

Supporting Information

VOPO₄·2H₂O as a new cathode material for rechargeable Ca-ion batteries

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Experimental section

Materials synthesis

VOPO₄·2H₂O was synthesized by one-step hydrothermal method. Firstly, 2.4 g V₂O₅ was added to 57.7 mL ultra-pure water. After stirred for 30 min, 13.3 mL H₃PO₄ was added to the above solution and stirred for another 2 h. The obtained solution was transferred into a 100 mL Teflon-lined stainless steel autoclave. The sealed autoclave was put into an oven at 120 °C for 17 h. After that, the sealed autoclave was cooled down naturally to room temperature, and the obtained bright yellow product was washed with deionized water for three times and acetone for three times, respectively. The obtained bright yellow product was stored under ambient conditions.

Material characterization

XRD measurement was performed using a Bruker AXS D8 Advance powder X-ray diffractometer with an area detector using Cu K α X-ray source. SEM images

were acquired by using a JEOL-7100F microscope. A Titan G2 60-300 instrument was used for transmission electron microscopy (TEM), high resolution TEM, HAADF images and energy dispersive X-ray spectroscopy (EDX) maps tests. VG Multi Lab 2000 instrument was used for XPS measurement. Renishaw INVIA micro-Raman spectroscopy system was used for Raman experiments. ICP measurements were conducted using a PerkinElmer Optima 4300DV spectrometer. The TGA was carried out on a NETZSCH-STA449F5 thermoanalyzer with a heating rate of 10 °C min⁻¹ and air atmosphere. Fourier Transform Infrared Spectroscopy spectrum of VOPO₄·2H₂O was obtained by FT-IR Spectrometer, Model Spectrum Two.

Electrochemical tests

The positive electrode was made with VOPO₄·2H₂O powder (70 wt%), acetylene black (AB, 20 wt%), and poly(vinylidene fluoride) (PVDF, 10 wt%). They were mixed and dispersed in N-methyl-2-pyrrolidinone (NMP) to form a slurry, and the slurry was cast onto Ti foil and dried at ambient temperature in a vacuum oven. Finally, the electrochemical performances for CIBs was tested by Swagelok-type cell (Fig. S3) assembled with the prepared positive electrode, GF/A as separator, 0.8 M Ca(TFSI)₂ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate (PC), ethylmethyl carbonate (EMC) with vol/vol/vol/vol = 2:3:2:3 as the electrolyte and ACC as both reference and counter electrode. GITT measurement was conducted with a multichannel battery testing system (LAND CT2001A). CV and galvanostatic discharge-charge tests were performed with an Autolab PGSTAT 302N electrochemical workstation. The Ca²⁺ diffusion coefficients (D^{GITT}) were calculated according to the GITT curves by the following equation:

$$D^{GITT} = \frac{4}{\pi t} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (1)$$

where the D^{GITT} (cm² s⁻¹) is Ca²⁺ diffusion coefficient, m_B , M_B , V_M , t , and S are the mass, molar mass, molar volume of VOPO₄·2H₂O, constant current pulse time, and electrode–electrolyte contact area, respectively.

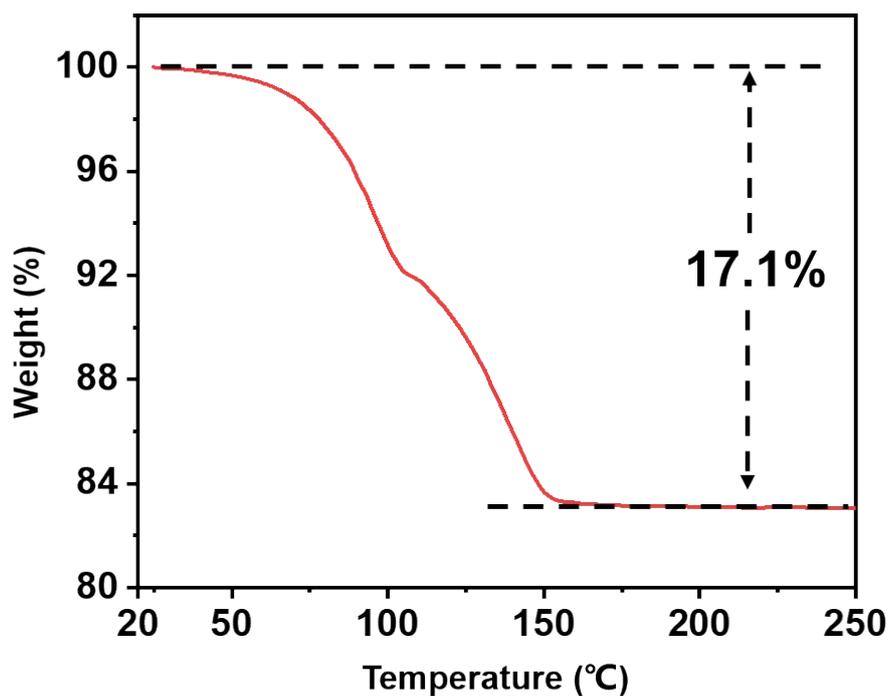


Fig. S1 TGA for VOPO₄·2H₂O with a heating rate of 10 °C min⁻¹ and air atmosphere.

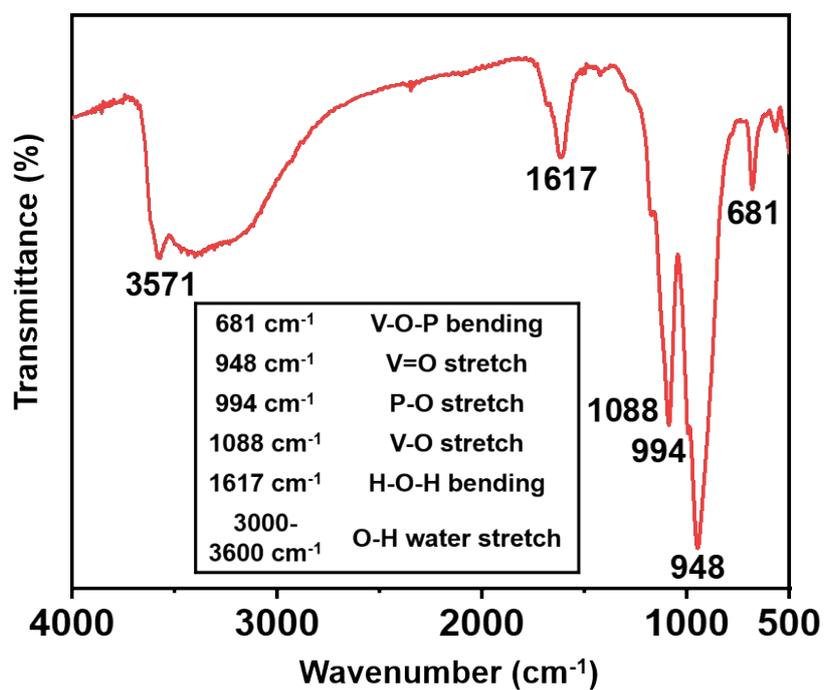


Fig. S2 FT-IR spectrum of VOPO₄·2H₂O.

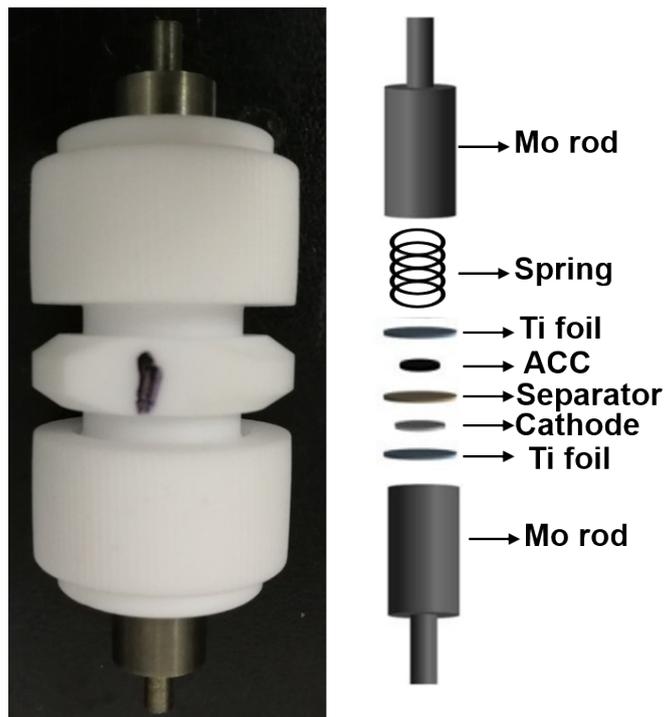


Fig. S3 The photograph and illustration of the Swagelok-type cell.

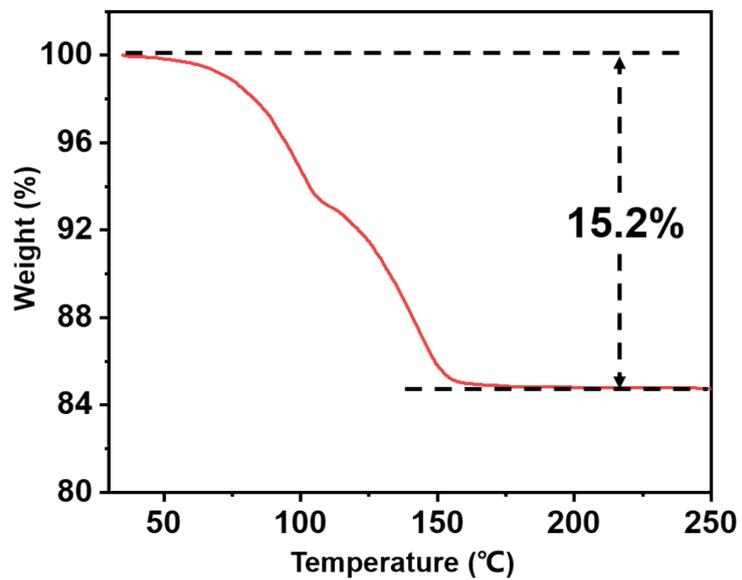


Fig. S4 TGA for $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ after aged for 5 hours.

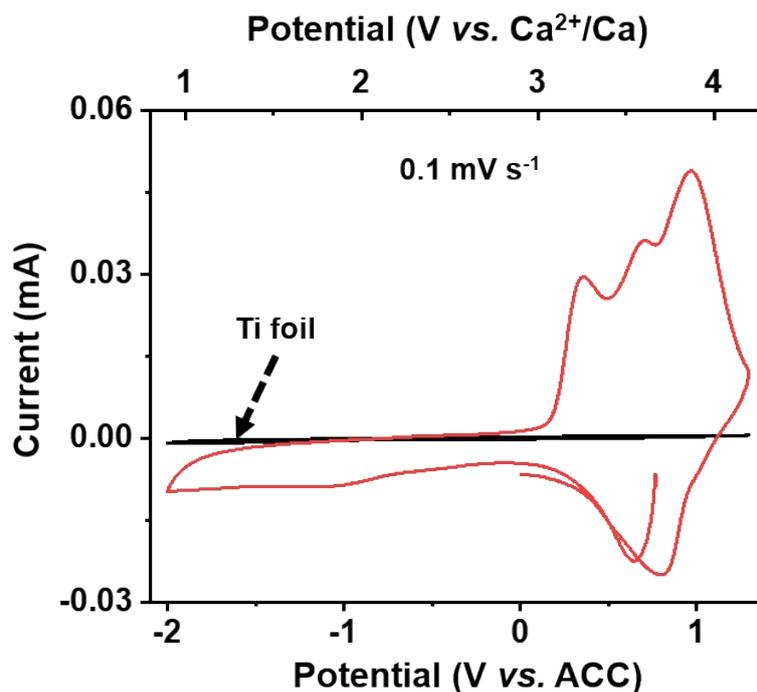


Fig. S5 CV curves of Ti foil and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ electrode at 0.1 mV s^{-1} .

The ICP result (Fig. S6) in the discharged state indicates that the molar ratio of Ca to V is 0.35 corresponding to a discharge capacity of 95 mA h g^{-1} , which is consistent with the discharge capacity obtained from the experiment.



Fig. S6 *Ex situ* ICP measurements at different states.

Tab. S1 The Ca²⁺ storage performance of VOPO₄·2H₂O and the reported cathode materials for CIBs with organic electrolyte.

Cathode material	Anode material	Reference electrode	Average working potential (V)	Reversible capacity (mAh g ⁻¹) /current density (mA g ⁻¹)	Cycles	Reference
VOPO ₄ ·2H ₂ O	ACC	/	-0.1	71.8/100	200	This work
Mg _{0.25} V ₂ O ₅ ·H ₂ O	ACC	/	-1.2	70.0/100	500	1
Na _x MnFe(CN) ₆	Ca _x Sn	/	0.8	85.0/10	35	2
K ₂ BaFe(CN) ₆	Carbon paper	Ag/AgCl	0.1	60.0/12.5	30	3
CaCo ₂ O ₄	V ₂ O ₅	/	-0.2	93/40	30	4
Na ₂ FePO ₄ F	BP2000 carbon	/	0.0	60/10	50	5
NH ₄ V ₄ O ₁₀	Pt	Ag/Ag ⁺	0.1	150/100	100	6
α-MoO ₃	Activated carbon	Ca	1.1	140/2	12	7
V ₂ O ₅	Activated carbon	Ag/Ag ⁺	-1	150/1.6	5	8
Fe ₄ [Fe(CN) ₆] ₃	Graphite rod	Fc/Fc ⁺	0.4	120/125	80	9

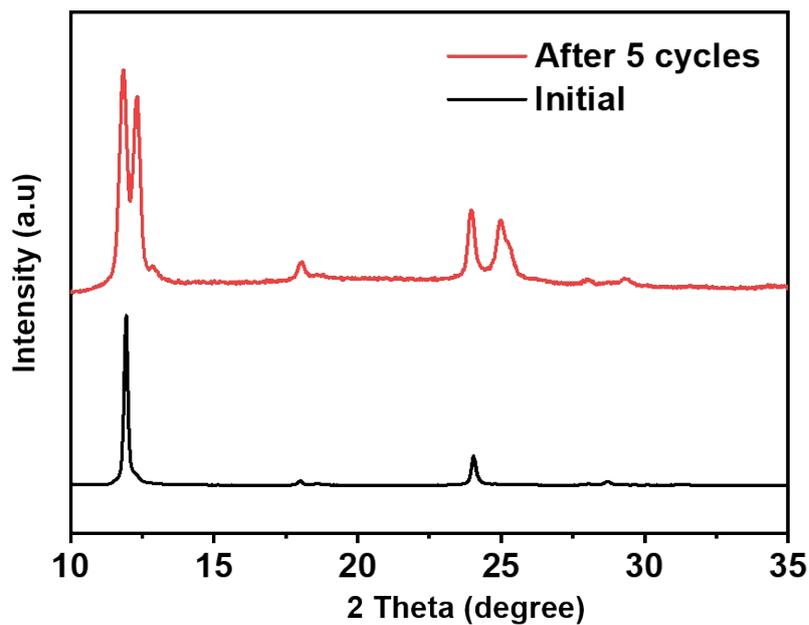


Fig. S7 XRD patterns of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ after 5 cycles.

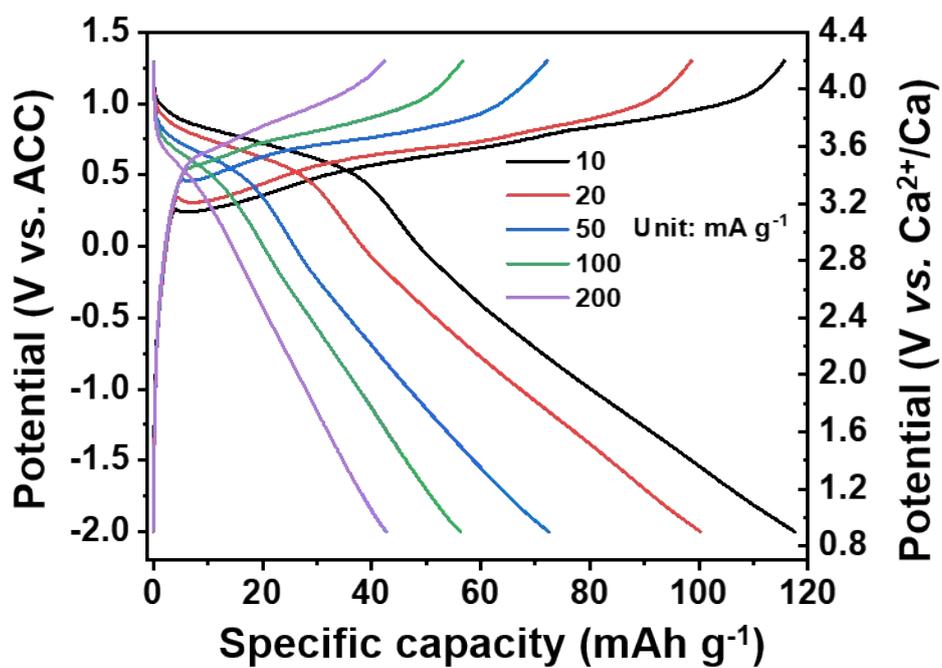


Fig. S8 Charge/discharge curves of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ electrode at different current densities.

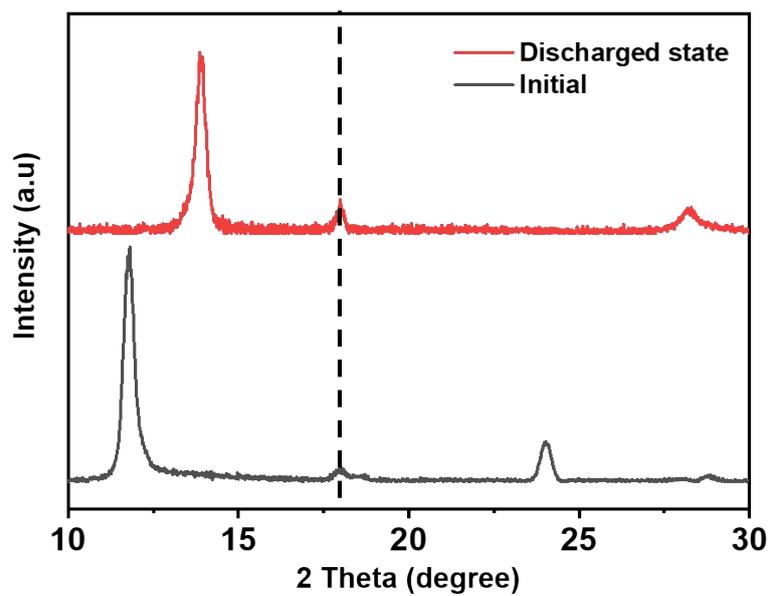


Fig. S9 *Ex situ* XRD patterns at different states.

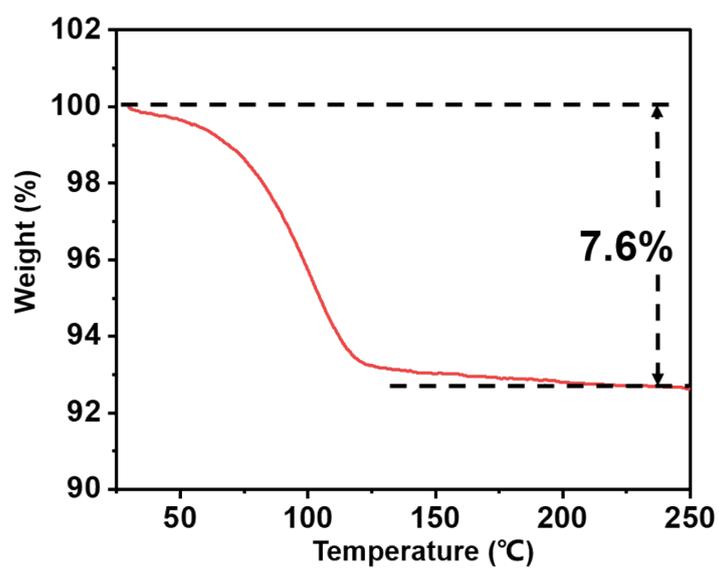


Fig. S10 TGA for the discharged $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

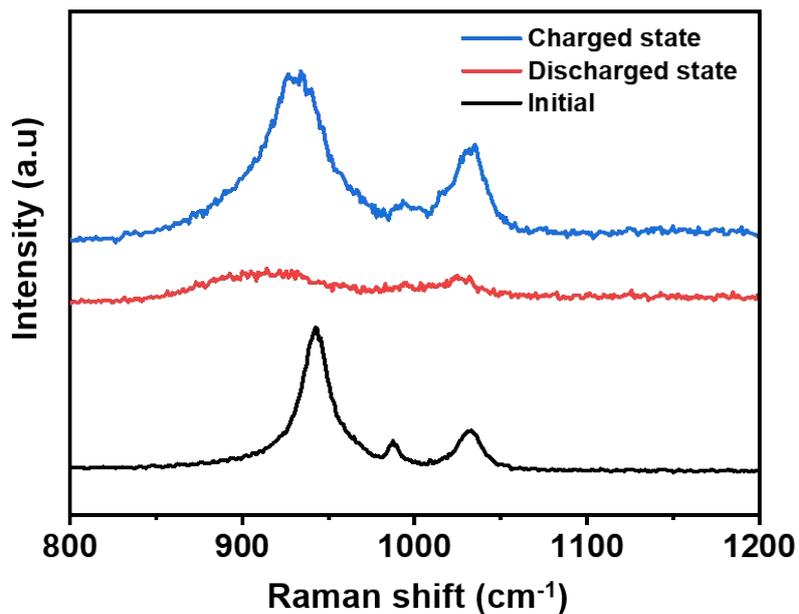


Fig. S11 *Ex situ* Raman spectrums at different states.

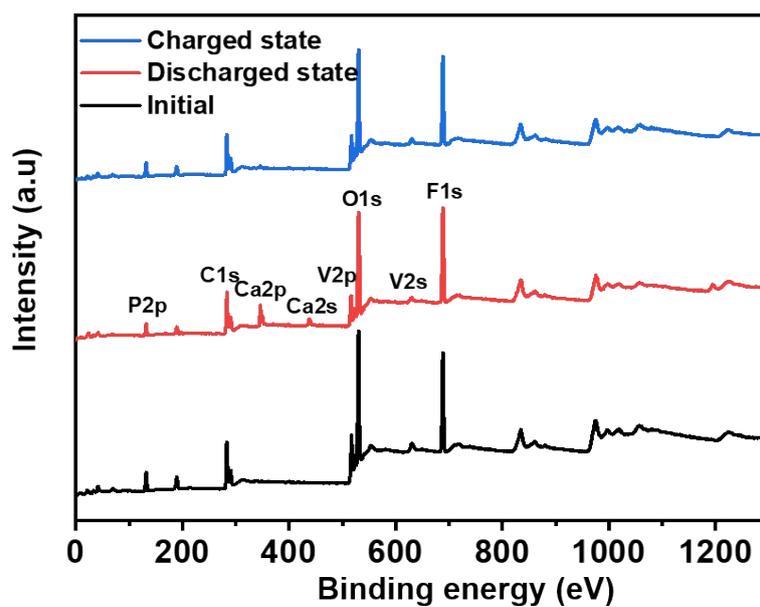


Fig. S12 *Ex situ* XPS spectra at different states.

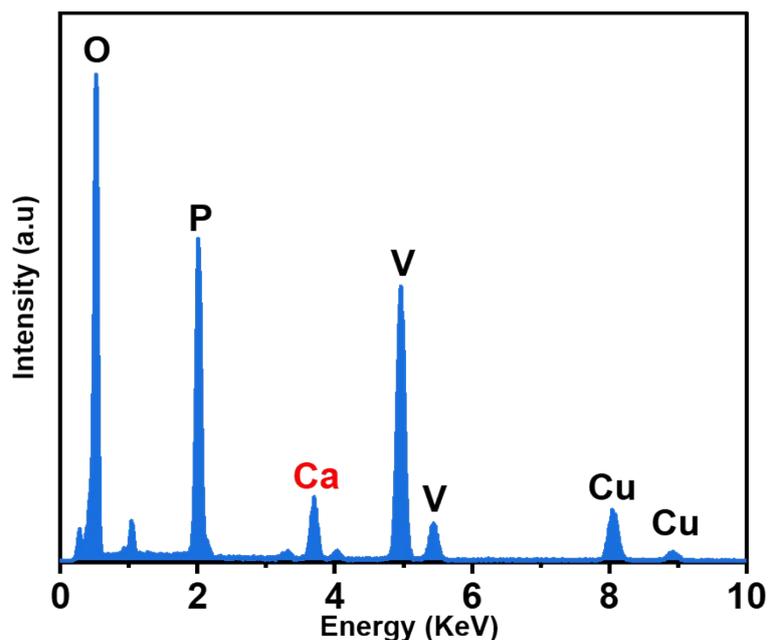


Fig. S13 EDX spectra for $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ at the discharged state.

References

- 1 X. Xu, M. Duan, Y. Yue, Q. Li, X. Zhang, L. Wu, P. Wu, B. Song and L. Mai, *ACS Energy Lett.*, 2019, **4**, 1328-1335.
- 2 A. L. Lipson, B. Pan, S. H. Lapidus, C. Liao, J. T. Vaughey and B. J. Ingram, *Chem. Mater.*, 2015, **27**, 8442-8447.
- 3 P. Padigi, G. Goncher, D. Evans and R. Solanki, *J. Power Sources*, 2015, **273**, 460-464.
- 4 M. Cabello, F. Nacimiento, J. R. González, G. Ortiz, R. Alcántara, P. Lavela, C. Pérez-Vicente and J. L. Tirado, *Electrochem. Commun.*, 2016, **67**, 59-64.
- 5 A. L. Lipson, S. Kim, B. Pan, C. Liao, T. T. Fister and B. J. Ingram, *J. Power Sources*, 2017, **369**, 133-137.
- 6 T. N. Vo, H. Kim, J. Hur, W. Choi and I. T. Kim, *J. Mater. Chem. A*, 2018, **6**, 22645-22654.
- 7 M. Cabello, F. Nacimiento, R. Alcántara, P. Lavela, C. Pérez Vicente and J. L. Tirado, *Chem. Mater.*, 2018, **30**, 5853-5861.
- 8 Y. Murata, S. Takada, T. Obata, T. Tojo, R. Inada and Y. Sakurai, *Electrochim. Acta*, 2019, **294**, 210-216.
- 9 N. Kuperman, P. Padigi, G. Goncher, D. Evans, J. Thiebes and R. Solanki, *J. Power Sources*, 2017, **342**, 414-418.