Supplementary Information (SI) for Journal of Materials Chemistry A.
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Supporting information for:

Small voltage hysteresis and flat plateaus in Ca-metal batteries using Ti-based NASICON cathode

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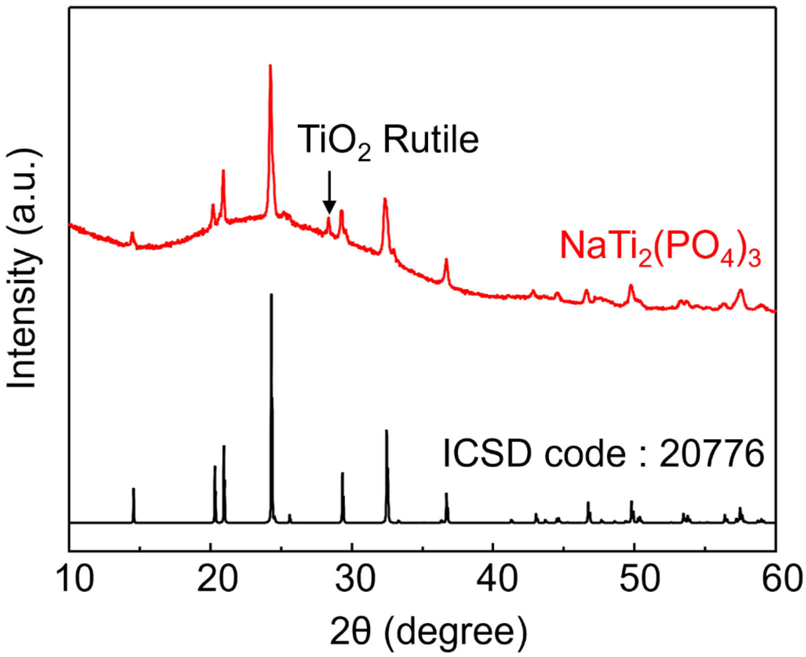


Figure S1. XRD profiles of lpNTP and ICSD pattern of NTP.

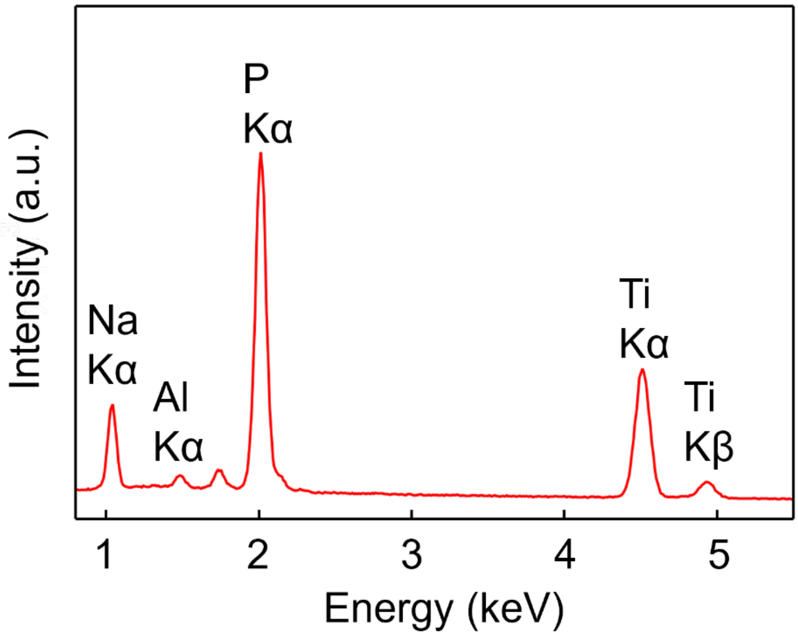


Figure S2. EDS spectrum of ncNTP.

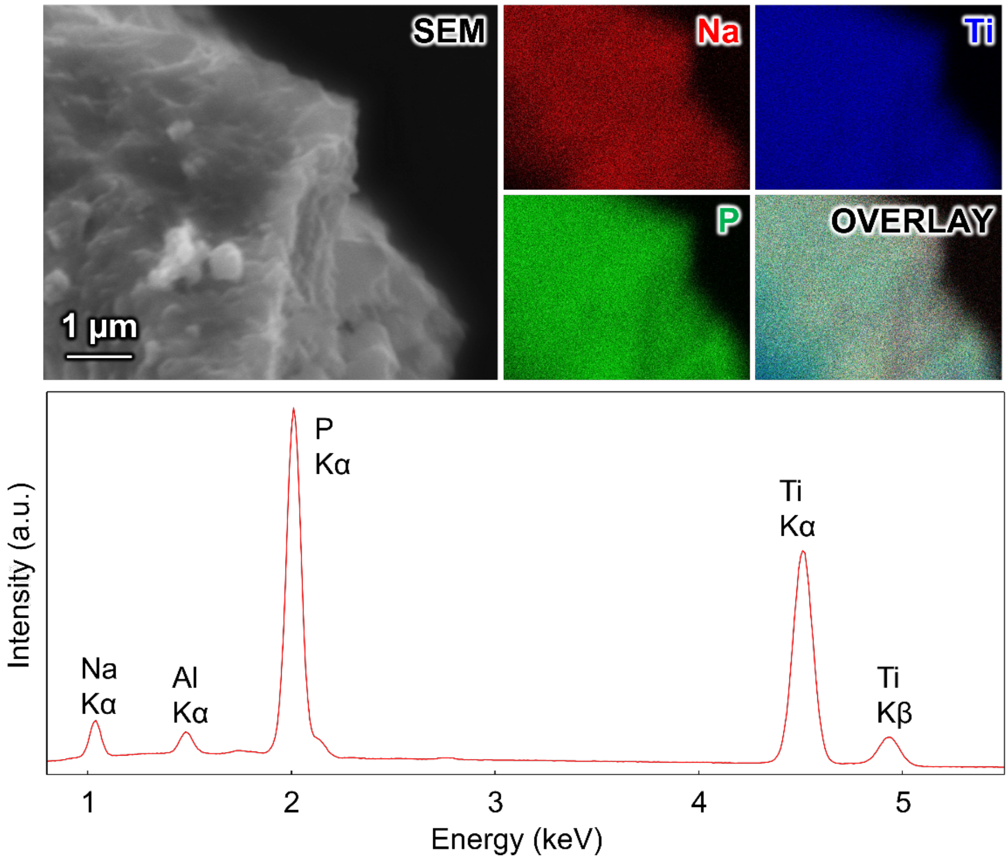


Figure S3. SEM image of lpNTP, along with EDS maps showing the distribution of Na, Ti, and P, and the corresponding EDS spectrum.

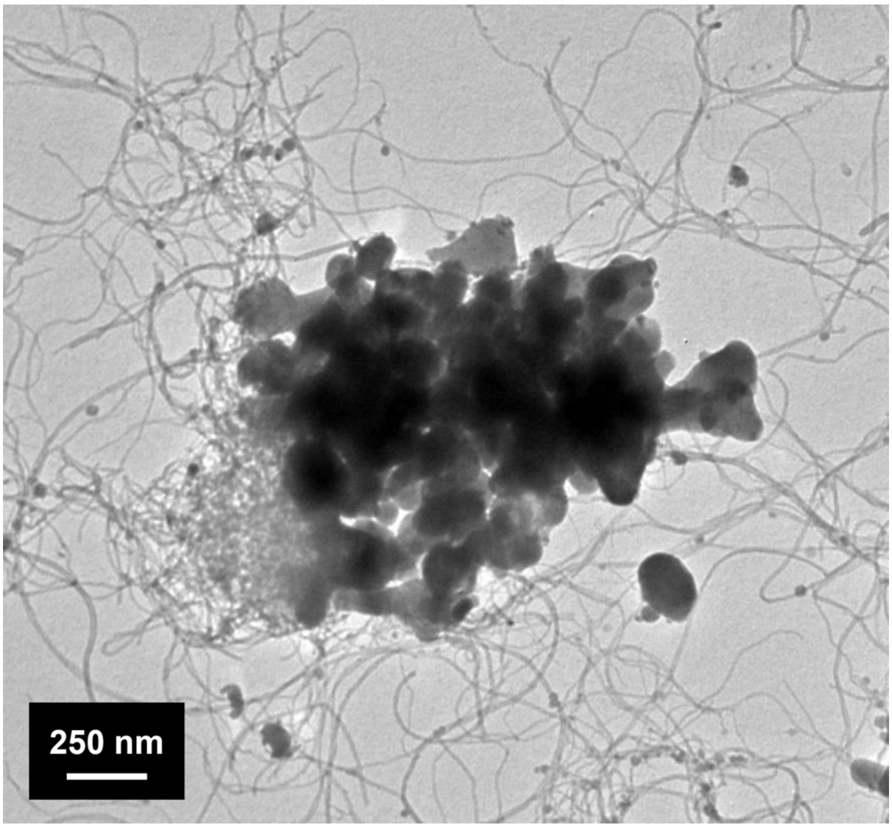


Figure S4. TEM image of ncNTP, highlighting the aggregated section.

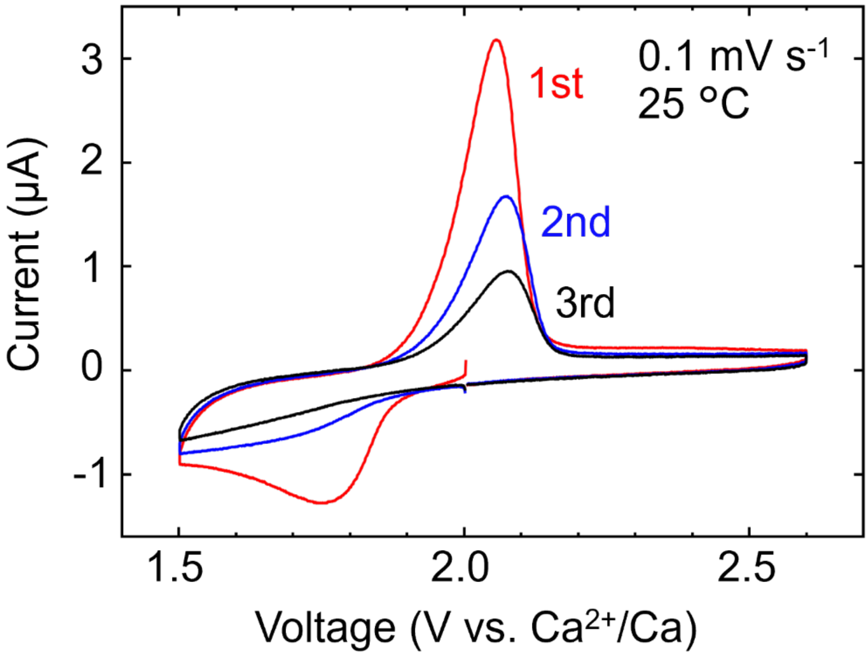


Figure S5. Cyclic voltammogram of ncNTP for the first to third cycles obtained at a scan rate of 0.1 mV s^{-1} in voltage range of 1.5–2.6 V vs. Ca^{2+}/Ca.

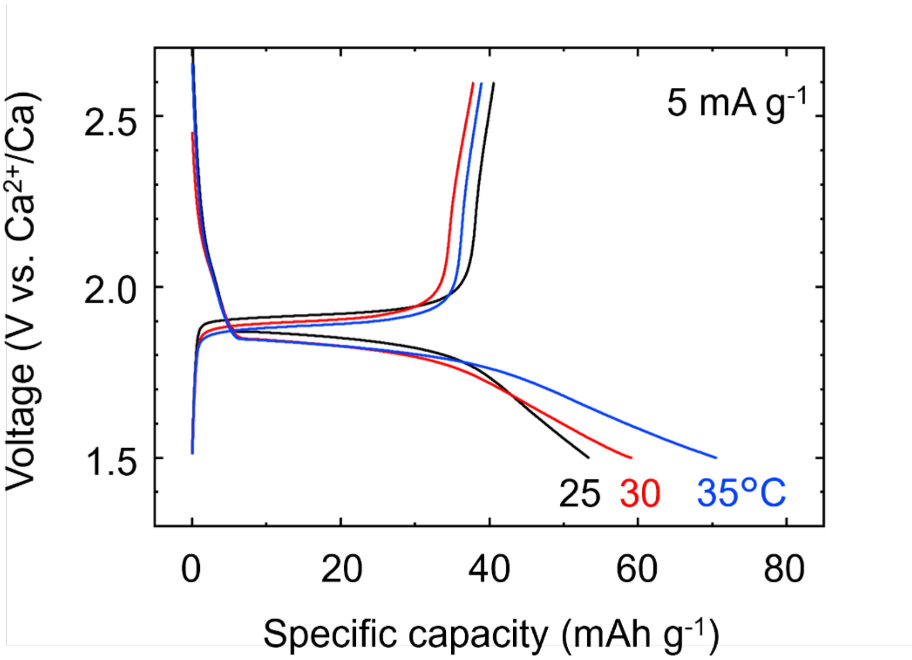


Figure S6. Temperature dependence of ncNTP. Voltage profiles for the 1st cycle at 5 mA g^{-1} in the voltage range of 1.5–2.6 V vs. Ca^{2+}/Ca at 25, 30, and 35 °C.

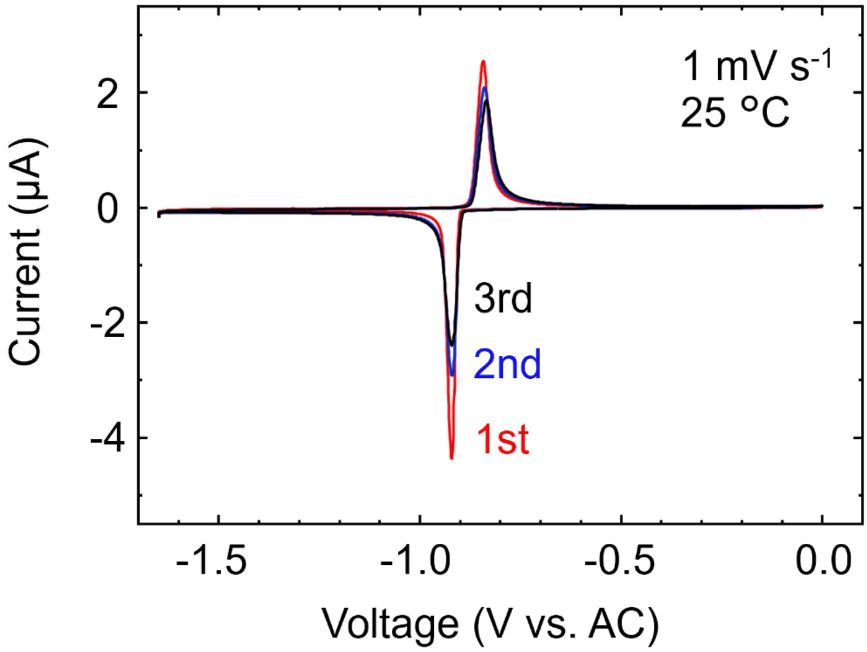


Figure S7. Cyclic voltammogram of ncNTP in Na half-cell using electrolyte of NaTFSI in DME with active carbon as counter and reference electrodes.

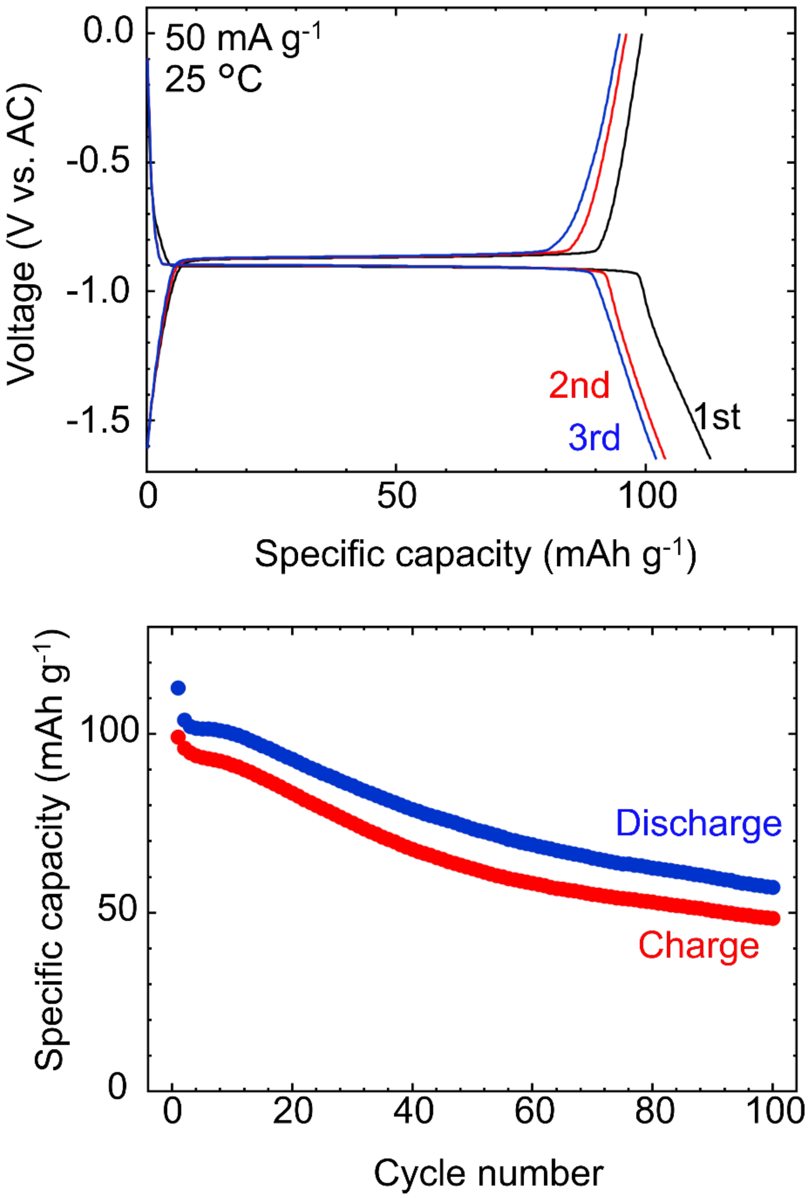


Figure S8. Voltage profiles of ncNTP using NaTFSI in DME electrolyte and activated carbon counter and reference electrode with voltage range of -1.65 V—0 V at a current density of 50 mA g^{-1}.

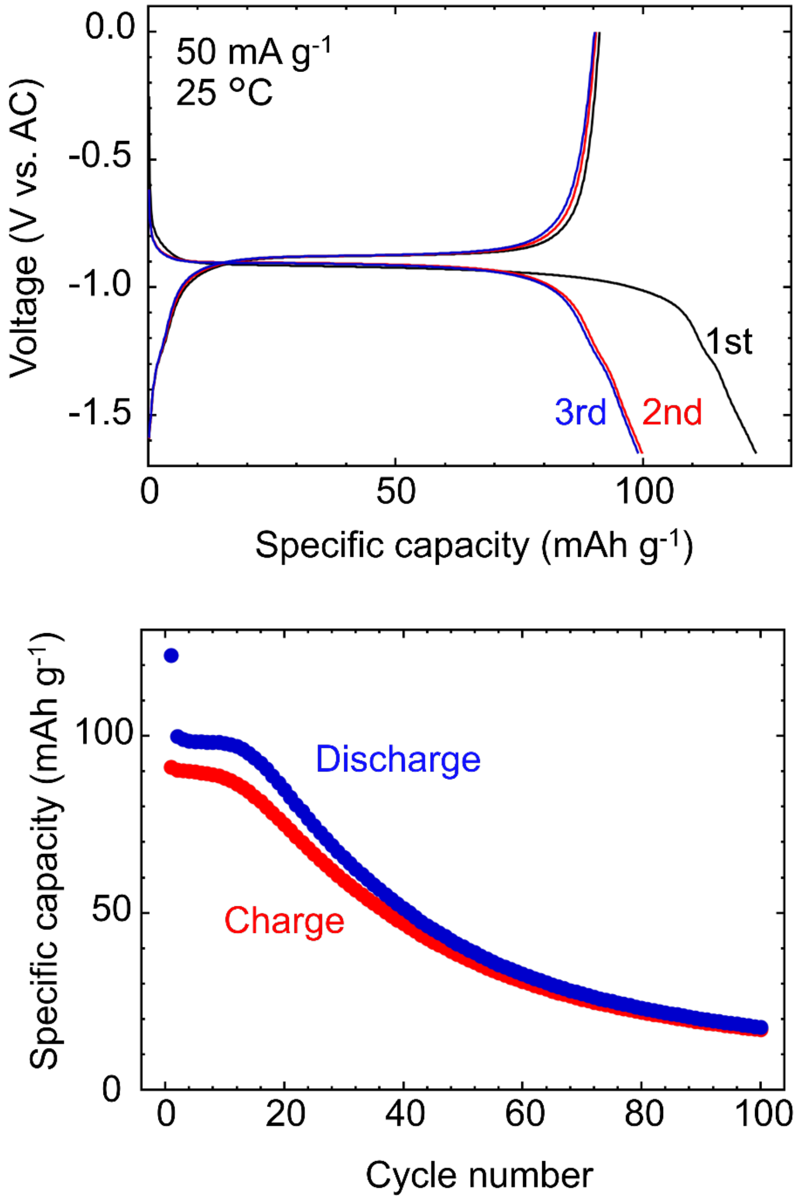


Figure S9. Voltage profiles of lpNTP using NaTFSI in DME electrolyte and activated carbon counter and reference electrode with voltage range of -1.65 V—0 V at a current density of 50 mA g^{-1}.

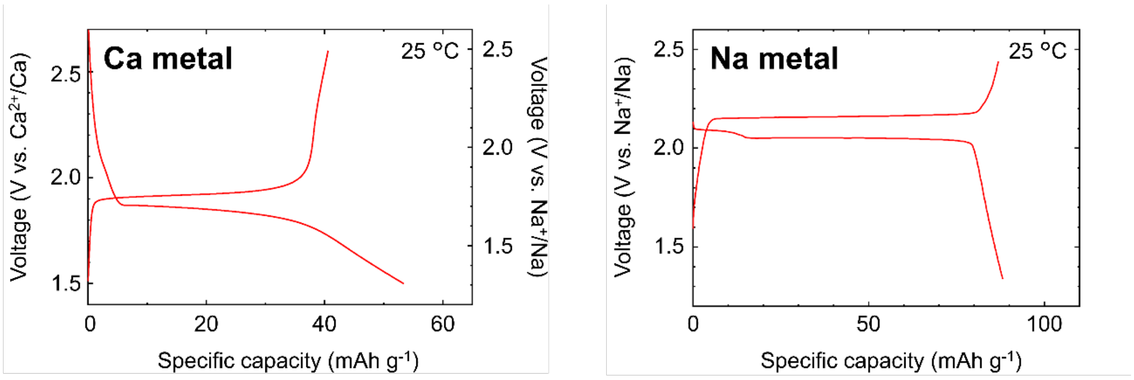


Figure S10. Voltage profile of Ca and Na metal batteries with ncNTP cathode at the current density of 5 mA g^{-1} for Ca and 50 mA g^{-1} for Na, in the voltage range of 1.5–2.6 V (vs. Ca^{2+}/Ca) for Ca and 1.34–2.44V (vs. Na^{+}/Na) for Na. The average reaction voltage for Ca is 1.7 V (vs. Na^{+}/Na), whereas Na exhibits 2.1 V (vs. Na^{+}/Na). This suggests that Ca operates at a lower potential, indicating a higher reaction energy for Ca insertion/extraction compared to Na.

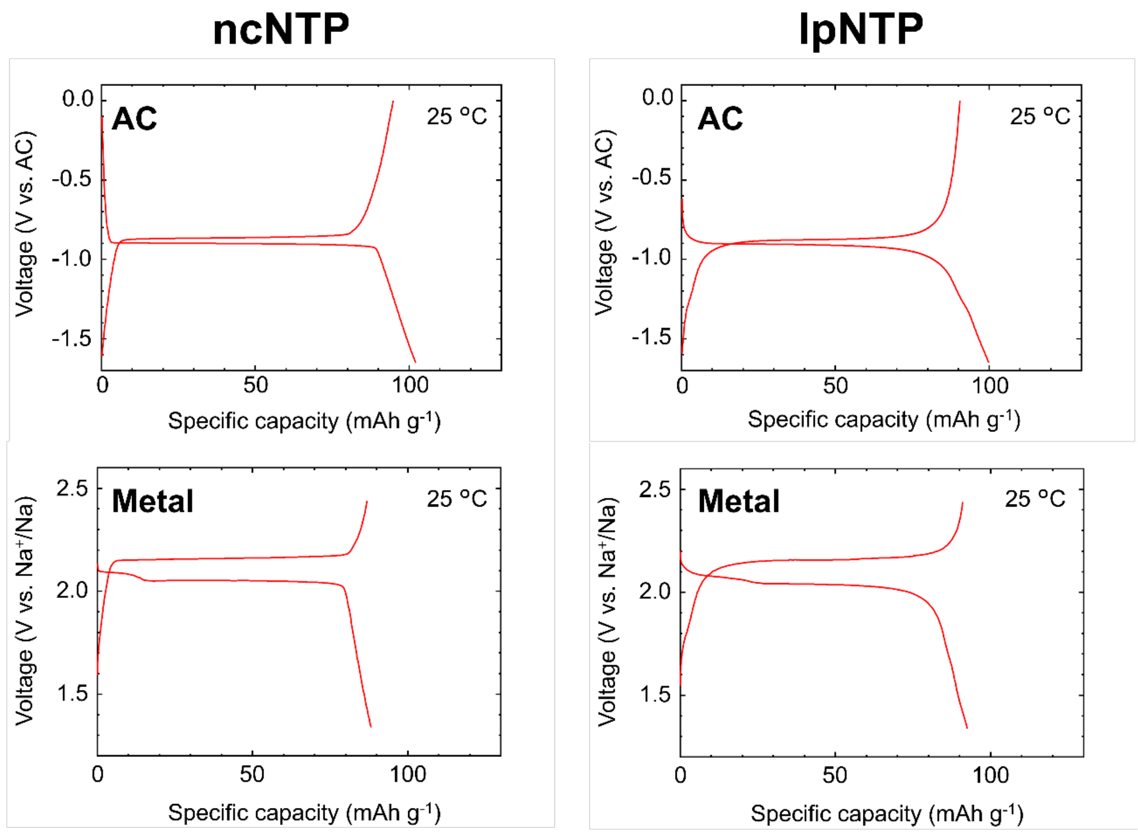


Figure S11. Voltage profile of ncNTP and lpNTP using AC and Na metal at the current density of 50 mA g^{-1} in the voltage range of 0 to –1.65 V for AC and 1.34 to 2.44V for Na. The Na metal-based system exhibits a voltage profile similar to the AC-based system, in both ncNTP and lpNTP, indicating that Na insertion/extraction process occur in AC-based system. This consistency validates the reliability of the AC-based system for Na-ion electrochemical analysis.

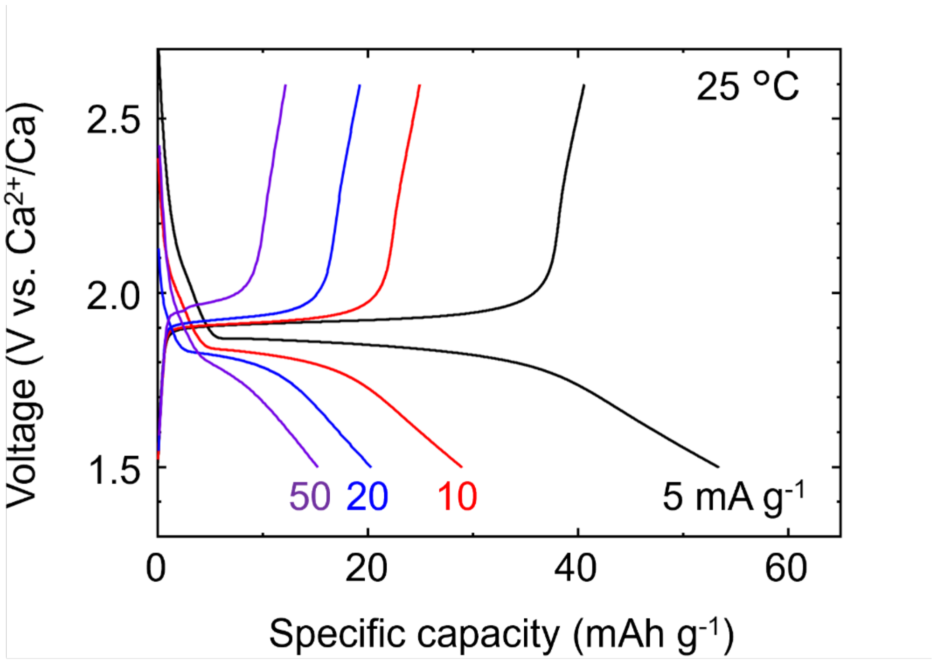


Figure S12. Rate performance of ncNTP at various current densities. Voltage profiles for the 1st cycle at a 5, 10, 20, and 50 mA g^{-1} in the voltage range of 1.5–2.6 V vs. Ca^{2+}/Ca at 25 °C.

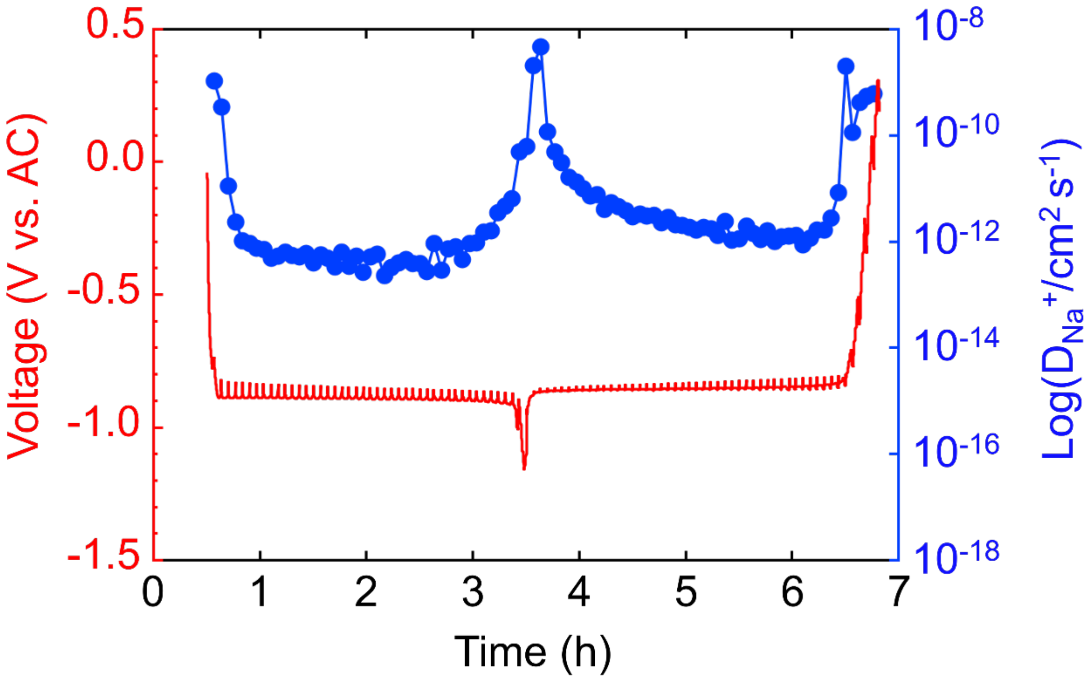


Figure S13. Galvanostatic intermittent titration-technique (GITT) test of ncNTP in Na half-cell using NaTFSI in DME electrolyte and activated carbon counter and reference electrode during first cycle for a rate of 50 mA g^{-1}.

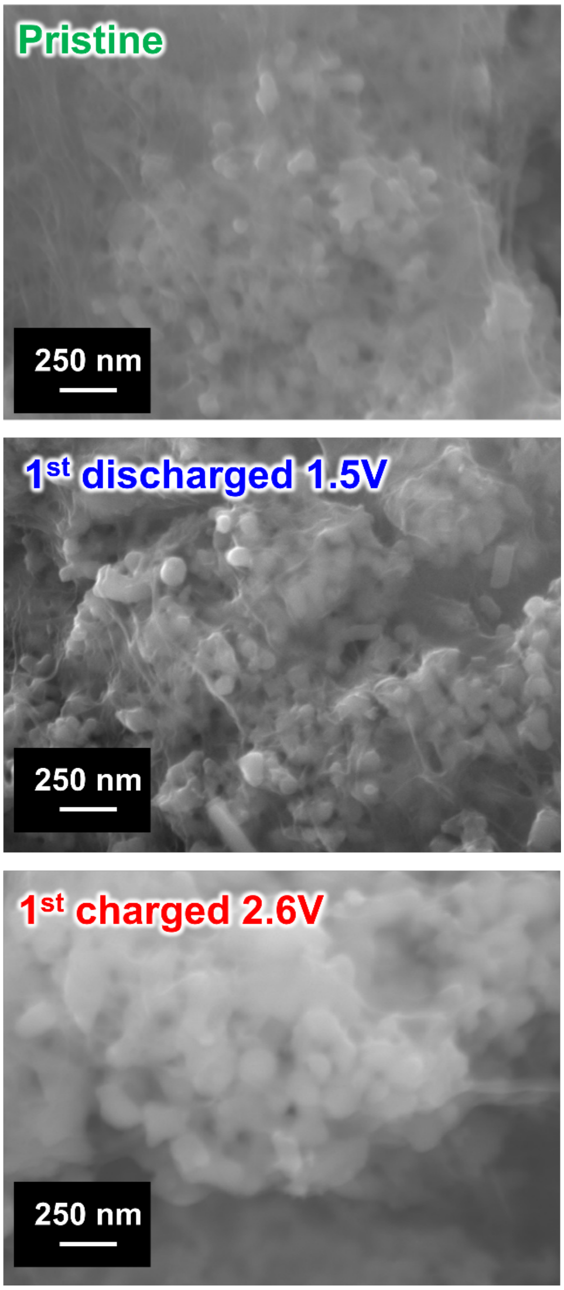
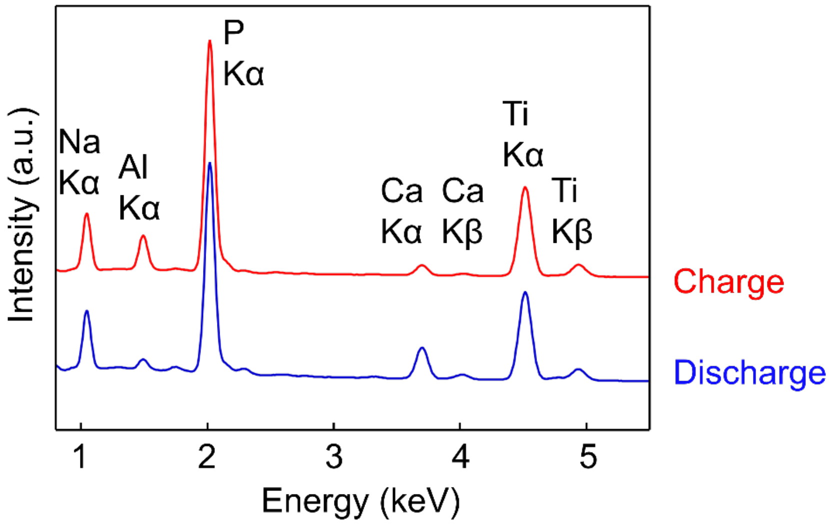


Figure S14. Ex situ FE-SEM images of ncNTP electrodes before and after discharge and charge.



	Na (mol)	Ca (mol)	
		EDS	Echem
Charge	1.02	0.15	0.10
Discharge	1.00	0.46	0.40

Figure S15. Ex situ EDS results of ncNTP electrodes after discharge and charge.

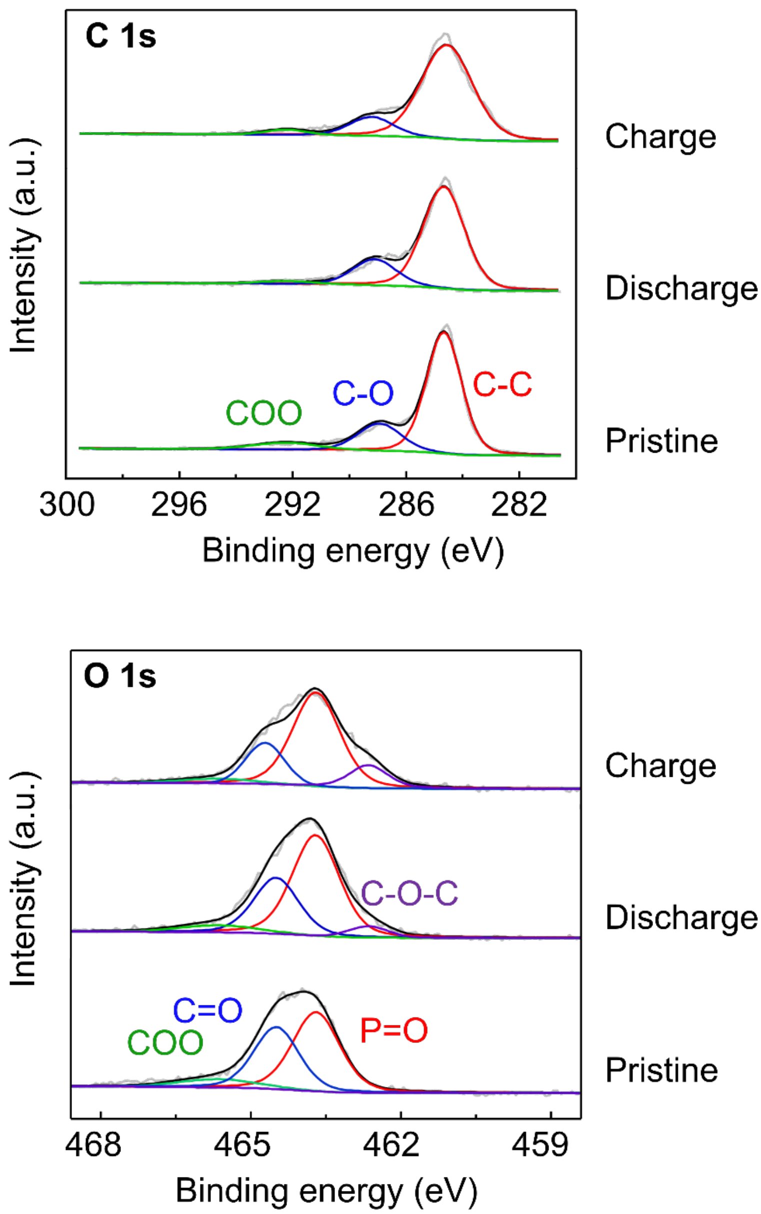


Figure S16. Ex situ XPS results for C 1s and O 1s of ncNTP electrodes before and after discharge and charge.

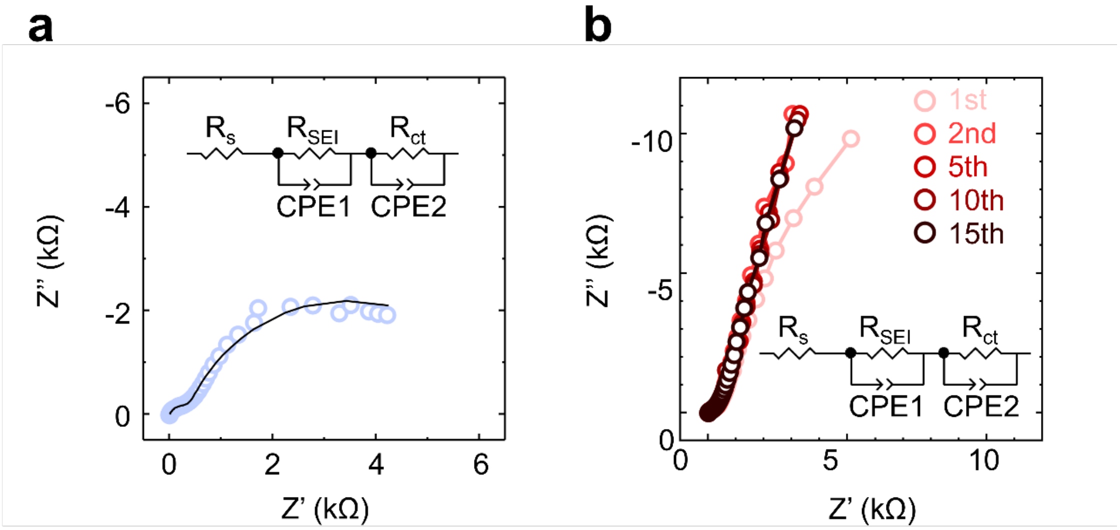


Figure S17. Nyquist plots of ncNTP measured at 25 °C with AC amplitude of 5 mV over a frequency range of 0.1 Hz to 1 MHz. (a) After discharge for the first cycle, including fitting results and the equivalent circuit. (b) After charge for each cycle.

Table S1. Refined parameters from Rietveld analysis for the diffraction pattern of $NaTi_2(PO_4)_3$ (space group #167, *R-3c*) collected using Cu Kα radiation.

Atom	Wyckoff	*x*	*y*	*z*	Occ.	B_{eq} (Å^2)
Na	6b	0	0	0	1	1.5(3)
Ti	12c	0	0	0.1461(1)	1	0.3(7)
P	18e	0.7109(4)	0	0.25	1	0.6(9)
O1	36f	0.2014(5)	0.1743(6)	0.3085(2)	1	0.7(2)
O2	36f	0.4730(5)	0.3032(6)	0.2476(3)	1	0.1(1)
a = 8.4828(2) Å, c = 21.7760(8) Å, V= 1357.03(6) Å^3, R_p = 16.6 R_{wp} = 9.99 R_{exp} = 8.89, S = 1.12						