Supporting Information

A simple pre-sodiation strategy to improve performance and energy density of sodium ion batteries with Na₄V₂(PO₄)₃ as cathode material

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Figure S1 (a) S.E.M. and (b) XRD pattern of as-synthesized $Na_3V_2(PO_4)_3/C$.



Figure S2 The crystal structure of monoclinic $Na_3V_2(PO_4)_3$ with the space group of P21/c



Figure S3 2D contour maps of *in-situ* XRD peak intensities at various 2θ ranges of $23.0^{\circ}-25.5^{\circ}$, $28.0^{\circ}-30.0^{\circ}$, $31.0^{\circ}-34.0^{\circ}$, and $34.0^{\circ}-37.0^{\circ}$ at 1.0-4.0 V (vs. Na⁺/Na).



Figure S4 Diagram of Swagelok three-electrode cell



Figure S5 3-electrode based tests for Na3VP|| H.C. full cell.



Figure S6 (a) SEM image and (b) XRD pattern of hard carbon (*KURANODETM*); (c) Rate performance; (d) Cycle performance of hard carbon (e) Charge and Discharge curves of Hard Carbon at 30 mA g⁻¹ in the first three cycles



Figure S7 Electrochemical performances of Na4VP||H.C. & Na3VP||H.C. full cells. Rate capabilities (a) calculated based on the total mass of electrodes (cathode and anode), (b) calculated with active mass of anode and (c) Cycling performance of Na4VP||H.C. full cell.(calculated based on the total mass of electrodes (cathode and anode), calcuted with active mass of anode.



Figure S8 Capacity retention along with Coulombic efficiency of Na3VP|| H.C. full cell



Figure S9 Energy efficiency at different C rates for both cells



Figure S10 Galvanostatic charge curves of Na4VP with various exposure time in Argon



Figure S11 Hard carbon salary losses contact with respect to time.

Air exposure time (hr)	OCV (V, vs Na ⁺ /Na)
0	0.0515
1	0.0893
3	0.0915
6	0.1085

Table S1 O.C.V. of sodiated H.C. with respect to the different air exposure time.