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

Peng Huang,\textsuperscript{a} Xin-Long Wang,\textsuperscript{b} De-Qing He,\textsuperscript{a} Hai-Yang Wu,\textsuperscript{a} Chao Qin,\textsuperscript{b,*} Meng Du,\textsuperscript{a} Chao Lai,\textsuperscript{a,*} and Zhong-Min Su\textsuperscript{b,*}

\textsuperscript{a} Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Department of Chemistry, School of Chemistry and Material Science, Jiangsu Normal University, Xuzhou, 221116, PR China, E-mail: laichao@jsnu.edu.cn
\textsuperscript{b} Institute of Functional Material Chemistry, National & Local United Engineering Lab for Power Battery, Northeast Normal University, Changchun, 130024 Jilin, People’s Republic of China. E-mail: qinc703@nenu.edu.cn; zmsu@nenu.edu.cn.

1. Materials and Methods
Precursors K\textsubscript{7}[Nb\textsubscript{6}O\textsubscript{19}]·13H\textsubscript{2}O,\textsuperscript{1} and Na\textsubscript{12}[\alpha-P\textsubscript{2}W\textsubscript{15}O\textsubscript{56}]·24H\textsubscript{2}O,\textsuperscript{2} 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 reived 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 Centaurt FT/IR spectrophotometer (KBr pellets) over the region of 400–4000 cm\textsuperscript{-1}. PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu K\textalpha\textsubscript{\lambda} (\lambda = 1.5418 Å) 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\textsuperscript{-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\textsuperscript{-2}. Lithium metal was used as the counter and reference electrode. The electrolyte was LiPF\textsubscript{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\textsuperscript{-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\textsubscript{9}[P\textsubscript{2}W\textsubscript{15}(NbO\textsubscript{2})\textsubscript{3}O\textsubscript{59}]·16H\textsubscript{2}O K\textsubscript{7}[Nb\textsubscript{6}O\textsubscript{19}]·13H\textsubscript{2}O (2.20 g, 1.10 mmol) was dissolved in an H\textsubscript{2}O\textsubscript{2} solution (12 mL of 30% aqueous H\textsubscript{2}O\textsubscript{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\textsubscript{12}[\alpha-P\textsubscript{2}W\textsubscript{15}O\textsubscript{56}]·18H\textsubscript{2}O (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 Cs₉[P₂W₁₅O₅₉(NbO₂)₃]·16H₂O (50 mg) and Cr(NO₃)₃·9H₂O (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 Cs₉[P₂W₁₅O₅₉(NbO₂)₃]·16H₂O. 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 Cr(NO₃)₃·9H₂O (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 Kα radiation (λ = 0.71073 Å) 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 F² 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: H₆₆Cs₅K₉Cr₄P₄Nb₆W₃₀O₁₉₆, Mr = 10454.4, Monoclinic, c2/m, a = 40.856(5) Å, b = 23.354(5) Å, c = 21.811(5) Å, α = 90.000(5)°, β = 113.632(5)°, γ = 90.000(5)°, V = 19066(6) Å³, Z = 4, Rcalcd = 3.592 g cm⁻³, final R₁ = 0.0548 and wR₂ = 0.1755 (Rint = 0.0924) for 55292 independent reflections (I > 2σ(I)). 2: H₅₅Cs₅K₅Na₆P₄Cr₄Nb₁₂W₆₀O₂₇₃, Mr = 18970.5, Triclinic, P-1, a = 23.8101(9) Å, b = 28.6573(11) Å, c = 30.7054(11) Å, α = 62.3380(10)°, β = 81.9910(10)°, γ = 81.8300(10)°, V = 18303.9(12) Å³, Z = 2, Rcalcd = 3.442 g cm⁻³, final R₁ = 0.0829 and wR₂ = 0.2564 (Rint = 0.0658) for 96321 independent reflections (I > 2σ(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 for 1 and 2.

5. **Calculation of the theoretical capacities**

The theoretical capacities were calculated according to equation:

\[ Q = \frac{nF}{3.6M} \times 96500n \]

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 $n = 93$, $Q_{POM} = 238.4$ 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 $n = 184$, $Q_{POM} = 255.6$ mA h g$^{-1}$. We found that the experimental capacities (466.6 mAh g$^{-1}$ for 1 and 282 mAh g$^{-1}$ for 2) are higher than the theoretical value (about 238.4 mA h g$^{-1}$ for 1 and about 255.6 mAh g$^{-1}$ for 2). The access capacities here possibly are the capacitive contribution derived from the pores of 1 and 2.$^{[3-6]}$
**Table S1.** Comparison of 1 and 2 with other pristine POMs and POMOFs based anodes.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Current density (mA g⁻¹)</th>
<th>Reversible capacity (mAh g⁻¹)/ Cycles</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (POM)</td>
<td>100</td>
<td>342.2/45</td>
<td>This work</td>
</tr>
<tr>
<td>2 (POM)</td>
<td>100</td>
<td>115.9/45</td>
<td>This work</td>
</tr>
<tr>
<td>Li₂[V₁₂O₃₆(CO₃)] (POM)</td>
<td>50</td>
<td>250/100</td>
<td>[3]</td>
</tr>
<tr>
<td>(NBu₄)₆[P₂W₁₈O₆₂] (POM)</td>
<td>100</td>
<td>50/100</td>
<td>[4]</td>
</tr>
<tr>
<td>POMOF-1 (POMOF)</td>
<td>1.25 C</td>
<td>350/500</td>
<td>[5]</td>
</tr>
<tr>
<td>Ag₂₆P₂W₁₈ (POMOF)</td>
<td>100</td>
<td>400/100</td>
<td>[4]</td>
</tr>
<tr>
<td>NENU-507 (POMOF)</td>
<td>100</td>
<td>640/100</td>
<td>[6]</td>
</tr>
</tbody>
</table>

**Fig. S1** The 3D architecture with 1D channels built by [Cr₃(H₂O)₁₂][P₂W₁₅Nb₃O₆₂] units, K and Cs cations for 1 (H atom, and water molecules are omitted for clarity). Color scheme: NbO₆ (orange), WO₆ (blue), PO₄ (bright green), CrO₆ (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}\text{]}_2}\} units, K and Cs cations for 2 (H atom, and water molecules are omitted for clarity). Color scheme: NbO$_6$ (orange), WO$_6$ (blue), PO$_4$ (bright green), CrO$_6$ (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