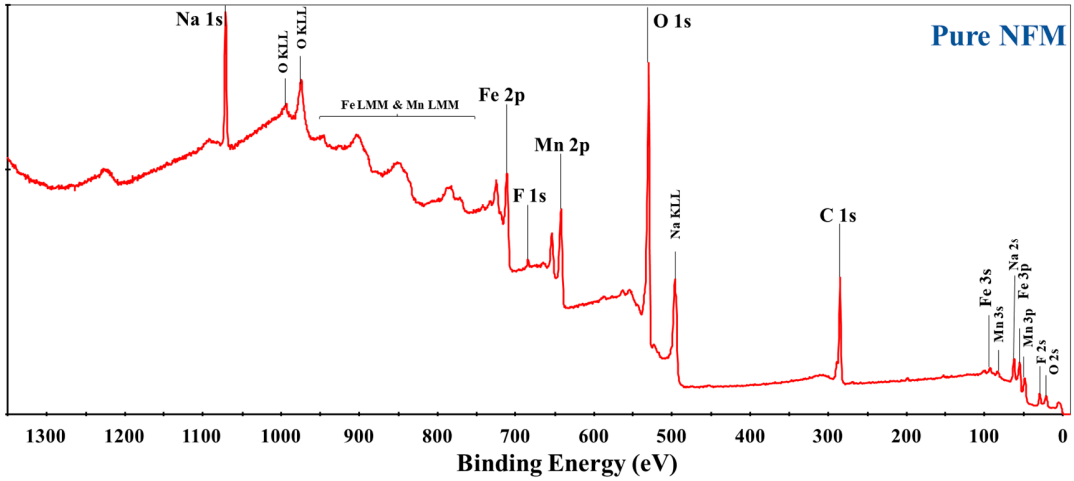


Figure S6. XPS Spectra for Pure NFM

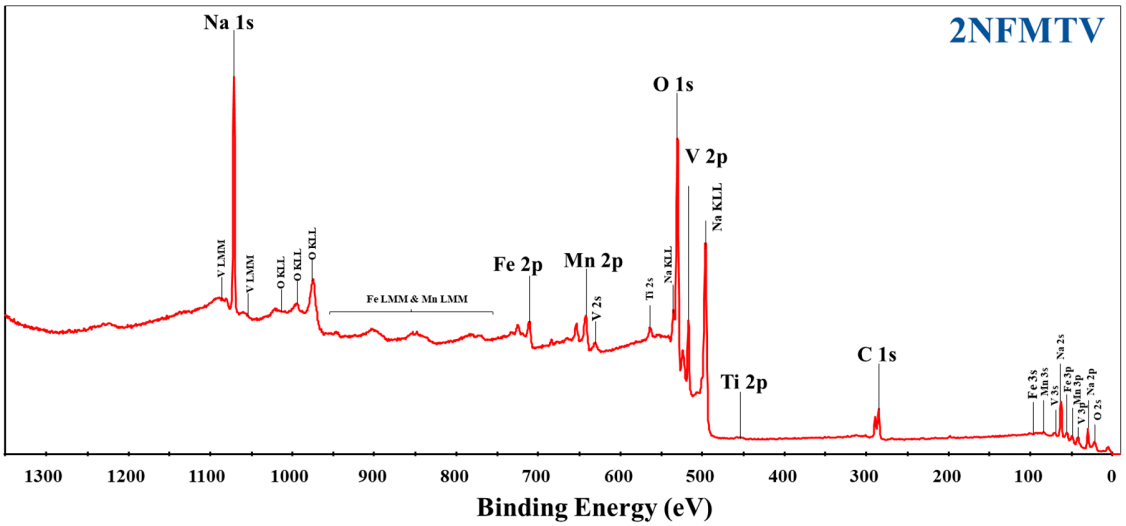


Figure S7. XPS Spectra for 2NFMTV

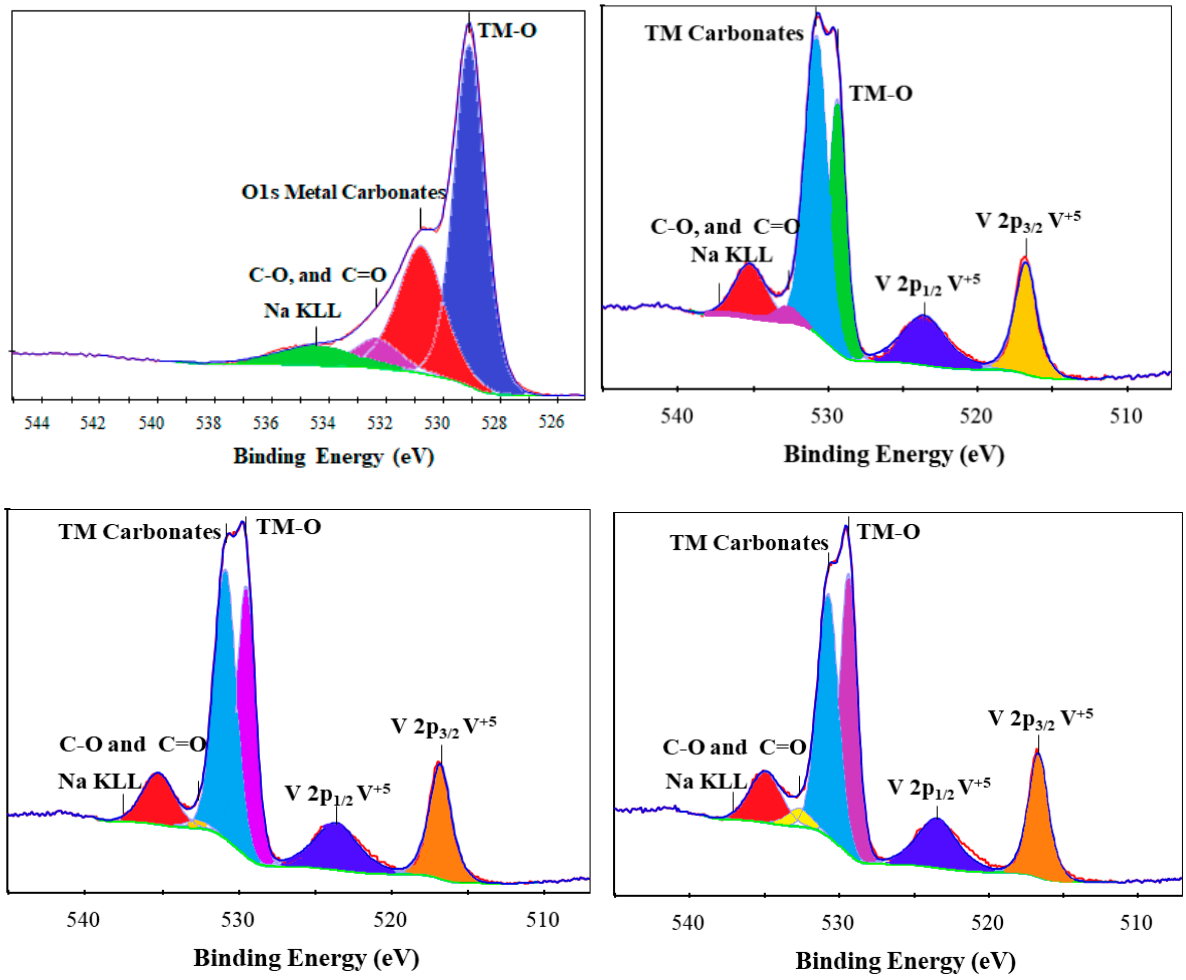


Figure S8. XPS Peak of O 1s in Pure NFM and Doped NFM

From Figure S7, it is seen that the O 1s peak at 529.3 eV corresponds to the lattice oxygen bound to metals, and peaks at 532.7 and 531.4 eV are related to $C-O$ and $C=O$ bond in active oxygen species (Na2CO3/ NaOH). The broad C 1 s region (298 to 280 eV) split into four component peaks: 284.8 (C–C), 286.7 (C–O), 288.7 (C=O), and 291.9 (C – F). The C 1s peaks at 288.7 attributed to Na2CO3 and 284.8 eV attributed to hydrocarbon contaminants on the powder surface. The peaks with higher energies (sp3 carbon) (C-O and C=O peaks) represents CO_2 and CO gases which are normally trapped in pores of materials.

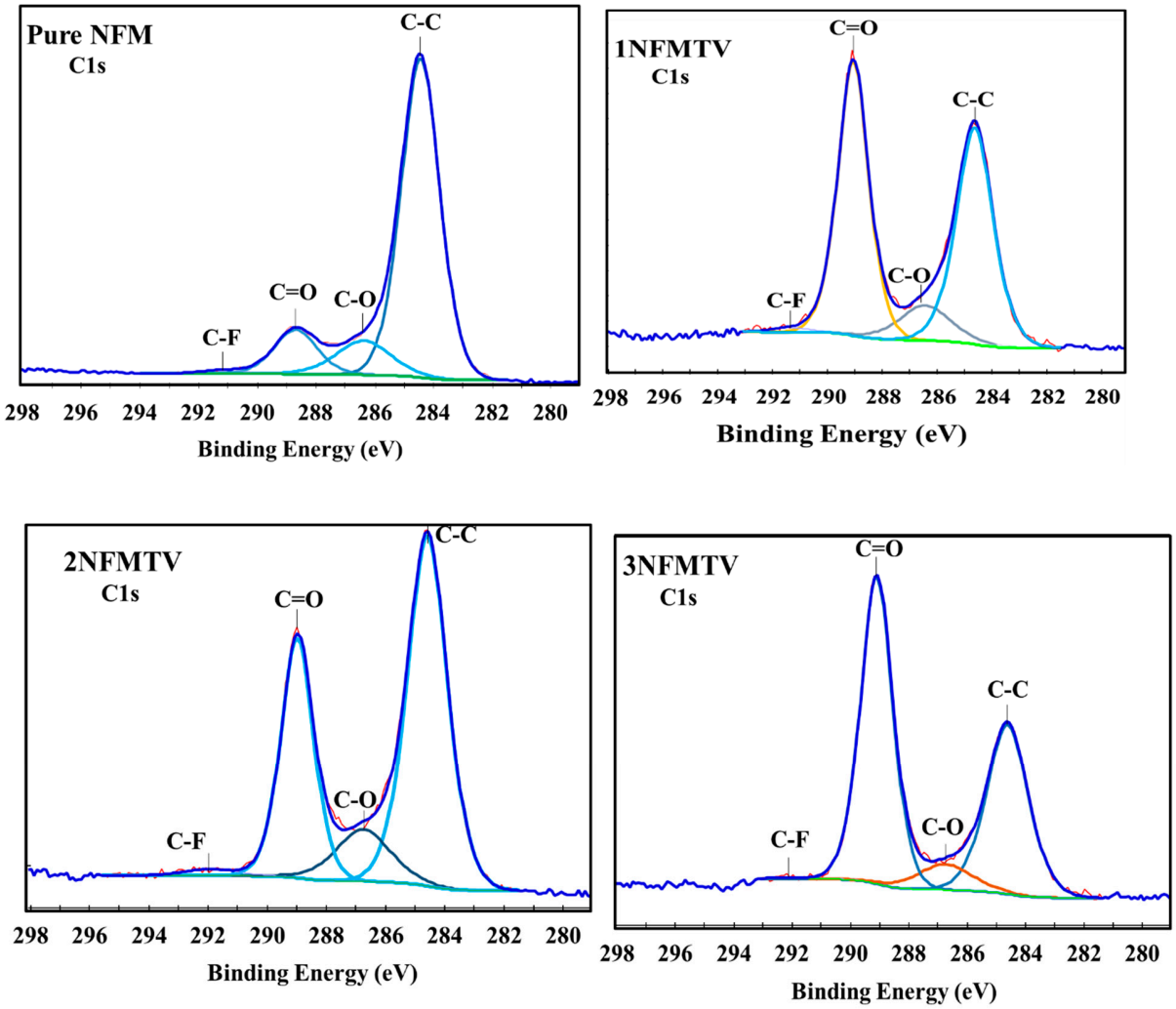


Figure S9. XPS Peak of C 1s in Pure NFM and Doped NFM

Estimating the content of substances by the area under the curves of the C 1s spectra as shown in Figure S8, significant reduction of residual Na on the surface after Ti and V doping. V and Ti doping effectively inhibit such unfavorable reaction through a robust (V + Ti) doped lattice structure facilitated by strong O covalent bonds (with the bonding energy of Ti - O = 662 kJ mol^{-1} and V- O = 644 kJ mol^{-1}). In this research, introduction to Ti and V in P2 $Na_{0.6}Fe_{0.5}Mn_{0.5}O_2$ has been considered to be an effective approach to suppress the detrimental J–T distortion to ameliorate its structural stability. The inactive Ti^{4+} and V^{5+} in the TMO_2 layers tends to halt the anisotropic change of the Mn–O bond and strengthen its bond, leading to a more stable configuration and contraction of TMO_2 layers.

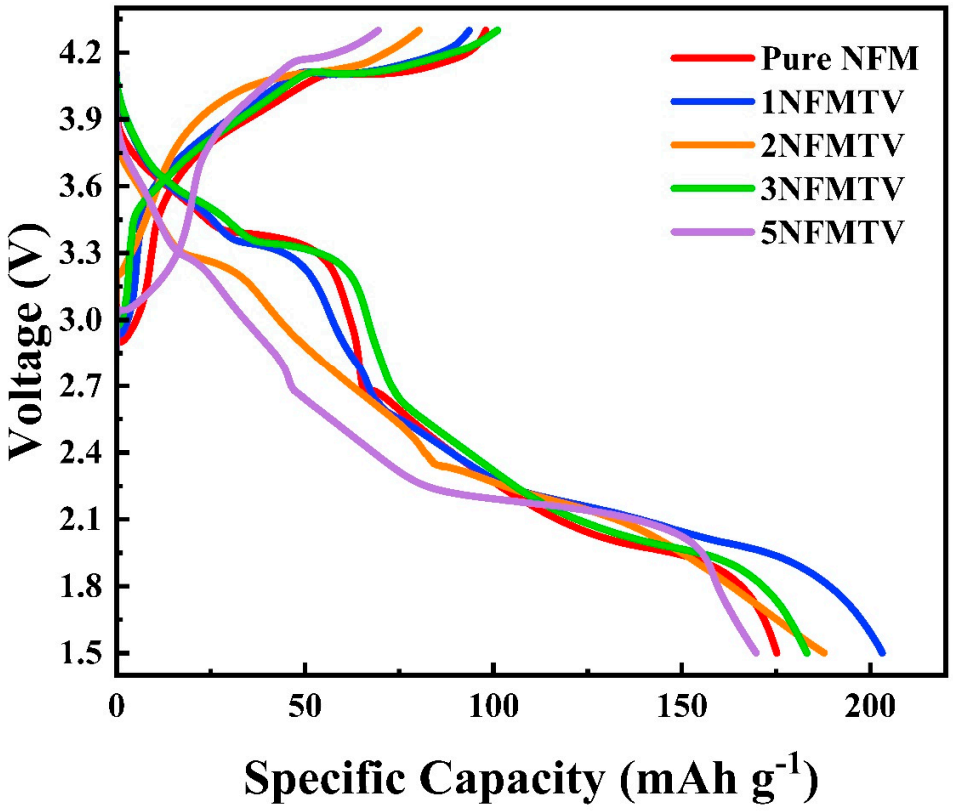


Figure S10. 1st Cycle Charge/Discharge Profiles for Pure NFM, 1NFMTV, 2NFMTV, 3NFMTV, 5NFMTV

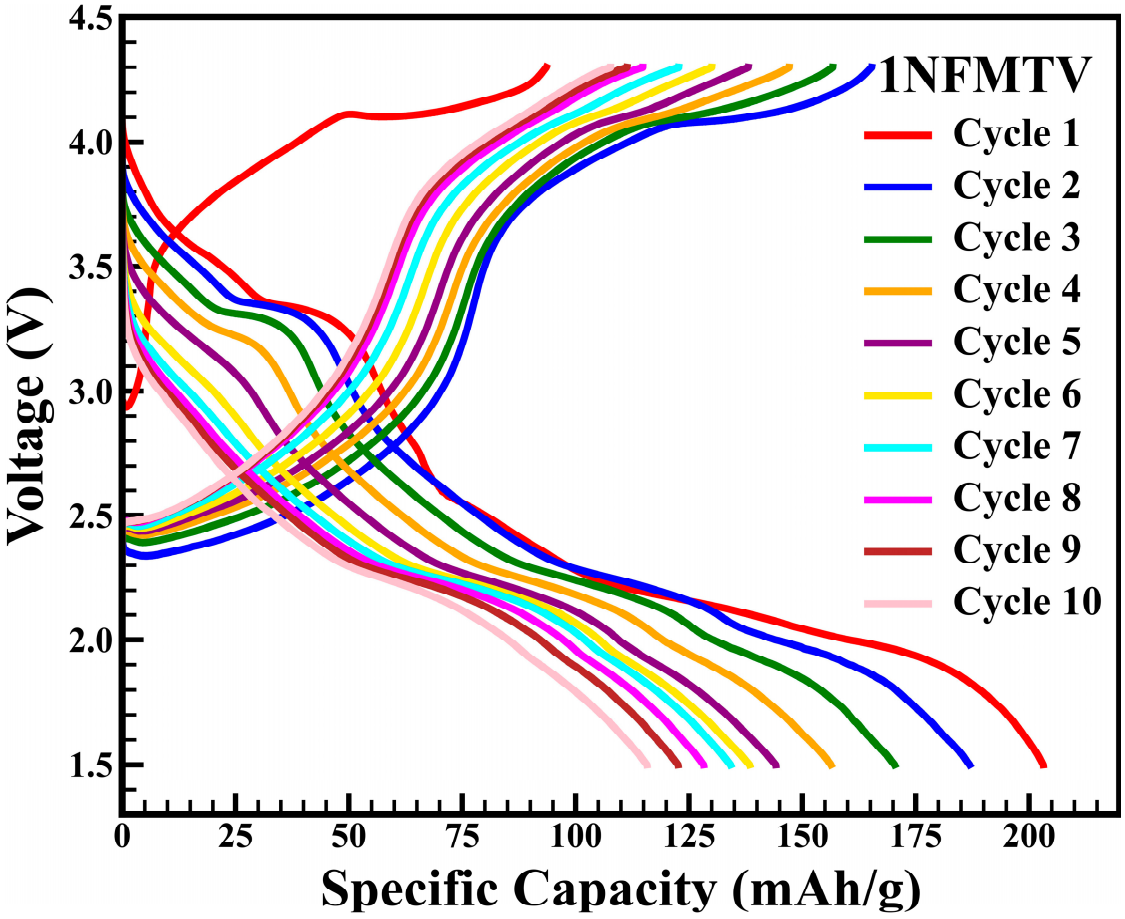


Figure S11. Cycling Profile for 1NFMTV

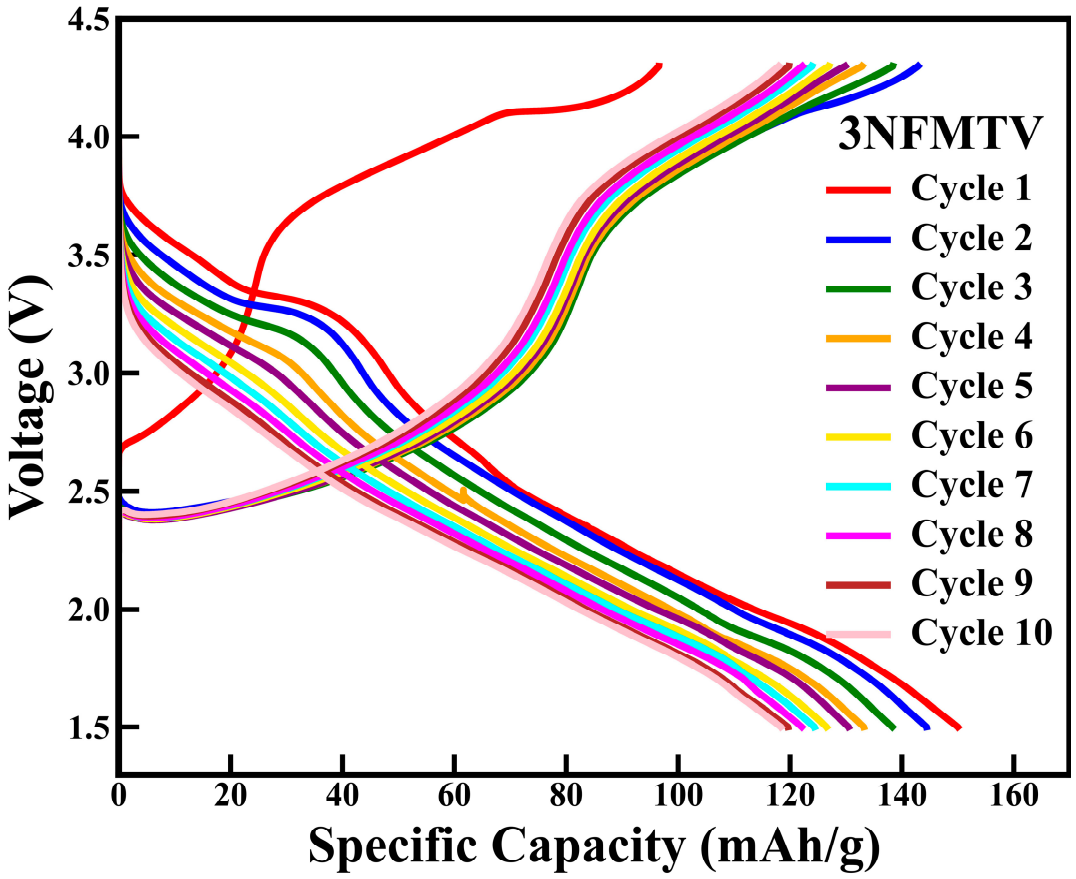


Figure S12. Cycling Profile for 3NFMTV

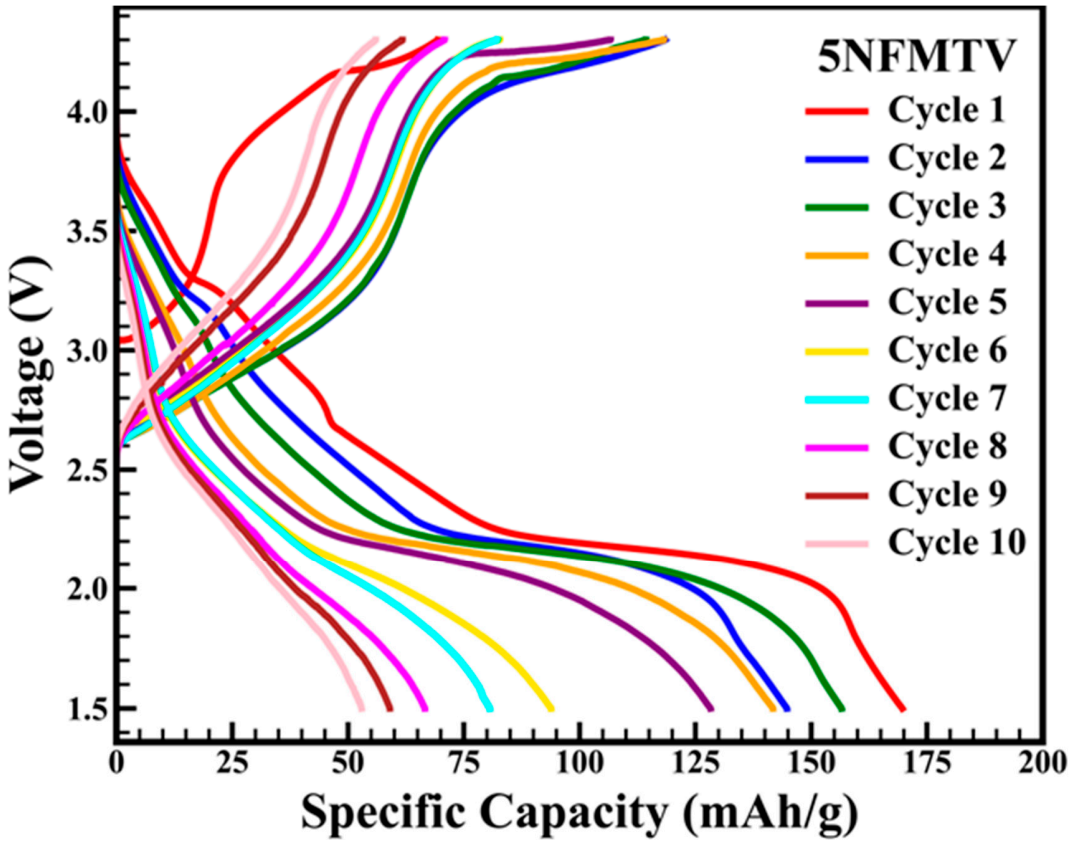


Figure S13. Cycling Profile for 5NFMTV

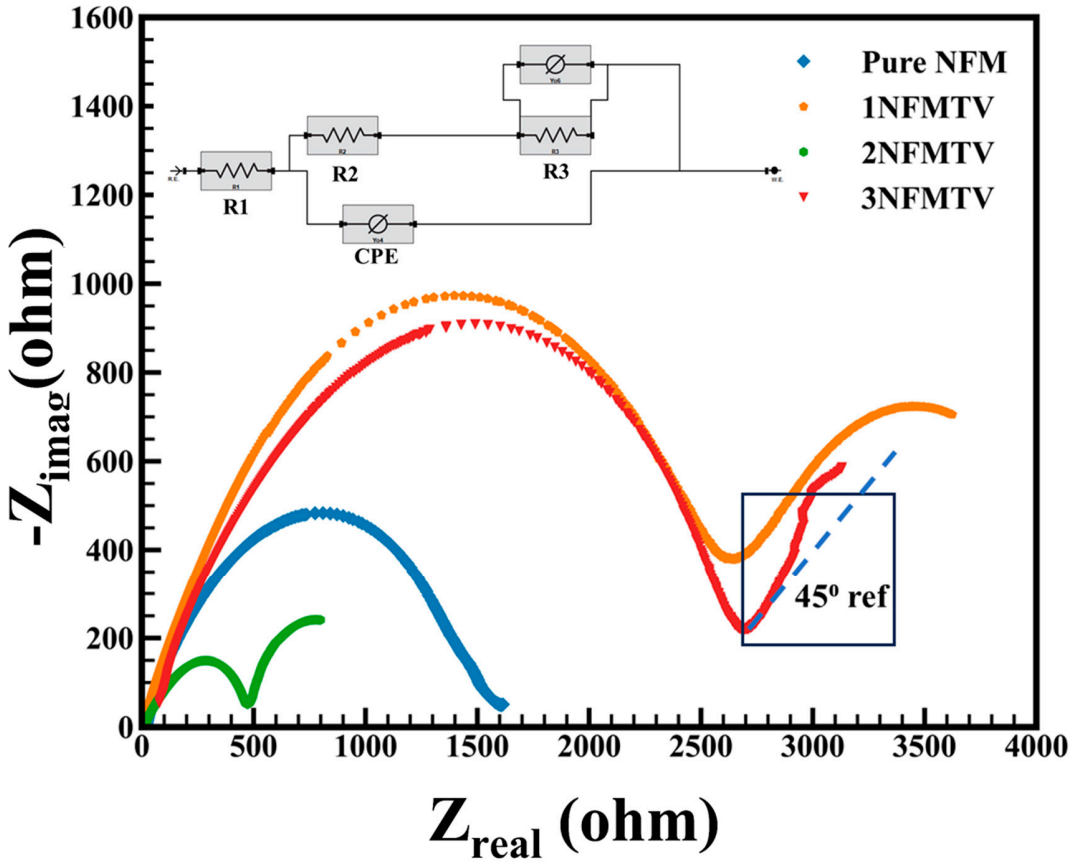


Figure S14. Nyquist plots from EIS analysis for Pure NFM, 1NFMTV, 2NFMTV, 3NFMTV over frequency range from 0.1 kHz to 100 kHz

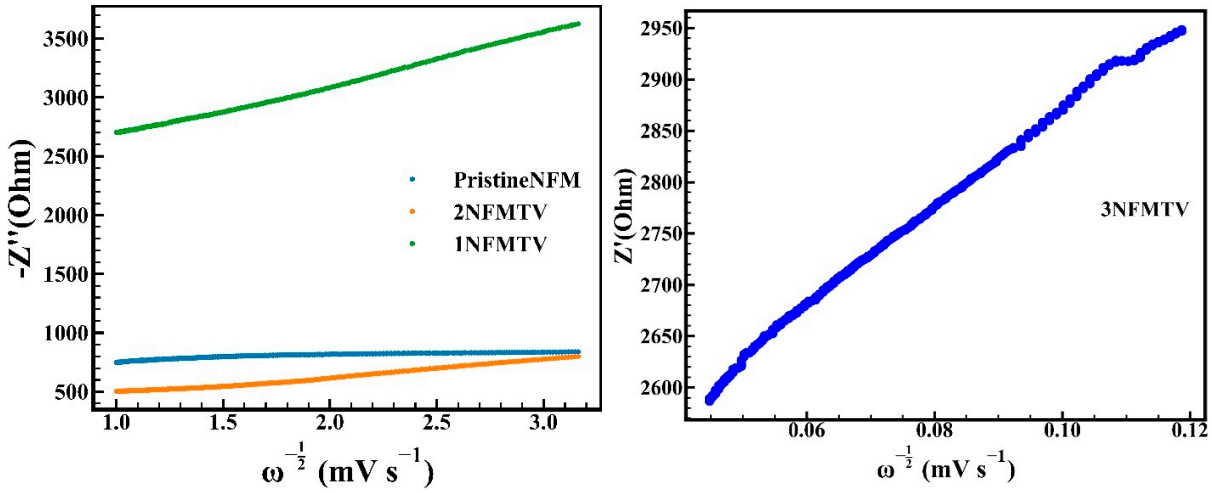


Figure S15. -Z'' vs. Angular Frequency response from EIS analysis for Pristine NFM, 1NFMTV, 2NFMTV, 3NFMTV

Table S1. Rietveld refinement results (lattice parameters, Na sites, and R-factors) for $Na_{0.6}Fe_{0.5}Mn_{0.5}O_2$

Pristine $Na_{0.6}Fe_{0.5}Mn_{0.5}O_2$					
Space Group: P63/mmc					
Atom	**Wyckoff Position**	**x**	**y**	**z**	**Occ.**
Na_f	2b	0	0	1/4	0.265
Na_e	2d	2/3	1/3	1/4	0.395
Fe	2a	0	0	0	0.50
Mn	2a	0	0	0	0.50
O	4f	1/3	2/3	0.083611	1.00
***a* (Å) = *b* (Å) =** 2.925, ***c* (Å)** = 11.29, **Unit Volume (Å^3) =** 83.3638 $\alpha = \beta = 90°$, $\gamma = 120°$					
R_{wp} = 7.8, **R_p** = 5, χ^2 = 4.7589					

Table S2. Rietveld refinement results (lattice parameters, Na sites, and R-factors) for $Na_{0.6}Fe_{0.49}Mn_{0.5}Ti_{0.005}V_{0.005}O_2$

$\boldsymbol{Na_{0.6}Fe_{0.49}Mn_{0.5}Ti_{0.005}V_{0.005}O_2}$					
Space Group: P63/mmc					
Atom	**Wyckoff Position**	**x**	**y**	**z**	**Occ.**
$\mathbf{Na_f}$	2b	0	0	1/4	0.265
$\mathbf{Na_e}$	2d	2/3	1/3	1/4	0.395
Fe	2a	0	0	0	0.49
Mn	2a	0	0	0	0.50
Ti	2a	0	0	0	0.005
V	2a	0	0	0	0.005
O	4f	1/3	2/3	0.089981	1.00
$\boldsymbol{a}$ **(Å)** = $\boldsymbol{b}$ **(Å)** = 2.92097, $\boldsymbol{c}$ **(Å)** = 11.29807, **Unit Volume (Å^3)** = 83.48128 $\boldsymbol{\alpha} = \boldsymbol{\beta} = 90°$, $\boldsymbol{\gamma} = 120°$					
$\mathbf{R_{wp}}$ = 5.82, $\mathbf{R_p}$ = 4.07, $\boldsymbol{\chi^2}$ = 5.004					

Table S3. Rietveld refinement results (lattice parameters, Na sites, and R-factors) for $Na_{0.6}Fe_{0.48}Mn_{0.5}Ti_{0.01}V_{0.01}O_2$

$\boldsymbol{Na_{0.6}Fe_{0.48}Mn_{0.5}Ti_{0.01}V_{0.01}O_2}$					
Space Group: P63/mmc					
Atom	**Wyckoff Position**	**x**	**y**	**z**	**Occ.**
$\mathbf{Na_f}$	2b	0	0	1/4	0.265
$\mathbf{Na_e}$	2d	2/3	1/3	1/4	0.395
Fe	2a	0	0	0	0.48
Mn	2a	0	0	0	0.50
Ti	2a	0	0	0	0.01
V	2a	0	0	0	0.01
O	4f	1/3	2/3	0.0934	1.00
$\boldsymbol{a}$ **(Å)** = $\boldsymbol{b}$ **(Å)** = 2.91538, $\boldsymbol{c}$ **(Å)** = 11.27331, **Unit Volume (Å^3)** = 82.97981 $\boldsymbol{\alpha} = \boldsymbol{\beta} = 90°$, $\boldsymbol{\gamma} = 120°$					
$\mathbf{R_{wp}}$ = 8.9, $\mathbf{R_p}$ = 6.05, $\boldsymbol{\chi^2}$ = 11.2189					

Table S4. Rietveld refinement results (lattice parameters, Na sites, and R-factors) for $Na_{0.6}Fe_{0.47}Mn_{0.5}Ti_{0.015}V_{0.015}O_2$

$\boldsymbol{Na_{0.6}Fe_{0.47}Mn_{0.5}Ti_{0.015}V_{0.015}O_2}$					
Space Group: P63/mmc					
Atom	**Wyckoff Position**	**x**	**y**	**z**	**Occ.**
$\mathbf{Na_f}$	2b	0	0	1/4	0.265
$\mathbf{Na_e}$	2d	2/3	1/3	1/4	0.395
Fe	2a	0	0	0	0.47
Mn	2a	0	0	0	0.50
Ti	2a	0	0	0	0.015
V	2a	0	0	0	0.015
O	4f	1/3	2/3	0.093474	1.00
$\boldsymbol{a}$ **(Å)** = $\boldsymbol{b}$ **(Å)** = 2.9217, $\boldsymbol{c}$ **(Å)** = 11.29141, **Unit Volume (Å^3)** = 83.47377, $\boldsymbol{\alpha} = \boldsymbol{\beta} = 90°$, $\boldsymbol{\gamma} = 120°$					
$\mathbf{R_{wp}}$ = 5.27, $\mathbf{R_p}$ = 3.9, $\boldsymbol{\chi^2}$ = 3.7443					

Table S5. Rietveld refinement results (lattice parameters, Na sites, and R-factors) for $Na_{0.6}Fe_{0.45}Mn_{0.5}Ti_{0.025}V_{0.025}O_2$

$\boldsymbol{Na_{0.6}Fe_{0.45}Mn_{0.5}Ti_{0.025}V_{0.025}O_2}$					
Space Group: P63/mmc					
Atom	**Wyckoff Position**	**x**	**y**	**z**	**Occ.**
$\mathbf{Na_f}$	2b	0	0	1/4	0.265
$\mathbf{Na_e}$	2d	2/3	1/3	1/4	0.395
Fe	2a	0	0	0	0.45
Mn	2a	0	0	0	0.50
Ti	2a	0	0	0	0.025
V	2a	0	0	0	0.025
O	4f	1/3	2/3	0.0926	1.00
$\boldsymbol{a}$ **(Å)** = $\boldsymbol{b}$ **(Å)** = 2.92103, $\boldsymbol{c}$ **(Å)** = 11.2909, **Unit Volume (Å^3)** = 83.4293 $\boldsymbol{\alpha = \beta} = 90°$, $\boldsymbol{\gamma} = 120°$					
$\mathbf{R_{wp}}$ = 5.46, $\mathbf{R_p}$ = 3.96, $\boldsymbol{\chi^2}$ = 4.1195					