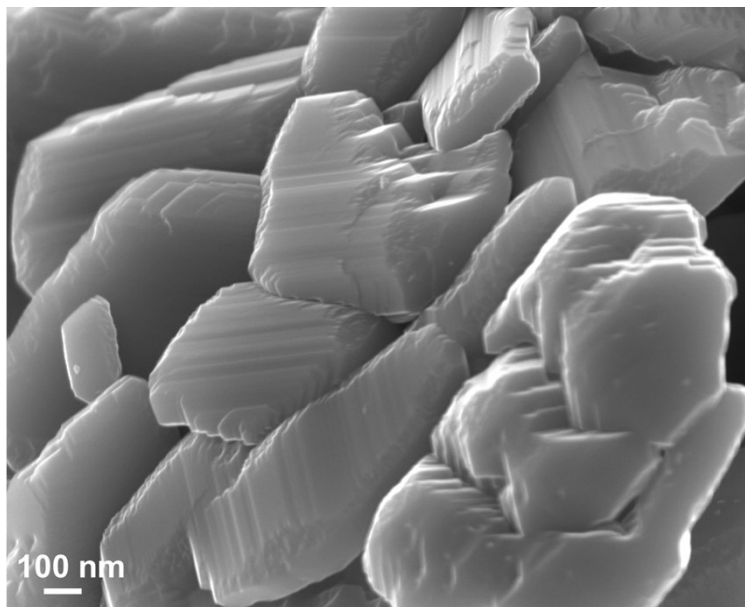
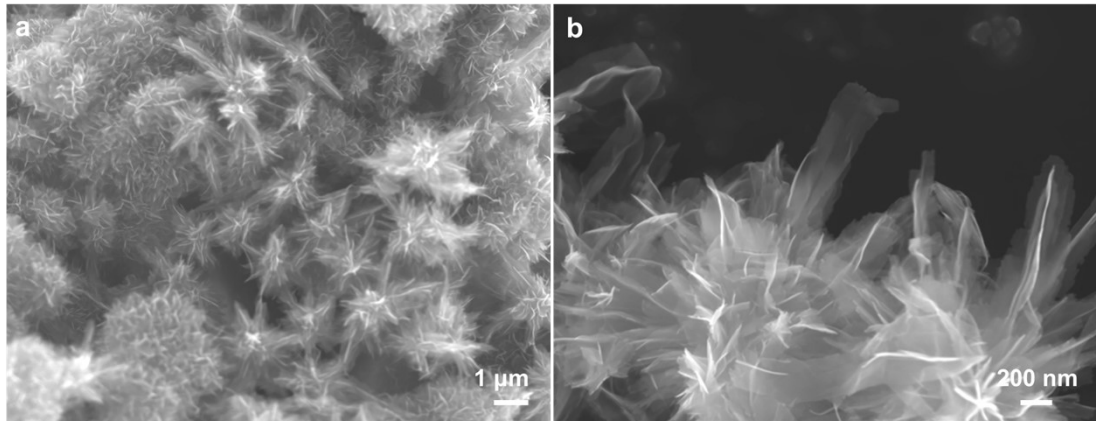


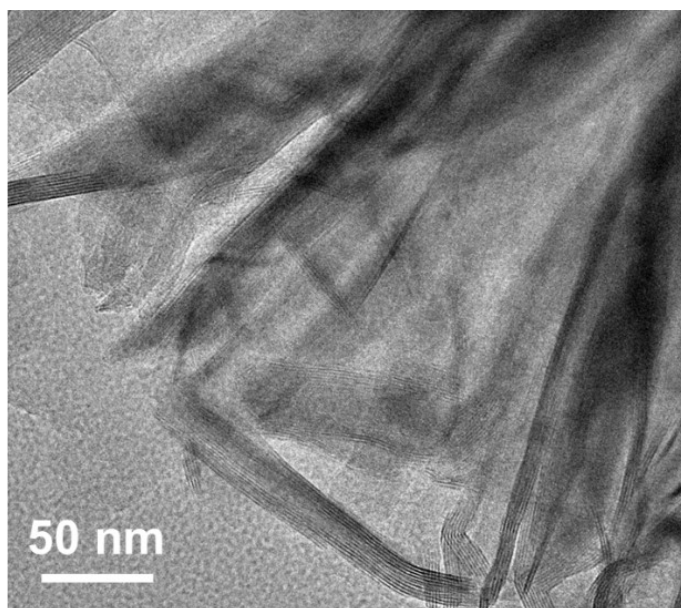
## Electronic supplementary information



**Fig. S1.** SEM image of V<sub>2</sub>O<sub>5</sub> nanoparticle.



**Fig. S2.** SEM images of P-VO<sub>x</sub> hybrid.



**Fig. S3.** TEM image of P-VO<sub>x</sub> hybrid.

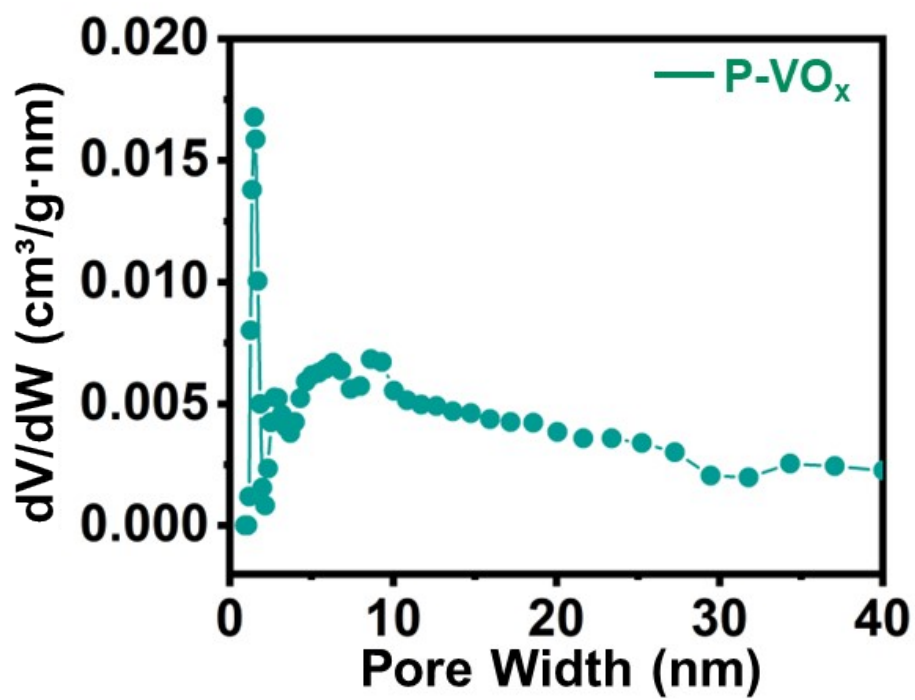


Fig. S4. Pore volume distribution of P-VO<sub>x</sub>.

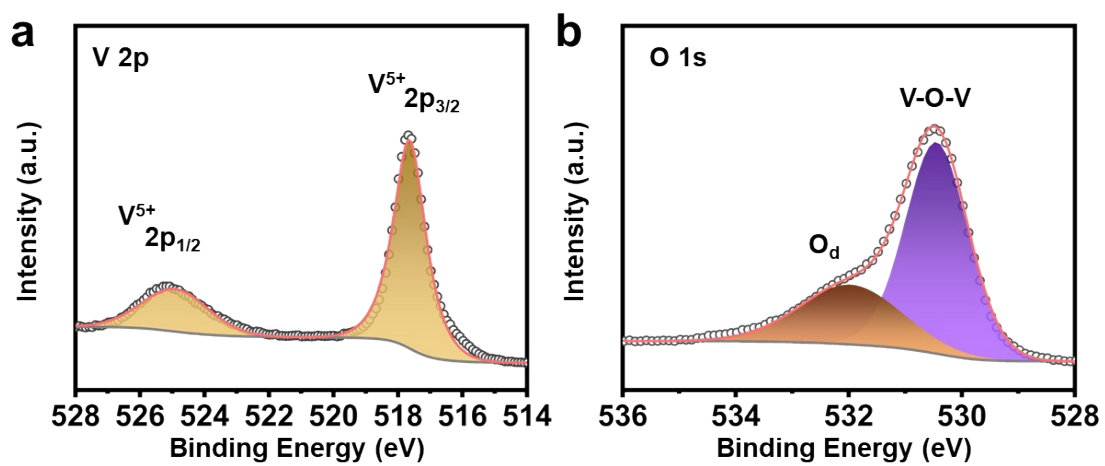
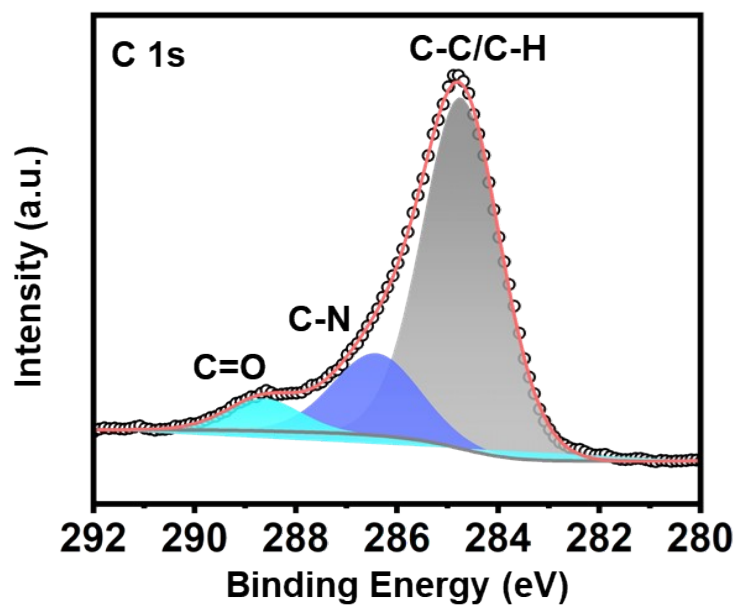
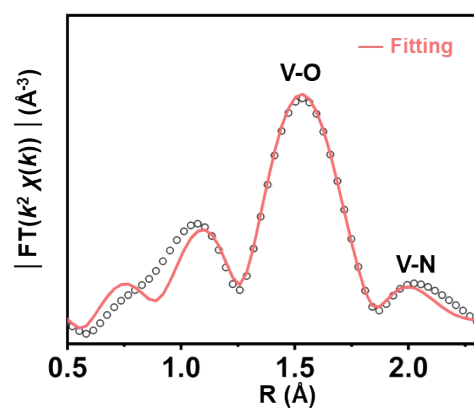


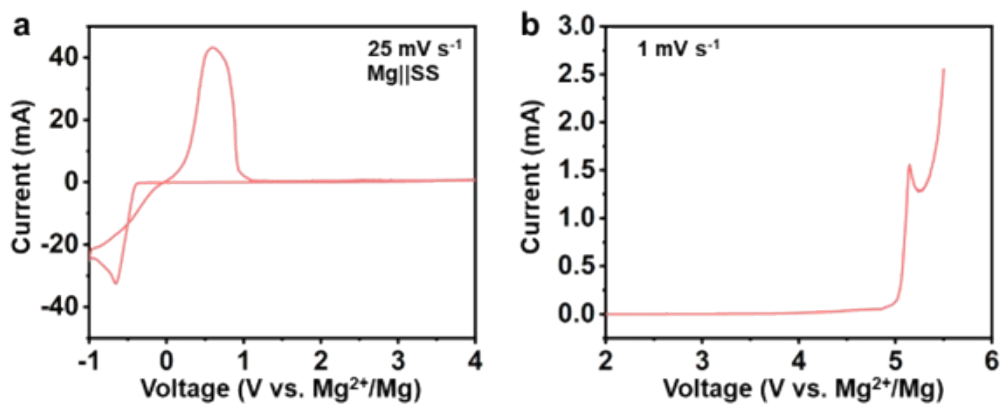
Fig. S5. (a) V 2p and (b) O 1s XPS spectra of  $V_2O_5$  nanoparticle.



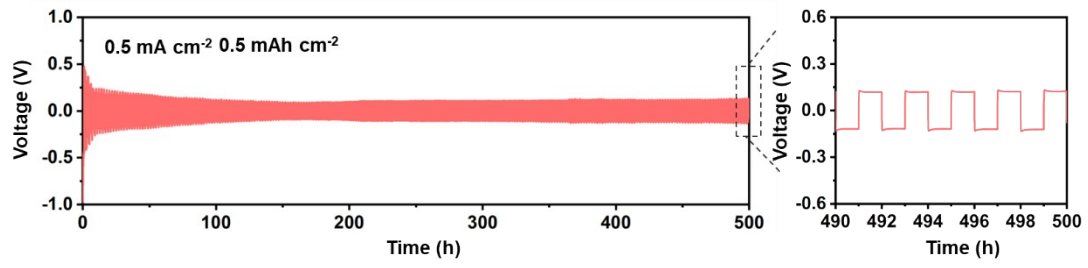
**Fig. S6.** C 1s XPS spectra of P-VO<sub>x</sub> hybrid.



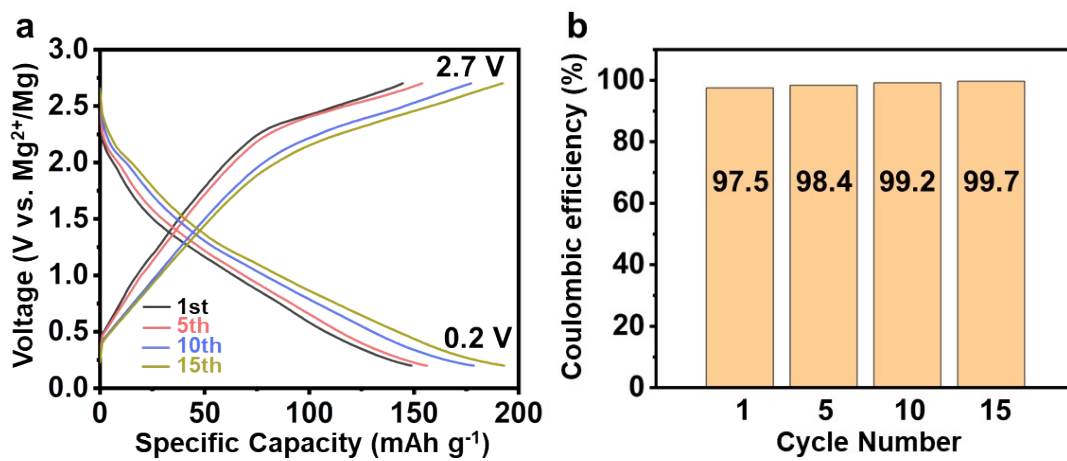
**Fig. S7.** Quantitative fitting of the V K-edge EXAFS for the P-VO<sub>x</sub> sample.



**Fig. S8.** (a) CV curves of Mg||SS cells at  $25 \text{ mV s}^{-1}$  with the  $\text{Mg}[\text{B}(\text{HFIP})_4]_2/\text{DME}$  electrolytes. (b) LSV curves of Mg||GC cells at  $1 \text{ mV s}^{-1}$  with carbon paper current collector as the working electrode substrate.



**Fig. S9.** Cycling performance of Mg||Mg cell at  $0.5 \text{ mA cm}^{-2}$  with  $0.5 \text{ mAh cm}^{-2}$ .



**Fig. S10.** (a) Charge-discharge curves under different cycles of P-VO<sub>x</sub> cathode in RMBs at a current density of 0.1 A g<sup>-1</sup> within a voltage window of 0.2-2.7 V. (b) Coulombic efficiency under different cycles.

**Table S1.** The Mg content determined by ICP-OES for P-VO<sub>x</sub> at different states.

<b>Samples</b>	<b>Weight of the electrodes (mg)</b>	<b>Weight of active materials (mg)</b>	<b>Constant volume (L)</b>	<b>Mg mass concentration (mg/L)</b>	<b>Mg content (wt%)</b>
Initial discharge	9.2	6.44	0.1	5.4538	8.46
Initial charge	7.4	5.18	0.1	0.9798	1.88
The 10th discharge	12.0	8.4	0.1	9.7258	11.57
The 10th charge	8.4	5.88	0.1	1.8228	3.1

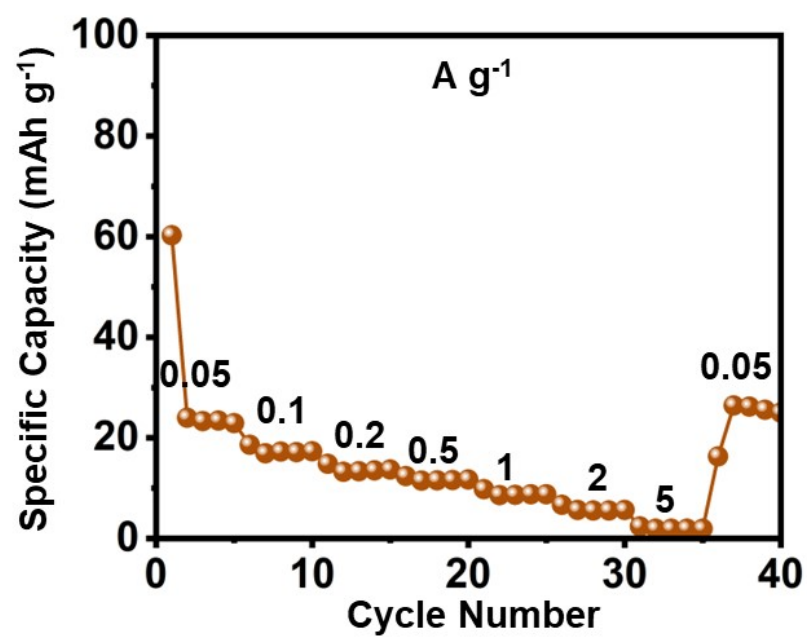
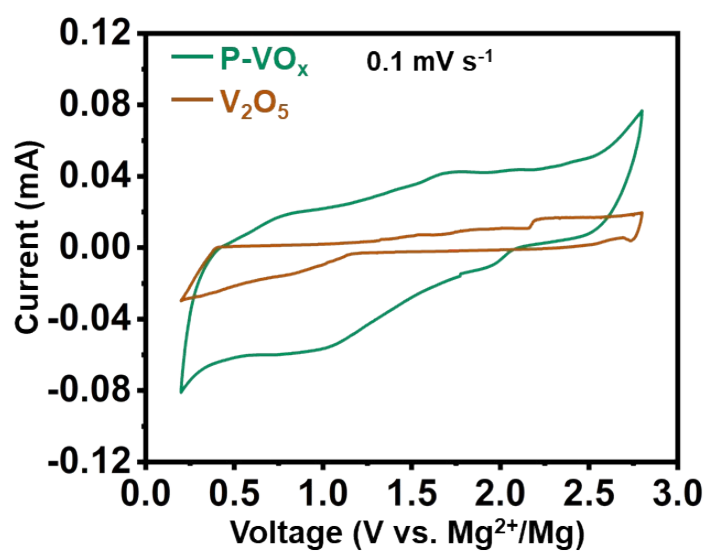
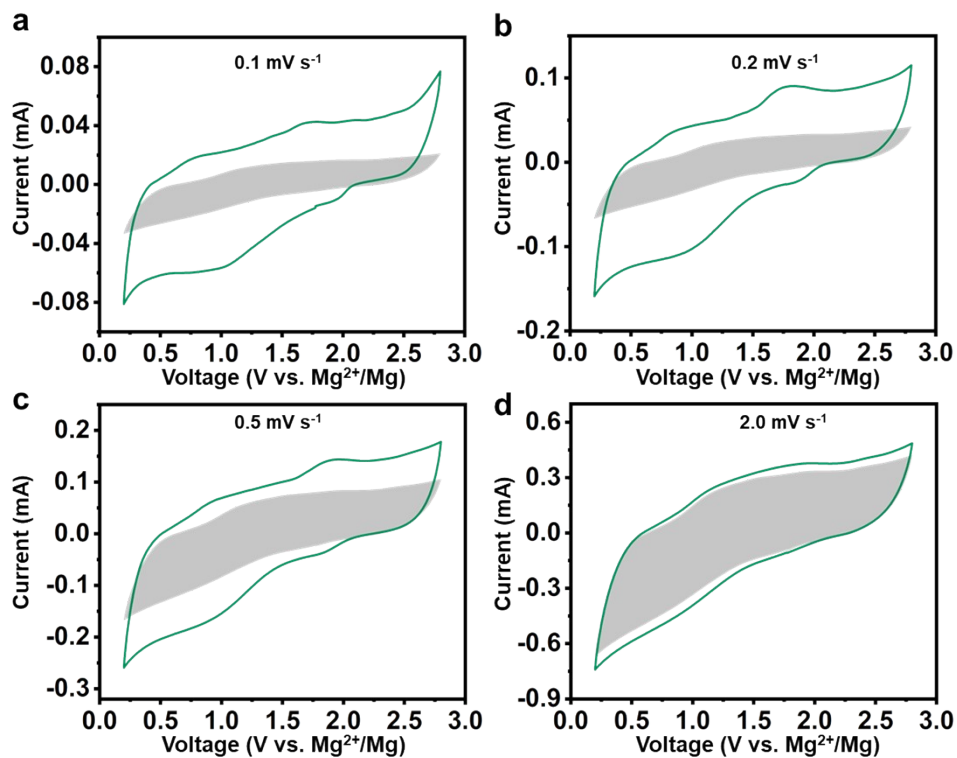


Fig. S11. Rate capability of V<sub>2</sub>O<sub>5</sub> nanoparticle.



**Fig. S12.** CV curves of V<sub>2</sub>O<sub>5</sub> and P-VO<sub>x</sub> cathodes at scan rates of 0.1 mV s<sup>-1</sup>.



**Fig. S13.** CV curve of P-VO<sub>x</sub> at the scan rate of (a) 0.1 mV s<sup>-1</sup>, (b) 0.2 mV s<sup>-1</sup>, (c) 0.5 mV s<sup>-1</sup> and (d) 2.0 mV s<sup>-1</sup>. The shaded area represents the capacitive current response ascribed from surface/near surface reaction.

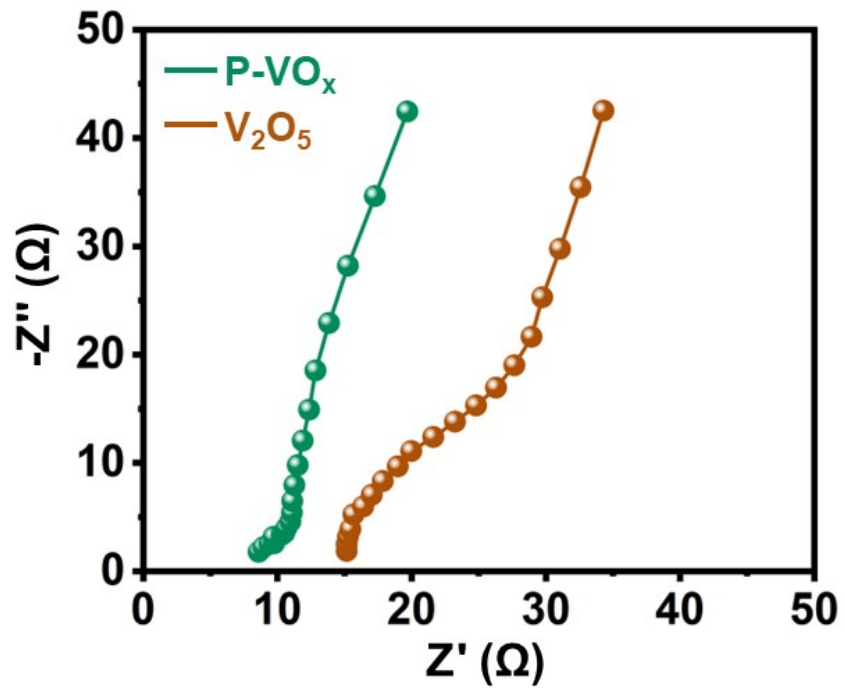
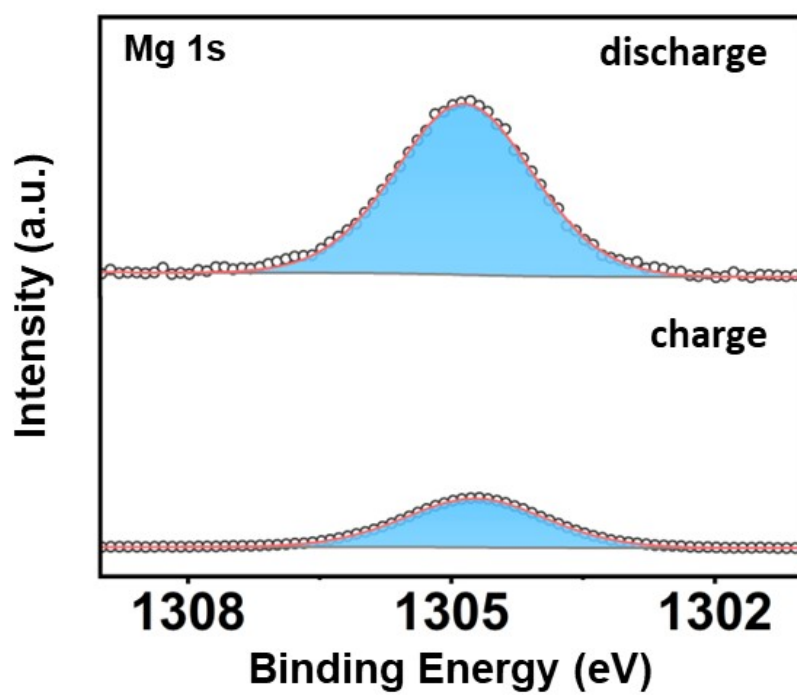
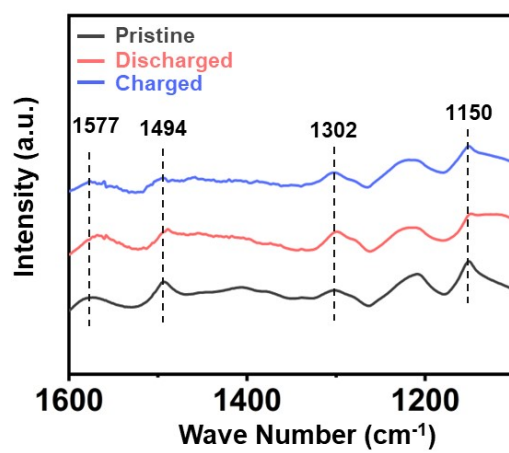


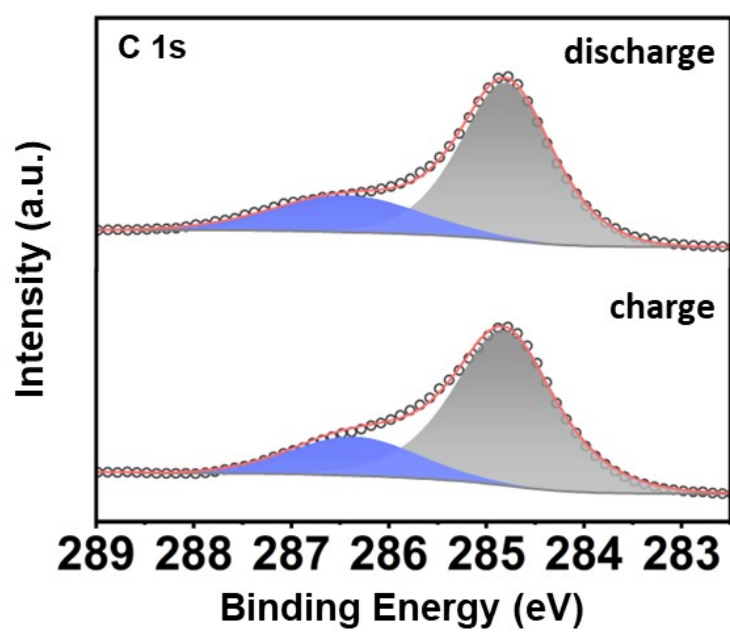
Fig. S14. Nyquist plots of  $V_2O_5$  and  $P-VO_x$  initial electrodes.



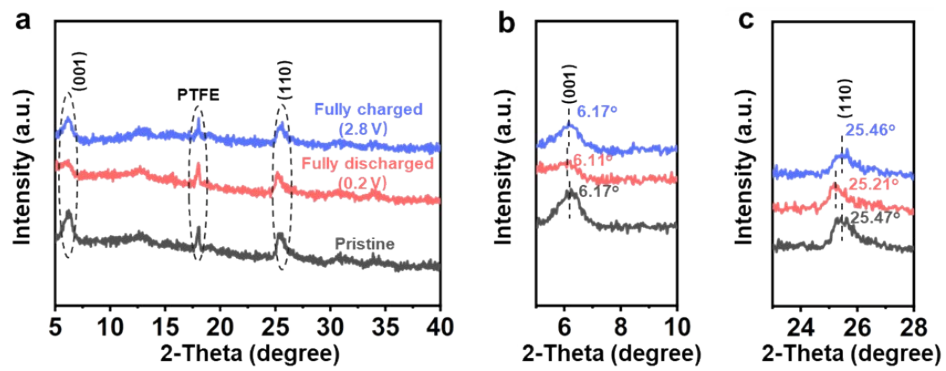
**Fig. S15.** Mg 1s XPS spectra of P-VO<sub>x</sub> electrode in discharged and charged states.



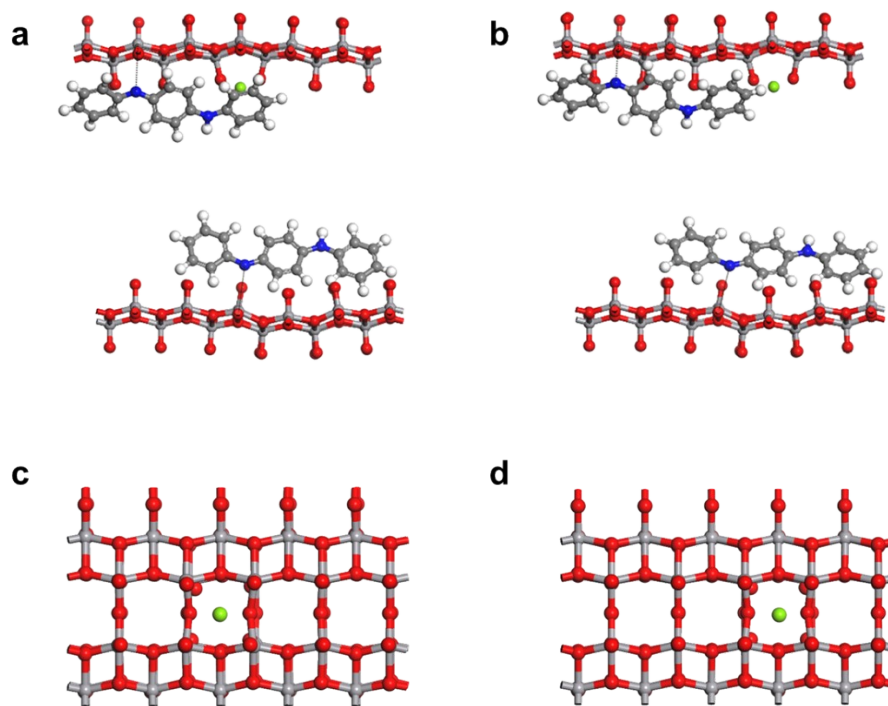
**Fig. S16.** Ex-situ FTIR of the P-VO<sub>x</sub> cathode before and after cycling.



**Fig. S17.** C 1s XPS spectra of P-VO<sub>x</sub> electrode in discharged and charged states.



**Fig. S18.** (a) XRD pattern of P-VO<sub>x</sub> electrode under different states. Fine variations of (b) (001) peak and (c) (110) peak.



**Fig. S19.** DFT-calculated (a) initial position and (b) final position of Mg<sup>2+</sup> along the migration path over P-VO<sub>x</sub>. DFT-calculated (c) initial position and (d) final position of Mg<sup>2+</sup> along the migration path over V<sub>2</sub>O<sub>5</sub>.