Supporting Information

In Operando Probing Sodium-incorporation in NASICON Nanomaterial: Asymmetric Reaction and Electrochemical Phase Diagram

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Figure S1. The schematic of the *in-situ* cell with a temperature range of 253 - 393 K. The used testing system is based on a Bruker D8 Discover X-ray diffractometer with VANTEC-500 detector. Beryllium window is selected as the current collector for the *in-situ* test on the XRD diffractometer. An electrochemical workstation is used to control the current and voltage of the *in-situ* cell during the electrochemical test. The homemade *in-situ* cell can achieve a temperature range of 253 - 373 K by using a chiller.



Figure S2. Nitrogen adsorption-desorption isotherm of the $Na_3V_2(PO_4)_3/C$ particles.



Figure S3. a) Cycle performance of $Na_3V_2(PO_4)_3$ at the current density of 5C. b) The charge discharge curves of $Na_3V_2(PO_4)_3$ at different cycle numbers.



Figure S4. XRD patterns of Na₃V₂(PO₄)₃ [a) Na₃V₂(PO₄)₃ and b) NaV₂(PO₄)₃] in the *in-situ* cell at 273, 283 and 293 K during the two theta range of $19 - 40^{\circ}$.



Figure S5. XRD patterns of $Na_3V_2(PO_4)_3$ [a) and b)] and $NaV_2(PO_4)_3$ [c) and d)] at 273 and 293 K.



Figure S6. XRD refinement of $NaV_2(PO_4)_3$ [a) and b)] and $Na_3V_2(PO_4)_3$ [c) and d)] at 273 and 293 K.



Figure S7. *In-situ* Raman of $Na_3V_2(PO_4)_3$ at 1C. a) One dimensional as well as b) two-dimensional images of the Raman patterns.



Figure S8. *Operando* XRD patterns of $Na_3V_2(PO_4)_3$ at a) 273 K, b) 293 K and c) 313 K with a charge/discharge rate of 3 C. *In-situ* XRD patterns at d) 273 K, e) 293 K and f) 313 K with a charge/discharge rate of 5 C.



Figure S9. *In-situ* XRD pattern of $Na_3V_2(PO_4)_3$ under 273 and 293 K. Images show the evolution of the charge-relax experiment, where a current equivalent to 10 C is applied for 90 s followed by an open-circuit relaxation of 10 min.