Controlling interlayer interactions in vanadium pentoxide-poly(ethylene oxide) nanocomposites for enhanced magnesium-ion charge transport and storage

Sanjaya D. Perera¹, Randall Archer¹, Craig A. Damin¹, Rubén Mendoza-Cruz²

and Christopher P. Rhodes^{1*}

¹ Department of Chemistry and Biochemistry, Texas State University, 601
University Drive, San Marcos, TX 78666

² Department of Physics and Astronomy, The University of Texas at San Antonio,
One UTSA Circle. San Antonio, TX 78249

* Corresponding author: Tel.: 512.245.6721, Fax: 512.245.2374, e-mail address:

cprhodes@txstate.edu

Revised manuscript submitted to the Journal of Power Sources

December 16, 2016

Abstract

Rechargeable magnesium batteries provide the potential for lower cost and improved safety compared with lithium-ion batteries, however obtaining cathode materials with highly reversible Mg-ion capacities is hindered by the high polarizability of divalent Mg-ions and slow solid-state Mg-ion diffusion. We report that incorporating poly(ethylene oxide) (PEO) between the layers of hydrated vanadium pentoxide (V_2O_5) xerogels results in significantly improved reversible Mg-ion capacities. X-ray diffraction and high resolution transmission electron microscopy show that the interlayer spacing between V_2O_5 layers was increased by PEO incorporation. Vibrational spectroscopy supports that the polymer interacts with the V_2O_5 lattice. The V_2O_5 -PEO nanocomposite exhibited a 5-fold enhancement in Mg-ion capacity, improved stability, and improved rate capabilities compared with V_2O_5 xerogels. The Mg-ion diffusion coefficient of the nanocomposite was increased compared with that of V_2O_5 xerogels and is attributed to enhanced Mg-ion mobility due to shielding interaction of PEO with the V_2O_5 lattice. This study shows that beyond only interlayer spacing, the nature of interlayer interactions of Mg-ions with V_2O_5 , PEO, and H_2O are key factors that affect Mg-ion charge transport and storage in layered materials. The design of layered materials with controlled interlayer interactions provides a new approach to develop improved cathodes for magnesium batteries.

Key words: Magnesium batteries; cathodes; vanadium pentoxide; poly(ethylene oxide); nanocomposites; electrochemical energy storage

1. Introduction

Electrochemical energy storage devices with low-cost, improved safety, high gravimetric specific energies, and high volumetric energy densities are needed for numerous applications including electric vehicles, consumer devices, and grid-level energy storage [1]. During the last two decades, lithium-ion (Li-ion) batteries have become widely utilized in mobile devices and electric vehicles due to their high specific energies and energy densities. Despite their successes, the high costs and significant safety issues of Li-ion batteries have resulted in research and development aimed at exploring alternative battery chemistries [2-4]. Electrical energy storage devices that are safe, utilize earth abundant elements, and provide high performance are of significant interest.

As an alternative to lithium-based systems, electrochemical energy storage systems based on the use of magnesium (Mg) have attracted significant interest and attention [5-8]. Magnesium batteries have significant advantages compared to Li-ion batteries including improved safety resulting from dendrite-free Mg deposition, the use of environmentally-friendly and abundant materials (abundance in the earth's crust is ~13.9% Mg compared to ~0.0007% Li), reduced cost (~\$ 2700/ton for Mg compared to \$64,000/ton for Li), high volumetric capacity (3833 mAh cm⁻³), and reasonable potential for Mg deposition (0.67 V vs Li⁺/Li) [6, 8-10]. In 2000, Aurbach *et. al.* demonstrated the first prototype rechargeable Mg battery using a Mo₆S₈ Chevrel phase cathode and a Mg metal anode, and the cell exhibited a reasonable energy density of ~60 Wh kg⁻¹ [8]. However, Chevrel phase cathodes have low voltages (~1.1 V vs Mg/Mg²⁺) and exhibit

only partial reversibility, as the capacity drops by ~40% after the first discharge cycle [11].

Obtaining cathodes that exhibit high capacities, high voltages, and excellent reversibility is a key challenge for the development of practical Mg batteries [12]. Subsequent to the demonstration of magnesium batteries using Chevrel phase Mo_6S_8 cathodes, a number of cathode materials including metal oxides, metal chalcogenides, polyanionic structures, and spinel compounds have been investigated [7, 10, 13-18]. However, most of these cathode materials suffer poor electrode kinetics and cycle performance due to low Mg^{2+} diffusion and structural instability [7]. Compared with a single valent Li^+ ion, a divalent Mg^{2+} ion has a high polarizability leading to strong interaction with the negatively charged host lattice [19, 20]. The strong interaction of Mg^{2+} with the host lattice results in high energy barriers for intercalation and low Mg-ion diffusion coefficients [10]. Unlike Li^+ which can lose its solvation shell upon intercalation [21], Mg^{2+} intercalation has been shown to involve co-intercalation of solvent molecules [22].

In order to reduce strong host interactions and improve poor electrode kinetics several approaches have been introduced. One approach is to introduce molecules with strong dipole moments to solvate Mg^{2+} ions [23-25]. Song *et.al.* demonstrated the capability to significantly improve the Mg-ion insertion and deinsertion by introducing a small amount of H_2O to the electrolyte, thereby decreasing Mg^{2+} polarization [23]. Trace H_2O within the electrolyte can passivate Mg metal and adversely affect further Mg anode activity[24, 26], therefore the use of H_2O within the electrolyte is not a viable approach for practical, rechargeable Mg batteries. Reducing particle dimensions to the nanoscale

(i.e. nanostructuring) can increase ion diffusion by significantly decreasing the diffusion length [18]. However, downsizing the electrode material particle size to the nanoscale significantly decreases the volumetric energy density [10]. Additional approaches are needed to overcome the poor electrode kinetics of magnesium cathodes while avoiding issues that arise from introducing H₂O into the electrolyte or nanostructuring.

Electrode materials with layered structures show significant potential as Mg-ion cathodes due to their ability to transport Mg-ions within the layers via different ion hopping mechanisms [27-30]. Among different types of layered metal oxides, vanadium pentoxide (V₂O₅) has attracted a significant attention as a cathode material for Mg batteries [13, 26, 31, 32]. Prior work has demonstrated that V₂O₅ can reversibly insert and de-insert Mg-ions [13, 26, 33]. Although large capacities have been reported for crystalline V₂O₅, the high capacities of crystalline V₂O₅ were shown to result from H₂O within the electrolyte [26]. Crystalline V₂O₅ evaluated with an electrolyte with low H₂O levels exhibited very low Mg-ion capacities (~10-60 mAh g⁻¹) [26].

V₂O₅ gels can be synthesized via sol-gel chemistry from both inorganic and metal-organic precursors [31, 34], and then dried under ambient conditions to form xerogels or supercritically dried to form aerogels. V₂O₅ xerogels (formula V₂O₅·nH₂O with n typically 1.6-2.0)[34] composed of V₂O₅ layers and structural interlayer H₂O have shown to possess among the highest Mg-ion capacities and rate capabilities of V₂O₅ materials [12, 22, 31]. Recent characterization of the structural changes that occur during reversible Mg-ion insertion into hydrated V₂O₅ xerogels showed that Mg-ions and solvent molecules co-intercalate between V₂O₅ layers which alters the interlayer spacing [22]. Monolithic hydrated V₂O₅ xerogels tested using a thin film electrode geometry that

minimizes ion diffusion lengths exhibited high Mg-ion capacities of 150 mAh g⁻¹ [13]; however, V₂O₅ xerogels tested within thicker electrode configurations using slurry-cast electrodes have been shown to exhibit Mg-ion capacities of ~40 mAh g⁻¹ [22]. The H₂O within the V₂O₅ structure plays a critical role in solvating the Mg²⁺ ions, shielding the interaction of the divalent Mg-ions with the V₂O₅ lattice, and facilitating insertion and deinsertion with the electrode structure as shown from calculations[35] and experiments [26]. The stability of structural interlayer H₂O during Mg-ion insertion/de-insertion within V₂O₅ varies between different studies [36, 37]. Le *et. al.* determined that structural interlayer water in hydrated V₂O₅ aerogels was retained upon cycling [37]. Novak *et. al.* reported that upon charging in hydrated V₂O₅ xerogel some H₂O molecules remained bound to Mg and are removed from the V₂O₅ lattice [36]. The potential for removal of H₂O from the structure upon cycling can ultimately lead to the structural failure and capacity fading [12]. Approaches that provide interlayers that (i) coordinate Mg²⁺, (ii) shield interaction with the negatively charged host lattice, and (iii) remain as stable interlayer scaffolds are of significant interest.

Nanocomposites of V₂O₅ with a number of polymers, including PEO [38], polyethylene glycol [39], poly(3,4-ethylenedioxythiophene) [40], polypyrrole [41], and polyaniline [41, 42] have been reported. The intercalation of PEO within the V₂O₅ xerogel layers was shown to increase the interlayer spacing and improve Li-ion intercalation [38]. Recently, Yao *et. al.* demonstrated that the physical mixing of PEO and exfoliated MoS₂ could be used to increase the interlayer spacing of MoS₂ improve the Mg-ion capacity of MoS₂ [10].

In this work, we report for the first time that the incorporation of PEO between the V_2O_5 layers can result in a significant improvement in Mg-ion charge storage. In contrast to physical mixing of exfoliated layers and the polymer, the polymer was introduced during the V_2O_5 sol-gel synthesis to allow intimate mixing of the PEO and V_2O_5 . The introduction of a polymer in the V_2O_5 interlayer was investigated as an approach to expand the interlayer spacing and reduce the interaction of divalent Mg^{2+} with the host V_2O_5 lattice. The expansion of the interlayer spacing resulting from the incorporation of the polymer was confirmed by TEM and x-ray diffraction analyses. The V_2O_5 -PEO nanocomposites were determined to provide significantly higher Mg-ion capacities than the V_2O_5 xerogel. The V_2O_5 -PEO nanocomposite showed an approximate ~500% increase in capacity compared to pure V_2O_5 xerogels, which is a significant improvement achieved without the use of additional solvent molecules (i.e. H_2O) within the electrolyte, reducing particle size, or using a thin film geometry. Direct interaction of the polymer with the V_2O_5 lattice was supported by infrared and Raman spectroscopy. The polymer and interlayer water were determined to play important roles in facilitating Mg-ion diffusion and improving Mg-ion charge storage. The design of layered materials with controlled interlayer interactions and spacing provides a new approach to altering the interaction between Mg^{2+} ions and the host lattice thereby improving electrochemical Mg-ion charge storage.

2. Experimental

Chemicals and Materials: Sodium metavanadate (NaVO_3), Dowex 50WX2-100 cation-exchange resin, poly(ethylene oxide) (PEO, avg. MW 400,000), magnesium

perchlorate, $\text{Mg}(\text{ClO}_4)_2$, and acetonitrile (anhydrous, 99.8%) were obtained from Sigma-Aldrich (St. Louis, MO) and used as received. Carbon fiber cloth (Spectracarb TM 2225 Type 700) was obtained from Engineering Fibers Technology (Shelton, CT).

Synthesis of vanadium pentoxide xerogels (V_2O_5): V_2O_5 xerogels were prepared from ion-exchange of NaVO_3 solutions by adapting previously reported methods [43]. To synthesize the V_2O_5 xerogels, 25 mL of a 1.0 M NaVO_3 aqueous solution was eluted thorough an ion-exchange column containing 50 g of cation-exchange resin (Dowex 50WX2-100) and 200 mL de-ionized water. The first light-colored 20 mL elution was discarded, and then the next 30 mL of dark orange-colored elution was collected. The 30 mL of the total collected elution was separated into five 6 mL portions and then diluted to 7 mL by adding 1 mL of de-ionized (DI) water. The additional water was added to result in the same vanadic acid concentration as used for the PEO-containing samples, as discussed below. The vanadic acid suspensions were allowed to gel for 24 hours, after which a wet V_2O_5 gel (hydrogel) was obtained. Following the formation of the V_2O_5 hydrogel, the sample was then dried at 60 °C under ambient atmosphere for approximately 16 hours to form the V_2O_5 xerogel.

Synthesis of V_2O_5 -PEO nanocomposites: The synthesis of the V_2O_5 -PEO nanocomposites was performed using a procedure similar to that used for the synthesis of the V_2O_5 xerogels. 6 mL elutions of vanadic acid were collected as described above. Separately, an aqueous PEO solution (50 mg mL^{-1} of PEO in DI water) was prepared. The V_2O_5 -PEO nanocomposites were synthesized by adding either 0.25 mL or 1 mL of the 50 mg mL^{-1} PEO solution. In order to keep the total volume and thus the total vanadic acid concentration constant, 0.75 mL of DI water was added to the sample containing

0.25 mL of PEO solution. The vanadic acid-PEO solutions were allowed to gel for 24 hours and then dried at 60 °C under ambient atmosphere for approximately 16 hours. The dried nanocomposites were notated as V₂O₅-PEO-1 and V₂O₅-PEO-2, for the samples prepared using 0.25 mL or 1 mL of PEO solution respectively. The concentration of PEO by mass was determined to be 5.8 wt % PEO and 20.0 wt % PEO for V₂O₅-PEO-1 and V₂O₅-PEO-2, respectively.

Structural and thermal characterization. X-ray powder diffraction (XRD) patterns were obtained using a Bruker (Billerica, MA) D8 Advance Eco X-ray Powder Diffractometer with Cu K α radiation. Scans were recorded for 2 θ values between 5 and 70°, using a step size of 0.02° and integration of 10 s per step. Scanning electron microscopy (SEM) images were obtained using a Helios NanoLab 400 DualBeam Field Emission Scanning Electron Microscope. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 1200EXII microscope. High resolution TEM (HRTEM) images were obtained a JEOL 2010F operated at 200 kV. TEM samples were prepared on lacey carbon grids by depositing a solution of the dried powder suspended in isopropanol. Samples were degassed at 120 °C for 16 h prior to characterization.

Thermogravimetric analysis (TGA, TA instruments Q50) was performed a constant heating rate of 10°C/min using air. Prior to TGA analysis, the V₂O₅ xerogel and V₂O₅-PEO nanocomposites were heated under vacuum at 120 °C for 16 h. For the V₂O₅ xerogel, the sample was determined to have 1.8 moles H₂O per mole of V₂O₅, notated as V₂O₅·1.8H₂O, from the TGA mass loss up to 500 °C (Figure S1) consistent with previous reports [34, 44, 45]. Since the onset of PEO decomposition occurs above ~200 °C, mass loss above 200 °C results from both PEO decomposition [38] and removal of structural

H₂O. To avoid the PEO decomposition region, the hydration levels for the V₂O₅-PEO nanocomposites were determined at 200 °C and compared with the hydration level of the V₂O₅ xerogel at 200 °C to allow for comparison. At 200 °C, the composition of the xerogel was determined to be V₂O₅ ·1.5H₂O, which indicates 0.3 moles of H₂O are removed from the structure above 200 °C.

Infrared spectra of the V₂O₅ xerogel, V₂O₅-PEO nanocomposites, and pure PEO were collected over the range of 4700-4000 cm⁻¹ using a Harrick Scientific (Pleasantville, NY) SplitPea attenuated total (internal) reflectance (ATR) microsampling accessory coupled to a Bruker (Billerica, MA) Tensor II FT-IR spectrometer that utilized a wide-band, liquid-nitrogen cooled mercury-cadmium-telluride (MCT) detector. The ATR accessory featured a silicon hemispherical internal reflection element (IRE), and the samples were brought into direct, optical contact with the IRE using a loading of 0.5 kg. The collected spectra represent the average of 64 individual scans collected at a spectral resolution of 4 cm⁻¹. Instrument control of the Tensor II FT-IR spectrometer and analysis of the resulting spectra were done using Bruker OPUS 7.5 software (version 7.5.18).

Raman spectra were obtained with a Horiba LabRam HR Evolution Confocal Raman Spectrometer equipped with an 1800 groove/mm grating. Sample excitation was performed using the 514 nm line of a Melles Griot (Carlsbad, CA) argon-ion laser. Raman scattered light was collected in a backscattering geometry using an Olympus (Center Valley, PA) 50× (0.75 NA) MPlan N objective. Spectra were obtained using a 25 second acquisition time and averaged over 10-20 accumulations. Laser-induced thermal effects were observed in prior Raman studies of vanadium pentoxide [46], and low laser powers are necessary to minimize spectral changes due to local heating. In order to avoid

sample degradation, the laser power was controlled below 0.30 mW using neutral density filters. Visual inspection of the samples, pre- and post-analysis, using white light illumination did not reveal any laser-induced changes. To further verify that the laser did not induce spectral changes, spectra were obtained at a laser power of below 0.03 mW using the same acquisition and sampling conditions as above; no differences were observed compared to the spectra taken at 0.3 mW.

Electrochemical testing. Electrodes were fabricated from a slurry composed of 80 wt% active material (typically ~150-200 mg of sample), 10 wt% conductive carbon (TIMCAL Super C65), and 10 wt% binder (Arkema, Kynar HSV900 – 5% in N-Methyl-2-pyrrolidinone (NMP)) using a similar method previously reported [47]. Excess NMP was added to control the viscosity of the slurry. The slurry was stirred overnight and then cast using a doctor blade (gap setting of 200 μm) on a cleaned 15 μm -thick aluminum foil current collector. The obtained electrode sheet was dried overnight in a fume hood and then transferred into an oven at 60°C and allowed to dry overnight to remove excess solvent. Electrodes were cut and then further dried at 120 °C under vacuum overnight. The average mass loading was 2.4 mg/cm^2 . The electrolyte, 1 M $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile (CH_3CN), was prepared by combining $\text{Mg}(\text{ClO}_4)_2$ (dried at 120 °C under vacuum for at least 16 hours prior to use) and dried acetonitrile within an inert atmosphere glovebox (Argon, ≤ 1 ppm H_2O). The dried acetonitrile was prepared by distillation and degassing and then stored over 4Å (8-12 mesh beads) dried molecular sieves within the glovebox. Electrochemical analysis was performed using standard three electrode cell configuration using 1 M $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile as the electrolyte and magnesium foil as the reference electrode. A Spectrocarb carbon cloth was used as the

counter electrode since previous studies evaluating magnesium deposition and stripping have shown that significant solvent reduction rather than magnesium plating occurs within electrolytes composed of magnesium salts in acetonitrile [48, 49]. Prior to use, the magnesium foil was roughened with sandpaper and thoroughly wiped using Kimwipes (Kimberly Clark, Irving, Texas). All electrochemical cell fabrication and testing was performed in an inert atmosphere glovebox (Argon, ≤ 1 ppm H₂O). For comparison, electrodes were tested using an Ag/AgCl reference electrode, and similar electrochemical results were obtained. Galvanostatic charge–discharge were collected over a voltage range of 1.0 to 3.0 V vs Mg/Mg²⁺ with a mass-normalized current of 10 mA g⁻¹ active material using an Arbin Instruments (College Station, TX) BT2043 test station. Cyclic voltammograms were determined using the same configuration over a voltage range of 1.0 to 3.0 V vs Mg/Mg²⁺ at scan rates of 2.5 to 7.5 mV/s. Coulombic efficiencies were determined from the average of the last 5 cycles of the cycling tests.

To evaluate whether PEO was maintained in the V₂O₅-PEO nanocomposite films after cycling within the electrolyte (1 M Mg(ClO₄)₂ in CH₃CN), FTIR-ATR spectra of V₂O₅-PEO-1 and V₂O₅-PEO-2 cast electrode films were obtained before and after cycling using the instrumental setup described above. The FTIR-ATR spectra were obtained using the same parameters except 128 scans rather than 64 scans were used for the spectral acquisition. The V₂O₅-PEO-1 and V₂O₅-PEO-2 electrodes were cycled five times in the electrolyte at a scan rate of 2.5 mV s⁻¹ over a voltage range of 1.0 to 3.0 V vs Mg. After cycling and prior to collecting FTIR-ATR spectra, the electrodes were rinsed three times with distilled acetonitrile (5 mL portions), allowed to dry inside the glovebox, and then placed inside the vacuum chamber of the glovebox for 2 hrs.

3. Results and Discussion

3.1. Approach for altering the interlayer spacing of V_2O_5 gels

The incorporation of a polymer between the V_2O_5 layers was investigated to increase the interlayer spacing between the V_2O_5 layers and decrease the interaction of highly polarized Mg^{2+} ions with the negatively charged V_2O_5 layer. To incorporate a polymer within the V_2O_5 layers, we introduced poly(ethylene oxide), PEO, during the growth of the V_2O_5 gels (represented graphically in Figure 1a,b). $V_2O_5 \cdot nH_2O$ nanosheets are formed from aqueous vanadic acid solutions [34]. At low pH, aqueous vanadic acid species such as tetrahedrally coordinated $VO(OH)_3$ species are generated [34]. The $VO(OH)_3$ species become 6-fold coordinate with water addition and combine via condensation reactions to form polyanions composed of edge or corner-sharing $[VO_4]^{3-}$ tetrahedral that further grow into extended $V_2O_5 \cdot nH_2O$ sheets that form an interconnected network [34].

Figure 1. Graphical representation of growth of hydrated V_2O_5 nanosheet formation from water addition and condensation reactions of $[VO_4]^{3-}$ polyanions in aqueous solution at low pH; (a) without poly(ethylene oxide) (PEO); (b) with PEO.

A representation of the process of incorporating PEO between the V_2O_5 nanosheets is shown in Figure 1b. Instead of exfoliating the nanosheets and adding PEO, the polymer was added directly to the vanadic acid solution. The V_2O_5 nanosheets were grown in the presence of PEO, thereby allowing the incorporation of PEO and H_2O between the V_2O_5 layers (Figure 1b). Prior work has shown that the ether oxygens of PEO strongly interact with vanadic acid species and V_2O_5 [34]. Using this *in-situ* approach facilitated the interaction of PEO with the V_2O_5 lattice. In order to determine the effect of polymer composition on the interlayer spacing and electrochemical properties, different amounts of PEO were introduced into the solution. The PEO-

containing materials are notated as V₂O₅-PEO-1 and V₂O₅-PEO-2 and are compared with the V₂O₅ xerogel without PEO.

All samples formed hydrated gels, which were dried as described in the experimental section to form xerogels. The dried V₂O₅ xerogel and V₂O₅-PEO nanocomposites are hydrates and can be represented as V₂O₅·nH₂O. TGA analysis (Figure S1) showed that for the V₂O₅ xerogel, n=1.8 based on the loss in sample mass up to 500°C, and we note that the measured hydration level is identical to similarly prepared xerogels [44]. Determining the degree of hydration for the V₂O₅-PEO nanocomposites from TGA was more complicated due to decomposition of PEO, however the V₂O₅-PEO nanocomposites and V₂O₅ xerogel showed a similar mass loss up to 200 °C (Figure S1), suggesting that the degree of hydration was similar between the samples. Based on the mass of PEO within the samples and H₂O evaluated at 200 °C from TGA, the molar ratios of V₂O₅, PEO and H₂O were represented by the formula (V₂O₅)_x(-OCH₂CH₂)_y·nH₂O and were determined to be V₂O₅·1.5H₂O, (V₂O₅)(-OCH₂CH₂)_{0.3}·1.5H₂O, and (V₂O₅)(-OCH₂CH₂)_{1.2}·2.0H₂O for the V₂O₅ xerogel, V₂O₅-PEO-1 and V₂O₅-PEO-2 samples respectively.

3.2. Scanning and transmission electron microscopy of V₂O₅ xerogels and V₂O₅-PEO nanocomposites

The morphologies of the V₂O₅ and V₂O₅-PEO samples were examined using SEM TEM, and HRTEM (Figure 2a-c). From the SEM images, nanosheets with crumpled morphologies were observed for the V₂O₅ xerogels and V₂O₅-PEO nanocomposites. Both nanocomposites with PEO, V₂O₅-PEO-1 and V₂O₅-PEO-2, exhibited similar

nanosheet structures as the V_2O_5 xerogel indicating that the inclusion of PEO during the V_2O_5 synthesis did not significantly alter the formation of V_2O_5 nanosheets. The lateral size of the V_2O_5 nanosheet was determined to be $\sim 2\text{-}3\ \mu\text{m}$. The nanosheet structure is further shown by the TEM images of V_2O_5 , V_2O_5 -PEO-1 and V_2O_5 -PEO-2 (Figure 2d-f). Based on analysis of the TEM images, the growth process results in several stacked nanosheet layers.

Figure 2. Scanning electron microscopy (SEM) images of V_2O_5 xerogel (a), V_2O_5 -PEO-1 (b), and V_2O_5 -PEO-2 nanocomposite (c); Transmission electron microscopy (TEM) images of V_2O_5 xerogel (d), V_2O_5 -PEO-1 (e), and V_2O_5 -PEO-2 nanocomposite (f); High-resolution TEM images showing d -spacings of V_2O_5 xerogel (g), V_2O_5 -PEO-1 (h), and V_2O_5 -PEO-2 nanocomposite (i).

A determination of the interlayer spacing (d -spacing) between the nanosheets was performed using the HRTEM images of the V_2O_5 xerogel and V_2O_5 -PEO nanocomposites (Fig. 2g-i). The high resolution TEM images show d -spacings of ~ 8.6 , 9.1 , and $10.8 \text{ \AA}$ for the V_2O_5 xerogel, V_2O_5 -PEO-1 nanocomposite, and V_2O_5 -PEO-2 nanocomposite respectively. The measured interlayer spacings are in the range of previously reported values [34, 38]. The interlayer spacing was increased with the incorporation of PEO within the structure, and higher amounts of PEO were observed to result in larger d -spacings.

Figure 3. Energy dispersive spectroscopy (EDS) elemental mapping of V_2O_5 -PEO-1 nanocomposite; (a) SEM image; corresponding EDS mappings of (b) carbon (C), (c) vanadium (V), and (d) oxygen (O) elements of V_2O_5 -PEO-1.

Energy dispersive spectroscopy (EDS) element mapping was used to evaluate the distribution of PEO within the nanocomposites. The SEM image and EDS mapping of the V_2O_5 -PEO-1 sample are shown in Figure 3. From the EDS analysis, carbon, vanadium, and oxygen are evenly distributed within the nanocomposite supporting that PEO is uniformly distributed within the V_2O_5 layers rather than forming a separate, distinct phase. We also observed a uniform distribution of PEO for V_2O_5 -PEO-2 that has the highest content of PEO (Figure S2). The uniform distribution of PEO within the V_2O_5 layers for both composition indicates the feasibility to obtain controlled PEO contents with uniform distributions during the growth of V_2O_5 nanosheets.

3.3. X-ray diffraction characterization of V_2O_5 xerogels and V_2O_5 -PEO nanocomposites

X-ray diffraction (XRD) was used to characterize long-range order within the V_2O_5 xerogels and V_2O_5 -PEO nanocomposites. The X-ray diffraction (XRD) powder patterns for the V_2O_5 xerogel and V_2O_5 -PEO-1 and V_2O_5 -PEO-2 nanocomposites are shown in Figure 4a. The relatively broad peak widths and high signal-to-noise ratios are a result of the low degree of crystallinity within the materials.

The XRD peak positions of the V_2O_5 xerogel are similar to those reported in earlier studies [50-52], and can be indexed to the $V_2O_5 \cdot nH_2O$ phase (JCPDS#:01-074-3093) with a monoclinic unit cell under space group $C/2m$ ($a=11.722 \text{ \AA}$, $b=3.570 \text{ \AA}$, $c=11.520 \text{ \AA}$, $\beta=88.65^\circ$) [53]. The observation of multiple 00ℓ reflections is consistent with the layered structure of hydrated V_2O_5 [54]. The absence of a (002) peak has been explained by a bilayer structure [55]. The $2\theta^\circ$ value of the highest intensity peak (001),

corresponds to a basal (d -spacing) of 11.6 Å and is consistent with intercalation of a single H₂O layer [52]. In addition to 00ℓ reflections, the position of peak at $2\theta^\circ=25.4$ is closest to $2\theta^\circ$ value of (110) planes and was previously identified as arising from in-plane (hkl) reflections [34].

Figure 4. (a) X-Ray diffraction (XRD) powder patterns of V₂O₅ xerogel, V₂O₅-PEO-1, and V₂O₅-PEO-2 nanocomposite; (b) Expanded region from $2\theta^\circ \sim 5-10$ showing shifting of the (001) peak to lower $2\theta^\circ$ values upon introduction of PEO.

For the XRD patterns of the V₂O₅-PEO-2 nanocomposites, the in-plane (hkl) reflections remained, however clear differences were observed in the peaks due to the 00ℓ reflections. The (001) peak was observed for the V₂O₅-PEO nanocomposites, however the (003) and (004) reflections were not observed, indicating a lower degree of long-range order between the V₂O₅ layers occurred upon incorporation of PEO. The polymer may induce disordered stacking between multiple layers [38]. The XRD patterns of the

V₂O₅-PEO nanocomposites show similar diffraction peaks to those previously reported for PEO- intercalated V₂O₅ [38] and polyaniline-intercalated V₂O₅ [56].

For the V₂O₅-PEO nanocomposites, the positions of the (001) peaks shift towards lower angles relative to the position of the (001) peak for the V₂O₅ xerogel (Figure 4b), which indicates an increase in the interlayer spacing between the nanosheets by incorporation of PEO within the structure. The interlayer distance (*d*-spacing) was calculated according to Bragg's law

$$d = \frac{n\lambda}{2 \sin \theta} \quad (1)$$

where *n* is an integer, λ is the X-ray wavelength (1.54 Å), and θ is the angle between the incident rays and the sample. The *d*-spacing increased from 11.6 Å for the V₂O₅ xerogel to 12.6 and 13.6 Å for V₂O₅-PEO-1 and V₂O₅-PEO-2 nanocomposites, respectively. In addition, the width of the (001) peak increased for the PEO-containing samples, which is indicative of less ordered layers. The gradual increase of *d*-spacing for the V₂O₅-PEO nanocomposites suggests that the interlayer spacing can be controlled by increasing the amount of PEO added during the synthesis. The correlation between the increased *d*-spacing and the increased PEO content observed from the XRD data is consistent with the results obtained using HRTEM. Previously reported calculations support that PEO chains can be arranged within V₂O₅ layers in either helical or zigzag conformations [57]. The PEO chains were found to possess a helical conformation at low polymer contents and zigzag conformations when the polymer content was high. The calculated results of this earlier study did not take into account the solvent, which may alter the polymer conformations from these idealized geometries.

3.4. Infrared spectroscopic analysis of V_2O_5 xerogels and V_2O_5 -PEO nanocomposites

Vibrational spectroscopy was used to characterize the structure of the V_2O_5 xerogels and V_2O_5 -PEO nanocomposites and particularly investigate the nature of V_2O_5 , PEO, and H_2O within the nanocomposite. The ATR-FTIR spectra of V_2O_5 xerogels, V_2O_5 -PEO nanocomposites, and pure PEO for comparison are shown in Figure 5. The FTIR spectra of the V_2O_5 -PEO nanocomposites exhibited bands due to V_2O_5 , PEO, and H_2O .

Figure 5. a) ATR-FTIR spectra of V_2O_5 xerogel, V_2O_5 -PEO nanocomposites, and PEO; Bands corresponding to C-O-C, C-H and $\nu_s(V=O_A)$ stretches are labeled; inset figure shows the expanded region from ~ 1020 - 1170 cm^{-1} corresponding to the C-O-C stretching bands; (b) Expanded region from 800 - 1100 cm^{-1} showing the $\nu_s(V=O)$ downshift.

Infrared spectra and vibrational mode assignments of V_2O_5 xerogels at various levels of hydration have been previously reported [45]. The ATR-FTIR spectra of the V_2O_5 xerogel showed a band centered at 998 cm^{-1} which is attributed to a symmetric

$\nu_s(\text{V}=\text{O}_\text{A})$ stretching mode, and band at 800 cm^{-1} which has been assigned to the asymmetric V-O-V stretching mode of bridging oxygens, $\nu_a(\text{VO}_\text{B}\text{V})$ [45, 58]. The frequency of the $\nu_s(\text{V}=\text{O}_\text{A})$ mode in V_2O_5 -PEO-1 and V_2O_5 -PEO-2 is observed at 988 cm^{-1} which is clearly downshifted to lower frequencies compared to the frequency of the $\nu_s(\text{V}=\text{O}_\text{A})$ mode in V_2O_5 xerogels (Figure 5b). The downshifting of the $\nu_s(\text{V}=\text{O}_\text{A})$ mode frequency is attributed to either direct interaction of the ether oxygen of PEO with the vanadyl oxygen in a similar manner as proposed for H_2O [45, 59], or from PEO interacting with H_2O that alters the strength of hydrogen bonding between H_2O coordinated to the vanadyl oxygen. Leroux et al. observed that for nanocomposites composed of alternating V_2O_5 sheets and polymer layers, the $\nu_s(\text{V}=\text{O}_\text{A})$ mode frequency shifted to lower wavenumbers with the incorporation of polymers [60]. The shift in the position of the $\nu_s(\text{V}=\text{O}_\text{A})$ mode was explained by a bonding interaction between the polymer and the inorganic V_2O_5 framework. A comparable shift of the frequency of the $\nu_s(\text{V}=\text{O}_\text{A})$ band was attributed to hydrogen bonding within a V_2O_5 -polypyrrole nanocomposite material [61]. Prior work has shown that frequency shifts of the vanadyl oxygen stretching mode can be correlated with changes in the vanadium-oxygen bond lengths [62]. The lower frequency of the $\nu_s(\text{V}=\text{O}_\text{A})$ mode within the V_2O_5 -PEO nanocomposites is consistent with a longer bond distance and lowering bond strength based on interaction with PEO. In addition to the primary band at 998 cm^{-1} within the infrared spectrum of the V_2O_5 xerogel, a band was observed at 925 cm^{-1} which has been attributed to a H_2O -V vibrational mode [63]. The absence of the band at 925 cm^{-1} within the V_2O_5 -PEO nanocomposites suggests that the interaction of H_2O with the V_2O_5 lattice within the nanocomposites has been altered compared with the V_2O_5 xerogels.

The infrared spectrum of PEO and assignments of PEO vibrational modes have been previously reported [64, 65]. The infrared spectrum of a pure, bulk PEO sample is shown in Figure 5. Absorptions located between 3000 and 2700 cm^{-1} correspond to C-H stretching modes [64]. The V_2O_5 -PEO nanocomposites show the presence of PEO within the samples as supported by the presence of bands at 2943 and 2880 cm^{-1} corresponding to C-H stretches of PEO. In pure PEO, the 1114 and 1078 cm^{-1} bands are associated with predominantly C-O-C stretching modes of PEO (Figure 4) [64]. The intensities of the C-O-C peaks are very weak in V_2O_5 -PEO-1 but increase with higher PEO content in V_2O_5 -PEO-2. The presence of triplet C-O-C stretching bands has been correlated with PEO within a crystalline phase [66-68]. The presence of triplet C-O-C stretching modes in the infrared spectrum of PEO indicates that the bulk PEO sample possessed either a crystalline or semi-crystalline phase, while PEO exists in an amorphous phase in V_2O_5 -PEO nanocomposites. Additional PEO absorptions were observed in the ATR-FTIR spectrum of the V_2O_5 -PEO-2 nanocomposite. In contrast to the 1360 and 1342 cm^{-1} CH_2 wagging absorptions observed in pure PEO, a single absorption at 1353 cm^{-1} was observed. The occurrence of a single CH_2 wagging absorption has been previously associated with an amorphous state of PEO [66]. The presence of PEO bands in the nanocomposite materials and the downshift of $\nu_s(\text{V}=\text{O}_A)$ stretching mode suggests that the PEO has been intercalated within the V_2O_5 layers and that the presence of PEO within the interlayer alters the vanadyl oxygen force constant and bond distance.

In addition to the presence of V_2O_5 and PEO vibrational modes, the ATR-FTIR spectrum of the V_2O_5 and V_2O_5 -PEO samples showed bands due to O-H stretching and H-O-H bending modes of chemically bound water within structure [69]. The presence of

structural water is consistent with the XRD and TGA data. The V_2O_5 xerogel shows a high frequency O-H stretching band at 3568 cm^{-1} , which has also been observed in previous infrared spectra of $V_2O_5 \cdot nH_2O$ [45, 70]. The high frequency mode at 3568 cm^{-1} has been attributed to the asymmetric stretching mode, $\nu_{as}(OH_2)$, of water and is proposed as originating from OH vibrations relatively free from hydrogen bonding [45]. The frequencies of the O-H stretching modes are affected by hydrogen bonding with $V=O$ groups [71]. The 3568 cm^{-1} band was not observed in the infrared spectra of the V_2O_5 -PEO nanocomposites. Instead, broad O-H absorptions were observed at $\sim 3300\text{ cm}^{-1}$, which supports that H_2O within V_2O_5 -PEO nanocomposites exhibit a greater degree of hydrogen bonding with either V_2O_5 , PEO or both.

3.5. Raman spectroscopic analysis of V_2O_5 xerogels and V_2O_5 -PEO nanocomposites

Raman spectroscopy was also used to probe the structure of the V_2O_5 -PEO nanocomposites. The vibrational mode assignments and Raman spectra of V_2O_5 xerogels at various levels of hydration have been previously reported [45] and have been shown to be related to vibrations of crystalline orthorhombic V_2O_5 [58]. The V_2O_5 structure can be described by packing of V_2O_5 layers along the c axis of the unit cell. Each layer is built up from edge and corner-sharing VO_5 square pyramids [58, 72]. Differences between the vibrations of crystalline orthorhombic V_2O_5 and hydrated V_2O_5 xerogels have been attributed to the interaction of coordinated water molecules which were trapped between layers and held firmly in place, thus restricting or altering certain Raman-active vibrations [59].

Figure 6 shows the Raman spectra of V_2O_5 and V_2O_5 -PEO nanocomposites. The vibrational bands observed for the Raman spectrum of the V_2O_5 xerogels (Figure 6a) are similar to those previously reported for $V_2O_5 \cdot 1.6H_2O$ xerogels [44, 45]. Compared with the bands of V_2O_5 xerogels, significant changes in the Raman spectra were observed for the V_2O_5 -PEO nanocomposites. Bands at 890, 512, and 670 cm^{-1} have been assigned to modes due to $\nu(V=O_A)$ stretching, symmetric stretching $\nu_s(V-O_B-V)$ of edge-shared oxygen and vanadium atoms, and $\nu(V_2-O)$ stretching of doubly coordinated oxygen, respectively [58, 72]. The interaction of V_2O_5 with H_2O occurs primarily with the vandyl oxygen bond, $V=O$, via either (i) hydrogen bonding to the vandyl oxygen or (ii) coordination of oxygen of H_2O with the axial vanadium of the vandyl oxygen, as supported by prior work [34, 59]. Based on these interactions, vibrational modes that are strongly influenced by coordination with the vandyl oxygen bond are expected to be more strongly affected than other vibrational modes.

In particular, bands 890 and 135 cm^{-1} were either significantly reduced in relative intensity or absent within the V_2O_5 -PEO nanocomposites. In crystalline V_2O_5 , bands at 145 and 146 cm^{-1} arise from lattice vibrational modes (restricted T_z and R_y) [58], and these bands are strongly associated with the layered structure [46]. Similar lattice vibrational modes are observed in V_2O_5 xerogels at 155 and 135 cm^{-1} [45]. The intensities of the lattice modes were found to decrease with Li intercalation [44]. In our case, the intensities of low frequency lattice vibrations were found to be significantly altered in both V_2O_5 -PEO-1 and V_2O_5 -PEO-2, which may be due to the interaction of PEO with the V_2O_5 lattice that alters the lattice vibrations. Changes in the relative intensity of the 135 cm^{-1} band provide insight into the nature of PEO and H_2O interaction with the V_2O_5

lattice. Prior work showed that the presence and intensity of the 135 cm^{-1} band in V_2O_5 xerogels is highly dependent on the amount of interlayer water [45]. The 135 cm^{-1} band was observed as a strong peak at relatively high levels of hydration, $\text{V}_2\text{O}_5 \cdot 1.2\text{H}_2\text{O}$ and $\text{V}_2\text{O}_5 \cdot 1.6\text{H}_2\text{O}$, however for $\text{V}_2\text{O}_5 \cdot 0.6\text{H}_2\text{O}$, the 135 cm^{-1} was observed as a shoulder and was not observed at $\text{V}_2\text{O}_5 \cdot 0.4\text{H}_2\text{O}$ and crystalline V_2O_5 [45].

Figure 6. (a) Raman spectra of V_2O_5 xerogel, $\text{V}_2\text{O}_5\text{-PEO-1}$ and $\text{V}_2\text{O}_5\text{-PEO-2}$ in the 100 cm^{-1} to 950 cm^{-1} region; (b) Representation of possible coordination of interlayer H_2O within V_2O_5 via hydrogen bonding; (c) Representation of possible coordination of V_2O_5

with both interlayer H₂O and PEO via hydrogen bonding; schematics do not represent steric effects and PEO chain conformation.

Our TGA analysis supports that the V₂O₅-PEO nanocomposites and V₂O₅ xerogel all contain a similar amount of structural H₂O (Figure S1), however the relative intensity of the 135 cm⁻¹ band is significantly different. The presence of a 135 cm⁻¹ shoulder within V₂O₅-PEO-1 suggests that both PEO and H₂O interact with the V₂O₅ lattice. However, the relative intensity of the 135 cm⁻¹ band in V₂O₅-PEO-1 is significantly lower than for the V₂O₅ xerogel, and for V₂O₅-PEO-2, the 135 cm⁻¹ band is not appreciably observed. Based on the correlation of the intensity of the 135 cm⁻¹ band with the amount of interlayer H₂O [45], the lower relative intensity of the 135 cm⁻¹ band for the V₂O₅-PEO-1 and V₂O₅-PEO-2 nanocomposites compared with the V₂O₅ xerogel despite similar amounts of H₂O suggests that PEO rather than H₂O preferentially coordinates with the V₂O₅ lattice. Based on this observation, it is possible that the interaction with PEO alters the relative intensity of V₂O₅ lattice modes. Prior work showed that by reducing the interaction of V₂O₅ layers resulted in the potential energy distribution of low frequency vibrational modes being redistributed to other coordinates [72].

Previous reports have characterized the nature interactions of H₂O with V₂O₅ and suggested specific types of hydrogen bonding configurations between H₂O and the vanadyl oxygen group [34, 59]. Based on these models, Figure 6b illustrates a coordination geometry of interlayer H₂O within V₂O₅ via hydrogen bonding. Figure 6c represents postulated coordination of interlayer PEO and H₂O with V₂O₅ via hydrogen bonding. Further analysis is needed to determine the specific coordination environments of H₂O and PEO within the V₂O₅ layers, which we expect to vary depending on the

relative composition of H₂O and polymer within the structure. Additionally, we did not observe the band at 822 cm⁻¹, corresponding to CH₂ rocking modes of PEO. This is mainly due to the combination of low excitation laser power used for the Raman analysis and the low concentration of PEO present in the composites.

3.6. Electrochemical evaluation of V₂O₅ xerogels and V₂O₅-PEO nanocomposites

The Mg-ion charge storage capacity of the V₂O₅ xerogels and V₂O₅-PEO nanocomposites were determined using galvanostatic charge/discharge tests. Vanadium pentoxide can reversibly electrochemically store Mg-ions and electrons within its structure, which can be described by the following equation.

Shown in Figure 7 are the galvanostatic charge/discharge profiles recorded at a mass-normalized current density of 10 mA/g. The sloping voltage profile is similar to that observed for Li-ion intercalation into V₂O₅·nH₂O xerogels [73]. For storage of Mg-ions within V₂O₅, prior calculations support that H₂O content can significantly influence voltage for Mg-ion insertion into V₂O₅ xerogels and can result in a sloping voltage profile [35]. We consider that due to the well-established ion coordination ability of PEO it is possible that interlayer PEO may affect the voltage of Mg-ion insertion into V₂O₅ in a manner similar to H₂O, however further investigation is needed to determine the effects of interlayer PEO and H₂O on Mg-ion insertion voltage.

The V₂O₅ xerogels showed a Mg-ion charge storage capacity of 19 mAh/g (C/10 discharge rate), which is in the range of previous reports [22]. Compared with the V₂O₅ xerogel, the V₂O₅-PEO-1 nanocomposite showed a significantly higher Mg-ion capacity

of 100.3 mAh g⁻¹, which is ~5 times higher than the V₂O₅ xerogel capacity. The V₂O₅-PEO-2 cathode exhibited a capacity of 53.7 mAh g⁻¹ which is higher than the V₂O₅ xerogel but lower than V₂O₅-PEO-1.

The Mg-ion capacity of 0.06, 0.34, and 0.18 per V₂O₅ formula unit was determined (i.e. x in Mg_xV₂O₅) for the V₂O₅ xerogel, V₂O₅-PEO-1, and V₂O₅-PEO-2 materials respectively. The higher Mg-ion storage capacity of V₂O₅-PEO-1 compared with V₂O₅ xerogel is related to the larger interlayer spacing and the specific nature of V₂O₅, polymer, and H₂O interactions within the structure, as discussed further below. Clearly, interlayer spacing is not the only factor since V₂O₅-PEO-2 showed higher interlayer spacing compared to V₂O₅-PEO-1 from XRD and TEM analysis, however V₂O₅-PEO-2 exhibited lower Mg-ion specific capacity than V₂O₅-PEO-1.

Figure 7. Galvanostatic charge-discharge voltage profiles of V₂O₅, V₂O₅-PEO-1 and V₂O₅-PEO-2 acquired at a mass-normalized current of 10 mA g⁻¹; electrolyte: 1 M Mg(ClO₄)₂ in dried acetonitrile; counter: carbon; reference: Mg metal.

In order to further understand the Mg-ion charge storage within V_2O_5 and V_2O_5 -PEO nanocomposites, cyclic voltammograms (CV) at different scan rates were acquired and analyzed. Figure 8a shows the CV curves of V_2O_5 , V_2O_5 -PEO-1 and V_2O_5 -PEO-2 at a scan rate of 2.5 mV/s. The V_2O_5 xerogels show an anodic peak at ~ 1.6 V vs Mg^{2+}/Mg . Compared to V_2O_5 xerogels and V_2O_5 -PEO-2, the V_2O_5 -PEO-1 nanocomposite showed higher current per mass of material indicating that the introduction of PEO within V_2O_5 improved the Mg-ion charge storage capacity.

Figure 8. (a) Cyclic voltammograms of V_2O_5 , V_2O_5 -PEO-1 and V_2O_5 -PEO-2 recorded at a scan rate of 2.5 mV/s; electrolyte: 1 M $Mg(ClO_4)_2$ in dried acetonitrile; counter: carbon cloth; reference: Mg metal; (b) Plot of the peak current density as a function of the square root of scan rate (v) showing a linear response (c) Cycling performance of V_2O_5 , V_2O_5 -PEO-1 and V_2O_5 -PEO-2 recorded at 10 mA/g constant current density for 30 cycles. All electrodes were pre-conditioned by charging and discharging 5 cycles prior to cycling.

At higher scan rates of 5.0 and 7.5 mV s⁻¹ (Figure S3), the V₂O₅-PEO-1 nanocomposite also showed higher currents than V₂O₅ xerogels and V₂O₅-PEO-2. At the higher scan rates, the peaks of the V₂O₅ xerogels and V₂O₅-PEO-2 were shifted to higher voltages, which is due to resistances within the electrode materials. We note that the scan rates applied to evaluate the Mg²⁺ ion storage capacity are much higher than that of previously reported scan rates used for thin film configurations [13], which suggests that the nanocomposite morphology provides an electrode architecture that can be used for practical electrodes rather than only thin films.

The Mg-ion charge storage kinetics were investigated by analysis of the cyclic voltammograms acquired at different scan rates. Shown in Figure 8b is the plot of peak current density vs. (scan rate, ν)^{1/2} for V₂O₅, V₂O₅-PEO-1 and V₂O₅-PEO-2 at different scan rates. The plots exhibit a linear response with respect to (scan rate)^{1/2}. V₂O₅-PEO-1 showed a higher slope than V₂O₅ or V₂O₅-PEO-2. Based on the linear trends of peak current density vs. (scan rate, ν)^{1/2}, Mg²⁺ diffusion coefficients were determined using the Randles-Sevcik equation:

$$I_p = 0.4463zFAC \sqrt{\frac{zF\nu D}{RT}} \quad (3)$$

where I_p is the peak current value (Amps), z is the number of exchanged electrons ($z=2$), F is the Faraday constant (96,485 C mol⁻¹), A is the electrode geometric area (cm²), C is the Mg²⁺ concentration within the lattice (mol cm⁻³), ν is the scan rate (V s⁻¹), D is the diffusion coefficient (cm² s⁻¹), R is the gas constant (J K⁻¹ mol⁻¹), and T is the temperature (K) [74]. The Mg²⁺ diffusion coefficients, $D_{Mg^{2+}}$, were obtained from the

slopes of the peak current vs. $v^{1/2}$ (Figure 8b). For the V_2O_5 xerogel, $D_{Mg^{2+}}$, was determined to be $2.4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, which is in the range of previously reported values for Mg^{2+} diffusion coefficients [10]. The V_2O_5 -PEO-1 nanocomposite showed a higher Mg^{2+} diffusion coefficient of $4.7 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, which is 2 times higher than the Mg^{2+} diffusion coefficient for the V_2O_5 xerogel. The V_2O_5 -PEO-2 nanocomposites had a Mg^{2+} diffusion coefficient of $2.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, which was lower than that observed for either the V_2O_5 xerogel or the V_2O_5 -PEO-1 nanocomposite.

The higher diffusion coefficient for V_2O_5 -PEO-1 compared with the V_2O_5 xerogel is consistent with more facile Mg^{2+} diffusion resulting from the larger interlayer spacing (Figures 2 and 4) and the interaction of the polymer with the negatively charged V_2O_5 host lattice which shields the Mg^{2+} from direct interaction with V_2O_5 . TGA indicates that V_2O_5 -PEO-1 and V_2O_5 xerogel contain similar amounts of structural water, however the Raman spectra (Figure 6a) support that polymer interacts preferentially with the V_2O_5 lattice leading to H_2O within the interlayer. For $V_2O_5 \cdot 1.4H_2O$ xerogels, prior work identified three different types of H_2O within the structure including H_2O that was hydrogen-bonded with other H_2O molecules rather than strongly associated with the lattice [72]. H_2O that is less strongly bound with V_2O_5 can result in improved ion transport due to the coupling of H_2O with higher freedom of motion with ion diffusion as supported by prior work [70]. The higher Mg-ion diffusion within V_2O_5 -PEO-1 is therefore attributed to improved mobility of Mg-ion within the expanded interlayer spacing due to coordination of Mg-ions with interlayer H_2O and polymer shielding of the interaction of Mg^{2+} with V_2O_5 .

The Mg^{2+} diffusion coefficient of V_2O_5 -PEO-2 was lower than that of the V_2O_5 xerogel or V_2O_5 -PEO-1. V_2O_5 -PEO-2 had the highest amount of PEO and the largest interlayer spacing. The lower diffusion coefficient and capacity V_2O_5 -PEO-2 compared with V_2O_5 -PEO-1 indicates that larger interlayer spacing is not the only contributor to electrochemical Mg-ion charge storage. Mg-ion diffusion is therefore not only affected by the interlayer spacing, but also the interlayer composition. Higher amounts of PEO may result in lower performance due to (i) lower diffusion of Mg-ions with PEO-rich regions, (ii) lower electronic conductivity by electronically insulating PEO, (iii) coordination of PEO with V_2O_5 lattice that blocks Mg-ion sites. The high peak current density of V_2O_5 -PEO-1 at 2.5, 5.0 and 7.5 mV/s scan rates indicates a fast charge transfer process due to the presence of a specific amount of PEO that interacts with the host lattice and enlarges interlayer spacing without hindering the electrochemical activity of V_2O_5 . Higher amounts of PEO results in lower electrochemical performance, especially at high rates (Figure S3).

To determine the reversibility of Mg-ion insertion within the materials, the cycling performance of the V_2O_5 -PEO nanocomposites were determined by galvanostatic charge-discharge conducted at a constant current density of 10 mA g^{-1} (Figure 8c). Prior to analyzing the cycling performance, the electrodes were conditioned for 5 cycles to establish stable electrochemistry. The higher specific capacity of V_2O_5 -PEO-1 over the other samples is maintained over 35 cycles. The initial specific capacity of V_2O_5 -PEO-1 gradually dropped from 125 mAh g^{-1} to 96 mAh g^{-1} over the first 12 cycles and maintained ~77 % of its initial specific capacity over 35 cycles. The incorporation of PEO therefore improved the reversible cycling of Mg-ion within the V_2O_5 structure.

While the V_2O_5 xerogel electrode slowly dropped its initial specific capacity of 18.5 to 4.3 mAh g^{-1} , V_2O_5 -PEO-2 electrode was constantly deteriorating its overall specific capacity from 76 mAh g^{-1} , which is higher than that of V_2O_5 , to 20 mAh g^{-1} with ~74% of capacity loss over 35 cycles. The average coulombic efficiency of the V_2O_5 -PEO-1 nanocomposite was 98.6 %, which was higher than the coulombic efficiencies of V_2O_5 and V_2O_5 -PEO-2, which showed coulombic efficiencies of 84.7 % and 89.2 % respectively. Changes in the capacity of V_2O_5 -PEO nanocomposites during the first few cycles may be due to a number of possible factors including changes in the interlayer spacing and composition due to intercalation of Mg^{2+} and potential solvent co-intercalation as previously reported for V_2O_5 xerogels [22].

To confirm that PEO was maintained within the V_2O_5 -PEO nanocomposites after cycling within the electrolyte, FTIR-ATR spectra were obtained of the V_2O_5 -PEO-1 and V_2O_5 -PEO-2 electrodes before and after cycling. As presented in Figure S4, FTIR-ATR spectra show the presence of C-O-C stretching bands originating from PEO at similar relative intensities when normalized to the relative intensity of the $\nu_s(\text{V}=\text{O}_\text{A})$ mode of V_2O_5 which provides evidence that PEO within nanocomposite materials is maintained after electrochemical cycling in the electrolyte. ~~The nature of structural changes of the V_2O_5 -PEO nanocomposites during cycling is currently under investigation by our group and will be reported in a separate publication.~~

4. Conclusions

The interlayer spacing and interlayer composition of hydrated V_2O_5 xerogels was altered by incorporating poly(ethylene oxide) within the V_2O_5 layers as an approach to

improve electrochemical storage of Mg-ions within the structure. The *in-situ* sol-gel synthesis method provides an effective approach to control the amount of PEO and interlayer spacing. From XRD, the interlayer spacing was shown to increase from 11.6 Å for the V₂O₅ xerogels to 12.6 Å and 13.6 Å for the V₂O₅-PEO-1 and V₂O₅-PEO-2 samples respectively. Higher amounts of PEO resulted in larger interlayer spacing. Infrared spectroscopy shows that the PEO interacts with the V₂O₅ lattice. Analysis of the Raman-active low frequency lattice modes of V₂O₅ supports that the polymer interacts with the V₂O₅ lattice and interaction of H₂O with V₂O₅ is reduced compared with the V₂O₅ xerogel with similar amounts of structural H₂O.

The V₂O₅-PEO nanocomposites were shown to exhibit higher Mg²⁺ diffusion coefficients compared with the V₂O₅ xerogel. The V₂O₅-PEO-1 nanocomposite showed 2 times higher diffusion coefficient compared with the V₂O₅ xerogel, which is attributed to the enhanced Mg-ion transport within the interlayer that is facilitated by structural H₂O that is not strongly bound with the V₂O₅ lattice. The incorporation of PEO between the V₂O₅ layers therefore shields the Mg²⁺ ions from strong interaction with the host lattice and improves Mg²⁺ mobility.

As a result of the structure of the V₂O₅-PEO nanocomposites, the Mg-ion charge storage capacity was ~5 times higher for V₂O₅-PEO-1 than the V₂O₅ xerogel. In particular, the V₂O₅-PEO-1 nanocomposite also exhibited significantly improved capacities compared with V₂O₅ xerogels at high scan rates. At higher PEO compositions, lower Mg-ion diffusion coefficients and capacities were observed which is attributed to higher resistances within the material. These results support that not only interlayer spacing but importantly the nature of interlayer interactions between the V₂O₅ lattice,

PEO, H₂O and Mg-ions, significant affect the Mg-ion charge transport and storage. Designing layered materials with controlled interlayer interactions provides a new approach to modify the interaction between Mg-ions and the host lattice and develop improved cathodes for rechargeable magnesium batteries. Further work is aimed at characterizing the structural changes occurring during Mg-ion insertion and de-insertion within the nanocomposite materials and evaluating the electrochemical Mg-ion charge storage of the cathodes within electrolytes that allow reversible anodic Mg deposition and stripping and have wide voltage windows to enable viable rechargeable magnesium batteries.

Acknowledgements

The authors gratefully acknowledge funding from the National Science Foundation PREM (Grant No. DMR-1205670) and the Texas State University Research Enhancement Program (REP).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/>

References

- [1] N. Nitta, F.X. Wu, J.T. Lee, G. Yushin, *Mater. Today*, 18 (2015) 252-264.
- [2] N. Liu, Z.D. Lu, J. Zhao, M.T. McDowell, H.W. Lee, W.T. Zhao, Y. Cui, *Nat. Nanotechnol.*, 9 (2014) 187-192.
- [3] X.L. Dong, L. Chen, J.Y. Liu, S. Haller, Y.G. Wang, Y.Y. Xia, *Sci. Adv.*, 2 (2016) 8.

- [4] E. McCalla, A.M. Abakumov, M. Saubanere, D. Foix, E.J. Berg, G. Rousse, M.L. Doublet, D. Gonbeau, P. Novak, G. Van Tendeloo, R. Dominko, J.M. Tarascon, *Science*, 350 (2015) 1516-1521.
- [5] D. Aurbach, G.S. Suresh, E. Levi, A. Mitelman, O. Mizrahi, O. Chusid, M. Brunelli, *Adv. Mater.*, 19 (2007) 4260-4267.
- [6] H.S. Kim, T.S. Arthur, G.D. Allred, J. Zajicek, J.G. Newman, A.E. Rodnyansky, A.G. Oliver, W.C. Boggess, J. Muldoon, *Nature communications*, 2 (2011) 427.
- [7] R. Zhang, T.S. Arthur, C. Ling, F. Mizuno, *J. Power Sources*, 282 (2015) 630-638.
- [8] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. urgeyman, Y. Cohen, M. M., E. Levi, *Nature*, 407 (2000) 724-726.
- [9] H.D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, D. Aurbach, *Energy Environ. Sci.*, 6 (2013) 2265-2279.
- [10] Y. Liang, H.D. Yoo, Y. Li, J. Shuai, H.A. Calderon, F.C. Robles Hernandez, L.C. Grabow, Y. Yao, *Nano. Lett.*, 15 (2015) 2194-2202.
- [11] P. Saha, M.K. Datta, O.I. Velikokhatnyi, A. Manivannan, D. Alman, P.N. Kumta, *Prog. Mater. Sci.*, 66 (2014) 1-86.
- [12] M.M. Huie, D.C. Bock, E.S. Takeuchi, A.C. Marschilok, K.J. Takeuchi, *Coord. Chem. Rev.*, 287 (2015) 15-27.
- [13] G. Gershinsky, H.D. Yoo, Y. Gofer, D. Aurbach, *Langmuir*, 29 (2013) 10964-10972.
- [14] P. Saha, P.H. Jampani, M.K. Datta, C.U. Okoli, A. Manivannan, P.N. Kumta, *J. Electrochem. Soc.*, 161 (2014) A593-A598.
- [15] R. Zhang, C. Ling, F. Mizuno, *Chem. Commun.*, 51 (2015) 1487-1490.
- [16] E. Lancry, E. Levi, A. Mitelman, S. Malovany, D. Aurbach, *J. Solid State Chem.*, 179 (2006) 1879-1882.
- [17] Y. NuLi, J. Yang, Y. Li, J. Wang, *Chemical communications*, 46 (2010) 3794-3796.
- [18] X. Sun, P. Bonnick, L.F. Nazar, *ACS Energy Lett.*, 1 (2016) 297-301.
- [19] R. Mohtadi, F. Mizuno, *Beilstein journal of nanotechnology*, 5 (2014) 1291-1311.
- [20] G.G. Amatucci, F. Badway, A. Singhal, B. Beaudoin, G. Skandan, T. Bowmer, I. Plitz, N. Pereira, T. Chapman, R. Jaworski, *J. Electrochem. Soc.*, 148 (2001) A940.
- [21] K. Xu, Y.F. Lam, S.S. Zhang, T.R. Jow, T.B. Curtis, *J. Phys. Chem. C*, 111 (2007) 7411-7421.
- [22] N. Sa, T.L. Kinnibrugh, H. Wang, G. Sai Gautam, K.W. Chapman, J.T. Vaughey, B. Key, T.T. Fister, J.W. Freeland, D.L. Proffit, P.J. Chupas, G. Ceder, J.G. Baren, I.D. Bloom, A.K. Burrell, *Chem. Mater.*, 28 (2016) 2962-2969.
- [23] J. Song, M. Noked, E. Gillette, J. Duay, G. Rubloff, S.B. Lee, *Phys. Chem. Chem. Phys.*, 17 (2015) 5256-5264.
- [24] P. Novak, J. Desilves, *J. Electrochem. Soc.*, 140 (1993) 140-144.
- [25] L. Yu, X. Zhang, *Journal of colloid and interface science*, 278 (2004) 160-165.
- [26] N. Sa, H. Wang, D.L. Proffit, A.L. Lipson, B. Key, M. Liu, Z. Feng, T.T. Fister, Y. Ren, C.-J. Sun, J.T. Vaughey, P.A. Fenter, K.A. Persson, A.K. Burrell, *J. Power Sources*, 323 (2016) 44-50.
- [27] P.S.E. Yeo, M.-F. Ng, *Chem. Mater.*, 27 (2015) 5878-5885.
- [28] S. Yang, D. Li, T. Zhang, Z. Tao, J. Chen, *J. Phys. Chem. C*, 116 (2012) 1307-1312.
- [29] S. Rasul, S. Suzuki, S. Yamaguchi, M. Miyayama, *Electrochim. Acta*, 82 (2012) 243-249.

- [30] V. Augustyn, J. Mater. Res., (in press) doi: 10.1557/jmr.2016.337 (2016).
- [31] J. Yin, C.J. Pelliccione, S.H. Lee, E.S. Takeuchi, K.J. Takeuchi, A.C. Marschilok, J. Electrochem. Soc., 163 (2016) A1941-A1943.
- [32] M. Inamoto, H. Kurihara, T. Yajima, Materials, 6 (2013) 4514-4522.
- [33] P.E. Tang, J.S. Sakamoto, E. Baudrin, B. Dunn, J. Non-Cryst. Solids, 350 (2004) 67-72.
- [34] J. Livage, Chem. Mater., 3 (1991) 578-593.
- [35] G.S. Gautam, P. Canepa, W.D. Richards, R. Malik, G. Ceder, Nano Lett., 16 (2016) 2426-2431.
- [36] P. Novak, W. Scheifele, F. Joho, O. Haas, J. Electrochem. Soc., 142 (1995) 2544-2550.
- [37] D.B. Le, S. Passerini, F. Coustier, J. Guo, T. Soderstrom, B.B. Owens, W.H. Smyrl, Chem. Mater., 10 (1998) 682-684.
- [38] E.M. Guerra, K.J. Ciuffi, H.P. Oliveira, J. Solid State Chem., 179 (2006) 3814-3823.
- [39] C.V.S. Reddy, J. Wei, Z. Quan-Yao, D. Zhi-Rong, C. Wen, S. Mho, R.R. Kalluru, Journal of Power Sources, 166 (2007) 244-249.
- [40] D.L. Chao, X.H. Xia, J.L. Liu, Z.X. Fan, C.F. Ng, J.Y. Lin, H. Zhang, Z.X. Shen, H.J. Fan, Adv. Mater., 26 (2014) 5794-5800.
- [41] F. Huguenin, R.M. Torresi, J. Phys. Chem. C, 112 (2008) 2202-2209.
- [42] L. Shao, J.W. Jeon, J.L. Lutkenhaus, J. Mater. Chem. A, 1 (2013) 7648-7656.
- [43] X. Rui, Z. Lu, Z. Yin, D.H. Sim, N. Xiao, T.M. Lim, H.H. Hng, H. Zhang, Q. Yan, Small, 9 (2013) 716-721.
- [44] E. Cazzanelli, G. Mariotto, S. Passerini, W.H. Smyrl, J. Non-Cryst. Solids, 208 (1996) 89-98.
- [45] L. Abello, E. Husson, Y. Repelin, G. Lucazeau, J. Solid State Chem., 56 (1985) 379-389.
- [46] X.Q. Liu, C.M. Huang, J.W. Qiu, Y.Y. Wang, Appl. Surf. Sci., 253 (2006) 2747-2751.
- [47] M. Stein, C.F. Chen, M. Mullings, D.J. Jamie, A. Zaleski, C.P. Rhodes, J. Electrochem. Energy Conv. Storage, 13 (2016) 031001.
- [48] Z. Lu, A. Schechter, M. Moshkovich, D. Aurbach, J. Electroanal. Chem., 466 (1999) 203-217.
- [49] T.T. Tran, W.M. Lamanna, M.N. Obrovac, J. Electrochem. Soc., 159 (2012) A2005-A2009.
- [50] F.J. Anaissi, G.J.F. Demets, E.B. Alvarez, M.J. Politi, H.E. Toma, Electrochim. Acta, 47 (2001) 441-450.
- [51] D.B. Le, S. Passerini, J. Guo, J. Ressler, B.B. Owens, W.H. Smyrl, J. Electrochem. Soc., 143 (1996) 2099-2104.
- [52] J.X. Wang, C.J. Curtis, D.L. Schulz, J.G. Zhang, J. Electrochem. Soc., 151 (2004) A1-A7.
- [53] V. Petkov, P.N. Trikalitis, E.S. Bozin, S.J.L. Billinge, T. Vogt, M.G. Kanatzidis, J. Am. Chem. Soc., 124 (2002) 10157-10162.
- [54] Y. Kim, Q.-T. Ta, H.-C. Dinh, P.K. Aum, I.-H. Yeo, W.I. Cho, S.-i. Mho, J. Electrochem. Soc., 158 (2011) A133.
- [55] T. Yao, Y. Oka, N. Yamamoto, Mater. Res. Bull., 27 (1992) 669-675.

- [56] Y. Chen, G. Yang, Z. Zhang, X. Yang, W. Hou, J.J. Zhu, *Nanoscale*, 2 (2010) 2131-2138.
- [57] Liu.Y.-J., S.J. L., D.D. C., K.C. R, H. W, K.M. G., *Chem. Mater.* , 8 (1996) 525-534.
- [58] L. Abello, E. Husson, Y. Repelin, G. Lucazeau, *Spectrochim. Acta Mol. Biomol. Spectrosc.*, 39 (1983) 641-651.
- [59] C.J. Fontenot, J.W. Wiench, M. Pruski, G.L. Schrader, *J. Phys. Chem. B*, 105 (2001) 10496-10504.
- [60] F. Leroux, G. Goward, W.P. Power, L.F. Nazar, *J. Electrochem. Soc.*, 144 (1997) 3886-3895.
- [61] J. Harreld, H.P. Wong, B.C. Dave, B. Dunn, L.F. Nazar, *J. Non-Cryst. Solids*, 225 (1998) 319-324.
- [62] F.D. Hardcastle, I.E. Wachs, *J. Phys. Chem.*, 95 (1991) 5031-5041.
- [63] F. Huguenin, E.A. Ticianelli, R.M. Torresi, *Electrochim. Acta*, 47 (2002) 3179-3186.
- [64] H. Matsuura, T. Miyazawa, *Bull. Chem. Soc. Jpn.*, 41 (1968) 1798-1808.
- [65] H. Matsuura, K. Fukuhara, *J. Polym. Sci. B*, 24 (1986) 1383-1400.
- [66] I. Pucić, T. Jurkin, *Radiation Physics and Chemistry*, 81 (2012) 1426-1429.
- [67] X. Li, S.L. Hsu, *J. Polym. Sci. Pt. B-Polym. Phys.*, 22 (1984) 1331-1342.
- [68] W. Wieczorek, D. Raducha, A. Zalewska, J.R. Stevens, *J. Phys. Chem.*, 102 (1998) 8725-8731.
- [69] V.L. Volkov, G.S. Zakharova, L.A. Perelyaeva, *Russ. J. Inorg. Chem.*, 51 (2006) 41-45.
- [70] N. Uchida, S. Kittaka, *J. Phys. Chem.*, 98 (1994) 2129-2133.
- [71] M.T. Vandenborre, R. Prost, E. Huard, J. Livage, *Mater. Res. Bull.*, 18 (1983) 1133-1142.
- [72] Y. Repelin, E. Husson, L. Abello, G. Lucazeau, *Spectrochim. Acta Mol. Biomol. Spectrosc.*, 41 (1985) 993-1003.
- [73] M. Giorgetti, S. Passerini, W.H. Smyrl, S. Mukerjee, X.Q. Yang, J. McBreen, *J. Electrochem. Soc.*, 146 (1999) 2387-2392.
- [74] D. Di Lecce, J. Hassoun, *J. Phys. Chem. C*, 119 (2015) 20855-20863.

Figure 1. Graphical representation of growth of hydrated V_2O_5 nanosheet formation from water addition and condensation reactions of $[VO_4]^{3-}$ polyanions in aqueous solution at low pH; (a) without poly(ethylene oxide) (PEO); (b) with PEO.

Figure 2. Scanning electron microscopy (SEM) images of V_2O_5 xerogel (a), V_2O_5 -PEO-1 (b), and V_2O_5 -PEO-2 nanocomposite (c); Transmission electron microscopy (TEM) images of V_2O_5 xerogel (d), V_2O_5 -PEO-1 (e), and V_2O_5 -PEO-2 nanocomposite (f); High-resolution TEM images showing d -spacings of V_2O_5 xerogel (g), V_2O_5 -PEO-1 (h), and V_2O_5 -PEO-2 nanocomposite (i).

Figure 3. Energy dispersive spectroscopy (EDS) elemental mapping of V_2O_5 -PEO-1 nanocomposite; (a) SEM image; corresponding EDS mappings of (b) carbon (C), (c) vanadium (V), and (d) oxygen (O) elements of V_2O_5 -PEO-1.

Figure 4. (a) X-Ray diffraction (XRD) powder patterns of V_2O_5 xerogel, V_2O_5 -PEO-1, and V_2O_5 -PEO-2 nanocomposite; (b) Expanded region from $2\theta^\circ \sim 5-10$ showing shifting of the (001) peak to lower $2\theta^\circ$ values upon introduction of PEO.

Figure 5. a) ATR-FTIR spectra of V_2O_5 xerogel, V_2O_5 -PEO nanocomposites, and PEO; Bands corresponding to C-O-C, C-H and $\nu_s(V=O_A)$ stretches are labeled; inset figure shows the expanded region from $\sim 1020-1170\text{ cm}^{-1}$ corresponding to the C-O-C stretching bands; (b) Expanded region from $800-1100\text{ cm}^{-1}$ showing the $\nu_s(V=O)$ downshift.

Figure 6. (a) Raman spectra of V_2O_5 xerogel, V_2O_5 -PEO-1 and V_2O_5 -PEO-2 in the 100 cm^{-1} to 950 cm^{-1} region; (b) Representation of possible coordination of interlayer H_2O within V_2O_5 via hydrogen bonding; (c) Representation of possible coordination of V_2O_5 with both interlayer H_2O and PEO via hydrogen bonding; schematics do not represent steric effects and PEO chain conformation.

Figure 7. Galvanostatic charge-discharge voltage profiles of V_2O_5 , V_2O_5 -PEO-1 and V_2O_5 -PEO-2 acquired at a mass-normalized current of 10 mA g^{-1} ; electrolyte: $1\text{ M Mg(ClO}_4)_2$ in dried acetonitrile; counter: carbon; reference: Mg metal.

Figure 8. (a) Cyclic voltammograms of V_2O_5 , V_2O_5 -PEO-1 and V_2O_5 -PEO-2 recorded at a scan rate of 2.5 mV/s ; electrolyte: $1\text{ M Mg(ClO}_4)_2$ in dried acetonitrile; counter: carbon cloth; reference: Mg metal; (b) Plot of the peak current density as a function of the square root of scan rate (v) showing a linear response (c) Cycling performance of V_2O_5 , V_2O_5 -PEO-1 and V_2O_5 -PEO-2 recorded at 10 mA/g constant current density for 30 cycles. All electrodes were pre-conditioned by charging and discharging 5 cycles prior to cycling.

Graphical abstract