Supplementary Information

An $Na_3VMn_{0.5}Ti_{0.5}(PO_4)_3$ NASICON cathode with multielectron reactions for sustainable energy storage

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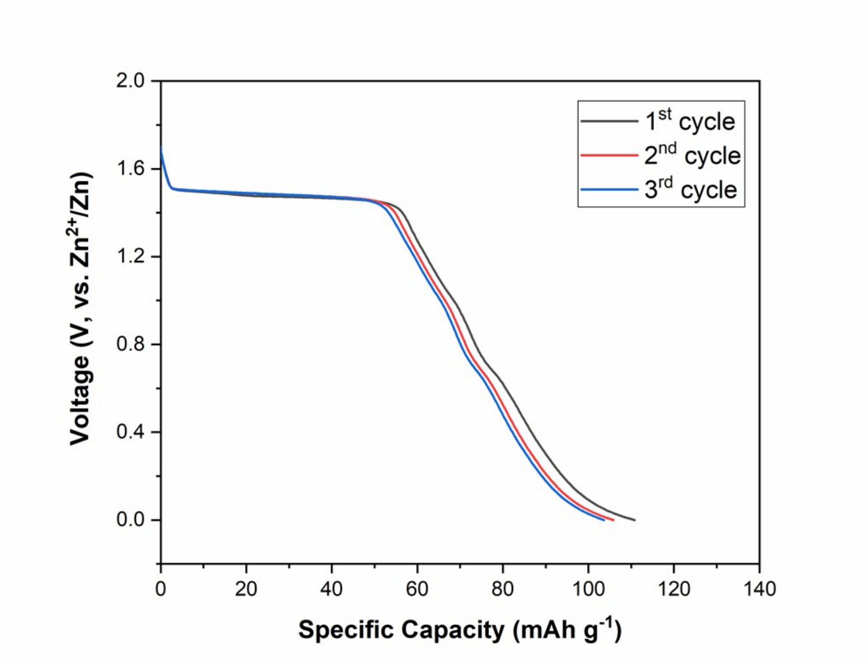

Figure S1. Voltage profile of $Na_3V_2(PO_4)_3$ electrode in hybrid cell.

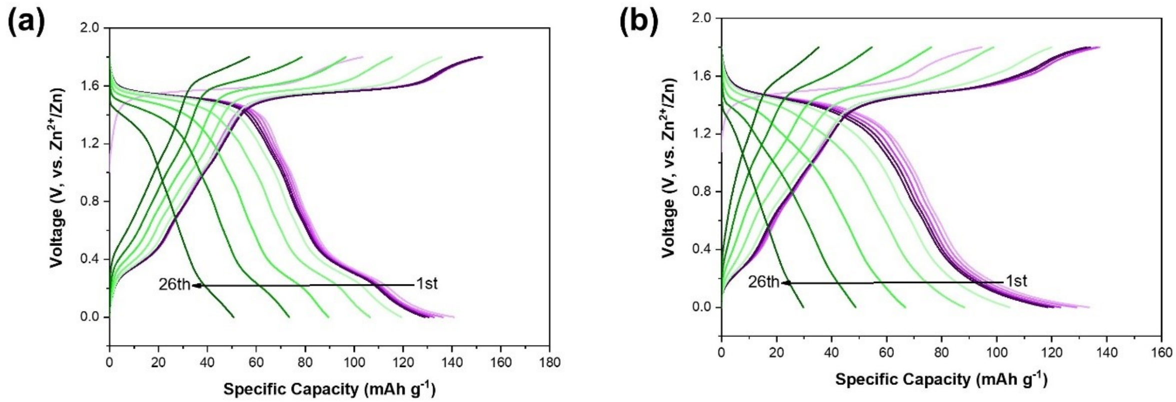

Figure S2. Voltage profiles of NVMTP cathodes in (a) ReHAB and (b) Zn-only electrolyte cells at various current rates of 50 (5 cycles), 100 (1), 200 (1), 500 (1), 1000 (1), and 2000 (1) mA g^{-1}.

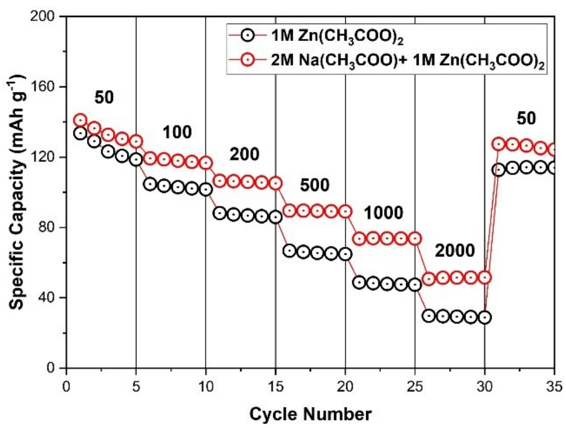

Figure S3. C-rate performance tests of NVMTP cathodes in ReHAB and Zn-only electrolyte cells at various current rates.

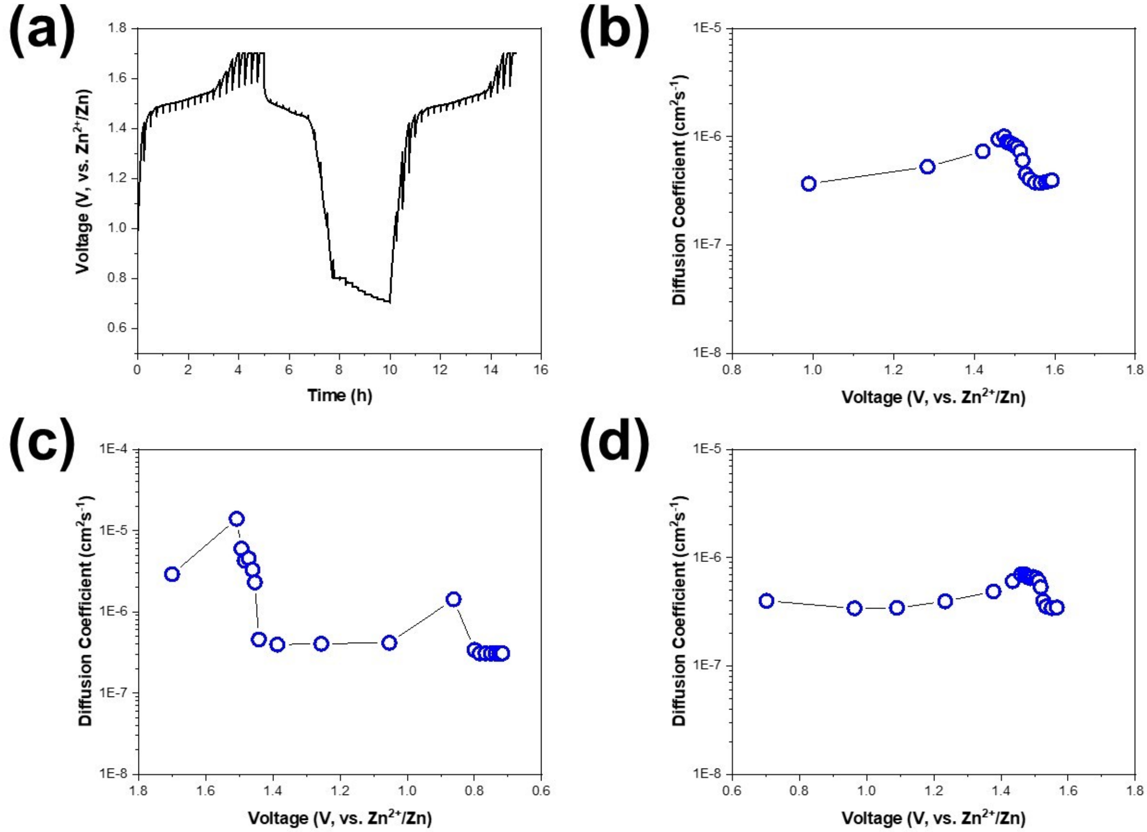

Figure S4. (a) Voltage profile during GITT at 20 mA g^{-1} current density in the voltage window of 0.8 to 1.7 V. Corresponding ionic diffusion coefficient calculated from GITT during (b) first charge, (c) first discharge, and (d) second charge.

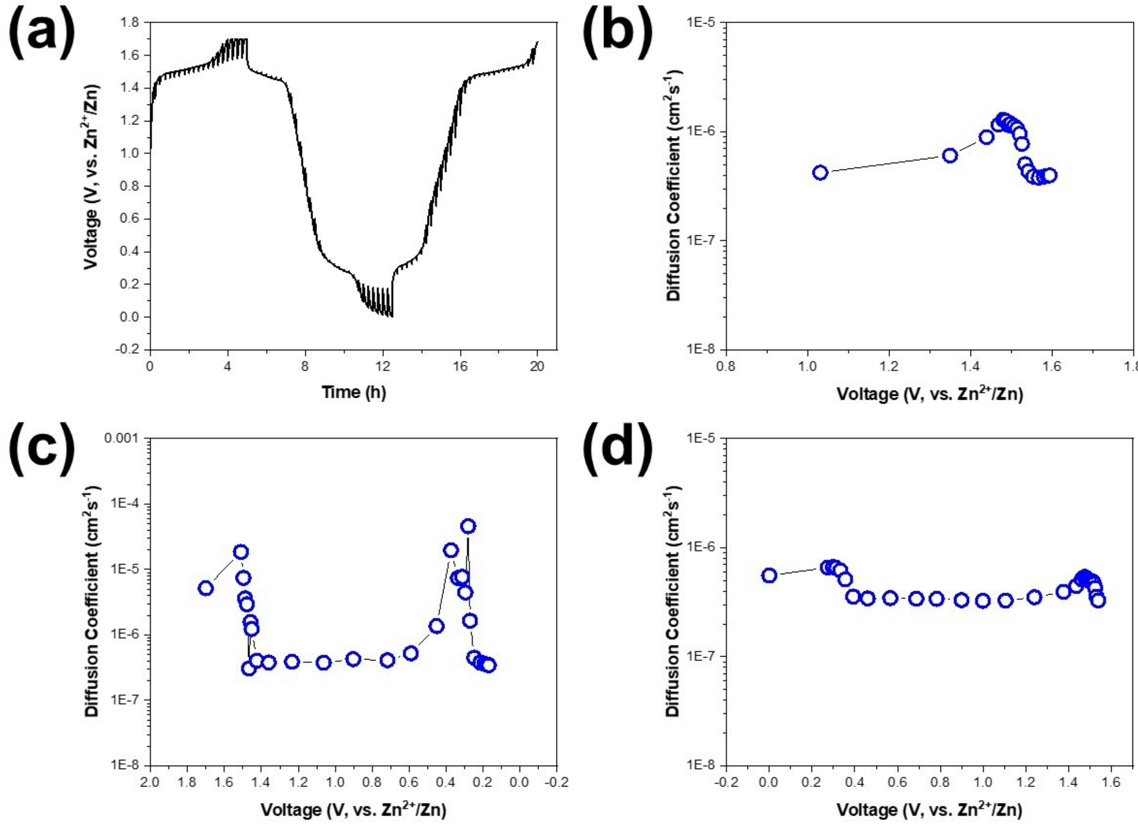

Figure S5. (a) Voltage profile during GITT at 11 mA g^{-1} current density in the voltage window of 0 to 1.7 V. Corresponding ionic diffusion coefficient calculated from GITT during (b) first charge, (c) first discharge, and (d) second charge.

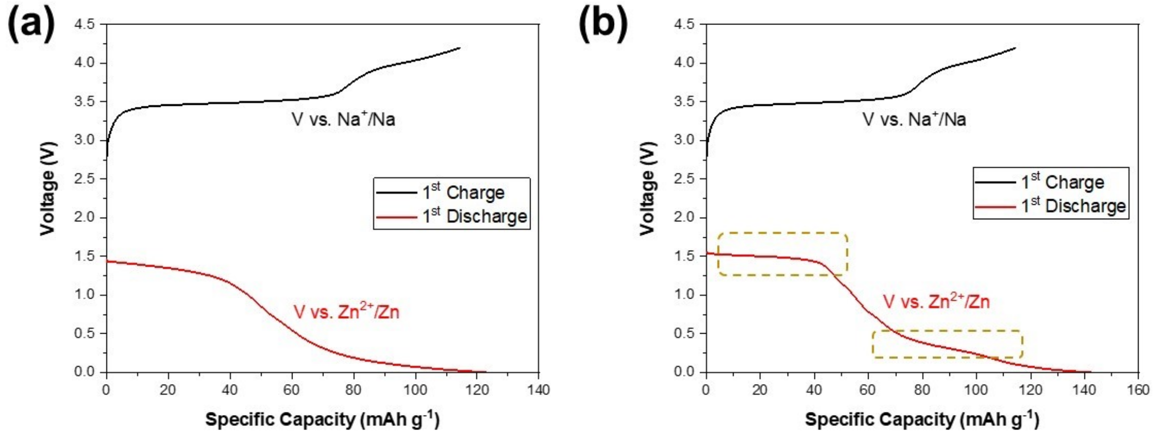

Figure S6. Voltage profile of NVMTP electrode in Na cell for initial charge reaction followed by subsequent discharge using (a) Zn-only and (b) Na/Zn hybrid electrolytes.

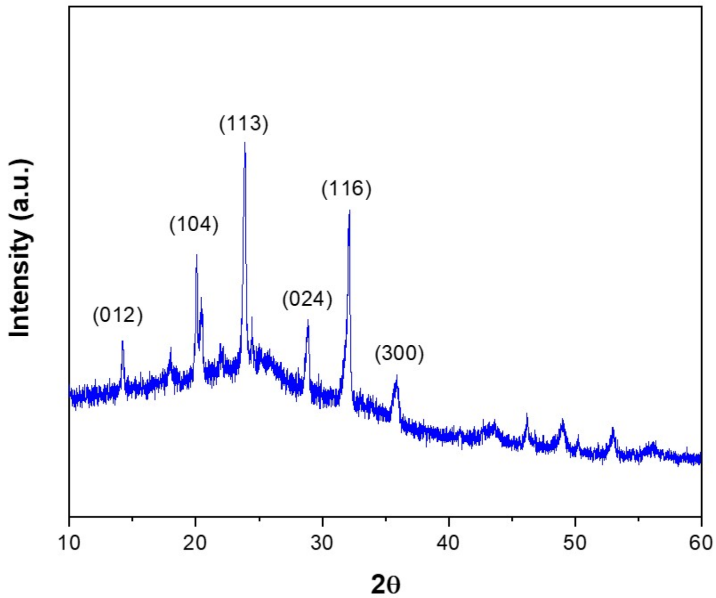

Figure S7. *Ex situ* XRD pattern of the NVMTP electrode after discharge to 0 V using a current rate of 20 mA g^{-1}.

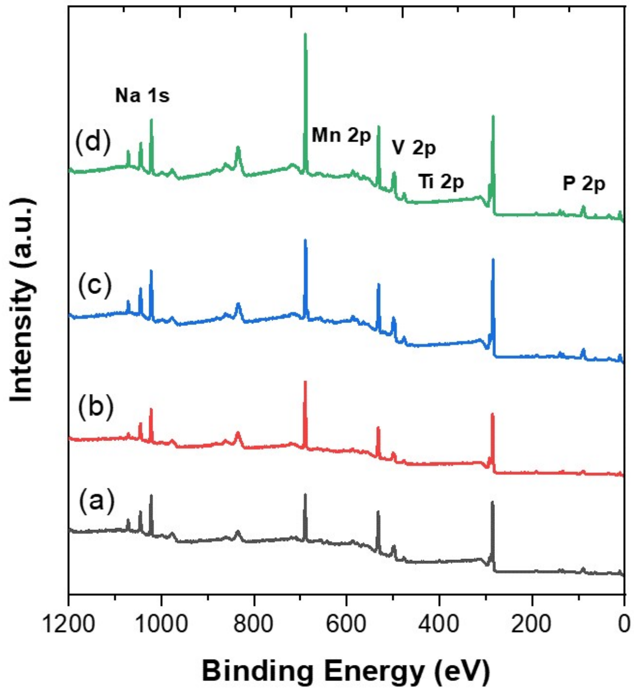

Figure S8. XPS spectra of NVTMP cathode after (a) first charge at 1.7 V, (b) first discharge at 0.8 V, (c) first discharge at 0 V, and (d) second charge at 1.7 V.

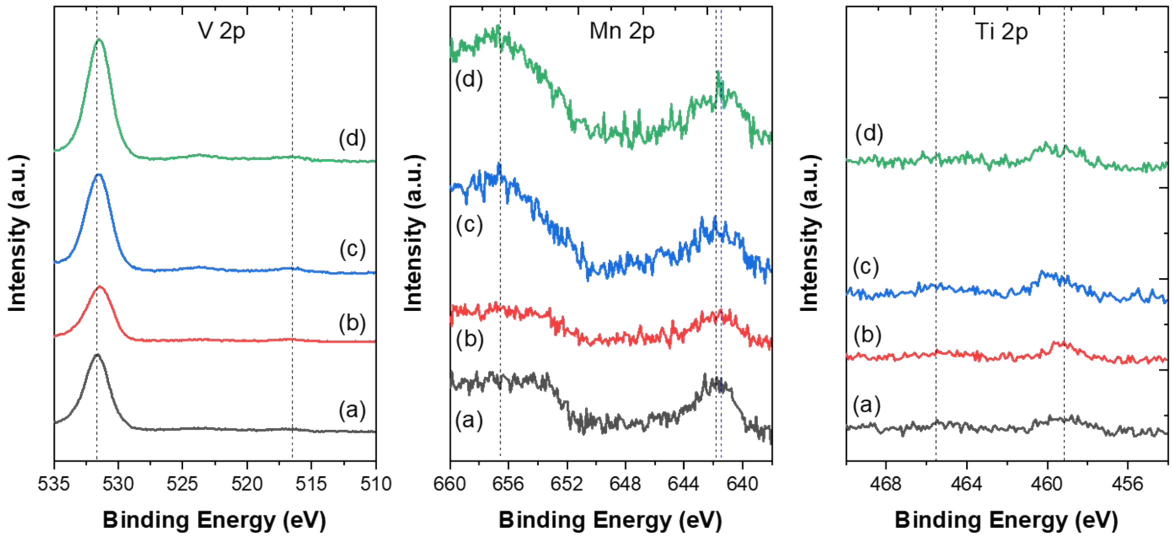

Figure S9. Selected XPS V 2p (left), Mn 2p (middle) and Ti 2p (right) spectra of the NVMTP electrode after (a) first charge at 1.7 V, (b) first discharge at 0.8 V, (c) first discharge at 0 V, and (d) second charge at 1.7 V.

Table S1. Crystallographic information of NVMTP sample obtained through Rietveld refinement.

Label	**Element**	**x**	**y**	**z**	**Fraction**
Na1	Na	0	0	0	1
Na2	Na	0.650840	0	0.25	0.5
Ti1	Ti	0	0	0.149780	0.25
V1	V	0	0	0.149780	0.5
Mn1	Mn	0	0	0.149780	0.25
P1	P	0.294550	0	0.25	1
O1	O	0.187940	0.173500	0.087460	1
O2	O	0.025780	0.209130	0.191250	1
Space group: R-3c; *a*=*b*=8.96490 Å; *c*= 21.47864 Å					

Table S2. EDX and ICP-OES analyses of NVMTP powder.

Element	Na	V	Mn	Ti	P	O
at.% (EDX)	16.24	6.70	1.77	1.55	15.55	58.15
at.% (ICP)	38.08	11.76	6.66	5.76	37.75	N.A.

Based on the EDX-derived atomic percentages, we estimated the empirical composition by normalizing each element to the lowest atomic percentage (Ti = 1.55). This yielded approximate atomic ratios of Na: 10.43, V: 4.31, Mn: 1.14, Ti: 1.00, P: 9.99, and O: 37.35. To facilitate comparison with the target stoichiometry of $Na_3VMn_{0.5}Ti_{0.5}(PO_4)_3$, we applied a uniform an average scaling factor[R1] of 3.08, resulting in a derived empirical formula of $Na_{3.38}V_{1.39}Mn_{0.37}Ti_{0.32}P_{3.32}O_{12.10}$. This composition exhibits deviations that fall within the experimental uncertainty of EDX analysis. To further confirm the elemental composition more accurately, inductively coupled plasma (ICP) analysis was conducted, offering complementary bulk data. The calculated empirical formula, approximately $Na_{3.02}V_{0.93}Mn_{0.53}Ti_{0.46}(PO_4)_3$, closely aligns with the intended stoichiometry of the target compound.

Table S3. *Ex situ* ICP-OES results of discharged NVMTP electrode after Na extraction using Na cell.

Electrolyte	Element	Wavelength (nm)	Concentration (wt%)
Zn-only	Zn	206.2	13.7
	Na	589.5	3.79
Na/Zn hybrid	Zn	206.2	9.14
	Na	589.5	6.87

Table S4. RDF and cumulative number of ions obtained from molecular dynamic simulation.

Entry	RDF Range (Å)	Highest RDF (Å)	Cumulative Number
Na-O1 (acetate)	2.10-3.68	2.42	2.43
Na-O2 (acetate)	2.10-3.62	2.42	2.30
Na-O (water)	2.06-3.02	2.32	1.58
Zn-O1 (acetate)	1.96-3.22	2.22	2.20
Zn-O2 (acetate)	1.98-3.22	2.22	2.18
Zn-O (water)	1.92-2.80	2.10	2.72

Table S5. *Ex situ* ICP-OES results of electrolyte after discharge cycle.

Element	Wavelength (nm)	Concentration (mg L^{-1})
V	290.8	121
Mn	257.6	3150
Ti	334.9	170

Reference

[R1] A. Laskin, J.P. Cowin, Automated single-particle SEM/EDX analysis of submicrometer particles down to 0.1 μm, Analytical Chemistry 73 (2001) 1023