



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



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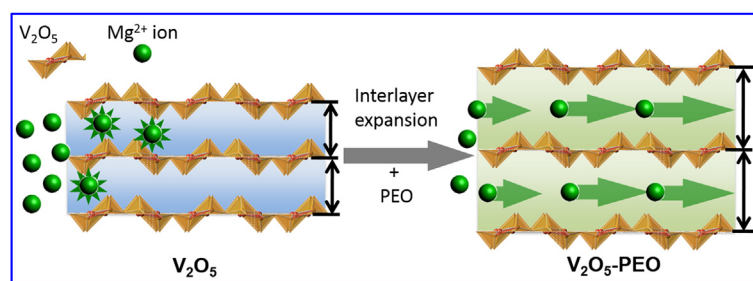
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HIGHLIGHTS

- V_2O_5 xerogels with different poly(ethylene oxide) compositions were synthesized.
- The incorporation of poly(ethylene oxide) increased spacing between V_2O_5 layers.
- Raman spectroscopy supports that the polymer interacts with the V_2O_5 lattice.
- V_2O_5 -PEO showed a higher Mg^{2+} diffusion coefficient compared with V_2O_5 xerogels.
- Mg-ion capacity of V_2O_5 -PEO-1 was 5 times higher than for V_2O_5 xerogels.

GRAPHICAL ABSTRACT



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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 which is attributed to enhanced Mg-ion mobility due to the 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.

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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 Mo₆S₈ 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 cathodes materials suffer poor electrode kinetics and cycle performance due to low Mg²⁺ diffusion and structural instability [7]. Compared with a single valent Li⁺ ion, a divalent Mg²⁺ ion has a high polarizability leading to strong interaction with the negatively charged host lattice [19,20]. The strong interaction of Mg²⁺ 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], Mg²⁺ 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 Mg²⁺ ions [23–25]. Song et al. demonstrated the capability to significantly improve the Mg-ion insertion and deinsertion by introducing a small amount of H₂O to the electrolyte, thereby decreasing Mg²⁺ polarization [23]. Trace H₂O within the electrolyte can passivate Mg metal and adversely affect further Mg anode activity [24,26], therefore the use of H₂O 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 and improve the Mg-ion capacity of MoS₂ [10].

In this work, we report for the first time that the incorporation of PEO between the V₂O₅ 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 V₂O₅ sol-gel synthesis to allow intimate mixing of the PEO and V₂O₅. The introduction of a polymer in the V₂O₅ interlayer was investigated as an approach to expand the interlayer spacing and reduce the interaction of divalent Mg²⁺ with the host V₂O₅ lattice. The expansion of the interlayer spacing resulting from the incorporation of the polymer was confirmed by transmission electron microscopy (TEM) and X-ray diffraction analyses. The V₂O₅-PEO nanocomposites were determined to provide significantly higher Mg-ion capacities than the V₂O₅ xerogel. The

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