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The Role of Structural Mg^{2+} on Battery Performance**

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Communication-Sol-Gel Synthesized Magnesium Vanadium Oxide, $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$: The Role of Structural Mg^{2+} on Battery Performance

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Abstract

Magnesium intercalated vanadium oxide xerogels, $\text{Mg}_{0.1}\text{V}_2\text{O}_5 \cdot 2.35\text{H}_2\text{O}$ and $\text{Mg}_{0.2}\text{V}_2\text{O}_5 \cdot 2.46\text{H}_2\text{O}$ were synthesized using an ion removal sol gel strategy. X-ray diffraction indicated lamellar ordering with turbostratic character. X-ray absorption spectroscopy indicated greater distortion of the local vanadium-oxygen coordination environment in the $\text{Mg}_{0.2}\text{V}_2\text{O}_5 \cdot 2.46\text{H}_2\text{O}$ material. Elemental analysis after cycling in Li^+ or Mg^{2+} based electrolytes revealed that the magnesium content was unchanged, indicating the structural Mg^{2+} ions are retained. The $\text{Mg}_{0.1}\text{V}_2\text{O}_5 \cdot 2.35\text{H}_2\text{O}$ material displayed a high voltage of 3.0 V vs. Mg^{2+}/Mg , high energy

density of 420 mWh/g, and discharge/charge efficiency, indicating promise as a cathode material for future magnesium based battery systems.

Introduction

The success of lithium ion batteries (LIB) has accelerated the development of portable electronics by providing lightweight and reliable power. Recently, utilization of LIB has expanded to include clean energy vehicles. Nevertheless, safety concerns, high cost, and the natural scarcity of lithium motivate consideration of substitutes for LIB. Magnesium ion batteries (MIB) possess several prospective advantages: the natural abundance of Mg, low cost, the promise of safe performance, and high capacity of Mg metal (3832 mAh/cm^3).^(1, 2)

One challenge associated with rechargeable magnesium batteries is the lack of high voltage cathode materials.⁽³⁾ Despite the cycle stability of Chevrel phase materials, they possess a low working voltage.⁽⁴⁾ The voltage of metal dichalcogenides is only $\sim 1.6 \text{ V}$, including MoS_2 ,^(5, 6) TiS_2 ,⁽⁷⁾ and WSe_2 ⁽⁸⁾. Silicate based cathodes have a similar operating voltage range.⁽⁹⁻¹¹⁾ Metal oxides may exhibit higher working voltages, for example, $\alpha\text{-MnO}_2$, and birnessite MnO_2 can be $>2.0 \text{ V}$,⁽¹²⁻¹⁵⁾ and MoO_3 is 1.8 V .⁽¹⁶⁾

Vanadium oxide xerogels ($\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) exhibit rich electrochemistry due to the wide range of oxidation states (II-V), with opportunity for multiple electron transfer yielding high energy density.^(17, 18) Crystalline V_2O_5 has an orthorhombic layered structure of edge shared distorted trigonal bipyramidal VO_5 units, forming $(\text{V}_2\text{O}_4)_n$ zigzag double chains along the (100) direction. However, hydrated $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and cation intercalated $\text{M}_x\text{V}_2\text{O}_5$ compounds have a different layer arrangement where two mono V_2O_5 layers comprised of square-pyramidal VO_5 units stack to form a bilayer slab with interatomic distance of $2.9 \text{ \AA}$, and the slabs stack to form a

monoclinic lattice (C2/m).(19) While the lithium ion diffusion coefficient is low in orthorhombic V_2O_5 ($10^{-12} \sim 10^{-13} \text{ cm}^2\text{s}^{-1}$),(20) cation diffusion can be facile in $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gel, reaching $10^{-8} \text{ cm}^2\text{s}^{-1}$.(21)

Previous research of V_2O_5 gels as cathode materials has demonstrated Mg^{2+} insertion into V_2O_5 at 2.2 V,(22-30) with a capacity of $\sim 170 \text{ mAh/g}$ in water-acetonitrile electrolyte.(27) V_2O_5 nanotubes showed an initial discharge capacity of $\sim 120 \text{ mAh/g}$ in 0.25 M $\text{Mg}(\text{AlBu}_2\text{Cl}_2)_2 / \text{THF}$ with 25% retention at the 5th cycle.(31, 32)

In this report, we study the role of Mg^{2+} (x) content for the first time. $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ materials were prepared by subtracting cations from a crystalline metal vanadate (e.g. NaVO_3 , MgV_2O_6) as an alternative strategy in order to adjust the cation amount in the structure, **Figure 1a**,(16, 33, 34) different than the usual $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ sol-gel method.(17). The as-prepared materials, $x = 0.1$ (**MVO-1**) and $x = 0.2$ (**MVO-2**), were characterized and their electrochemical activity in lithium and magnesium electrolytes was determined. Post mortem analysis was done to determine the magnesium vanadium ratio after cycling. The implications for use of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in lithium and magnesium based battery systems will be discussed, with particular focus on the structural role of the Mg^{2+} ion.

Experimental

Synthesis and characterization. $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ was synthesized via a novel sol gel based process (33) Briefly, magnesium vanadate (MgV_2O_6),(35) was dissolved in water, then treated with an ion exchange resin. Characterization included x-ray diffraction (XRD), crystallite size determination using the Scherrer equation,(36) thermogravimetric analysis (TGA) using a TA

Instruments Q600 and determination of elemental composition via a Thermo Scientific ICAP inductively-coupled plasma optical emission spectroscopy (ICP-OES).

X-ray absorption spectroscopy (XAS) measurements of as prepared coatings of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ were acquired at the V K-edge (5.465 keV) in transmission mode at the National Synchrotron Light Source at Brookhaven National Laboratory. XAS scans of each sample were aligned to a vanadium metal foil measured simultaneously and merged in Athena. (37, 38) A V_2O_5 powder reference material was measured for comparison. Each merged XAS spectrum was normalized in Athena utilizing the AUTOBK algorithm to minimize background below $R_{\text{bkg}} = 1.0$. The edge position was selected as the maximum of the second peak in the first derivative of $\chi\mu(E)$ (ca. 5.482 – 5.483 keV). After background removal, the data was Fourier transformed into R-space using a Hanning window with a k-range of 2 – 11 Å⁻¹. Theoretical models were created using FEFF6(39) using the standard orthorhombic V_2O_5 crystal structure(40) and fit to the experimental data.

Electrochemical testing. Working electrodes were prepared using $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, carbon and binder. Cyclic voltammetry (CV) was conducted using a three electrode system: the working electrode was $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, and lithium counter and reference electrodes with a scan rate of 0.1 mV/s and a voltage window of 2.0 to 4.0 V. The lithium based electrolyte was 1.0 M LiPF_6 in ethylene carbonate (EC) / dimethyl carbonate (DMC) (v/v 30/70). In Mg^{2+} containing electrolyte Ag/AgNO_3 reference and carbon auxiliary electrodes were used with voltage limits of –1.0 and +0.85 V using a scan rate of 0.1 mV/s. The magnesium based electrolyte was 0.5 M magnesium bis(trifluoromethylsulfonylimide) ($\text{Mg}(\text{TFSI})_2$) /0.5 M dipropylene glycol dimethyl ether (dipro-glyme) in acetonitrile. Two electrode lithium cells were used for galvanostatic

cycling between voltage limits of 2.0 V and 3.8 V at rates of 0.1 C and 0.5 C, 1C was set as 200 mA/g. In magnesium based electrolyte a 0.1 C (1 C = 200 mAh/g) rate for both discharge and charge was used, between voltage limits of -1.0 and +0.85 V in a three electrode set up versus Ag^+/Ag , corresponding to ~2.1 to 3.9 V versus Mg^{2+}/Mg .

Results and discussion

$\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ samples were synthesized via a novel sol gel based process using ion removal,

Fig. 1. The chemical composition of the as-synthesized $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels was determined through TGA/DSC and ICP-OES as $\text{Mg}_{0.1}\text{V}_2\text{O}_5 \cdot 2.35\text{H}_2\text{O}$ (**MVO-1**) and $\text{Mg}_{0.2}\text{V}_2\text{O}_5 \cdot 2.46\text{H}_2\text{O}$ (**MVO-2**). X-ray diffraction patterns indicated typical lamellar ordering with turbostratic character.(19, 33, 41) The broad peak located at ~6 degrees 2 theta can be indexed as the (001) peak(19) and was utilized to calculate the crystallite size. The **MVO-1** and **MVO-2** samples had crystallite sizes of 8 nm, and similar interlayer spacings of 14.5 and 14.3 Å, respectively.

The x-ray absorption near edge structure, (XANES) of the samples and V_2O_5 standard indicate no change in the absorption edge position suggesting no formal oxidation state change, **Fig. 2a**. The amplitude of the sharp pre-edge peak at ~5.470 keV is lower in **MVO-1** while **MVO-2** is very similar to V_2O_5 . This pre-edge peak results from a normally forbidden dipole electron transition, but becomes an allowed transition due to broken symmetries and orbital mixing.(42, 43) In the case of the vanadium K-edge, this pre-edge peak is likely due to a 1s-3d transition from the mixing of the 2p orbitals of the oxygens with the 3d π orbitals of the vanadium ions.(44) A reduction in this peak intensity suggests a subtle change in the local electronic environment around each vanadium atom that may be due to variations in the interatomic distance between vanadium and oxygen atoms,(45) or slight change in the coordination environment.(46)

Additionally, the samples have an increased “white-line” at ~5.488 keV compared to V_2O_5 indicative of changes in the electron transition induced from the absorption event, here the 1s - 4p transition. This is likely due to variations in the bonding environment of the vanadium ions and the neighboring oxygen atoms.(42) Unlike the pre-edge peak, **MVO-2** shows lower white line intensity, but is shifted from the V_2O_5 crystal structure.

The extended x-ray absorption fine structure (EXAFS) is shown in **Fig. 2b** as $|\chi(R)|$ (Fourier transform of $\chi(k)$). In the V_2O_5 structure, oxygen atoms are located 1.59, 1.78, 1.88 and 2.02 Å from each vanadium atom, and neighboring vanadium atoms are 3.08 and 3.42 Å away. In the synthesized $Mg_xV_2O_5 \cdot nH_2O$ gels, there is a shift in the first V-O peak to a larger distance, and a contraction of the second shell V-V/V-O peak. The V_2O_5 structure was used to fit each sample using Artemis.(39) In agreement with the XANES interpretation, there is disorder in the V-O environment dependent on the Mg content. The **MVO-1** sample exhibits minimal shifts in $|\chi(R)|$, while the **MVO-2** sample shows a larger shift in the first shell V-O peak suggesting greater distortion.

Cyclic voltammetry (CV) in Li^+ containing electrolyte, **Fig. 3a**, showed cathodic peaks at 2.85 V and 3.50 V in both **MVO-1** and **MVO-2**, and anodic peaks at 3.03 V and 2.68 V. **MVO-1** consistently displayed higher peak current than **MVO-2**. Galvanostatic cycling testing was conducted at 0.1 C and 0.5 C where **MVO-1** and **MVO-2** delivered 174 and 148 mAh/g respectively, **Fig. 3b**. On Cycling, **Fig. 3c**, **MVO-1** delivered 137 mAh/g capacity at 0.1 C, and 95 mAh/g at 0.5 C, while **MVO-2** delivered 120 mAh/g at 0.1 C, and 82 mAh/g at 0.5 C. The capacity retention of **MVO-1** after ten cycles was 82 % at 0.1 C and 77 % at 0.5 C, and 68 % at 0.1 C and 55 % at 0.5 C for **MVO-2**. **Fig. 3d** compares the Mg and Li content per formula unit determined by ICP-OES for as prepared material, material recovered after discharge, after charge,

and after soaking in Li^+ containing electrolyte. Notably, the magnesium content remained consistent in all cases, indicating the structural Mg^{2+} ions are retained during the electrochemical Li^+ cycling, and did not exchange with Li^+ ion upon electrolyte exposure.

The electrochemical performance of the as-synthesized $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels in Mg^{2+} containing electrolyte was measured using a three electrode configuration, **Fig. 4a**. **MVO-1** showed a major cathodic peak at 0.1 V with a weaker peak at -0.65 V, while **MVO-2** had one broad cathodic peak at 0.05 V, the anodic peak of both samples was at 0.6 V. **Fig. 4b** displays typical discharge voltage curves of **MVO-1** and **MVO-2** where the capacity of **MVO-1** was 125 mAh/g (0.53 Mg^{2+} insertion), yet the value of **MVO-2** was only 46 mAh/g (0.20 Mg^{2+} insertion). The difference between the two materials at the 10th cycle was ~2.5 fold, **Fig. 4a**.

Notably, the capacity of **MVO-1** and **MVO-2** increased in the initial cycles from 90 mAh/g to 143 mAh/g, and became steady from the 5th to 10th cycle. Previous research on V_2O_5 based materials attributed this to gradual penetration of electrolyte into the electrode, resulting in a larger active area for the insertion reaction, and higher electronic conductivity after extended cycling.(16, 47) **Fig. 4d** compares the Mg content after full discharge, the results are very close to the theoretical values calculated from capacity, indicating that the discharge capacity is attributable to Mg^{2+} insertion rather than side reactions. The ICP-OES results in **Fig. 4d** show similar Mg/V ratio between cathode before cycling and after full charge, indicating the Mg^{2+} in the as-prepared material maintained a structural role and did not participate in electrochemical activity with the Mg^{2+} electrolyte, consistent with the behavior in Li^+ electrolyte, **Fig. 3d**. Considering the cycling performance of **MVO-1**, this material with an average voltage of 3.0 V (vs Mg^{2+}/Mg) and 420 mWh/g energy density is a promising high voltage cathode material for MIB.

Summary

A novel sol gel synthetic strategy was successfully utilized in the preparation of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels with adjustable Mg content where $x = 0.1$ or 0.2 . Structural analysis showed a lamellar structure with turbostratic ordering along c-axis. The XANES of each spectrum showed there is no change in the absorption edge position between the samples suggesting no formal oxidation state change. Analysis of the EXAFS region in conjunction with the XANES indicated that there is Mg-based distortion primarily manifested on the local V-O coordination, and not the relative structure between the vanadium oxide clusters within the 2D layers. **MVO-1** showed high discharge capacity of 140 mAh/g with near 100% efficiency, a high voltage of 3.0 V and high energy density of 420 mWh/g, showing promise as a cathode material for Mg-ion battery.

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Figure 1. Illustration of the two synthetic strategies of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ gels: The novel ion subtraction strategy (top red) and conventional ion-exchange strategy (bottom blue).

Figure 2. a) XANES of $Mg_xV_2O_5 \cdot nH_2O$ gels and V_2O_5 standard. The inset shows first derivative of $\chi_{\mu}(E)$. b) $|\chi(R)|$ for $Mg_xV_2O_5 \cdot nH_2O$ gels. The distances are not correct for phase shifts, and are represented to be shorter than the actual interatomic distance.

Figure 3 a). Cyclic voltammetry test of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ in 1 M LiPF_6 in EC/DMC (30/70) at 0.1 mV/s scan rate. **b)** Cycle 1 discharge voltage curve of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ versus lithium in 1 M LiPF_6 in EC/DMC (30/70) at 0.1 C, and corresponding c) Specific capacity versus cycle number. d) Mg and Li content per $\text{Mg}_x\text{V}_2\text{O}_5$ formula unit of the cathodes measured by ICP-OES under different conditions.

Figure 4. a) Cyclic voltammetry test of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ versus Ag^+/Ag reference in 0.5 M $\text{Mg}(\text{TFSI})_2$ in acetonitrile/0.5 M dipro-glyme at 0.1 mV/s scanning rate. b) Discharge voltage curve of $\text{Li} / \text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ electrochemical cells in 0.5 M $\text{Mg}(\text{TFSI})_2$ in acetonitrile/0.5 M dipro-glyme and corresponding. c) Cycling performance of $\text{Mg}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ versus Ag^+/Ag reference in 0.5 M $\text{Mg}(\text{TFSI})_2$ in acetonitrile/0.5 M dipro-glyme; d) Mg content per $\text{Mg}_x\text{V}_2\text{O}_5$ formula unit of the cathodes measured by ICP-OES.