# Self-assembly and lithium storage performance of a nanoscale polyoxometalate based on the {MnTa<sub>18</sub>} cluster

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### 1. Materials and Methods

All reagents and solvents for the syntheses were purchased from commercial sources and used as received. Precursors  $Cs_3K_{3.5}H_{0.5}[SiW_9(TaO_2)_3O_{37}]\cdot 9H_2O$ ,<sup>1</sup> were synthesized according to the procedures described in the literature, their purity was characterized by IR spectra, thermogravimetric analyses, and elemental analysis. Elemental analyses (Cs, K, Si, Mn, Ta, and W) 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<sup>-1</sup>. PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu K $\alpha$  ( $\lambda$  = 1.5418 Å) radiation in the range 3–50°. 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<sup>-1</sup>

## 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<sup>-2</sup>. Lithium metal was used as the counter and reference electrode. The electrolyte was LiPF<sub>6</sub> (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 and the cycle life of working electrodes at room temperature, cyclic voltammetry test with CHI760e electrochemical analyzer. The cutoff potentials for charge and discharge were set at 3.0 and 0.01 V (vs. Li+/Li), respectively.

## 3. Synthesis

Synthesis of  $Cs_{12}K_3H_7[MnTa_{18}Si_6W_{54}O_{231}]\cdot 61H_2O$  (1) The mixture of  $Cs_3K_{3.5}H_{0.5}[SiW_9(TaO_2)_3O_{37}]\cdot 9H_2O$  (50 mg) and  $MnCl_2\cdot 4H_2O$  (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 products were purple block crystals (yield: 52%). Anal. Calc: Si, 0.84; Ta 16.35; W, 49.83; Mn, 0.27; Cs, 8.01; K, 0.59. Found: Si, 0.61; Ta 16.99; W, 48.15; Mn, 0.41; Cs, 8.82; K, 0.27. IR (KBr disks): 532, 697, 781, 900, 962 cm<sup>-1</sup> (Fig. S3)

#### 4. Single-Crystal Studies

Intensity data of **1** was collected on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293 K. Absorption corrections were applied using multiscan techniques. Their structures were solved by direct methods of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.<sup>2</sup> 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**: H<sub>129</sub>Cs<sub>12</sub>K<sub>3</sub>MnSi<sub>6</sub>Ta<sub>18</sub>W<sub>54</sub>O<sub>292</sub>, *M*r = 19921.88, triclinic, *P*-1, *a* = 21.631(2) Å, *b* = 23.063(2) Å, *c* = 31.541(3) Å, *α* = 80.614(2)°,  $\beta$  = 81.403(2)°,  $\gamma$  = 70.344(2)°, *V* = 14544(3) Å<sup>3</sup>, *Z* = 2,  $\rho_{calcd}$  = 4.520 g cm<sup>-3</sup>, final *R*<sub>1</sub> = 0.0968 and *wR*<sub>2</sub> = 0.3022(*R*<sub>int</sub> = 0.1821) for 41770 independent reflections (*I* > 2*σ*(*I*)). CCDC 1058416 (**1**), contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambrige Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif for **1**.



**Fig. S1** Ball-and-stick presentations of **1**. (W: blue, Mn: pale green, Ta: yellow, O: gray, Si: invisible green)



**Fig. S2** Ball-and-stick presentations of **1**. (a) Nine bridging O atoms (red) linked six basic unit in the molecule. (b) A different viewing angle of (a). (c) Six bridging O atoms (red) distributed in the Antarctic and the Arctic. (In order to make the picture clearer, only half of the molecule is shown.) (d) A different viewing angle of (c). (W: blue, Mn: green, Ta: yellow)



Fig. S3 IR spectra of 1.



Fig. S4 The XRPD patterns for as-synthesized (top) and simulated (bottom) 1.



Fig. S5 TGA curve of 1.



Fig. S6 Electrochemical impedance spectroscopy of compound 1 electrode in LIBs.



**Fig. S7** Equivalent circuits used for fitting the experimental date. (a) Before cycling. (b) After cycleing.

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	Before cycling	Error (%)	After cycling	Error (%)
Re	5.734	4.232	3.051	3.426
Rf			9.83	15.483
Rct	455.0	2.942	109.9	3.120
Sum	460.7		122.8	

Table S1 The fitting errors of the simulated equivalent circuit of 1 anodes



**Fig. S8** IR spectra of anode material (70 wt% active material of compound **1**, 20 wt% Super-P, and 10 wt% PVDF) before cycling (Black) and after cycling (Red).

Theoretical capacities were calculated according to equation:

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

Q: Reversible charging-discharging capacity; n: Number of electrons; M: Molecular weight. Owing to the intercalation mechanism for Li storage, we consider the redox reactions of metal ions (W, Ta and Mn) and perform X-ray photoelectron spectroscopy (XPS) studies to detect the change of element valence during cycling test (Fig. S9). For compound **1**, W<sup>6+</sup>, Ta<sup>5+</sup>, and Mn<sup>2+</sup> can be reduced to W<sup>5+</sup>, Ta<sup>4+</sup> and Mn, respectively, with maximum of n = 74, Q = 105.4 mAh/g. We found that the experimental capacities are higher than the theoretical value, which is quite common in LIBs of nano materials. The schematic diagrams of the mechanism for Li storage have been given (Fig. S11).<sup>3-15</sup>



**Fig. S9** The XPS spectra of compound **1**. (a) W (before cycling); (b) Ta (before cycling); (c) Mn (before cycling); (d) W (after cycling); (e) Ta (after cycling); (f) Mn (after cycling).



**Fig. S10** The 3D architecture with 1D channels built by  $[MnTa_{18}Si_6W_{54}O_{231}]$  unit (K, Cs, H, and water molecules are omitted for clarity). Color scheme: TaO<sub>6</sub> (yellow), WO<sub>6</sub> (blue), SiO<sub>4</sub> (pink), MnO<sub>6</sub> (brown).



Maximum of 74-electrons

Fig. S11 Schematic diagrams of the mechanism for Li storage of compound 1.

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