# **Supplementary Information**

# Fine Valance Regulation of Hydrated Vanadium Oxide as A

# Novel Cathode for Stable Potassium-ion Storage

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# **Experimental section**

#### Synthesis of VOH-G and VOH-S

VOH-S and VOH-G were both synthesized through a simple hydrothermal reaction.<sup>S1</sup> In a typical process to synthesize the VOH-S, 1 g V<sub>2</sub>O<sub>5</sub> (obtained by annealing of NH<sub>4</sub>VO<sub>3</sub> at 500 °C for 6 h) and 1 g sucrose were added in 70 ml DI water with stirring for 1 h. Subsequently, the yellow suspension was transferred to a 100 mL Teflon-lined stainless-steel autoclave and heated to 100 °C for 12 h in an electric oven. After colling to room temperature, the dark green precipitation was washed three times respectively with DI water and ethanol, and then dried at 60 °C in a vacuum oven. In order to control the valance of vanadium, VOH-G was synthesized by the same process, while the 1 g sucrose was replaced by 5 g glucose. All chemicals were used as received without further purification.

## **Material Characterization**

The obtained VOH-S and VOH-G samples were characterized with an X-ray diffractometer (XRD, Rigaku TTR-III, Cu K $\alpha$  radiation,  $\lambda$ =1.5406 Å). The morphology and microstructure of the samples were studied by scanning electron microscope (SEM, FEI Apreo) and transmission electron microscope (JEM-2100F). Further information of the chemical bonding condition and element valance was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos AXIS with an Al K $\alpha$  X-ray source). Thermogravimetric analysis (TGA, NETZSCH TG 209F1 Libra) was carried out from 25 °C to 800 °C in N<sub>2</sub>. Fourier transform infrared (FTIR) spectroscopy was employed to characterize the structure of samples over the range of 4000-500 cm<sup>-1</sup>. The elemental compositions were detected by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 7300 DV).

### **Electrochemical Measurements**

The electrochemical tests were carried out in CR2032-type coin cells. The active material VOH (70 wt%), acetylene black (20 wt%), and polyvinylidene fluoride (10 wt%) were mixed thoroughly. The resultant slurry was then pasted onto the carbon coated aluminum foils with a mass loading of ~1.5 mg cm<sup>-2</sup> and dried at 80 °C for 12 h in an oven. Coin cells were assembled in an Ar-filled glovebox (MBraun Labmaster 130). Metallic K was used as the counter electrode to assemble the half cells, which was separated from the cathode by glass fibre (Whatman, GF/D). 1.5 M KFSI in EC/DEC (1:1 by volume) was employed as the electrolyte. Cyclic voltammetry (CV) tests (2.0-4.0 V vs. K<sup>+</sup>/K, at a scan rate of 0.1–1.0 mV s<sup>-1</sup>) were conducted on a CHI660E workstation (Shanghai Chenhua Co. Ltd., China). Galvanostatic charge/discharge tests in the voltage range of 2.0-4.0 V were performed at room temperature with the battery test system (Neware BTS-2300, Shenzhen). The galvanostatic intermittent titration technique (GITT) was tested by a series of (dis)charge process at a current density of 10 mA g<sup>-1</sup> for 10 min, followed by a 20 min relaxation process. All the specific capacity and current density in this study were

calculated on the basis of the mass of active material. Also, in order to disclose the electronic conductivity of the VOH samples, we measured the electronic conductivity by a four-probe method (Powder Resistivity Tester, ST2722-SZ, Suzhou Jinge).

#### The Measurement of Pseudo-capacitance Contribution

Theoretically, the peak current (i) and scan rate (v) in the CV curve follows the rule:

$$i = av^b \tag{1}$$

where *a* and *b* are adjustable values. By using the equation of log  $(i) = b \log(v) + \log(a)$  derived from Eq. (1), the ion diffusion and capacitive contributions can be discriminated. A *b* value of 0.5 indicates an ion diffusion governed mechanism, while a *b* value of 1.0 suggests a capacitive storage process. To further quantify the contribution of capacitance  $(k_1v)$  and diffusion  $(k_2v^{1/2})$  at a specific scan rate, Eq. (1) can be divided into two halves to form Eq. (2):

$$i(V) = k_1 v + k_2 v^{1/2} \tag{2}$$

where  $k_1$  and  $k_2$  are constants at a certain scan rate.

To accurately calculated the capacitive contribution, previous work on the calibration of charge storage mechanism is referred.<sup>S2</sup>

## **Figures and tables**



**Fig. S1** XRD patterns of VOH samples prepared by adding different amounts (1, 2 and 5 g) of sucrose (a) and glucose (b).

In addition to  $V_{10}O_{24}$ ·nH<sub>2</sub>O,  $V_6O_{13}$  phase is also formed when 2 g or 5 g sucrose is added. Moreover, only when 5 g glucose is added, pure  $V_{10}O_{24}$ ·nH<sub>2</sub>O can be obtained. Thus, 1 g sucrose and 5 g glucose are chosen to obtain a pure phase of  $V_{10}O_{24}$ ·nH<sub>2</sub>O, which are named as VOH-S and VOH-G, respectively.



Fig. S2 TGA results of VOH samples.

The amount of structural water can be calculated from the TGA curves. The mass loss below 100 °C can be attributed to physically absorbed water, while the weight loss after that is due to the crystal water. Therefore, VOH-S contains ~2.81 mole crystal water, while VOH-G loss ~3.39 mole during the heating process.



Fig. S3 SEM-EDS elemental mapping images of the VOH-S sample.



**Fig. S4** Further characterization and comparison: (a) FTIR, (b) Raman, (c)V 2p, and (d) O 1s XPS spectra of VOH-S and VOH-G.



Fig. S5 Wide-scan XPS spectra of (a) VOH-S and (b) VOH-G.

The wide-scan XPS spectra indicate no other elements in the samples, further confirm the pure phase of VOH-S and VOH-G.



Fig. S6 SEM images of VOH-S electrode after 500 cycles at 500 mA g<sup>-1</sup>.



**Fig. S7** GCD curves at 10 mA  $g^{-1}$  and cycling performances at a current density 500 mA  $g^{-1}$  under high mass-loading of (a, b)2.5 mg cm<sup>-1</sup> and (c, d)4.3 mg cm<sup>-1</sup>.

At 10 mA g<sup>-1</sup>, they deliver high capacities of 106.6 and 103.5 mA h g<sup>-1</sup>, which are about 96.91% and 94.09% of the capacity under low mass-loading. At a current density of 500 mA g<sup>-1</sup>, the batteries also display a stable discharge capacity for 250 cycles.



**Fig. S8** Optical images of the VOH-S solutions soaked for different periods. After soaking into the 1.5 M KFSI in EC/DEC electrolyte for 7 days, the solution maintained colourless and transparent, indicating the stability of VOH-S electrode in the electrolyte.



**Fig. S9** Optical images of the separators on the cathode side (a) rested for 6 h and (b) cycled for 500 cycles at 500 mA  $g^{-1}$ .

We disassembled a cell rested for 6 h and another one cycled for 500 times to evaluate the color changes of the separators. There is barely color change on the cathode side after 500 cycles, also indicating little V dissolution during cycling.



Fig. S10 Rate profiles of VOH-G at various current densities.



Fig. S11 EIS spectra of VOH-S//K and VOH-G//K fresh cells.

The charge-transfer resistance  $(R_{ct})$  of VOH-S is significantly lower than that of VOH-G cathode, corresponding to the faster electronic transfer property of VOH-S.



**Fig. S12** (a) Comparation of (002) peak of VOH-S at 1<sup>st</sup> fully charged state and its pristine state; (b) The XRD pattern of the carbon coated Al foil.



Fig. S13 SEM image and EDS elemental mapping images of the VOH-S cathode at 1<sup>st</sup> fully charged state.

	Voltage		Consoity	Capacity	Rate		
Cathode	range	Electrolyte			capacity	Ref.	
	(V vs. K <sup>+</sup> /K)		$(\mathbf{m}\mathbf{A} \mathbf{n} \mathbf{g}^{T})$	retention	(mA h g <sup>-1</sup> )		
VOH	2.0-4.0	1.5 M KFSI-	~110@	99.2%@700	~43	This	
		EC/DEC	(10 mA g <sup>-1</sup> )	$(0.5 \text{ A } \sigma^{-1})$	(1 A g <sup>-1</sup> )	work	
		(1:1)			(119)	work	
$K_{0.83}V_2O_5$	1.5-4.3	7 M KFSI-	~90	81.7%@200	~53	<b>S</b> 3	
		EC/DEC (1:1)	(10 mA g <sup>-1</sup> )	$(0.1 \text{ A g}^{-1})$	$(0.1 \text{ A g}^{-1})$		
K <sub>2</sub> V <sub>3</sub> O <sub>8</sub> /C	1.0-4.2	0.5 M KPF6-	~75	80%@200	~45	6.4	
		EC/DEC (1:1)	(20 mA g <sup>-1</sup> )	$(0.02 \text{ A g}^{-1})$	$(0.2 \text{ A g}^{-1})$	84	
$K_{0.5}V_2O_5$	1.5-3.8	1.5 M KFSI-	~90	81%@250	~45	0.5	
		EC/DEC (1:1)	(10 mA g <sup>-1</sup> )	(0.1 A g <sup>-1</sup> )	$(0.2 \text{ A g}^{-1})$	22	
K <sub>0.3</sub> Mn <sub>0.95</sub> Co <sub>0.05</sub> O <sub>2</sub>	2.0-3.6	0.8 M KPF6-	~100	75%@500	~45	<b>S</b> 6	
		EC/DEC (1:1)	(22 mA g <sup>-1</sup> )	$(0.17 \text{ Ag}^{-1})$	$(0.44 \text{ A g}^{-1})$		
K2[(VO)2(HPO4)2		0.1 M KClO <sub>4</sub>	~81	83%@200	~30		
$(C_2O_4)]$	2.0-4.6	-PC	(5 mA g <sup>-1</sup> )	$(0.02 \text{ Ag}^{-1})$	$(0.2 \text{ A g}^{-1})$	57	
VOPO4·H2O	1.5-4.8	1M KPF6-					
		EC/DMC	~97	61.1%@650	~67	<b>S</b> 8	
		(1:1)	(45 mA g <sup>-1</sup> )	$(0.09 \text{ Ag}^{-1})$	$(0.45 \text{ A g}^{-1})$		
		5%FEC					
K <sub>0.6</sub> CoO <sub>2-x</sub> N <sub>x</sub> porous nanoframe	1.5-4.2	0.8 M KPF6-	0.6		20		
		EC/DEC/PC	~86	77.3%@400	30	<b>S</b> 9	
		(1:1:1)	$(20 \text{ mA g}^{-1})$	$(0.05 \text{ Ag}^{-1})$	$(0.5 \text{ A g}^{-1})$		

Table S2. V concentration of VOH-S solutions at different periods.				
Sample	V Concentration (mg L <sup>-1</sup> )			
3 Days	0.3			
7 Days	0.96			
The V concentration of VOUS colution	and officer 2 and 7 days are apply 0.2 and 0.06 ma I -			

The V concentration of VOH-S solutions after 3 and 7 days are only 0.3 and 0.96 mg  $L^{-1}$ , respectively, corresponding to about 0.05% and 0.16% of V being dissolved from the VOH-S electrode, indicating the good stability of VOH-S in the electrolyte.

Table S3. Distribution ratio of V before and after 500 cycles.

Sample	Distribution ratio of V before cycling	V Concentration after 500 cycles (mg L <sup>-1</sup> )	Distribution ratio of V after 500 cycles
Electrode	100 %	57.7742	97.611 %
Separator	0 %	1.414	2.389 %

To get exact proportion of the vanadium dissolved after 500 cycles, the V concentrations of the electrode (corresponding to the V remained in the electrode) and the separator (corresponding to the V dissolved in the electrolyte and some residual powder attached to the separator) are respectively tested by ICP, and it can be calculated that only 2.389% of V is detected in the separator, which is the evidence of the stability of our VOH-S during cycling. Note that the

detected V here also contains some VOH-S particles detached from the electrode and thus the value 2.389% should be an over-estimate.

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