Electronic Supplementary Information (ESI): Amorphous V_2O_5-P_2O_5 as high-voltage cathodes for magnesium batteries

Timothy S. Arthur,*[a] Keiko Kato,[a] Jason Germain,[a] Jinghua Guo,[b] Per-Anders Glans,[b] Yi-Sheng Liu,[b] Daniel Holmes,[c] Xudon Fan,[d] and Fuminori Mizuno[a]

Experimental Methods:

Materials: V_2O_5 and P_2O_5 powder were purchased from Sigma-Aldrich and used as received. 1 M $Mg(ClO_4)_2$ / Acentonitrile with less than 50 ppm of water was purchased from KishidaChemicals. All chemicals were stored in an Ar-filled glovebox.

Ball-milling: V_2O_5 and P_2O_5 powders (total mass of 1 g) were loaded into a 45 ml ZrO_2 ball-milling vessel with 10 x 10mm and 10 x 5mm ZrO_2 balls in an Ar-glove box. Powders were milled for 20 h at 370 rpm using Fritsch© Planetary Ball-mill P7.
Cathode preparation: The cathode was prepared by mixing the active material or SiO_2, Acetylene Black (HS-100, Denkikagaku Kogyo) and PVDF binder (KF polymer, 5 wt % in NMP, Kureha) in a 2:1:1 wt. ratio. The resulting paste was painted onto a SUS mesh current collector, dried for 1 h at 120 ^oC and finally dried under vacuum for 12 h at 120 ^oC. Typical active material loading is ~ 2 mg/cm^2.

Methods: X-ray photoelectron spectroscopy was collected using a Phi 5600 and analyzed using the Multipack software. For peak de-convolution, the spectra were aligned using a SiO_2 standard and FWHM of the fitted peaks were constrained within 1.5-1.7 eV. X-ray diffraction was collected on a Rigaku SmartLab system. Differential scanning calorimety was collected on a TA Instruments DSC-Q100 in hermetically sealed aluminum pans. The temperature was ramped from 30 ^oC to 450 ^oC at a rate of 5 ^oC min^{-1}, then reversed from 450 ^oC to 30 ^oC and finally from 30 ^oC to 450 ^oC again. X-ray absorption spectra were collected at beamline 6.3.1.2 at the Advanced Light Source using a total electron yield (TEY) detector. Energies are aligned by periodically collecting an O *K*-edge spectra of a TiO_2 reference. Scanning electron microscopy was collected with a JEOL 77800F FE-SEM equipped with an energy dispersive X-ray detector. Transmission electron microscopy was collected on a JOEL 2200FS microscope at the Center for Advanced Microscopy at Michigan State University. TEM grids were prepared by drop-casting the cathode from acetonitrile. Magic-angle spinning nuclear magnetic resonance was collected on a Varian Infinity-Plus 400 MHz and aligned to a H_3PO_4 standard.

Electrochemistry: Three-electrode cyclic voltammetry (CV) was performed in an argon-filled glovebox. Magnesium foil was used as counter electrode, Ag/Ag^+ (0.1 M $AgNO_3$ and 0.01 M tetrabutylammonium perchlorate as reference solution) was used as a reference electrode, and 1 M $Mg(ClO_4)_2$ / Acetonitrile was used as electrolyte. CV was tested within [-1.6V, 1V] potential window at the scanning rate of 0.25 mV s^{-1}. Potentials are converted to Mg/Mg^{2+} by using a ferrocene standard (0.087 V vs. Ag/Ag^+). The current density (mA g-1) of the cathodes is normalized to the mass of the active material, or SiO_2, in the cathode.

i. Additional Results:

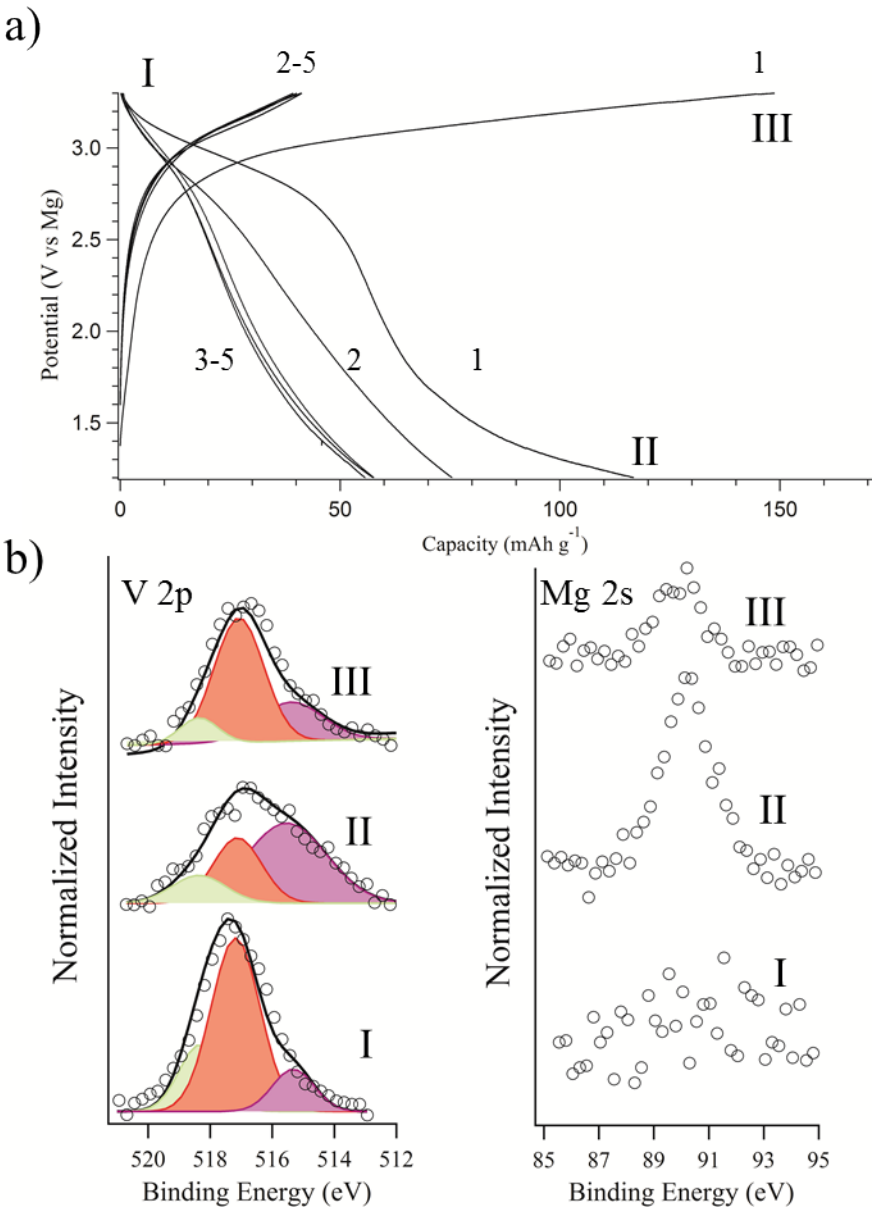

Fig. S1 – a) Three-electrode galvanic charge/discharge of 75:25 V_2O_5:P_2O_5. b) V 2p and Mg 2s XPS of the electrode taken at I-As-prepared, II-After 1st discharge and III-After 1st charge.

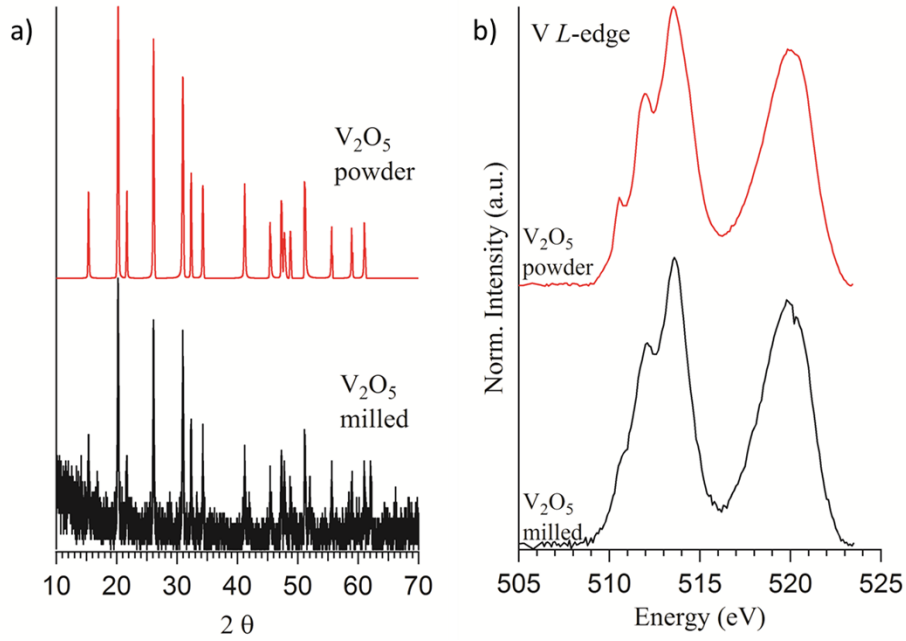

Fig. S2 – a) XRD patterns and b) V L_3 NEXAFS for V_2O_5 powders before and after milling.

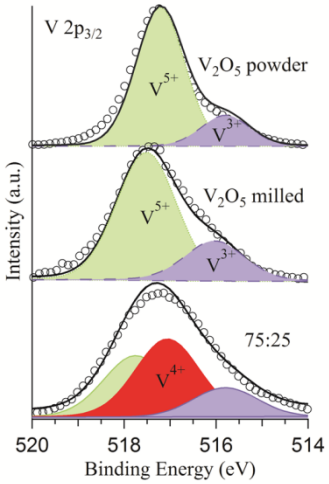

Fig. S3 - V $2p_{3/2}$ XPS spectra and peak-fitting of commercial and milled V_2O_5 compared to a V_2O_5: P_2O_5 (75:25) powder.

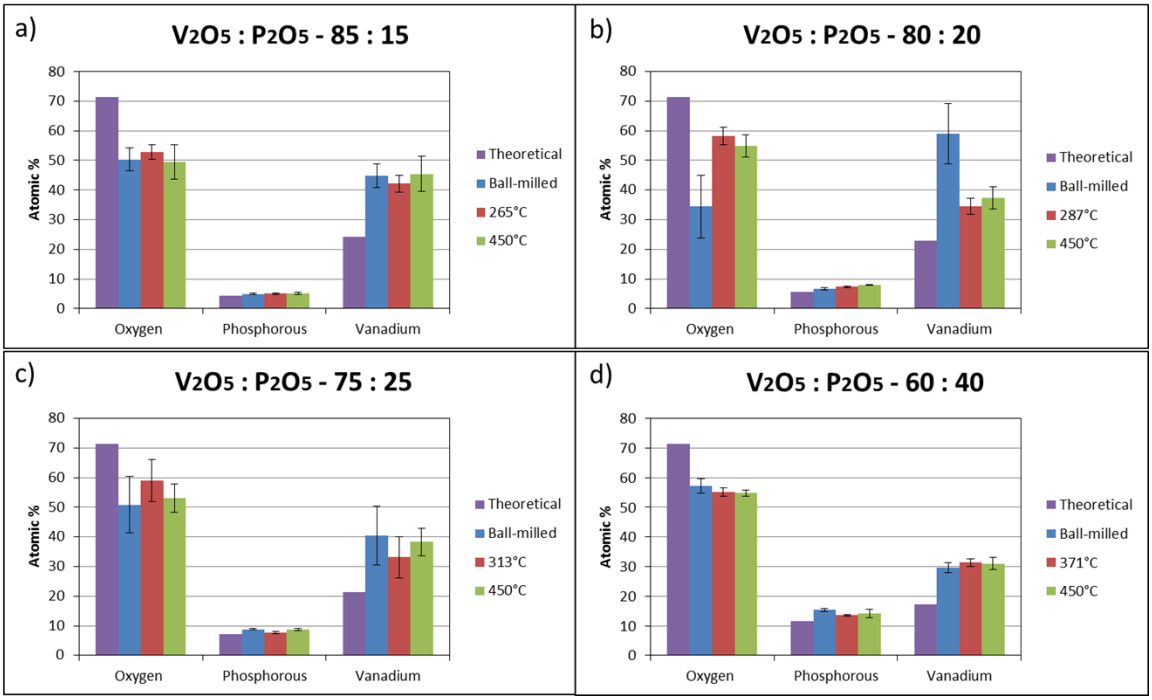

Fig. S4 - Atomic ratios calculated by Energy dispersive X-ray spectroscopy (EDS) for a) 85:15, b) 80:20, c) 75:25 and d) 60:40 V_2O_5 : P_2O_5 ratios.

Table S1 – T_g, ΔT and T_c temperatures for the amorphous V_2O_5-P_2O_5 system

V:P	T_g (°C)	T_{c1} (°C)	$\Delta T(T_{c1}-T_g)$	T_{c2} (°C)
85:15	234.7	265.2	30.6	423.1
80:20	236.1	287.0	51.0	390.8
75:25	244.5	313.3	68.9	391.4
70:30	256.8	409.4	152.7	----
65:35	285.5	389.3	103.8	----
60:40	309.8	371.3	61.5	----

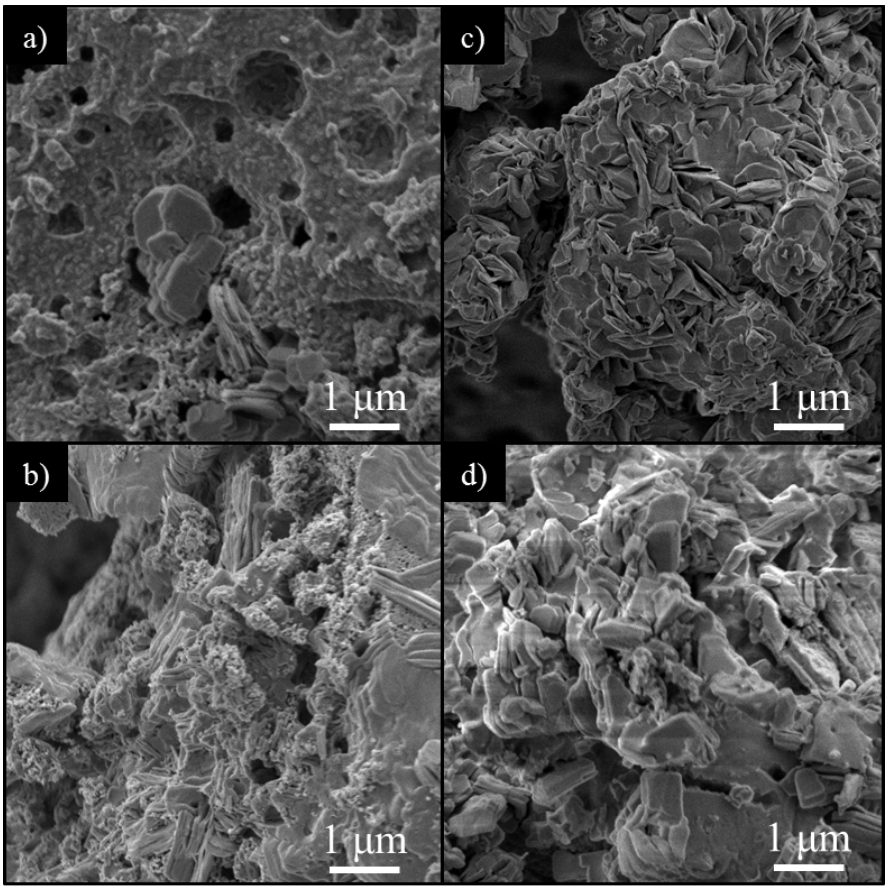

Fig. S5 – SEM images of a V_2O_5: P_2O_5 (75:25) powders annealed to a) 313 °C and b) 450 °C, and V_2O_5: P_2O_5 (60:40) annealed to c) 371 °C and d) 450 °C.

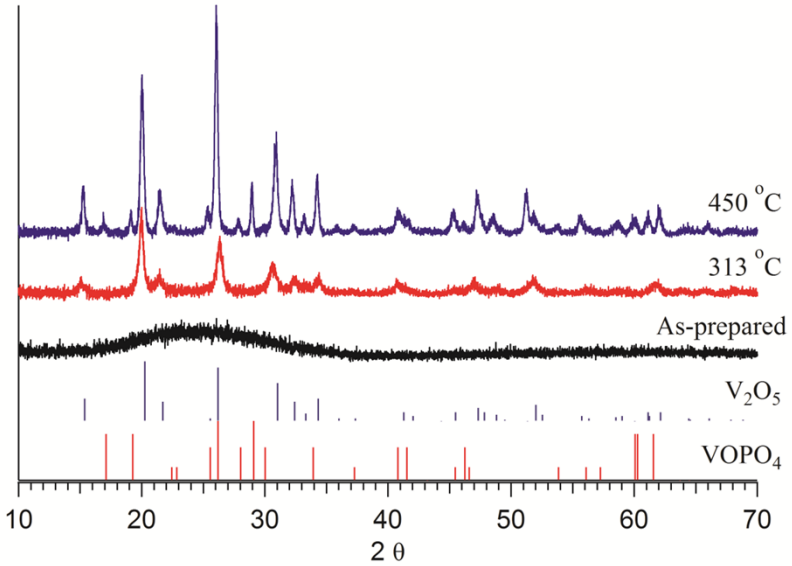

Fig. S6 – XRD patterns for V_2O_5:P_2O_5 (75:25) as prepared and after annealing at 313 °C and 450 °C. The reference patterns are assigned to PDF 00-009-0387 for V_2O_5 and PDF 00-027-0948 for $VOPO_4$.