Supporting Information

Bilayered $Mg_{0.25}V_2O_5 \cdot H_2O$ as a Stable Cathode for Rechargeable Ca-ion Batteries

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Experimental section

Material synthesis. The parallelogram shaped $Mg_{0.25}V_2O_5 \cdot H_2O$ was synthesized using an one-step hydrothermal method. In a typical synthesis, 0.364 g (2 mmol) of V_2O_5 was dispersed in 13 mL of deionized water, and then 5 mL of H_2O_2 (30%) was added with stirring. After stirred for about 20 min, a clear solution with orange red color was obtained. Then 0.03 g of polyethylene glycol (PEG-4000) and 30.5 g (150 mmol) of $MgCl_2 \cdot 6H_2O$ were added into the solution, and stirred for another 2 h. The finally obtained solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. The sealed autoclave was put into an oven with the condition of 200 °C for 48 h. After that, the autoclave was cooled down naturally to room temperature, and the obtained black product was washed with deionized water and ethanol for several times. After dried at 70 °C for 24 h, the final product was obtained.

Material characterization. The XRD patterns were collected using a Bruker D8 Discover X-ray diffractometer equipped with a Cu Kα radiation source. XRD refinement was conducted using the software TOPAS 5.0. SEM images were collected using a JEOL-7100F microscope at an acceleration voltage of 20 kV. TEM, HRTEM images, SAED patterns and EDX mapping were recorded using a Titan G2 60-300 with EDS image corrector. XPS measurements were performed using a VG MultiLab 2000 instrument. TGA analysis was performed using a Netzsch STA 449F3 simultaneous thermal analyzer in Ar atmosphere. ICP measurements were conducted using a PerkinElmer Optima 4300DV spectrometer.

Electrochemical measurements. The electrochemical measurements were conducted in a glove box filled with pure Ar gas at room temperature based on three-electrode system and Swagelok-type cell, respectively. The work electrodes were composed of 70% active material, 20% acetylene black and 10% polyvinylidene fluoride (PVDF). The slurry was spread on a Al foil and dried at 70 °C for 24 h, and then were punched to small wafers with a diameter of 1.0 cm. The active mass loading was 1.0–1.5 mg cm^{-2}. Activated carbon cloth (ACC) was used as counter electrode both in

three-electrode system and Swagelok-type cell. In three-electrode system, a Ag^+/Ag electrode (as shown in Figure S6a) was applied as reference electrode. In Swagelok-type cell, a Whatman glass microfiber filter (GF/A) was used as the separator, and Al foil was used as the current collector. The electrolyte was composed of 0.8 M $Ca(TFSI)_2$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), propylene carbonate (PC), ethylmethyl carbonate (EMC) (vol/vol/vol/vol = 2:3:2:3). CV and galvanostatic charge/discharge measurements were performed with a multi-channel electrochemical workstation (Bio-Logic SAS VMP-3). GITT measurement was conducted with a multi-channel battery testing system (LAND CT2001A).

In situ XRD test. To carry out the in situ XRD measurement, a freestanding work electrode with the same composition as mentioned above was prepared without the Al foil, which was realized by using a roll press. The electrochemical cell assembled for in situ XRD measurement is similar to the Swagelok-type cell in configuration, with ACC as the counter electrode and GF/A glass microfiber filter as the separator. But a X-ray-transparent Be window was used both as the current collector and part of the cell housing. The work electrode was placed behind the Be window. During the in situ testing, the electrochemical cell was cycled at a current density of 20 mA g^{-1} using a multi-channel battery testing system (LAND CT2001A). Meanwhile, the XRD patterns of the electrodes were collected with a planar detector very 2 min in a still mode using the X-ray diffractometer (Bruker D8 Discover).

***Ab initio* calculations.** All *ab initio* calculations were based on the density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP).[1-2] The electron-ion interaction was described with the projector augmented wave (PAW) method.[3-4] The electron exchange and correlation energies were treated with the spin-polarized generalized gradient approximation and Perdew-Burke-Ernzerhof functional (GGA-PBE).[5] A plane-wave basis was employed with a kinetic energy cutoff of 520 eV. For calculations on the binding energy of $M_{0.25}V_2O_5 \cdot H_2O$ system (M

= Mg, Ca, Figure 1b in the main text), the van der Waals interactions[6-7] with a Hubbard U correction of 3.1 eV was added to remove the spurious self-interaction of the vanadium d-electrons.[8-9] We chose a (1 × 2 × 2) supercell and a k-point mesh of 2 × 2 × 1. All geometries were optimized and then total energy was calculated. The convergence of the electronic self-consistent was set as 10^{-5} eV and the ionic relaxation criterion was set as 0.02 eV·Å^{-1}, and the convergence of total energy was set as 5×10^{-4} eV.

Atomic coordinates of ground states for the (1 × 2 × 2) supercell of $Mg_{0.25}V_2O_5\cdot H_2O$ structure. All atomic positions are given in fractional coordinates defined by the lattice parameters a = 10.76065 Å, b = 16.2534 Å, c = 21.94866 Å; α = 90.03840°, β = 93.94756°, γ = 89.98683°.

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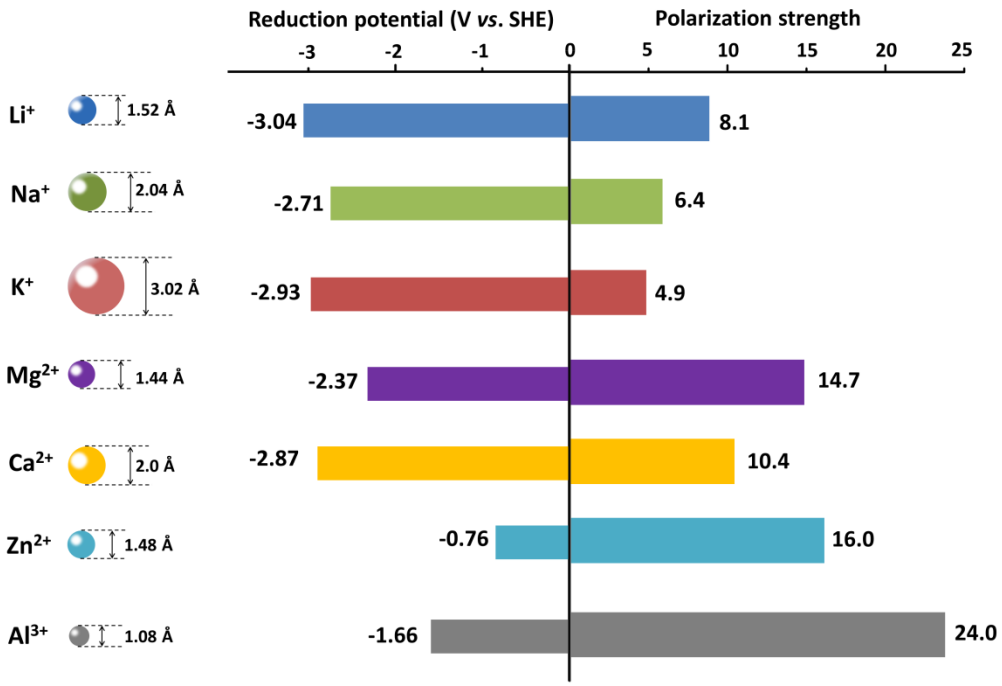

Figure S1. The comparison of ionic diameter, reduction potential and polarization strength of different metals or metal ions.

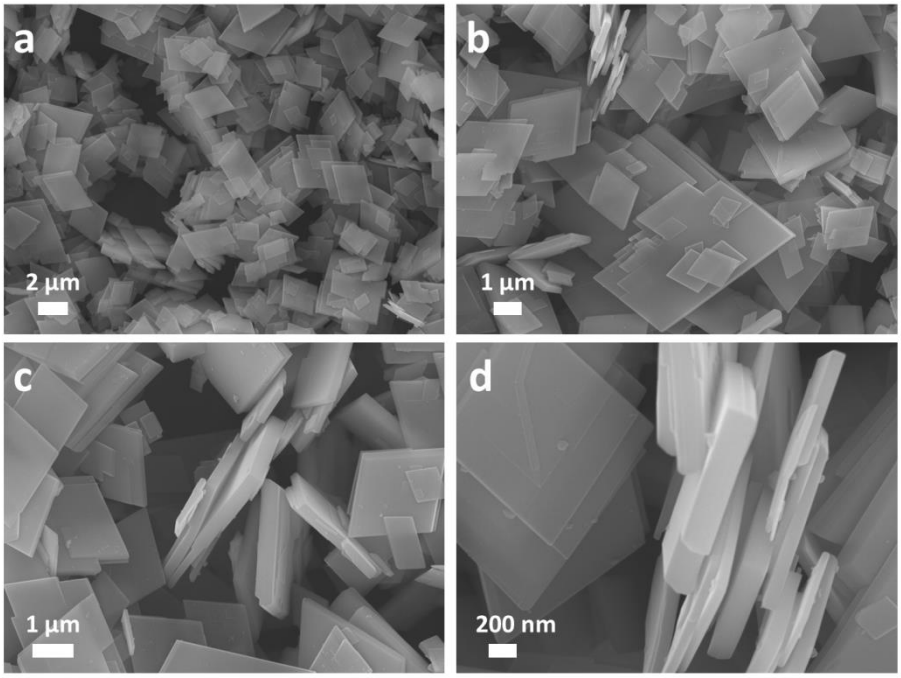

Figure S2. SEM images of the as-synthesized parallelogram shaped $Mg_{0.25}V_2O_5 \cdot H_2O$ plates.

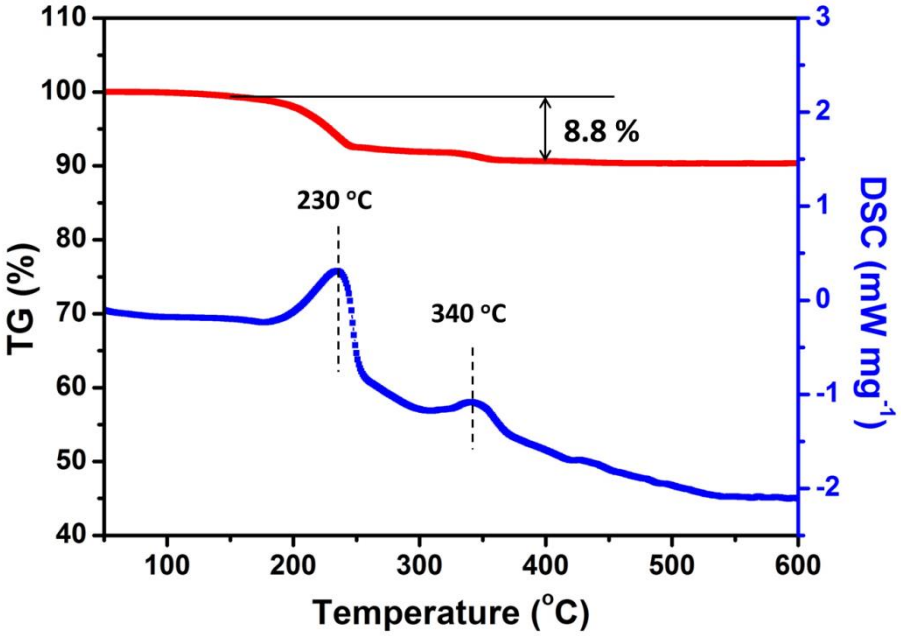

Figure S3. TG/DSC curves of the $Mg_{0.25}V_2O_5 \cdot H_2O$ at Ar atmosphere.

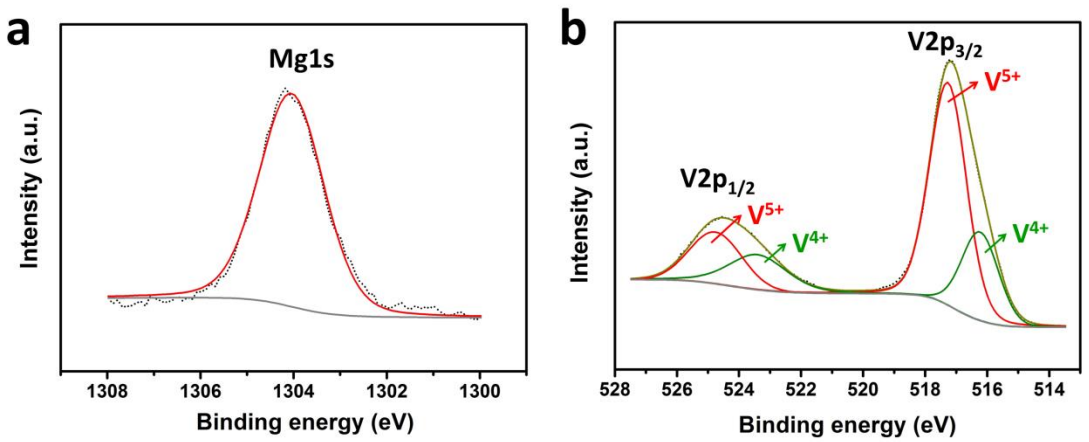

Figure S4. XPS spectra of $Mg_{0.25}V_2O_5 \cdot H_2O$ powder. (a) Mg1s spectrum. (b) V2p spectrum.

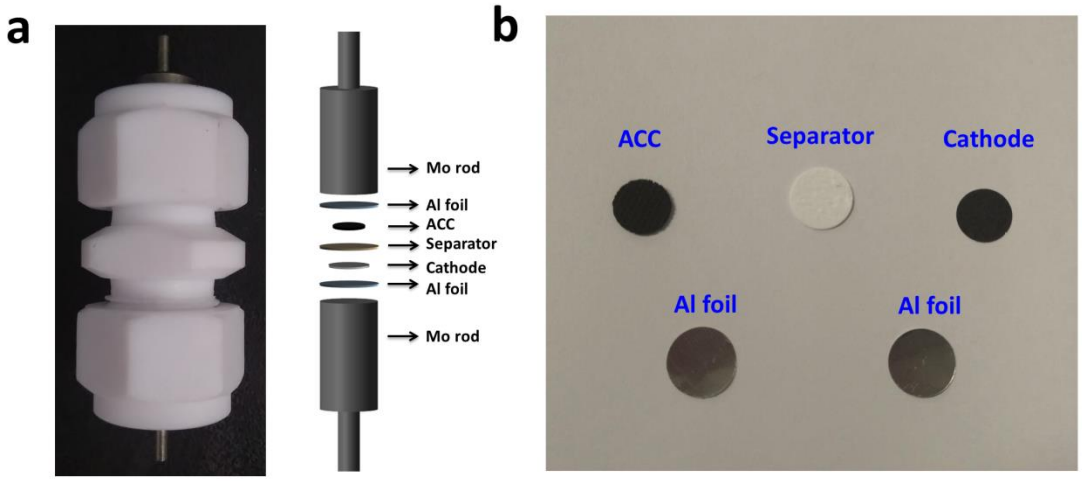

Figure S5. (a) The photograph and illustration of the Swagelok-type cell. (b) The photograph of each part for the assembly of Swagelok-type cell.

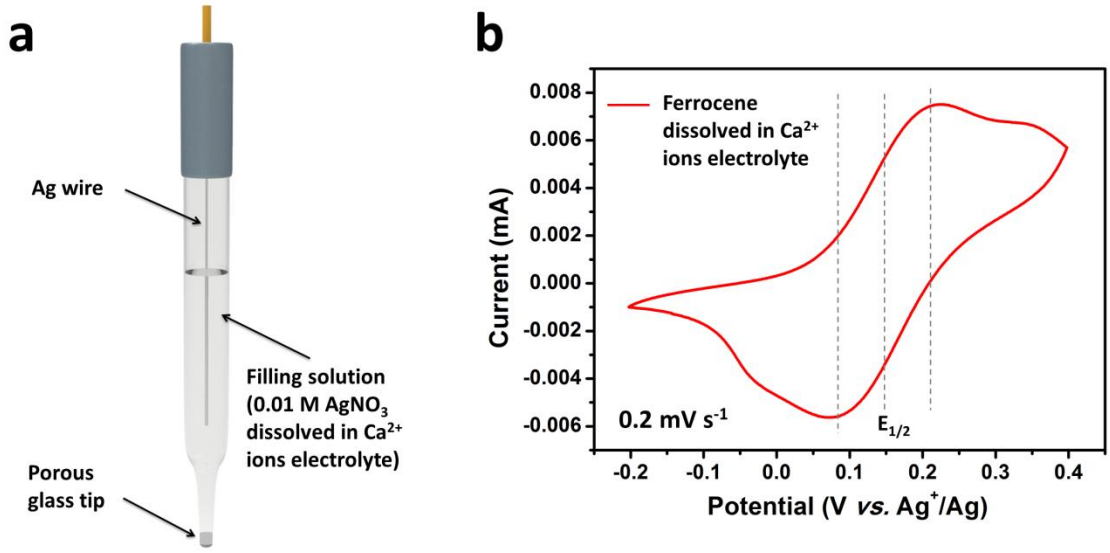

Figure S6. (a) The illustration of Ag^+/Ag reference electrode. (b) CV curve of 10 mM ferrocene dissolved in the Ca^{2+} ions electrolyte (the work, counter and reference electrodes are Al foil, ACC and Ag^+/Ag electrode, respectively).

Since the standard potential of Ag^+/Ag reference is unknown, the redox potential of ferrocene was utilized to calibrate it. From the CV test of ferrocene in electrolyte (Figure S6b), it is found that the redox potential of ferrocene is about 0.15 V *vs.* Ag^+/Ag. And based on the previous study, the ferrocene redox potential is about 2.8 V *vs.* Ca^{2+}/Ca in ester carbonate electrolyte.[10] Therefore, the potential of Ag^+/Ag reference electrode used here can be roughly regarded as ~2.65 V *vs.* Ca^{2+}/Ca.

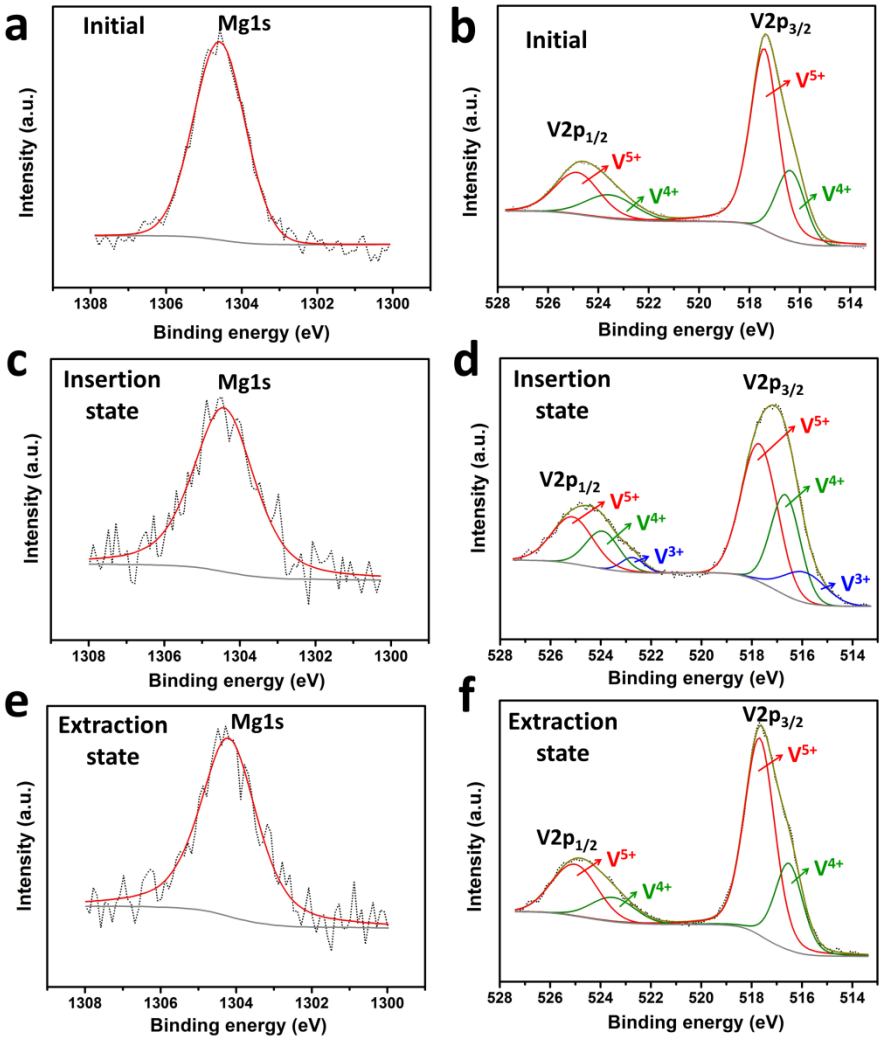

Figure S7. High-resolution Mg1s and V2p spectra of $Mg_{0.25}V_2O_5 \cdot H_2O$ electrodes at initial, insertion and extraction states, respectively.

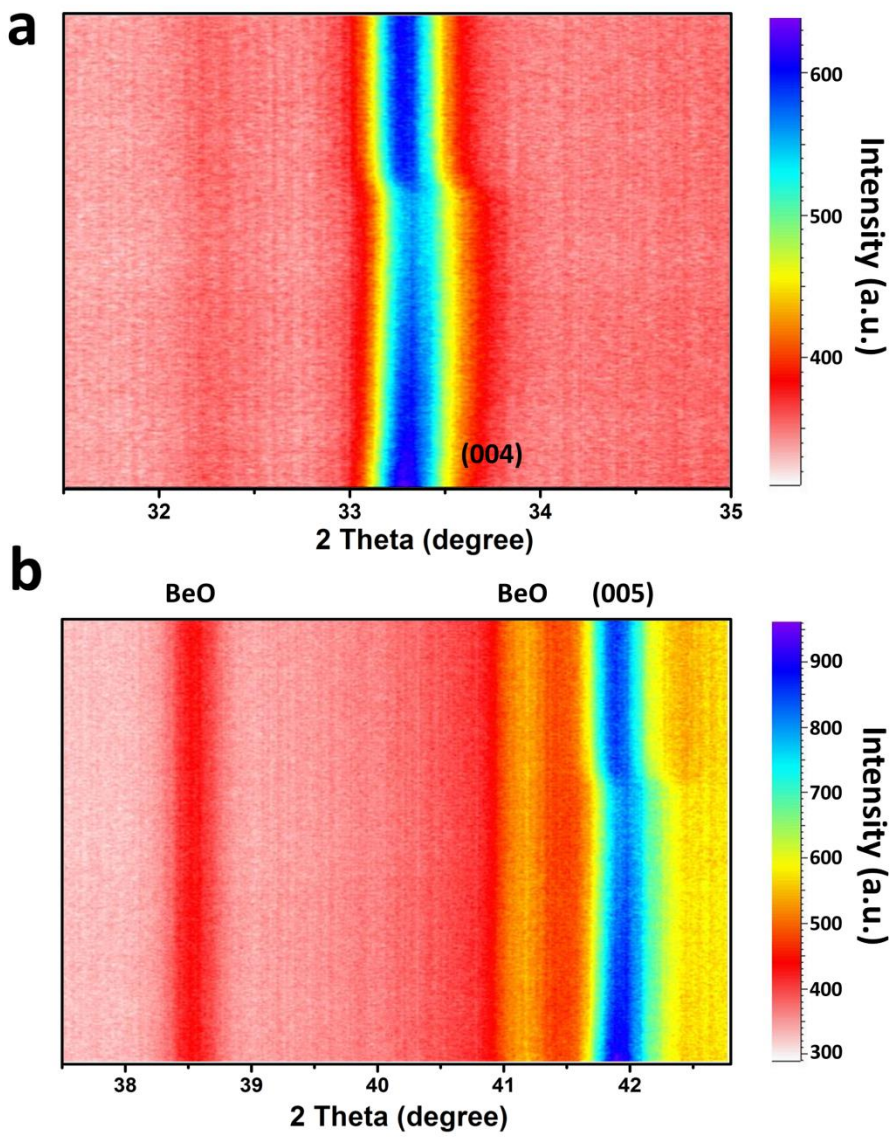

Figure S8. The zoom-in images of (004) and (005) peaks from in situ XRD results of $Mg_{0.25}V_2O_5 \cdot H_2O$.

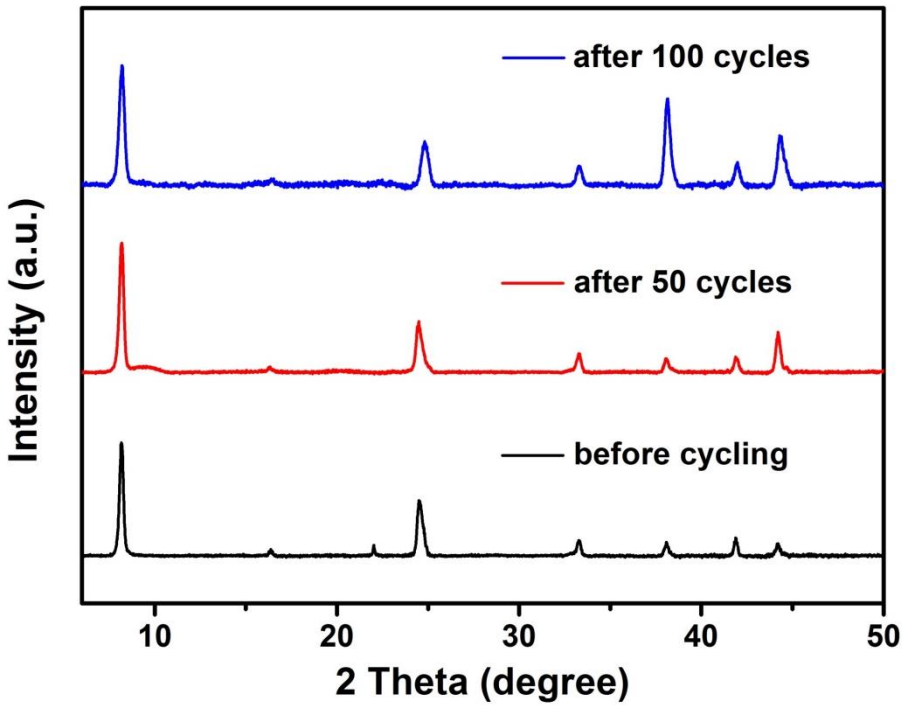

Figure S9. Ex situ XRD results of $Mg_{0.25}V_2O_5 \cdot H_2O$ electrodes before cycling, after 50 cycles and after 100 cycles for Ca^{2+} storage.

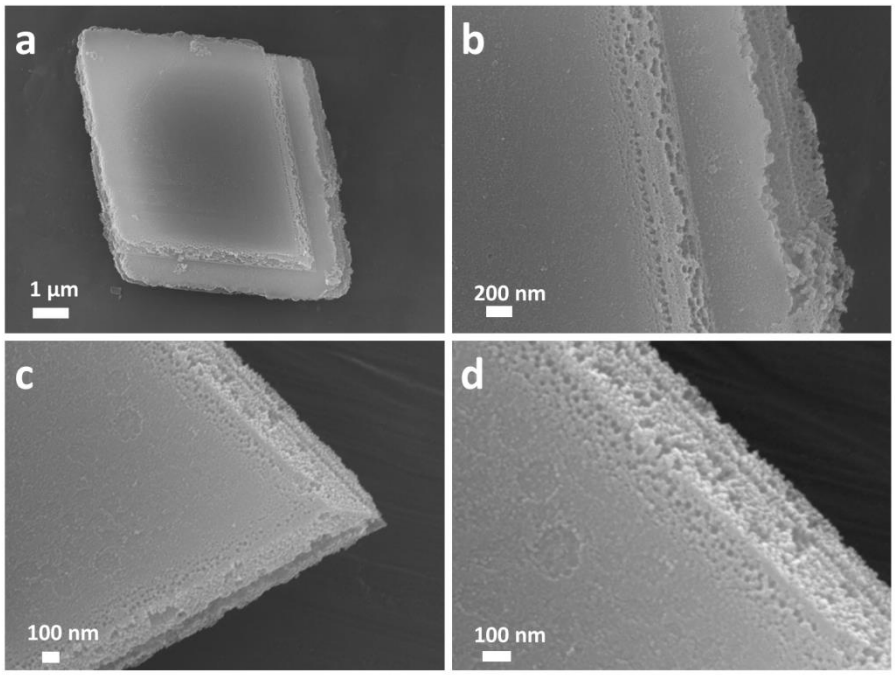

Figure S10. Ex situ SEM images of $Mg_{0.25}V_2O_5 \cdot H_2O$ after 50 cycles.

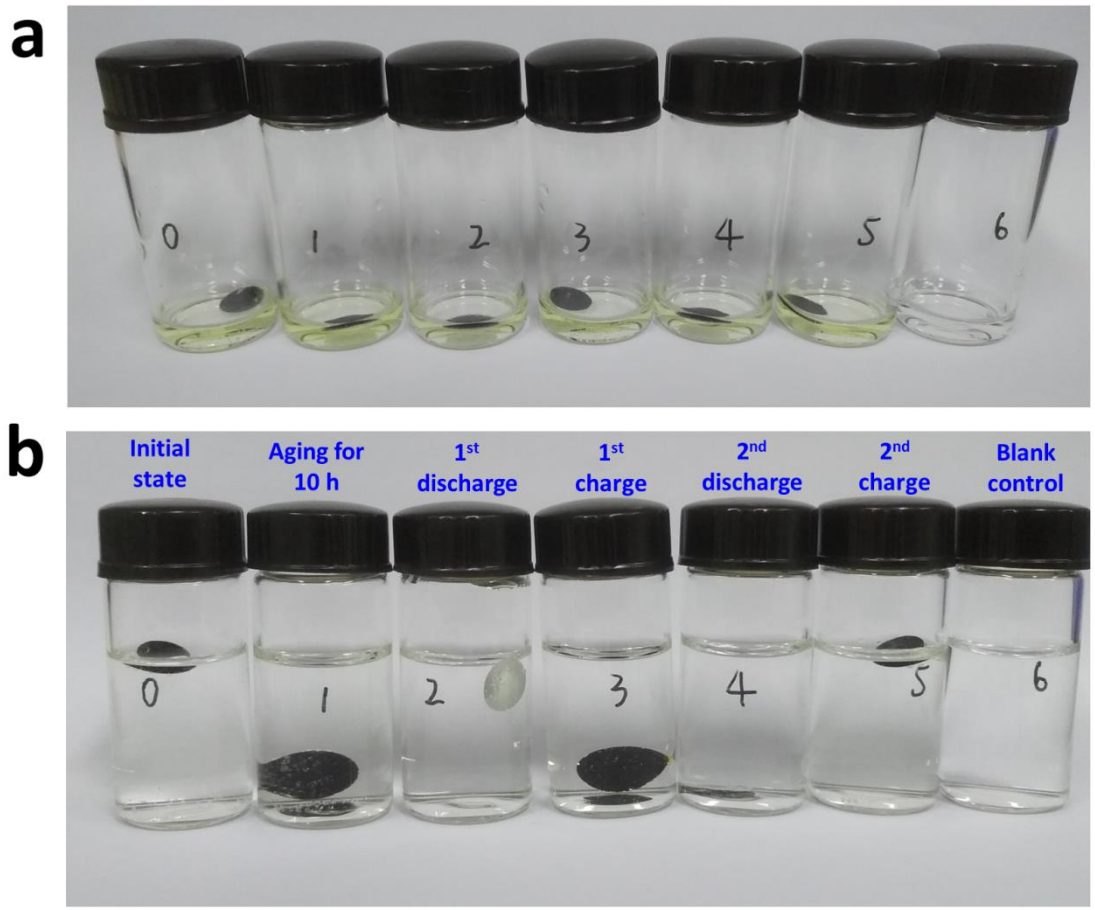

Figure S11. The photographs of the samples prepared for ex situ ICP measurements. (a) The $Mg_{0.25}V_2O_5 \cdot H_2O$ electrodes at different states were immersed in the same amount of H_2O_2 for active material dissolution. (b) The solution with dissolved material was diluted by same amount of ultrapure deionized water. (The sample IDs are the same as those in Table S2.)

Table S1. Comparison of the Ca^{2+} storage performance of $Mg_{0.25}V_2O_5 \cdot H_2O$ in this work and previously reported Ca^{2+} storage cathodes with organic electrolyte.

Materials	Current density (mA g^{-1})	Initial highest reversible capacity (mAh g^{-1})	Cycle number, retained capacity	Reference
$Mg_{0.25}V_2O_5 \cdot H_2O$	20	122	20 cycles, 110 mAh g^{-1}	This work
	50	91	100 cycles, 97 mAh g^{-1}	
	100	70	500 cycles, 61 mAh g^{-1}	
$Na_xMnFe(CN)_6$	10	~100	35 cycles, ~50 mAh g^{-1}	*Chem. Mater.* **2015**, 27, 8442
$MnFe(CN)_6$	/	~60	20 cycles, ~20 mAh g^{-1}	*J. Phys. Chem. C* **2015**, 119, 27946
$K_2BaFe(CN)_6$	12.5	~60	30 cycles, 55.8 mAh g^{-1}	*J. Power Sources* **2015**, 273, 460
$CaCo_2O_4$	40	~93	30 cycles, ~80 mAh g^{-1}	*Electrochem. Commun.* **2016**, 67, 59
$K_xNiFe(CN)_6 \cdot nH_2O$	/	~50	12 cycles, ~42 mAh g^{-1}	*Electrochim. Acta* **2016**, 207, 22
Na_2FePO_4F	10	~60	50 cycles, ~79 mAh g^{-1}	*J. Power Sources* **2017**, 369, 133
$Fe_4[Fe(CN)_6]_3$	125	~120	80 cycles, ~100 mAh g^{-1}	*J. Power Sources* **2017**, 342, 414
Na-doped $NH_4V_4O_{10}$	100	~150	100 cycles, ~150 mAh g^{-1}	*J. Mater. Chem. A* **2018**, 6, 22645
α-MoO_3	2	~140	12 cycles, ~100 mAh g^{-1}	*Chem. Mater.* **2018**, 30, 5853

Table S2. The ICP results of the $Mg_{0.25}V_2O_5 \cdot H_2O$ electrodes at different states.

Sample	Elements	Concentration (mg L^{-1})	Molar ratio (Mg : Ca : V)
#0 Initial state	Mg	1.3961	0.453 : 0.001 : 2
	Ca	0.0069	
	V	12.9907	
#1 Aging for 10 h	Mg	0.7853	0.430 : 0.034 : 2
	Ca	0.1028	
	V	7.7152	
#2 1st discharge	Mg	1.0632	0.473 : 0.356 : 2
	Ca	1.3169	
	V	9.4746	
#3 1st charge	Mg	2.1712	0.448 : 0.045 : 2
	Ca	0.3602	
	V	20.3722	
#4 2nd discharge	Mg	1.6566	0.478 : 0.358 : 2
	Ca	2.0455	
	V	14.6027	
#5 2nd charge	Mg	1.5541	0.443 : 0.028 : 2
	Ca	0.1592	
	V	14.769	
#6 Blank control	Mg	-0.0039	
	Ca	-0.0063	
	V	0.0623	

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