**Ca2+ Pre-Intercalated Bilayered Vanadium Oxide for High-Performance Aqueous Mg-Ion Batteries**

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**Figure S1** Selected area electron diffractions (SAEDs) of carbon coated CaVOnH nanowires



**Figure S2** Thermogravimetric analysis (TGA, inset: V 2p XPS of pristine CaVOnH) (a) and TGA-MS of m/z signals (b) of pristine CaVOnH under Ar atmosphere



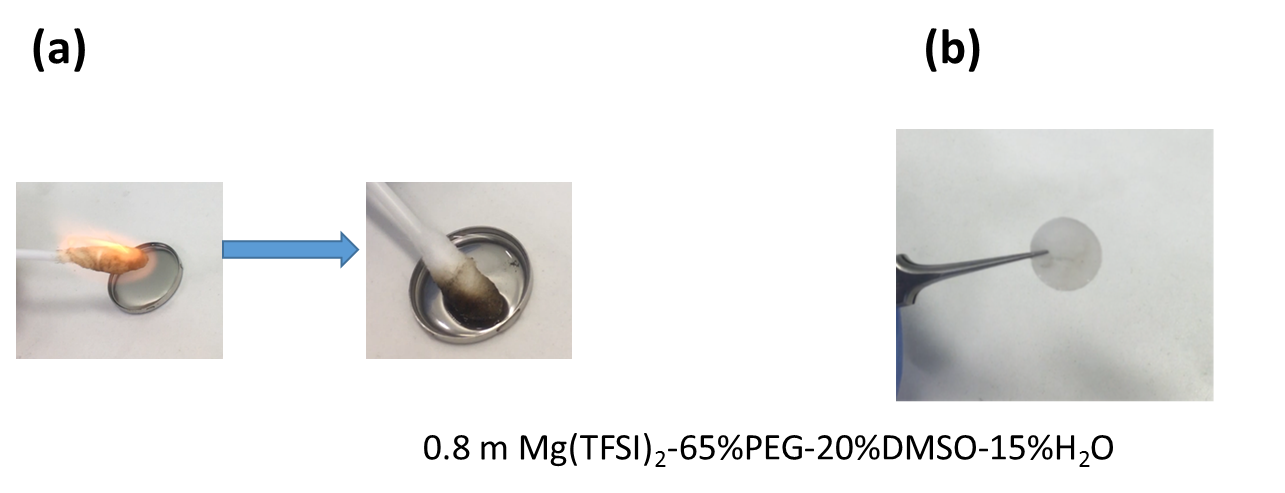
**Figure S3** Field scans (a) and time dependent magnetization (b) at various temperatures in CaVOnH



**Figure S4** ESW of 0.8 m Mg(TFSI)2-(85%-y)PEG-yDMSO-15%H2O (y=0, 10%, 20%, and 35%) AMEs between -0.42 V and 4.78 V *vs* Mg2+/Mg on GC at 0.5 mV s−1, where the experiments were conducted in the potentials between –3.0 V and 2.2 V vs the used reference electrode AgCl/Ag and the potentials have been converted to Mg2+/Mg reference for convenience based on the voltage difference of 2.58 V between AgCl/Ag and Mg2+/Mg.



**Figure S5** 1H NMR spectra of 0.8 m Mg(TFSI)2-(85%-y)PEG-yDMSO-15%H2O (y=0, 10%, 20%, and 35%) AMEs; DMSO solvent shows a single 1H chemical shift peak at 2.74 ppm.



**Figure S6** **Flammability evaluation**. (a) A burning cotton swab was soaked in the 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O (snapshot of Video S1), where the fire of cotton swab was extinguished. (b) Flammability testing of glass fiber immersed in 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O (snapshot of Video S2)



**Figure S7** The comparison of pristine powder CaVOnH and the 1st pattern from *in operando* synchrotron diffraction, where the wavelength was converted to Mo Kα1 radiation, λ=0.70932 Å.



**Figure S8** A linear combination fitting (LCF) of the V K-edge XANES spectrum of CaVOnH at the pristine (a) and the end of discharge (b) with a fit range between 5458 and 5486 eV

LCF shows the pristine CaVOnH consists of 83.7% V2O5 and 16.3% VO2, therefore, the oxidation state of V in the pristine CaVOnH is determined as +4.85.

LCF shows the discharged CaVOnH consists of 17.8% V2O3 and 82.2% VO2, therefore, the oxidation state of V in the end of discharge CaVOnH is determined as +3.82.



**Figure S9** *Ex situ* X-ray absorption spectroscopy (XAS) for the V K-edge (a, b) and phase-uncorrected Fourier transforms (FT) of V K-edge EXAFS (k3-weighted) (c, d) of CaVOnH at different discharge/charge states (pristine, 2.0 V, 1.58 V, 2.7 V, and 3.68 V); the isosbestic points in (a, b) are indicated by red arrows.

**Table S1** Hydrogen-bonds (HBs) contribution of both electrolytes and lifetime of HBs from molecular dynamics (MD) calculations

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Electrolyte | Origin of HBs contribution | | | | lifetime of HBs |
|  | TFSI--H2O | H2O-H2O | PEG-H2O | DMSO-H2O |  |
| 0.8 m Mg(TFSI)2-85%PEG-15%H2O[1] | 1.6/TFSI- | 1/H2O | 1.9/PEG | -- | 79 ps |
| 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O | 1.6/TFSI- | 1/H2O | 1.7/PEG | 0.5/DMSO | 82 ps |

**Table S2** The first peak position and corresponding integrated coordination numbers (ICN) of solvation structure in both electrolytes from MD calculations

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Electrolyte | First peak position (nm)/corresponding ICN | | | |
| Mg2+-H2O | Mg2+- TFSI- | Mg2+-PEG | Mg2+-DMSO |
| 0.8 m Mg(TFSI)2-85%PEG-15%H2O[1] | 0.20/3.5 | 0.21/0.73 | 0.19/2.0 |  |
| 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O | 0.19/3.0 | 0.22/0.40 | 0.19/1.4 | 0.21/1.0 |

**Table S3** Comparison of discharge capacities of CaVOnH and V2O5 materials in both 0.8 m Mg(TFSI)2-85%PEG-15%H2O and 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O electrolytes at different currents

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Discharge capacities (mAh g−1) in 0.8 m Mg(TFSI)2-85%PEG-15%H2O | | Discharge capacities (mAh g−1) in 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O | |
|  | CaVOnH | V2O5[1] | CaVOnH | V2O5 |
| 1st cycle | 273 | 359 | 281 | 376 |
| 50 mA g−1 | 253 | 242 | 264 | 229 |
| 100 mA g−1 | 206 | 178 | 212 | 168 |
| 200 mA g−1 | 157 | 147 | 167 | 128 |
| 500 mA g−1 | 87 | 101 | 126 | 97 |
| 1000 mA g−1 | 41 | 54 | 102 | 76 |
| Returning to 50 mA g−1 | 253 | 225 | 279 | 183 |

**Video S1:** Flammability testing of the 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O electrolyte. The fire of an ignited cotton swab was extinguished after being immersed in the 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O electrolyte, indicating that the electrolyte is non-flammable and safe.

**Video S2**: Flammability of 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O. 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O electrolyte soaked glass fiber was not ignited, indicating that 0.8 m Mg(TFSI)2-65%PEG-20%DMSO-15%H2O electrolyte shows superior safety.

**References:**

[1] Q. Fu, X. Wu, X. Luo, S. Indris, A. Sarapulova, M. Bauer, Z. Wang, M. Knapp, H. Ehrenberg, Y. Wei, S. Dsoke, High-Voltage Aqueous Mg-Ion Batteries Enabled by Solvation Structure Reorganization. *Advanced Functional Materials* **32**, 2110674 (2022).