

Supporting Information

Synergistic W and Ti Dual Doping for P2/Tunnel Intergrowth Formation: A Pathway to High Stability Sodium Ion Battery Cathodes

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Keywords: Sodium ion batteries - cathode materials - P2/tunnel intergrowth - dual doping

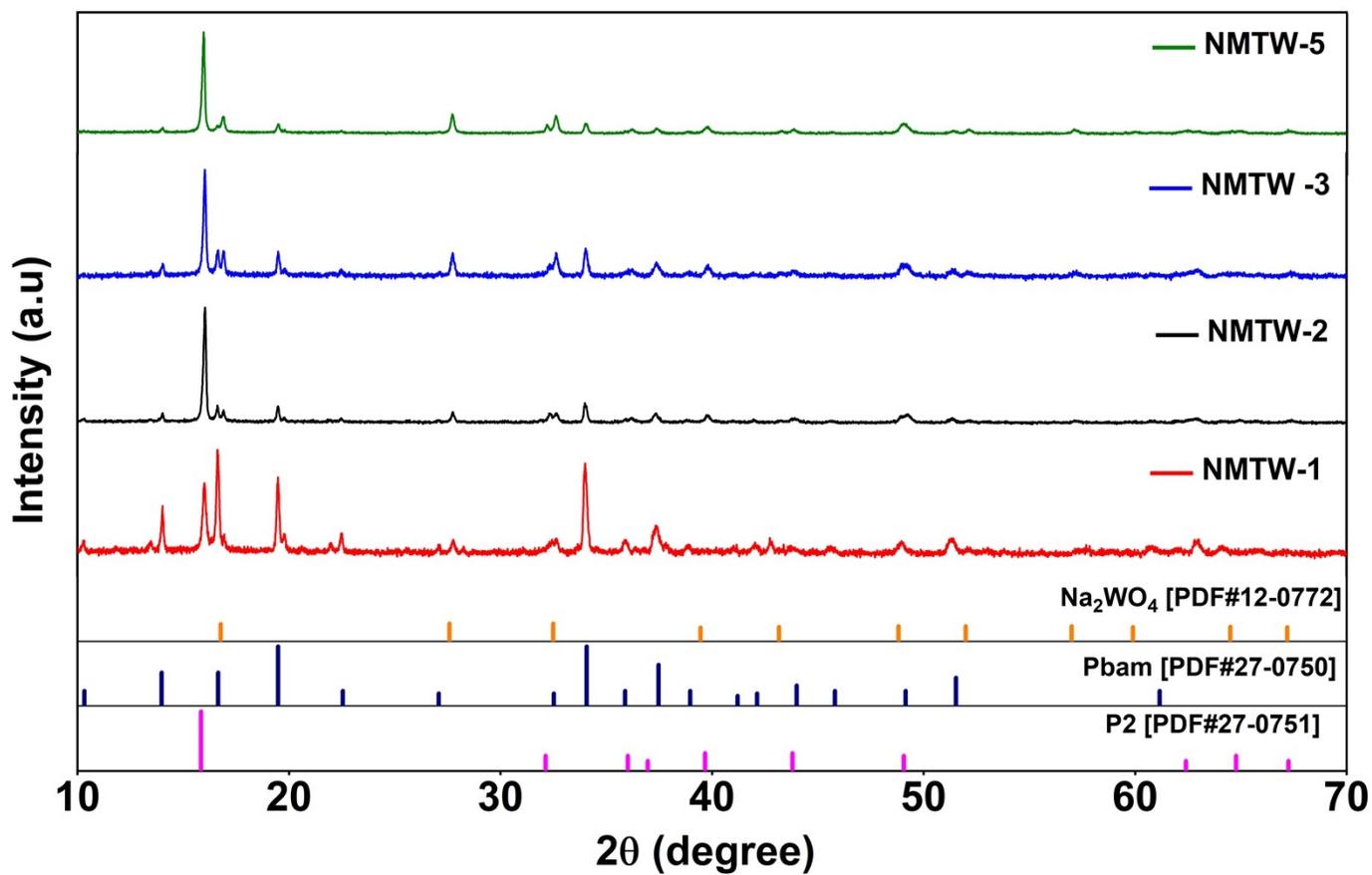


Figure S1. XRD patterns of the samples after second calcination (ca2).

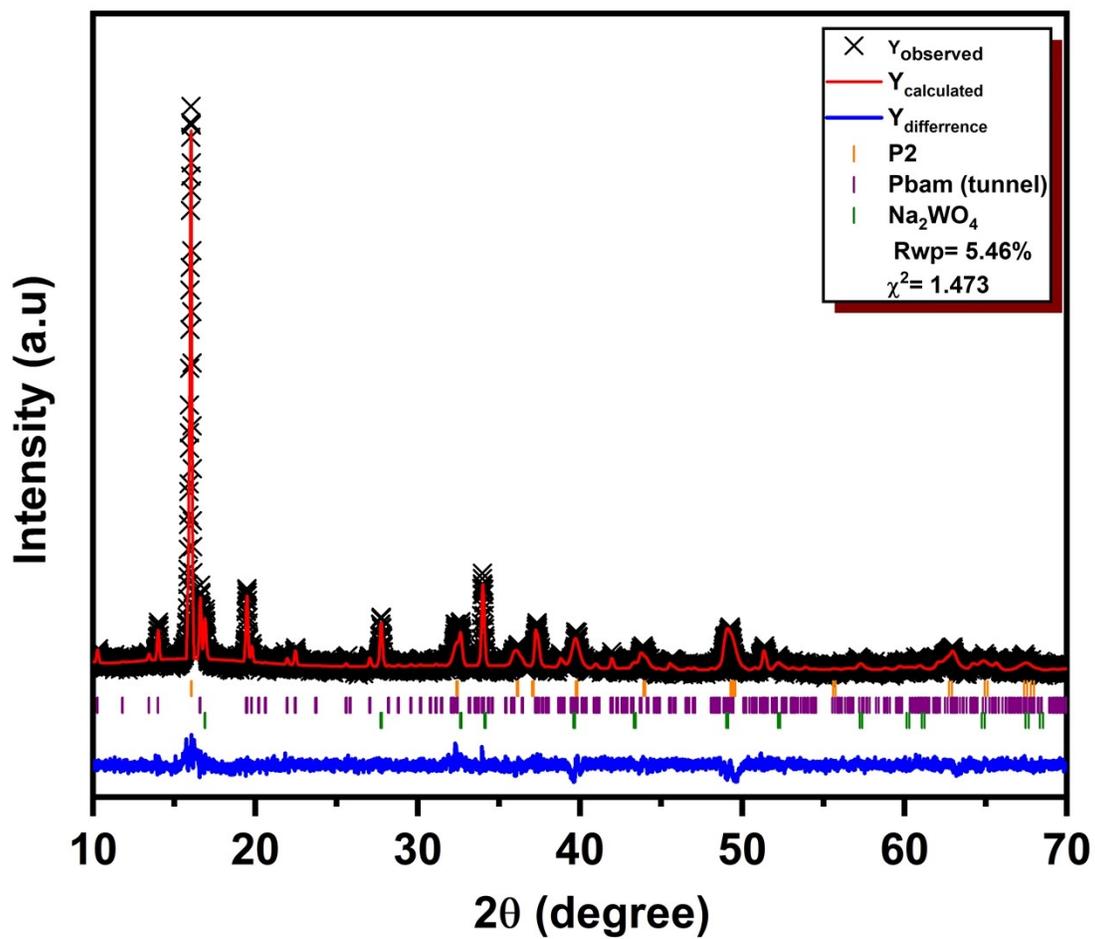


Figure S2. Rietveld refinement of NMTW-2 ca2.

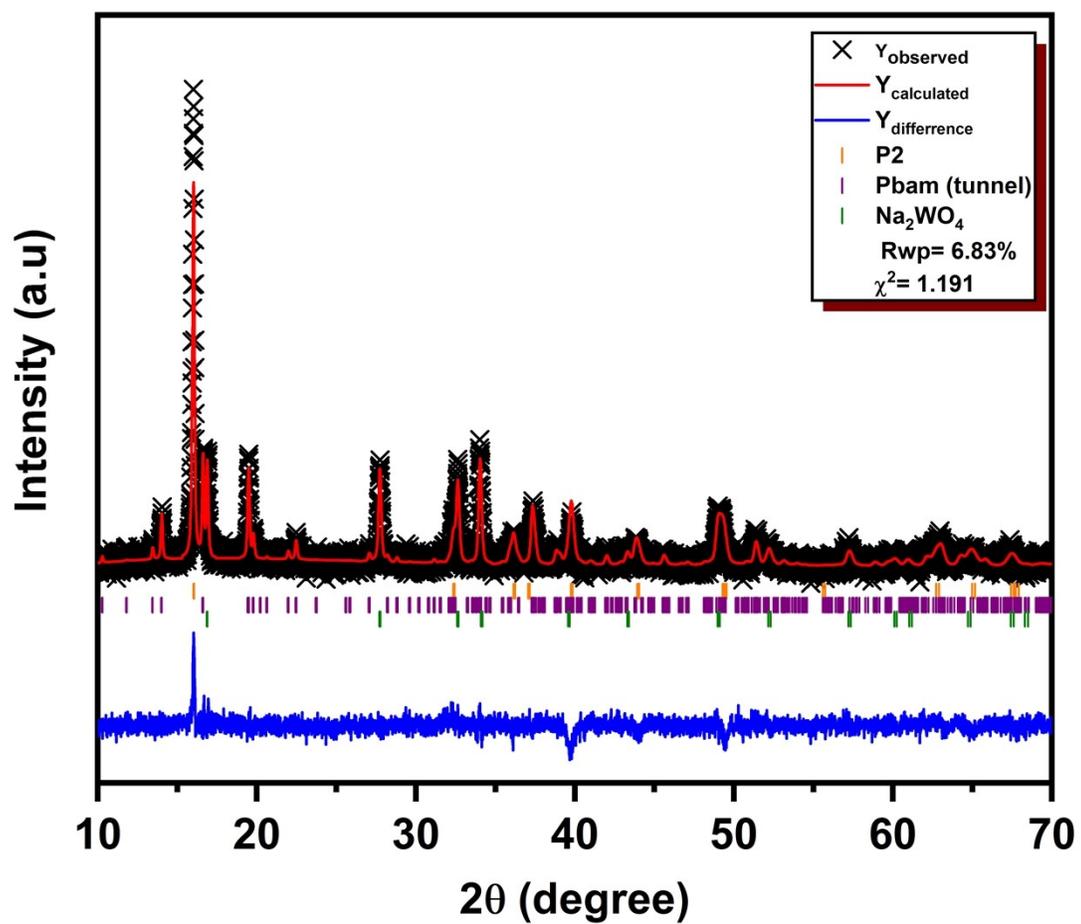


Figure S3. Rietveld refinement of NMTW-3 ca2.

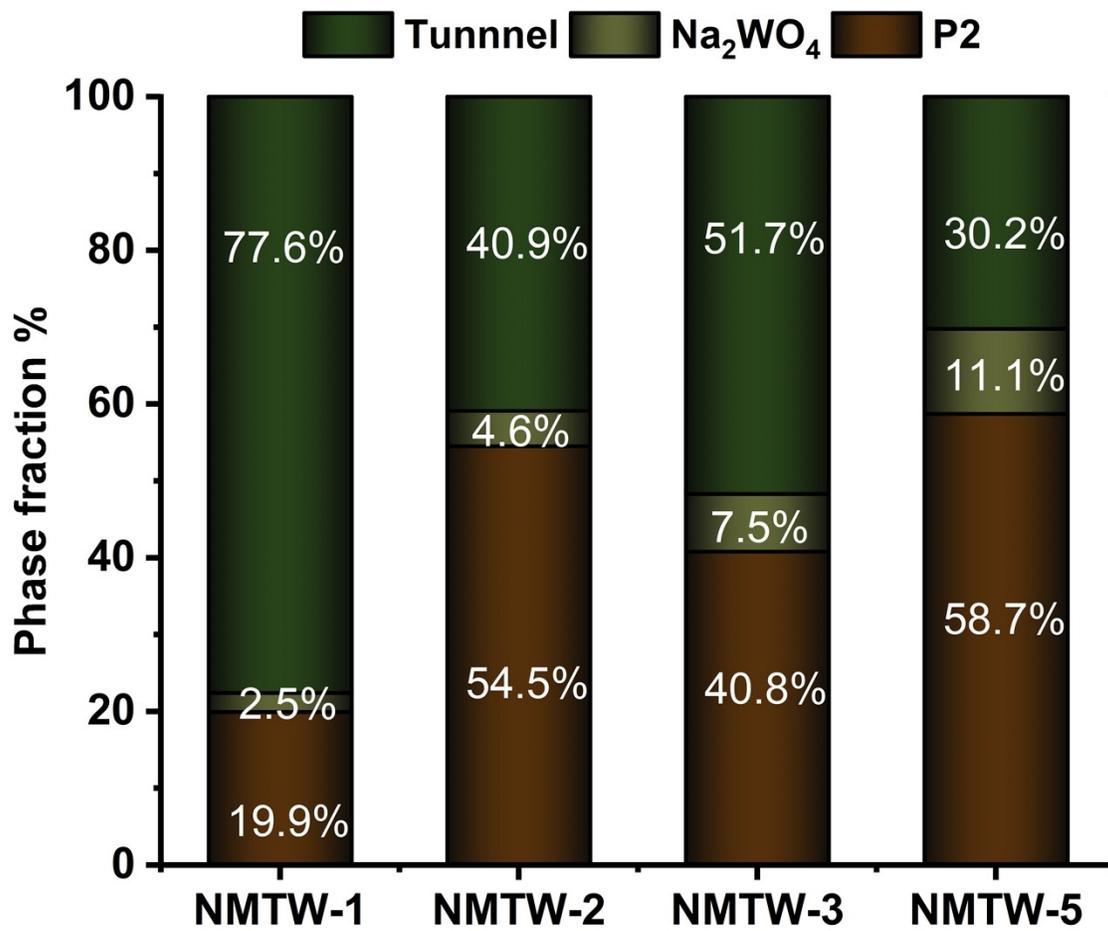


Figure S4. Phase fraction % for ca2 samples.

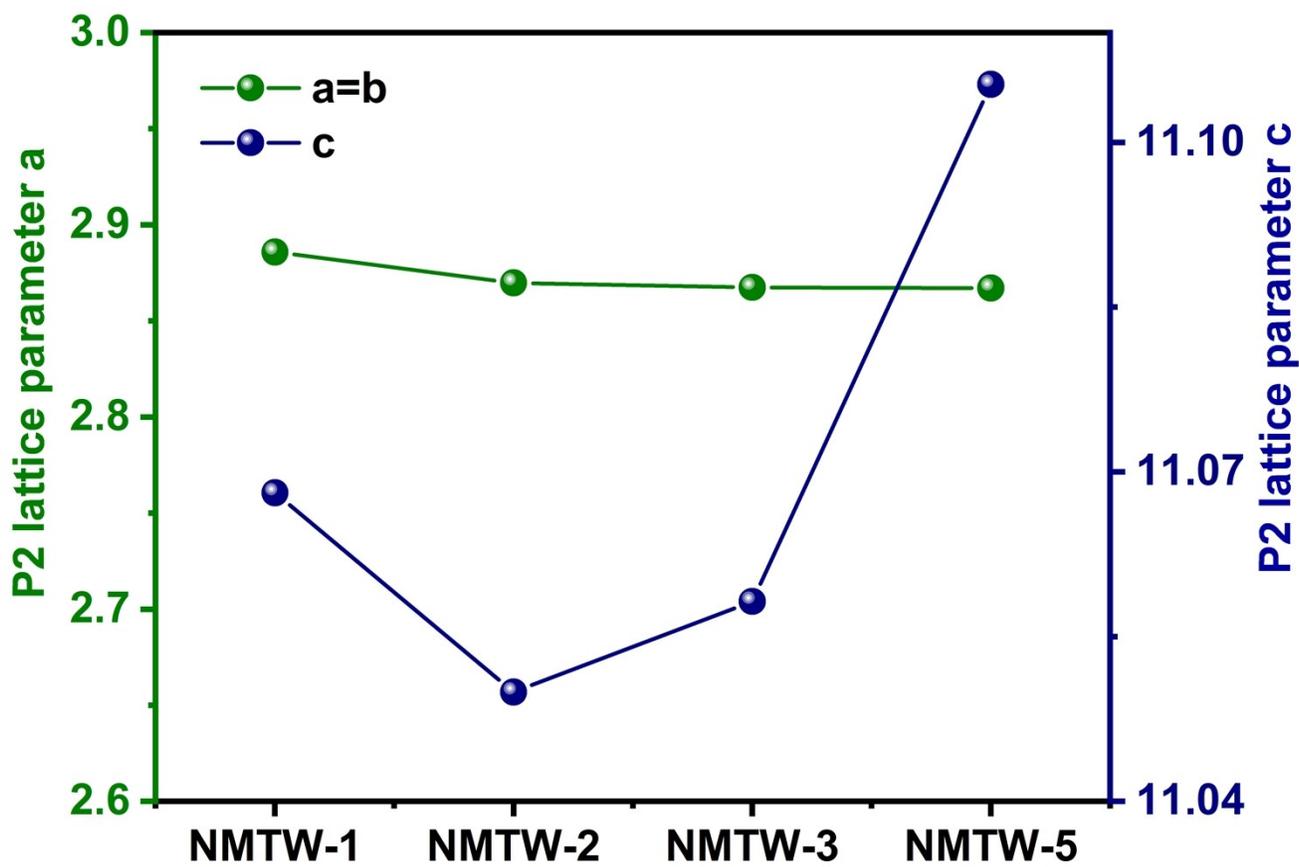


Figure S5. P2 lattice parameters for ca2 samples

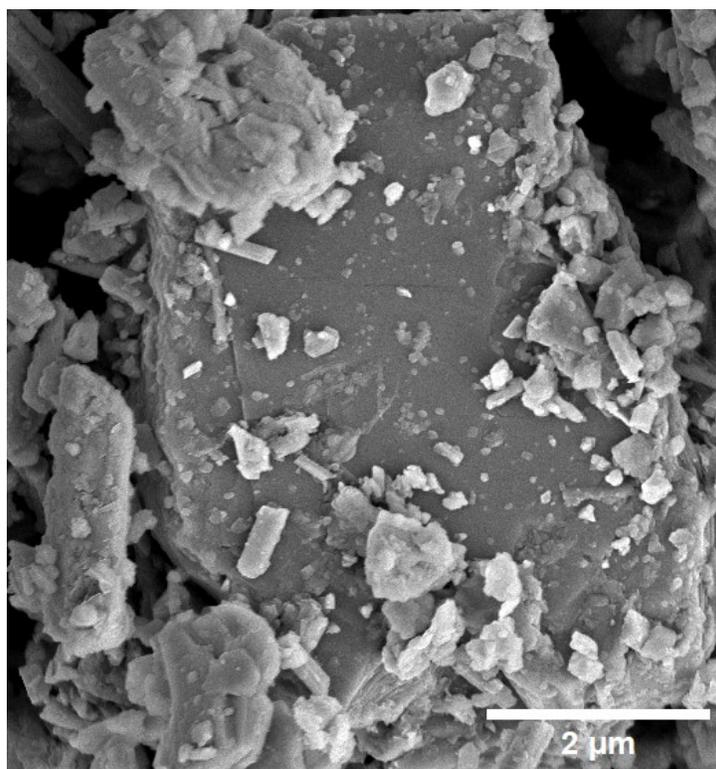


Figure S6. SEM image of NMTW-5 ca2.

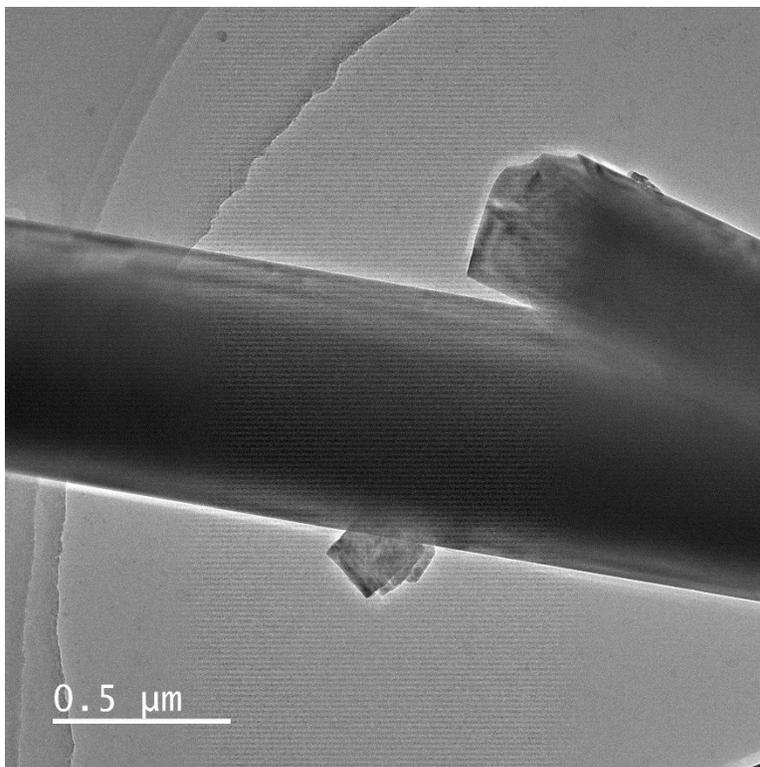


Figure S7. TEM image of NMTW-3 ca2.

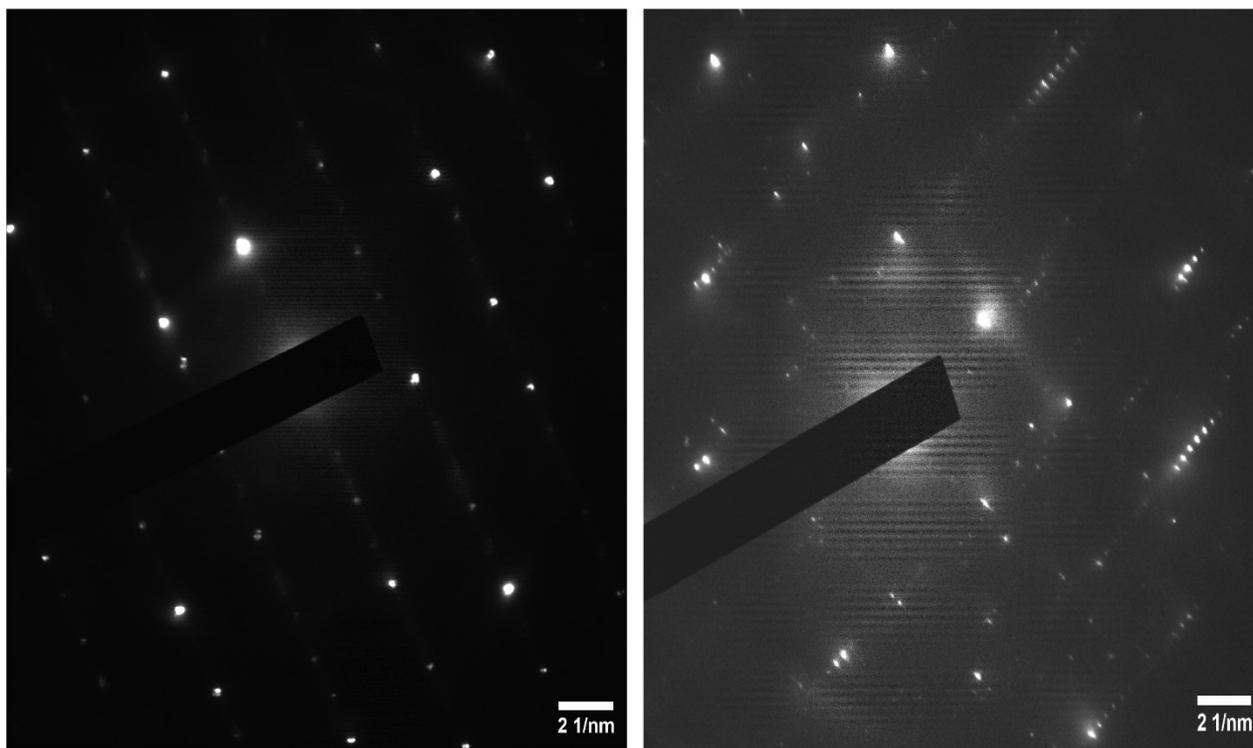


Figure S8. Selected area electron diffraction (SAED) image of NMTW-3 ca2.

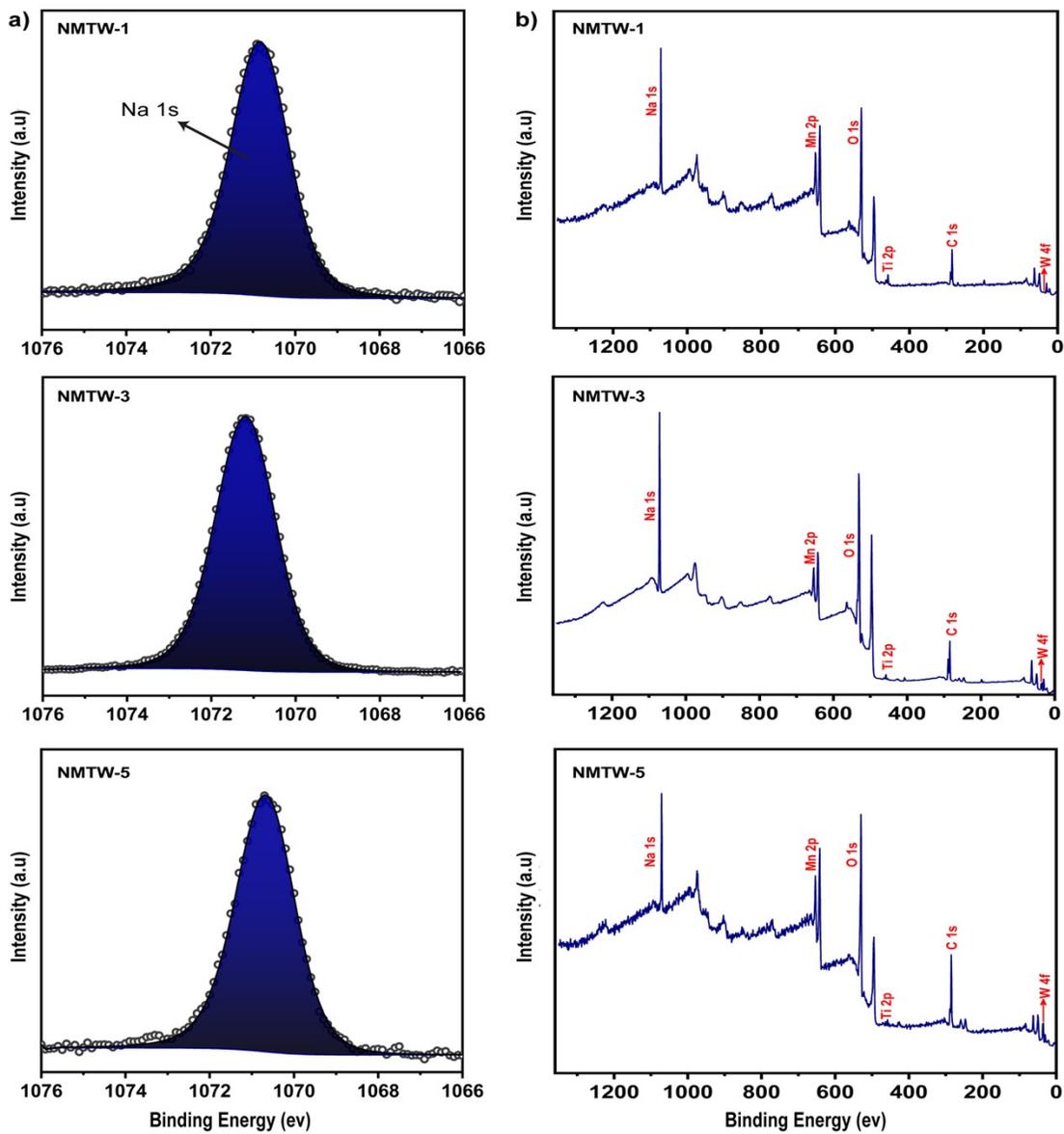


Figure S9. (a) Na 1s high resolution XPS and (b) XPS survey spectra for ca2 samples NMTW-1, NMTW-3, and NMTW-5.

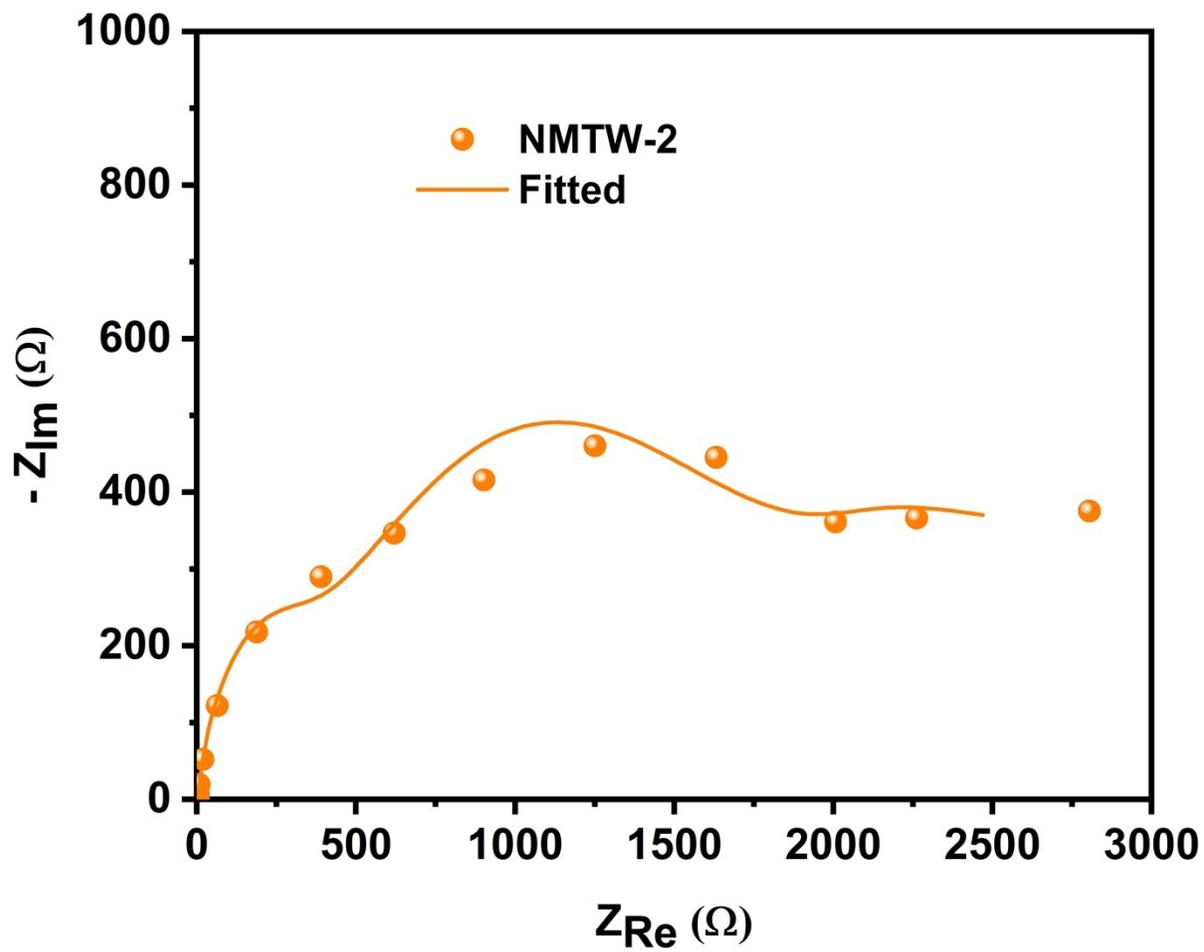


Figure S10. Nyquist plot of NMTW-2 ca2.

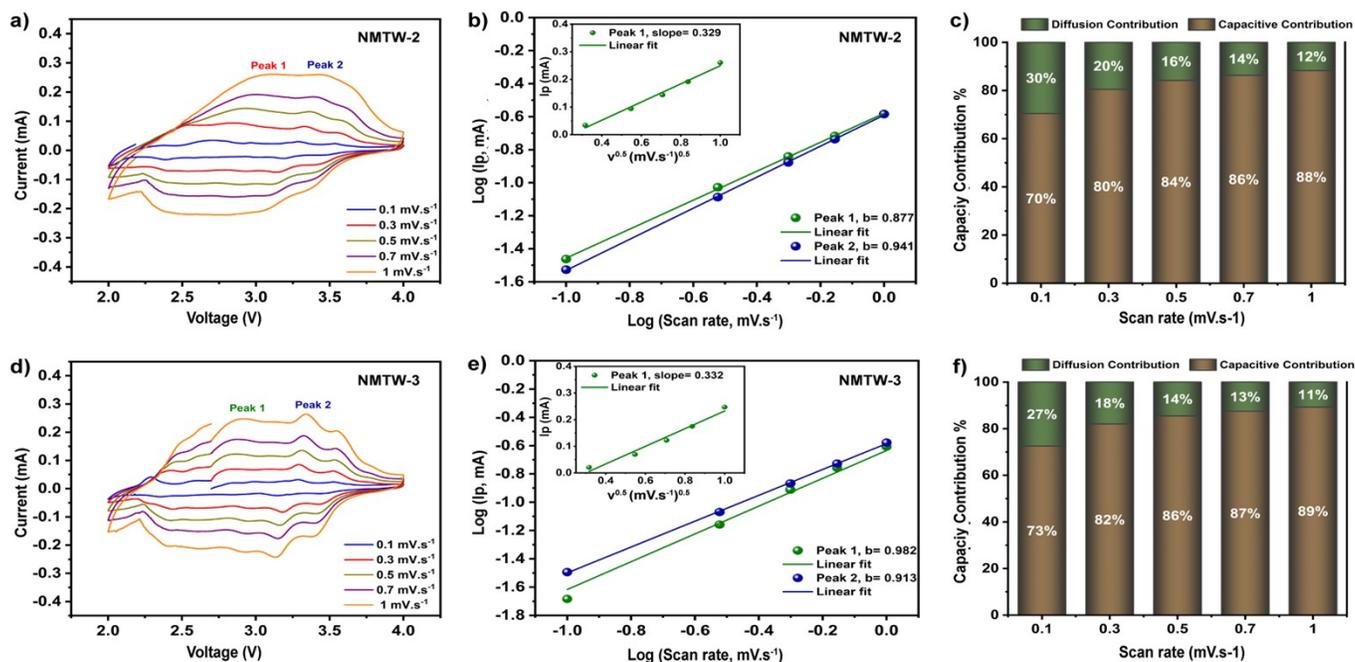


Figure S11. Kinetics analysis including (a) CV profiles for NMTW-2 at different sweep rates, (b) Log peak current (I_p) vs Log scan rate (v) plot at various oxidation peaks with I_p vs $v^{0.5}$ inset, (c) diffusion and capacitive contribution at different scan rates; (d-f) corresponding results for NMTW-3.

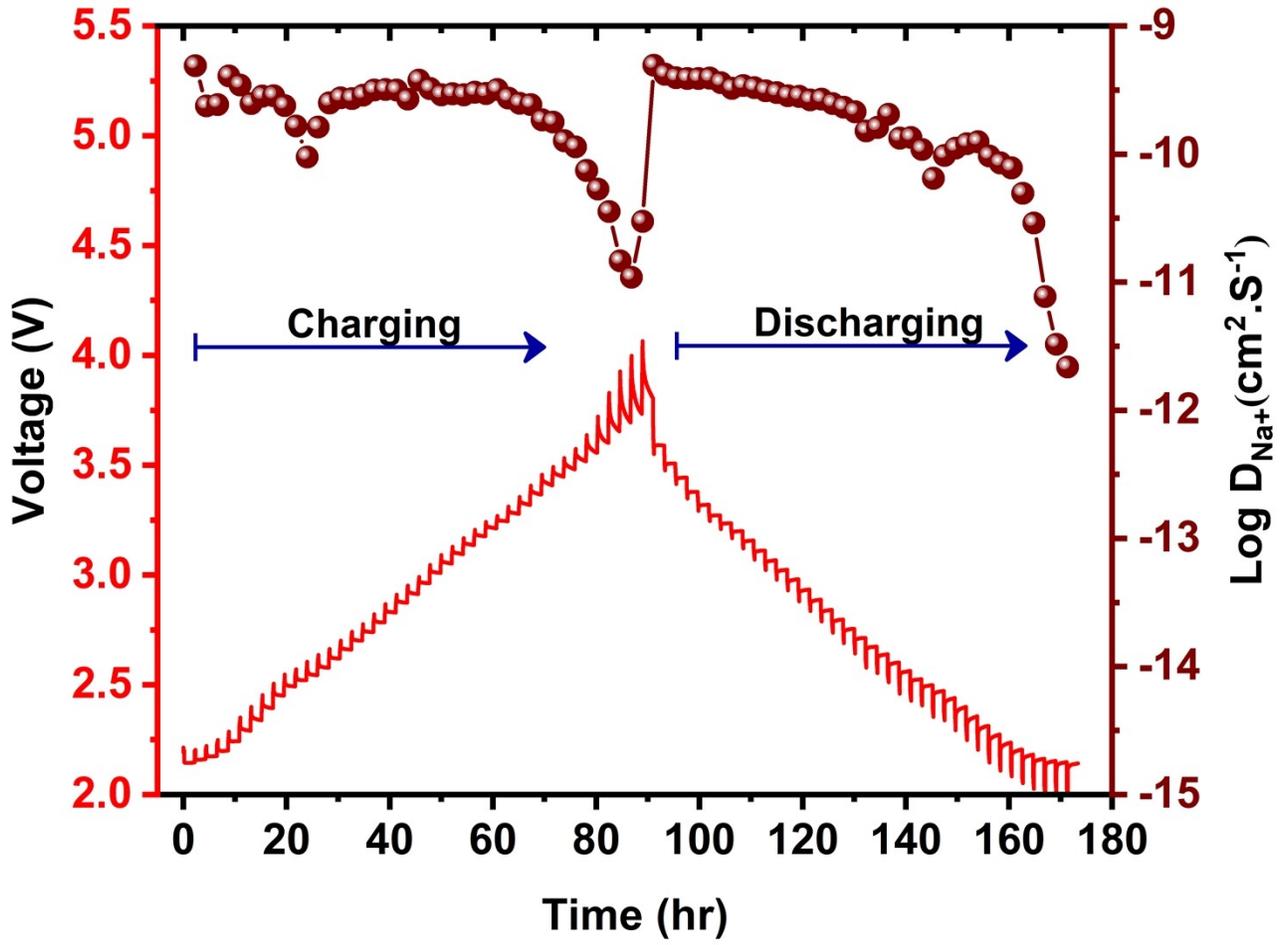


Figure S12. GITT profile and Log (Na⁺ diffusion coefficient) for NMTW-2

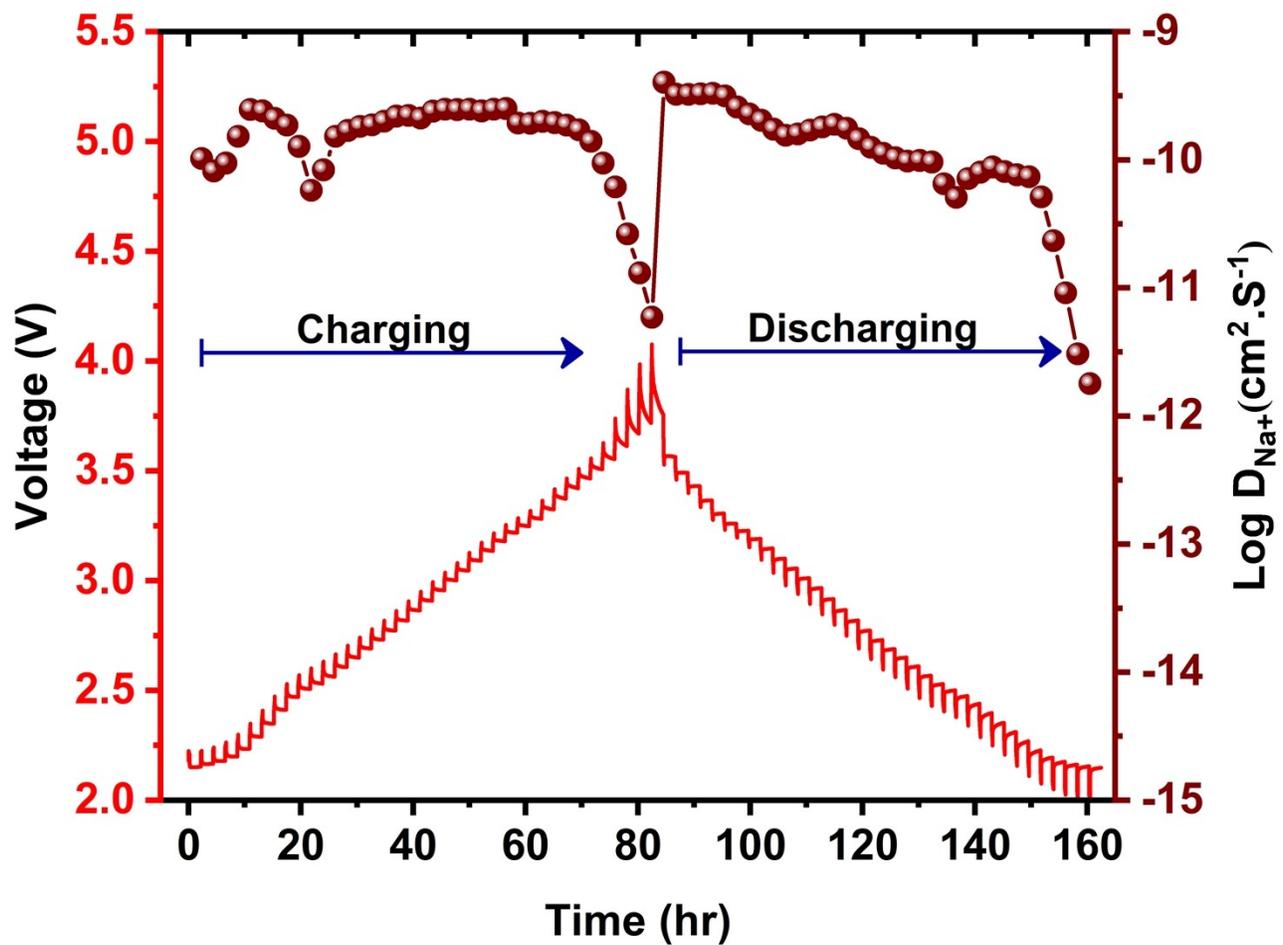


Figure S13. GITT profile and Log (Na^+ diffusion coefficient) for NMTW-3

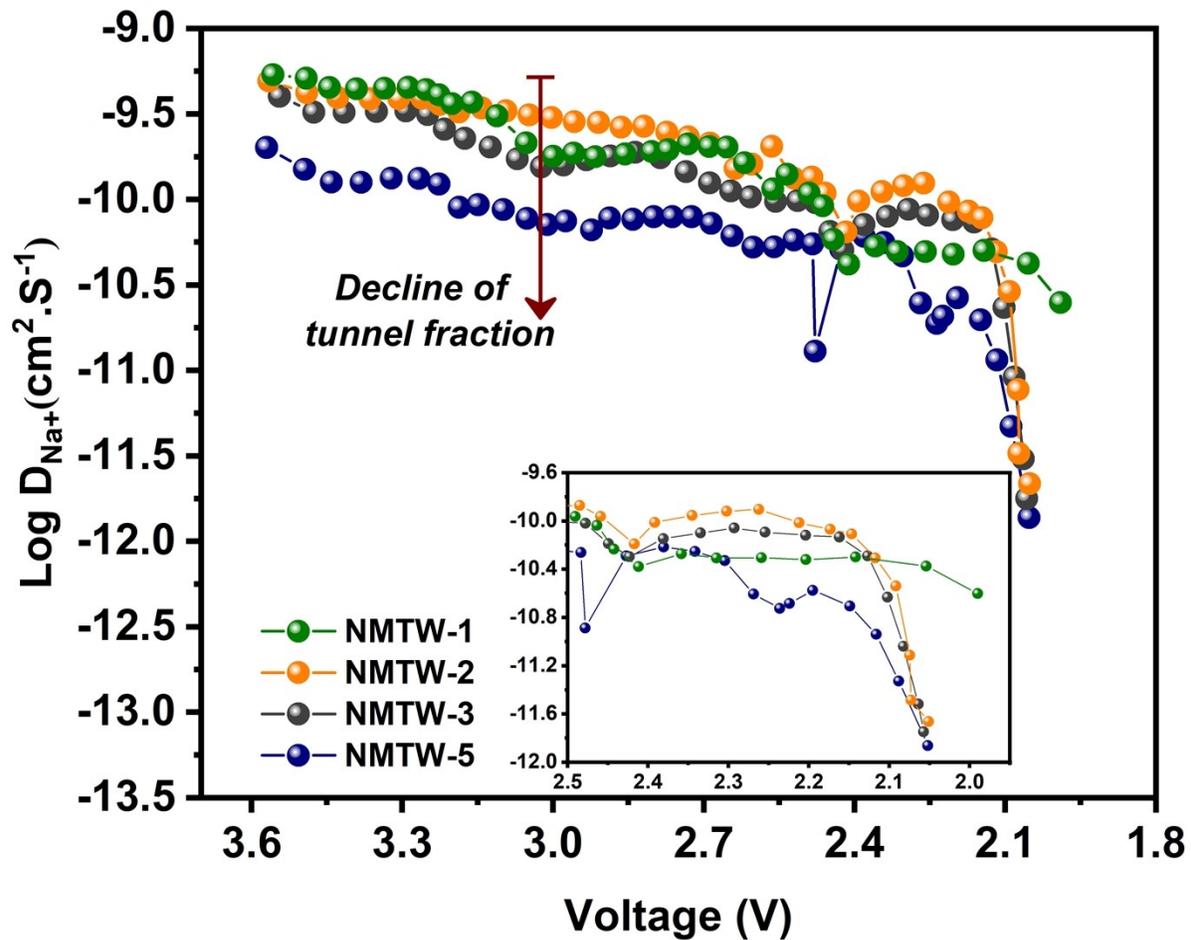


Figure S14. Log (Na^+ diffusion coefficient) across all samples during discharging.

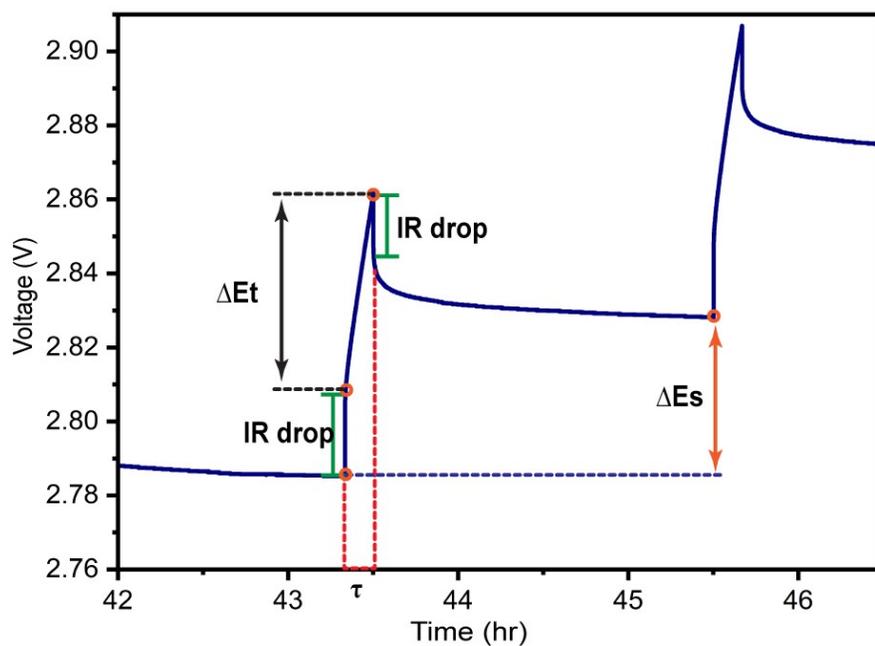


Figure S15. Time versus voltage profile for a single titration during charging.

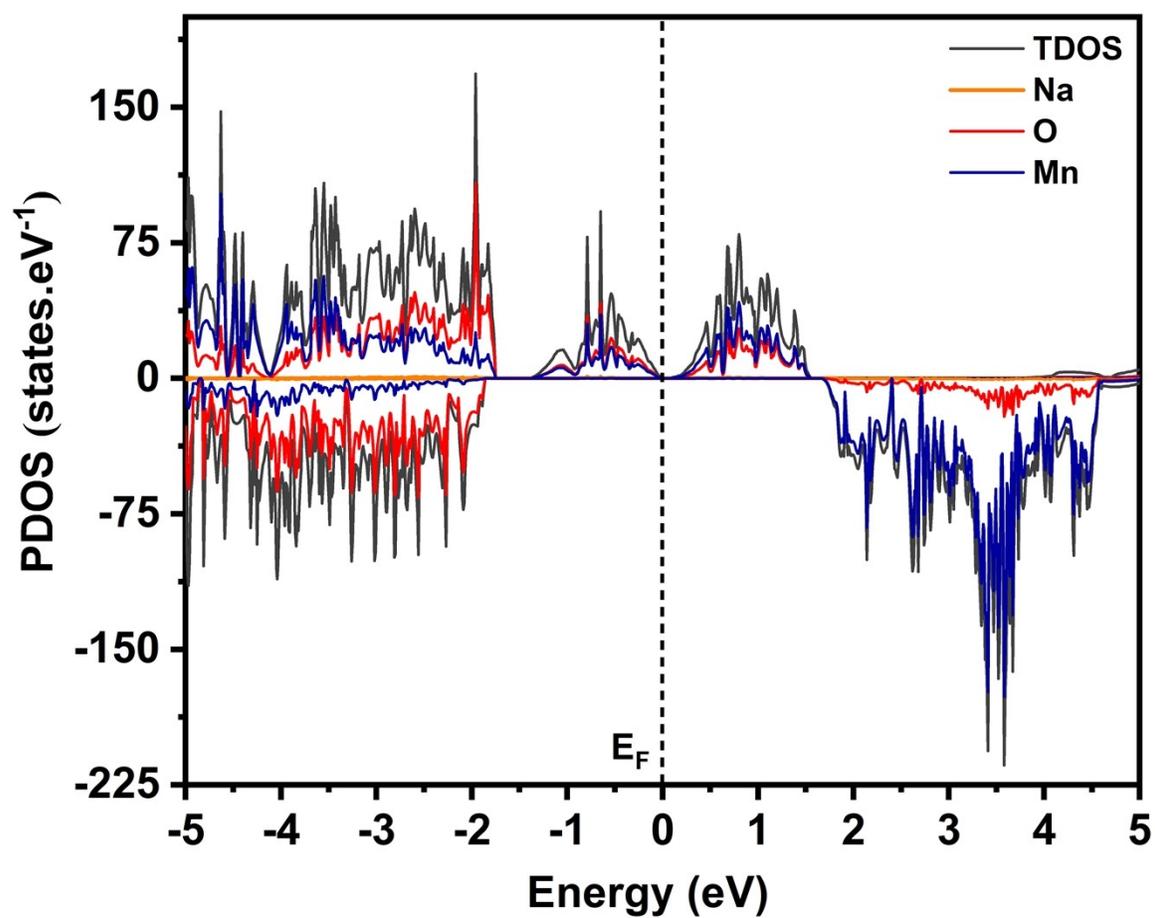


Figure S16. Projected density of states (PDOS) of the pristine P2 Na_{2/3}MnO₂.

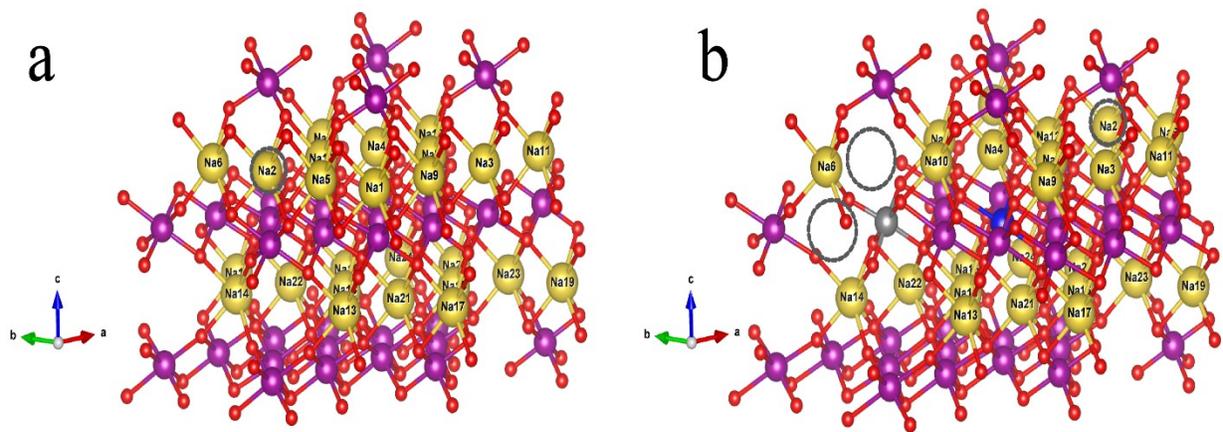


Figure S17. DFT optimized structures of (a) pristine $\text{Na}_{2/3}\text{MnO}_2$ and (b) dual doped NMTW-5. Color scheme: Mn (purple), Na (yellow), W (gray), Ti (blue), and O (red).

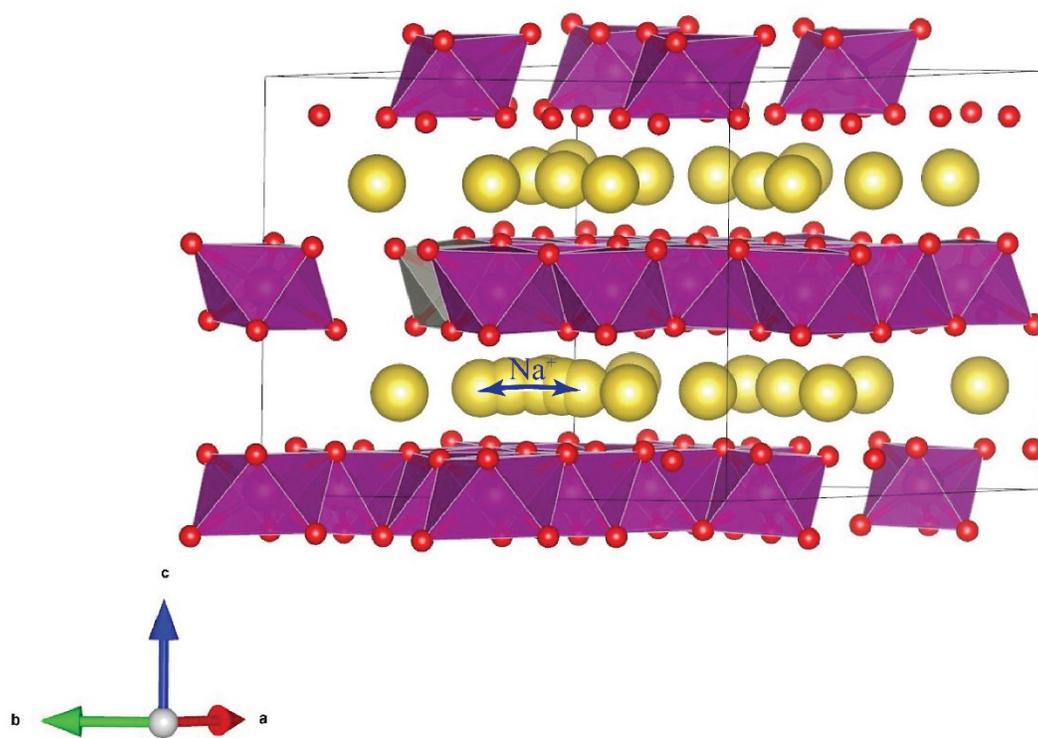


Figure S18. NEB calculated Na^+ migration pathway between two Na sites within NMTW-5.

Table S1. Crystallographic parameters of P2 phase (P63/mmc) of NMTW-5 ca2 refined by the Rietveld method.

Atom	Site	x	y	z	Occ.
Na _f	2b	0.0	0.0	0.25	0.19002
Na _e	2d	0.33333	0.66667	0.75	0.42343
O	4f	0.33333	0.66667	0.0836	1
Mn	2a	0	0	0	0.9
Ti	2a	0	0	0	0.05
W	2a	0	0	0	0.05
a = 2.86709 Å		c = 11.10528 Å		Vol = 79.058 Å³	

Table S2. Crystallographic parameters of Na₂WO₄ phase (Fd-3m, origin choice 2) of NMTW-5 ca2 refined by the Rietveld method.

Atom	Site	x	y	z	Occ.
Na	16c	0	0	0	1
W	8b	0.375	0.375	0.375	1
O	32e	0.2590(9)	0.2590(9)	0.2590(9)	1
a = 9.10953 Å				Vol = 755.94 Å³	

Table S3. Crystallographic parameters of tunnel phase (Pbam) of NMTW-5 ca2 refined by the Rietveld method.

Atom	Site	x	y	z	Occ.
Na1	4g	0.152(8)	0.2027(29)	0	0.82
Na2	4h	0.243(12)	0.401(4)	0.5	0.43
Na3	4g	0.130(11)	0.004(4)	0	0.51
Mn1	4g	-0.0011(23)	0.3061(10)	0	1
Mn2	4h	0.3619(27)	0.0914(8)	0.5	1
Mn3	2c	0	0.5	0	1
Mn4	4h	0.3427(28)	0.3052(11)	0.5	1
Mn5	4g	0.0126(29)	0.1130(8)	0	1
O1	4h	0.342(6)	-0.0009(27)	0.5	1
O2	4g	0.195(6)	0.1097(26)	0	1
O3	4h	0.077(7)	0.1789(27)	0.5	1
O4	4h	0.450(6)	0.1900(30)	0.5	1
O5	4h	0.152(6)	0.2935(30)	0.5	1
O6	4g	0.467(9)	0.2688(23)	0	1
O7	4g	0.327(7)	0.3417(23)	0	1
O8	4g	0.500(8)	0.0727(22)	0	1
O9	4h	0.448(8)	0.4371(21)	0.5	1
a = 9.1187 Å		b = 26.3686 Å		c = 2.8338 Å	
Vol = 681.37 Å³					

Table S4. Equivalent circuit fitted results for EIS data for all samples.

Circuit component	NMTW-1	NMTW-2	NMTW-3	NMTW-5
Bulk resistance (R_{bulk}, Ω)	3.475	3.343	3.33	3.287
Solid electrolyte interphase resistance (R_{sei}, Ω)	232.1	450	157	167
Charge transfer resistance (R_{ct}, Ω)	250	500	146.6	102.2