

## Two nanoscale Nb containing polyoxometalates based on the $\{P_2W_{15}Nb_3O_{62}\}$ clusters and Chromium Cations

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### 1. Materials and Methods

Precursors  $K_7H[Nb_6O_{19}] \cdot 13H_2O$ ,<sup>1</sup> and  $Na_{12}[\alpha-P_2W_{15}O_{56}] \cdot 24H_2O$ ,<sup>2</sup> were synthesized according to the procedures described in the literature, and their purity was characterized by IR spectra, thermogravimetric analyses, and elemental analysis. All other reagents were readily available from commercial sources and were used as received without further purification. Elemental analyses (Cs, P, K, Cr, W, and Nb) were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded on Alpha Centaur FT/IR spectrophotometer (KBr pellets) over the region of 400–4000  $cm^{-1}$ . PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu  $K\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation in the range 3–50°. UV-vis absorption spectroscopy was obtained on a U-3010 spectrophotometer (Hitachi, Japan). Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA 7 analyzer heated from room temperature to 800 °C under a nitrogen gas atmosphere with a heating rate of 10 °C  $min^{-1}$ .

### 2. Electrochemical Measurement

The working electrodes were prepared by compressing a mixture of active materials, acetylene black, and binder (polytetrafluoroethylene, PTFE) in a weight ratio of 70:20:10. The composite cathodes were cut into wafers with diameter of 8 mm with mass loading of 5  $mg\ cm^{-2}$ . Lithium metal was used as the counter and reference electrode. The electrolyte was  $LiPF_6$  (1.0 M) dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) with a volume ratio of 1:1:1. The LAND-CT2001A galvanostatic testers were employed to measure the electrochemical capacity at a current density of 100  $mA\ g^{-1}$  and the cycle life of working electrodes at room temperature. The cutoff potentials for charge and discharge were set at 2.8 and 0.05 V (vs.  $Li^+/Li$ ), respectively.

### 3. Synthesis

**Synthesis of  $Cs_9[P_2W_{15}(NbO_2)_3O_{59}] \cdot 16H_2O$**   $K_7H[Nb_6O_{19}] \cdot 13H_2O$  (2.20 g, 1.10 mmol) was dissolved in an  $H_2O_2$  solution (12 mL of 30% aqueous  $H_2O_2$  in 160 mL of water). With vigorous stirring, HCl (aq. 1.0 M) was added in one aliquot (14 mL), followed by the immediate addition of  $Na_{12}[\alpha-P_2W_{15}O_{56}] \cdot 18H_2O$  (9.50 g, 2.20 mmol). The resulting mixture was stirred with heating at 40 °C for

1 h, cooled to room temperature, and then filtered to remove some white precipitate. To the yellow filtrate was added CsCl (25 g), and the mixture was stirred for 1 h and then filtered to collect the yellow precipitate formed. The precipitate was washed first with ethanol (12 mL) and then diethyl ether (12 mL), and dried in air to give the product as a yellow powder (56% yield based on Nb precursor).

**Synthesis of 1.** The mixture of  $\text{Cs}_9[\text{P}_2\text{W}_{15}\text{O}_{59}(\text{NbO}_2)_3]\cdot 16\text{H}_2\text{O}$  (50 mg) and  $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (10 mg) were put in a 5-cm high vial, which was then transferred and sealed in a Teflon-lined autoclave with 3 mL HCl (aq. 1.0 M) and heated at 120 °C for 3 days followed by slow cooling to room temperature. The resulting green crystals were separated from the solution and washed with distilled water several times, yielding 62% based on  $\text{Cs}_9[\text{P}_2\text{W}_{15}\text{O}_{59}(\text{NbO}_2)_3]\cdot 16\text{H}_2\text{O}$ . Anal. Calc: P, 1.18; Nb 5.33; W, 52.75; Cr, 1.49; Cs, 6.35; K, 1.49. Found: P, 1.03; Nb 5.58; W, 51.32; Cr, 1.35; Cs, 6.56; K, 1.41.

**Synthesis of 2.** Compound **2** was prepared following the procedure described for **1**, but by using a larger quantity of  $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (20 mg). The resulting products were green block crystals (yield: 68%). Anal. Calc: P, 1.30; Nb 5.87; W, 58.14; Cr, 1.09; Cs, 9.10; Na, 0.12; K, 1.03. Found: P, 1.17; Nb 5.82; W, 57.01; Cr, 0.99; Cs, 8.83; Na, 0.13; K, 1.12.

#### 4. Single-Crystal Studies

Intensity data of **1** and **2** were collected on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K. Absorption corrections were applied using multiscan techniques. Compound **1** was solved by Direct Method of SHELXS-2017 and compound **2** was solved by Direct Method of SHELXS-2014. They all further refined by full-matrix least-squares refinement on  $F^2$  using the SHELXTL package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms, with the exception of some oxygen atoms. Hydrogen atoms attached to lattice water molecules were not located. Crystallization water molecules were estimated by thermogravimetry, and only partial oxygen atoms of water molecules were achieved with the X-ray structure analysis. **1**:  $\text{H}_{144}\text{Cs}_5\text{K}_4\text{Cr}_3\text{P}_4\text{Nb}_6\text{W}_{30}\text{O}_{196}$ ,  $M_r = 10454.4$ , Monoclinic,  $c2/m$ ,  $a = 40.856(5) \text{ \AA}$ ,  $b = 23.354(5) \text{ \AA}$ ,  $c = 21.811(5) \text{ \AA}$ ,  $\alpha = 90.000(5)^\circ$ ,  $\beta = 113.632(5)^\circ$ ,  $\gamma = 90.000(5)^\circ$ ,  $V = 19066(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 3.592 \text{ g cm}^{-3}$ , final  $R_1 = 0.0548$  and  $wR_2 = 0.1755$  ( $R_{\text{int}} = 0.0924$ ) for 55292 independent reflections ( $I > 2\sigma(I)$ ). **2**:  $\text{H}_{55}\text{Cs}_{13}\text{K}_5\text{NaP}_8\text{Cr}_4\text{Nb}_{12}\text{W}_{60}\text{O}_{273}$ ,  $M_r = 18970.5$ , Triclinic,  $P-1$ ,  $a = 23.8101(9) \text{ \AA}$ ,  $b = 28.6573(11) \text{ \AA}$ ,  $c = 30.7054(11) \text{ \AA}$ ,  $\alpha = 62.3380(10)^\circ$ ,  $\beta = 81.9910(10)^\circ$ ,  $\gamma = 81.8300(10)^\circ$ ,  $V = 18303.9(12) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 3.442 \text{ g cm}^{-3}$ , final  $R_1 = 0.0829$  and  $wR_2 = 0.2564$  ( $R_{\text{int}} = 0.0658$ ) for 96321 independent reflections ( $I > 2\sigma(I)$ ). CCDC 1490204 (**1**) and 1490205 (**2**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) for **1** and **2**.

#### 5. Calculation of the theoretical capacities

The theoretical capacities were calculated according to equation:

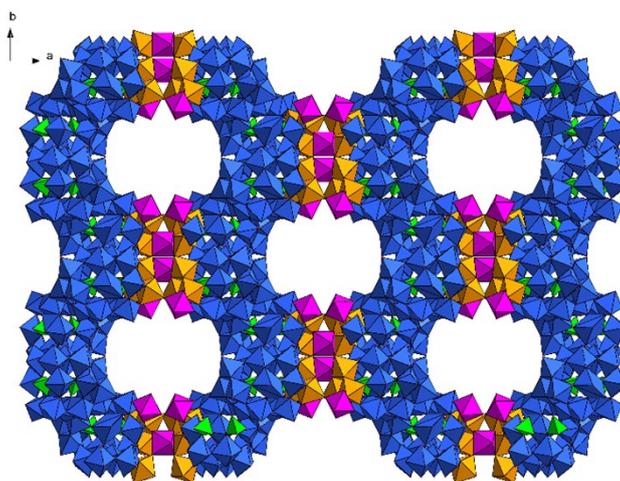
$$Q = \frac{nF}{3.6M} = \frac{96500n}{3.6M}$$

Q: Reversible charging-discharging capacity;  $n$ : Number of electrons;  $M$ : Molecular weight. As we know, niobium is not electrochemically active. Owing to the intercalation mechanism for Li

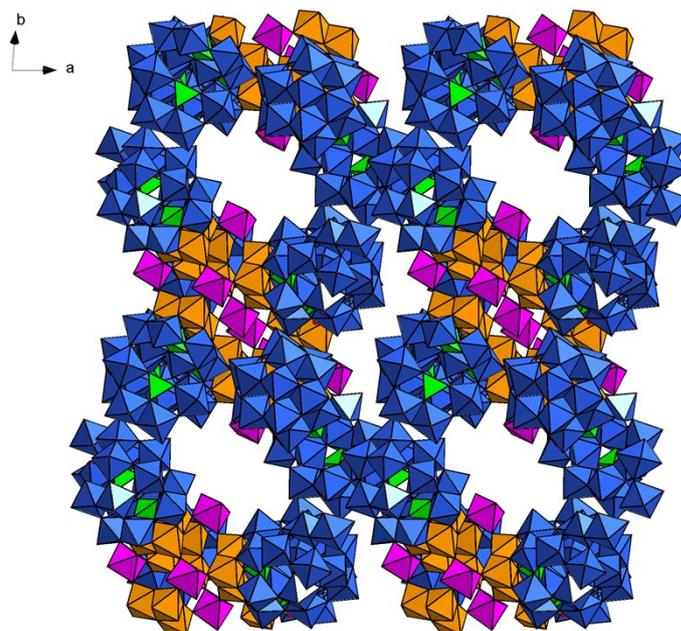
storage, we consider the redox reactions of metal ions (W and Cr). If thirty  $W^{6+}$ , and three  $Cr^{3+}$  in **1** may can be reduced to  $W^{3+}$  and  $Cr^{2+}$ , respectively, maximum of  $n = 93$ ,  $Q_{POM} = 238.4 \text{ mA h g}^{-1}$ . For **2**, if sixty  $W^{6+}$ , and four  $Cr^{3+}$  may can be reduced to  $W^{3+}$  and  $Cr^{2+}$ , respectively, maximum of  $n = 184$ ,  $Q_{POM} = 255.6 \text{ mA h g}^{-1}$ . We found that the experimental capacities ( $466.6 \text{ mAh g}^{-1}$  for **1** and  $282 \text{ mAh g}^{-1}$  for **2**) are higher than the theoretical value (about  $238.4 \text{ mA h g}^{-1}$  for **1** and about  $255.6 \text{ mAh g}^{-1}$  for **2**). The access capacities here possibly are the capacitive contribution derived from the pores of **1** and **2**.<sup>[3-6]</sup>

**Table S1.** Comparison of **1** and **2** with other pristine POMs and POMOFs based anodes.

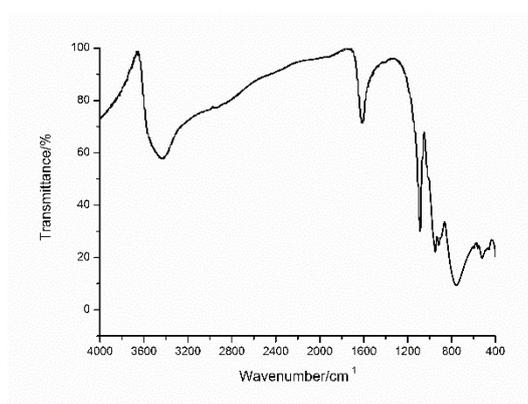
Materials	Current density ( $\text{mA g}^{-1}$ )	Reversible capacity ( $\text{mAh g}^{-1}$ )/ Cycles	Reference
<b>1 (POM)</b>	<b>100</b>	<b>342.2/45</b>	<b>This work</b>
<b>2 (POM)</b>	100	115.9/45	This work
$\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ (POM)	50	250/100	[3]
$(\text{NBu}_4)_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ (POM)	100	50/100	[4]
POMOF-1 (POMOF)	1.25 C	350/500	[5]
$\text{Ag}_{26}\text{P}_2\text{W}_{18}$ (POMOF)	100	400/100	[4]
NENU-507 (POMOF)	100	640/100	[6]



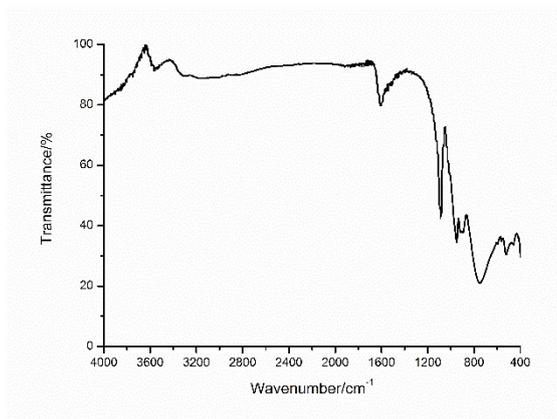
**Fig. S1** The 3D architecture with 1D channels built by  $\{\text{Cr}_3(\text{H}_2\text{O})_{12}[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]_2\}$  units, K and Cs cations for **1** (H atom, and water molecules are omitted for clarity). Color scheme:  $\text{NbO}_6$  (orange),  $\text{WO}_6$  (blue),  $\text{PO}_4$  (bright green),  $\text{CrO}_6$  (pink).



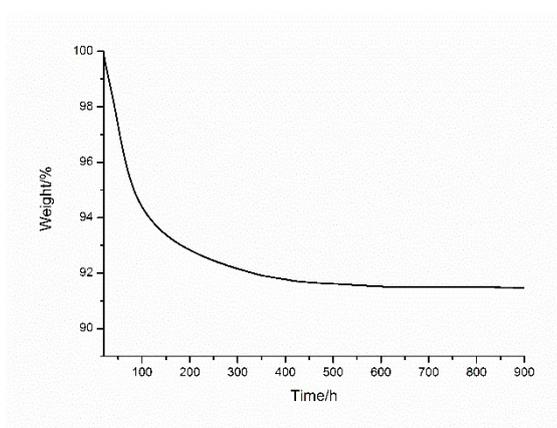
**Fig. S2** The 3D architecture with 1D channels built by  $\{\text{Cr}_3(\text{H}_2\text{O})_{12}[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]_2\}$  units, K and Cs cations for **2** (H atom, and water molecules are omitted for clarity). Color scheme: NbO<sub>6</sub> (orange), WO<sub>6</sub> (blue), PO<sub>4</sub> (bright green), CrO<sub>6</sub> (pink).



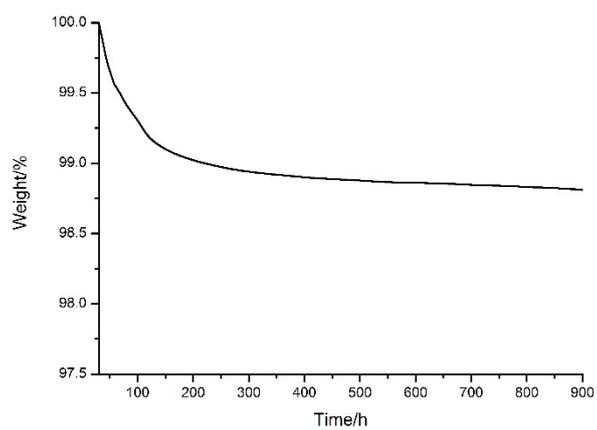
**Fig. S3** The IR spectrum of **1**.



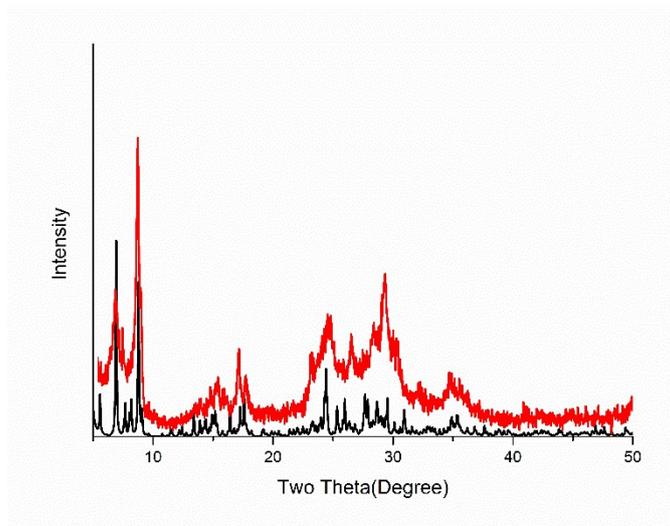
**Fig. S4** The IR spectrum of **2**.



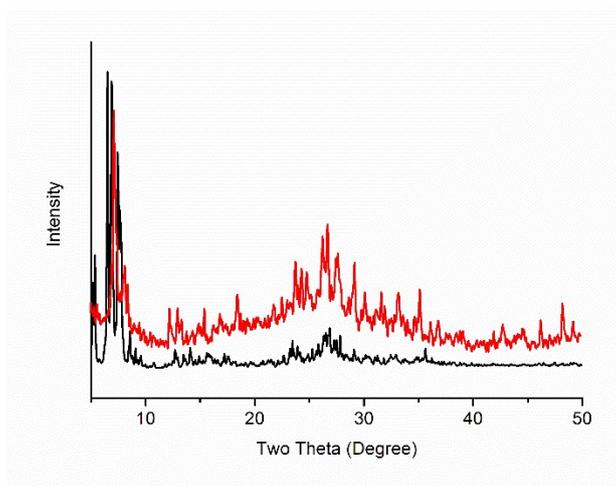
**Fig. S5** The TGA curve of **1**.



**Fig. S6** The TGA curve of **2**.



**Fig. S7** The XRPD pattern (top) and simulated pattern (bottom) of **1**.



**Fig. S8** The XRPD pattern (top) and simulated pattern (bottom) of **2**.

## References

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