

Electronic Supplementary Information (ESI)

**Superior electrochemical sodium storage of V_4P_7 nanoparticle as an anode
for rechargeable sodium-ion batteries**

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Experimental

Synthesis of V₄P₇ Nanoparticles:

The V₄P₇ nanoparticles were synthesized by high energy mechanical milling (HEMM, Fritsch Pulverisette-6) with vanadium (99.95%, Alfa Aesar) and red phosphorus (98.9%, Alfa Aesar) under an Ar atmosphere. Stoichiometric amount of precursors was put into a hardened steel vial (80 cm³) with hardened steel balls (3/8 in. in diameter). The weight ratio of milling balls to powder was 20:1. The phase pure V₄P₇ was obtained after milling for 60 h at a rotation speed of 300 rpm. The final product was collected, softly ground, and stored in a glove box to minimize the surface oxidation.

Synthesis of VO₂(B) Nanorods:

The VO₂(B) nanorods were synthesized by a hydrothermal method. 1.6 mmol of vanadium pentaoxide (V₂O₅, 99.6%, Sigma-Aldrich) was dissolved in 50 mL of deionized water. After stirring for 30 min using a magnetic stirrer, 16.0 mmol of glycerol (99.5%, Sigma-Aldrich) was added into solution and additional stirring was conducted for 30 min. Then, the obtained solution was transferred into a Teflon-lined stainless steel autoclave (100 mL capacity) and hydrothermally treated at 180 °C for 24 h with a ramping rate of 5 °C min⁻¹. As-obtained blue black powder was collected by centrifugation and washed with deionized water and ethanol for several times. The final product was dried in vacuum oven at 80 °C for 24 h.

Materials Characterization: The phase of as-synthesized V₄P₇ nanoparticles, VO₂(B) nanorods, and electrodes was characterized by X-ray diffractometer (XRD, D8-Advance, BRUKER MILLER Co.) using Cu K α radiation ($\lambda=1.5406$ Å). The valence states of vanadium and phosphorus for as-prepared V₄P₇ nanoparticles were characterized by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo scientific) equipped with an Al K α X-ray source ($h\nu = 1486.6$ eV). The morphology of nanoparticles, nanorods, and electrodes was examined by field emission scanning electron microscopy (FE-SEM, SU70, Hitachi) and transmission electron microscopy (TEM, JEM-2100F, JEOL). The V and P content in as-synthesized V₄P₇ nanoparticles and were determined using inductively coupled plasma atomic emission

spectrometer (ICP-AES, OPTIMA 8300, Perkin-Elmer). The ex-situ measurement of V K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) was carried out with a transmission mode at the 7D beamline of Pohang accelerator laboratory (PAL, Korea) in a storage ring of 2.5 GeV with a ring current of 330-360 mA.

Electrochemical Measurements: The electrochemical properties of the V_4P_7 and $VO_2(B)$ electrodes were evaluated using 2032 coin-type half cells, which were fabricated inside an argon-filled glove box by employing poly-propylene (Welcose, Korea) separator and sodium foil counter/reference electrode. The V_4P_7 and $VO_2(B)$ working electrodes were prepared by mixing 70% active material, 15% Super P carbon black, and 15% carboxymethyl cellulose (CMC) binder by weight to form a slurry, which cast onto a piece of copper foil and followed by drying in a vacuum oven at 80 °C overnight. The mass loading of the active material on the copper foil was 1.5-2 mg cm⁻². The electrolyte was 1.0 M NaClO₄ dissolved in a solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) with the addition of 5 vol.% of fluoroethylene carbonate (FEC) additive. Galvanostatic cycling and cyclic voltammetry tests were performed with a battery testing system (Wonatech, Korea) within voltage ranges of 0.01–2 V and 0.01–3 V (vs. Na/Na⁺). Electrochemical impedance spectroscopy (EIS) experiment was carried out at a frequency range of 100 kHz to 0.1 Hz with an AC amplitude of 5 mV using an impedance analyzer (Zive, SP1). For the ex-situ XRD, SEM, and TEM analyses, the electrode materials were collected by disassembling the test cells in the argon-filled glove box, rinsing with DMC several times, and drying at room temperature.

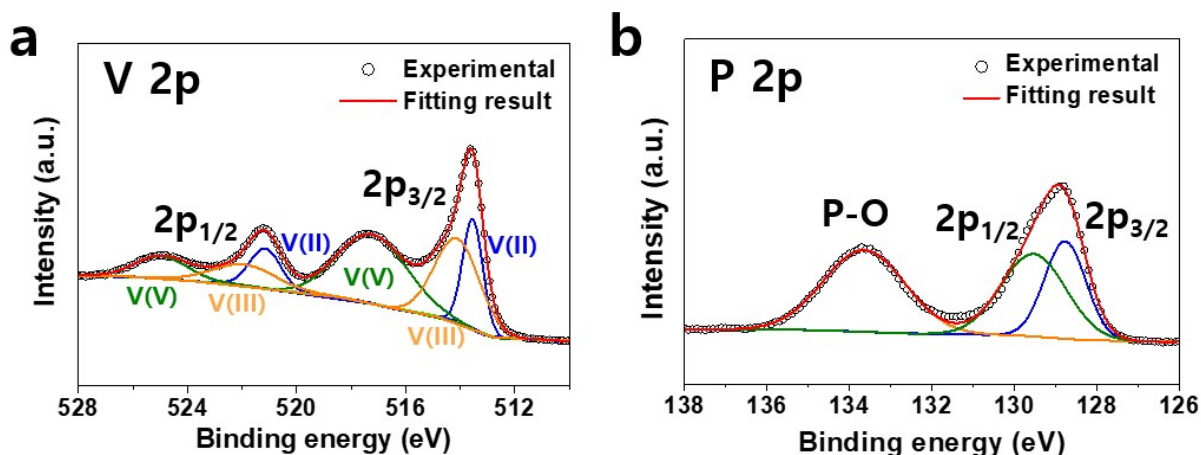


Fig. S1. (a) V 2p and (b) P 2p XPS spectra of as-prepared V_4P_7 nanoparticles.

(The valence states of V and P in as-synthesized V_4P_7 powder were characterized by X-ray photoelectron spectroscopy (XPS). The V2p core level spectrum shows the characteristic peaks of V^{2+} ($2p_{3/2}$ at 513.4 and $2p_{1/2}$ at 521 eV), V^{3+} ($2p_{3/2}$ at 514.5 and $2p_{1/2}$ at 522.7 eV), and V^{5+} ($2p_{3/2}$ at 517.3 and $2p_{1/2}$ at 524.7 eV), respectively (Fig. S1a).^[1,2] The P2p XPS spectrum exhibits two peaks at 129.1 and 130 eV corresponding P $2p_{3/2}$ and P $2p_{1/2}$, respectively (Fig. S1b). The peaks around 133.7 eV in P2p spectrum can be assigned to oxidized P species arising from oxidation as a result of air contact.^[3] The V_4P_7 phase has two partial occupancy sites for phosphorus ions, thus the near-neighbor environments of all 'equivalent' atoms are slightly different, depending on the actual occupancy of the near split-atom positions.^[4] The various valence states of vanadium ions could be derived from the partial occupied sites of phosphorus ions in the crystal structure.

[1] *Appl. Surf. Sci.* 2010, **257**, 887-898.

[2] *J. Elect. Spectro. Related Phenom.* 2004, **135**, 167-175.

[3] *J. Mater. Chem. A.* 2016, **4**, 4686-4690.

[4] *Acta Cryst.* 1976, **B32**, 1499-1505.)

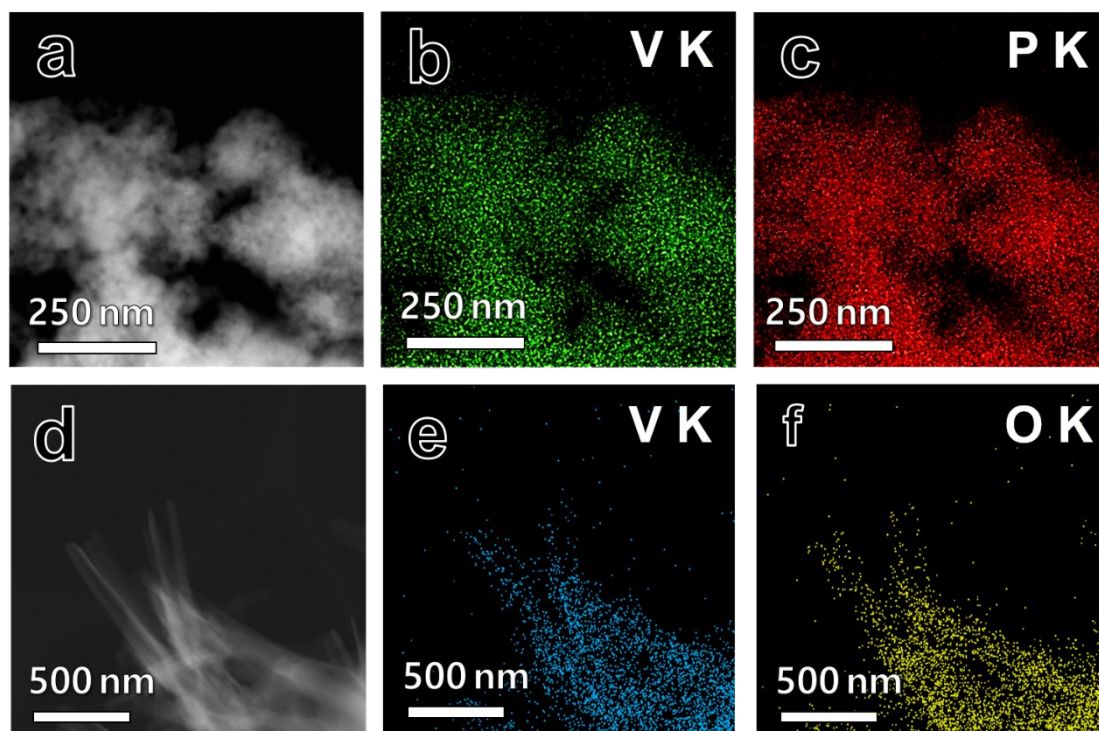


Fig. S2. (a) STEM image of V_4P_7 nanoparticles, (b) V K, and (c) P K EDS mapping of (a) and (d) STEM image of $VO_2(B)$ nanorods, (e) V K, and (f) O K EDS mapping of (d).

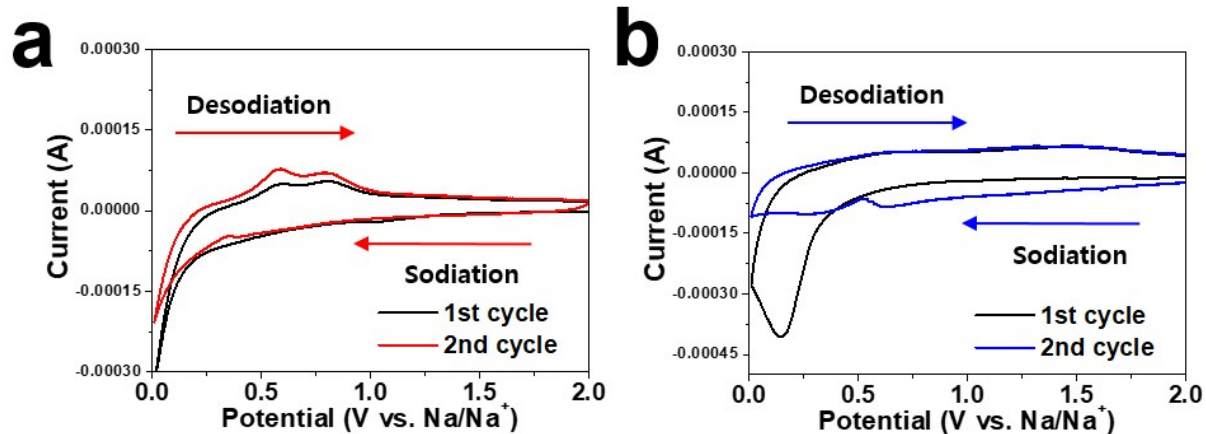


Fig. S3. Cyclic voltammetry (CV) plots at a scan rate of 0.1 mV s^{-1} for (a) V₄P₇ electrode and (b) VO₂(B) electrode, respectively.

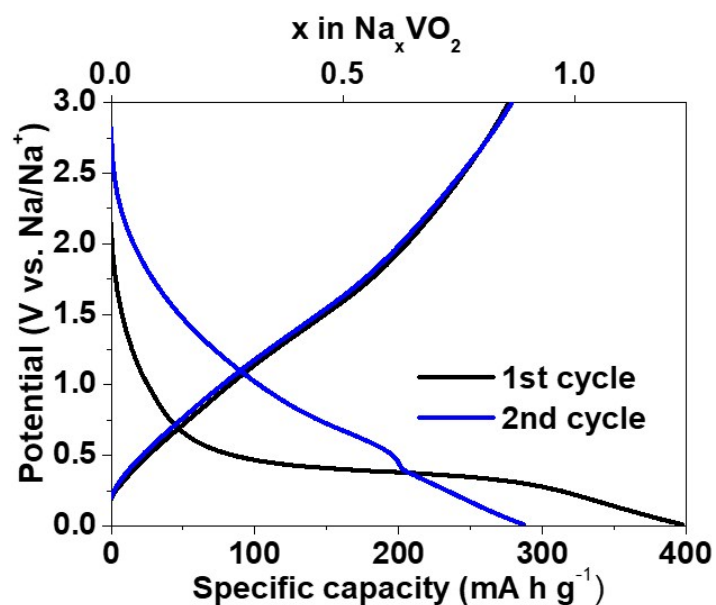


Fig. S4. Galvanostatic discharge/charge voltage profiles of $\text{VO}_2(\text{B})/\text{Na}$ cell at current density of 50 mA g^{-1} with operational potential range from 0.01 to 3.0 V.

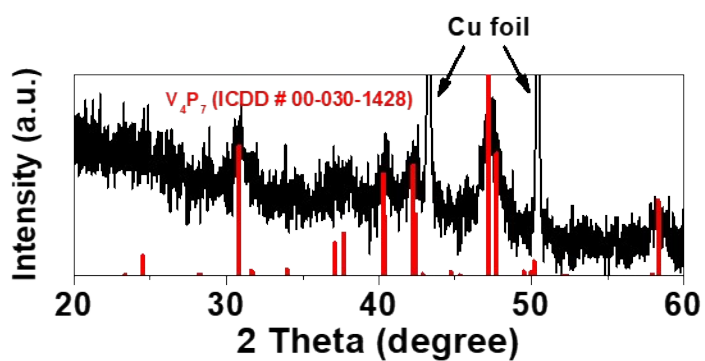


Fig. S5. XRD pattern of V_4P_7 electrode after discharged to 0.01 V after 20th cycle.

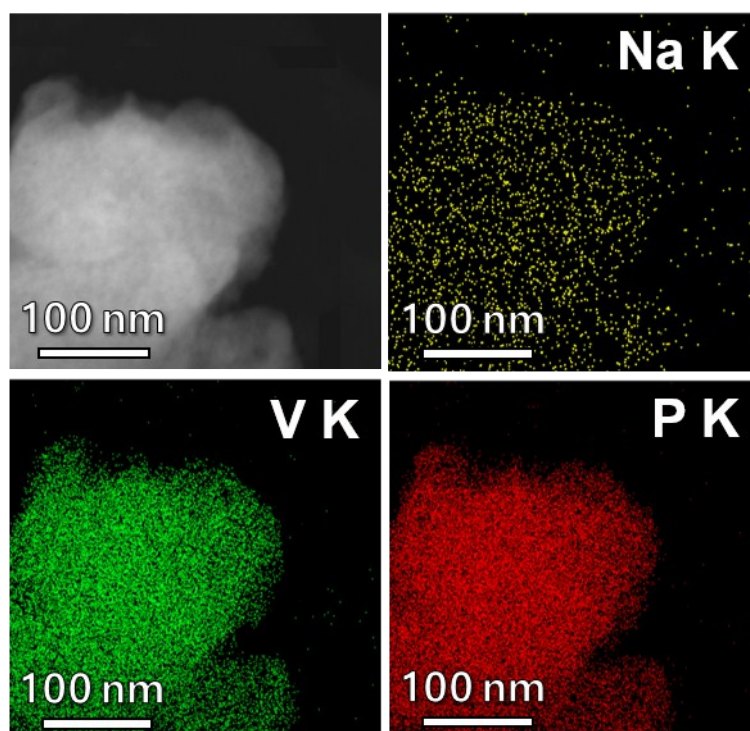


Fig. S6. STEM image and NaK, VK, and PK EDS mapping of V_4P_7 electrode after 1st discharged to 0.01 V.

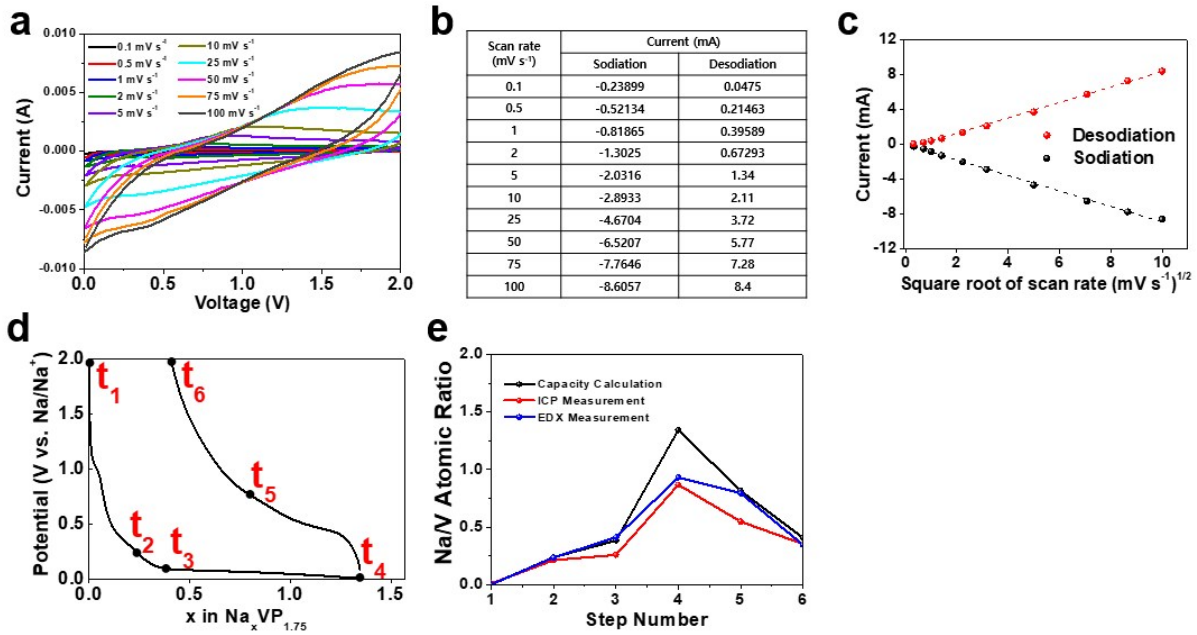


Fig. S7 (a) Cyclic voltammetry (CV) plots as a function of the scan rate, (b) corresponding measured current values, (c) current versus square root of the scan rate, (d) galvanostatic discharge/charge voltage profiles of V_4P_7/Na cell, and (e) Na/V atomic ratio of electrodes by ICP-AES, EDS, and capacity calculation, stopped at various discharge/charge states as shown in (d).

(To identify the successful insertion of Na^+ into bulk V_4P_7 nanoparticles, cyclic voltammetry (CV) test was performed as a function of the scan rate from 0.1 to 100 $mV s^{-1}$ (Fig. S7a, b). Fig. S7c showed the current values as a function of the square root of the scan rate ($v^{1/2}$). Assuming that the current obeys a power-law relationship with the voltage sweep rate leads to $i=av^b$, Fig. S7c showed a linear relation for both the sodiation and desodiation currents with $v^{1/2}$ indicating that Na^+ ions/electrons are stored in the bulk of V_4P_7 as diffusion-controlled reaction rather than at the surface as capacitive reaction ($b=1, i \propto v$).

The cycle tested cell was disassembled in argon-filled glove box and the electrode was washed with dimethylcarbonate (DMC) and acetonitrile to clean the solid electrode interface layer and

surface attached Na-salt and NaClO₄. The atomic ratio of Na/V measured by ICP-AES for the Na/V₄P₇ cell, which did not operate the galvanostatic test, just assembled and de-assembled one is only 0.08 (t₁ of Fig. S7d), indicating very little existence of surface attached NaClO₄ in the electrode, which seems to be negligible. Fig. S7e shows that the atomic ratio of Na/V in the electrode at discharge state increased with decreasing the voltage to 0.01 V (from t₁ to t₄), which means the electrochemical Na ion insertion occurred in the bulk V₄P₇ electrode during the discharge process. On the other hand, Na/V ratio in the electrode at charge state decreased with increasing the voltage to 2.0 V (from t₄ to t₆), which means the electrochemical Na-ion extraction occurred in the bulk V₄P₇ electrode during the charge process.)

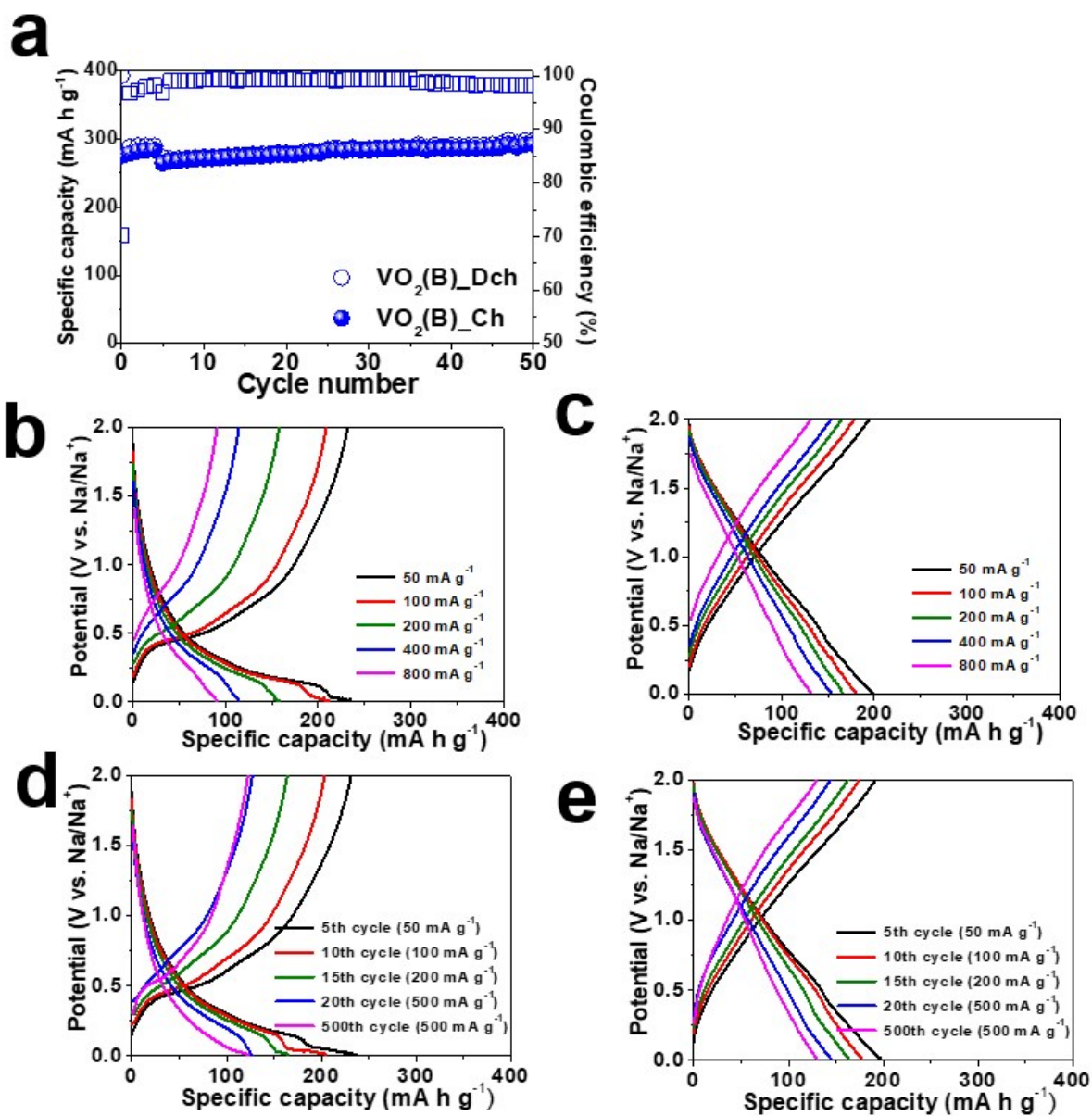


Fig. S8 (a) Cycling performance tested at a current density of 100 mA g⁻¹ in the voltage range of 0.01-3.0 V for VO₂(B) electrode and discharge/charge voltage profiles of rate capability and long-term cycle retention tested at current density of 500 mA g⁻¹ for (b,d) V₄P₇ and (c,e) VO₂(B) electrodes, respectively.

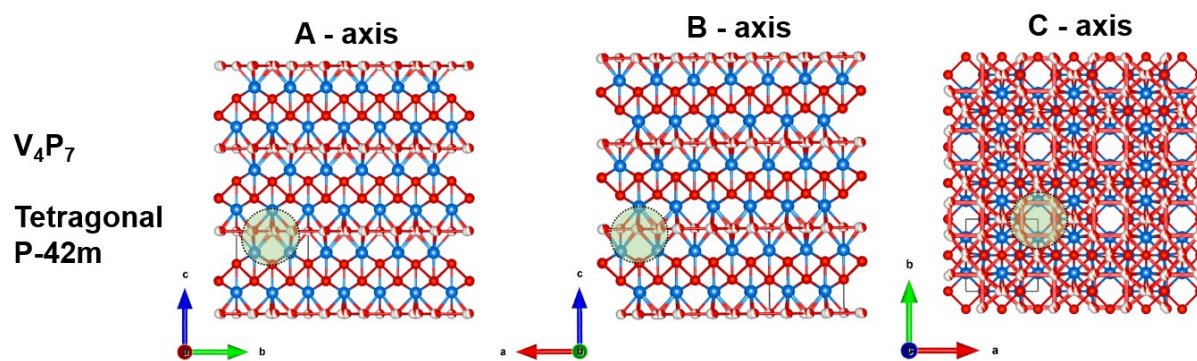


Fig. S9 The crystal structure of V_4P_7 tetragonal phase along a, b, and c-axis.