Supporting Information

Controllable Synthesis of Na-Enriched $Na_4V_2(PO_4)_3$ Cathode for High-Energy Sodium-Ion Batteries: A Redox-Potential-Matched Chemical Sodiation Approach

*Mingli Xu[a], Fengxue Zhang[b], Yanhui Zhang[b], Chen Wu[a], Xue Zhou[c], Xinping Ai[a], Jiangfeng Qian[a]**

[a] *Hubei Key Laboratory of Electrochemical Power Sources, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, China*
[b] *Hubei Baijierui Advanced Materials Co., Ltd., Wuhan, Hubei 430072, China*
[c] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, China*
**Corresponding authors. Email: jfqian@whu.edu.cn*

Keywords:
sodium-ion battery, $Na_3V_2(PO_4)_3$ cathode, Na-enriched $Na_4V_2(PO_4)_3$ cathode, chemical sodiation approach, redox-potential matching principle

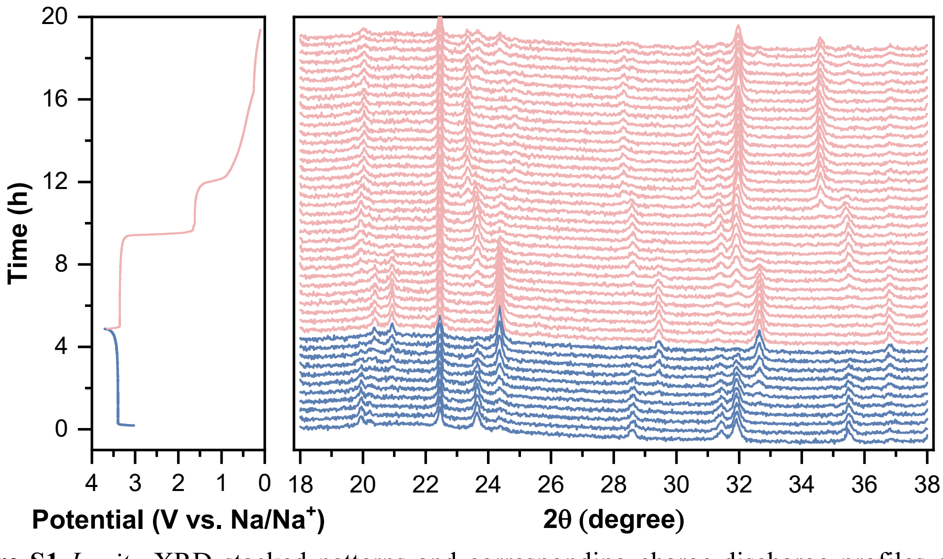

Figure S1 *In-situ* XRD stacked patterns and corresponding charge-discharge profiles of Na_3VP cathode in half cell.

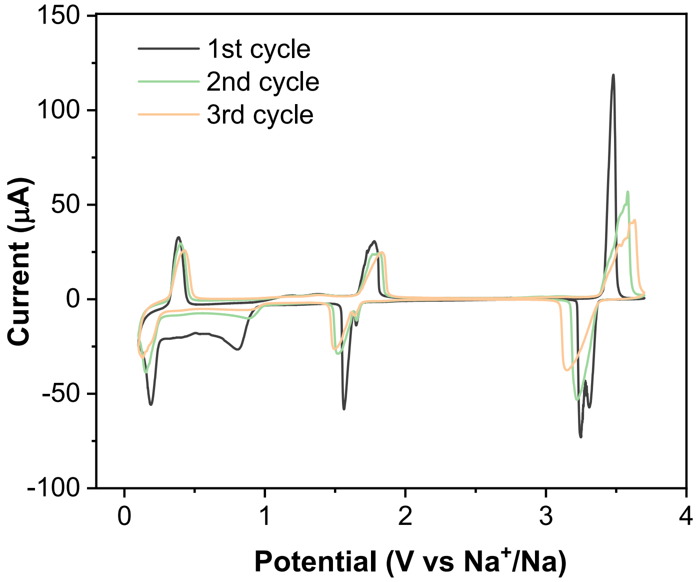

Figure S2 Cyclic voltammetry profiles of Na_3VP in the potential range of 0.1-3.7 V vs. Na^+/Na at scan rate of 0.1 mV/s.

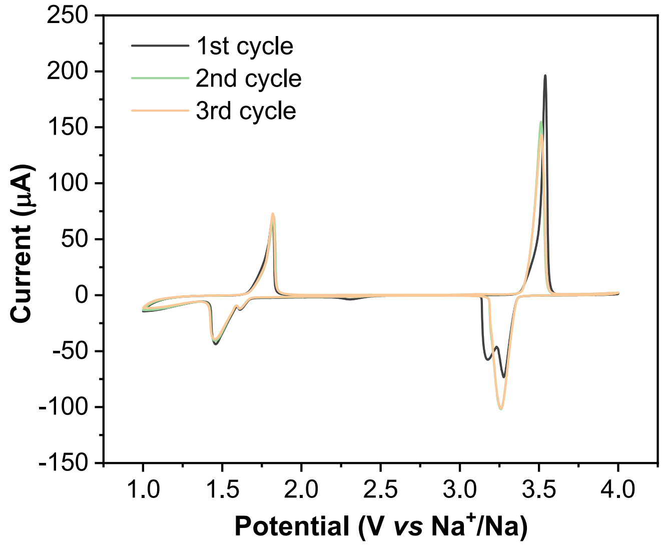

Figure S3 Cyclic voltammetry profiles of Na_3VP in the typical potential range of 1.0-4.0 V vs. Na^+/Na at scan rate of 0.1 mV/s.

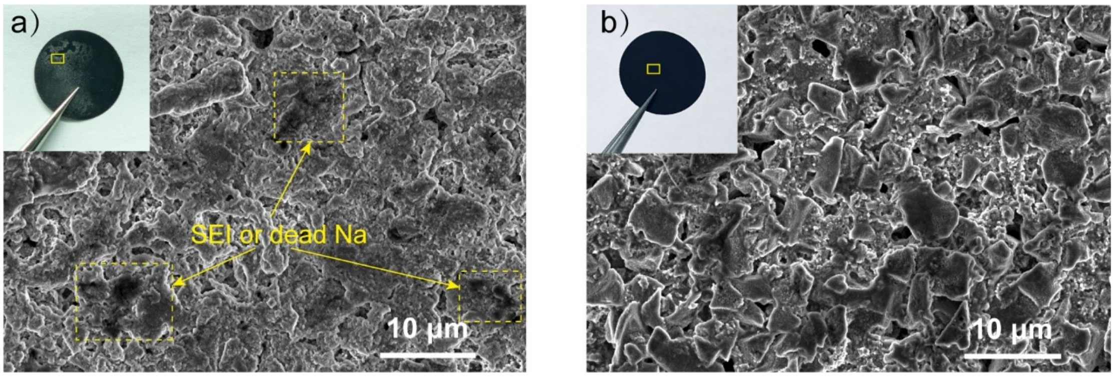

Figure S4 SEM images of HC anodes attained from (a) Na_5VP||HC and (b) Na_4VP||HC full cells after initial cycle.

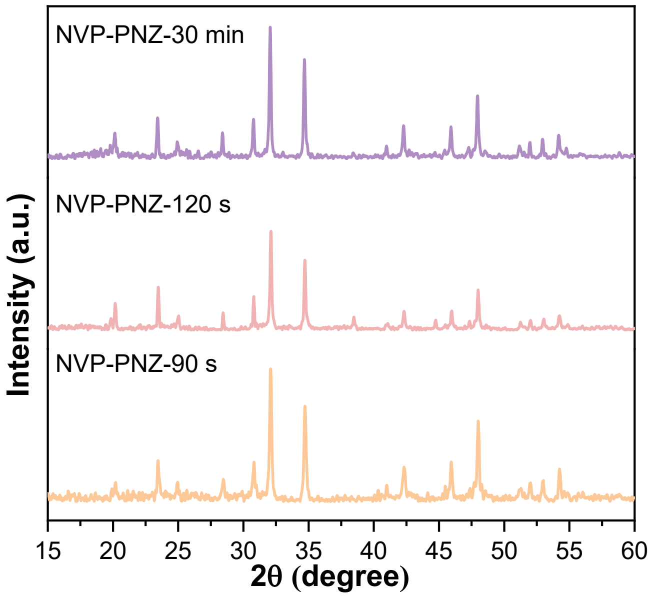

Figure S5 XRD patterns of presodiated electrodes with different treatment time (90 s, 120 s, and 30 min).

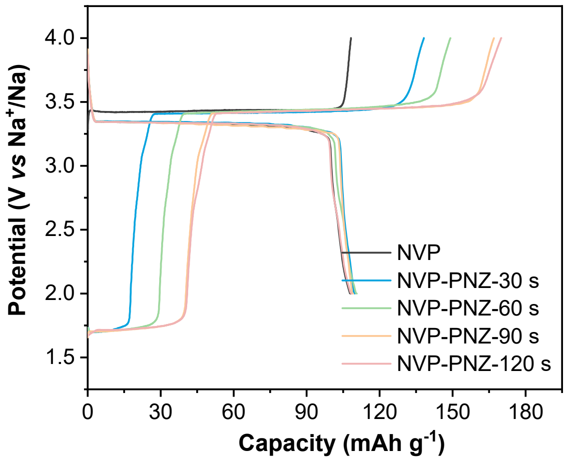

Figure S6 Initial charge-discharge curves of the Na*x*VP electrodes with different presodiation time (0 s, 30 s, 60 s, 90 s, and 120 s).

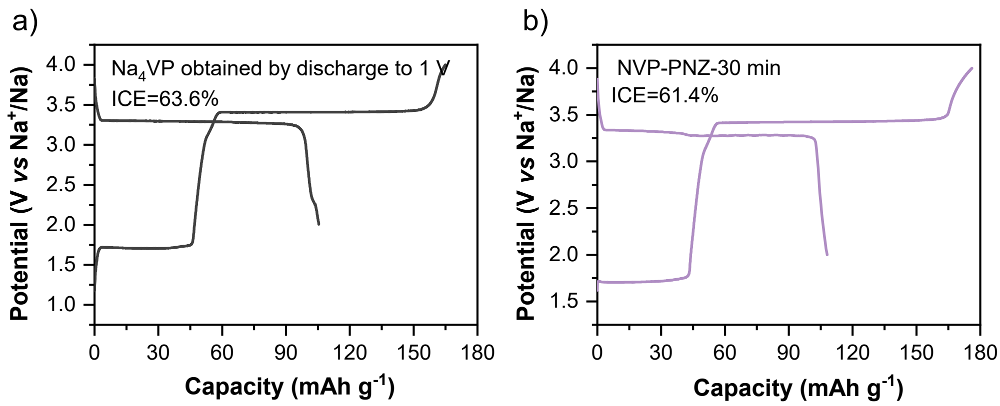

Figure S7 (a) Charge-discharge curves of the Na_4VP obtained by electrochemical presodiation. (b) Charge-discharge curves of the Na_4VP obtained by chemical presodiation with extended treatment time of 30 min.

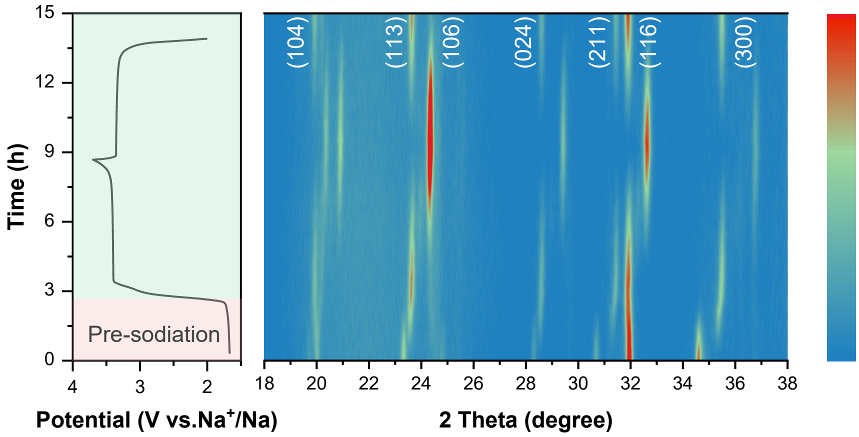

Figure S8 In-situ XRD counter maps and corresponding charge-discharge profiles of a PNZ-Na presodiated Na_4VP||Na half cell

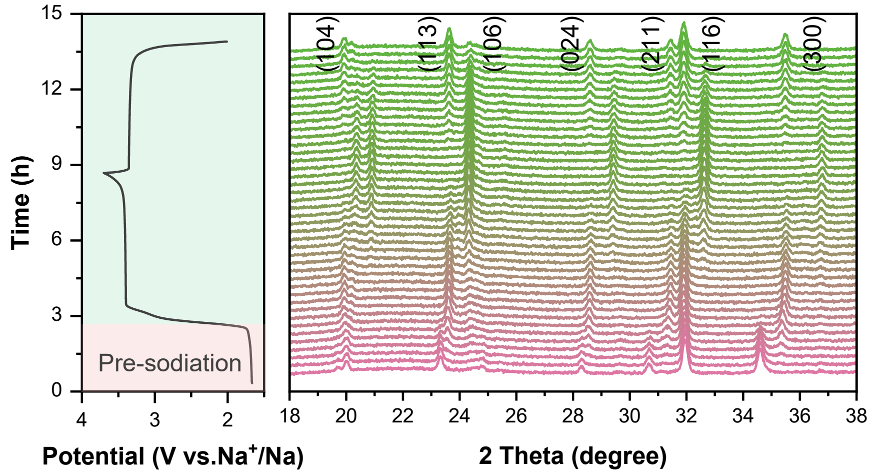

Figure S9 *In-situ* XRD stacked patterns and corresponding charge-discharge profiles of a PNZ-Na presodiated Na_4VP||Na half cell

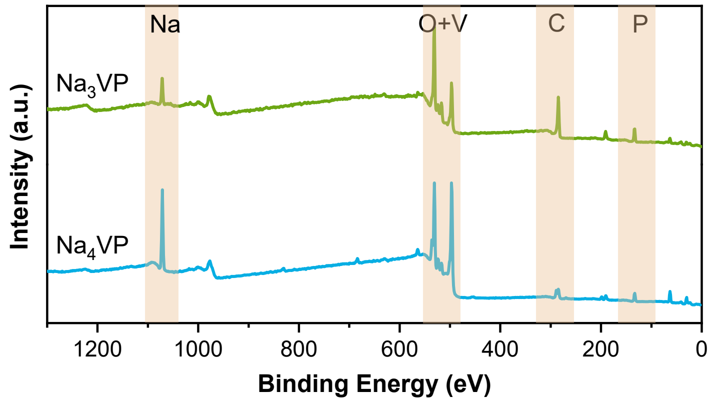

Figure S10 XPS full spectrum of the Na_3VP and Na_4VP.

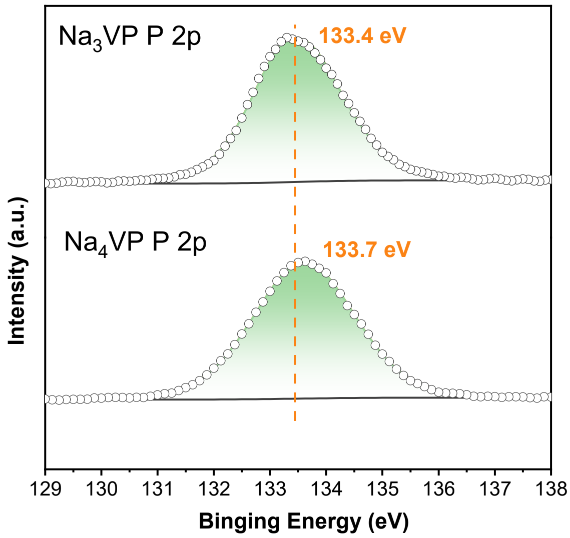

Figure S11 XPS P 2p spectra of the Na_3VP and Na_4VP.

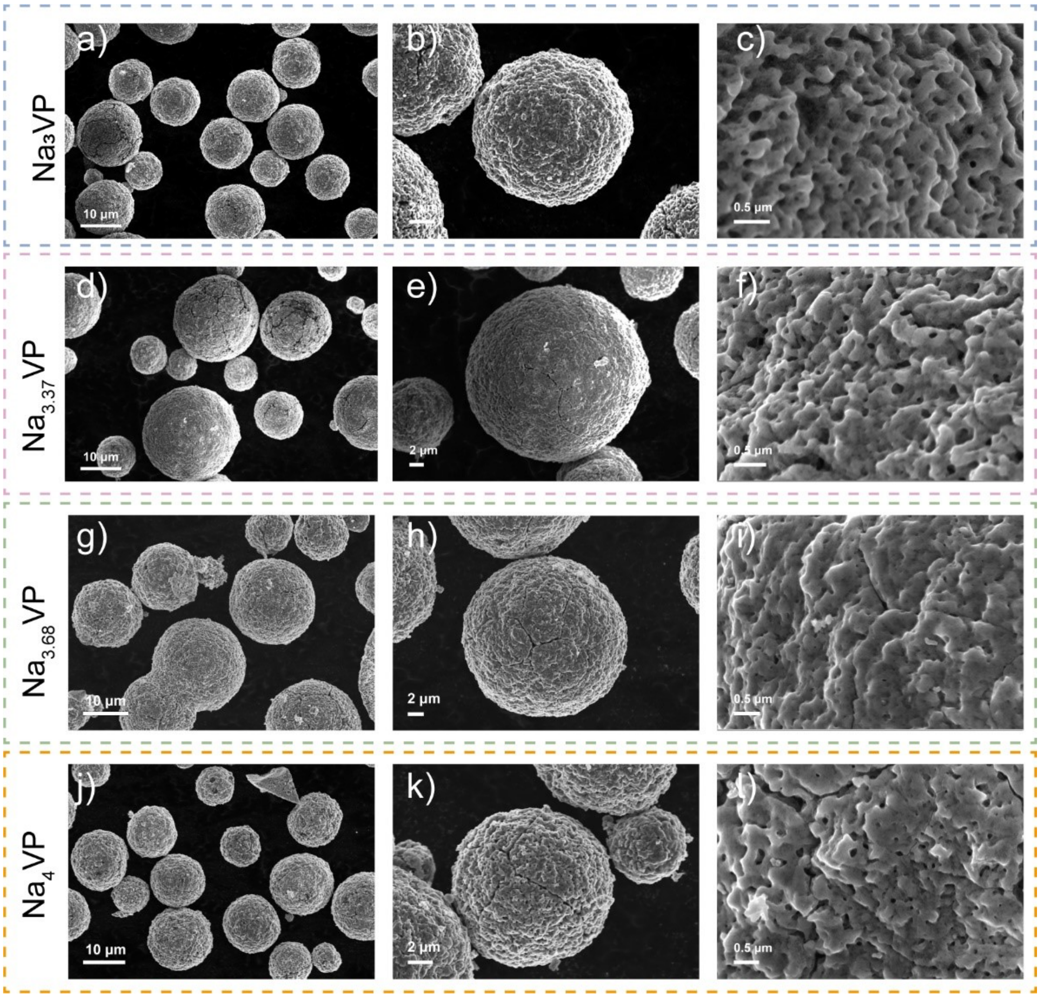

Figure S12 SEM images of Na*x*VP with different sodiation depth.

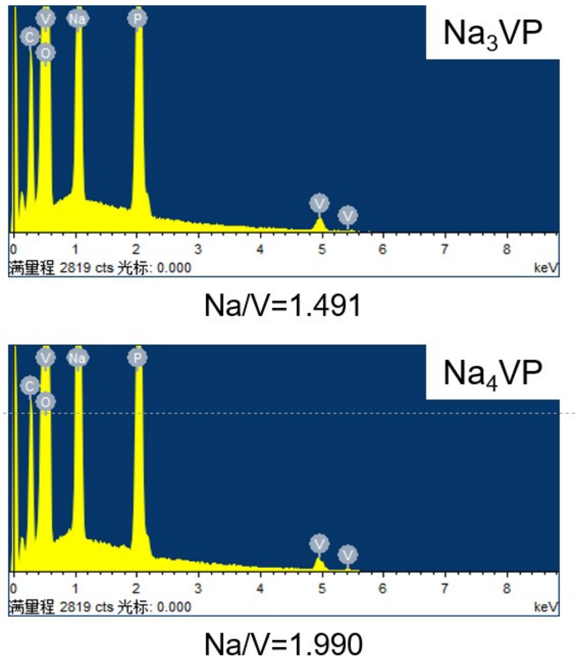

Figure S13 EDX images of the Na_3VP and Na_4VP and corresponding relative element ratio.

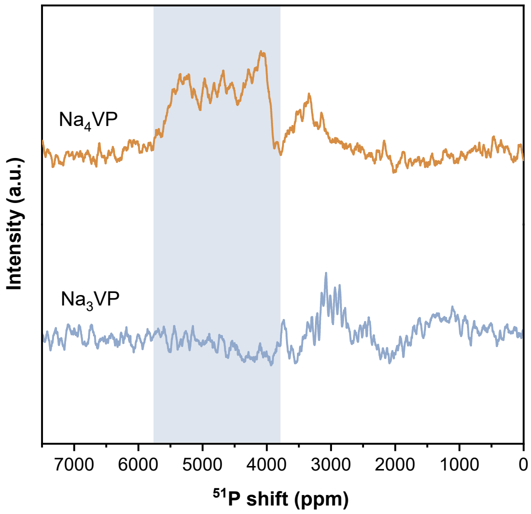

Figure S14 ^{31}P ssNMR spectra of the Na_3VP and Na_4VP.

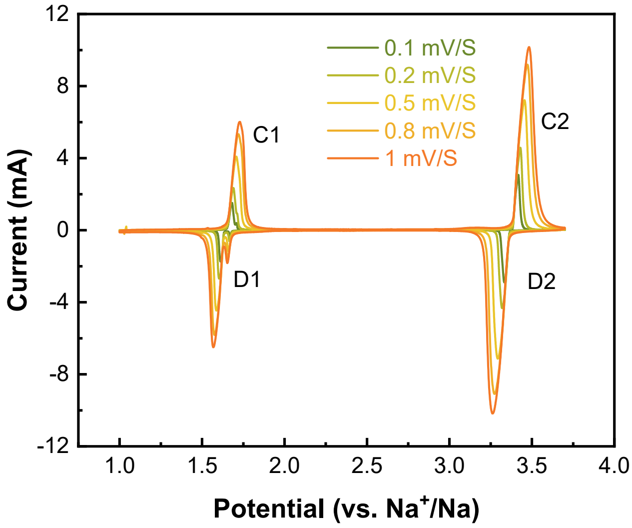

Figure S15 CV curves of Na_3VP at various scan rates in the potential range of 1-3.7 V vs. Na^+/Na.

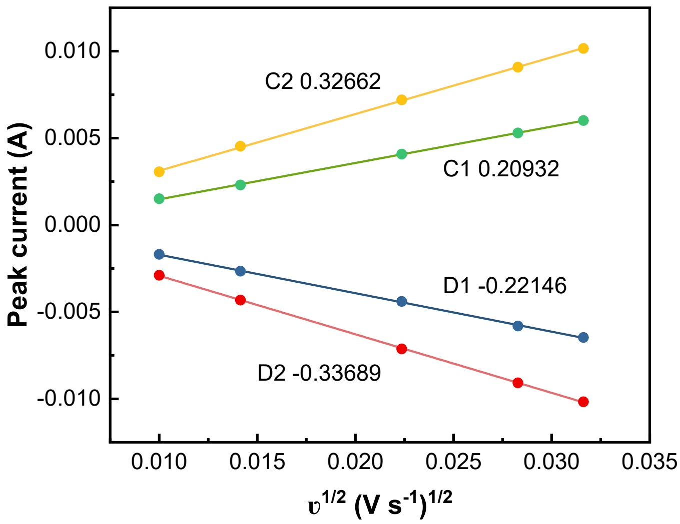

Figure S16 Corresponding relationships between I_p and $\upsilon^{1/2}$

Na^+ duffusion coefficients (D_{Na}) can be estimated by the Randles-sevick equation (Eq 1):

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{Na}^{1/2} C \upsilon^{1/2} \qquad \text{(Eq 1)}$$

where I_p and υ correspond to the peak current (A) and scan rate (mV/s), respectively. n is the number of transferred electron, A is the electrode area (cm^2), C is the molar concentration of sodium ion (mol/cm^3). The remarkably correlated linearly between I_p and $\upsilon^{1/2}$ indicates typical diffusion controlled behavior in Na3VP. According to the fitted slope, the calculated D_{Na} are 1.18×10^{-9}, 2.89×10^{-9}, 1.33×10^{-9}, and 3.07×10^{-9} cm^2/s, associated with the peaks of C1, C2, D1, and D2. Therefore, the Na^+ diffusion in the Na_3VP is faster than in the Na_4VP.

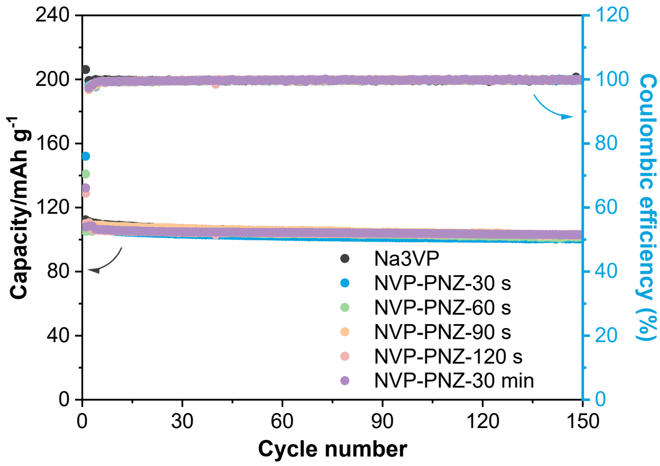

Figure S17 Cycling performance of the Na*x*VP electrodes with different presodiation time (0 s, 30 s, 60 s, 90 s, 120 s and 30 min).

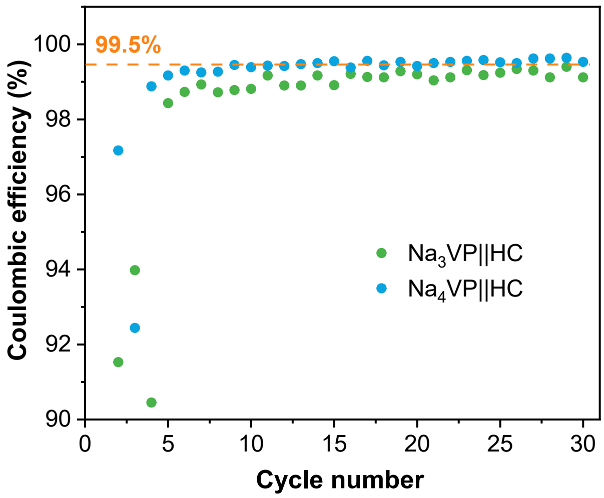

Figure S18 Coulombic efficiency of $Na_3VP||HC$ and $Na_4VP||HC$ full cells.

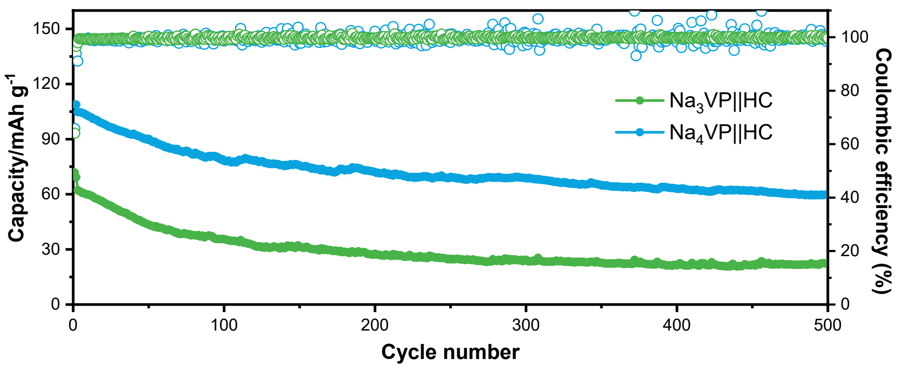

Figure S19 Long-term cycling stability at 2C of Na_3VP||HC and Na_4VP||HC full cells.

Table S1 Comparison of the electrochemical performance of NVP-based sodium-ion batteries reported in literatures

Cathode||Anode	ICE (%)	Energy density (Wh/kg)	Electrochemical performance	Ref
Na3VP||Pb-C	~70	170	~36% after 300th @ 2C	[1]
Na3VP thin film||MoSe2	~50	213.6	~50% after 50th @ 22.2 mA/cm^2	[2]
Na3VP||graphite	~88	78	~48% after 200th @ 50 mA/g	[3]
Na3VP||hard carbon	70.6	143.7	~89% after 300th @ 100 mA/g	[4]
Na3VP||hard carbon	50	120	~55% after 550th @ 2C	[5]
Na3VP||hard carbon	~50	151	~65% after 100th @ 1C	[6]
Na3VP||hard carbon	71.5	169	62% after 70th @ 0.2C	[7]
Na3VP||hard carbon	43.5	~90	~70% after 50th @ 50 mA/g	[8]
Na3VP||hard carbon	60	159.4	58.5% after 100th @ 1C	Our work
Na3VP||presodiated hard carbon	~94	251.1	73.3% after 450th @ 1 A/g	[9]
Na3VP||presodiated hard carbon	~95	218	~55% after 550th @ 2C	[5]
Na3VP||presodiated hard carbon	82.6	~191	83.3% after 50th @ 50 mA/g	[8]
Electrochemical presodiated Na4VP||hard carbon	~50	265	78% after 100th @ 1C 66% after 200th @ 1C	[6]
Biph-Na presodiated Na4VP||hard carbon	62.7	218.4	70% after 500th @ 1C (using excess cathode)	[7]
PNZ-Na presodiated Na4VP||hard carbon	65	251.1	78% after 100th @ 1C 57% after 500th @2C	Our work

Reference

1. B. Pandit, M. T. Sougrati, B. Fraisse and L. Monconduit, Exploration of a $Na_3V_2(PO_4)_3$/C –Pb full cell Na-ion prototype, *Nano Energy*, 2022, **95**, 107010.
2. J. A. Sam Oh, Q. Sun, C. Tian, X. Song, B. Chua, K. Zeng and L. Lu, Aerosol-deposited Freestanding $Na_3V_2(PO_4)_3$ Thin-film Microbattery, *Materials Today Energy*, 2022, **27**, 101006.
3. K. Subramanyan, M. Akshay, Y. S. Lee and V. Aravindan, Na-Ion Battery with Graphite Anode and $Na_3V_2(PO_4)_3$ Cathode via Solvent-Co-Intercalation Process, *Advanced Materials Technologies*, 2022, **7**, 2200399.
4. X. Jiang, X. Liu, Z. Zeng, L. Xiao, X. Ai, H. Yang and Y. Cao, A Bifunctional Fluorophosphate Electrolyte for Safer Sodium-Ion Batteries, *iScience*, 2018, **10**, 114.
5. M. Liu, J. Zhang, S. Guo, B. Wang, Y. Shen, X. Ai, H. Yang and J. Qian, Chemically Presodiated Hard Carbon Anodes with Enhanced Initial Coulombic Efficiencies for High-Energy Sodium Ion Batteries, *ACS Appl Mater Interfaces*, 2020, **12**, 17620.
6. S. Mirza, Z. Song, H. Zhang, A. Hussain, H. Zhang and X. Li, A Simple Pre-sodiation Strategy to Improve the Performance and Energy Density of Sodium Ion Batteries with $Na_4V_2(PO_4)_3$ as the Cathode Material, *Journal of Materials Chemistry A*, 2020, **8**, 23368.
7. Y. Liu, X. Wu, A. Moeez, Z. Peng, Y. Xia, D. Zhao, J. Liu and W. Li, Na-Rich $Na_3V_2(PO_4)_3$ Cathodes for Long Cycling Rechargeable Sodium Full Cells, *Advanced Energy Materials*, 2022, **13**, 2203283.
8. B. Xiao, F. A. Soto, M. Gu, K. S. Han, J. Song, H. Wang, M. H. Engelhard, V. Murugesan, K. T. Mueller, D. Reed, V. L. Sprenkle, P. B. Balbuena and X. Li, Lithium-Pretreated Hard Carbon as High-Performance Sodium-Ion Battery Anodes, *Advanced Energy Materials*, 2018, **8**, 1801441.
9. X. Yin, Y. Zhao, X. Wang, X. Feng, Z. Lu, Y. Li, H. Long, J. Wang, J. Ning and J. Zhang, Modulating the Graphitic Domains of Hard Carbons Derived from Mixed Pitch and Resin to Achieve High Rate and Stable Sodium Storage, *Small*, 2021, **18**, 2105568.