Is Alpha-V₂O₅ a Cathode Material for Mg Insertion Batteries?

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Abstract: When designing a high energy density battery, one of the critical features is a high voltage, high capacity cathode material. In the development of Mg batteries, oxide cathodes that can reversibly intercalate Mg, while at the same time being compatible with an electrolyte that can deposit Mg reversibly are rare. Herein, we report the compatibility of Mg anodes with α -V₂O₅ by employing magnesium bis(trifluoromethane sulfonyl)imide in diglyme electrolytes at very low water levels. Electrolytes that contain a high water level do not reversibly deposit Mg, but interestingly these electrolytes appear to enable much higher capacities for an α -V₂O₅ cathode. Solid state NMR indicates that the major source of the higher capacity in high water content electrolytes originates from reversible proton insertion. In contrast, we found that lowering the water level of the magnesium bis(trifluoromethane sulfonyl)imide in diglyme electrolyte is critical to achieve reversible Mg deposition and direct evidence for reversible Mg intercalation is shown. Findings we report here elucidate the role of proton intercalation in water-containing electrolytes and clarify numerous conflicting reports of Mg insertion into α -V₂O₅.

1. Introduction

Development of a higher energy density, rechargeable battery is important for the future advancement of mobile energy storage systems. Although lithium-ion batteries (LIBs) are widely used for energy storage in many consumer electronic applications, issues associated with manufacturing a cost-competitive battery of sufficient energy density have slowed their development in large volume applications such as electric vehicles (EV).[1] One solution to greater energy density in LIBs would be to replace the current graphite anode with lithium

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4 metal. However, this solution has a long history of undesirable cycling behavior related to
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6 dendrite formation and the reactivity of Li metal with the electrolyte.[2] While techniques that
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8 incorporate Li metal anodes into LIBs are being investigated, magnesium (Mg) has started to
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10 draw sufficient attention as an inexpensive and earth-abundant metal that is potentially a safer
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12 anode alternative than lithium.[3, 4] Mg shares many properties with lithium, but has more to
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14 offer: for instance, Mg is the eighth most abundant element in the earth's crust, making
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16 manufacturing cost efficient energy storage systems possible. In addition, Mg offers a
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18 reasonable alternative to Li with its fairly low reduction potential (-2.37 V vs. SHE) and a high
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20 theoretical volumetric capacity (3833 mAh/cm³).[5] A major difference as compared to lithium
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22 is that Mg metal has been proposed to not form dendrites during deposition, which makes it
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24 potentially longer lasting and substantially safer than a Li metal anode.[6, 7]
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34 While advantages of Mg have been recognized for a long time, research towards the
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36 development of Mg batteries is still at a very early stage, with many technological challenges
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38 ahead. Even though the Grignard or halogen-containing electrolyte systems works well with a
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40 Mg metal anode, at least in terms of cycling efficiency, and are compatible with a Chevrel phase
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42 cathode (1.1 V vs Mg),[3, 8-11] however, two issues exist: 1) the use of ethereal solutions of
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44 Grignard/halogen based electrolytes are corrosive to cell components; and 2) they are not
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46 compatible with metal oxide cathodes.[12, 13] Meanwhile, conventional electrolytes, based
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48 upon Mg(ClO₄)₂ or Mg(NO₃)₂ salts, show evidence of Mg intercalation with metal oxide
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50 cathodes, but have yet to be proven for reversible Mg deposition.[14-17] In a more recent
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52 work, Toyota demonstrated the utility of a halogen-free electrolyte based on a stable anionic
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54 boron cluster in a full cell.[18] However, the carborane anion involves a complex preparation
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procedure, which hinders its practical application. Herein, we utilize a more accessible system with a non-corrosive, halogen-free electrolyte, magnesium bis(trifluoromethane sulfonyl)imide in diglyme ($\text{Mg}(\text{TFSI})_2/\text{D2}$), that can reversibly plate/strip Mg and at the same time is compatible with a high voltage orthorhombic V_2O_5 cathode (2.56 V vs. Mg). In particular, our findings show that lowering the water level in the electrolyte is a critical step in achieving successful plating/stripping of Mg, and thus permits compatibility with both the Mg metal anode and the V_2O_5 cathode. Although near theoretical capacity can be achieved with a high water content electrolyte for the V_2O_5 cathode, such a system fails to incorporate Mg metal as anode. Results from solid state NMR spectroscopy have shown that the gain in capacity in a high water content system is mostly due to reversible proton intercalation. Furthermore, real and reversible Mg intercalation into V_2O_5 for $\text{Mg}(\text{TFSI})_2/\text{D2}$ at a low water level was demonstrated and confirmed by X-ray absorption near edge spectroscopy (XANES), energy dispersive spectroscopy (EDX) and X-ray diffraction (XRD).

2. Experimental

2.1 Preparation of the orthorhombic V_2O_5 cathode

Vanadium oxide electrodes were prepared by casting an 8:1:1 weight-ratio slurry of vanadium oxide (Fluka, > 99%), Timcal Super C45 carbon black, and polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidinone (NMP) onto a 304 stainless steel current collector. These laminates were then dried at 75 °C in an oven for at least one hour before being punched as 7/16" diameter electrodes. Average mass load of V_2O_5 is 2 mg/cm².

2.2 Electrolyte synthesis

Magnesium bis(trifluoromethane sulfonyl)imide (99.5%, Solvionic, France) was dried in a vacuum oven at 170°C overnight before use. Diglyme (Aldrich, anhydrous, 99.5%) solvent was pretreated with molecular sieves (Aldrich, 3Å beads, 4-8 mesh) overnight and then added into the dried Mg(TFSI)₂. The as-prepared electrolyte was then stirred overnight before use. Water levels of the as prepared electrolytes were determined from Karl-Fischer analysis.

2.3 Electrochemical characterizations

A three electrode setup with a Pt disk as the working electrode (2 mm in diameter, CH instruments, Austin, TX) and polished Mg ribbon as the counter and reference electrode (99.9% purity, Sigma-Aldrich) is used to measure the cyclic and linear voltammograms of the electrolyte. Galvanostatic cycling of V₂O₅ vs. Mg in coin cells was performed using a Maccor series 4000 cycler at 20 μA/cm². A three electrode Swagelok cell configuration is used for the cyclic voltammetry measurement, with V₂O₅ on a stainless steel current collector as the working electrode, and a polished magnesium disk (7/16" diameter) as the counter and reference electrode. Electrochemical characterization was carried out using a multichannel potentiostat (Parstat MC, Princeton Applied Research, TN) under a pure argon atmosphere in a glove box where H₂O and O₂ level is kept under 1 ppm.

2.4 X-ray Diffraction

High energy X-ray diffraction (XRD) was carried out at Beamline 11-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The X-ray energy was 114.76 keV (corresponding to 0.10804 Å, the fixed wavelength for this station), which has a large

penetration capability that allowed for the detection of structural changes of the bulk material. The V_2O_5 powder was collected and sealed with kapton tape. An incident X-ray beam size of 0.5 mm $\times$ 0.5 mm was used. A Perkin Elmer area X-ray detector was used to collect the 2-dimensional diffraction patterns in transmission mode. The measured 2D diffraction patterns were calibrated using a standard CeO_2 sample and converted to one-dimensional intensity versus scattering angle patterns using Fit2D software.[19] XRD patterns of cycled V_2O_5 at charged, discharged and recharged states are shown in Figure S1.

2.5 X-ray absorption near edge structure (XANES)

Ex-situ vanadium (V) K-edge X-ray absorption spectroscopy was performed to detect the change of the V valence states for charged and discharged cathodes at beamline 20-BM-B at APS (ANL). The measurements were carried out in transmission mode with a vanadium metal foil as a reference, which provides internal calibration for the X-ray energy. Coin cells with V_2O_5 as the cathode and Mg metal as the anode were cycled at a constant current mode, 20 $\mu A/cm^2$, for 10 cycles before holding at certain charged/discharged potentials. V_2O_5 powder was then collected and mixed homogeneously with cellulose at a mass ratio of 1:5 and pressed into pellets for the measurement. The XANES spectra were normalized and analyzed using the ATHENA software package.[20] The full range XANES spectra shown in Figure S2 indicate good normalization. The V metal K-edge position, located at the maximum of the first derivative, was defined as 5465 eV.

2.6 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

Scanning electron microscopy and energy-dispersive X-ray spectroscopy characterization were performed using a Hitachi S4700-II scanning electron microscope equipped with an EDX detector mounted at a 30° take-off angle. Elemental composition was determined using a standardless ZAF (atomic number, absorption and fluorescence) corrected analysis. Both EDX and SEM were performed at an electron energy of 30 keV. Cathode materials collected from cycled coin cells were soaked and rinsed with acetone to remove any electrolyte residue on the surface prior to the EDX analysis.

2.7 NMR characterization

^1H NMR experiments were performed using a Bruker Avance III spectrometer operating at a magnetic field strength of 11.7 T, corresponding to a ^1H Larmor frequency of 300 MHz with a Bruker HX double resonance 1.3 mm MAS probe. ^1H NMR spectra were referenced relative to acetone at 2.05 ppm. A hahnecho pulse sequence was used to acquire all ^1H NMR spectra. A recycled delay of 2 sec was used in all experiments. Experiments were only performed after a stable probe temperature was reached (10°C). Samples were carefully scraped off the stainless steel current collector and packed into a 1.3 mm rotor for signal acquisition, and the weight of the sample was recorded every time. The ^1H NMR spectra are normalized to the weight of the active materials in the sample holders.

3. Results and discussion

3.1 Investigation of effective Mg plating and stripping of $\text{Mg}(\text{TFSI})_2/\text{D2}$ at various water level

Besides effective magnesium plating and stripping, the primary characteristics required for a magnesium electrolyte are a wide electrochemical window and compatibility with current collectors, as pointed out by Ha. *et al.* recently.[21] In addition, we have found that the water content in the $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte is critical to achieve reversible Mg deposition. For instance, **Figure 1 (a, b)** show typical cyclic voltammetry curves with 1 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ at water contents of 2600 and 300 ppm, where no clear electrochemical evidence of reversible Mg deposition can be observed. The same electrolyte at a lowered water level, 15 ppm, shows significant improvement of Mg plating/stripping as presented in **Figure 1c**. Several issues need to be identified for practical consideration of utilizing $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte in a Mg battery. Firstly, water level of electrolyte needs to be strictly regulated since cyclic voltammograms show that even trace water can passivate Mg metal and thus shut down the further activity of the Mg anode. Secondly, even though $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte at a low water content gives reversible Mg deposition, the large overpotential and low coulombic efficiency are problems that still need to be solved. To understand the possible compatibility of the $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte with a high voltage oxide cathode, its anodic stability was investigated by Linear sweep voltammetry (LSV), presented in **Figure 1d**. Oxidation onset potential was determined to be 4.2 V (vs. Mg/Mg^{2+}), in agreement with reported literature.[21] As compared to the complex ether based organomagnesium electrolytes, where the largest window *versus* magnesium metal was limited to ~ 3.5 V. [22-24] An anodic stability larger than 4 V is of critical importance to allow the use of high voltage cathodes materials. It is worth noting that the mechanism of reversible deposition for $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte has not been fully described and further details will be presented in a future publication. We believe the diglyme solvent plays a critical

factor by providing a well-solvated environment for Mg ions and therefore facilitates efficient Mg deposition and dissolution. Detailed solvation structure analysis for this system can be found from a pair distribution function study reported recently;[25] nevertheless, its halogen-free nature provides a simple approach to electrolyte design and exhibits promising potential for application in a cell containing a high voltage metal oxide cathode.

3.2 Performance of an α -V₂O₅ cathode for Mg intercalation in wet and dry electrolyte systems

Vanadium pentoxide (V₂O₅) is one of the classical intercalation cathodes due to its potential insertion properties with divalent cations, with reports beginning in the late 1980s.[26, 27] However, insertion of Mg²⁺ into a V₂O₅ cathode was claimed mainly using Mg(ClO₄)₂ based electrolytes, which contains a high water content and does not plate and strip Mg metal.[26-28] As a consequence, Mg metal was not used as the anode in these studies.[26-32] In addition, several publications report the necessity of water in the electrolyte to enable Mg intercalation.[29, 30, 33] For instance, Novak and Desilvestro reported reversible cycling of V₂O₅ with Ag/AgCl as a reference electrode and noted that the presence of water was critical to give reversible electrochemical response.[33] Large capacity was reported in these systems, however, no clear evidences of structural changes were given beyond electrochemical cycling data to indicate true Mg intercalation had occurred.

In this work we perform two sets of experiments of cycling α -V₂O₅ as cathode. One in Mg(TFSI)₂/D2 electrolyte with high water content (wet electrolyte) and another in low water content electrolyte (dry electrolyte). Firstly, V₂O₅ cell using 1 M Mg(TFSI)₂/D2 with 2600 ppm water as an electrolyte is constructed. Galvanostatic cycling of a coin cell composed of V₂O₅ and

the high surface area carbon as capacitive anode is shown in **Figure 2a**, where the cell's capacity can be achieved in close equivalent to theoretical value, ~ 260 mAh/g (ESI^+). It is worth mentioning that, the addition of water in the electrolyte necessitates replacing the Mg metal with a high surface carbon, as cells containing water are not compatible with Mg anodes. For comparison with the wet electrolyte system, galvanostatic cycling of V_2O_5 against a carbon electrode is performed in 1.0 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte with 15 ppm H_2O . Results presented in **Figure 2b** indicate a discharge capacity of ~ 60 mAh/g is achieved in the dry electrolyte system. To further understand the different performance of the dry electrolyte *versus* the wet electrolyte for an $\alpha\text{-V}_2\text{O}_5$ cathode, galvanostatic cycling of V_2O_5 with a magnesium metal anode was performed in 1.0 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte with 15 ppm H_2O , to investigate Mg intercalation in a prospective full cell design. (ESI^+) A three electrode setup is used with V_2O_5 as cathode and Mg metal as reference and counter electrode and cycling results show reversible Mg insertion as presented in **Figure 2c**. The discharge capacity for the 1st cycle is ~ 80 mAh/g and 94% of capacity was maintained starting from the 2nd to the 10th cycle at ~ 50 mAh/g, as shown in **Figure 2d**. The observed discharge capacity is significantly lower for the dry electrolyte as compared to the wet electrolyte system, but falls in good agreement with the capacity from the V_2O_5 cell with a carbon anode in the dry electrolyte system. At varied voltage escalation rates, oxidation peaks and reduction peak showed a slight voltage drift (less peak splitting at lowered rate), ascribed to the slow kinetics for Mg insertion. Capacity loss after the 1st cycle is due to the partially reversible insertion for magnesium intercalation and the likely film formation on the magnesium anode.[24, 34, 35] Potential correction for the Mg reference electrode is done by adding ferrocene, which is a redox couple that can be used as an internal

standard. Cyclic voltammetry results indicate a 1.0 V potential shift to the lower value in $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte with the Mg metal as reference (ESI^+).

3.3 Characterization of cycled V_2O_5 in a wet versus dry electrolyte

The significant capacity difference observed for the dry electrolyte (1 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ with 15 ppm H_2O) *versus* wet electrolyte (1 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ with 2600 ppm H_2O) with the V_2O_5 cathode requires further understanding. Therefore, ^1H solid state NMR spectroscopy was carried out for electrochemically cycled V_2O_5 from a hybrid half-cell running against the carbon counter electrode with wet electrolyte, and a full V_2O_5 cell against Mg anode in a dry electrolyte. **Figure 3a** shows the ^1H NMR spectra for pristine, charged and discharged V_2O_5 cycled in the wet electrolyte. The growth and decay of the proton features upon charge and discharge, relative to the pristine state, indicates that protons participate in cell cycling. Three peaks can be resolved upon deconvolution, appearing at -1.3 ppm, 1.8 ppm and 4.4 ppm, respectively (ESI^+). The peak at -1.3 ppm is ascribed to the participated proton co-intercalation in lattice. The features at 1.8 and 4.4 ppm are ascribed to the adsorbed surface water and the –OH bond in the V_2O_5 lattice. The disappearance of the -1.3 ppm peak for the charged state confirms the proton de-intercalation, indicating the added water from the electrolyte participates in cycling. In contrast, the ^1H NMR spectra remained essentially unchanged for electrochemically cycled V_2O_5 in the dry electrolyte, as shown in **Figure 3b**, the slight changes observed are assigned simply to the change of adsorbed water at the cathode surface. Based on the spectroscopic evidence and the electrochemical performance, it is hypothesized that the

significant improvement in capacity from cells with high water content is due to proton intercalation into the V_2O_5 lattice.

It is crucial to verify that the source of measured current is contributed from real reversible Mg intercalation for the dry electrolyte system, rather than conversion[36] or side-reactions[12] due to the fact that much of the literature relating to Mg intercalation are ambiguous and errors have been reported in the past.[36, 37] X-ray absorption near edge spectroscopy (XANES) was applied to inspect changes of the vanadium (V) oxidation state in pristine, charged, and discharged V_2O_5 using dry electrolyte. The electrochemically charged/discharged V_2O_5 cathodes were collected from the cells cycled with the dry electrolyte followed with XANES measured in transmission mode (ESI[†]). Normalized vanadium K absorption edge spectra from **Figure 4a** shows a ~0.8 eV edge shift (calculated by the first derivative of the normalized energy) of the main line towards lower energy for the discharged V_2O_5 electrode at 0 V (red), as compared with the pristine V_2O_5 (black). This change is accompanied by a 0.27 eV shift of the pre-edge peak toward lower energy. Lowered edge energy upon discharge indicates a partial reduction of the V oxidation state upon magnesium intercalation. In addition, the asymmetry of the pre-edge and reduction in fine structure in the near-edge region of the discharged electrode indicates a mixture of reduced and pristine vanadium states. A reduced pre-edge intensity for both charged and discharged states is observed, which is ascribed to the distortion of the square pyramidal coordination of V^{5+} with the nearby five oxygen atoms, since the pre-edge peak is considered to be a fingerprint that reflects the global symmetry around the V ions.^[38, 39] The pre-edge peak energy in the discharged state shifted back to higher energy for the electrode charged back to 2.8 V (blue),

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4 indicating an increase of the vanadium oxidation state and the reversibility of magnesium
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6 insertion into V_2O_5 . [40] However, the edge position and intensity at the charged state did not
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8 completely recover and overlap to the pristine state (0.06 eV difference), attributed to the
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10 incomplete extraction of Mg upon charging. The Fourier-transformed (FT) extended X-ray
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12 absorption fine structure (EXAFS) is shown in **Figure 4b**. The decrease in intensity of the first
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14 and second FT peaks for the discharged state reflects the structural disorder intrinsic to
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16 heterogeneous Mg insertion. EXAFS suggests that the V_2O_5 lattice structure remains largely
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18 undisturbed after cycling. The nearly complete reversibility of the local atomic structure
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20 following charging is further evidence of reversible Mg intercalation in V_2O_5 through an
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22 intercalation pathway. The amount of Mg insertion is calculated to be about 0.2 mole per V_2O_5
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24 based on the change of the vanadium valence state. This finding is consistent with the capacity
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26 value from the electrochemical cycling results and, as a consequence the capacity from the Mg
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28 anode based V_2O_5 cell is mainly contributed from Mg intercalation pathway.
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38 EDX was applied to directly probe the presence of Mg in the discharged V_2O_5 electrode.
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40 **Figure 5a** shows the signature spectra of elements C, O, Mg and V. An increase in the
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42 characteristic peak of Mg for the discharged V_2O_5 is clearly observed as compared to the
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44 charged and pristine electrodes, indicating the existence of a higher concentration of Mg in the
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46 discharged state. A minor amount of Mg remained in the charged electrode due to the
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48 incomplete removal of Mg, and this finding is in agreement with the XAS and the diffraction
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50 results (ESI[†]). EDX suggested that nearly pure Mg is being deposited on the Mg anode during
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52 the plating process, shown in **Figure 5**. Surface morphology and elemental analysis for the Mg
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54 metal anode that went through 10 cycles *versus* V_2O_5 was examined to study the morphology
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1 evolution on the Mg anode. The surface of the Mg anode appeared reasonably smooth without
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3 obvious dendrite formation formed, as shown in the inset image of **Figure 5b**. Interestingly,
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5 upon a closer inspection, **Figure S7** (SI), pinholes that are hundreds of nanometers in diameter
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7 were observed. These pinholes are attributed to the stripping process of the Mg anode during
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9 cycling, and similar pinhole morphology was observed and reported for stripping Mg using
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11 $\text{Mg}(\text{TFSI})_2$ in the mixture of glyme solvents as electrolyte.[21] Consistent with the XAS and EDX
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13 results, X-ray diffraction (XRD) shows the formation of a new phase for discharged V_2O_5
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15 electrodes, as well as the presence of a MgV_2O_5 phase structure. Detailed discussions regarding
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17 this part can be found in the ESI[†].
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28 **4. Conclusions**

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32 In conclusion, it is demonstrated that water level in the $(\text{MgTFSI})_2/\text{D2}$ electrolyte plays
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34 an important role for plating/stripping Mg. Using this electrolyte, we have demonstrated that
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36 Mg intercalation is occurring, but at capacities much lower than what has been reported
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38 previously. In contrast, $\text{Mg}(\text{TFSI})_2/\text{D2}$ with a high water content gives higher capacity, with
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40 protons participating in intercalation, but such a system lacks the potential for leveraging the
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42 Mg metal anode. The presence of proton involvement in the capacity of the V_2O_5 system is for
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44 the first time report and should be considered a caution for future investigations of possible Mg
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46 intercalation cathodes. Results presented in this work provide informative insights for designing
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48 beyond lithium energy storage systems and offer potential guidance for compatibility of metal
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50 oxide cathodes with Mg anode. We believe such full cell prototype provides a solid foundation
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for further understanding and development of Mg full cell with high voltage cathodes reasonable for commercial Mg batteries.

Figures

Figure 1. Cyclic voltammograms (CV) of Mg(TFSI)₂/D2 at 1 M, (a) with 2600 ppm water; (b) with 300 ppm water; (c) with 15 ppm water. Arrows indicate the scan direction and sequence; (d) Linear sweep voltammetry (LSV) of Mg(TFSI)₂/D2 at 1 M with 15 ppm water (the inset shows the enlargement region between 3.3 V to 5.5 V). Dash line with arrow indicates the breakdown potential; CV and LSV were conducted with applying Pt disk as the working electrode and Mg ribbons as the reference and counter electrodes at scan rate of 25 mV/sec.

Figure 2. Cycling performance of a V_2O_5 cathode in $Mg(TFSI)_2/D2$ electrolyte. (a) Cyclic voltammetry with V_2O_5 as the working electrode and Mg disks as the counter and reference electrodes at sweep rates of 2 mV/sec (red) and 5 mV/sec (black). 1 M $Mg(TFSI)_2/D2$ with 15 ppm H_2O is used as electrolyte; (b) Discharge capacity vs cycle number for the V_2O_5 vs Mg anode coin cell at 20 $\mu A/cm^2$ in 1 M $Mg(TFSI)_2/D2$ with 15 ppm; (c) Galvanostatic cycling of a V_2O_5 vs carbon coin cell in 1 M $Mg(TFSI)_2/D2$ with 2600 ppm H_2O at 20 $\mu A/cm^2$; (d) Galvanostatic cycling of a V_2O_5 vs carbon coin cell in 1 M $Mg(TFSI)_2/D2$ of 15 ppm H_2O at 20 $\mu A/cm^2$.

Figure 3. ^1H NMR spectra of electrochemically cycled V_2O_5 electrodes at charged/discharged states: (a) V_2O_5 electrodes were harvested upon cycling against a carbon counter electrode in a wet $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte (2600 ppm H_2O) at 1 M; (b) discharged and charged V_2O_5 electrodes were harvested upon cycling against a Mg metal anode in a dry $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte (15 ppm H_2O) at 1 M. All cells were cycled at a current density of $20 \mu\text{A}/\text{cm}^2$. Spectra reported here are normalized to the mass of the sample.

Figure 4. (a) XANES spectra for pristine (black), charged (blue), and discharged (red) V_2O_5 at the vanadium K-edge; (b) the Fourier transform of the extended fine structure of pristine, charged, and discharged V_2O_5 at the vanadium K-edge. The spectra have not been phase-shifted.

Figure 5. (a) Normalized EDX spectrum for discharged (black), charged (red) and pristine (blue) V_2O_5 , with insets of both magnified and offset data from the boxed area, and a SEM image of the discharged electrode; (b) SEM image and EDX spectrum of the cycled Mg anode.

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Supplementary information

Available online

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Figure 1. Cyclic voltammograms (CV) of $\text{Mg}(\text{TFSI})_2/\text{D2}$ at 1 M, (a) with 2600 ppm water; (b) with 300 ppm water; (c) with 15 ppm water. Arrows indicate the scan direction and sequence; (d) Linear sweep voltammetry (LSV) of $\text{Mg}(\text{TFSI})_2/\text{D2}$ at 1 M with 15 ppm water. Dash line with arrow indicates the breakdown potential; CV and LSV were conducted with applying Pt disk as the working electrode and Mg ribbons as the reference and counter electrodes at scan rate of 25 mV/sec.

Figure 2. Cycling performance of a V_2O_5 cathode in $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte. (a) Cyclic voltammetry with V_2O_5 as the working electrode and Mg disks as the counter and reference electrodes at sweep rates of 2 mV/sec (red) and 5 mV/sec (black). 1 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ with 15 ppm H_2O is used as electrolyte; (b) Discharge capacity vs cycle number for the V_2O_5 vs Mg anode coin cell at $20 \mu\text{A}/\text{cm}^2$ in 1 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ with 15 ppm; (c) Galvanostatic cycling of a V_2O_5 vs carbon coin cell in 1 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ with 2600 ppm H_2O at $20 \mu\text{A}/\text{cm}^2$; (d) Galvanostatic cycling of a V_2O_5 vs carbon coin cell in 1 M $\text{Mg}(\text{TFSI})_2/\text{D2}$ of 15 ppm H_2O at $20 \mu\text{A}/\text{cm}^2$.

Figure 3. ^1H NMR spectra of electrochemically cycled V_2O_5 electrodes at charged/discharged states: (a) V_2O_5 electrodes were harvested upon cycling against a carbon counter electrode in a wet $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte (2600 ppm H_2O) at 1 M; (b) discharged and charged V_2O_5 electrodes were harvested upon cycling against a Mg metal anode in a dry $\text{Mg}(\text{TFSI})_2/\text{D2}$ electrolyte (15 ppm H_2O) at 1 M. All cells were cycled at a current density of $20 \mu\text{A}/\text{cm}^2$.

Figure 4. (a) XANES spectra for pristine (black), charged (blue), and discharged (red) V_2O_5 at the vanadium K-edge; (b) the Fourier transform of the extended fine structure of pristine, charged, and discharged V_2O_5 at the vanadium K-edge. The spectra have not been phase-shifted.

Figure 5. (a) Normalized EDX spectrum for discharged (black), charged (red) and pristine (blue) V_2O_5 , with insets of both magnified and offset data from the boxed area, and a SEM image of the discharged electrode; (b) SEM image and EDX spectrum of the cycled Mg anode.