

# Supporting information

## Anisotropic Proton Conduction Realized by a Layered Vanadium

### Selenite Single Crystal

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## Experimental Section

### Materials and Reagents.

Vanadium pentoxide (99%, Sinopharm Chemical Reagent Co., Ltd), selenious acid (AR, Tianjin Yingda Chemical Reagent Co., Ltd (A), ethanol R, Sinopharm Chemical Reagent Co., Ltd) and acetone (AR, Sinopharm Chemical Reagent Co., Ltd) were used as received without further purification. And the distilled water is produced by WP-UP-LH-10 ultrapure water equipment.

### Synthesis and Characterization.

0.091 g (0.5 mmol) of  $V_2O_5$  and 0.129 g (1 mmol) of selenious acid are mixed in 0.5 mL distilled water. The mixture was transferred into a 20 mL Teflon-lined autoclave, which was kept at 200 °C for 4 days. After cooling to room temperature with the rate of 9 °C/h, the light-brown-green hexagonal prismatic crystals of **1** were obtained along with some yellow powder. Crystals were washed with distilled water and dried in air. Anal. calc. for  $(H_3O)(VO_2)_3(SeO_3)_2$  (**1**): H, 0.58%. Found: H, 0.67%.

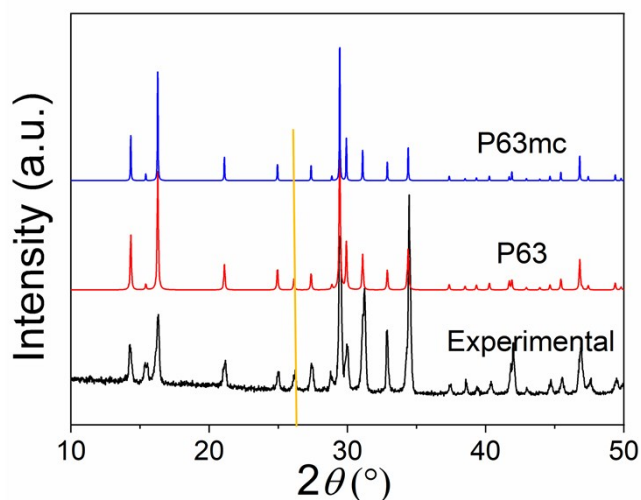
### Analytical Methods.

Powder X-ray diffraction (PXRD) patterns were measured with scan speed of 2°/min on a Rigaku Miniflex-II diffractometer in the angular range of  $2\theta = 5 - 65^\circ$  with Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Data processing were performed in Origin 8.0. Elemental analysis (EA) was carried out with a German Elementary Vario EL III instrument. Elemental ratios of V and Se were determined by energy dispersive X-ray spectroscopy (EDS) with JEOL JSM-6700F scanning electron microscope. Thermogravimetric analysis (TGA) was performed with a heating rate of 10 K/min on NETZSCH STA 449F3 unit under  $N_2$  atmosphere in the temperature range of 20 - 600 °C.

### X-ray Crystallographic Study

Under the optical microscope, a suitable single crystal was selected carefully and glued to glass fiber. Single-crystal X-ray diffraction data collection and the determination of crystal axes for compound **1** was conducted on a SuperNova CCD diffractometer at 298 K, with graphite-monochromated  $MoK\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the *SHELX-2018* program package.<sup>1</sup> All the three hydrogen atoms of  $[H_3O]^+$  were disorder with 1/3 site occupancy. Besides, the empirical formula was further verified through EDS, TGA and EA experiments. The crystallographic data and details of structural refinements are listed in Table S1. It should be noted that, the structure could be solved and refined in both the space groups of  $P6_3$  and  $P6_3mc$ . However, structural refinements in  $P6_3$  gave much lower  $R1$  values (0.0413 in  $P6_3$  and 0.0799 in  $P6_3mc$ ). Moreover, Fig. S1 compares the experimental PXRD pattern of **1** with the simulated ones from single crystal structures under different space groups ( $P6_3$  and  $P6_3mc$ ). It can be seen that there is an extra diffraction peak at around  $26^\circ$  of  $2\theta$  in both the experimental PXRD pattern of **1** and the

simulated one in  $P6_3$ , while there is none at the same position for the simulated one in  $P6_3mc$ . Thus,  $P6_3$  is more suitable for the single crystal structure of **1**.



**Fig. S1** Comparison of the experimental PXRD pattern of **1** with the simulated ones from single crystal structures under different space groups ( $P6_3$  and  $P6_3mc$ ).

#### Proton Conductivity Measurement

Ac impedance technique was applied to measure proton conductivity with a Solartron 1260 impedance/gain-phase analyzer. Gold wires were connected to both sides of the crystalline to form four end terminals (quasi-four-probe method). Crystal sizes were determined by LW500LT microscope. The measured crystal was clean with acetone after the test for another direction measurement. The bulk conductivity was obtained by semicircle fittings of Nyquist plots. The conductivities could be expressed by the equation:

$$\sigma = L/SR \text{ (Eq. S1)}$$

where  $\sigma$  represent the conductivity ( $S \text{ cm}^{-1}$ ),  $R$  was the resistance value ( $\Omega$ ),  $L$  and  $S$  were the thickness (cm) of the measured sample and the electrode area ( $\text{cm}^2$ ), respectively.

Arrhenius equation could be described by the equation:

$$\ln(\sigma T) = \ln A - E_a/(k_B T) \text{ (Eq. S2)}$$

where  $\sigma$  represent the proton conductivity,  $E_a$  represent the proton-transport activation energy,  $k_B$  is the Boltzmann constant,  $T$  and  $A$  are temperature and pre-exponential factor, respectively.

**Table S1. Crystallographic data and structural refinement details for 1.**

Compound	1
Structural formula	(H <sub>3</sub> O)(VO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub>
Empirical formula	H <sub>3</sub> V <sub>3</sub> Se <sub>2</sub> O <sub>13</sub>
Formula Mass	521.76
Crystal system	hexagonal
Space group	<i>P</i> 6 <sub>3</sub>
<i>a</i> /Å	7.1368(5)
<i>c</i> /Å	11.4944(13)
<i>V</i> /Å <sup>3</sup>	507.02(9)
<i>Z</i>	2
$\lambda$ /Å	0.71073
<i>T</i> /K	298
<i>F</i> (000)	488
<i>D<sub>c</sub></i> / Mg·m <sup>-3</sup>	3.418
$\mu$ /mm <sup>-1</sup>	9.958
No. of Reflection collected	3824
No. of Reflection unique	870
No. of parameters	56
<i>R</i> <sub>int</sub>	0.0513
<sup>[a]</sup> <i>R</i> <sub>1</sub> value ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0413
<sup>[b]</sup> <i>wR</i> ( <i>F</i> <sup>2</sup> ) value ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0985
<i>R</i> <sub>1</sub> value (all data)	0.0453
<i>wR</i> ( <i>F</i> <sup>2</sup> ) value (all data)	0.0985
<i>GOF</i>	1.010
CCDC Number	1976286

$$^{[a]}R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ^{[b]}wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

**Table S2 Selected bond lengths (Å) and bond angles (°) for 1.**

1			
Se(1)-O(1)	1.709(10)	V(1)-O(2)	1.933(10)
Se(1)-O(1)#1	1.709(9)	V(1)-O(1)	1.949(9)
Se(1)-O(1)#2	1.709(10)	V(1)-O(4)#1	2.131(14)
Se(2)-O(2)	1.708(9)	V(1)-O(3)#3	2.155(14)
Se(2)-O(2)#3	1.708(9)	O(5)-H(5A)	0.8234
Se(2)-O(2)#4	1.708(9)	O(5)-H(5B)	0.8200
V(1)-O(3)	1.672(13)	O(5)-H(5C)	0.8228
V(1)-O(4)	1.690(14)		
O(1)-Se(1)-O(1)#1	102.8(4)	O(3)-V(1)-O(3)#3	81.8(5)
O(1)-Se(1)-O(1)#2	102.8(4)	O(4)-V(1)-O(3)#3	80.8(5)
O(1)#1-Se(1)-O(1)#2	102.8(4)	O(3)-V(1)-O(3)#3	89.6(5)
O(2)-Se(2)-O(2)#3	102.8(4)	O(4)-V(1)-O(3)#3	167.5(5)
O(2)-Se(2)-O(2)#4	102.8(4)	O(2)-V(1)-O(3)#3	81.5(5)
O(2)#3-Se(2)-O(2)#4	102.8(4)	O(1)-V(1)-O(3)#3	81.1(5)
O(3)-V(1)-O(4)	102.9(4)	O(4)#1-V(1)-O(3)#3	76.5(4)
O(3)-V(1)-O(2)	97.4(6)	V(1)-O(3)-V(1)#4	140.9(6)
O(4)-V(1)-O(2)	97.8(5)	Se(1)-O(1)-V(1)	129.8(6)
O(3)-V(1)-O(1)	96.1(5)	Se(2)-O(2)-V(1)	130.0(6)

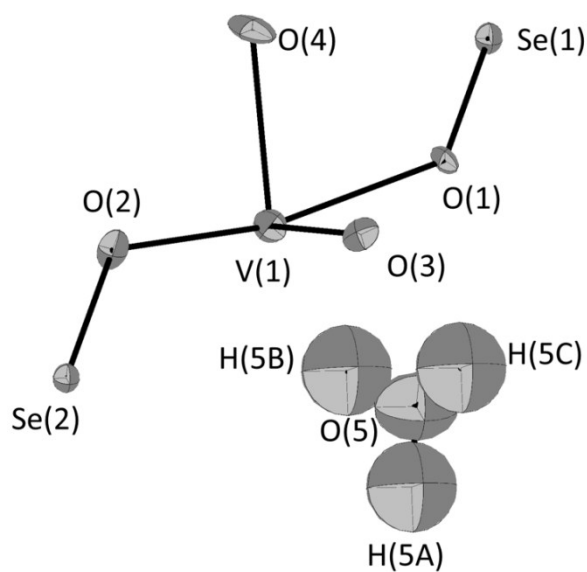
O(4)-V(1)-O(1)	96.2(6)	V(1)-O(4)-V(1)#2	141.4(7)
O(2)-V(1)-O(1)	157.8(4)	H(5A)-O(5)-H(5B)	115.2
O(3)-V(1)-O(4)#1	166.0(6)	H(5A)-O(5)-H(5C)	115.0
O(4)-V(1)-O(4)#1	91.0(7)	H(5B)-O(5)-H(5C)	115.3

Symmetry transformations used to generate equivalent atoms: #1  $-y+1, x-y+1, z$ ; #2  $-x+y, -x+1, z$ ; #3  $-x+y+1, -x+2, z$ ; #4  $-y+2, x-y+1, z$

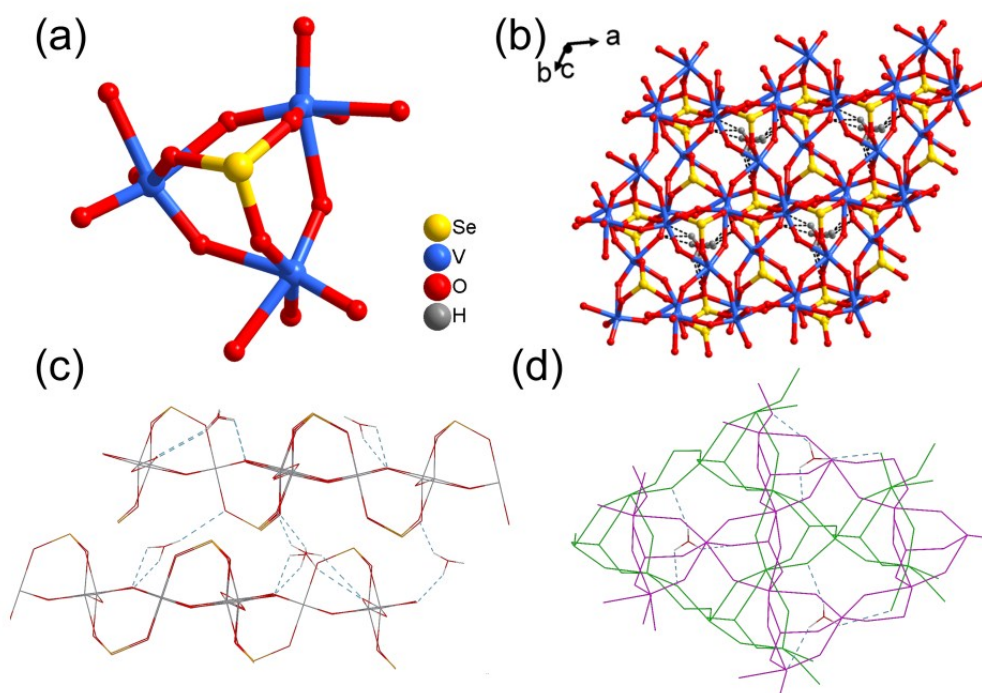
**Table S3 Hydrogen bond parameters of 1.**

1				
D-H...A	d(H...A)	d(D...A)	d(D-H)	< (DHA)
O(5)-H(5A)...O(3)#5	2.59	3.15(2)	0.82	126.7
O(5)-H(5B)...O(3)#6	2.37	3.15(2)	0.82	159.6
O(5)-H(5C)...O(2)#7	2.37	3.15(2)	0.82	147.2

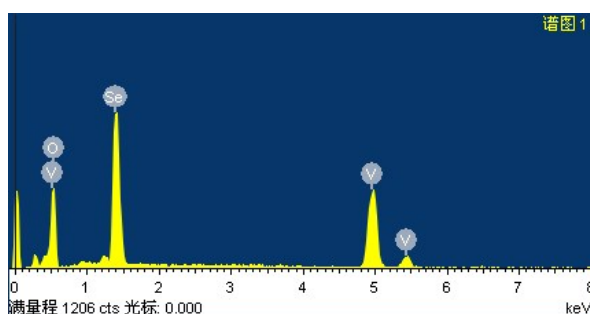
Symmetry transformations used to generate equivalent atoms: #5  $-x+y+1, -x+1, z$ ; #6  $-y+1, x-y, z$ ; #7  $x-y+1, x, z-1/2$



**Fig. S2** ORTEP plot showing the crystallographically asymmetric unit of **1**. Thermal ellipsoids are given at the 50% probability level.



**Fig. S3** (a) The trinuclear cluster is formed by three edge-sharing  $[VO_6]$  octahedra. The  $[SeO_3]$  pyramid is capped on the trinuclear cluster. (b) Packing view of **1** along the  $c$  axis;  $O-H\cdots O$  H-bonds are shown in black dashed lines. Views of  $O-H\cdots O$  H-bonding network in **1** along the  $[100]$  (c) and  $[001]$  (d) directions, respectively;  $O-H\cdots O$  H-bonds are shown in navy dashed lines.



**Fig. S4** Energy dispersive spectroscopy (EDS) image of **1**.

**Table S4** Energy dispersive spectroscopy (EDS) data of compound **1**.

Element	Weight percentage (%)	Atomic percentage (%)	Atomic ratio (calc.)
V	48.78	59.61	1.00 (1.00)
Se	51.22	40.39	0.68 (0.67)

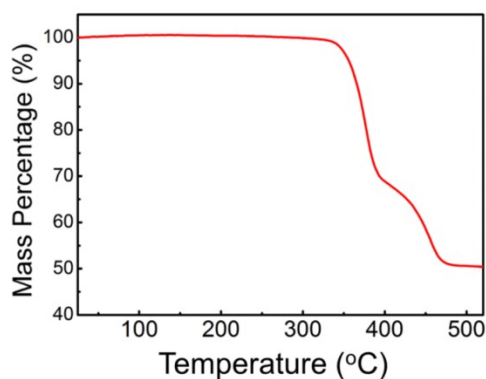


Fig. S5 Thermogravimetric curve for 1.

Table S5 Proton conductivity ( $\sigma$ ) values of 1 at 80 °C under varied RH conditions.

[100] direction					
RH %	70	80	85	90	95
$\sigma$ (S cm <sup>-1</sup> )	$1.36 \times 10^{-5}$	$2.98 \times 10^{-5}$	$3.88 \times 10^{-5}$	$4.66 \times 10^{-5}$	$4.82 \times 10^{-5}$
[001] direction					
RH %	70	80	85	90	95
$\sigma$ (S cm <sup>-1</sup> )	$7.25 \times 10^{-8}$	$6.02 \times 10^{-7}$	$1.53 \times 10^{-6}$	$2.18 \times 10^{-6}$	$3.43 \times 10^{-6}$

Table S6 Proton conductivity ( $\sigma$ ) values of 1 under 95% RH and at different temperatures.

[100] direction					
T/°C	60	70	80	85	90
$\sigma$ (S cm <sup>-1</sup> )	$2.95 \times 10^{-5}$	$3.64 \times 10^{-5}$	$4.02 \times 10^{-5}$	$4.82 \times 10^{-5}$	$5.95 \times 10^{-5}$
[001] direction					
T/°C	60	70	80	85	90
$\sigma$ (S cm <sup>-1</sup> )	$4.07 \times 10^{-6}$	$6.38 \times 10^{-6}$	$9.13 \times 10^{-6}$	$1.18 \times 10^{-5}$	$1.67 \times 10^{-5}$

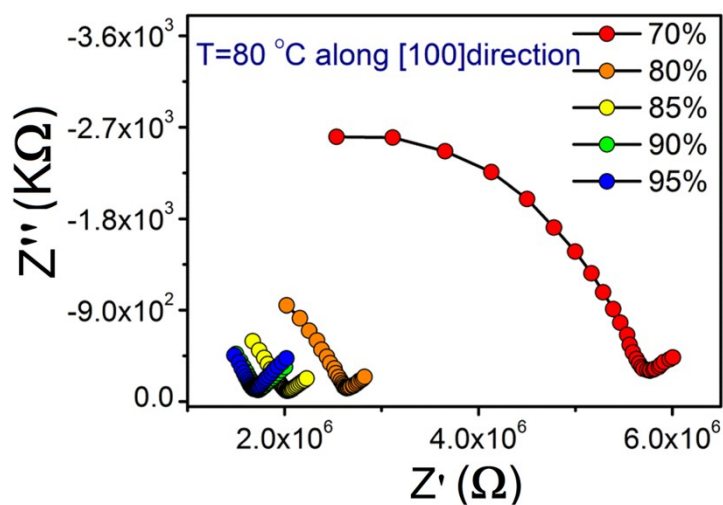
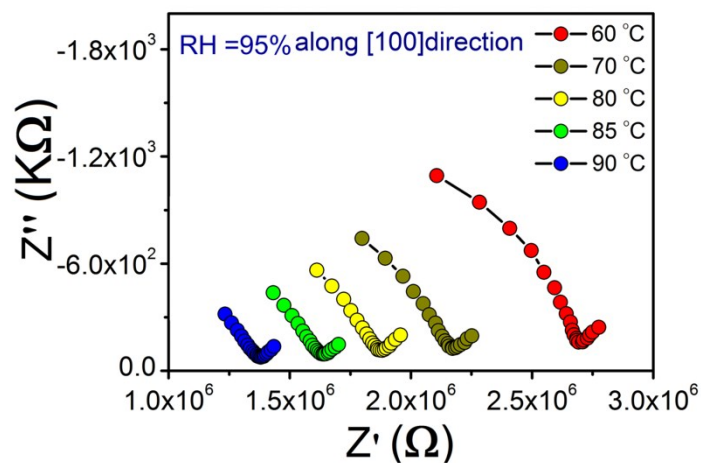
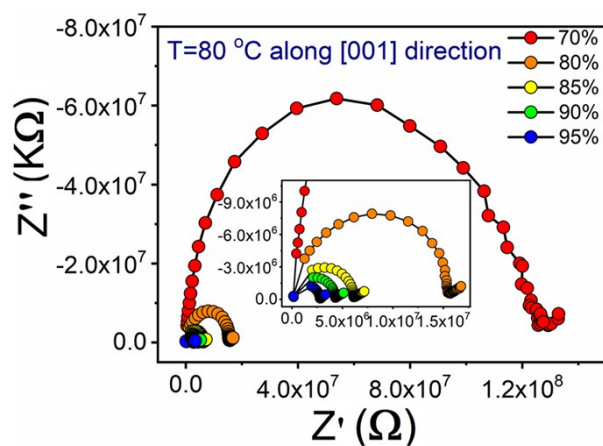


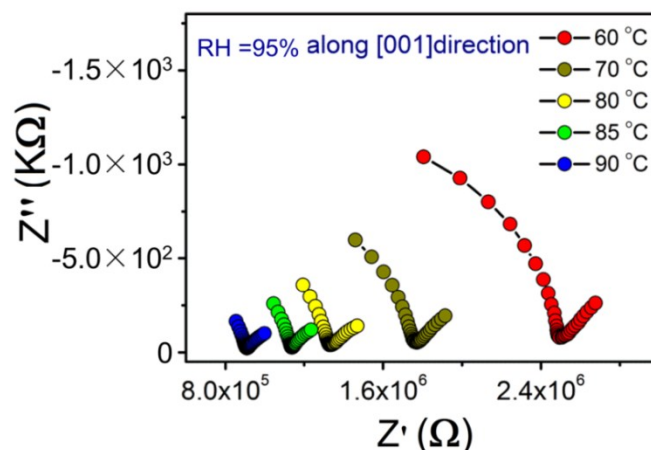
Fig. S6 Impedance spectra of 1 along [100] direction under different relative humidities at 80 °C.



**Fig. S7** Impedance spectra of 1 along [100] direction under different temperature conditions at 95% RH.



**Fig. S8** Impedance spectra of 1 along [001] direction under different relative humidities at 80 °C. Inset is the enlarged image of part of impedance spectra for clarity.



**Fig. S9** Impedance spectra of 1 along [001] direction under different temperature conditions at 95% RH.

**Reference:**

1. G.M. Sheldrick, crystal structure refinement with SHELXL, *Acta Cryst.* 2015, **C71**, 3-8.