Supporting Information

Unraveling the Magnesium-Ion Intercalation Mechanism in Vanadium Pentoxide in a Wet Organic Electrolyte by Structural Determination

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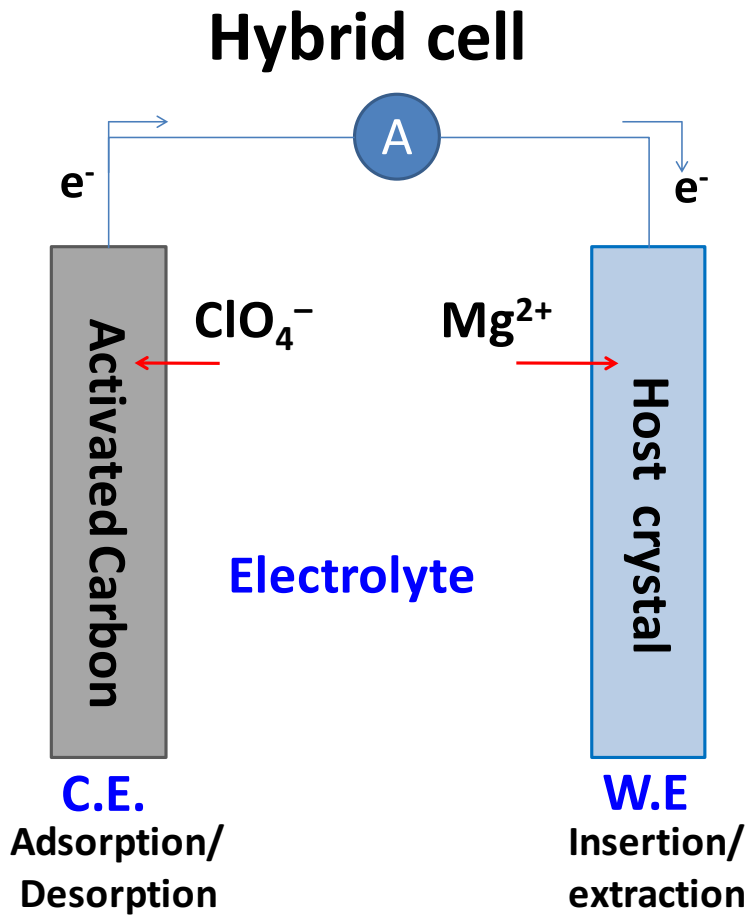

Figure S1. Scheme of the electrochemical test cell, where the activated carbon in the counter electrode acts as a capacitor.

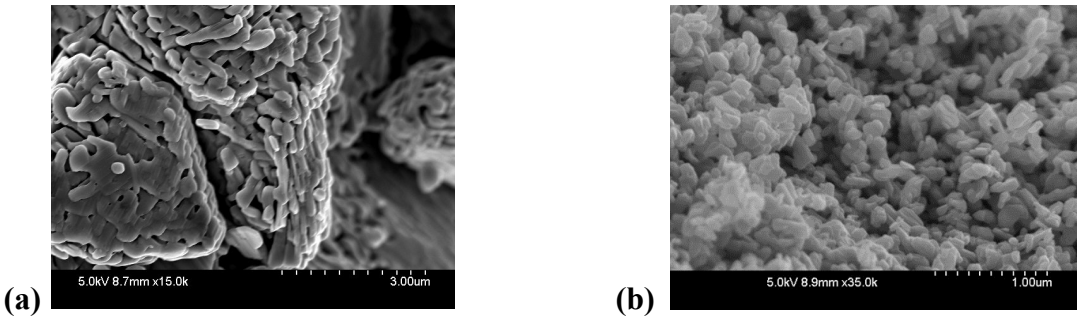

Figure S2. SEM images of V_2O_5 particles (a) as-purchased, and (b) synthesized using oxalic acid treatment in this work.

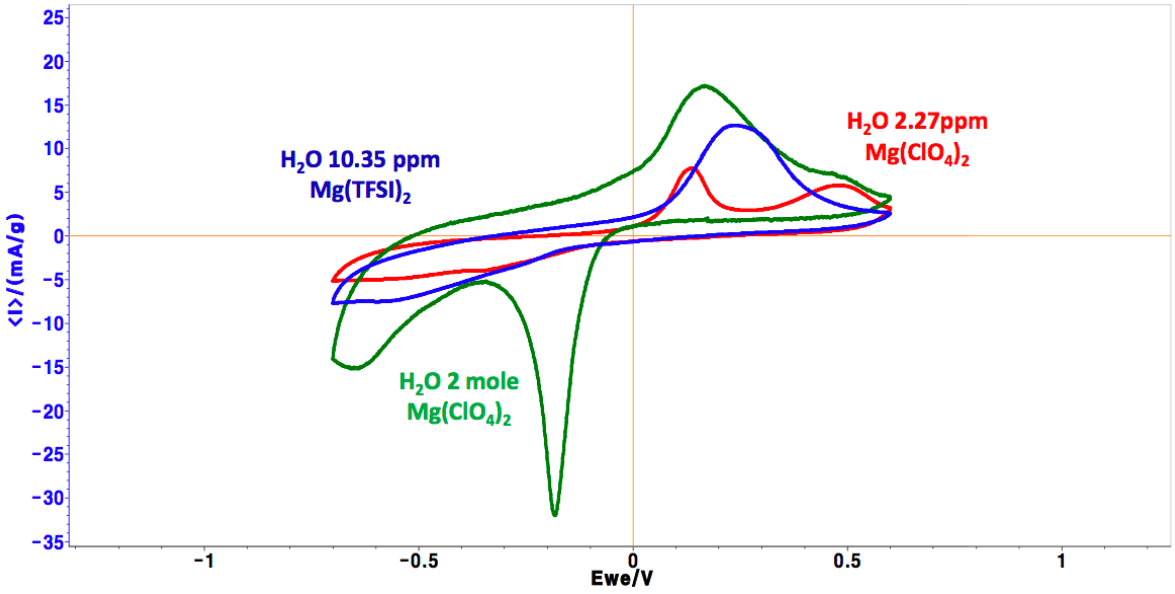

Figure S3. Comparison of CVs for V_2O_5 performed in different electrolytes: Green (0.5 M $Mg(ClO_4)_2$ + 2M H_2O in AN); Red (0.5 M $Mg(ClO_4)_2$ in AN, 2.27 ppm H_2O); Blue (0.5 M $Mg(TFSI)_2$ in AN, 10.35 ppm H_2O).

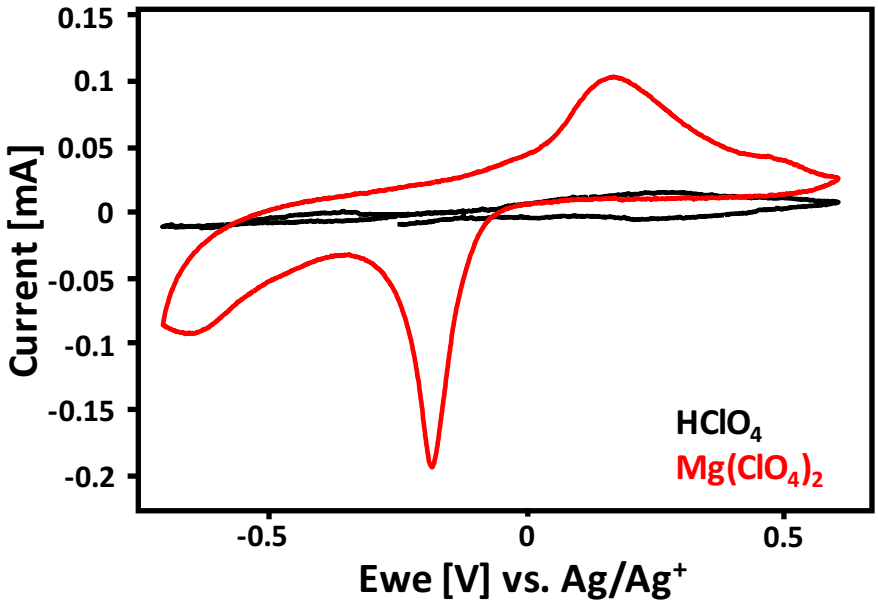

Figure S4. Comparison of CVs for V_2O_5 performed in two electrolytes: Red (0.5 M $Mg(ClO_4)_2$ + 2M H_2O in AN); Black (2M H_2O in AN with pH of 5.5 that was adjusted with $HClO_4$).

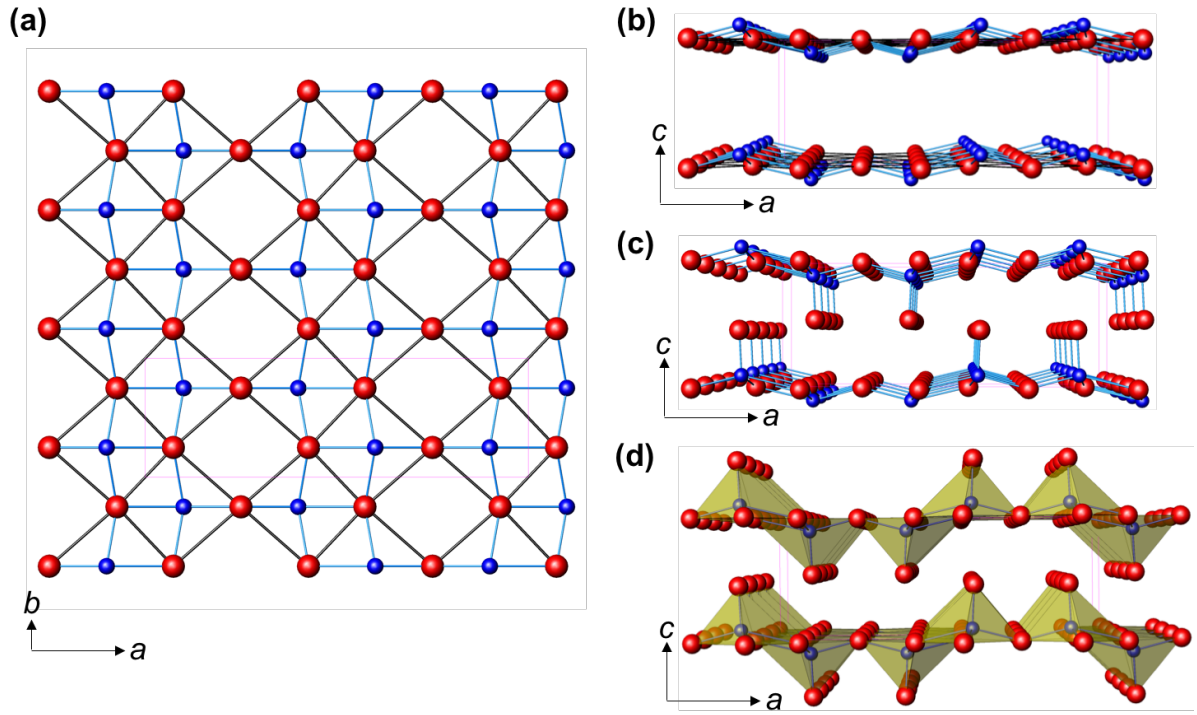

Figure S5. The description of α-V_2O_5 structure. (a) single layer of square VO_4 network of V_2O_5 in *ab*-plane (001 view); (b) Stacking of two layers with a spacing of 4.37 Å (010 view); (c) interlayer oxygen atoms added to (b) to construct the complete V_2O_5 structure; (d) Square-pyramid polyhedral representation of (c) with a slightly wider region. Note that V and O atoms are shown as blue and red spheres, respectively. The pink lines denote the unit cell.

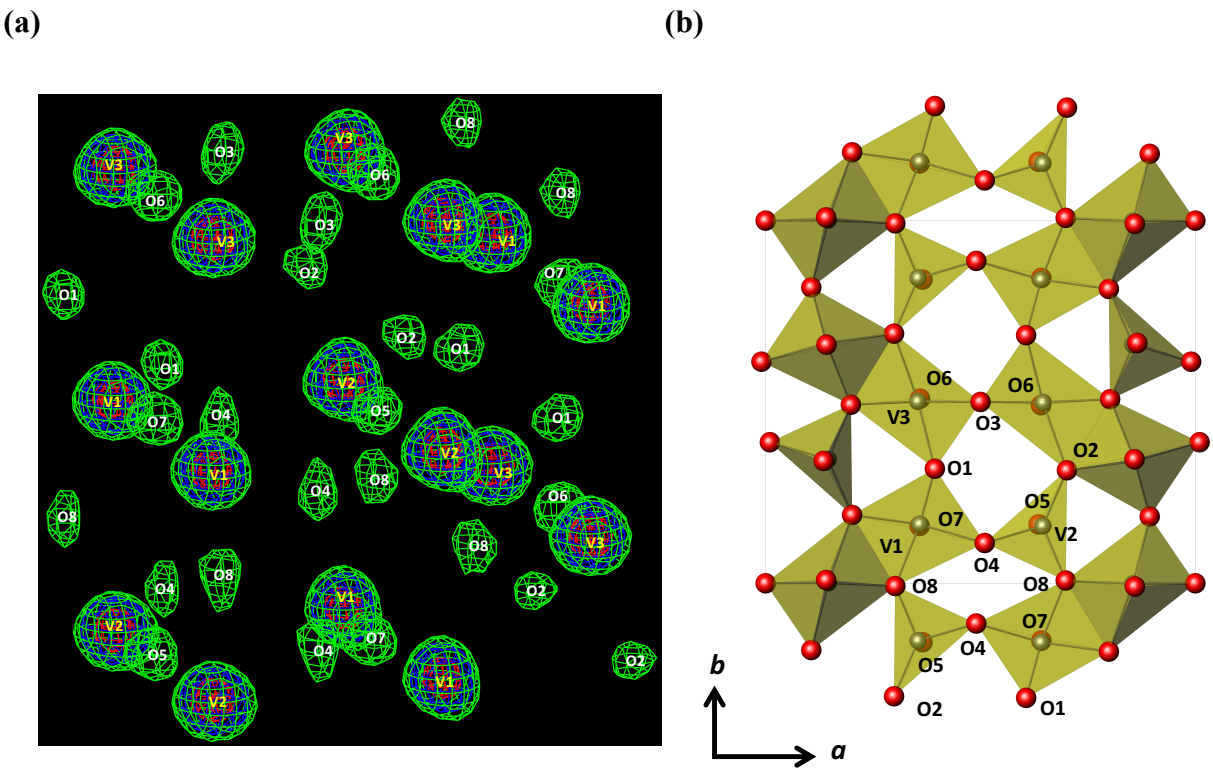

Figure S6. (a) Fourier (observed) electron density maps; (b) unit cell structure of magnesium-inserted V_2O_5 ($Mg_{0.17}H_xV_2O_5$). Note that the electron density maps showed no appreciable densities other than vanadium or oxygen atoms.

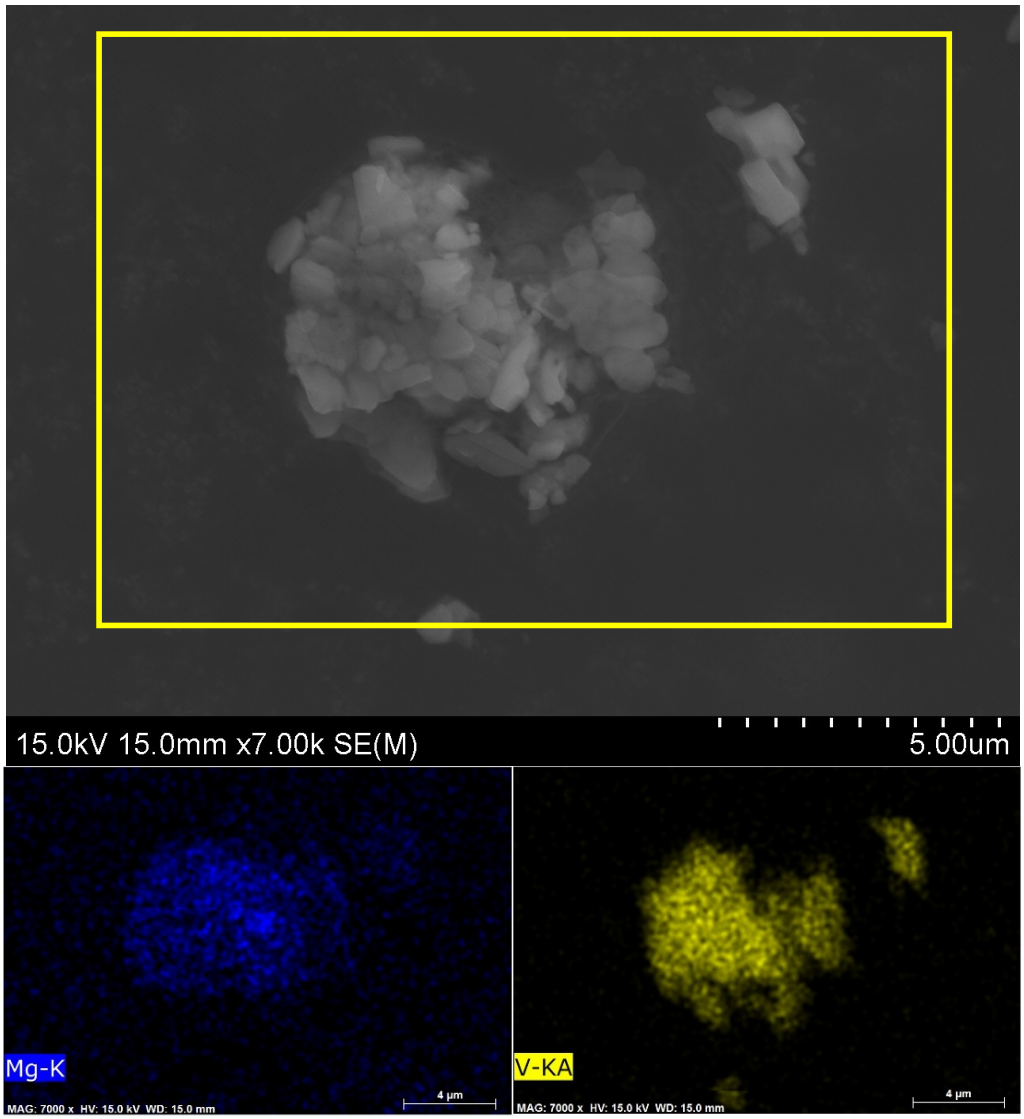

Figure S7. The HR FE-SEM EDX elemental mapping of $Mg_{0.17}H_xV_2O_5$ electrode. Note that magnesium atoms are well distributed over the particles.

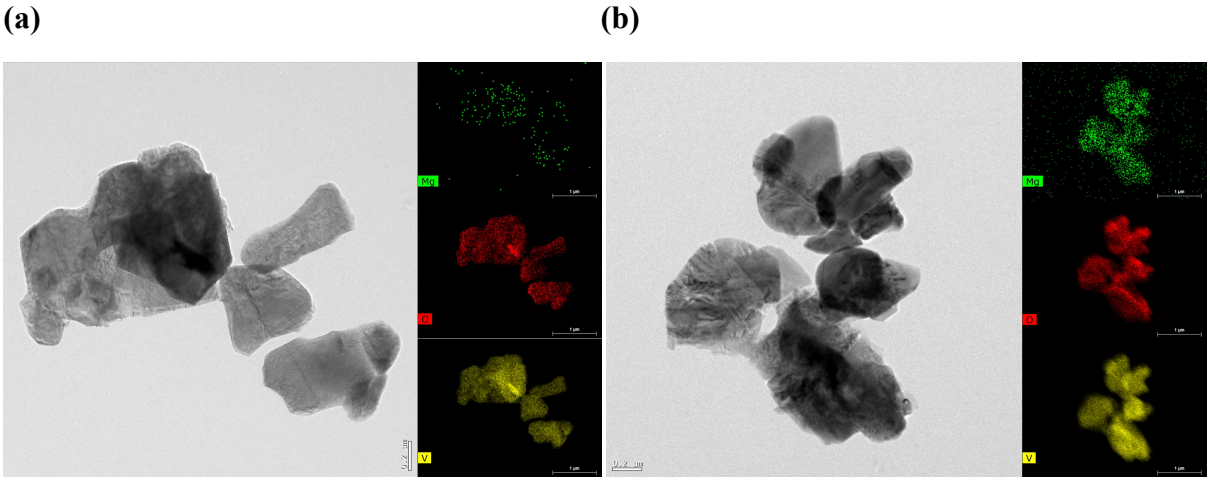

Figure S8. HR TEM EDX elemental mappings of (a) pristine V_2O_5 powder and (b) $Mg_{0.17}H_xV_2O_5$ (sample at point 5 in Figures 2 and 3).

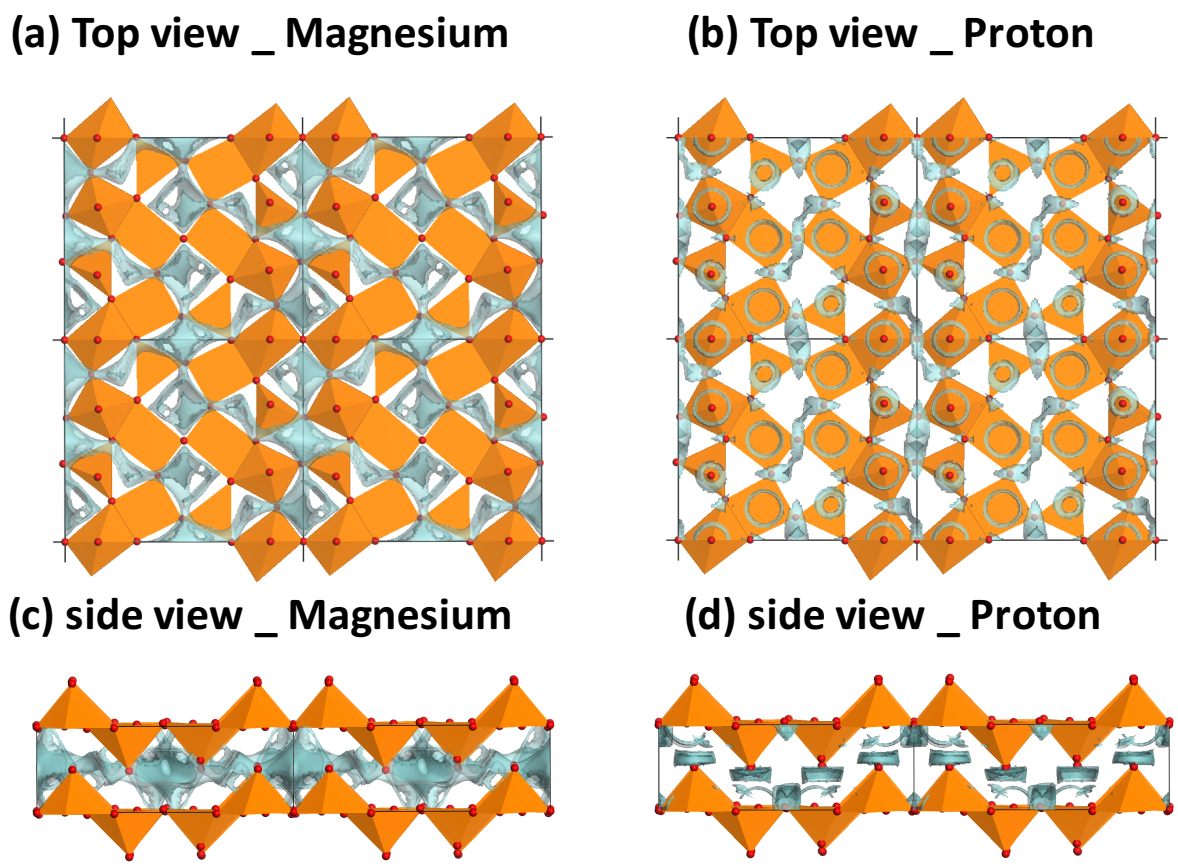

Figure S9. 3D bond valence difference map isosurfaces (sky-blue color) for $Mg_{0.17}H_xV_2O_5$ with the isosurfaces of $|0.1|$ v.u. for Mg ions (a and c), and for protons (b, and d). The orientation arrangement of atoms is the same as in Figure 5b or Figure S6b. Oxygen atoms are denoted as red balls, and vanadium atoms—not seen in this figure—are in the centers of the orange-colored polyhedra.

Table S1. Crystallographic data and Rietveld refinement results for pristine V_2O_5 by powder XRD data: atomic coordinates, site occupancies, isotropic displacement parameters and reliability factors at room temperature.

Crystal System			Orthorhombic			
Space Group			*P m m n* (no. 59)			
Lattice Parameters, Volume, Z			a = 11.5123(3) Å, b = 3.5641(3) Å, c = 4.3681(3) Å V = 179.21(1) Å^3, Z = 2			
Atoms	*x*	*y*	*z*	Wyckoff	Occupancy	$U_{iso}\times100$
V	0.1012(8)	0.2500	0.8917(2)	*4f*	1.00	1.9(5)
O1	0.1043(4)	0.2500	0.5310(1)	*4f*	1.00	2.4(1)
O2	–0.0689(3)	0.2500	0.0030(1)	*4f*	1.00	1.7(7)
O3	0.2500	0.2500	0.0010(2)	*2b*	1.00	2.3(9)

*$R_p = 0.08$, $R_{wp} = 0.118$, $R_{exp} = 0.03$, $R(F^2) = 0.0414$, $\chi^2 = 1.68$

Table S2. Selected interatomic distances (Å) for pristine V_2O_5.

V1–O1 × 1	1.576(1) Å	V1–O2 × 2	1.878(2) Å
V1–O3 × 2	1.778(1) Å		

Table S3. Selected interatomic distances (Å) for $Mg_{0.17}H_xV_2O_5$ (x = 1).

V1–O1	1.753 (1) Å	O1-V1	1.7530(1) Å
V1–O2	2.034 (1) Å	O1-V3	2.0730(1) Å
V1–O4	2.026 (1) Å	O1-Mg3	2.587(15) Å
V1–O7	1.617 (1) Å	O1-Mg3	2.030(18) Å
V1–O7	2.550 (19) Å	O2-V1	2.034(1) Å
V1–O8	1.969 (1) Å	O2-V2	1.802(1) Å
V2–O2	1.802 (1) Å	O2-V3	2.1360(1) Å
V2–O4	1.806 (1) Å	O3-V3 x 2	1.869(1) Å
V2–O5	2.565 (4) Å	O4-V1	2.026(1) Å
V2–O5	1.612 (1) Å	O4-V2	1.806(1) Å
V2–O8	1.743 (1) Å	O5-V2	1.612(1) Å
V3-O1	2.073(1) Å	O5-V2	2.565(4) Å
V3-O2	2.136(1) Å	O5-H1	1.00(1) Å
V3-O3	1.869(1) Å	O5-Mg3	2.303(25) Å
V3-O6	1.614(1) Å	O6-V3	1.614(1) Å
V3-O6	2.556(3) Å	O6-H2	1.03(3) Å
H1-O5	1.01(2) Å	O6-Mg3	1.94(4) Å
H2-O6	1.03(3) Å	O7-V1	2.550 (19) Å
H3-O7	1.00(3) Å	O7-H3	1.00(3) Å
Mg3-O1	2.587(15) Å	O7-Mg3	1.940(1) Å
Mg3-O1	2.030(18) Å	Mg3-O6	1.94(4) Å
Mg3-O5	2.303(25) Å	Mg3-O7	1.940(1) Å

Table S4. Elemental ratios estimated from HR FE-SEM EDX elemental analysis for $Mg_{0.17}H_xV_2O_5$ samples.

Sample #	**Atomic (%)**		**Relative atomic ratio**
	V	Mg	**Mg / V_2**
A	91.1	8.9	0.20
B	88.9	11.1	0.24
C	92.2	7.8	0.16
			Average 0.20

Table S5. Elemental ratios estimated from ICP (Inductively coupled plasma) analysis for $Mg_{0.17}H_xV_2O_5$ samples.

	Mass ratio (%)		**Relative atomic ratio**
	Mg	V	**Mg / V_2**
Sample			
D	3.77	96.33	**0.159**
E	4.24	95.76	**0.186**
			Average 0.173

Table S6. Optimized fraction coordinates and insertion energies for magnesium and proton ions for $Mg_{0.17}H_xV_2O_5$ (x = 1) by DFT calculations.

	x	*y*	*z*	Total energy (eV)	Insertion energy (eV)
Mg1	0.5	0	0.41435	-350.420	-6.55
Mg2	0.48956	0.38070	0.38614	-349.526	-5.65
Mg3	0.81810	0.16803	0.56619	-348.110	-4.24
H5	0.56637	0.13734	0.42015	-359.369	-2.01
H6	0.65005	0.40222	0.43074	-357.290	0.07
H7	0.88607	0.26286	0.61047	-358.632	-1.27
reduced V_2O_5*				-343.835	
Mg atom				-0.038	
$2H_2$				-13.523	

*$Mg_{0.17}H_xV_2O_5$ structure excluding Mg and H atoms.

Table S7. Optimized fraction coordinates and insertion energies for magnesium and proton ions for $Mg_{0.17}H_xV_2O_5$ (x = 1) by DFT calculations using optB86b-vdW functional for checking the validity of selected D3 correction scheme.

	x	*y*	*z*	Total energy (eV)	Insertion energy (eV)
Mg1	0.5	0	0.41913	-304.196	-6.68
Mg2	0.49127	0.37268	0.38566	-303.246	-5.73
Mg3	0.81685	0.16795	0.56522	-301.754	-4.24
H5	0.56642	0.13671	0.41871	-312.896	-1.68
H6	0.65005	0.40186	0.42957	-310.786	0.48
H7	0.88793	0.26330	0.61012	-312.144	-0.88
reduced V_2O_5*				-297.719	
Mg atom				0.207	
$2H_2$				-13.548	