Supporting Information

Unexpectedly high electrochemical performances of monoclinic $Na_{2.4}V_2(PO_4)_3$/Conductive polymer composite for Na-ion batteries

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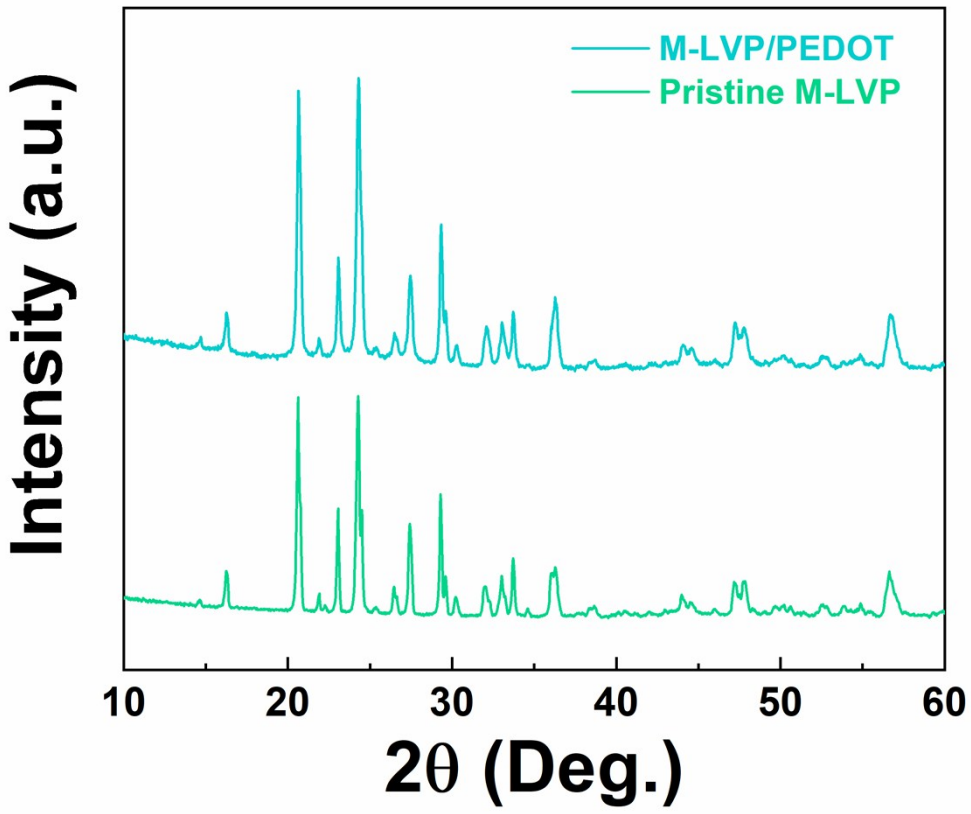
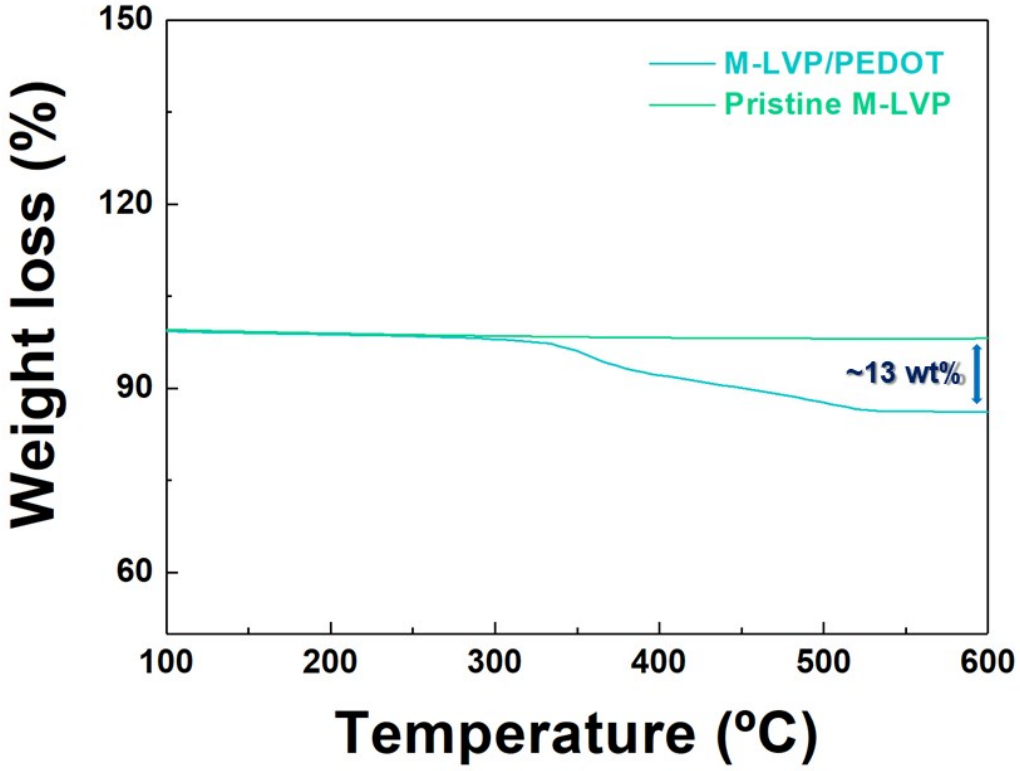
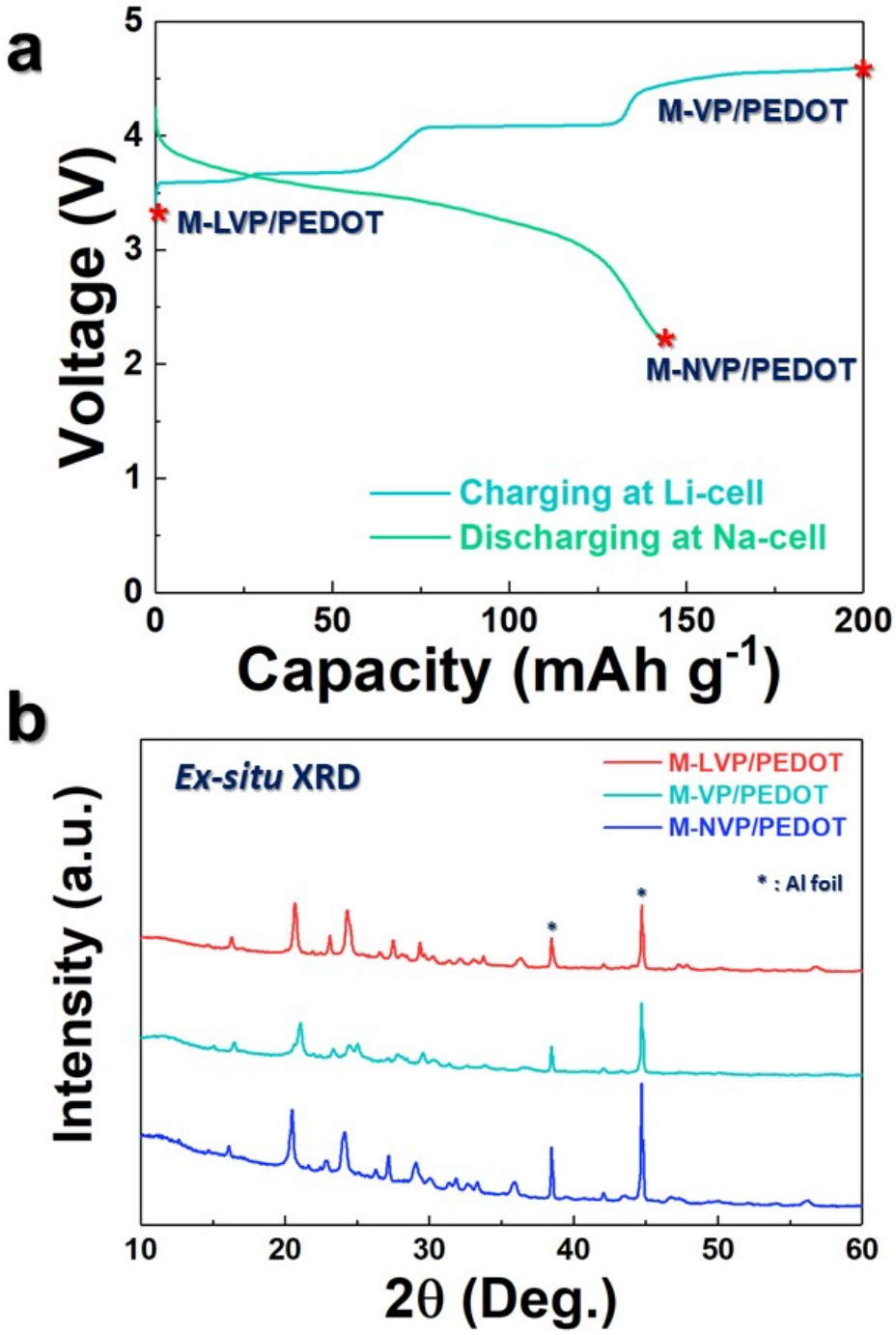


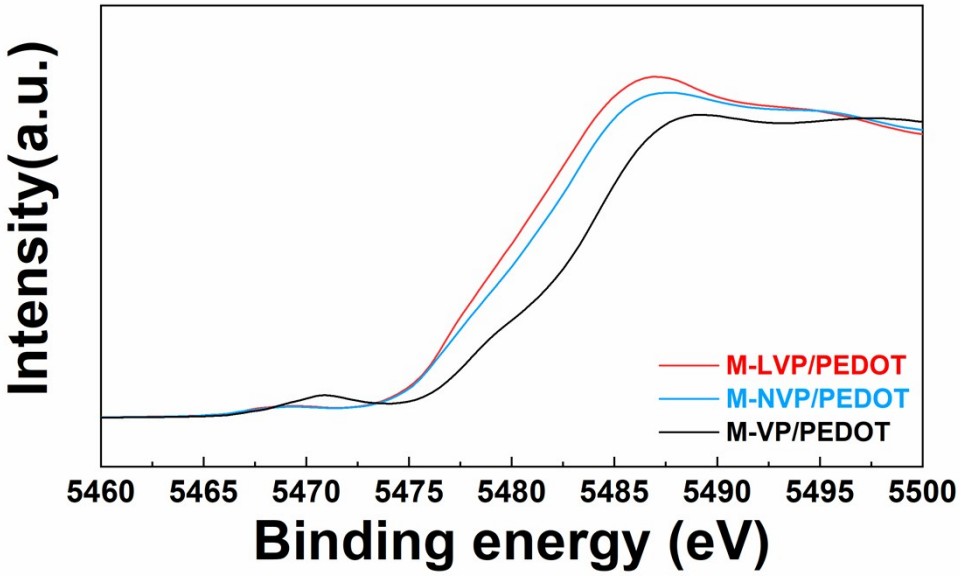
Supporting Figure S1 XRD patterns of M-LVP/PEDOT composite and pristine M-LVP.



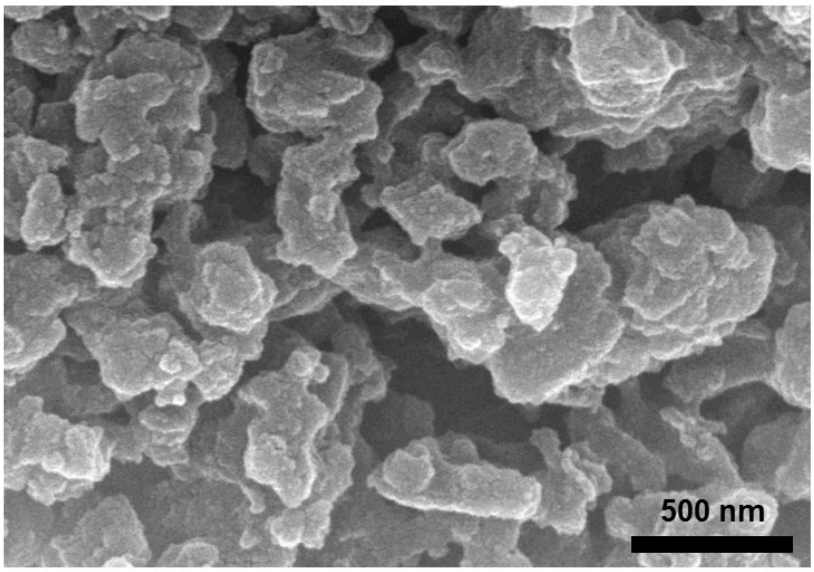
Supporting Figure S2 TGA profile of M-LVP/PEDOT composite and pristine M-LVP.



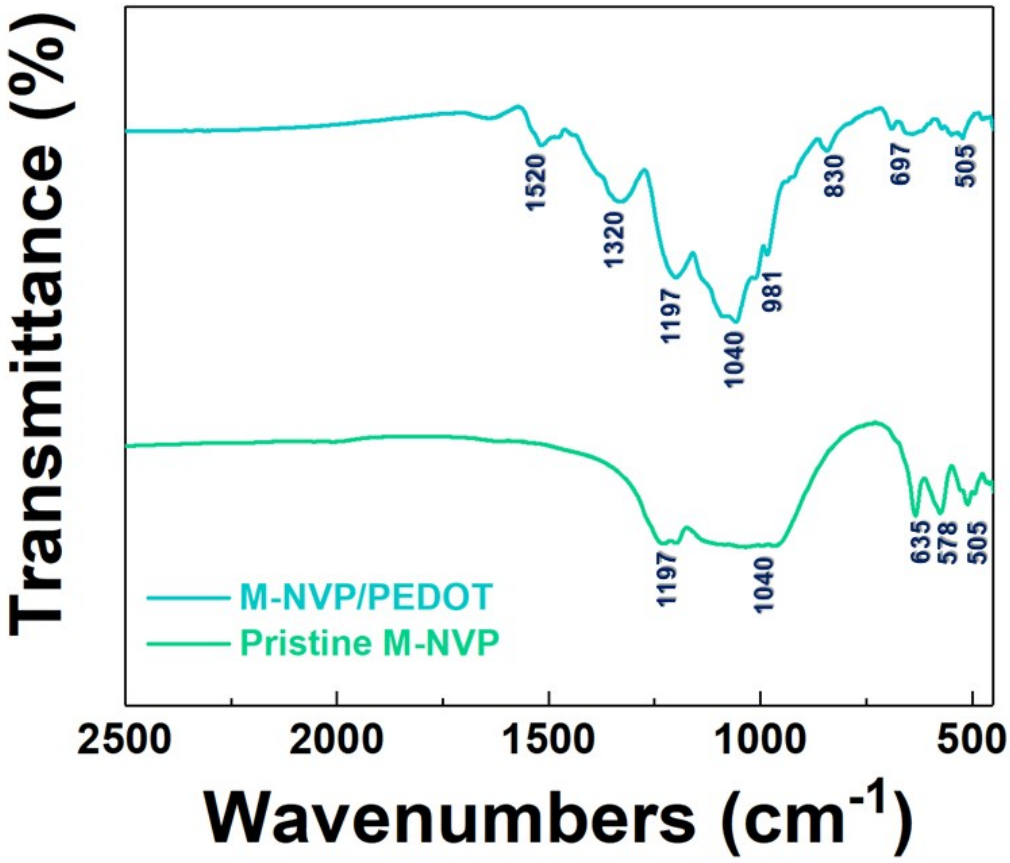
Supporting Figure S3 (a) Preparation process of M-NVP/PEDOT composite through electrochemical ion-exchange, (b) *Ex-situ* XRD patterns of M-LVP/PEDOT, M-VP/PEDOT and M-NVP/PEDOT



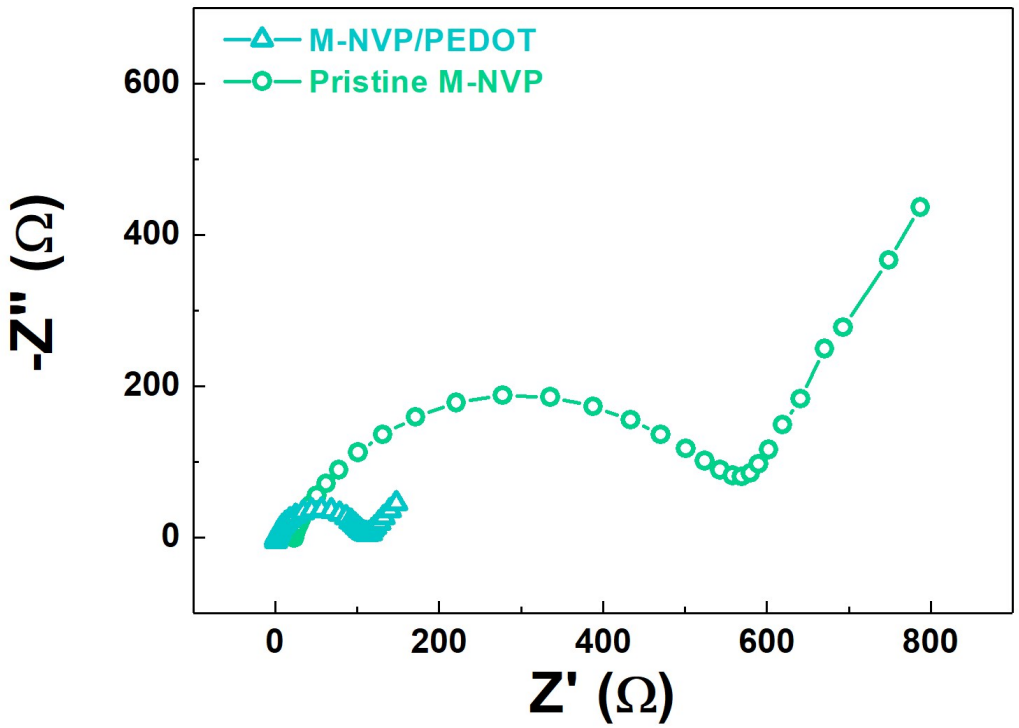
Supporting Figure S4 V K-edge XANES analyses of M-LVP/PEDOT, M-NVP/PEDOT and M-VP/PEDOT.



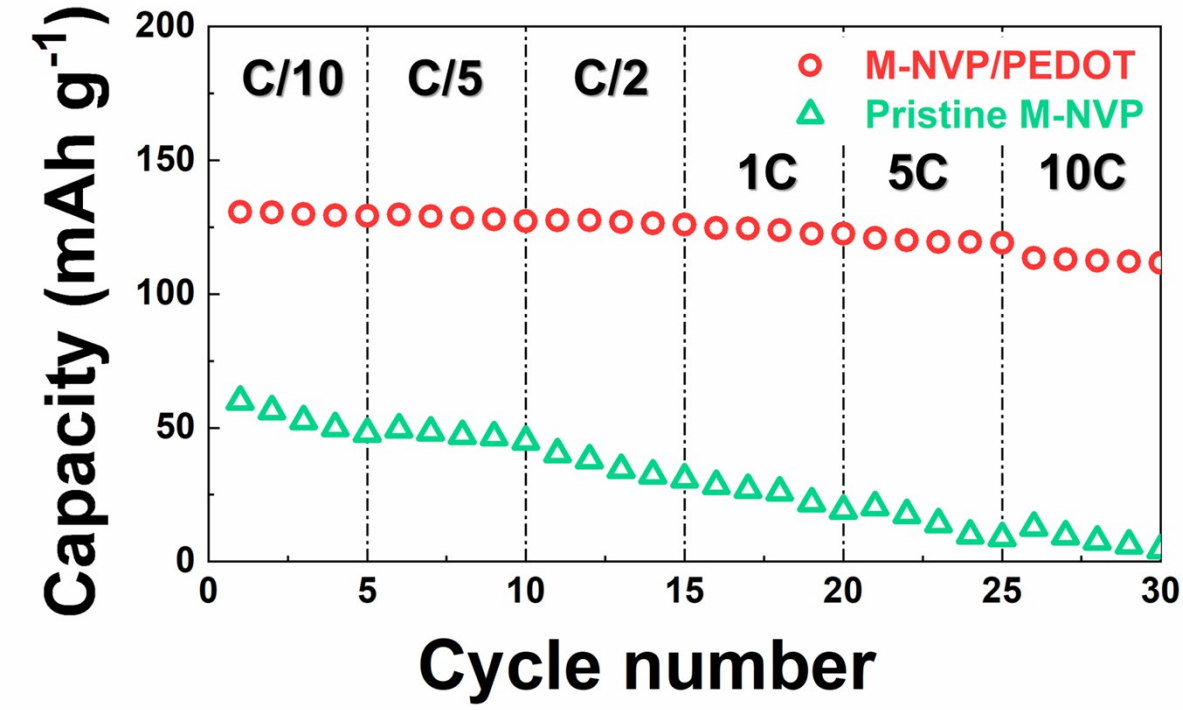
Supporting Figure S5 The SEM images of M-NVP/PEDOT



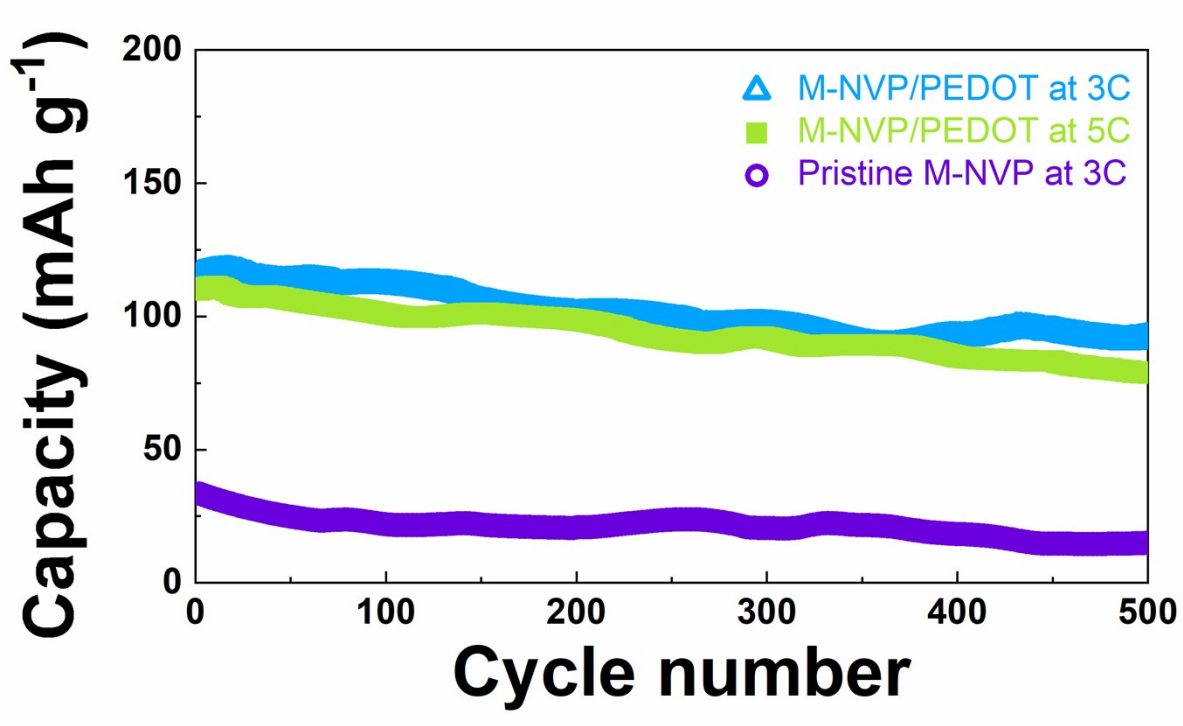
Supporting Figure S6 FT-IR spectra of M-NVP/PEDOT and Pristine M-NVP



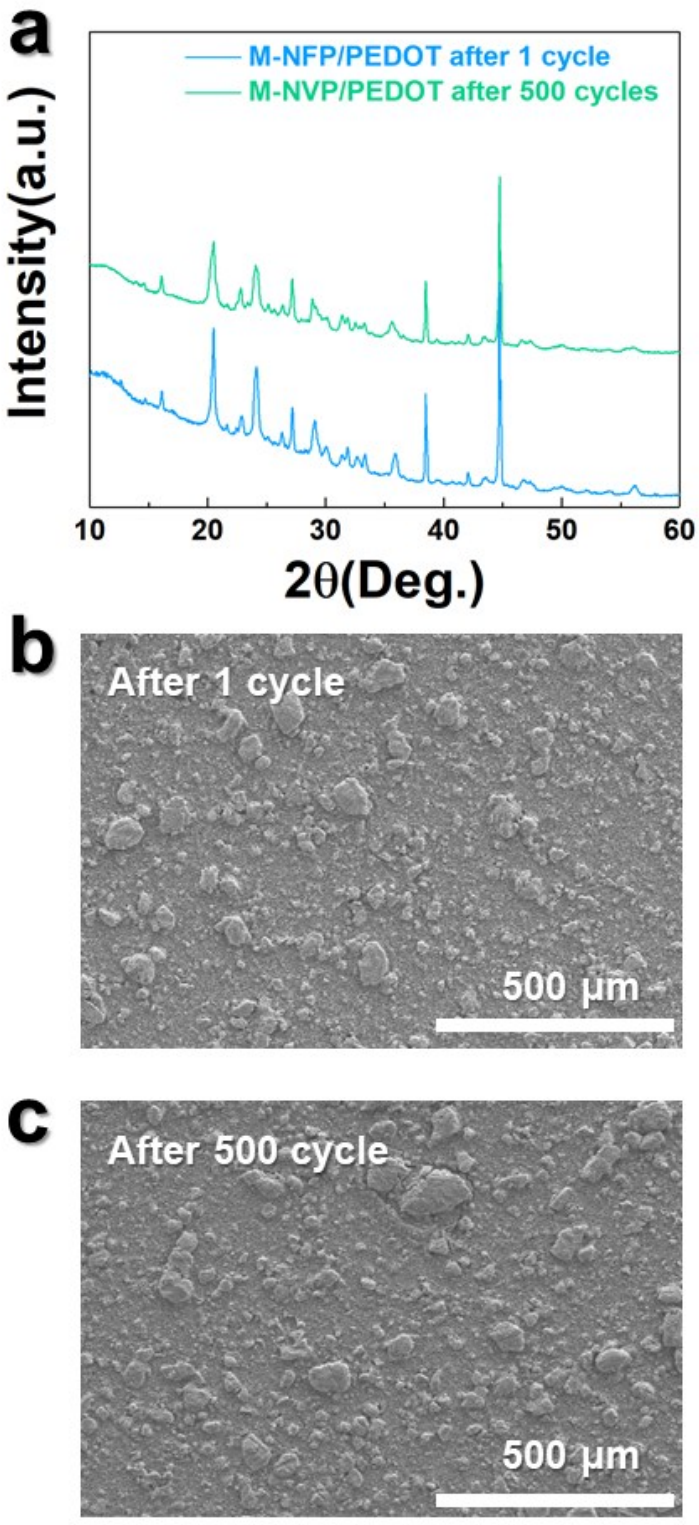
Supporting Figure S7 EIS measurement of M-NVP/PEDOT and Pristine M-NVP that shows their charge-transfer resistance.



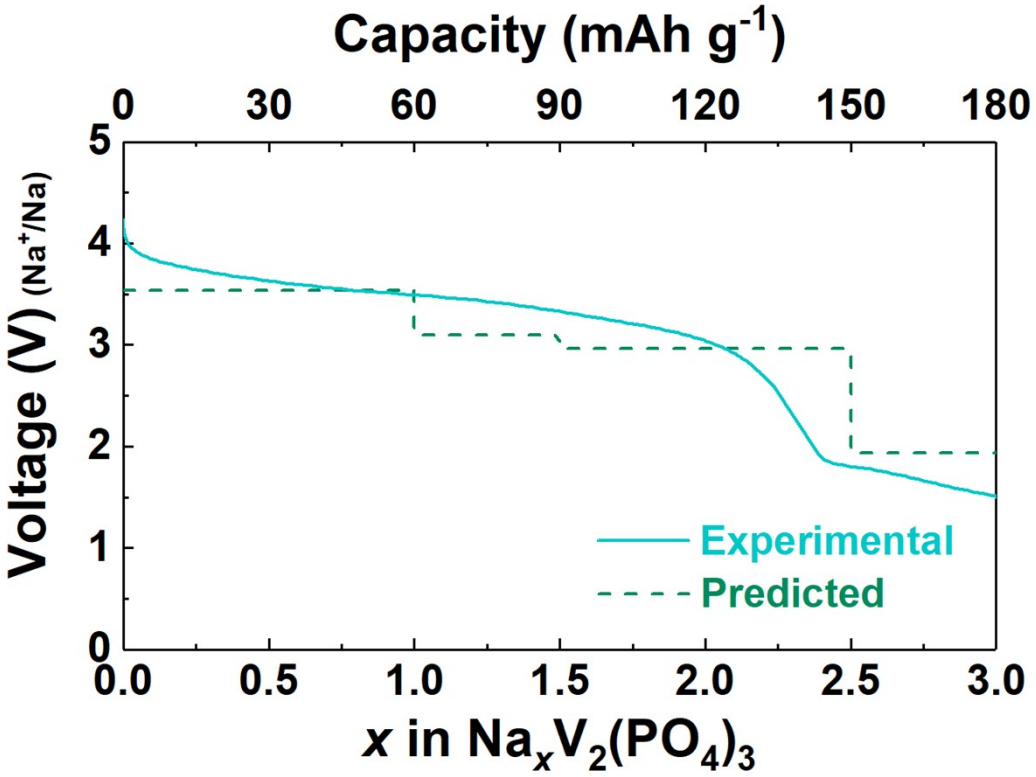
Supporting Figure S8 The rate cycling performance of M-NVP/PEDOT composite and pristine M-NVP from C/10 to 10C.



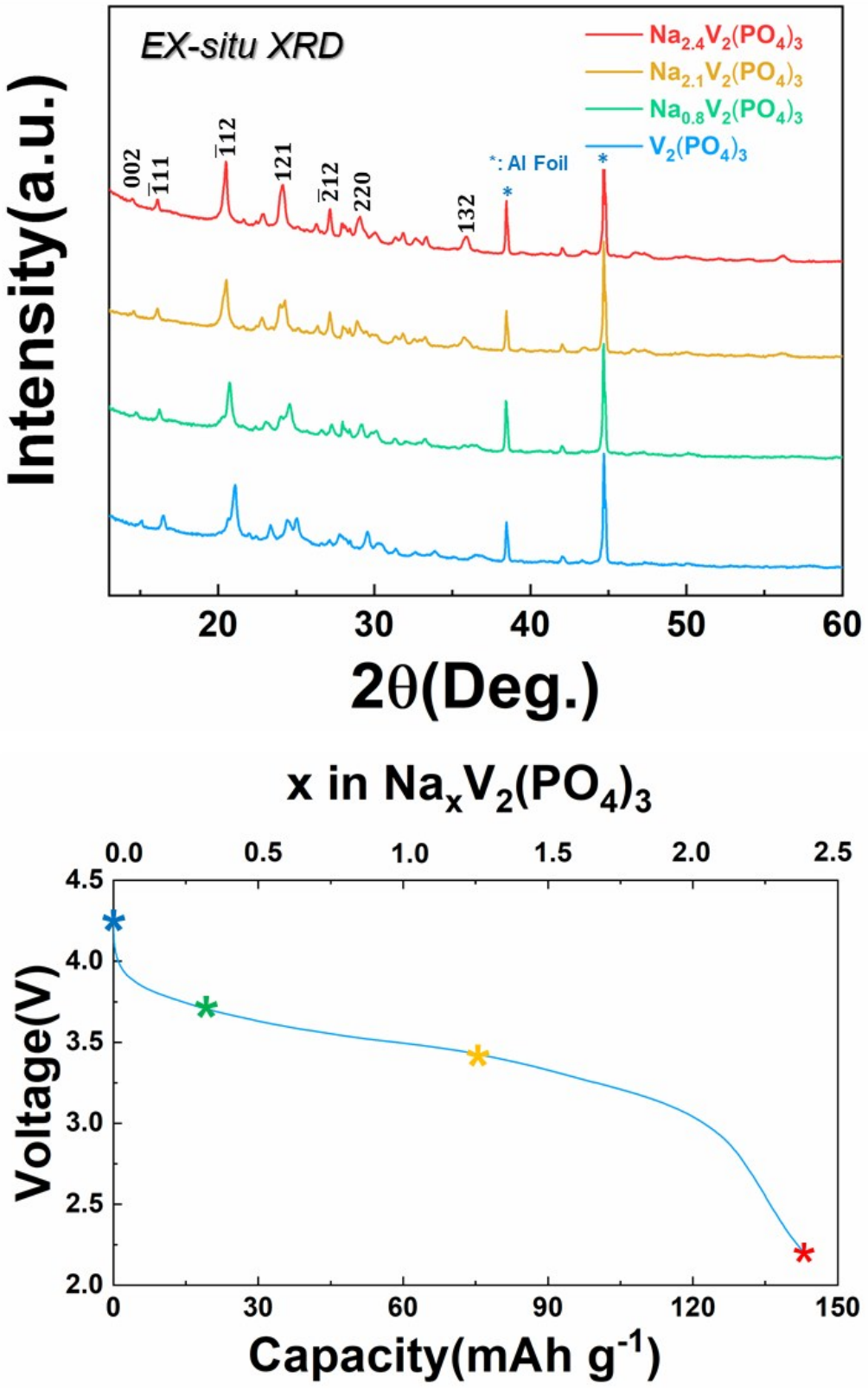
Supporting Figure S9 Cyclic performance of M-NVP/PEDOT and pristine M-NVP at various current densities.



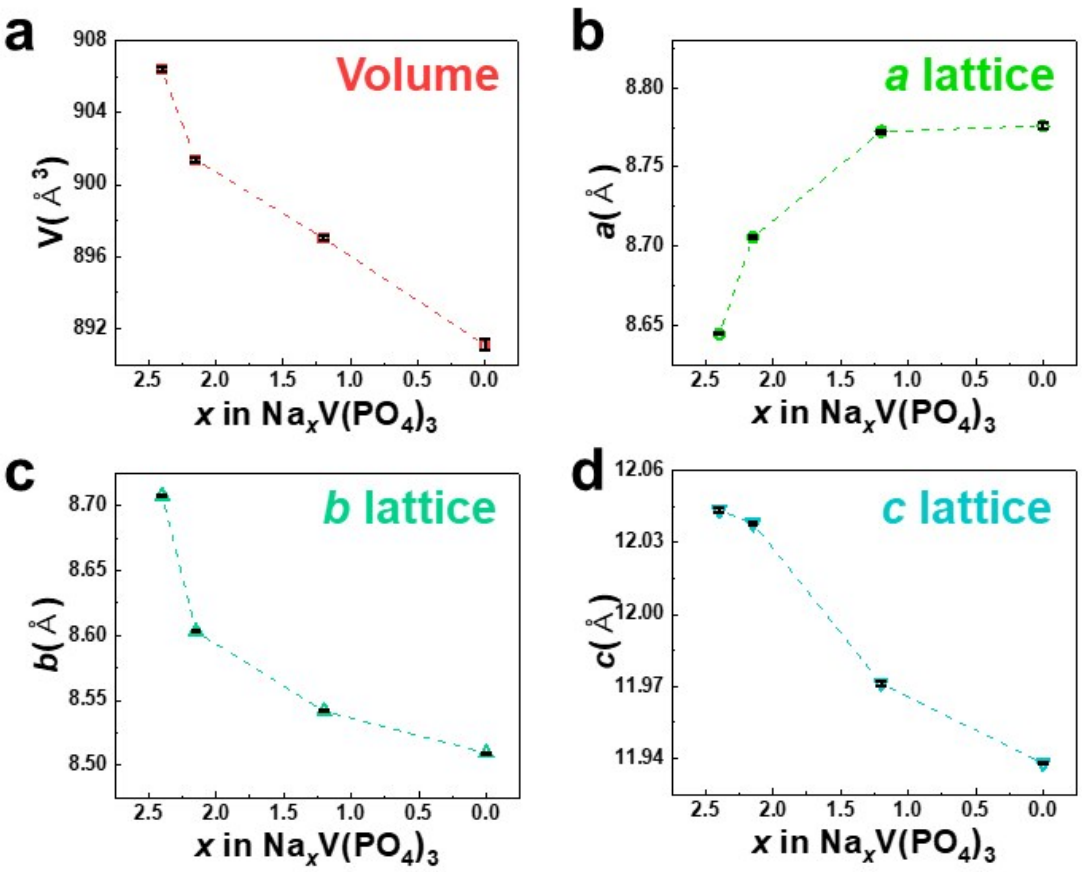
Supporting Figure S10 The comparison of (a) XRD patterns and (b-c) SEM images of M-NVP/PEDOT electrode measured after 1 cycle and 500 cycles.



Supporting Figure S11 Experimentally measured and discharge curve of M-NVP/PEDOT composite at the voltage range between 4.25 V and 1.5 V (*vs.* Na/Na^+) and its predicted curve obtained using first-principles calculations



Supporting Figure S12 Ex situ XRD patterns of M-NVP/PEDOT at various voltages.



Supporting Figure S13 Change in (a) volume, (b) *a* lattice parameter, (c) *b* lattice parameter, and (d) *c* lattice parameter of $Na_xV_2(PO_4)_3$ ($0 \leq x \leq 2.4$) samples with standard deviations.

	Na	Li	V	P
M-LVP/PEDOT	0	2.979	1.997	2.983
M-VP/PEDOT	0	0.008	1.993	2.991
M-NVP/PEDOT	2.413	0.007	1.998	2.987

Supporting Table T1 ICP analyses on the atomic ratio of Na, Li, V, P in the M-LVP/PEDOT, M-VP/PEDOT and M-NVP/PEDOT.

Atom	Multiplicity	x	y	z	B_{iso}	Occupancy
Na1	4e	0.3817	0.2397	0.3442	1.328	0.620
Na2	4e	0.2903	0.4918	0.5494	1.328	0.898
Na3	4e	0.2586	0.2716	0.0639	1.328	0.891
V1	4e	0.1073	0.4599	0.2428	0.842	1.000
V2	4e	0.3911	0.4683	0.7618	0.842	1.000
P1	4e	0.1443	0.1052	0.1055	0.824	1.000
P2	4e	0.3463	0.1139	0.6020	0.824	1.000
P3	4e	0.5002	0.2509	0.0358	0.824	1.000
O1	4e	0.3366	0.0993	0.4299	0.448	1.000
O2	4e	0.1522	0.1098	0.9210	0.448	1.000
O3	4e	0.2590	0.4867	0.3579	0.448	1.000
O4	4e	0.2136	0.4989	0.8038	0.447	1.000
O5	4e	0.0404	0.0642	0.1696	0.448	1.000
O6	4e	0.4739	0.0808	0.6394	0.448	1.000
O7	4e	0.0629	0.3794	0.4449	0.448	1.000
O8	4e	0.4019	0.3257	0.9326	0.448	1.000
O9	4e	0.4290	0.1638	0.1835	0.448	1.000
O10	4e	0.0914	0.1586	0.6157	0.448	1.000
O11	4e	0.1838	0.2693	0.1793	0.448	1.000
O12	4e	0.3199	0.2847	0.6356	0.448	1.000

Supporting Table T2 detailed structural information of N-NMP/PEDOT.

	a (Å)	*b* (Å)	*c* (Å)	*β* (Å)
M-LVP/PEDOT	8.5932(5)	8.5904(4)	12.0292(6)	90.465(3)
M-VP/PEDOT	8.7760(18)	8.5095(7)	11.938(2)	91.716(15)
M-NVP/PEDOT	8.6445(5)	8.7076(3)	12.0433(10)	90.991(7)

Supporting Table T3 The comparison of lattice parameters of M-LVP/PEDOT, M-VP/PEDOT and M-NVP/PEDOT composites calculated by Rietveld refinement