Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Stabilization of $VOPO_4 \cdot 2H_2O$ voltage and capacity retention in aqueous zinc batteries with a hydrogen bond regulator

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Experimental Procedures

$VOPO_4 \cdot 2H_2O$ was synthesized by a reflux process. Typically, 0.8 g of V_2O_5, 4.4 mL of H_3PO_4 (85%) and 30 mL of H_2O were refluxed for 8 h. The precipitation was filtered, washed with ethanol and deionized water for several times and dried at 60 °C in a vacuum oven.

Characterizations

X-ray diffraction (XRD) data was collected on a PANalytical Empyrean diffractometer with Cu-Kα radiation. Morphologies were characterized by a scanning electron microscope equipped with an energy dispersive X-ray spectroscopy (EDS) detector (SU8010, HITACHI, Japan). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an XPS spectrometer with Al-Kα radiation (8.34 Å) as the excitation source (ESCALAB 250Xi, Thermo Scientific Escalab, USA). The Fourier transform infrared (FT-IR) spectra were collected on Lambda 650S (UK PerkinElmer). Raman spectra were obtained on a LabRAM HR Evolution series high-resolution Raman spectrometer (Nano Wizard Ultra Speed & inVia Raman, Germany) with a laser wavelength of 633 nm.

Electrochemical Measurements

$VOPO_4 \cdot 2H_2O$ and Ketjen Black were mixed with a weight ratio of 2:1 in water and drop casted on carbon paper substrates. Galvanostatic charge-discharge was carried out in coin cells with $VOPO_4 \cdot 2H_2O$ and Zn foil as the cathode and anode, respectively. Electrochemical impedance spectroscopy (EIS) was recorded in three-electrode cells with Zn as the counter and reference electrodes. Electrochemical studies were performed on the Bio-logic VMP3 or Land CT-2001A battery cyclers.

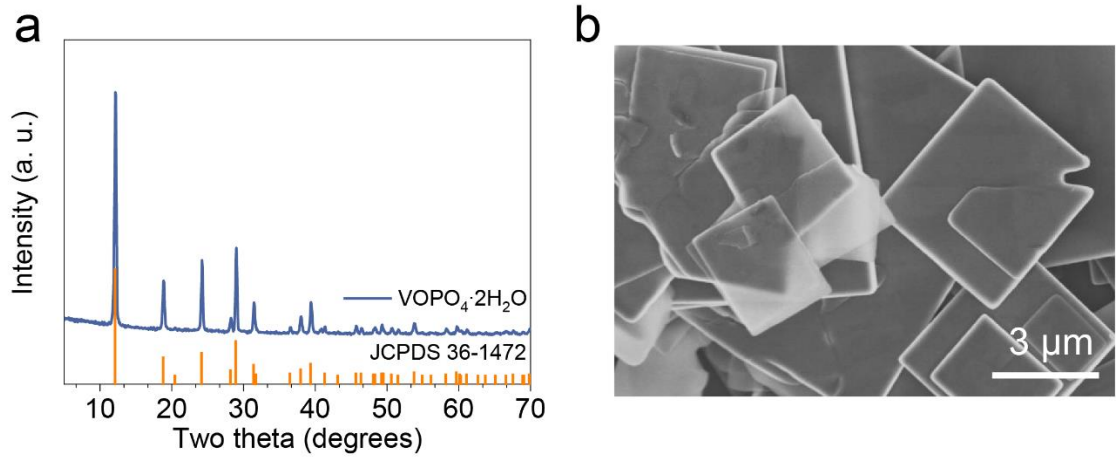

Figure S1. a) XRD pattern and b) SEM image of $VOPO_4 \cdot 2H_2O$.

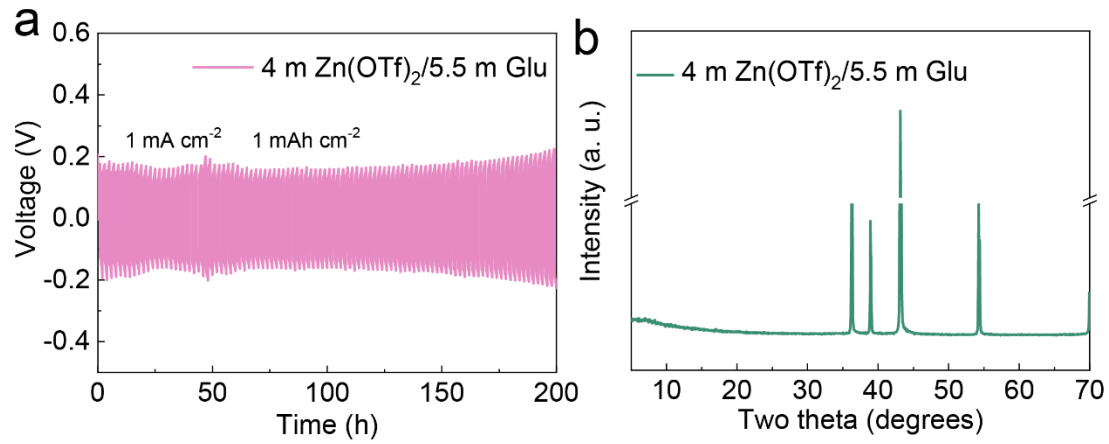

Figure S2. a) Zn plating/stripping behavior in the symmetric cell at current density of 1 mA cm^{-2} and capacity of 1 mA h cm^{-2}. b) XRD of Zn electrode after 20 cycles.

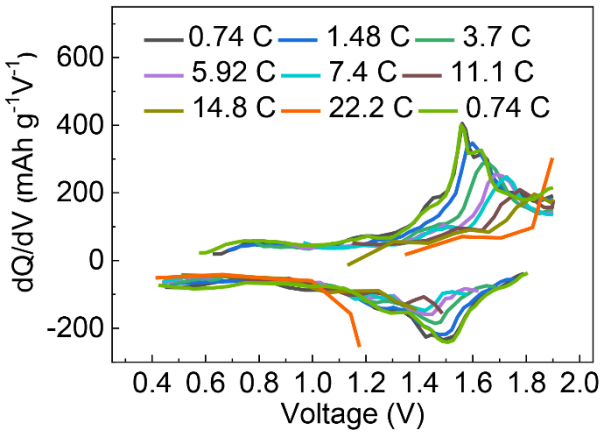

Figure S3. Differential capacity curves of $VOPO_4 \cdot 2H_2O$ in 4 m $Zn(OTf)_2$/5.5 m Glu electrolyte at various current densities.

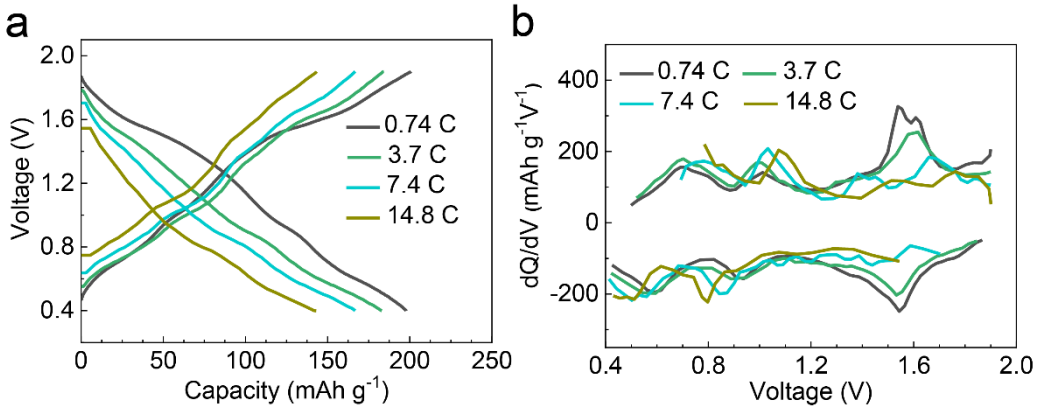

Figure S4. a) Charge-discharge and b) differential capacity curves of $VOPO_4{\cdot}2H_2O$ in 4 m $Zn(OTf)_2$ electrolyte at various current densities.

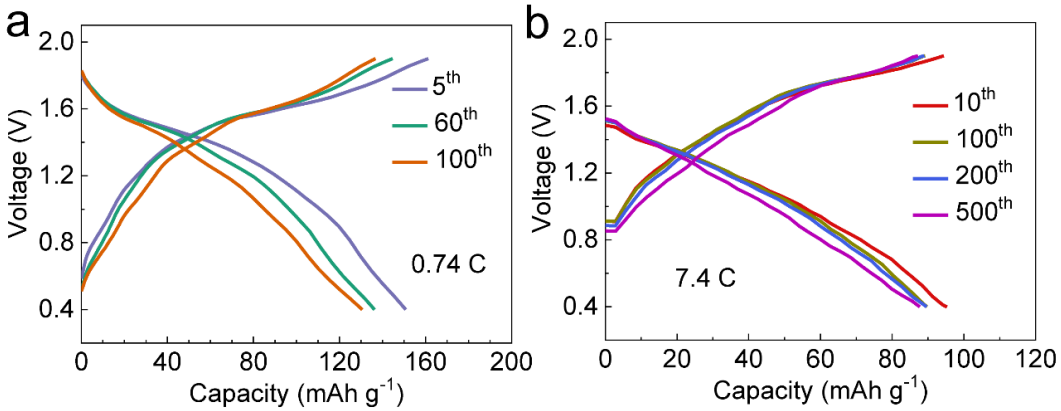

Figure S5. Charge-discharge curves of $VOPO_4{\cdot}2H_2O$ at different cycles in 4 m $Zn(OTf)_2$/5.5 m Glu at a) 0.74 C and b) 7.4 C.

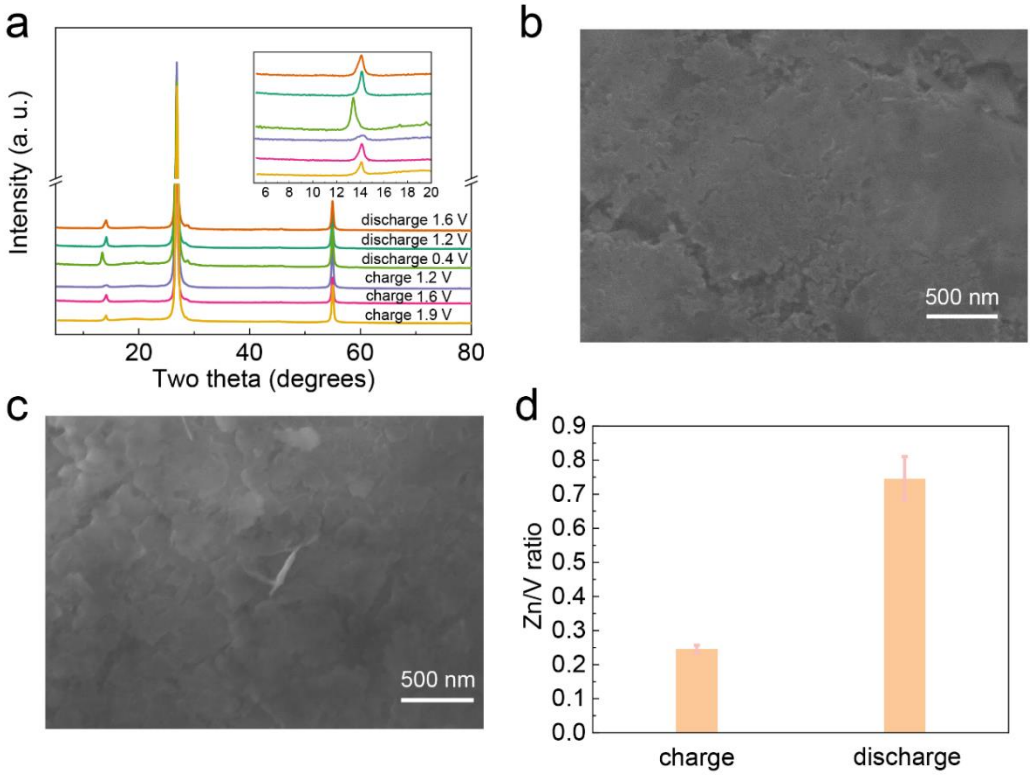

Figure S6. Characterizations of the $VOPO_4 \cdot 2H_2O$ cathode at different states of the 30th cycle in the 4 m $Zn(OTf)_2$/5.5 m Glu electrolyte: a) XRD, SEM images of the b) charged and c) discharged electrodes, d) EDS Zn/V ratios.

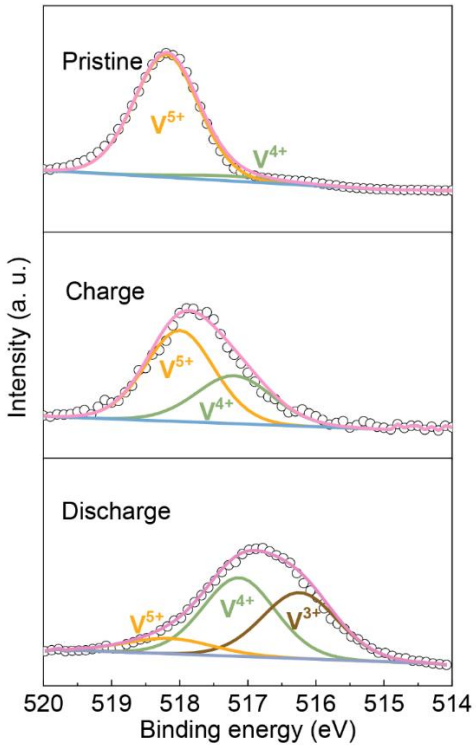

Figure S7. V $2p_{3/2}$ XPS of $VOPO_4 \cdot 2H_2O$ cathode at different states of the 30th cycle in the 4 m $Zn(OTf)_2$/5.5 m Glu electrolyte.

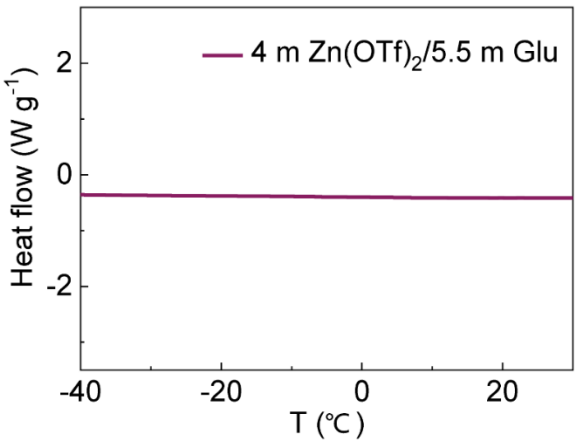

Figure S8. Differential scanning calorimetry (DSC) curve of the 4 m $Zn(OTf)_2$/5.5 m Glu solution.

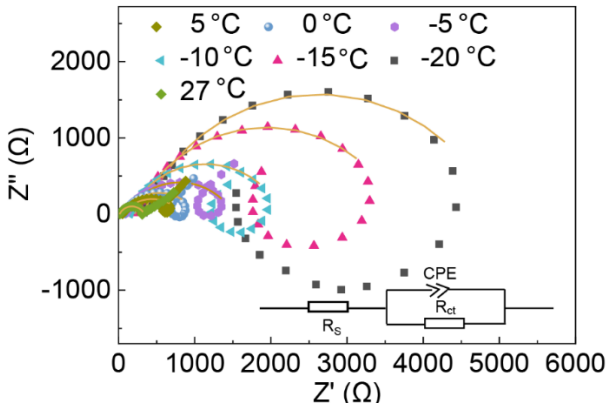

Figure S9. Nyquist plots and the fitted curves of the $VOPO_4{\cdot}2H_2O$ electrode in the 4 m $Zn(OTf)_2$/5.5 m Glu electrolyte at different temperatures.

Table S1. The R_{ct} values from the fittings of Nyquist plots.

Temperature (°C)	-20	-15	-10	5	0	5	27
R_{ct} (Ω)	4620	3477	2012	1427	945	786	321

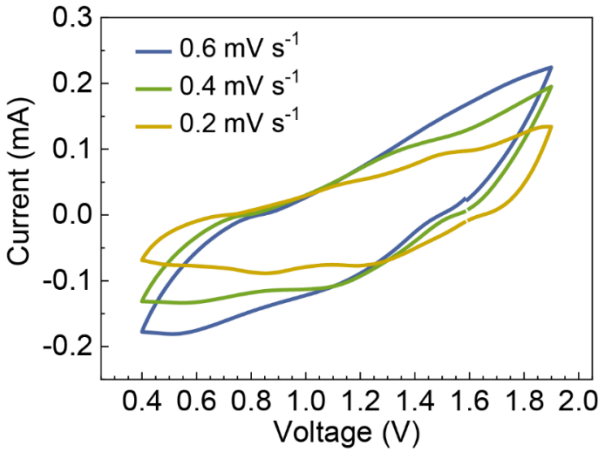

Figure S10. CV curves of $VOPO_4 \cdot 2H_2O$ in the 4 m $Zn(OTf)_2$/5.5 m Glu electrolyte at different scan rates under -20 °C.