

Supplementary Information

A vanadium-based metal-organic phosphate framework material:

$\text{K}_2[(\text{VO})_2(\text{HPO}_4)_2(\text{C}_2\text{O}_4)]$ as a cathode for potassium-ion battery

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Experimental section

Materials synthesis

2 mmol V_2O_5 and 6 mmol oxalic acid were added to 50 mL of deionized water, and maintained at 70 °C for 1 h with vigorous stirring to form a blue solution. After cooling down to room temperature, 12 mmol KH_2PO_4 (200% excess) was added to the solution, and then transferred into a 80 mL Teflon-lined stainless steel autoclave and sealed. The autoclave was maintained at 160 °C for 12 h with natural cooling outside the oven. A light green precipitate of KVPC-L was washed with deionized water and ethanol for several times, and then dried in air at room temperature. The KVPC-S was synthesized by the same way, but the precursor concentration was tenfold higher. The KVPC-L and KVPC-S samples were further vacuum dried at 120 °C for better electrochemical performance.

Characterization

The phases of as-obtained KVPC samples were characterized with an X-ray diffractometer (Philips X'Pert Pro Super, Cu $K\alpha$ radiation). The morphology of the samples was studied with a scanning electron microscope (SEM, JSM-6390LA) and a transmission electron microscope (TEM, JEM-2100F). The elemental compositions were analyzed by energy dispersive X-ray spectroscopy (EDS) attached to the SEM instrument. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C min^{-1} in the temperature range of 25-600 °C under flowing N_2 atmosphere (DTG-60H, Shinadzu). FTIR (Magna-IR 750 spectrometer) was performed in the range of 400-4000 cm^{-1} . The N_2 -adsorption/desorption isotherms were measured with an ASAP 2020 Accelerated Surface Area instrument.

Electrochemical evaluation

The KVPC electrodes were prepared by mixing the active material (70 wt. %), acetylene black (20 wt. %) and poly(vinylidene fluoride) (10 wt. %) binder in N-

methyl-2-pyrrolidinone to obtain slurries, which were coated on an aluminium foil collector and vacuum dried at 120 °C. The typical KVPC loading was about 1.5 mg cm⁻². The electrochemical properties of the obtained KVPC-L and KVPC-S materials were evaluated in coin-type cells (CR2032 size), which were assembled in an argon filled glove box (MBraun Labmaster 130). For the fabrication of potassium half cells, potassium metal was used as the counter electrode, 0.1 mol L⁻¹ (saturated) KClO₄ in PC was used as the electrolyte and a Whatman glass-fiber separator was used. The cyclic voltammetry (CV) of the cells were conducted on a CHI 660C electrochemical workstation in a voltage range from 2.0 to 4.6 V at a scan rate of 0.1 mV s⁻¹. The cells were also galvanostatically cycled on a multi-channel battery test system (Neware BTS-2300, Shenzhen) in the voltage range from 2.0 to 4.6 V at 30 °C.

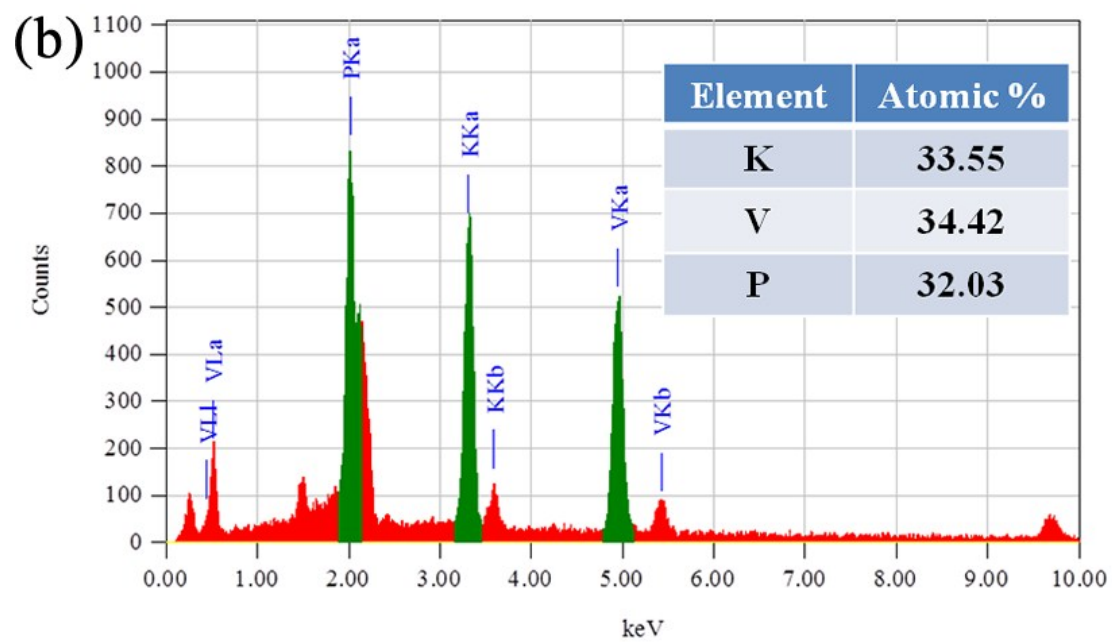
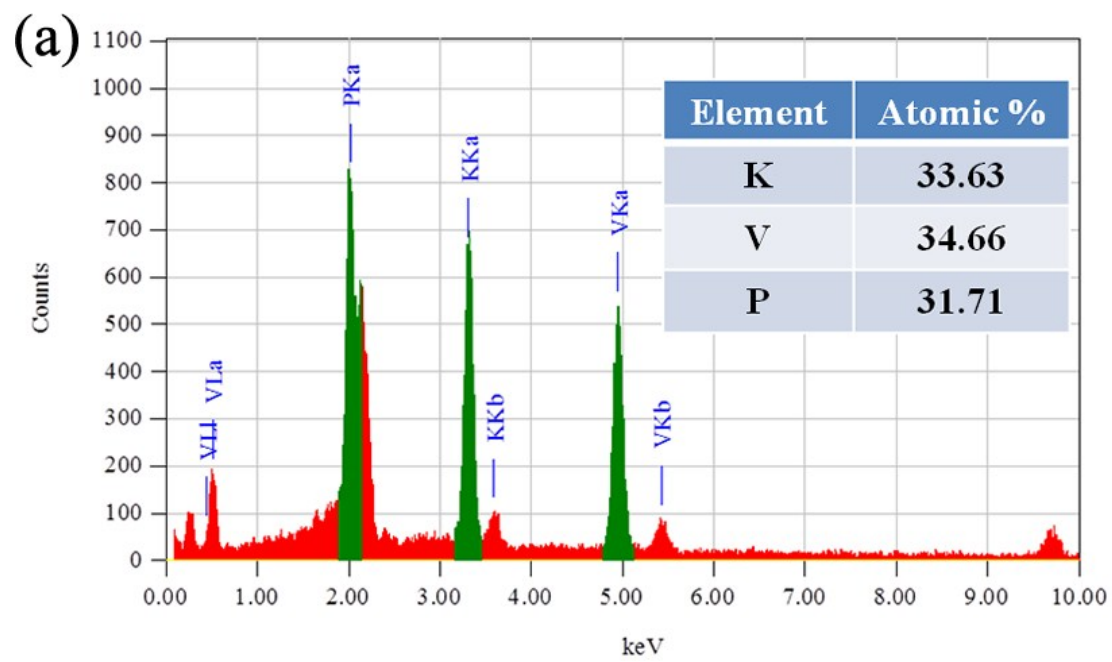


Fig. S1. EDS results of KVPC-L (a) and KVPC-S (b).

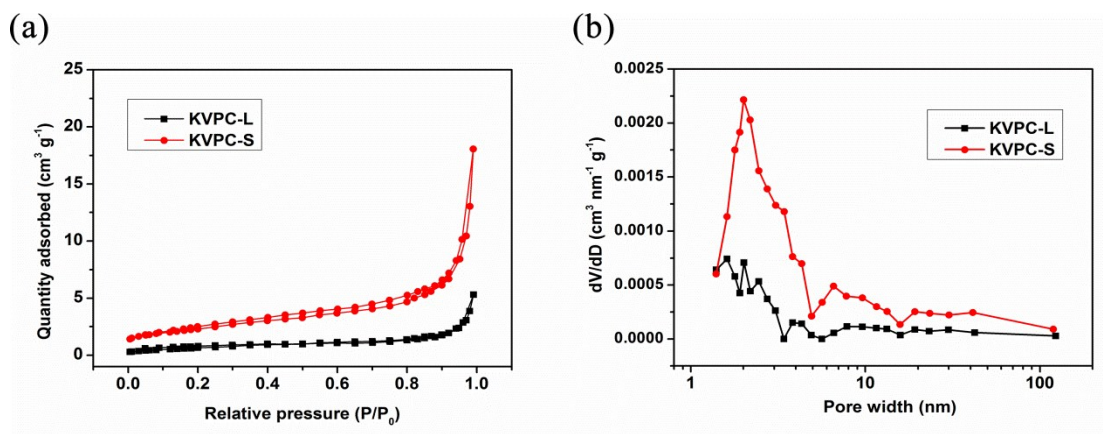


Fig. S2. N₂ adsorption-desorption isotherms (a) and pore size distribution curves (b) of KVPC-L and KVPC-S.

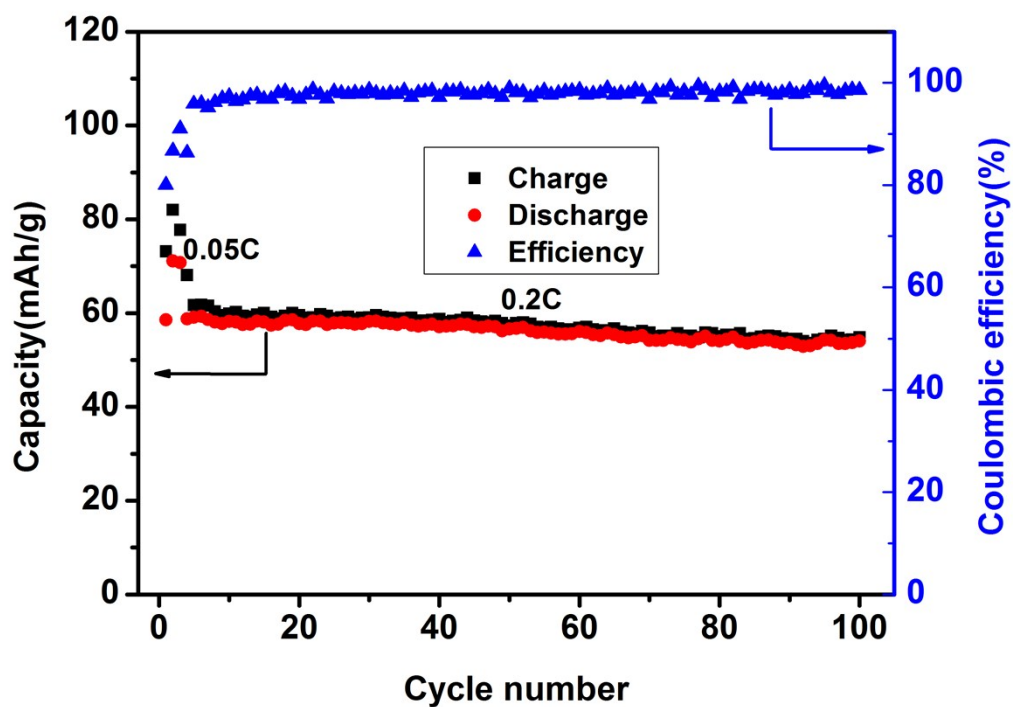


Fig. S3. Cycling performances of KVPC-L in the voltage range of 2.0-4.6 V in 0.1 mol L⁻¹ KClO₄-PC (It was activated three times at a low current density of 0.05C and then cycled at 0.2C, 1C=109 mAh g⁻¹).

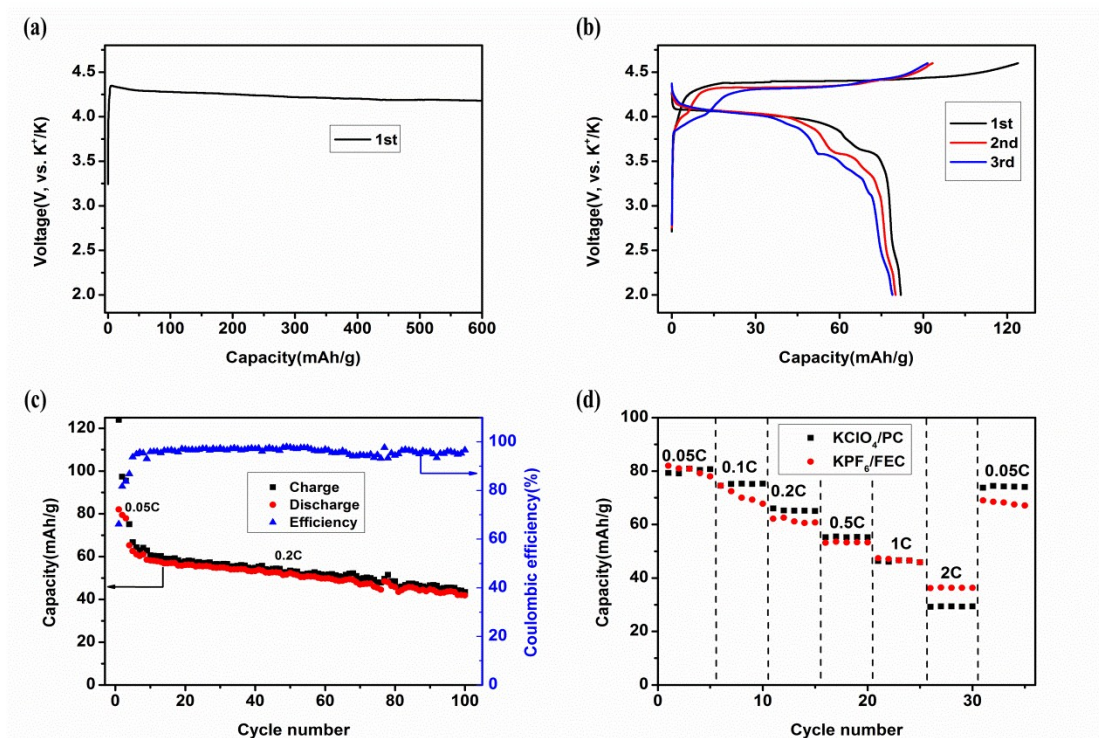


Fig. S4. Charge-discharge curves of KVPC-S in 0.8 mol L⁻¹ KPF₆-EC/DEC (+2%FEC) (a) and 0.3 mol L⁻¹ KPF₆-FEC (b); (c) Cycling performances of KVPC-S in 0.3 mol L⁻¹ KPF₆-FEC; (d) Comparison of the rate capability of KVPC-S in different electrolyte.

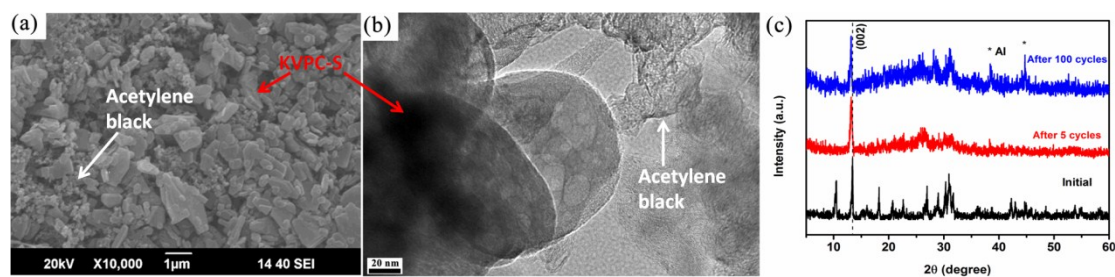


Fig. S5. SEM image (a) and TEM image (b) of KVPC-S after the 100th cycle. The XRD patterns of KVPC-S after the 5th and 100th cycles are also presented in (c).

Table S1. Comparison of the electrochemical performance of KVPC with layered and polyanionic cathodes in KIBs

Composition	Capacity (mAh g ⁻¹)	Average discharge voltage (V)	Average capacity decay rate per cycle (current density)	Reference	Classification
P2-K _{0.3} MnO ₂	136	2.7	0.84% (27.9 mA g ⁻¹)	[2]	Layered
P2-K _{0.6} CoO ₂	78	2.7	0.33% (100 mA g ⁻¹)	[3]	
P3-K _{0.5} MnO ₂	97	2.6	0.60% (20 mA g ⁻¹)	[4]	
P3-K _{0.67} Ni _{0.17} Co _{0.17} Mn _{0.66} O ₂	76.5	2.9	0.13% (20 mA g ⁻¹)	[5]	
K _{0.7} Fe _{0.5} Mn _{0.5} O ₂	178	2.3	0.67% (20 mA g ⁻¹)	[6]	
P2-K _{0.65} Fe _{0.5} Mn _{0.5} O ₂	149	2.5	0.06% (100 mA g ⁻¹)	[7]	
P3-K _{0.69} CrO ₂	100	2.5	0.04% (100 mA g ⁻¹)	[8]	
V ₂ O ₅ ·0.6H ₂ O	224.4	2.2	0.11% (50 mA g ⁻¹)	[29]	
KVOPO ₄	84	4.0	0.22% (6.65 mA g ⁻¹)	[10]	Polyanionic
KVPO ₄ F	92	4.1	0.06% (6.65 mA g ⁻¹)	[10]	
K ₃ V ₂ (PO ₄) ₃	54	3.5	0.22% (20 mA g ⁻¹)	[11]	
KVP ₂ O ₇	60	4.2	0.18% (25 mA g ⁻¹)	[14]	
K ₃ V ₂ (PO ₄) ₂ F ₃	100	3.7	0.06% (20 mA g ⁻¹)	[15]	
K ₂ [(VO) ₂ (HPO ₄) ₂ (C ₂ O ₄)]	81	3.6	0.08% (21.8 mA g ⁻¹)	This work	