## **Supplemental Information**

## Vanadium Oxide Pillared by Interlayer Mg<sup>2+</sup> lons and Water as

## **Ultralong Life Cathodes for Magnesium Ion Batteries**

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Figure S1. XRD diffraction patterns of  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$ ,  $V_2O_5 \cdot nH_2O$  and  $Mg_{0.3}V_2O_5$ .

**Table S1.** Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) analysis of Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>·1.1H<sub>2</sub>O and Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>.

Elements Samples	Mg (W/%)	V (W/%)	Mg/V
Mg <sub>0.3</sub> V <sub>2</sub> O <sub>5</sub> ·1.1H <sub>2</sub> O	2.92	40.69	0.3/2
$Mg_{0.3}V_2O_5$	2.99	41.90	0.3/2



**Figure S2.** TGA-DTA analysis of the pristine  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$ . The  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$  shows stepwise loss of lattice water corresponding to an overall 9.51% weight loss, equivalent to 1.1 molecule of water per formula unit.



**Figure S3.** (A) Survey XPS spectrum and (B) high-resolution XPS spectrum of V2p peak for the resulting  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$ .



Figure S4. Energy dispersive X-ray (EDX) spectrum of the Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>·1.1H<sub>2</sub>O.



Figure S5. (A) FESEM image, (B) TEM images and (inset of B) SAED pattern of V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O.



**Figure S6.** (A) FESEM image, (B,C) TEM images, (inset of C) HRTEM image and (D) SAED pattern of Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>.



**Figure S7.** Nitrogen adsorption-desorption isotherms of (A)  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$ , (B)  $V_2O_5 \cdot nH_2O$  and (C)  $Mg_{0.3}V_2O_5$ .



**Figure S8.** CV curves of (A)  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$ , (B)  $V_2O_5 \cdot nH_2O$  and (C)  $Mg_{0.3}V_2O_5$  for the first two cycle at a scanning rate of 0.1 mV s<sup>-1</sup> between 1.4 and 3.4 V vs.  $Mg/Mg^{2+}$ .



**Figure S9.** Discharge-charge curves (A,C) and cycling performances (B,D) of  $Mg_{0.3}V_2O_5$ ·1.1H<sub>2</sub>O at 0.2 and 0.5 A g<sup>-1</sup>, respectively.



**Figure S10.** Cycling performances of (A)  $V_2O_5 \cdot nH_2O$  and (B)  $Mg_{0.3}V_2O_5$  at 0.5 A g<sup>-1</sup>, respectively.



Figure S11. SEM images of the (A)  $V_2O_5 \cdot nH_2O$  and (B)  $Mg_{0.3}V_2O_5$  single nanowire devices, respectively.



**Figure S12.** (A) SEM image, (B) TEM image, (insets of B) HRTEM image and (C) SAED pattern of  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$  after 500 cycles at 0.1 A g<sup>-1</sup>. (D) SEM image, (E) TEM image, (insets of E) HRTEM image and (F) SAED pattern of  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$  after 10000 cycles at 1 A g<sup>-1</sup>.



**Figure S13**. (A) TEM-EDX element mapping images of Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>·1.1H<sub>2</sub>O nanowires at full charge state in 10<sup>th</sup> cycle, and (B) corresponding energy dispersive X-ray (EDX) spectrum. (C) TEM-EDX element mapping images of Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>·1.1H<sub>2</sub>O nanowires at full discharge state in 10<sup>th</sup> cycle, and (D) corresponding energy dispersive X-ray (EDX) spectrum.



**Figure S14**. Thermogravimetry analysis (TGA) curves of  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$  nanowires after charging and discharging.



**Figure S15**. <sup>13</sup>C MAS NMR spectra collected for pristine  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$  (black line),  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$  after full discharging (red line) and full charging (blue line).



**Figure S16.** Discharge/Charge profiles of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> in APC electrolyte at 20 mA g<sup>-1</sup>. During the first discharge process, Mg<sup>2+</sup> intercalation with irreversible Na<sup>+</sup> deintercalation (Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> + Mg<sup>2+</sup> + e<sup>-</sup>  $\rightarrow$  MgNaTi<sub>3</sub>O<sub>7</sub> + Na<sup>+</sup>). In subsequent charge/discharge processes, the reversible 0.5 M Mg<sup>2+</sup> insertion–extraction occurs (MgNaTi<sub>3</sub>O<sub>7</sub>  $\leftrightarrow$  Mg<sub>0.5</sub>NaTi<sub>3</sub>O<sub>7</sub> + 0.5Mg<sup>2+</sup> + e<sup>-</sup>). The calculated theoretical capacity is of 88 mA h g<sup>-1</sup>, and the practical test is of 83 mA h g<sup>-1</sup> in this work.



**Figure S17**. (A) TEM-EDX element mapping images of MgNaTi<sub>3</sub>O<sub>7</sub> anode in charging state in MgNaTi<sub>3</sub>O<sub>7</sub>/Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>·1.1H<sub>2</sub>O full cell, and (B) corresponding energy dispersive X-ray (EDX) spectrum. (C) TEM-EDX element mapping images of MgNaTi<sub>3</sub>O<sub>7</sub> anode in discharging state in MgNaTi<sub>3</sub>O<sub>7</sub>/Mg<sub>0.3</sub>V<sub>2</sub>O<sub>5</sub>·1.1H<sub>2</sub>O full cell, and (D) corresponding energy dispersive X-ray (EDX) spectrum.



Figure S18. EDX spectrum of  $Mg_{0.3}V_2O_5 \cdot 1.1H_2O$  cathode in discharging state in  $MgNaTi_3O_7/Mg_{0.3}V_2O_5 \cdot 1.1H_2O$  full cell.