Rationally Designed Vanadium Pentoxide as High Capacity Insertion Material for Mg-Ion

Ayan Mukherjee, Sarah Taragin, Hagit Aviv, Ilana Perelshtein, and Malachi Noked*

Owing to high energy density and economic viability, rechargeable Mg batteries are considered alternatives to lithium ion batteries. However besides the chevrel phase, none of the conventional inorganic cathode materials demonstrate reversible intercalation/deintercalation of Mg\(^{2+}\) ions in an anhydrous electrolyte system. The lack of high voltage and high capacity cathode frustrates the realization of Mg batteries. Previous studies indicate that vanadium pentoxide (V\(_2\)O\(_5\)) has the potential to reversibly insert/extract Mg ions. However, many attempts to utilize V\(_2\)O\(_5\) demonstrate limited electrochemical response, due to hindered Mg ion mobility in solid. Here, monodispersed spherical V\(_2\)O\(_5\) with a hierarchical architecture is rationally designed, through a facile and scalable approach. The V\(_2\)O\(_5\) spheres exhibit initial discharge capacity of 225 mA h g\(^{-1}\) which stabilizes at ≈190 mA h g\(^{-1}\) at 10 mA g\(^{-1}\), much higher than previous reports. The V\(_2\)O\(_5\) spheres exhibit specific discharge capacity of 55 mA h g\(^{-1}\) at moderate current rate (50 mA g\(^{-1}\)) with negligible fading after 50 cycles (=5%) and 100 cycle (=13%), while it retains ≈95% coulombic efficiency after 100 cycles demonstrating excellent stability during Mg\(^{2+}\) ion intercalation/deintercalation. Most interestingly, exact phase and morphology are completely retained even after repeated Mg\(^{2+}\) ion intercalation/deintercalation at different current rates, demonstrating pronounced electrochemical activity in an anhydrous magnesium electrolyte.

1. Introduction

Promising alternatives to lithium ion batteries (LIB) for energy storage applications are multivalent batteries as they rely on the transfer of multi-electron during the electrochemical reaction and offer high volumetric energy density when conjugated with metallic anodes.\(^{[1,2]}\) Among various multivalent compounds, magnesium (Mg) metal is considered as the most promising option due to its (1) high specific volumetric capacity (3833 mA h g\(^{-1}\)), and (2) extensive and widespread abundance.\(^{[3,4]}\)

Nevertheless, though Mg batteries are under investigation for few decades now, their realization is restricted due to lack of suitable high voltage cathode material that can tackle the limitations associated with the sluggish Mg\(^{2+}\) ion diffusion into the host.\(^{[5–10]}\) This limitation is due to the high migration barrier induced by high charge to radius ratio of Mg\(^{2+}\) ions. It is expected that these limitations can be mitigated through rational engineering of cathode materials composed of morphologically tuned nanomaterial, open tunnel structures, and layered materials.\(^{[11]}\)

The first prototype of Mg battery was demonstrated using Mo\(_5\)S\(_4\) as cathode, that exhibits excellent performance but within low operating voltage (1.1 V vs Mg),\(^{[12]}\) and limited capacity. Hence, it is desirable to find high voltage cathode host that can reversibly intercalate the divalent Mg\(^{2+}\) ion for realization of Mg batteries in practical devices.\(^{[13]}\) Previous reports on reversible Mg\(^{2+}\) intercalation hosts showed that oxides of transition metals could be promising candidates for high voltage cathode.\(^{[14–17]}\) Owing to the high working voltage and energy density of vanadium pentoxides (V\(_2\)O\(_5\)) it is considered as extremely attractive for Mg batteries.\(^{[18,19]}\)

The orthorhombic V\(_2\)O\(_5\) exhibits spin ladder configuration consisting of distorted corners and edges sharing VO\(_3\) square pyramids connected by weak interlayer bonding, providing large interstitial space for ion intercalation (Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\)). The large interstitial space arises due to weak V–O interaction between three oxygen atoms (O1, O2, O3) and vanadium atom. Previous studies confirm that Li intercalation into orthorhombic V\(_2\)O\(_5\) lattice undergoes several first order phase transition, of which reversible, \(\alpha \leftrightarrow \epsilon \leftrightarrow \delta\) within \(0 \leq x_{Li} \leq 1\) and irreversible, \(\delta \rightarrow \gamma \rightarrow \omega\) at \(x_{Li} \geq 1\) and \(x_{Li} \geq 2\), respectively.\(^{[20–25]}\) The \(\epsilon\) and \(\delta\) phases of V\(_2\)O\(_5\) are orthorhombic containing [VO\(_3\)] square pyramid but higher puckering within the interlayers than \(\alpha\) phase. The irreversible \(\gamma\) phase belongs to the same crystal structure with [VO\(_3\)] square pyramid but even higher puckered interlayers, whereas the \(\omega\) phase belongs to tetragonal structure with completely different atomic arrangement than that of orthorhombic V\(_2\)O\(_5\).\(^{[26]}\) It is evident from some recent studies that orthorhombic V\(_2\)O\(_5\) is a potential host for reversible Mg intercalation with a limit of \(x_{Mg} \approx 0.5\)\(^{[11,16,26–29]}\) which is significantly lower than the Li system. However, the extent of intercalation and hence the specific capacity of V\(_2\)O\(_5\)
can be bumped up using a bilayered xerogel phase (V₂O₅ ⋅ 1.8 H₂O)²⁹,³⁰ which incorporate the water molecules within the interlayers of V₂O₅ polymorph.³¹ Eventually the water molecules not only expand the interlayer spacing of V₂O₅ from 4.37 to 11.53 Å³¹ but also coordinate to the Mg²⁺ ion, screening the charge and facilitating intercalation of Mg²⁺ ion. For instance, Tang et al.³² reported the discharge capacity of 180 mA h g⁻¹ in surface modified V₂O₅ aerogel. Novák³³ demonstrated discharge capacities of ≈170 mA h g⁻¹ using Mg(ClO₄)₂ in water containing acetonitrile (AN) electrolyte (1 m Mg(ClO₄)₂ + 1 m H₂O). Yu and Zhang³⁴ showed similar discharge capacity (≈158.6 mA h g⁻¹) using Mg(ClO₄)₂ in water containing propylene carbonate (PC) electrolyte (1 m Mg(ClO₄)₂ + 1.79 m H₂O/PC). Nevertheless, the strategy of water containing electrolytes and aerogels is not suitable for system with Mg metal anode, therefore its utilization, even as a model system, is important scientifically but not practically.

Several works have been done on V₂O₅ as cathode material for Mg batteries with anhydrous electrolyte, but limited in achieving stable and significant specific discharge capacity.³⁶,³⁷,³⁸,³⁹ The studies clearly evident the choice of nanostructured materials and thin films of V₂O₅ as promising strategy to overcome the sluggish mobility of Mg ions into the cathode. Recently Fu et al.³⁶ demonstrated reversible Mg intercalation in V₂O₅ nanowires with discharge capacity of 130 mA h g⁻¹ at C/20 after few activation cycles using Mg(ClO₄)₂ and AN electrolyte with capacity retention of >90% after 100 cycles. Banerjee et al.³⁷ synthesized a metastable phase of V₂O₅ (z-phase) nanowires and demonstrated 1st discharge capacity of 140 mA h g⁻¹, and retained 90 mA h g⁻¹ after 100 cycles using magnesium bistrifluoromethylsulfonylimide (Mg-(TFSI)₂) as electrolyte. Gershinsky et al.³⁶ found a reversible capacity of 150 mA h g⁻¹ in monolithic V₂O₅ thin film with 20–50 nm primary particle using Mg-(TFSI)₂ in AN. Nevertheless, thin film methodologies are limited in loading of active material, hence reducing the practical capacity of the cell.

In the present study, we demonstrated a facile and scalable approach to synthesize monodispersed orthorhombic V₂O₅ spheres and study the electrochemical activity of this material in dry Mg(ClO₄)₂-AN electrolyte system. The V₂O₅ spheres exhibit the highest reported 1st and 2nd discharge capacity (>190 mA h g⁻¹) and very good long-term stability without any noticeable degradation even upon long cycling at different current rates. Detailed phase evolution with pre- and post-galvanostatic cycling results of structural and morphological study witness the potential of our V₂O₅ as a cathode material in next generation Mg batteries.

2. Result and Discussions

The formation of spherical morphology is governed through the oriented aggregation by particle assembling into the microstructure. Specifically, at the initial stage of reaction, the precursors are grown to layer structure of V(OH)₃·NH₂ through the precipitation reaction of NH₄VO₃, HCl, and N₂H₄·H₂O at room temperature. With the elapse of time the number of layers increase and assembled together where the edges are etched by the solvent simultaneously. As time passes, these layer-by-layer structures transforms into spherical morphology.³⁸ Finally calcination at 350 °C leads to complete oxidation of V(OH)₃·NH₂ to V₂O₅.³⁹ It is worthy to mention here that the precursor concentration, pH value (10 in this case), and reaction time play the pivotal role in the formation of spherical morphology. The morphology of V₂O₅ is depicted by SEM study, shown in Figure 1a,b. The V₂O₅ shows uniform spherical morphology of diameter 230–250 nm and the monodispersity is maintained throughout the sample. The formation of the nanospheres is governed by the orientation of the aggregated nanoparticles assembly trailed by Oswald ripening. In order to dig inside the particle architecture, TEM image shown in Figure 1c confirms that V₂O₅ retains its spherical morphology with excellent crystallinity. The lattice fringes shown in the HRTEM image (Figure 1d) matches with the (0 1 0) plane of orthorhombic V₂O₅. The X-ray diffraction pattern of V₂O₅ spheres is shown in Figure 2a, indicating a phase pure, highly crystalline polyno- morph that crystallizes in orthorhombic crystal structure (space group Pmnm) with simulated lattice parameters are a = 11.52 Å, b = 4.38 Å, and c = 3.57 Å. The pattern discards the possibility of any lattice water content as it differs significantly from hydrated V₂O₅.²⁶

The local structure of V₂O₅ is determined using Raman spectroscopy, shown in Figure 2b of the composite slurry containing V₂O₅ spheres, Super P carbon black, poly(vinylidene fluoride) (PVDF), and N-methyl-2-pyrrolidone (NMP). The V₂O₅ polyhedra exhibit four types of V–O bonds and occupy four sites in the [VO₃] slab depending on the bond lengths. Among the bonds V–O₁ is the short and strong apical, the V–O₂ bond forms both ladder step and interchain within the [VO₂] slab, and V–O₃ forms the bridge between two V atoms. The high frequency mode appears at 994 cm⁻¹ is denoted as ν(1), arises due to z displacement of O₁ atoms and belongs to in-phase stretching vibration of apical bond. The mode located at 798 cm⁻¹ arises due to the formation of V–O₃–V bridge. The band located at 699 cm⁻¹ arises due to the antiphase stretching of V–O₂ bond. The Aₓ mode located at 529 cm⁻¹ originates from the stretching vibration and displacement of O₂ atom along the x direction. The bending vibration of bridge angle V–O₃–V is observed from the band located at 485 cm⁻¹. The band appears at 405 and 284 cm⁻¹ due to the x and y displacement of O₁ atom and the band at 305 cm⁻¹ is due to the z displacement of O₂ atom. Further the band at 405 cm⁻¹ corresponds to V–O₁ rocking along the xx plane and the band at 302 cm⁻¹ corresponds to the combined oscillation of O₁ atom along y direction and O₂ atom along z direction. The low frequency band at 197 cm⁻¹ belongs to Aₓ and Bₓ modes whereas the intense band at 133 cm⁻¹ belongs to Bᵧ and B₂ᵧ modes.⁴⁰ The peak positions are well consistent to previous studies on orthorhombic V₂O₅.¹⁶,⁴¹ validating the XRD results. The claim and surface analysis is further preciously studied using X-ray photoelectron spectroscopy (XPS). Mendialdua et al.⁴¹ demonstrate successfully that in order to determine the oxidation of vanadium, O1s signal is a better choice of reference energy than that of Cls or even the difference in binding energy between the O1s and V2p3/2 core level to determine the oxidation state of vanadium more precisely. Figure 2c shows the
XPS spectra of V2p and O1s core level of the composite slurry and fitted following the procedure of Silversmit et al. [42] The intense peak of O1s and V2p 3/2 is positioned at 529 and 516 eV respectively, indicating that vanadium in the present case exists only in +5 oxidation state. [42] The small shoulder peak of C=O positioned at ≈ 530.2 eV arises due to the composite slurry. The XPS full spectra of the composite slurry shown in Figure 2d are consistent with the composition.

In order to study and in-depth interpretation of the magnesium electrochemistry, it is essentially desired and convenient to study the lithium electrochemistry which acts as accurate and delicate marker for the intercalation/deintercalation behavior of our V2O5 spheres. For this purpose, a coin cell assembly is fabricated (Li/V2O5) in LP57 electrolyte. A stable open circuit voltage (OCV) of 3.42 V versus Li indicates complete oxidation of vanadium. [43] A typical cyclic voltammogram (CV) of V2O5 spheres at 0.25 mV s−1 is shown in Figure S1 (Supporting Information). The CV curve shows two distinct reduction peaks at 3.34 V, and 3.14 V versus Li along with a shoulder peak at 3.08 V versus Li, indicating the reduction of V5+ into a mixture of V4+ and V3+ along with the formation of ε-LixV2O5 and δ-LixV2O5. During anodic sweep the reversibility of the phase transformation is well retained and validated through the appearance of peaks at 3.34 and 3.49 V versus Li along with the shoulder at 3.25 V versus Li, similar to previous report by Madhavi et al. [44] and Aurbach et al. [45] Subsequent cycling clearly recites negligible capacity fading and high reversibility of the V2O5 spheres. Further, in order to study the magnesium electrochemistry, a three electrode flooded cell is used (Figure S2, Supporting Information) using V2O5 spheres coated in Pt electrode as working electrode (WE), AC (= 4 times weight of active mass) as counter electrode (CE), AC (= 2 times weight of active mass) as reference electrode and 0.2 M Mg(ClO4)2 in AN as electrolyte (the pre-measurement treatment of the AC and electrolyte is mentioned in experimental section). Figure 3a displays the first galvanostatic charge/discharge profile of V2O5 spheres that exhibit specific discharge capacity of 225 mA h g−1 with distinct and flat charge and discharge plateaus demonstrating significantly improved kinetics than previous reports. [26,37,43,46,47] Further in order to understand the charge/discharge mechanism, the differential capacity (dQ/dV) is plotted versus voltage from the galvanostatic data (Figure 3b). During intercalation, two distinct peaks are observed that are positioned at ≈ 2.04 V (vs Mg/Mg2+) and ≈ 2.01 V (vs Mg/Mg2+2), while during deintercalation, three peaks appear at 2.17 V (vs Mg/Mg2+), 2.18 V (vs Mg/Mg2+), and 2.20 V (vs Mg/Mg2+2). Further, CV data of V2O5 spheres as working, Mg metal as counter, and reference electrodes are recorded in APC electrolyte is shown in Figure S3 (Supporting Information). The CV shows reversible intercalation/deintercalation of Mg2+ ions in V2O5 lattice even in APC electrolyte through the appearance of reduction peaks at 1.67 V (vs Mg/Mg2+) and 1.57 V (vs Mg/Mg2+) and oxidation peaks at
1.86 V (vs Mg/Mg$^{2+}$) and 1.9 V (vs Mg/Mg$^{2+}$) with a shoulder at 1.8 V (vs Mg/Mg$^{2+}$). The detailed characterization and electrochemical studies of the V$_2$O$_5$ spheres in APC electrolyte are beyond the scope of this article.

In order to approximate the phase formation during insertion of Mg$^{2+}$ ion into the layers of V$_2$O$_5$ spheres, we conducted ex situ ICP, XRD, and Raman study of a discharged cell. The WE after discharge, washed with AN for several times and dried in dynamic vacuum overnight. The structural phase evolution is determined from the XRD study shown in Figure 4a. It is observed that all the peaks corresponding to $\alpha$-V$_2$O$_5$ disappear completely and new peaks appear that match with Mg$_{0.45}$V$_2$O$_5$ (ICDD no. 040-1171). The molar ratio of Mg:V, estimated from ICP is 0.176, suggesting 0.352 Mg per V$_2$O$_5$ unit, which is in reasonable agreement with the XRD. The broadening of the peaks is due to slight amorphous nature of the discharged V$_2$O$_5$ spheres, which is the signature of magnesiated V$_2$O$_5$, confirmed previously from scanning tunneling electron microscopy (STEM) and electron diffraction. The broad hump at 40° is due to the presence of carbon in the composite slurry. In order to study the local disorder, Raman study is carried out in V$_2$O$_5$ spheres after Mg$^{2+}$ intercalation shown in Figure 4b that compares the Raman spectra of pristine V$_2$O$_5$ and Mg$^{2+}$ intercalated V$_2$O$_5$. The peaks corresponding to V$_2$O$_5$ becomes relatively weak and few are even disappear (485 and 644 cm$^{-1}$) after Mg$^{2+}$ intercalation, indicating a significant change in the local structure.

Figure 2. a) XRD pattern, b) Raman spectra, c) XPS spectra of V2p and O1s, and d) survey spectra of V$_2$O$_5$ spheres.

Figure 3. a) 1st galvanostatic profile at 10 mA g$^{-1}$, b) dQ/dV of 5th cycle at 10 mA g$^{-1}$ of V$_2$O$_5$ spheres.
structure, similar to previous report on operando Raman study of Li intercalated V$_2$O$_5$.[48] The changes and also appearance of a major peak at $\approx900$ cm$^{-1}$ due to the formation of a magnesiumated V$_2$O$_5$ ($\varepsilon$-Mg$_{0.6}$V$_2$O$_5$) are well established from previous studies.[16,26,36] The Mg$^{2+}$ ions are intercalated into the interlayers of the V$_2$O$_5$ spheres and coordinated with the oxygen atom to form a magnesiated V$_2$O$_5$ phase ($\varepsilon$-Mg$_x$V$_2$O$_5$) after discharging, while after charging, it reverts back to its initial phase ($\alpha$-V$_2$O$_5$). However, the extent of reversible Mg$^{2+}$ ion intercalation/deintercalation depends entirely on the stability of the V$_2$O$_5$, which arises from tailored monodispersed morphology of the spherical V$_2$O$_5$. The aligned interlayers of the monodispersed spheres facilitated the intercalation/deintercalation of Mg$^{2+}$ ions and accounted for excellent reversibility and high specific capacity. The electrochemical analysis of $dQ/dV$ indicates that magnesiation and de-magnesiation in V$_2$O$_5$ spheres undergo multiple intercalation/deintercalation processes with different thermodynamics and kinetics along with different phase transition. Novák et al.[11] identified ten different phases in the Mg-V$_2$O$_5$ phase diagram, but a more detailed study of multi-steps phase formation with exact kinetics and thermodynamics is undergoing and is beyond the scope of the present study.

The rate performance of V$_2$O$_5$ spheres as shown in Figure 5 reveals that with increasing the current density from 10 mA g$^{-1}$ $\rightarrow$ 30 mA g$^{-1}$ $\rightarrow$ 50 mA g$^{-1}$ $\rightarrow$ 80 mA g$^{-1}$ and reverse back to 10 mA g$^{-1}$ reversibility is retained excellently. Specifically, the first discharge capacity of V$_2$O$_5$ spheres is as high as 225 mA h g$^{-1}$ due to the decomposition of electrolyte on the cathode interface and formation of a thin cathode electrolyte interface (CEI) layer. The high specific discharge capacity stabilizes at $\approx190$ mA h g$^{-1}$. Further increasing the current density, specific discharge capacity of $\approx100$, 60, and 40 mA h g$^{-1}$ is achieved at 30, 50, and 80, respectively. It is important to note that the specific discharge capacity of $\approx55$, 95, and 187 mA h g$^{-1}$ is recovered at 50, 30, and 10 mA g$^{-1}$ respectively, demonstrating excellent rate capability of the V$_2$O$_5$ spheres. A feeble decrease in specific discharge capacity during the initial cycles is attributed due to the fact the few Mg$^{2+}$ ions are trapped at the dead sites and cannot deintercalate from the V$_2$O$_5$ lattice during subsequent charging. However, these trapped Mg$^{2+}$ ions act as layer pillars which improve the stability of the V$_2$O$_5$ structure and provide excellent rate capability.[39]

The voltage profiles versus specific capacity of the 10th, 50th, 100th cycle of V$_2$O$_5$ spheres at current density of 50 mA g$^{-1}$ are shown in Figure 6a. The profiles exhibit two distinct charge/discharge plateaus which correspond to intercalation/deintercalation of Mg$^{2+}$ ions into the V$_2$O$_5$ layers. The specific discharge capacity is 55, 52, and 42 mA h g$^{-1}$ after 10th, 50th, 100th cycle. It is observed that the capacity fading is very feeble up to 50 cycles ($\approx$5%) and 100 cycle ($\approx$13%) demonstrating excellent capability of Mg$^{2+}$ ion intercalation/deintercalation of the V$_2$O$_5$ spheres during crude electrochemical cycling. The cycling stability or round trip efficiency of V$_2$O$_5$ spheres is further validated from Figure 6b. It is observed that V$_2$O$_5$ spheres retained $\approx95$% columbic efficiency after 100 cycles demonstrating excellent stability during Mg$^{2+}$ ion intercalation/deintercalation. The performance of the V$_2$O$_5$ spheres in Mg battery is compared with state-of-the-art report, as given in Table S1 (Supporting Information) and it is observed that the uniform spherical morphology exhibits superior activity as compared to others. The excellent performance is attributed to the fact that uniform spherical morphology increases the effective contact area between electrode and electrolyte and leads to complete utilization of active material which facilitates rapid diffusion of Mg$^{2+}$ ions into the V$_2$O$_5$ lattice.

Figure 4. a) XRD pattern and b) Raman spectra of 1st discharged V$_2$O$_5$ spheres.

Figure 5. Rate performances of V$_2$O$_5$ spheres.
Post-cycling analysis is done on the cycled V$_2$O$_5$ electrodes after washing the electrode with AN and drying overnight to check the structural, morphological, and compositional changes due to crude electrochemical cycling (several galvanostatic charge/discharge cycles in various current rates). Figure 7a–c shows the XRD pattern of uncycled V$_2$O$_5$ spheres (black) and cycled V$_2$O$_5$ spheres (red), zoomed in 2$\Theta$ = 20–21° and 2$\Theta$ = 25.6–26.8°, respectively. The pattern reveals that after cycling the V$_2$O$_5$ spheres retained their initial phase and crystal structure with small shifting of the whole pattern toward lower angle side. The shifting of the pattern supports the claim of multiple intercalation/deintercalation of Mg$^{2+}$ ions and accounted for obvious increase in the interplanar spacing ($d$). The pattern of pristine V$_2$O$_5$ sphere (Figure S4a, Supporting Information) shows the low magnification and high magnification SEM image of the cycled V$_2$O$_5$ electrode. It is distinctly observed that the V$_2$O$_5$ retained its spherical morphology and monodispersion eventually after the electrochemical cycling. Figure 8 distinctly compares the pre- and post-cycling XPS study of the V$_2$O$_5$ spheres. After the cycling, the peak position of V2p and the difference of V2p and O1s are retained without any shift in binding energy. The postmortem analysis validates the stability of the V$_2$O$_5$ spheres while cycling in Mg electrolyte. The certain decrease in specific capacity and columbic efficiency during long cycles might be accounted for the formation of CEI layer due to some electrolyte decomposition and other parasitic reactions that limit the penetration of Mg ion into the active material. The CEI formation is further validated through the postmortem XPS analysis of the C1s spectra as shown in Figure S5 (Supporting Information). The C1s spectra of pristine V$_2$O$_5$ sphere (Figure S5a, Supporting Information) contain three major peaks, of which the peak positioned at 284.6 eV (C–C, C=C) belongs to conductive
In summary, we demonstrate a facile and scalable synthesis approach for spherical V$_2$O$_5$. Owing to the monodispersed size of ~250 nm and spherical geometry, the V$_2$O$_5$ exhibits pronounced Mg$^{2+}$ ion intercalation/deintercalation. The reversible phase transformation from α- V$_2$O$_5$ to ε- V$_2$O$_5$ is established from the ex situ XRD and Raman studies. A high specific discharge capacity of 225 mA h g$^{-1}$ is achieved at 10 mA g$^{-1}$ for 1st cycle, which stabilizes at ~190 mA h g$^{-1}$, while at high current density of 80 mA g$^{-1}$, it exhibits stable specific discharge capacity of ~40 mA h g$^{-1}$. The columbic efficiency of ~95% explicitly supports the excellent reversibility of the V$_2$O$_5$ spheres in anhydrous Mg electrolyte. Post-cycling structural and morphological analysis is evident from the excellent stability and sustainability of the spherical V$_2$O$_5$ during repeated Mg$^{2+}$ ion intercalation/deintercalation at different current density. Our study paves the way for rational design of meso-scaled architecture cathodes for rechargeable Mg batteries.

4. Experimental Section

**Synthesis of V$_2$O$_5$ Spheres:** The precursors were purchased from Sigma Aldrich and used without further purification. In a typical synthesis of monodispersed spherical V$_2$O$_5$, 0.01 moles of ammonium metavanadate (NH$_4$VO$_3$) undergo vigorous stirring in 100 ml ultrapure water (MilliQ 18.2 MQ) till a transparent solution was achieved. A transparent yellow solution was obtained by adding 3 ml of 1 M HCl solution slowly under vigorous stirring. The pH of the solution was adjusted by adding appropriate amount of hydrazine (N$_2$H$_4$.H$_2$O), which was further subjected to vigorous stirring for 3 h till a gray precipitate of V(OH)$_3$.NH$_2$ was obtained. The precipitate was washed several times with copious amount of water and ethanol and dried overnight at 60 °C. The obtained precursor was calcined at 350 °C for 2 h @ 5 min$^{-1}$ to get spherical V$_2$O$_5$.

**Physical Characterization:** The exact phase and crystal structure were studied by X-ray diffraction (XRD) using Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation (λ = 1.5414 Å). The simulation of lattice parameters was done using Rietveld refinement method using Maud software. The background parameters were fitted with polynomial of degree four and convergence of the parameters were continued till goodness of fit (f1) was achieved, similar to previous reports.$^{57-59}$

The surface morphology and monodispersity of the V$_2$O$_5$ spheres were established using environmental scanning electron microscope (ESEM, Quanta 2000, from FEI). The highly crystalline nature of the V$_2$O$_5$ was further confirmed through high resolution transmission electron microscopy (HR-TEM, JEM 2000, JEOL, Accelerating Voltage 200 kV, Gatan US& 4000 4 x 4k camera). The binding energy and valance state of vanadium were determined using X-ray photoelectron spectroscopy (XPS) study (Thermo Scientific Nexsa spectrometer). The local environment of the V$_2$O$_5$ spheres was manifested by Raman spectroscopy using micro-Raman (LabRam HR) with excitation wavelengths of 332 nm. The final composition of the intercalated V$_2$O$_5$ spheres was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) technique (Ultima-2 spectrometer (JobinVyon Horiba)).

**Electrode Preparation:** The slurry was prepared by mixing 80% of the active material (V$_2$O$_5$ spheres), 10% of Super P carbon black, and 10% of poly(vinylidene fluoride) (PVDF). The slurry was diluted to appropriate concentration by N-methyl-2-pyrrolidone (NMP). The mixture was mixed homogeneously using a Thinky mixer (ARV-310/ARV-310 LED) at 2000 rpm, 30 kPa for 3 min several times by adding NMP. Few clean platinum plates (8 x 8 mm) was coated with slurry and dried overnight at 100 °C to remove the NMP. The dried coated Pt electrodes were then subjected to vacuum drying again at 100 °C for 15 h to remove any traces of moisture. In order to build the electrodes for coin cell, a clean and polished Al foil was coated (60 µm thick) with the prepared slurry doctor blade and dried for overnight at 100 °C. The dried coated slurry was rolled uniformly and electrodes of diameter 9 mm were punched and again dried for 15 h under vacuum at 100 °C.

Based on the measurement conditions using magnesium perchlorate (MgClO$_4$)$_2$ in acetonitrile (AN) as electrolyte system and previous studies$^{61}$ to construct the 3-electrode flooded cell, high surface area (2000 m$^2$ g$^{-1}$) activated carbon (AC) cloth (507–20 type) procured from Kynol as quasi-reference electrode (RE) and counter electrode (CE) was considered. Prior to use the AC, it was dried for 48 h at 100 °C under dynamic vacuum.

**Electrolyte Preparation:** High purity anhydrous MgClO$_4$ and AN were procured from Sigma Aldrich. In order to ensure moisture free electrolyte system, the MgClO$_4$ was subjected to heat treatment at 150 °C under dynamic vacuum for 48 h, and AN was dried in molecular sieves (4 Å) for several days inside Ar filled glovebox. A 0.2 M MgClO$_4$ solution in AN was prepared by stirring for 24 h inside Ar filled glovebox. Since drying perchlorate was not trivial, but a methodology was established that was well documented and reported by the team in Bar-Ilan University at literature. Over the years this process enabled production of dozens of dried electrolyte solution with typical values of less than 18 and 117 ppm for AN and electrolyte solution, respectively.$^{63,64}$ All phenyl complex (APC) electrolyte solution was prepared by slow addition of AlCl$_3$ into PhMgCl/THF solution. The final electrolyte concentration was 0.25 m AlCl$_3$ and 0.5 m PhMgCl in THF. The resulting solution was stirred for 24 h at room temperature inside Ar-filled glovebox.

**Figure 8.** XPS spectra of pre- and post-cycling V$_2$O$_5$ spheres.
Electrochemical Measurement: In 3-electrode assembly, comprising spherical V2O5 as working electrode (WE), AC as both counter electrode (CE) and reference electrode (RE), electrochemical measurements were carried out using multi-potentiostat/galvanostat instruments (VMP-3 potentiostat, Bio-Logic). The measurement was done inside Ar filled glovebox. The 2032-coin cell was constructed using 9 mm V2O5 electrode as WE, metallic Li as CE, and LP57 as electrolyte. Two pieces of polypropylene separators of diameter 18 mm were placed between WE and CE. The cell construction was done inside glovebox and measured in BCS-805 battery cycler (Bio-Logic Science Instruments).

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

Acknowledgements
The authors acknowledge financial support through European Union’s Horizon 2020 research and innovation program under grant agreement No. 824066 (E-MAGIC). A.M. acknowledges Planning and Budget Committee (PBC) Israel for fellowship.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
electrochemistry, Mg battery, spherical morphology, vanadium pentoxide

Received: April 22, 2020
Revised: May 19, 2020
Published online: July 15, 2020

[1] R. Van Noorden, Nature 2014, 507, 26.
[2] J. Muldoon, C. B. Bucur, T. Gregory, Chem. Rev. 2014, 114, 11683.
[3] M. Matsui, J. Power Sources 2011, 196, 7048.
[4] C. Ling, D. Banerjee, M. Matsui, Electrochim. Acta 2012, 76, 270.
[5] P. Canepa, G. Sai Gautam, D. C. Hannah, R. Malik, M. Liu, K. G. Gallagher, K. A. Persson, G. Ceder, Chem. Rev. 2017, 117, 4287.
[6] P. Canepa, G. S. Gautam, R. Malik, Z. Rong, K. R. Zavadil, K. Persson, G. Ceder, Chem. Mater. 2015, 27, 3317.
[7] G. S. Gautam, P. Canepa, A. Urban, S. Bo, G. Ceder, Chem. Mater. 2017, 29, 7918.
[8] Z. Rong, R. Malik, P. Canepa, G. S. Gautam, M. Liu, A. Jain, K. Persson, G. Ceder, Chem. Mater. 2015, 27, 6016.
[9] R. D. Bayliss, B. Key, G. S. Gautam, P. Canepa, B. J. Kwon, S. H. Lapidus, F. Dogan, A. A. Adil, A. S. Lipton, P. J. Baker, G. Ceder, J. T. Vaughey, J. Cabana, Chem. Mater. 2020, 32, 663.
[10] P. Canepa, S. Bo, G. S. Gautam, W. D. Richards, T. Shi, Y. Tian, Y. Wang, J. Li, B. Key, G. Ceder, Nat. Commun. 2017, 8, 1759.
[11] R. Imhof, O. Haas, P. Novák, Electrochim. Acta 1999, 45.
[12] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moskovich, E. Levi, Nature 2000, 407, 724.
[13] D. Aurbach, G. S. Suresh, E. Levi, A. Mitelman, O. Mizrahi, O. Chusid, M. Brunelli, Adv. Mater. 2007, 19, 4260.
[46] R. Attias, M. Salama, B. Hirsch, R. Pant, Y. Gofer, D. Aurbach, ACS Energy Lett. 2019, 4, 209.
[47] H. D. Yoo, J. R. Jokisaari, Y. S. Yu, B. J. Kwon, L. Hu, S. Kim, S. D. Han, M. Lopez, S. H. Lapidus, G. M. Nolis, B. J. Ingram, I. Bolotin, S. Ahmed, R. F. Klie, J. T. Vaughey, T. T. Fister, J. Cabana, ACS Energy Lett. 2019, 4, 1528.
[48] R. Baddour-Hadjean, J. P. Pereira-Ramos, C. Navone, M. Smirnov, Chem. Mater. 2008, 20, 1916.
[49] A. Mukherjee, T. Sharabani, R. Sharma, S. Okashy, M. Noked, Batteries Supercaps 2020, https://doi.org/10.1002/batt.201900202.
[50] A. Mukherjee, T. Sharabani, I. Perelshtein, M. Noked, Batteries Supercaps 2020, 3, 52.
[51] A. Nurpeissova, D.-I. Park, S.-S. Kim, Y.-K. Sun, J. Electrochem. Soc. 2016, 163, A171.
[52] B. Deng, H. Wang, W. Ge, X. Li, X. Yan, T. Chen, M. Qu, G. Peng, Electrochim. Acta 2017, 236, 61.
[53] L. Yang, B. Ravdel, B. L. Lucht, Electrochem. Solid-State Lett. 2010, 13, A95.
[54] R. D. Bayliss, B. Key, G. Sai Gautam, P. Canepa, B. J. Kwon, S. H. Lapidus, F. Dogan, A. A. Adil, A. S. Lipton, P. J. Baker, G. Ceder, J. T. Vaughey, J. Cabana, Chem. Mater. 2020, 32, 663.
[55] T. Chen, G. Sai Gautam, P. Canepa, Chem. Mater. 2019, 31, 8087.
[56] T. Chen, G. Ceder, G. S. Gautam, P. Canepa, Front. Chem. 2019, 7, 24.
[57] A. Mukherjee, S. Chakrabarty, W.-N. Su, S. Basu, Mater. Today Energy 2018, 8, 118.
[58] M. Banerjee, A. Mukherjee, A. Banerjee, D. Das, S. Basu, New J. Chem. 2017, 41, 10983.
[59] A. Mukherjee, S. Basu, P. K. Manna, S. M. Yusuf, M. Pal, J. Mater. Chem. C 2014, 2, 5885.