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High-Voltage Aqueous Mg-Ion Batteries Enabled by Solvation Structure Reorganization

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Herein, an eco-friendly and high safety aqueous Mg-ion electrolyte (AME) with a wide electrochemical stability window (ESW) =3.7 V, containing polyethylene glycol (PEG) and low-concentration salt (0.8 m Mg(TFSI)$_2$), is proposed by solvation structure reorganization of AME. The PEG agent significantly alters the Mg$^{2+}$ solvation and hydrogen bonds network of AMEs and forms the direct coordination of Mg$^{2+}$ and TFSI$^{-}$, thus enhancing the physicochemical and electrochemical properties of electrolytes. As an exemplary material, V$_2$O$_5$ nanowires are tested in this new AME and exhibit initial high discharge/charge capacity of 359/326 mAh g$^{-1}$ and high capacity retention of 80% after 100 cycles. The high crystalline $\alpha$-V$_2$O$_5$ shows two 2-phase transition processes with the formation of $\varepsilon$-Mg$_{0.5}$V$_2$O$_5$ and Mg-rich Mg$_x$V$_2$O$_5$ ($x=1$) during the first discharge. Mg-rich Mg$_x$V$_2$O$_5$ ($x=1$) phase formed through electrochemical Mg-ion intercalation at room temperature is for the first time observed via XRD. Meanwhile, the cathode electrolyte interphase (CEI) in aqueous Mg-ion batteries is revealed for the first time. MgF$_2$ originating from the decomposition of Mg$^{2+}$ is identified as the dominant component. This work offers a new approach for designing high-safety, low-cost, eco-friendly, and large ESW electrolytes for practical and novel aqueous multivalent batteries.

1. Introduction

Aqueous magnesium-ion batteries (AMIBs) have become very attractive recently due to the low cost, high safety, high conductivity of aqueous electrolytes, and rich resources of Mg. Generally, the specific energy of AMIBs largely depends on the capacity and working potential of the cathode material. Among numerous cathode materials under investigation, vanadium pentoxide (V$_2$O$_5$) has been considered as a promising one owing to its large theoretical capacity (294 mAh g$^{-1}$ when considering 1 mol of Mg$^{2+}$ per mol V$_2$O$_5$) and high average working voltage of $\approx 2.4$ V,[1] which results in a large specific energy ($> 600$ Wh kg$^{-1}$). Practically, in contrast to theoretical predictions, the V$_2$O$_5$ nanocarbon/carbon composites show an initial discharge capacity of 300 mAh g$^{-1}$ in the voltage range of 0.5–2.8 V versus Mg$^{2+}$/Mg$^{0}$. Despite this, the cycle stability of this kind of high voltage cathode material has been seriously limited by the low electrochemical stability window (ESW, 1.3–2 V) of aqueous Mg-ion electrolyte (AME).[2a,3] The ESW of aqueous electrolytes strongly depends on the salts and solvents, electrolyte-electrode interphases, and electrolyte additives.[4,5] Suo et al.[4a] proposed water-in-salt electrolytes (WiSE) to expand the ESW of aqueous Li-ion electrolytes to $\approx 3.0$ V using 21 m ("m" means "mol/kg") lithium bis(trifluoromethanesulfonyl) imide (LiTFSI). The hydrate molten salt Li-ion electrolytes were reported to show a very high ESW (3.8[4c] and 5 V[4d]) for aqueous electrolytes recently where a molecular crowding agent polyethylene glycol 400 (PEG 400) was added into LiTFSI-H$_2$O, which...
had an expanded ESW of 3.2 V and therefore enabled high-efficient working of a LiMn2O4/LiTi2O4 full cell over 300 cycles. Inspired by this work, herein, we propose an eco-friendly and high-safety AME using the PEG and low-salt concentration Mg(TFSI)2 salt. The optimized 0.8 m Mg(TFSI)2-xPEG-15%H2O electrolyte owns a wide ESW of ≈3.7 V. Hence, it enables the usage of high-voltage V2O5 cathode material, which exhibits a mechanism of vanadium oxide cathode material in AMIBs.

2. Results and Discussion

2.1. Solvation Structure Reorganization of Aqueous Mg-Ion Electrolytes (AMEs)

PEG 400 is considered an ideal crowding agent for AMEs due to its unique advantages such as miscibility with water, inertness, low toxicity, and low cost. To study the properties of AMEs, a series of 0.8 m Mg(TFSI)2-xPEG-(1-x)H2O (x = 0%, 75%, 80%, 85%, 90%, and 95%) were prepared. With the addition of PEG, the viscosity of the electrolytes strongly increases and the ionic conductivity notably decreases (Figure S1 and Table S1, Supporting Information), which well matches with the Walden's rule. The Ionic conductivity of the electrolytes with 75–85%PEG is close to that of Li-ion WiSEs and liquid Mg-ion electrolytes and much higher than that of solid/gel Mg-ion electrolytes (Table S2, Supporting Information). The ESWs of the electrolytes are determined by linear sweep voltammetry (LSV) using glassy carbon (GC) as a working electrode. Compared to PEG-free 0.8 m Mg(TFSI)2-100%H2O, the ESW of the AME expands with increasing the amount of PEG, where both the O2 and H2 evolution potentials are pushed beyond the thermodynamic stability of water (Figure 1a). The electrolyte with 95%PEG (Figure 1b) shows an onset of reduction at 1.07 V versus Mg2+/Mg and then reaches a plateau at 0.48 V versus Mg2+/Mg. Different from the other electrolytes, the absence of H2 evolution could be due to the lack of “free” water in this electrolyte. It seems TFSI− reduction for the electrolytes with 80–95%PEG results in a passivation process, similar to the 21m-LiTFSI WiSE reported by Suo et al. Consequently, the plateau current reduces from 11.9 (80%PEG) to 4.9 (85%PEG), 3.7 (90%PEG), and 3.5 µA cm−2 (95%PEG). This passivation, in turn, suppresses H2 evolution. O2 evolution at the cathode side is also suppressed by the presence of PEG, but a clear passivation process is not observed (Figure 1c). Overall, an ESW of ≈3.7 V is obtained for 0.8 m Mg(TFSI)2-85%PEG-15%H2O, which is 2.3 times as wide as that of ≈1.6 V for the PEG-free electrolyte.

This ESW is the widest value up-to-date reported for AMEs and also much wider than most representative non-aqueous Mg-ion electrolytes (Table S3, Supporting Information), highlighting the great potential of 0.8 m Mg(TFSI)2-85%PEG-15%H2O as a high voltage Mg-ion electrolyte. Moreover, the use of low-salt concentration and low-cost solvent significantly reduces the cost of AMIBs.

Flammability test shows that this electrolyte is non-flammable demonstrating its superior safety properties (Figure S2 and Videos S1–S4, Supporting Information). Furthermore, LSV test of 0.8 m Mg(TFSI)2-85%PEG-15%H2O was also performed on stainless steel foil (SS) since SS is a common current collector. The electrolyte shows on SS an overall ESW of ≈2.3 V (Figure S3, Supporting Information). Besides, a plateau-like curve is seen at ≈4.2 V versus Mg2+/Mg due to the passivation process related to the oxidation of TFSI−.

Nuclear magnetic resonance (NMR) and Fourier-transform infrared spectroscopy (FTIR) were carried out to reveal how the PEG crowding agent impacts the physicochemical properties of the AMEs. 1H spectrum of 0.8 m Mg(TFSI)2-100%H2O exhibits a chemical shift at 4.84 ppm (Figure 2a), corresponding to H2O solvent. Upon adding PEG from 75% to 85%, the 1H peak of H2O weakens and shifts to higher values, indicating the decrease of electron density around H atoms and the shortening of H–O bond in H2O. Meanwhile, one 1H peak of PEG can be observed at 3.74 ppm and initially does not show any shift in the range of 75–85%PEG, showing a slightly higher value compared with pure PEG solvent (3.70 ppm). By further adding PEG (90–95%), the 1H peak of H2O disappears and the one of PEG shows strong broadening and becomes almost invisible due to the high viscosity and disordered environment. The trend of the

![Figure 1](https://example.com/figure1.png)

**Figure 1.** The linear sweep voltammetry (LSV) of 0.8 m Mg(TFSI)2-xPEG-(1-x)H2O (x = 0%, 75%, 80%, 85%, 90%, and 95%) on glassy carbon (GC) between −3.0 and 2.2 V versus AgCl/Ag at 0.5 mV s−1, where potentials have been converted to Mg2+/Mg for convenience based on the voltage difference of 2.58 V between AgCl/Ag and Mg2+/Mg. a) The overall ESW and enlarged regions of [−0.22 V, 1.58 V] and [3.58 V, 4.58 V] versus Mg2+/Mg in both anodic and cathodic sides.
\[ ^1H \text{NMR peak of } H_2O \text{ shifting to higher values for increasing PEG content is different from } ^1H \text{NMR observations on LiTFSI-PEG-H}_2O^{[8]} \text{ and LiTFSI-based WiSE}^{[11]} \text{ both of which show shifts to lower values due to the different environment of hydrogen in these electrolytes. This may be attributed to the interactions of } Mg^{2+}, \text{TFSI}^-, \text{ and PEG with } H_2O, \text{ each of which could influence the solvent structures especially coordination and hydrogen bonds (HBs). To prove this, molecular dynamics (MD) calculations were performed to study the HBs of different electrolytes (Table S4, Supporting Information). The HBs of 0.8 m Mg(TFSI)\_2-100\%H\_2O are contributed by TFSI^-H_2O interaction (≈5.4 per TFSI^-) and H\_2O-H\_2O interaction (≈1.5 per H\_2O). While 0.8 m Mg(TFSI)\_2-85\%PEG-15\%H\_2O shows an additional interaction of PEG-H\_2O (≈1.9 per PEG) and the contributions from TFSI^-H\_2O and H\_2O-H\_2O are reduced to ≈1.6 (per TFSI^-) and ≈1 (per H\_2O), respectively. The changes of HBs, therefore, affect the \(^1\text{H} \) chemical shift of the electrolytes, as observed in the NMR experiments. Besides, the lifetime of HBs increases from 50.86 ps (0.8 m Mg(TFSI)\_2-100\%H\_2O) to 79.33 ps (0.8 m Mg(TFSI)\_2-85\%PEG-15\%H\_2O), which demonstrates that the PEG crowding agent improves the stability of the AMEs.

Figure 2b,c shows the FTIR spectra of different electrolytes. The FTIR spectrum of H\_2O is dominated by two broad peaks at 3297 and 1636 cm\(^{-1}\), which are attributed to the stretching and bending vibrations of H\_2O bond, respectively. PEG shows three FTIR peaks at 3451, 2864, and 1454 cm\(^{-1}\), corresponding to H\_2O stretching, C-H stretching, and C-H bending, respectively. Upon adding PEG, the C-H stretching and bending peaks of PEG exhibit intensities decrease but their peak positions remain unchanged, demonstrating the structural stability of PEG. In contrast, the H-O stretching and bending peaks of H\_2O shift to 3399 and 1658 cm\(^{-1}\) with the increase of PEG to 85\%, accompanied by intensities reduction. This significant blueshift demonstrates the strengthening of the H-O bond, which could be ascribed to the interaction between PEG and H\_2O (PEG-H\_2O) and the reorganization of the proton donor framework, as well as the coordination of Mg\(^{2+}\), H\_2O, and PEG. Due to the inductive effect of the alkyl groups in PEG,\(^{[12]}\) the O atom in PEG has a higher negative charge density than that in H\_2O, which promotes the H atom in H\_2O to donate electrons and therefore forms HBs between H\_2O and PEG. Consequently, the PEG crowding agent strengthens the H-O bond of the AME. Overall, a higher potential is required to break the H-O bond (water decomposition), expanding the ESW of the electrolytes.

Furthermore, density functional theory (DFT) and MD calculations were conducted to monitor the structure changes and dissolution mechanism of electrolytes at the atomic level. The simulated geometrical structures of 0.8 m Mg(TFSI)\_2-100\%H\_2O and 0.8 m Mg(TFSI)\_2-85\%PEG-15\%H\_2O are shown in Figure 3a,b. Total energy calculations and root-mean-square deviation (RMSD) of Mg\(^{2+}\) confirm that both electrolyte systems are stabilized at equilibrium states (Figure S4, Supporting Information). To quantitatively analyze the solvation structure, short-range correlations of the electrolytes including radial distribution function (RDF) and corresponding integrated coordination numbers (ICN) are presented (Figure 3c,d and Table S5: Supporting Information). The g(r) profiles of Mg\(^{2+}\)-H\_2O in 0.8 m Mg(TFSI)\_2-100\%H\_2O and 0.8 m Mg(TFSI)\_2-85\%PEG-15\%H\_2O exhibit a dominant peak at 0.20 nm, corresponding to the first solvation shell of Mg\(^{2+}\). After adding PEG, an additional

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**Figure 2.**

\[ ^1H \text{NMR and b,c) FTIR spectra of 0.8 m Mg(TFSI)\_2-xPEG-(1-x)H\_2O (x = 0\%, 75\%, 80\%, 85\%, 90\%, and 95\%) and their comparison with pure Mg(TFSI)\_2 and PEG. PEG solvent reference shows \(^1\text{H} \) chemical shift at 4.20 ppm (OH-) and 3.70 ppm (CH\_2) and Mg(TFSI)\_2 has no \(^1\text{H} \) chemical shift. \]
peak appears at 0.19 nm, corresponding to Mg\(^{2+}\)-PEG with an ICN \(= 2\), and the ICN of Mg\(^{2+}\)-H\(_2\)O sharply decreases from 5.47 to 3.5. This implies that 36% of the water in the first solvation shell is replaced by two PEG molecules, confirming the significant changes of Mg\(^{2+}\) solvation structure. Conversely, 0.73 TFSI\(^-\) is coordinated with the first solvation shell of Mg\(^{2+}\) in 0.8 m Mg(TFSI)\(_2\)-100%H\(_2\)O (Figure S4e, Supporting Information), demonstrating the “quasi-water-in-salt” property of this electrolyte due to the direct coordination of Mg\(^{2+}\) and TFSI\(^-\). The results identify that all water molecules in 0.8 m Mg(TFSI)\(_2\)-100%H\(_2\)O are connected while dissociated Mg\(^{2+}\) cations and TFSI\(^-\) anions are fully solvated with water. The addition of PEG breaks the water networking and allows direct contacts between Mg\(^{2+}\) and TFSI\(^-\), while part of water molecules are replaced and PEG and TFSI\(^-\) do form a new network through the bonding with H\(_2\)O and Mg\(^{2+}\).

2.2. Electrochemical Properties of V\(_2\)O\(_5\) Nanowires Using the High Voltage AME

To demonstrate the applicability of Mg(TFSI)\(_2\)-85%PEG-15%H\(_2\)O electrolyte, V\(_2\)O\(_5\) nanowires synthesized via hydrothermal method were selected as a cathode material for AMIBs. X-ray powder diffraction (XRD) demonstrates the V\(_2\)O\(_5\) nanowires crystallize in an orthorhombic structure with space group \(Pnm2_1\) and an interplanar spacing of 4.4 Å (Figure S5a, Supporting Information). Rietveld refinement exhibits the lattice parameters are \(a = 11.514\) Å, \(b = 4.375\) Å, and \(c = 3.567\) Å. Scanning electron microscopy (SEM) demonstrates that V\(_2\)O\(_5\) has an average length of more than 10 μm and a width of \(\approx\) 30 nm (Figure S5b, Supporting Information). Figure 4a shows cyclic voltammograms (CVs) of V\(_2\)O\(_5\) at 0.05 mV s\(^{-1}\) where V\(_2\)O\(_5\) exhibits two very broad reduction peaks at 2.25 and 1.76 V and one oxidation peak at 3.0 V for the first scan. In the following two scans, both reduction and oxidation peaks show notable changes with the strong decrease with their intensities, indicating the large irreversible capacity. In contrast, CV displays significant differences in the 0.8 m Mg(TFSI)\(_2\)-100%H\(_2\)O electrolyte (Figure S6, Supporting Information), where it shows two broad reduction peaks at 1.92 and 2.44 V (with a shoulder at 2.50 V) and two oxidation peaks at 2.49 and 2.80 V for the first scan. In the following two scans, those peaks show strong decrease in intensity and one pair of redox peaks appear at 2.28/2.32 V. With the scan rate increase, the overall CVs of V\(_2\)O\(_5\) nanowires in Mg(TFSI)\(_2\)-85%PEG-15%H\(_2\)O do not change much (Figure 4b), but the redox peaks become wider and move toward lower/higher potentials for reduction/oxidation. Generally, peak current (i) and scan rate (v) obey the power-law relationship \(i = av^b\) of \(i = av^b\). According to the linear fitting of log(i) versus log(v), the oxidation/reduction of V\(_2\)O\(_5\) exhibits \(b\) values of 0.56/0.62 (Figure 4c), indicating a diffusion-controlled process.

Charge-discharge cycling of the V\(_2\)O\(_5\) nanowires was performed in the potential window of 1.58–3.68 V versus Mg\(^{2+}\)/Mg. The electrode displays two clear plateaus (at 2.41 and 1.93 V, respectively) on the first discharge profile and one slope-like plateau at around 2.74 V on the first charge profile (Figure 5a).
During subsequent cycling, the plateau at 2.41 V in charge becomes shorter and the plateau at 1.93 V in discharge gradually transforms into a sloped profile. Meanwhile, the slope-like charge plateau gradually becomes shorter with a slight increase of slope-plateau. The electrode shows a first discharge/charge capacity of 359/326 mAh g\(^{-1}\), resulting in \(\approx 91\%\) initial coulombic efficiency (Figure 5a). Afterward, the discharge capacity decreases to 286 mAh g\(^{-1}\) after 100 cycles, yielding 80% capacity retention (Figure 5b), which exhibits superior performance compared with that in 0.8 m Mg(TFSI)\(_2\)-100%H\(_2\)O (Figure S7, Supporting Information). Rate capability test (Figure 5d) demonstrates that the V\(_2\)O\(_5\) nanowires can deliver an average discharge capacity of 242, 178, 147, 101, and 54 mAh g\(^{-1}\) at current densities of 50, 100, 200, 500, and 1000 mA g\(^{-1}\), respectively. When the current returns to 50 mA g\(^{-1}\), V\(_2\)O\(_5\) delivers a specific capacity of \(\approx 225\) mAh g\(^{-1}\), followed by a slow increase of capacity to \(\approx 250\) mAh g\(^{-1}\) at the 40th cycle and then a gradual capacity fading to \(\approx 214\) mAh g\(^{-1}\) at 60th cycle. The electrode exhibits larger and larger electrode polarization along with the increase of current densities (Figure 5c), suggesting the kinetics properties of V\(_2\)O\(_5\) nanowires at high current densities strongly depend on electrolyte’s properties, particularly ionic conductivity. Compared with recent literature (Table S6, Supporting Information), our AMIB cell using V\(_2\)O\(_5\) cathode material exhibited much improved electrochemical performance in terms of discharge capacity and cycling stability. As a result, the high voltage aqueous electrolyte reported in this work makes it possible to develop high-performance AMIBs with better cycle stability.

### 2.3. Reaction Mechanism of Vanadium Oxide Cathodes in AMIBs

Ex situ XRD was performed on V\(_2\)O\(_5\) at different discharge/charge states to study their structure evolution during Mg\(^{2+}\) intercalation/deintercalation (Figure 6a). Some new reflections appear at 2.41 V (about 25% of depth of discharge).
Upon discharge to 2.15 V (about 50% of depth of discharge), all reflections of V₂O₅ disappear and the obtained reflections of the formed Mg-rich MgₓV₂O₅ (x ≈ 0.6) (see Rietveld refinement Figure S8a (Supporting Information), space group Pmn2₁, lattice parameters a = 12.503 Å, b = 4.180 Å, and c = 3.526 Å) are in good match with ε-Mg₀.₆V₂O₅ from our previous work,[2] indicating a 2-phase transition process. With further Mg²⁺ intercalation to 1.93 and 1.58 V (about 75% and 100% of depth of discharge), the disappearance of new reflections from MgₓV₂O₅ (x ≈ 0.6) suggests a second 2-phase transition process to form Mg-rich MgₓV₂O₅ (x ≈ 1.0) phase (Figure S8b, Supporting Information). This is the first report of this MgₓV₂O₅ (x = 1.0) phase formed at room temperature via electrochemical Mg-ion intercalation and detected via XRD. Upon charging to 2.76 V (50% of depth of charge), the reflections of V₂O₅ re-appear and co-exist with Mg-rich MgₓV₂O₅ (x ≈ 1.0) phase (Figure S8c, Supporting Information) and finally, all reflections at 3.68 V (100% of depth of charge) recover to their initial positions with lower intensities, implying a reversible 2-phase transition but asymmetry during cycling.

Figure 6. a) Ex situ XRD, b) Raman spectra, c,d) X-ray absorption spectroscopy (XAS) for the V K-edge, e,f) phase-uncorrected Fourier transforms (FT) of V K-edge EXAFS (k²-weighted), and g,h,i) V 2p, F 1s and Mg 1s X-ray photoelectron spectra of V₂O₅ at different discharge/charge states (Mo Kα radiation, λ = 0.70932 Å); the isobestic points in (c,d) are indicated by red arrows.

Mg-rich MgₓV₂O₅ (x = 1.0) phase (Figure S8b, Supporting Information). This is the first report of this MgₓV₂O₅ (x = 1.0) phase formed at room temperature via electrochemical Mg-ion intercalation and detected via XRD. Upon charging to 2.76 V (50% of depth of charge), the reflections of V₂O₅ re-appear and co-exist with Mg-rich MgₓV₂O₅ (x = 1.0) phase (Figure S8c, Supporting Information) and finally, all reflections at 3.68 V (100% of depth of charge) recover to their initial positions with lower intensities, implying a reversible 2-phase transition but asymmetry during cycling.
To investigate the local structure of the materials during Mg$^{2+}$ (de)intercalation, Raman scattering was performed on the pristine and cycled samples. V$_2$O$_5$ nanowires display typical Raman peaks (Figure 6b) as reported in previous work.[14] Significant structural changes are detected for V$_2$O$_5$ after Mg$^{2+}$ intercalation (Figure 6b). Upon Mg$^{2+}$ intercalation to 2.15 V, the peak at 140 cm$^{-1}$ shifts to 138 cm$^{-1}$ with the decrease of the intensity, meanwhile, some new peaks appear at 174, 427, 753, 869, and 954 cm$^{-1}$. With further Mg$^{2+}$ intercalation to 1.58 V, only some small and broad peaks (115, 153, 237, 268, 389, 834, 871, 939, and 997 cm$^{-1}$) are observed due to local structure in the Mg$_x$V$_2$O$_5$ (x=1.0) phase. Upon charging (2.76 and 3.68 V), the Raman spectra show reversible changes and finally return to its original state of V$_2$O$_5$, indicating the high reversibility.

The electronic and structural environments of V-ions at various charged/discharged states are studied by X-ray absorption spectroscopy (XAS). The edge position of the initial state V$_2$O$_5$ is slightly lower than that of the V$_2$O$_3$ reference. Herein, the oxidation state of V is confirmed to be mainly +5, in agreement with the XPS result for pristine V$_2$O$_5$. Upon Mg$^{2+}$ intercalation into V$_2$O$_5$, the edge energy of V K-edge and pre-edge peak shift toward lower values, implying reduction of V ions to V$^{4+}$ (Figure 6c). The intensity decrease of the pre-edge peak indicates an increase in the symmetry of V ions due to the decreased probability of the 1s and bound p hybridized d-state transitions.[15] Meanwhile, two broad peaks of edge resonance (B) emerge to a single broad peak with the increase of intensity, which is ascribed to energy absorption by core electrons.[15b] Moreover, distinct isosbestic points are detected for both discharge at $\approx 5474$ and $\approx 5503$ eV and charge at $\approx 5504$ eV processes, indicating a 2-phase reaction.[16] The edge position of the electrode at 1.58 V (100% of depth of discharge) overlaps with that of VO$_2$ reference, indicating that the oxidation state of V is confirmed to be +4. Upon Mg$^{2+}$ deintercalation, the edge energy of V K-edge, pre-edge peak, and edge resonance display reversible behavior, indicating the oxidation of V ions and reversibility of local structure (Figure 6d). The local structural changes of V-ion were further studied by analyzing the phase-uncorrected Fourier transform (FT) (k$^3$-weighted) of the V K-edge extended X-ray absorption fine structure (EXAFS). The pristine V$_2$O$_5$ shows two FT peaks at 1.0 and 1.53 Å, corresponding to the V–O bonds in VO$_2$ octahedra, and one FT peak at 2.76 Å assigned to the V–V shell.[17] During discharge, the V–O features shift to lower and higher radial distances with strongly decreased (peak at 1.0 Å) and slightly increased amplitudes (peak at 1.53 Å) (Figure 6e), indicating the overall symmetry increase of the local structure around V. Meanwhile, the V–V feature decreases its amplitude with shifts to lower value. These results indicate that the intercalated Mg$^{2+}$ affect both V–O and V–V shell structure. During charging, they show reversible behavior and almost return to their initial positions (Figure 6f), demonstrating the high reversibility of V$_2$O$_5$.

The surface chemistry and elemental composition of the pristine and cycled cathodes are studied by X-ray photoelectron spectroscopy (XPS). The V 2p spectrum of pristine V$_2$O$_5$ can be fitted by two doublets with V 2p$_{3/2}$ at 517.2 and 515.9 eV,[18] respectively, resulting in an average oxidation state of V$^{4+}$.[19] (Figure 6g–i). The V ions are gradually reduced to V$^{4.86+}$ when discharged to 2.15 V. Meanwhile, the V 2p$_{3/2}$ peak gradually decreases in intensity and totally disappears at the end of discharge, indicating that the surface of the V$_2$O$_5$ cathode is covered by a newly formed cathode electrolyte interphase (CEI) film. The F 1s spectrum of pristine V$_2$O$_5$ shows one peak at 687.3 eV related to C–F bond, which is attributed to the PVDF binder.

Upon discharge, two new peaks at 684.7 (refers to F–Mg bond) and 1303 eV (refers to Mg–F bond) are observed for F 1s and Mg 1s. These new XPS signals confirm that the main component of the CEI film is MgF$_2$, which could be attributed to the decomposition of TFSI$^{-}$. Upon charge to 2.76 and 3.68 V, V 2p$_{3/2}$ peak reappears and increases in intensity with oxidation state of V$^{4.60+}$ and V$^{4.86+}$, respectively. Surprisingly, it is noticed that along with the decrease/increase of the V 2p$_{3/2}$ peak, the F 1s peak increases/decreases accordingly. This indicates reversible formation/decomposition of the CEI film during discharge-charge cycling. Overall, the V$_2$O$_5$ cathode returns to its pristine state accompanied by reversible CEI formation and decomposition during cycling.

3. Conclusion
A series of AMEs show a stable ESW of $\approx 3.7$ V using a low-salt concentration of 0.8 m Mg(TFSI)$_2$. The electrochemical/physicochemical properties of AME and water splitting suppression are strongly affected by the addition of PEG 400 molecular crowding agent. V$_2$O$_5$ nanowires show a discharge capacity of 286 mAh g$^{-1}$ after 100 cycles with capacity retention of 80% at 50 mA g$^{-1}$ in the 0.8 m Mg(TFSI)$_2$-85%PEG-15%H$_2$O AME. A Mg-rich Mg$_x$V$_2$O$_5$ (x=1.0) phase is for the first time observed via XRD through electrochemical Mg-ion intercalation at room temperature. Meanwhile, a reversible formation/decomposition of CEI in AMIBs is revealed for the first time, where MgF$_2$ originating from the decomposition of TFSI$^{-}$ is identified as the dominant component. Not only electrolyte but also the crystal structure can affect the electrochemical performance, particularly at high current densities. This work paves the way to novel multivalent aqueous batteries by using a low-salt concentration AME and provides an approach for designing high-performance cathode materials and eco-friendly, high-voltage, high-safety, and low-cost aqueous electrolytes for sustainable large-scale energy storage.

4. Experimental Section

**Synthesis of V$_2$O$_5$ Nanowires:** V$_2$O$_5$ nanowires were prepared via a hydrothermal method. Briefly, 0.5 g of commercial V$_2$O$_5$ powder (Alfa Aesar, 99.99%) was added to 25 mL of deionized water under vigorous stirring for 10 min to form a light orange suspension. Then, 5 mL 30% hydrogen peroxide (H$_2$O$_2$) was dropwise added to the above suspension with stirring for 20 min to get a transparent reddish-brown solution. The obtained solution was transferred to a 45 mL Teflon-lined stainless-steel autoclave and kept at 220 °C for 48 h. The precipitate was washed with deionized H$_2$O and ethanol several times and dried at 75 °C for 12 h.

**Preparation and Characterizations of the Electrolyte:** Mg(TFSI)$_2$ was dissolved into a series of polyethylene glycol 400 (PEG 400) and pure H$_2$O solvent with vigorous stirring overnight at room temperature to form 0.8 m Mg(TFSI)$_2$-xPEG-(1-x)H$_2$O (x = 0%, 75%, 80%, 85%, 90%, and 95%). Ionic conductivity was measured by using Mettler Toledo InLab 738 ISM at 25 °C.
Fourier-transform infrared spectroscopy (FTIR) was performed on a Bruker Alpha-P instrument with attenuated total reflection (ATR) technology in the frequency range of 4000–400 cm⁻¹. The viscosity of various electrolytes was measured on a Bohlin Gemini 200 Nano rheometer at 25 °C with 40/1° cone geometry by using a solvent evaporation protection cover. Measurements were conducted with the shear rate varied from 1 to 200 s⁻¹ (viscosity is generally independent of shear rate).¹¹ H nuclear magnetic resonance (NMR) spectroscopy was performed on the electrolyte samples with a Bruker Avance 300 MHz spectrometer at a magnetic field of 7.0 T. Samples were placed inside 5 mm glass tubes and chemical shifts are given relative to that of tetrathylsilane at 0 ppm.

Samples were prepared in an argon-filled glove box and transferred under argon atmosphere during the measurement, using electrons of 8 eV energy of 15 keV. The structural characterizations were performed with a Zeiss Supra 55 Scanning Electron Microscope (SEM) with primary energy of 15 keV. The structural characterizations were performed on a STOE STADI P diffractometer operated with Mo Kα radiation (λ = 0.70932 Å). The powders were filled in 0.5 mm Ø boro-silicate capillaries, and diffraction patterns were collected in capillary geometry. A LabRam HR Evolution Raman microscope from Horiba Scientific equipped with HeNe laser (633 nm, 17 mW) and a CCD detector (Horiba) was used to collect the Raman scattering of the samples. Meanwhile, a 600 g/µm grating was used to split the measurement signal with a x100 objective (NA 0.95) for all the pristine and cycled samples. The washed and dried electrodes after discharge and charge were sealed in an in situ cell with a quartz window inside a glovebox, where the quartz window is suitable for ex situ Raman measurements. X-ray photoelectron spectroscopy (XPS) was performed using a K-Alpha spectrometer (ThermoFisher Scientific, UK) equipped with a microfocused, monochromated Al Kα, X-ray source (λ = 1486.6 eV) with a spot size of 400 µm. A charge compensation system was employed during the measurement, using electrons of 8 eV energy and low-energy argon ions to prevent localized charge accumulation. All samples were prepared in an argon-filled glove box and transferred under argon atmosphere into the spectrometer. Thermo Advantage software was used in data acquisition and processing, as described elsewhere.[¹⁸] The analyzer transmission function, Scofield sensitivity factors, and effective attenuation lengths for photoelectrons were applied for quantification.[¹⁹] The standard TPP-2M formalism was used for the calculation of effective attenuation lengths.[²¹] All spectra were referenced to the carbonaceous C 1s peak (C−C/C−H) at 285.0 eV binding energy.

Electrochemical Characterizations: The electrode was prepared by coating slurry mixture on stainless steel foil, which consists of active material V₂O₅ with C₆₅ (Timcal) and polyvinylidene difluoride (PVDF) coating slurry mixture on stainless steel foil, which consists of active material V₂O₅ with C₆₅ (Timcal) and polyvinylidene difluoride (PVDF) coating slurry mixture on stainless steel foil, which consists of active material V₂O₅ with C₆₅ (Timcal) and polyvinylidene difluoride (PVDF) coating slurry mixture on stainless steel foil, which consists of active material V₂O₅ with C₆₅ (Timcal) and polyvinylidene difluoride (PVDF) coating. The electrode was dried at 65 °C overnight and then cut electrodes into 12 mm diameter (mass loading of ~1 mg cm⁻²). The electrode was dried at 65 °C overnight and then cut electrodes into 12 mm diameter (mass loading of ~1 mg cm⁻²). Activated carbon (AC) electrode was prepared using AC, C₆₅ (Timcal) and polytetrafluoroethylene (PTFE, 60 wt% solution in water from Sigma–Aldrich) in a weight ratio of 8:1:1 with solvent isopropanol in a DAC150.1 FVZ model from SpeedMixer with 800 rpm for 10 min. The paste mixture was kneaded manually on a glass plate and finally was rolled to a uniform thickness electrode. The electrodes were finally dried at 70 °C overnight under vacuum before use. The LSVs of various electrolytes were performed using a glass cell consisting of glassy carbon (GC) and stainless steel foil working electrode, Pt plate counter electrode, and AgCl/Ag reference electrode. Three-electrode Swagelok-type cells for electrochemical measurements were assembled in air at room temperature. The cells were built with V₂O₅ positive electrode, AC counter electrode, AgCl/Ag reference electrode (3 m NaCl), 0.8 m Mg(TFSI)₂, 85%PEG-15%H₂O or 0.8 m Mg(TFSI)₂-100%H₂O as an electrolyte (700 µL), and a piece of glass microfiber (Whatman) as the separator. The mass of AC was intentionally in excess with a large µMg(Mg²⁺/Mg) reference for convenience based on the voltage difference of 2.58 V between AgCl/Ag and Mg²⁺/Mg. Sample Preparation for Ex Situ Characterizations: The V₂O₅ cells at 25% (2.41 V), 50% (2.15 V), 75% (1.93 V), 100% (1.58 V) depth of discharge and 50% (2.76 V), 100% (3.68 V) depth of charge were disassembled and then the cathode was washed with acetonitrile in an Ar-filled glovebox. After drying in a vacuum chamber, the electrode composite was peeled off and filled into 0.5 mm Ø boro-silicate capillaries for ex situ XRD measurements. Note that the reference electrode was removed before putting the cells into glovebox.

Ex situ X-ray absorption spectroscopy (XAS) measurements were carried out at PETRA-III beamline P65 at DESY in Hamburg. XAS spectra were recorded in quick-XAS (6 min/spectrum) mode in fluorescence geometry using a PIPS diode. The K-edge of V₂O₅ at different states (sealed in two pieces of Kapton foils) was measured and the energy was calibrated using the absorption edge of V foil, as it is commonly employed in XAS experiments. V₂O₅, VO₂, and V₂O₃ were used as standard materials. All data were collected at room temperature with a Si (111) double crystal monochromator and all XAS spectra were processed using DEMETER software package.[²³]

Molecular Dynamics Simulations: All atomistic molecular dynamics (MD) simulations were performed with the GROMACS 4.6.7 package.[²⁴] The GROMOS force field[²⁵] was used for all components. The MD simulations were carried out using cubic cells with a linear dimension of 2.83 nm for 0.8 m Mg(TFSI)₂-H₂O (containing 9 mG(TFSI)₂ and 600 H₂O) and 2.18 nm for 0.8 m Mg(TFSI)₂-85%PEG-15%H₂O (containing 10 mG(TFSI)₂, 100 H₂O, and 25 PEG) using the software package PACKMOL.[²⁶] In all simulations, the temperature was kept constant at T = 300 K by an improved velocity-rescaling thermostat,[²⁷] using a coupling time constant of 0.1 ps. The pressure was kept constant at p = 1 bar by a semi-isotropically Parrinello-Rahman barostat[²⁸] with coupling time constant of 2 ps and compressibility 4.5× 10⁻¹ bar¹. Electrostatic interactions were treated through the Particle Mesh Ewald method[²⁹] with a real-space cut-off of 1.0 nm and a grid spacing of 0.16 nm with fourth-order interpolation scheme. Lennard-Jones interactions were truncated at 1.0 nm and shifted to zero. A Leapfrog algorithm with an elementary time step of 2 fs was used for numerical integration. All bonds were constrained by the LINCS algorithm.[³⁰] Prior to production runs, an energy minimization was first performed using a conjugate-gradient method, followed by an equilibration of the system for 10 ns under constant volume constant temperature conditions, and a subsequent equilibration run of 10 ns under constant temperature and constant pressure conditions. These final production runs at constant temperature and pressure had a length of more than 150 ns each.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Q.F. conceived the idea and discussed with X.W., X.L., S.I., A.S., M.B., Z.W., M.K., H.E., Y.W., and S.D.; Q.F. performed material synthesis, electrolyte/sample preparation, characterizations, electrochemical measurements, and analyzed the data. Z.W. carried out X-ray fluorescence measurements and analyzed x-ray fluorescence data. M.B. performed FTIR and analyzed the data. S.I. conducted NMR and analyzed the data. X.L. performed XPS and Raman measurements and analyzed the XPS data and Q.F. analyzed the Raman data. A.S. and Q.F. analyzed the Raman data. A.S. and Q.F. carried out XAS and Raman measurements. S.I. conducted NMR and analyzed the data. X.L. carried out DFT and MD calculations and revised the manuscript. All authors contributed to interpreting the findings, reviewing, and commenting on the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aqueous Mg-ion batteries, aqueous Mg-ion electrolytes, molecular dynamics simulations, nuclear magnetic resonance, vanadium oxide, X-ray absorption spectroscopy

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