Supporting Information

Experiments

Sample preparation

The preparation of P-VPO.

Preparation of $VOPO_4 \cdot 2H_2O$: $VOPO_4 \cdot 2H_2O$ is synthesized by a conventional hydrothermal method. First 1.68 g of V_2O_5 and 9.5 ml of H_3PO_4 were added to 43 ml of deionized H_2O with continuous stirring for 2 h. The homogeneous solution obtained was transferred to a 100 mL Teflon-lined stainless-steel autoclave and kept at 120 °C for 17 h. Finally, it was collected by centrifugation and washed with deionized H_2O to obtain yellow powder, which was dried in a vacuum at 60 °C overnight.

Preparation of P-VPO: 0.4 g of the prepared $VOPO_4 \cdot 2H_2O$ was taken and added to 40 ml of isopropanol and stirred for 5 min, then 6 ml of phenylamine was added and stirred for 30 min, and the obtained solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave and kept at 60 °C for 3 h. Finally, it was collected by centrifugation and washed with deionized H_2O to obtain dark grey powder, which was dried in a vacuum at 60 °C overnight.

Electrochemical measurements.

The CR2032-type coin cells were assembled for electrochemical measurements. P-VPO cathode was prepared by mixing active material, carbon black (Super P) and polyvinylidene fluoride (PVDF) in the mass ratio 7:2:1 with N-methyl-2-pyrrolidone on Ti foil and then drying overnight at 100 °C in a vacuum oven. The AC anode was

prepared by mixing commercial activated carbon (AC), carbon black (Super P) and polyvinylidene fluoride (PVDF) in the mass ratio of 8:1:1 with N-methyl-2-pyrrolidone and coating on Ti foil, which was then dried overnight at 100 °C in a vacuum oven. A glass fibrous membrane was used as a spacer. An aqueous solution of 1M $Ca(ClO_4)_2$ was used as the electrolyte. (3M $Al(CF_3SO_3)_3$ was used for the aqueous aluminium ion batteries system), and the cells of both systems were tested in the ranges of -1.4-1.6 V (Vs AC) and -1.1-1.2 V (Vs AC), respectively. Cyclic voltammetry (CV) was performed on a ChenHua CHI 660 electrochemical workstation.

Characterization

The crystal structure of all the samples was investigated by X-ray powder diffractometer (XRD, Bruker D8) with Cu Kα (λ = 0.15406 nm). The elemental composition and valence states of P-VPO and VPO were characterized by the X-ray photoelectron spectrum (XPS, VG Scientific with 300 W Al Kα source). The morphology features of simples were tested by scanning electron microscopy (SEM, Hitachi-SU8000) and transmission electron microscopy (TEM, JEOL-2100F). Thermogravimetric analysis (TGA, TA Instruments Q5000) was performed at a heating rate of 10 °C min^{-1} under Nitrogen atmosphere. Fourier Transform infrared spectroscopy (FTIR, Nicolet 6700) was investigated to analyze chemical bonds.

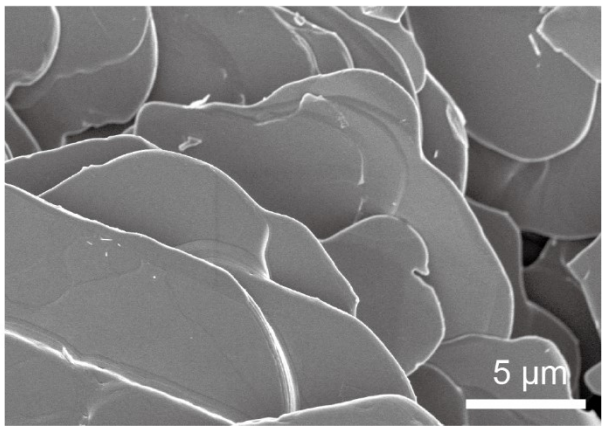

Figure.S1 The SEM image of VPO.

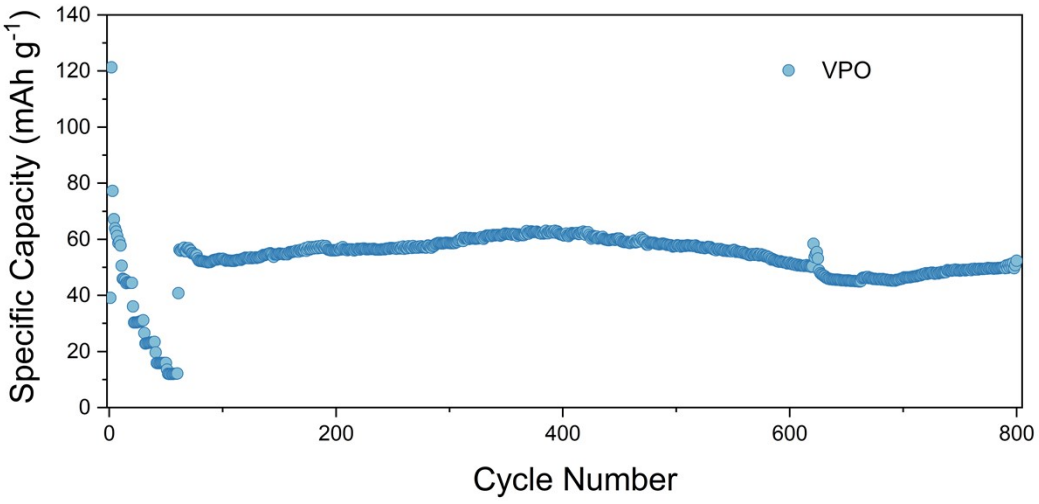

Figure.S2 Long-term cyclic stability at 0.1 A g^{-1} of ACIBs.

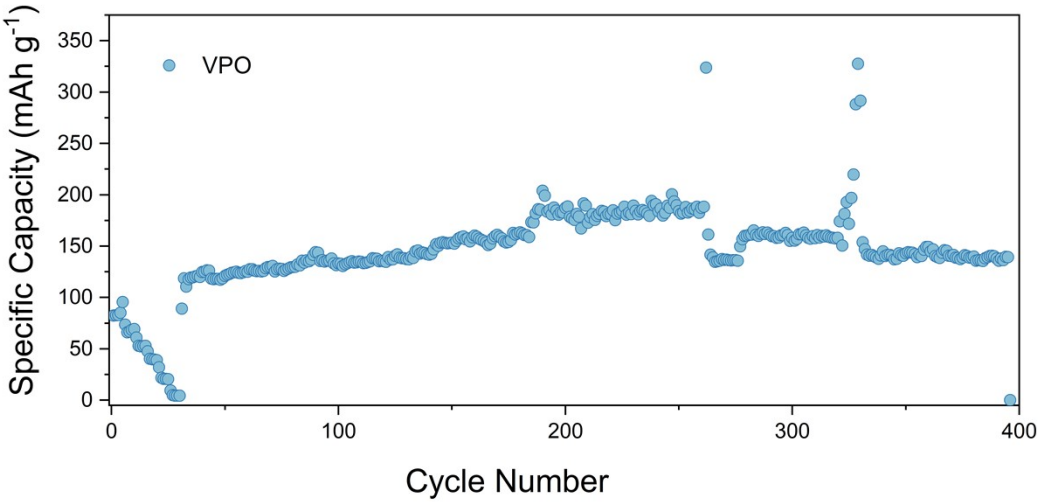

Figure.S3 Long-term cyclic stability at 0.1 A g^{-1} of AAIBs.

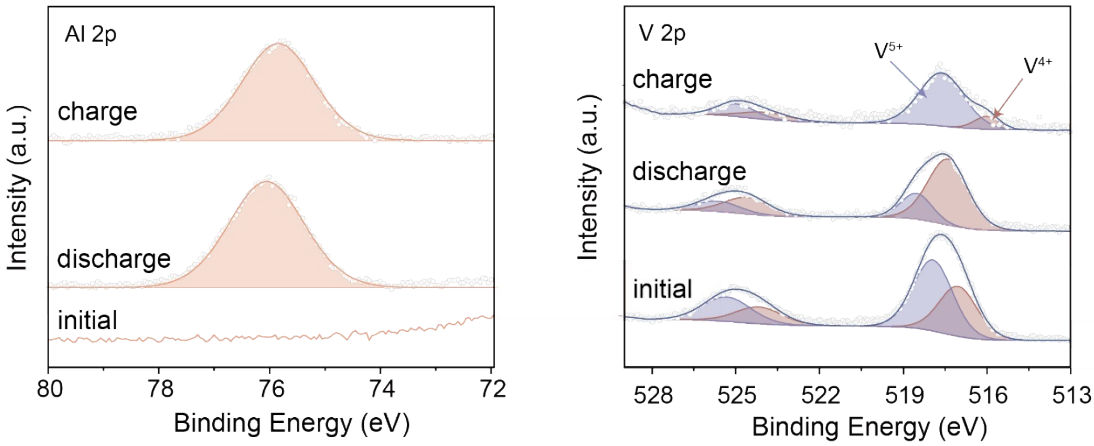

Figure.S4 Al 2p and V 2p XPS spectra at different charged/discharged states.

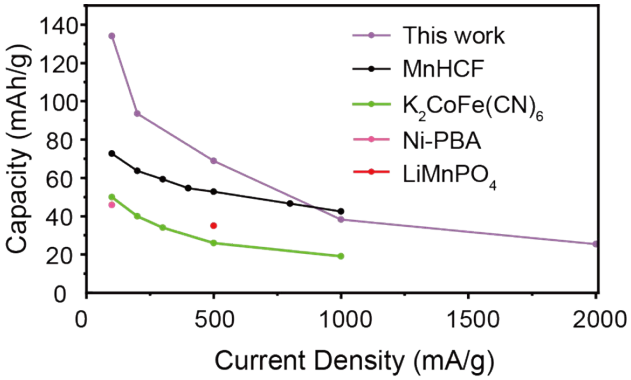

Figure.S5 Comparison on specific capacity of similar cathodes for AAIBs.

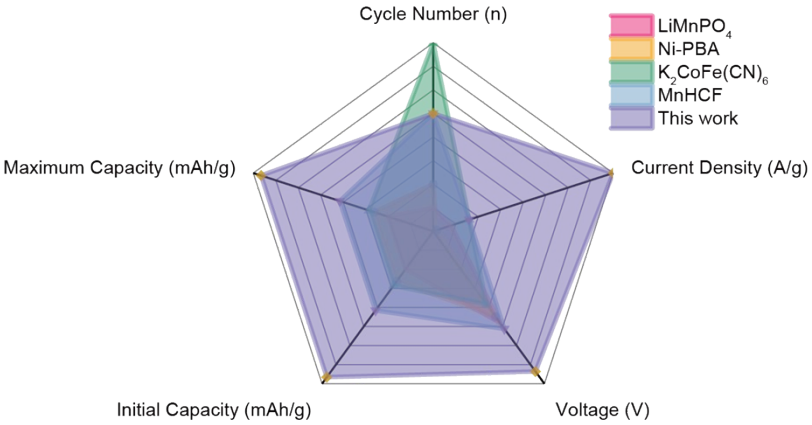

Figure.S6 Comparison on comprehensive properties of similar cathodes for AAIBs.[1-4]

References

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