Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

A phosphite based layered framework as a novel positive electrode material for Na-ion Batteries

A. Shahul Hameed,[ab] Mirai Ohara,[a] Kei Kubota,[ab] and Shinichi Komaba*[ab]

[a]*Department of Applied Chemistry, Tokyo University of Science, Tokyo 162-8601, Japan.*

[b]*ESICB, Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan*

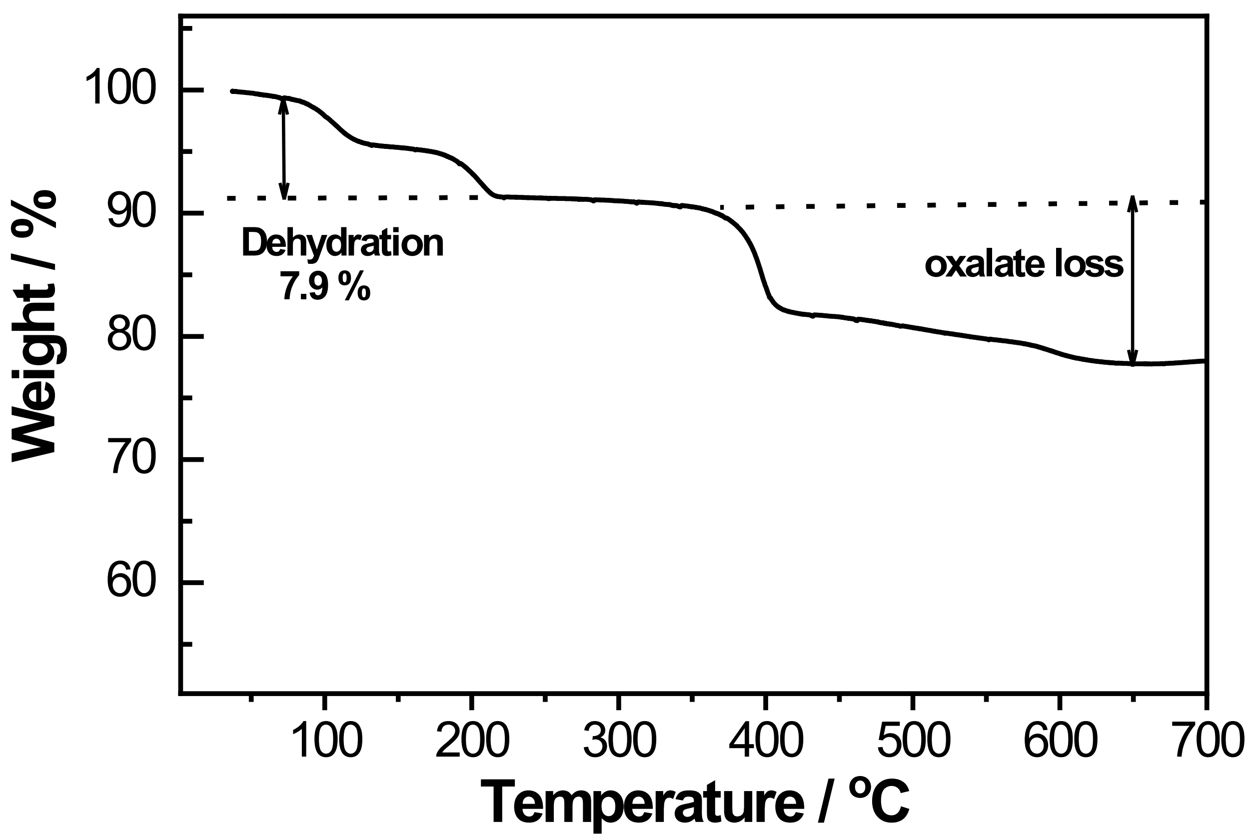

Fig. S1: TGA of p-NVPox in nitrogen atmosphere at a scan rate of 5 ºC min^{-1}

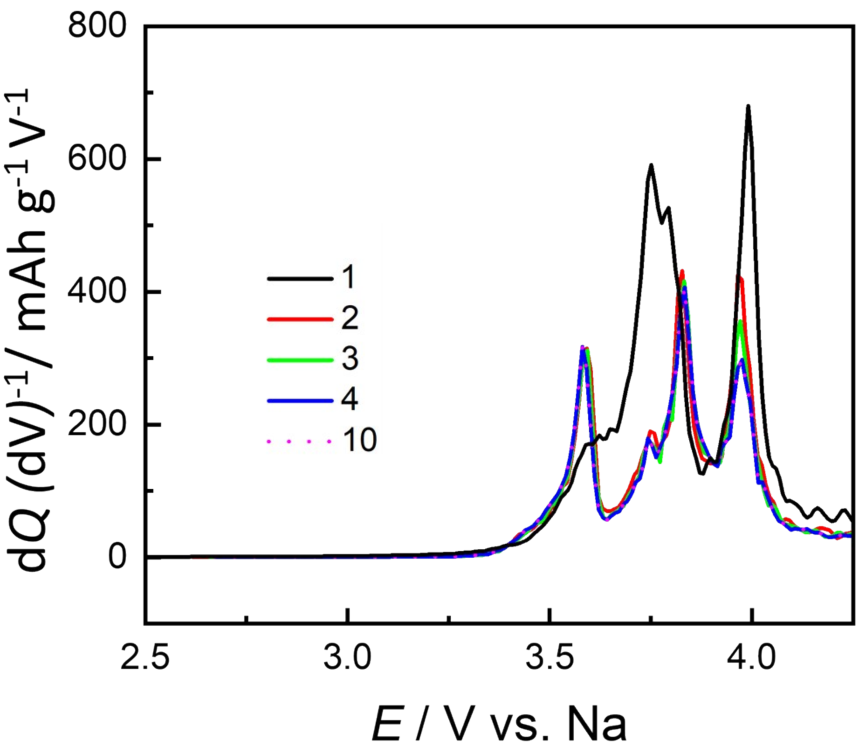

Fig. S2: The d*Q*/d*V* plots of p-NVPox (charge curves) for selected cycles

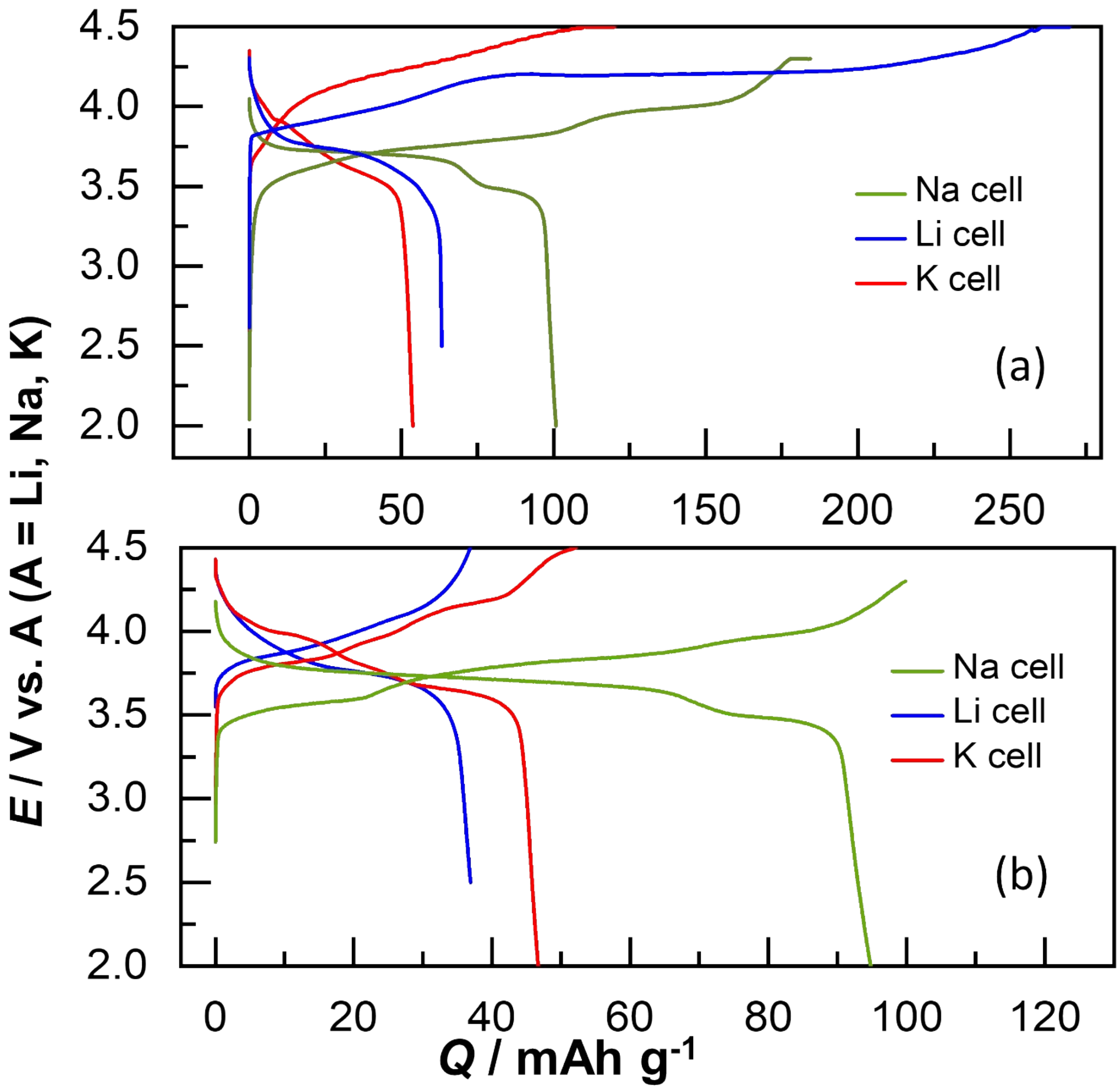

Fig. S3: Comparison of charge-discharge profiles of p-NVPox in Li-, Na- and K-half cells at 0.1 C for (a) 1^{st} cycle, and (b) 10^{th} cycle.

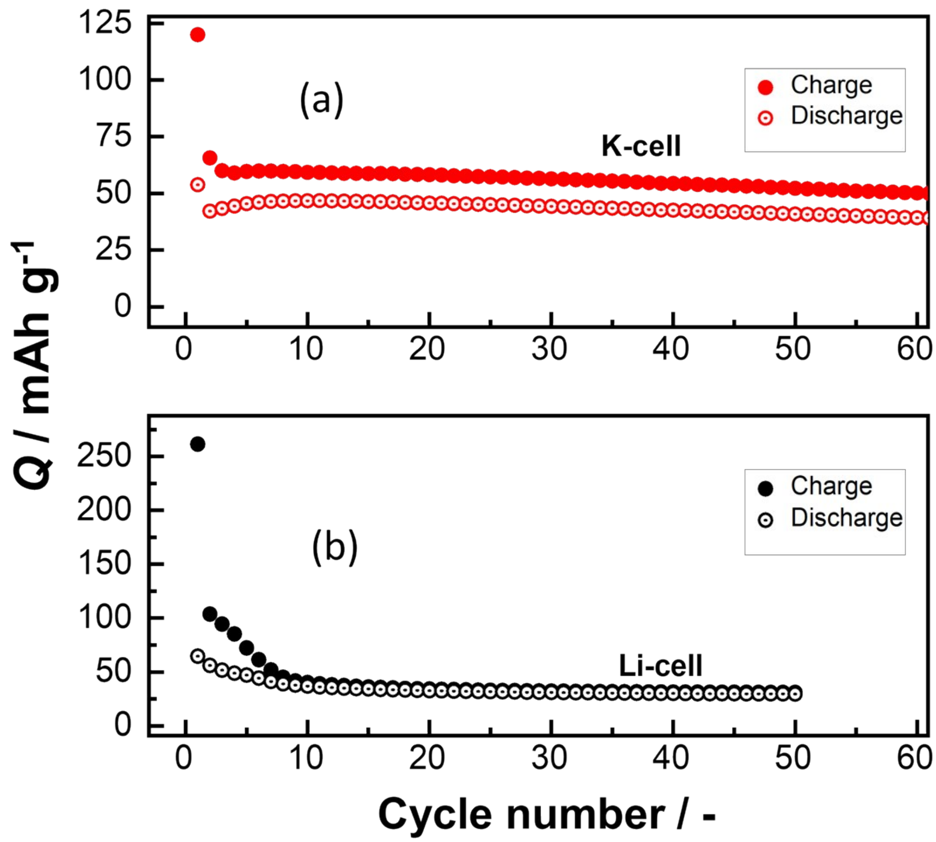

Fig. S4: Capacity retention plots of p-NVPox at 0.1 C in (a) K- half cell and (b) Li-half cell.

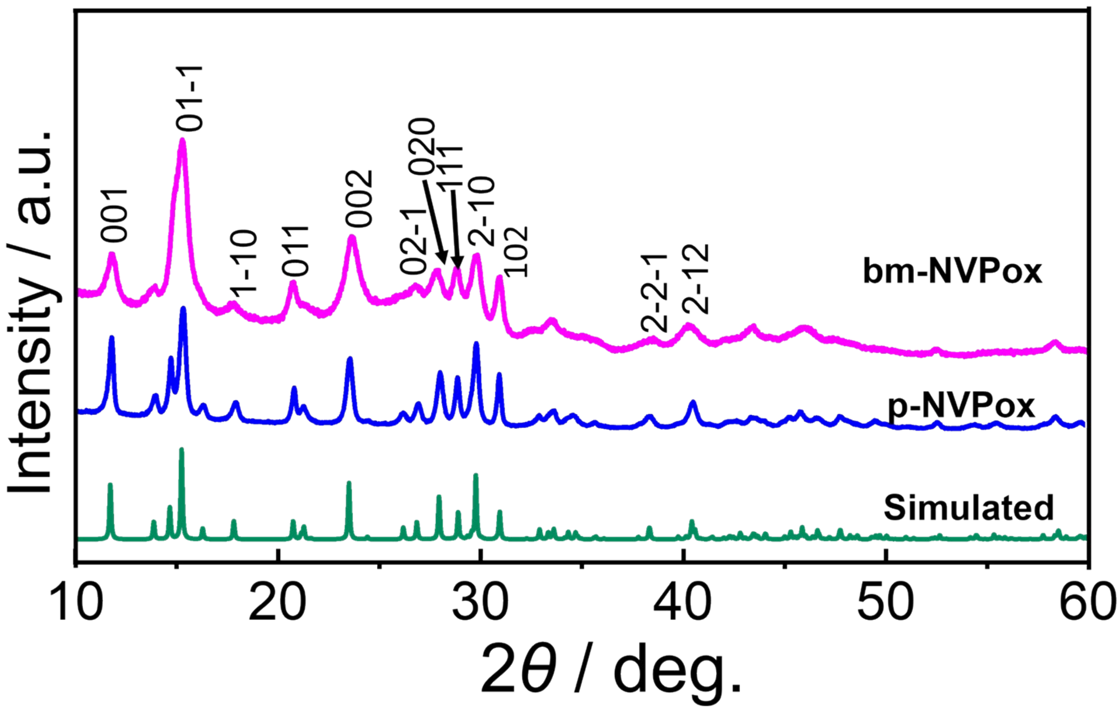

Fig. S5: Comparison of XRD patterns of bm-NVPox and p-NVPox with the simulated pattern of $Na_2[(VOHPO_3)_2(C_2O_4)]\cdot 2H_2O$

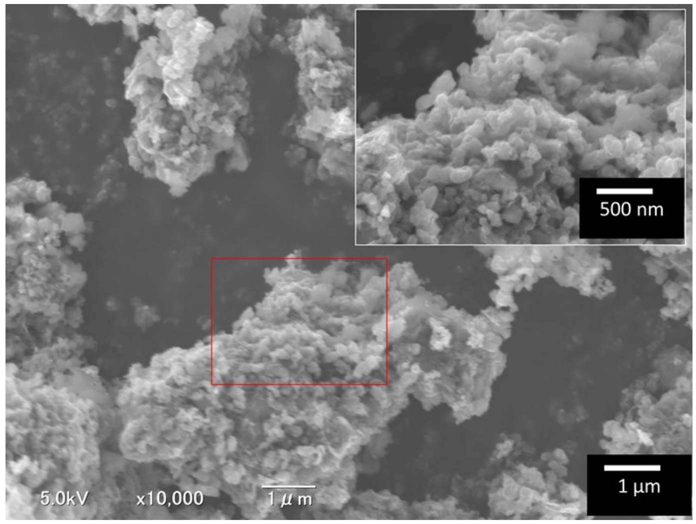

Fig. S6: SEM micrograph of bm-NVPox. The inset shows a higher magnification image (x30,000) of the selected area.

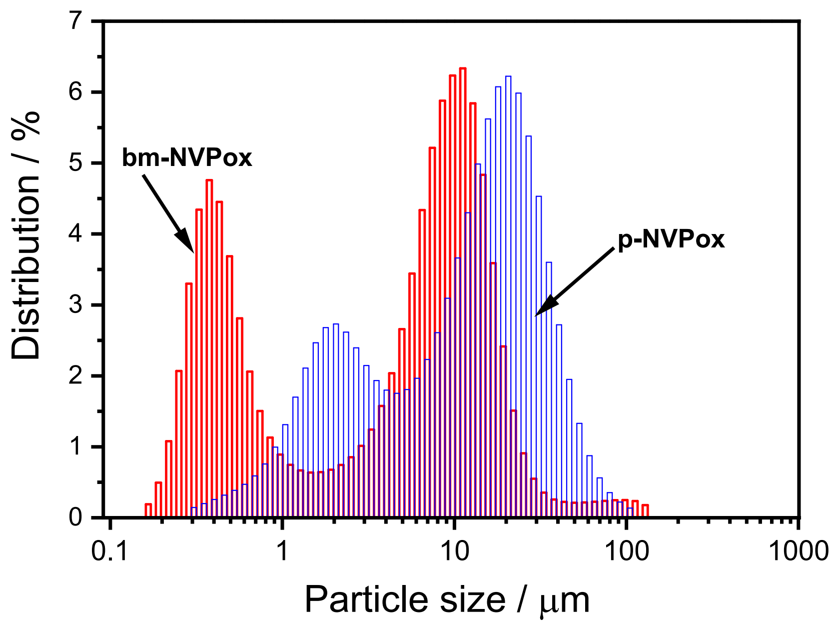

Fig. S7: Comparison of particle size of ball milled NVPox and the pristine sample.

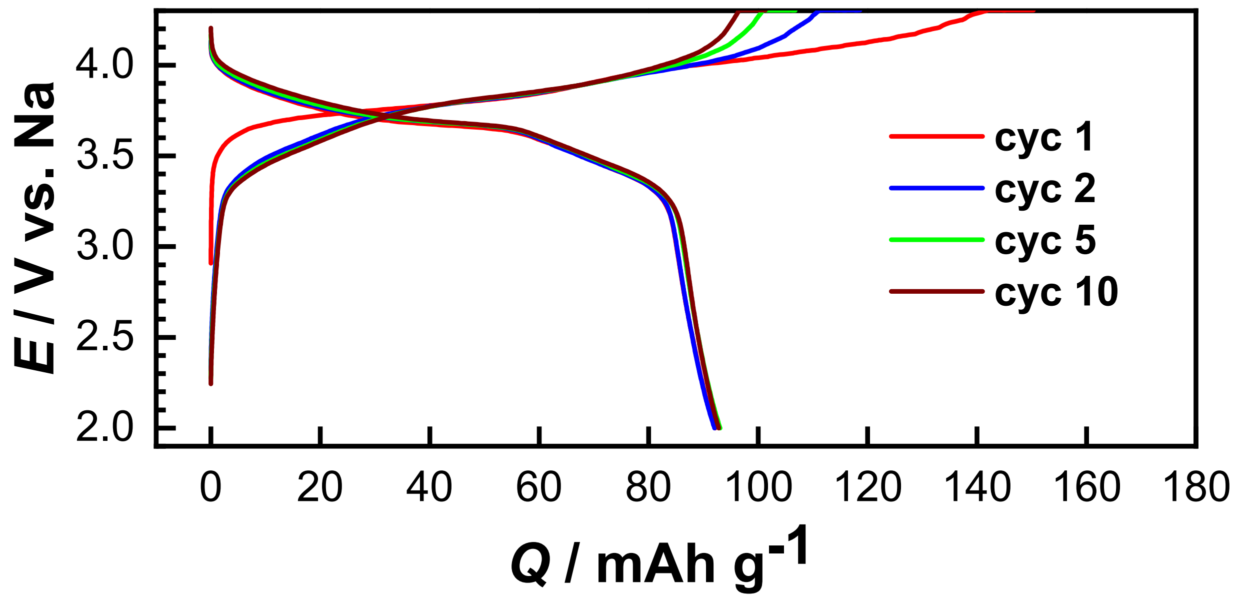

Fig. S8: Charge-discharge profiles of bm-NVPox for 10 cycles at 0.1 C current rate in the potential range of 2.0-4.3 V.

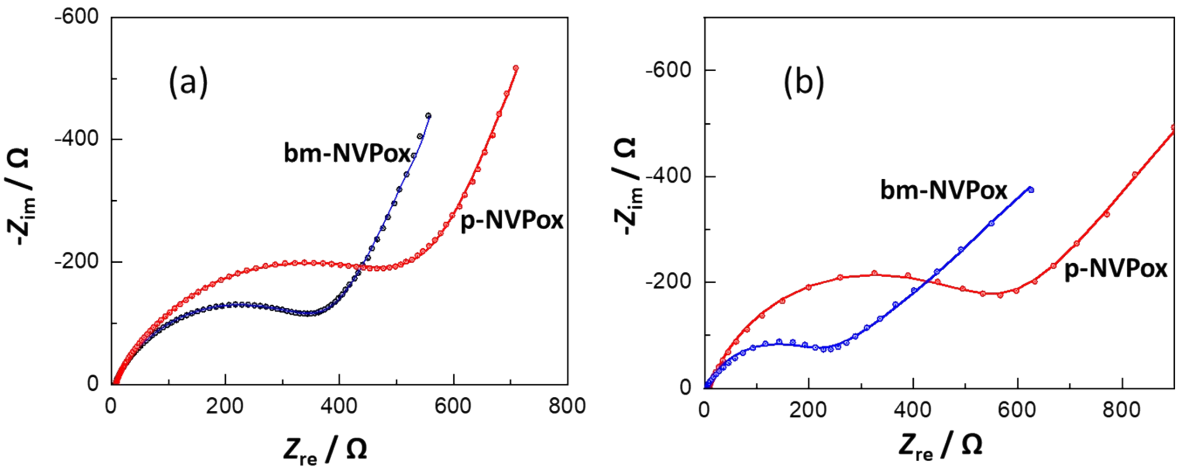

Fig. S9: Nyquist plots of p-NVPox and bm-NVPox during first cycle: (a) charged state (4.3V) and (b) discharged state (2.0 V). The circles represent experimental values and the solid line represent fitted results.

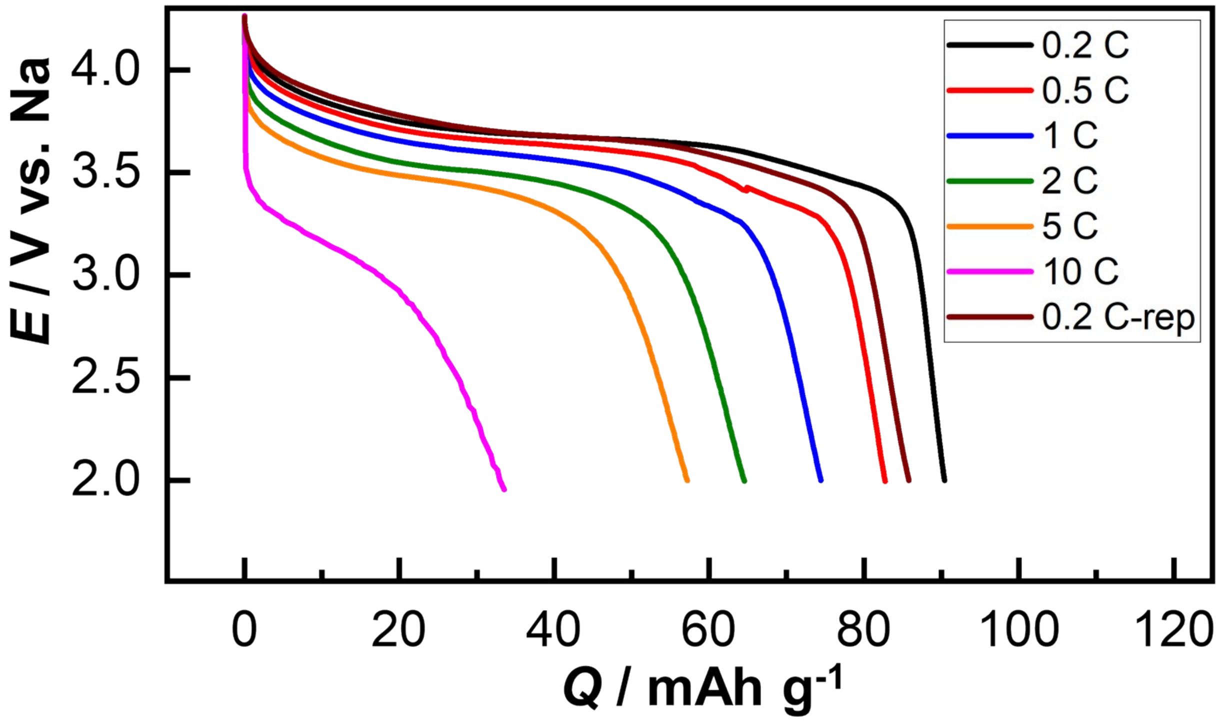

Fig. S10: Comparison of discharge profiles of p-NVPox at different current rates.

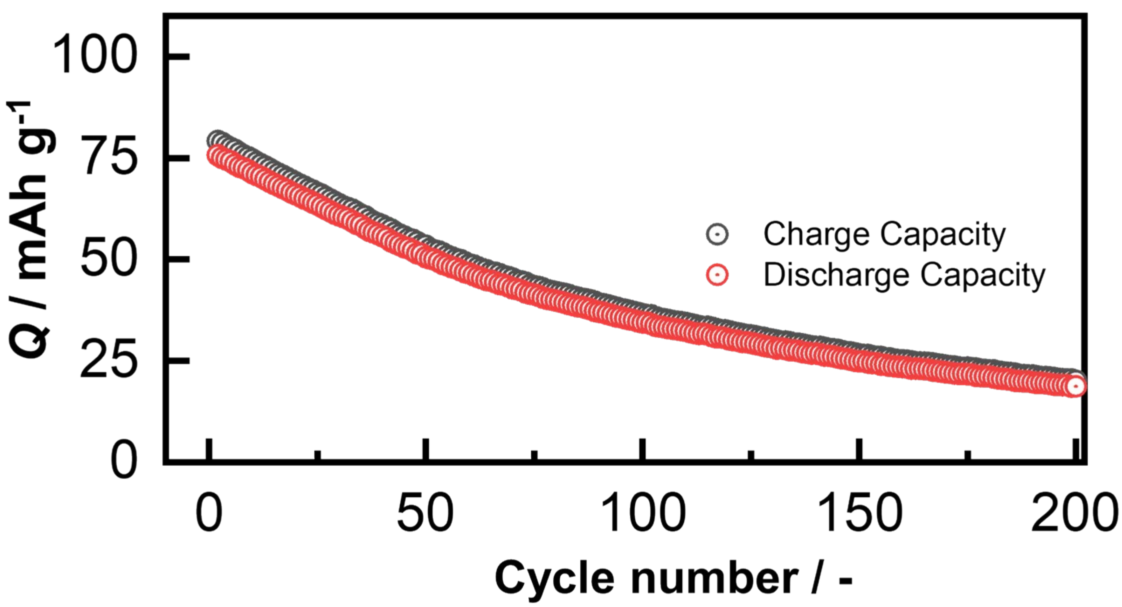

Fig. S11: Long term cycling of p-NVPox at 2 C rate showing charge and discharge capacities for 200 cycles.

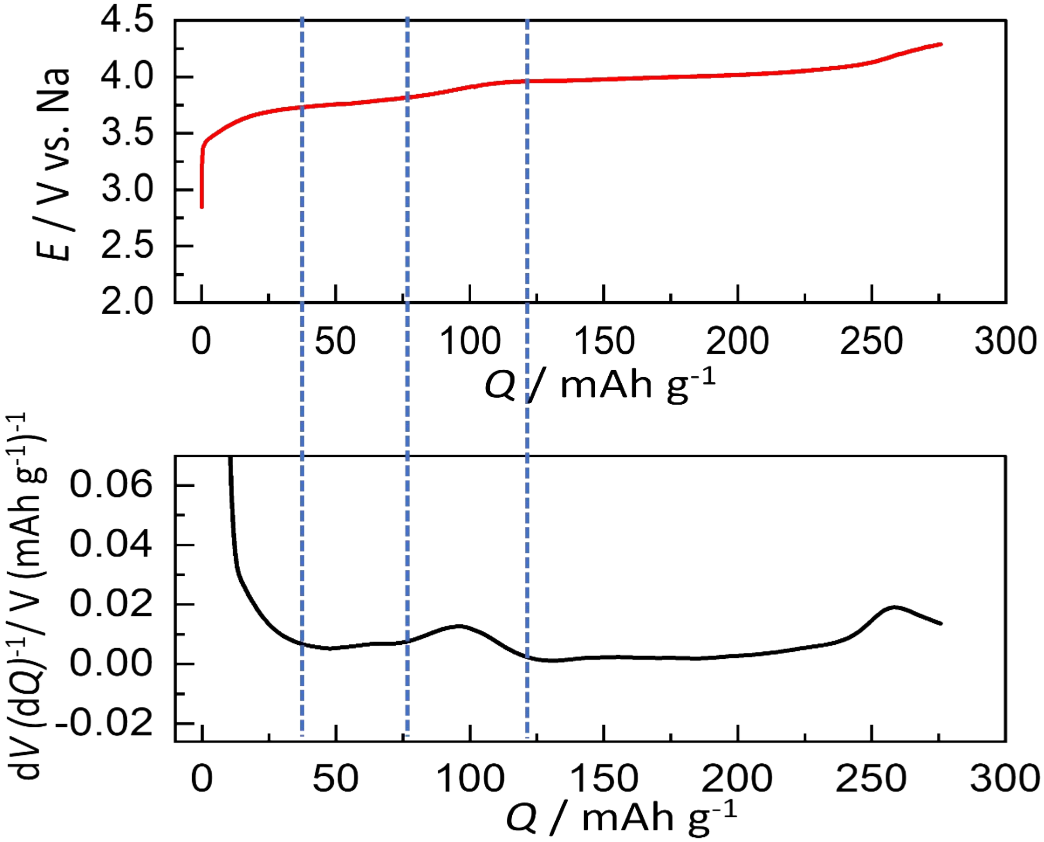

Fig. S12: Differential voltage analysis (dV/dQ) of the first charge curve of p-NVPox during the operando XRD measurement.

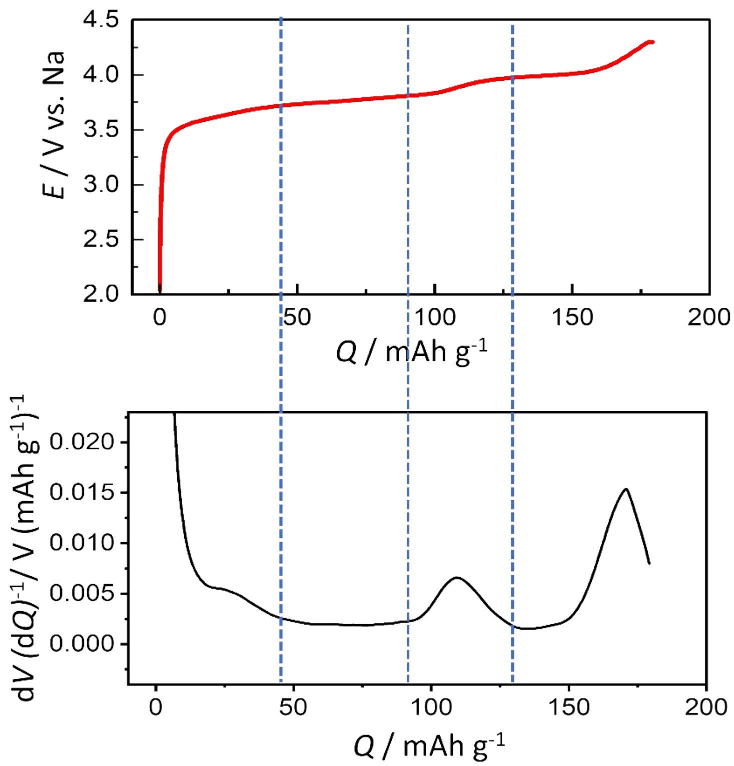

Fig. S13: Differential voltage analysis (dV/dQ) of the first charge curve of p-NVPox in a coin cell.

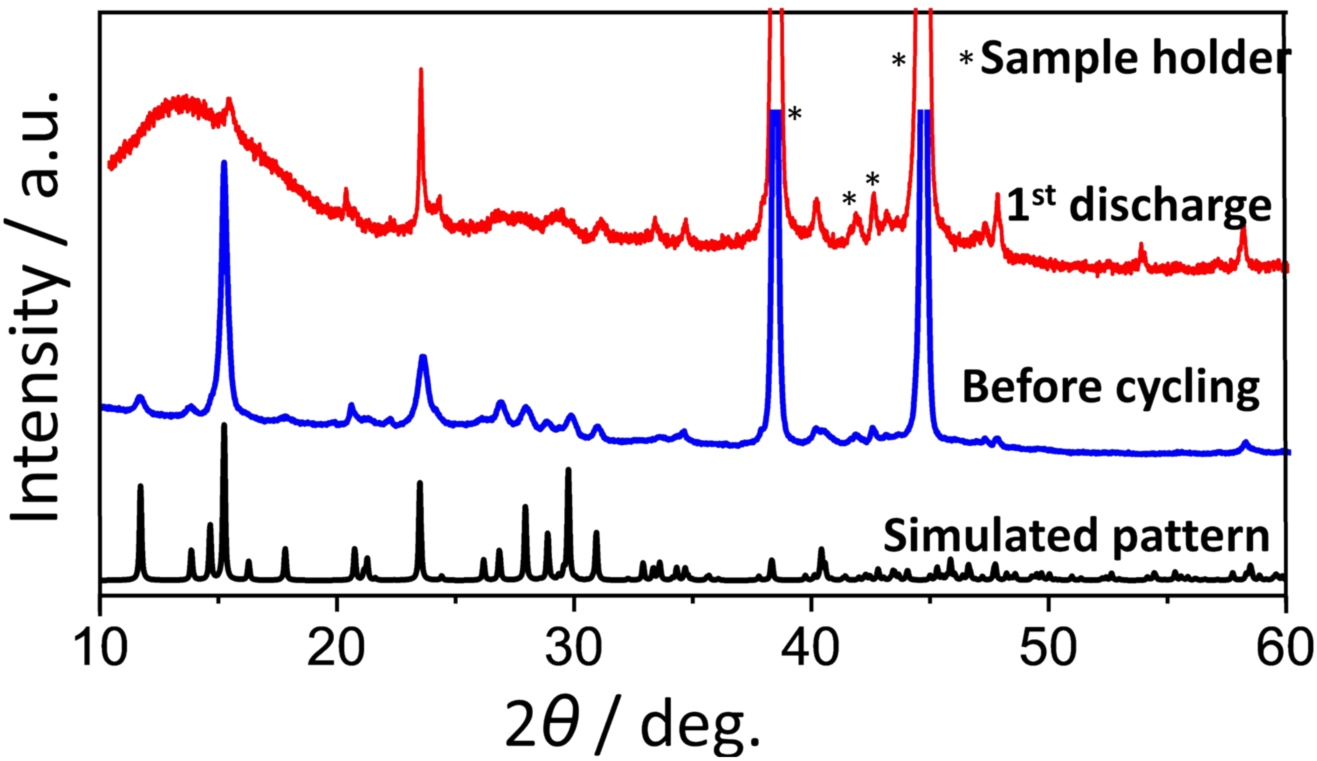

Fig. S14: XRD patterns of p-NVPox electrode before cycling and at the end of first discharge compared with the simulated pattern of NVPox.

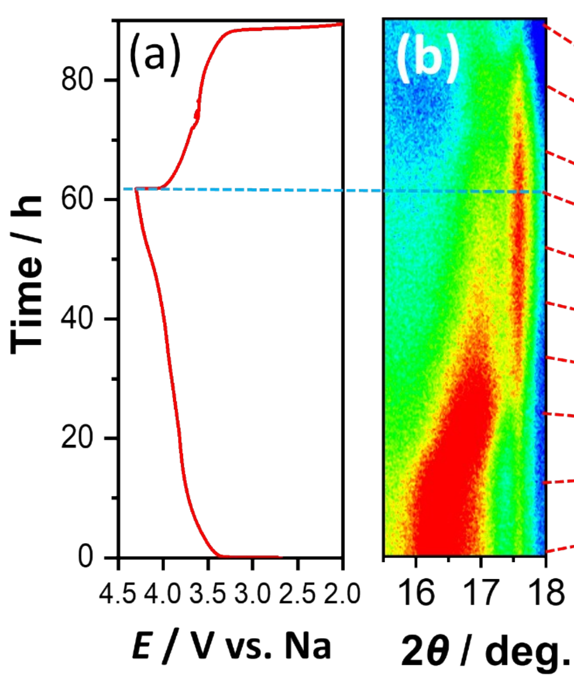

Fig. S15: Structural evolution during second Na extraction/insertion: a) Charge-discharge profile during the operando XRD measurement, (b) contour maps of operando XRD for selected 2θ regions and c) XRD patterns at selected SOC.

Synthesis of c-$NaTi_2(PO_4)_3$

0.01 M $Ti(OBu)_4$ was added to 40 mL of 30% H_2O_2 with constant stirring and 15 mL of 28% NH_4OH was added and stirred. Then stoichiometric amounts of citric acid, $(NH_4)_2HPO_4$ and Na_2CO_3 were added, followed by ethylene glycol. After stirring for few hours, the resulting solution was dried at 80 ^oC in air under constant stirring. The powder was calcined at 350 ^oC for 3h in air and then at 700 ^oC for 12h in air to obtain the white $NaTi_2(PO_4)_3$.(NTP) powder. The carbon coating was carried out by hydrothermal treatment of NTP(200 mg) with sucrose (500 mg) at 180 ^oC for 6h, followed by calcination at 800 ^oC for 1h in Ar.

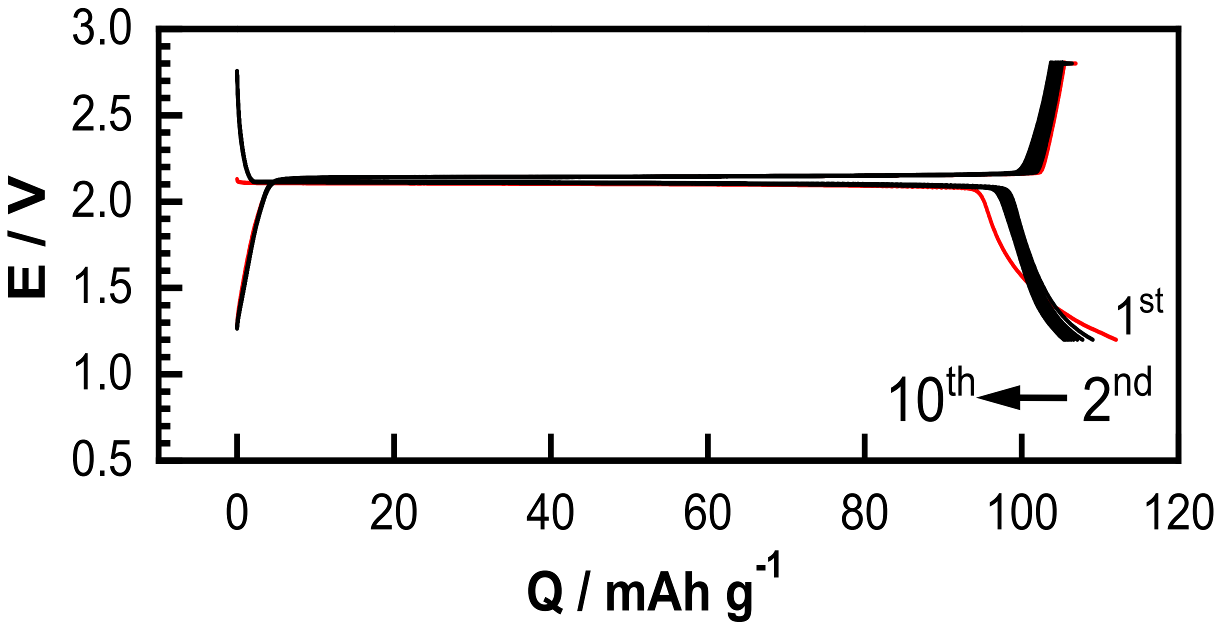

Fig. S16: Charge-discharge profiles of a $NaTi_2(PO_4)_3$ (NTP) half-cells

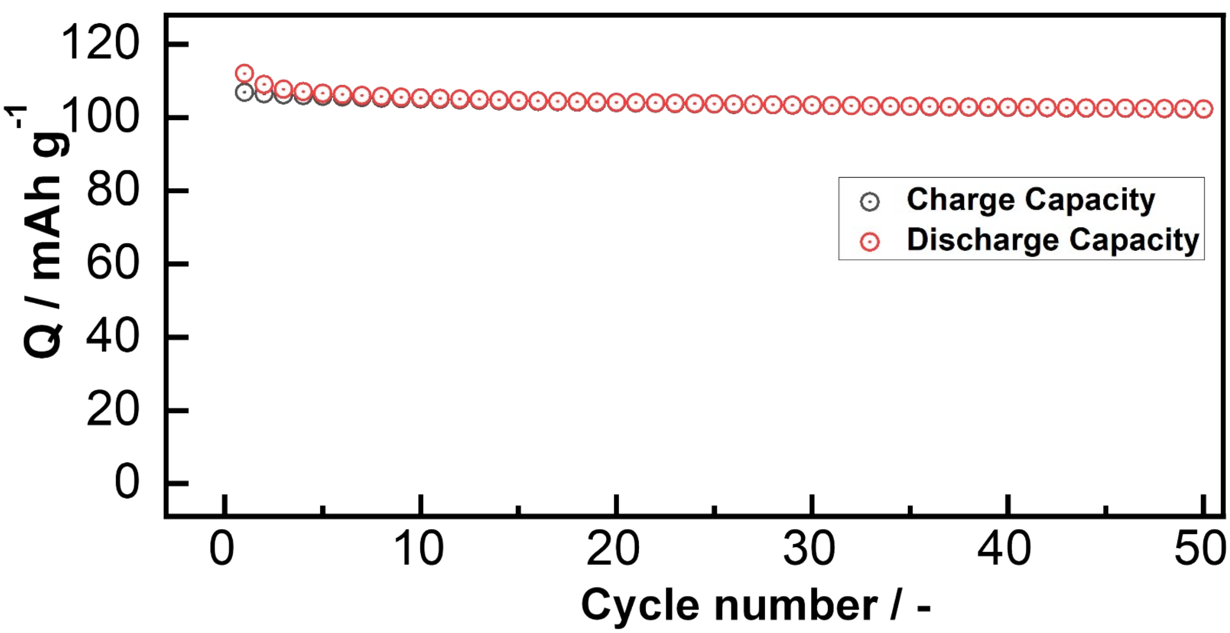

Fig. S17: Capacity retention plots of a $NaTi_2(PO_4)_3$ (NTP) half-cell.