

***In operando* Synchrotron Diffraction and *in operando* X-ray Absorption  
Spectroscopy Investigations of Orthorhombic V<sub>2</sub>O<sub>5</sub> Nanowires as Cathode  
Materials for Mg-Ion Batteries**

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## Abstract:

Orthorhombic  $\text{V}_2\text{O}_5$  nanowires were successfully synthesized via a hydrothermal method. A cell-configuration system was built utilizing  $\text{V}_2\text{O}_5$  as the cathode and 1 M  $\text{Mg}(\text{ClO}_4)_2$  electrolyte within acetonitrile, together with  $\text{Mg}_x\text{Mo}_6\text{S}_8$  ( $x \approx 2$ ) as the anode to investigate the structural evolution and oxidation state and local structural changes of  $\text{V}_2\text{O}_5$ . The  $\text{V}_2\text{O}_5$  nanowires deliver an initial discharge/charge capacity of 103 mAh  $\text{g}^{-1}$ /110 mAh  $\text{g}^{-1}$  and the highest discharge capacity of 130 mAh  $\text{g}^{-1}$  in the 6<sup>th</sup> cycle at C/20 rate in the cell-configuration system. *In operando* synchrotron diffraction and *in operando* X-ray absorption spectroscopy together with *ex situ* Raman and X-ray photoelectron spectroscopy reveal the reversibility of magnesium insertion/extraction and provide the information on the crystal structure evolution and changes of the oxidation states during cycling.

**Keywords:** Orthorhombic  $\text{V}_2\text{O}_5$  Nanowires; *In operando* Synchrotron Diffraction; *In operando* X-ray Absorption Spectroscopy; Mg-Ion Batteries

## 1. Introduction

Since the early 1990s, Lithium-ion batteries (LIBs) have been the most significant and widespread used secondary battery. Low-cost, high-safety and high-energy density batteries are highly required and in demand for storage of the intermittent energy from renewable resources, such as solar and wind power. However, the application of LIBs in large-scale energy storage, for instance, power grid, is still limited by the price, resources, and safety issues<sup>1-4</sup>. Because of significantly notable advantages of Mg metal such as the abundant resources, lower cost, high theoretical volumetric capacity (3833 mAh cm<sup>-3</sup>) and high safety, magnesium-ion batteries (MIBs) have been considered as a very promising alternative to replace LIBs<sup>5-8</sup>. Gregory et al.<sup>9</sup> initiated the usable Mg rechargeable battery systems in the 1980s and they developed the electrolyte solutions containing Mg-organo-borate moieties (the first breakthrough in the field), Mg(BBu<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub> within tetrahydrofuran (THF). Although this electrolyte was capable of the reversible deposition/ dissolution and, therefore, the usage of metallic Mg as an anode, the electrochemical window was narrow (< 2 V). The second breakthrough in this field was done by Aurbach et al. in 2000<sup>10</sup>, who introduced the electrolyte solutions formed by the reaction of AlCl<sub>3-n</sub>R<sub>n</sub> Lewis acid with R<sub>2</sub>Mg Lewis base in ethers (THF or glymes). Hence, the first rechargeable magnesium battery composed of Mg metal, Chevrel phase cathode, and Mg(AlCl<sub>2</sub>BuEt)<sub>2</sub> electrolyte was demonstrated. The Mg battery showed excellent cycle life (>3500), low capacity fading with cycling, and very low self-discharge, as well as a wide temperature operating range. Afterward, another advanced electrolyte solution with a wide electrochemical window (>3 V), the all-phenyl-complex (APC) electrolyte, was developed by Aurbach et al.<sup>11</sup>. Despite the potential advantages of Mg and great progress in MIBs, many challenges need to be overcome before the commercialization of MIBs. One of the major issues is the lack of suitable cathode materials and incompatibility of electrolytes with high-voltage cathodes and metallic Mg anodes. Moreover, the most common Mg-ion electrolytes exhibit high corrosion to the battery casing and current collectors. For example, stainless steel would be corroded above 2 V vs Mg<sup>2+</sup>/Mg within the known APC electrolyte<sup>12</sup>. The amount of promising Mg-insertion materials is also limited due to sluggish Mg-ion solid diffusion in the solids originated from the Mg-ion's divalent character of its high charge density and high Mg<sup>2+</sup> migration barriers. The high charge density of Mg<sup>2+</sup> probably contributes to larger desolvation energy of charge transfer at the cathode/electrolyte interface<sup>13-14</sup>, which could give a higher

charge transfer resistance and hinder the ion mobility. The rate capability of the Mg-insertion cathodes can be improved to some extent by using nanomaterials, open tunnel structure or employing layered materials<sup>15</sup>. Thanks to their proven high working voltage and high energy density within LIBs, vanadium oxide materials are extremely attractive for MIBs.

Vanadium pentoxide ( $V_2O_5$ ) has large enough interstitial vacancies to adopt various guest species, such as  $Li^+$ ,  $K^+$ ,  $Na^+$ , as well as  $Mg^{2+}$ <sup>16-18</sup>. For  $V_2O_5$  aerogel, the uptake of 4 mol of  $Mg^{2+}$  per mol  $V_2O_5$  was demonstrated in a chemical magnesiation test<sup>19</sup>. In the past ten years, a lot of work<sup>17, 20-28</sup> has been done on the  $V_2O_5$  as cathode materials for MIBs. However, up to now, only limited capacities have been achieved for this kind of cathode material in electrochemical cells with a Mg electrolyte. For instance, Tang and co-workers<sup>17</sup> reported a discharge capacity of 180 mAh g<sup>-1</sup> for aero-gel  $V_2O_5$  dominated by the surface morphology, such as thin and mesoporous solid phase. Yu and Zhang<sup>20</sup> reported that the electrochemical performance of  $V_2O_5$  in a  $Mg(ClO_4)_2$  electrolyte with propylene carbonate (PC) is determined by  $H_2O$  content in the electrolyte. The highest first discharge capacity of 158.6 mAh g<sup>-1</sup> in this study was demonstrated for a 1 M  $Mg(ClO_4)_2$  + 1.79 M  $H_2O$ /PC electrolyte. Highly reduced  $VO_x$  nanotube delivered an initial discharge capacity of 218 mAh g<sup>-1</sup> in  $Mg(ClO_4)_2$ /acetonitrile electrolyte, as reported by Kim and co-workers<sup>21</sup>. Very recently, Banerjee et al.<sup>24</sup> reported that a metastable  $V_2O_5$  ( $\zeta$ - $V_2O_5$ , space group  $C2/m$ ) delivered an initial discharge capacity of 140 mAh g<sup>-1</sup> and retained discharge capacity of 90 mAh g<sup>-1</sup> after 100 cycles. The  $V_2O_5$  nanoclusters within a porous carbon support with a molecular energy storage mechanism were demonstrated to deliver an initial discharge capacity of 300 mAh g<sup>-1</sup> in the working potential range of 0.5-2.8 V<sup>25</sup>. Gershinsky et al.<sup>28</sup> reported a reversible capacity of ~150 mAh g<sup>-1</sup> for  $V_2O_5$  thin film within a working potential range of 2.2 - 3.0 V vs  $Mg^{2+}/Mg$ . In Gershinsky's work<sup>28</sup>, the weakened intensity of reflections and main reflection shift of 010 to lower angle were observed for  $V_2O_5$  film material via *ex situ* X-ray diffraction (XRD). However, a detailed investigation of structural changes of  $V_2O_5$  in the discharging and charging processes is still missing. *In operando* synchrotron diffraction serves as a highly powerful technique to look into the structural changes of a battery material<sup>29-30</sup>. In order to get a better understanding of the structural evolution of a battery material in "real time", *in operando* synchrotron powder diffraction should be performed. In addition, *in operando* X-ray absorption spectroscopy (XAS) serves as another powerful technique to reveal the local structure and oxidation state during the electrochemical reaction.

Orthorhombic  $\text{V}_2\text{O}_5$  ( $\alpha\text{-V}_2\text{O}_5$ ) has the space group  $Pmn2_1$  and it is composed of  $[\text{VO}_5]$  square pyramid layers connected by sharing edges and corners (distorted) and alternating in an up-up-down-down sequence with every third row being vacant<sup>31</sup>. In addition, there are three different oxygens, O1, O2, and O3, in the structure and the  $\text{V}_2\text{O}_5$  sheet is held together via a weak vanadium-oxygen interaction, which can provide accommodating interlayer space for the intercalation reactions. Concerning lithium-ion batteries, the structural evolution of orthorhombic  $\text{V}_2\text{O}_5$  during Li-ion intercalation has been well investigated<sup>4, 32-36</sup>. The  $\alpha$ -phase is discovered at  $x < 0.1$ , and the  $\varepsilon$ -phase is detected at  $0.35 < x < 0.7$ , while the  $\delta$ -phase is obtained at  $x = 1$  for  $\text{Li}_x\text{V}_2\text{O}_5$ . Beyond  $x = 1$ , an irreversible transformation from  $\delta$ -phase to  $\gamma$ -phase is observed and the  $\gamma$ -phase is capable of being reversibly cycled for  $0 \leq x \leq 2.0$  while remaining within the  $\gamma$ -type structure. The irreversible formation of  $\omega$ -phase with a rocksalt-type structure emerges upon the third lithium insertion into the  $\text{V}_2\text{O}_5$  structure. Among these phases, the  $\alpha$ -,  $\varepsilon$ -, and  $\delta$ -phases composed of  $[\text{VO}_5]$  square pyramids are orthorhombic with an increased puckering in the layers. The  $\gamma$ -phase is also made up of  $[\text{VO}_5]$  square pyramids as well, but it is highly puckered and irreversible (metastable  $\gamma'$ -phase upon complete deintercalation), while the  $\omega$ -phase is tetragonal, which differs greatly from the initial orthorhombic  $\text{V}_2\text{O}_5$  phase. However, some authors suggested the coexistence of  $\text{Li}_x\text{VO}_2$  and  $\text{Li}_3\text{VO}_4$  compounds rather than the  $\gamma$ - and  $\omega$ -phase<sup>36-37</sup>.

To the best of our knowledge, *in operando* techniques have not yet been applied to study the reaction mechanism of  $\text{V}_2\text{O}_5$  materials in MIBs in detail. In the present work, two strategies are proposed to improve the  $\text{Mg}^{2+}$  intercalation into the  $\text{V}_2\text{O}_5$  cathode and to investigate the electrochemical mechanism during cycling: (1) to prepare nanosized  $\text{V}_2\text{O}_5$  materials. It has been demonstrated, by first-principles calculations, that the diffusion barrier of  $\text{Mg}^{2+}$  can be reduced to 0.20 eV in single layered  $\text{V}_2\text{O}_5$ <sup>38</sup> and the  $\text{Mg}^{2+}$  ions' hopping barrier in  $\text{V}_2\text{O}_5$  is 1.26 eV<sup>39-40</sup>, which is 3 times higher than that of 0.35 eV for  $\text{Li}^+$  ions. In addition, it is well known that nanosized materials provide short diffusion lengths for cation insertion, which results in higher capacities. Generally, numerous nanostructured vanadium oxide materials as reported in the literature displayed a superior electrochemical performance because of their high specific areas and short Mg-ion migration pathways. (2) to build a cell-configuration system in a chosen "standard" polar aprotic electrolyte. As reported in several publications<sup>9, 41-42</sup>, passivation films could be formed on the metal for a vast majority of organic solvents and normal salts, such as carbonates and nitriles,  $\text{Mg}(\text{SO}_3\text{CF}_3)_2$  and  $\text{Mg}(\text{ClO}_4)_2$ , respectively. The APC electrolyte

developed by Aurbach has an electrochemical window  $\sim 3.3$  V vs  $\text{Mg}^{2+}/\text{Mg}$ , but it will corrode the stainless steel based cell casing above 2.0 V for  $\text{V}_2\text{O}_5$ . Due to the incompatibility of metallic Mg with chosen "standard" electrolyte, it is necessary to avoid the use of metallic Mg as an anode by adopting a cell-configuration system. In the present study, we studied the electrochemistry of  $\text{V}_2\text{O}_5$  nanowires in 1M  $\text{Mg}(\text{ClO}_4)_2$  in acetonitrile (AN) electrolyte together with  $\text{Mg}_x\text{Mo}_6\text{S}_8$  ( $x \approx 2$ ) anode. The evolution of the crystal structure, oxidation state and local structural changes were studied by *in operando* synchrotron diffraction and *in operando* XAS.

## 2. Experimental

**Synthesis of  $\text{V}_2\text{O}_5$  nanowires:** The  $\text{V}_2\text{O}_5$  nanowires were synthesized via a modified hydrothermal method as reported earlier<sup>43</sup>. Briefly, ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ , 0.3 g), HCl (2 M, 1.0 ml), surfactant P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , where PO and EO are propylene oxide, and ethylene oxide respectively, 0.5 g) and 30 ml of deionized water were mixed (with ultrasonication for 10 mins) and stirred for 1 h. Afterward, the mixtures were put into 50ml Teflon-lined autoclaves and kept for 24 h at 120 °C in an oven. The resultant precipitates were filtered and rinsed three times with distilled water and acetone. The product was annealed at 400 °C for 2 h in the air with a heating rate of 10 °C/min after drying at 120 °C for 24 h under vacuum.

**Synthesis of  $\text{Mo}_6\text{S}_8$ :**  $\text{Mo}_6\text{S}_8$  was synthesized according to the reported work<sup>44</sup>. The  $\text{Cu}_2\text{Mo}_6\text{S}_8$  was synthesized through a molten salt synthesis using KCl as salt. Typically, CuS (0.398 g), Mo (0.602 g),  $\text{MoS}_2$  (1 g), and KCl (2 g) were ground in the glovebox and annealed in an alumina crucible under argon atmosphere. The mixtures were kept at 850 °C for 60 h with a ramping rate of 150 °C/h and then the furnace was cooled down to the room temperature. The residual salt was washed two times with hot distilled water. Then the powder was put into a 6 M HCl solution with strong stirring for 7 h and bubbled with  $\text{O}_2$ , which was required to leach Cu and to obtain the  $\text{Mo}_6\text{S}_8$  product. Finally, the remaining powders were washed with distilled water and dried at 120 °C for 2 h.

**Preparation of two electrolytes:** The preparation of electrolytes was conducted in glove box (Ar atmosphere) with very low  $\text{H}_2\text{O}$  and  $\text{O}_2$  ( $\leq 2$  ppm). APC electrolyte, 0.4 M  $(\text{PhMgCl})_2\text{-AlCl}_3$ , was prepared by dissolving a certain amount of aluminium chloride powder ( $\text{AlCl}_3$ ) and 2 M

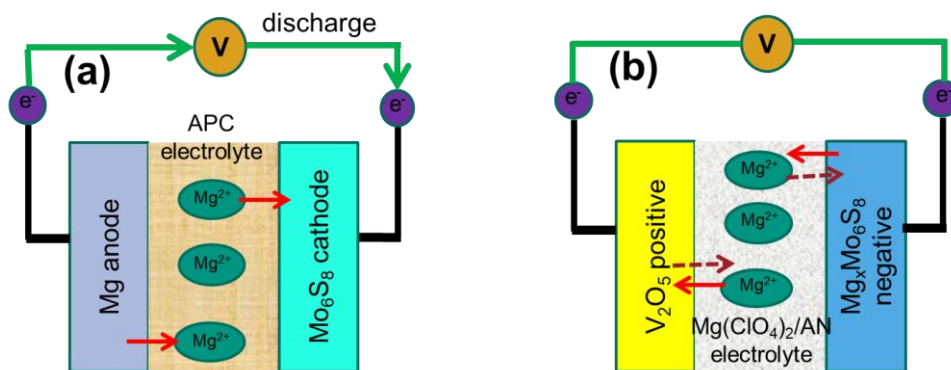
phenylmagnesium chloride solution of tetrahydrofuran ( $\text{PhMgCl}$ )<sub>2</sub>/THF in tetrahydrofuran (THF). All these chemicals were water-free grade and purchased from Sigma-Aldrich. A 1 M  $\text{Mg}(\text{ClO}_4)_2/\text{AN}$  was prepared by dissolving a certain amount of anhydrous  $\text{Mg}(\text{ClO}_4)_2$  (Fox-Chemicals) in anhydrous acetonitrile (Alfa Aesar) with vigorous stirring at room temperature in the Ar-filled glovebox, where  $\text{Mg}(\text{ClO}_4)_2$  and AN are water free without further drying.

**Morphological, Structural and Surface Characterization:** The morphology of materials was characterized with Zeiss Supra 55 scanning electron microscope (SEM) with primary energy of 15 keV. The structural characterizations were done utilizing synchrotron radiation ( $\lambda = 0.4132 \text{ \AA}$ , 30 keV) at the Material Science and Powder Diffraction beamline (MSPD) at ALBA synchrotron (Barcelona, Spain)<sup>45</sup>. The powder diffraction patterns were collected in capillary geometry with powders filled in 0.5 mm  $\varnothing$  boro-silicate capillaries. Raman scattering of the products was recorded on a microscope type HORIBA LabRam Evolution HR with a laser source ( $\lambda = 523 \text{ nm}$ , 10 mW) from 100 to 1100  $\text{cm}^{-1}$ . The washed and dried electrodes after discharging and charging were sealed in a cell with a quartz window inside a glovebox. The window is suitable for *ex situ* Raman measurement. X-ray photoelectron spectroscopy (XPS) was performed utilizing an XPS spectrometer (K-Alpha<sup>+</sup>) with a micro-focused, monochromatized Al  $K_\alpha$  X-ray source (ThermoFisher Scientific, East Grinstead, UK). The sample storage and transportation for XPS characterization were done in an airtight transport vessel under Ar to the spectrometer. Thermo Advantage software was used to perform data acquisition and processing as mentioned elsewhere<sup>46</sup>. One or more Voigt profiles were used to fit the spectra. The graphite C 1s peak at 284.4 eV binding energy is reference for all spectra, which was controlled employing the peaks of metallic Ag, Cu, and Au, respectively. The binding energy uncertainty of intense peaks was about  $\pm 0.1 \text{ eV}$  and the uncertainty of weak peaks was estimated to be  $\pm 0.2 \text{ eV}$ . The Scofield's sensitivity factors<sup>47</sup>, analyzer transmission function, and effective attenuation lengths (EALs) for photoelectrons were employed for quantification and the standard TPP-2M formalism was used to calculate the EALs<sup>48</sup>.

**Electrochemical Characterization:** The electrodes were prepared through mixing  $\text{V}_2\text{O}_5$  nanowires or  $\text{Mo}_6\text{S}_8$  active material, respectively, with Super C65 (TIMCAL) and polyvinylidene difluoride (PVDF) binder with a ratio of 70:20:10 within N-Methyl-2-pyrrolidone solvent. After drying, the cathode materials (active  $\text{V}_2\text{O}_5$  of 3.71 mg with total average thickness of 126  $\mu\text{m}$

and  $\text{Mo}_6\text{S}_8$  of 11.10 mg with total average thickness of  $142\ \mu\text{m}$ ) were pressed on a current collector of 12 mm stainless steel mesh with a thickness of  $60\ \mu\text{m}$  before assembling the 2-electrode Swagelok cells (modified cell design from our previous work<sup>49</sup>, for details see **Fig. S1**). As displayed in **Scheme 1**, before assembling the cell configuration  $\text{V}_2\text{O}_5 \mid \text{Mg}(\text{ClO}_4)_2/\text{AN} \mid \text{Mg}_x\text{Mo}_6\text{S}_8$  ( $x \approx 2$ ), a cell consisting of  $\text{Mo}_6\text{S}_8 \mid \text{APC} \mid \text{Mg}$  was made and discharged to obtain the  $\text{Mg}_x\text{Mo}_6\text{S}_8$  negative electrode. Then, the cell was disassembled and the  $\text{Mg}_x\text{Mo}_6\text{S}_8$  electrode was washed using THF solvent and dried in the glovebox. In the rebuild  $\text{V}_2\text{O}_5 \mid \text{Mg}(\text{ClO}_4)_2/\text{AN} \mid \text{Mg}_x\text{Mo}_6\text{S}_8$  cell configurations, the mass of  $\text{Mg}_x\text{Mo}_6\text{S}_8$  was intentionally in excess (10-15 % capacity excess of  $\text{Mg}_x\text{Mo}_6\text{S}_8$  based on 1 mol of  $\text{Mg}^{2+}$  per mol  $\text{V}_2\text{O}_5$ ). *Note that specific capacities in this work were calculated in terms of the weight of the  $\text{V}_2\text{O}_5$  active cathode material.* A multichannel electrochemical workstation (Bio-Logic VMP) was used to conduct galvanostatic cycling and cyclic voltammetry (long cycling with a rate of C/20; for *ex situ* Raman and XPS with a rate of C/80).

**Ex situ Raman and ex situ XPS Sample Preparation:** the rebuild cell configurations, consisting of  $\text{V}_2\text{O}_5$  and  $\text{Mg}_x\text{Mo}_6\text{S}_8$  with a  $\text{Mg}(\text{ClO}_4)_2/\text{AN}$  electrolyte, were disassembled and washed with AN in Ar-filled glovebox for the 1<sup>st</sup> discharged state at 0.01 V and the 1<sup>st</sup> charged state at 1.6 V with C/80 rate. (For discharged/charged samples, the active  $\text{V}_2\text{O}_5$  of 3.185 mg/2.996 mg with total average thickness of  $\sim 110\ \mu\text{m}$  and  $\text{Mo}_6\text{S}_8$  of 9.24 mg/8.939 mg with total average thickness of  $\sim 135\ \mu\text{m}$ )



**Scheme 1** The compositions of the half-cell for the electrochemical preparation of the  $\text{Mg}_x\text{Mo}_6\text{S}_8$  anode (a) and  $\text{V}_2\text{O}_5 \mid \text{Mg}(\text{ClO}_4)_2/\text{AN} \mid \text{Mg}_x\text{Mo}_6\text{S}_8$  ( $x \approx 2$ ) cell configuration (b)

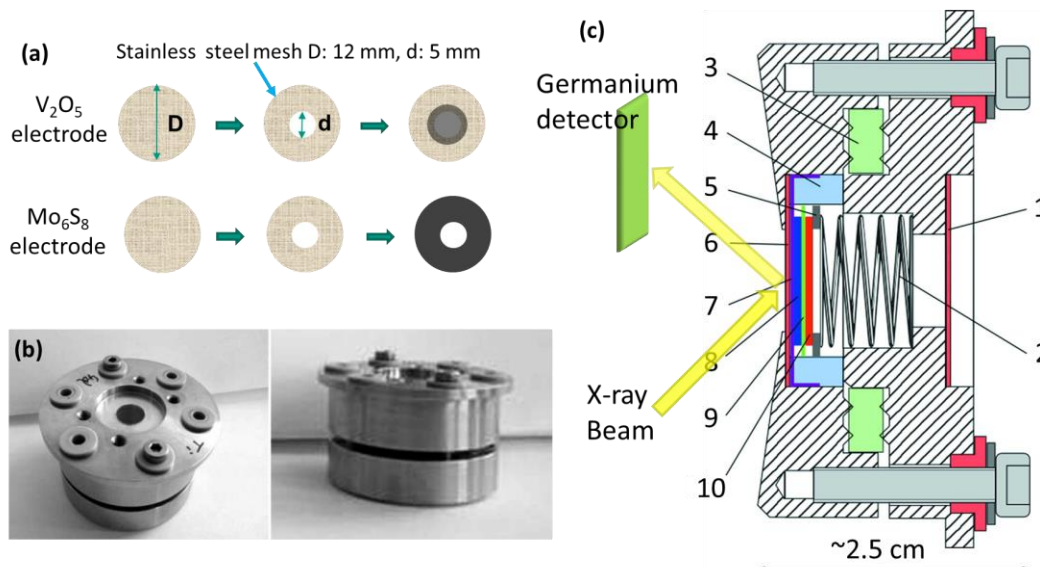


***In operando Synchrotron Diffraction and in operando X-ray Absorption Spectroscopy (XAS):***

*In operando* synchrotron diffraction during cycling was performed at MSPD at ALBA synchrotron. The *in operando* cells for XRD were built by using 2025-type coin cells with a 5 mm diameter beam entrance covered by glass windows. The cathode material ( $V_2O_5$  mixture, in total 4.4 mg with average thickness of 140  $\mu m$ ) was prepared by pressing the mixture on a stainless steel mesh within a 5 mm hole in the center, and a  $Mg_xMo_6S_8$  anode (pure  $Mo_6S_8$  mass: 9.94 mg with total average thickness of 155  $\mu m$ ) was made in the same way, but with a 5 mm hole in the center (**Fig. 1a**). In this way, only the  $V_2O_5$  material will be detected during the *in operando* synchrotron measurements. More details of this setup can be found elsewhere<sup>30</sup>. *In operando* synchrotron diffraction patterns were collected at room temperature and  $\lambda = 0.4132$  Å wavelength (30 keV), utilizing the position sensitive detector MYTHEN. Data were collected with effective exposure time of 60 s in steps of  $0.006^\circ$  over angular range of  $1.8^\circ - 42^\circ$  in 2theta during the first two cycles with C/25 rate. In order to improve the powder averaging (increasing the number of crystallites contribution), the coin cells were continuously oscillated  $\pm 5^\circ$  around the incoming beam direction.

The diffraction data analysis was carried out by the Rietveld method with applying the Fullprof software package<sup>50</sup>. The same model was used for the Rietveld refinement of Mg-poor and Mg-rich phases with different lattice parameters, where the positions of the Mg ions were clarified by Shklover and Haibach<sup>51</sup>. For the Rietveld refinement, the occupancy of Mg was determined and fixed according to the charge and capacity in the electrochemical data, where x in  $Mg_xV_2O_5$  is recorded by EC lab software for each diffraction pattern. *In operando* XAS measurements were conducted at synchrotron at the KIT, Karlsruhe. Photographs and schematic drawing of a modified *in operando* cell set up from our previous work is shown in **Fig. 1b** and **c**<sup>29</sup>. *In operando* XAS measurements were carried out during the first discharge-charge processes with C/25 rate (active  $V_2O_5$  of 3.493 mg with average thickness of 145  $\mu m$  and pure  $Mo_6S_8$  mass of 10.15 mg with average total thickness of 155  $\mu m$ ). XAS spectra of Vanadium K-edge were recorded in quick-XAS (6 min/spectrum) mode in fluorescence geometry using a germanium detector, since the penetration depth is several  $\mu m$  thick (bulk method), and the chances of a fluorescence photon to reach the detector are excellent. The V K-edge for  $V_2O_5$  was measured during the electrochemical cycling and the energy was calibrated using a vanadium foil as commonly employed in XAS experiments.  $V_2O_3$ ,  $VO_2$ , and  $V_2O_5$  were used as standard materials. All the

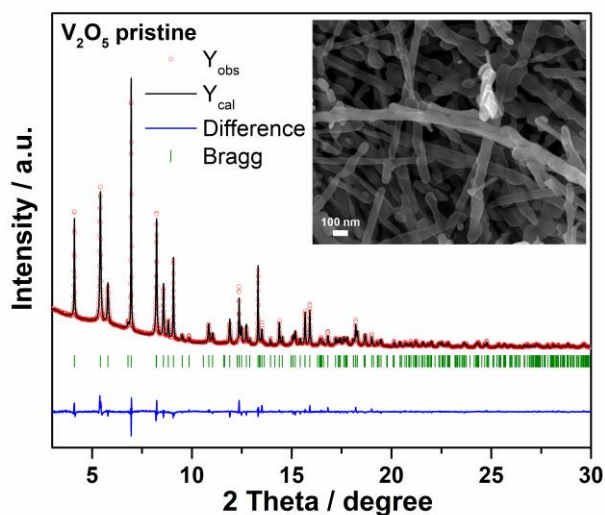
data were collected at room temperature with a Si (111) double crystal monochromator and all the XAS spectra were analyzed and processed utilizing the DEMETER software package<sup>52</sup>.



**Figure 1** Electrode preparation used for *in operando* cell (a), photographs and schematic diagram of the *in operando* cell design (b, c): (1) and (6) 125  $\mu$ m Kapton windows, (2) contact spring (stainless steel), (3) plastic sealing ring, (4) insulating PTFE ring, (5) and (7) current collector and current collector of stainless steel mesh with 9 mm hole in the center, (8) working electrode (WE), (9) Whatmann separator, and (10) counter electrode (CE) (modified cell design from our previous work<sup>29</sup>).

### 3. Results and Discussion

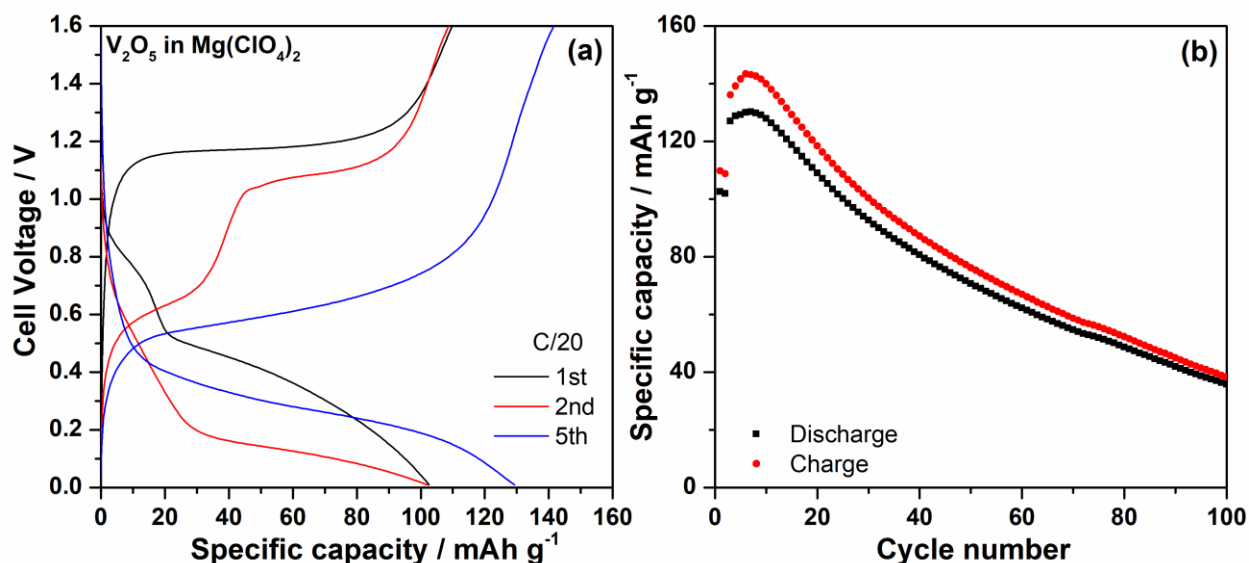
#### 3.1 Structural and Morphological Characterization



**Figure 2** Rietveld refinement from synchrotron diffraction data of  $V_2O_5$  nanowires (inset: SEM image)

The synchrotron diffraction pattern of pristine  $V_2O_5$  nanowires powder is displayed in **Fig. 2**, indicating a high crystallinity of the material. All reflections can be indexed in the orthorhombic  $\alpha$ - $V_2O_5$  structure model with space group  $Pmn2_1$ , and the lattice parameters are  $a=11.511$  Å,  $b=4.373$  Å, and  $c=3.565$  Å, in accordance with a previously published work<sup>51</sup>. It is quite different from the bilayered  $V_2O_5 \cdot nH_2O$ <sup>53</sup> that only has few reflections due to its low crystallinity, implying the water-free crystalline  $V_2O_5$  in the present work. SEM (inset in **Fig. 2**) demonstrates that the  $V_2O_5$  is composed of nanowires. The diffraction confirms that the synthesized  $Mo_6S_8$  crystallizes in space group  $R-3$  (see **Fig. S2**) with lattice parameters  $a=b=9.195$  Å,  $c=10.884$  Å (hexagonal setting, Bragg R-factor=3.74,  $R_f$ -factor=1.81). Two small reflections at  $13.34^\circ$  and  $16.99^\circ$  indicate a very small amount of impurity.

### 3.2 Electrochemical properties



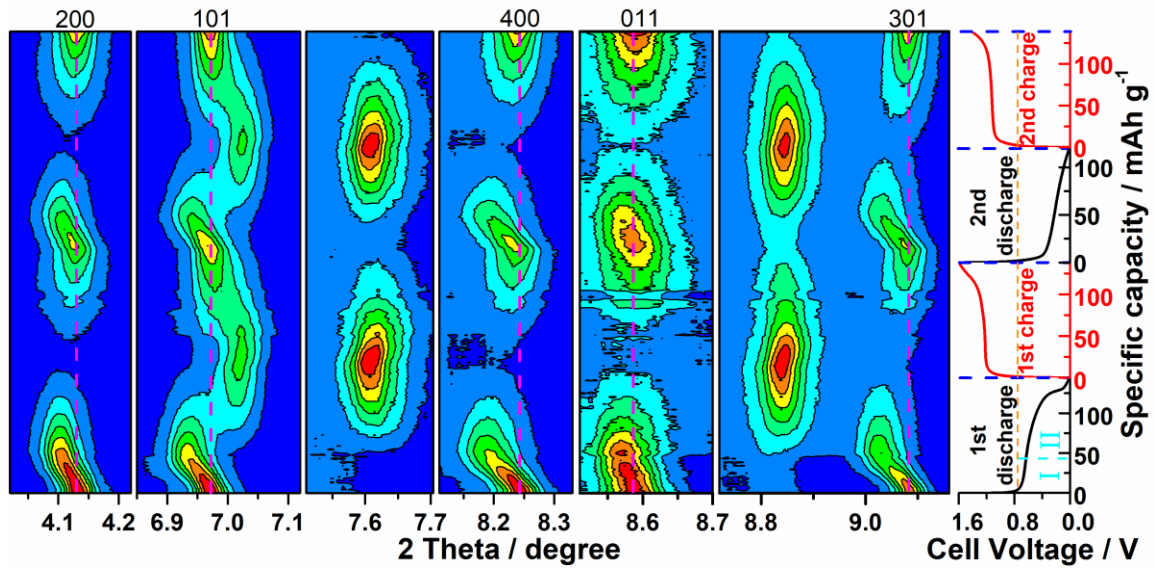
**Figure 3** Discharge-charge profiles (a) and cycling performance (b) of  $V_2O_5 \mid Mg(ClO_4)_2/AN \mid Mg_xMo_6S_8$  ( $x \approx 2$ ) cell configuration (C/20) in the voltage range of 1.6 - 0.01 V.

**Fig. S3** shows the voltage-capacity curve for magnesiation of the  $Mo_6S_8$  electrode in APC electrolyte at C/50. During the 1<sup>st</sup> discharge,  $Mo_6S_8$  exhibits one plateau at around 0.9 V with a first discharge capacity of  $125 \text{ mAh g}^{-1}$  (theoretical capacity of  $128 \text{ mAh g}^{-1}$ ), which is in good agreement with previous works<sup>10-11</sup>. **Fig. 3** displays the cycling behavior of  $V_2O_5$  electrode in a cell configuration with  $Mg(ClO_4)_2/AN$  electrolyte at C/20. During the 1<sup>st</sup> discharge, a short

plateau at around 0.9 V and a long plateau at around 0.4 V are observed. In contrast, only one flat plateau appears at about 1.1 V for the 1<sup>st</sup> charge process. V<sub>2</sub>O<sub>5</sub> delivers an initial discharge/charge capacity of 103 mAh g<sup>-1</sup> (0.35 Mg<sup>2+</sup>)/110 mAh g<sup>-1</sup> and the highest discharge capacity of 130 mAh g<sup>-1</sup> in the 6<sup>th</sup> cycle. The cell exhibits a similar discharge capacity of 102 mAh g<sup>-1</sup> in the second discharge with a lower plateau compared with that of the 1<sup>st</sup> discharge. Since the capacity or the amount of Mg-ion insertion not only depends on the plateau but also depends on the working voltage range, it shows a capacity increase in the following few cycles at C/20, and after 100 cycles, the cell still delivers a capacity of 36 mAh g<sup>-1</sup> as shown in **Fig. 3b**. The possible reason responsible for capacity decay could be attributed to unwanted side reaction<sup>54</sup>, for example, the dissolution of electrode materials V<sub>2</sub>O<sub>5</sub><sup>55-56</sup>, a small contribution of structural irreversibility of V<sub>2</sub>O<sub>5</sub>. The “capacity match” between cathode and anode materials might also play an important role in an “unideal state”<sup>54</sup>. However, understanding the cause of capacity fading with cycling is rather complicated for current operating cell configuration. The real reason responsible for the significant capacity decrease with cycling is required to be understood in the future and it can be the object of the following paper. In the present work, the current density of the C/20 rate is around 14.73 mA g<sup>-1</sup>, suggesting that the Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> could easily provide enough Mg-ions for the intercalation into the V<sub>2</sub>O<sub>5</sub> host structure. This indicates fast kinetics and good rate capability for Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub><sup>7, 10</sup>. Moreover, the 10-15 % excess capacity of Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> could provide enough Mg-ions for all V<sub>2</sub>O<sub>5</sub> particles based on 1 Mg-ion insertion per formula unit. The voltage profiles of the cell configuration are determined by the curves of V<sub>2</sub>O<sub>5</sub> and Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> in half-cells. As the state of charge x in the Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> anode is different for the investigated cell-configurations, different voltage profiles are observed in spite of the same initial V<sub>2</sub>O<sub>5</sub> electrodes. This difference could be caused by the different capacity ratio between cathode and anode materials and the different polarizations resulting from different C rates employed. However, the reaction mechanism of V<sub>2</sub>O<sub>5</sub> would be expected to be the same despite the observation of different voltage profiles when a similar amount of Mg-ions is inserted into the same V<sub>2</sub>O<sub>5</sub> electrode. One has to note that the plateaus cannot be easily distinguished and assigned since cathode V<sub>2</sub>O<sub>5</sub> and anode Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> materials have their peculiar electrochemistry characteristics in the cell-configuration system. In our case, sluggish Mg-ion solid diffusion cannot be avoided despite V<sub>2</sub>O<sub>5</sub> nanowires, but the electrochemical performance can be improved because of their high reaction areas and short Mg-ion migration pathways of the V<sub>2</sub>O<sub>5</sub>

nanowires. We suppose a serious capacity degradation of the cell at higher C rates due to the sluggish Mg-ion solid diffusion. Although the charge/discharge rate of C/20 is too slow for the practical application, it is suitable using such slow rate of C/20 to demonstrate that the cell configuration can work with such configuration and, therefore, **can be used for analyzing V<sub>2</sub>O<sub>5</sub> through *in operando* techniques**.

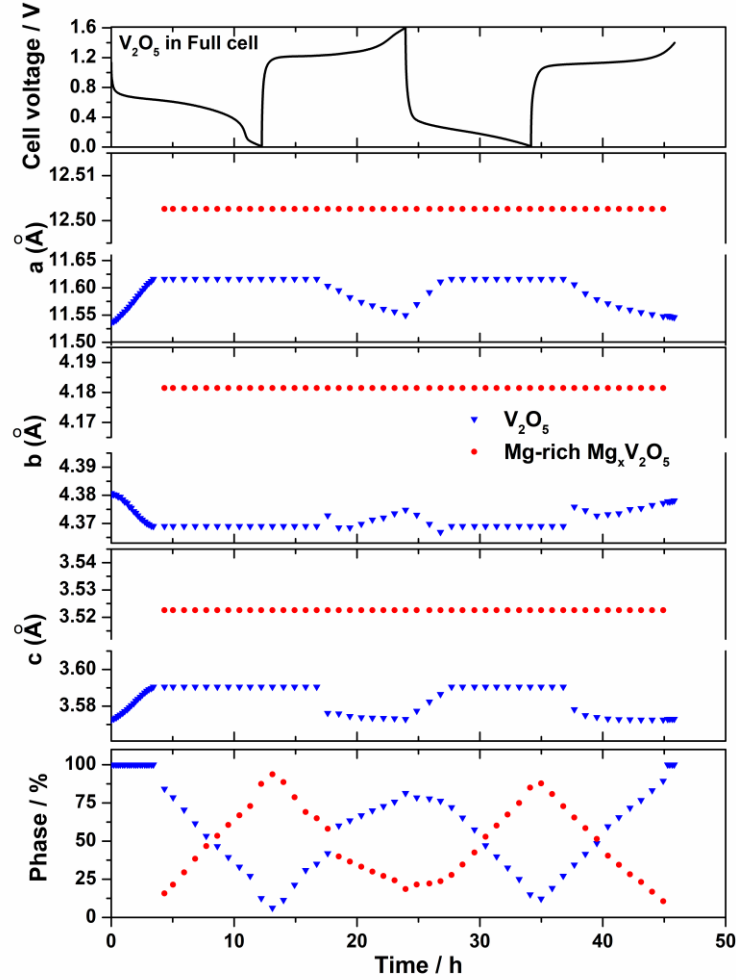
### 3.3 Electrochemical mechanism



**Figure 4** Contour maps of *in operando* synchrotron diffraction of V<sub>2</sub>O<sub>5</sub> collected during the first two discharge-charge processes and the corresponding discharge-charge profiles at C/25 at a cell voltage of 0.01 - 1.6 V

*In operando* synchrotron diffraction was performed to clarify the electrochemical mechanism during the Mg ions insertion and extraction in V<sub>2</sub>O<sub>5</sub>. Contour maps in the selected ranges during the first two cycles are shown in **Fig. 4**. At the initial stage of discharge, all the reflections could be indexed based on an orthorhombic  $\alpha$ -V<sub>2</sub>O<sub>5</sub> phase with space group  $Pmn2_1$  (see the Rietveld refinement of pristine V<sub>2</sub>O<sub>5</sub> in **Fig. S4a**). In the beginning of the 1<sup>st</sup> discharge (Mg insertion), most reflections of V<sub>2</sub>O<sub>5</sub> gradually shift to lower angles, indicating a solid solution process with an expansion of the unit cell (**Region I**). The Mg content of the Mg-poor phase at the end of the solid solution regime was estimated as Mg<sub>0.14</sub>V<sub>2</sub>O<sub>5</sub> with lattice parameters of  $a=11.616$  Å,  $b=4.369$  Å, and  $c=3.591$  Å, according to the diffraction patterns and corresponding electrochemical profile (see the Rietveld refinement of Mg<sub>0.14</sub>V<sub>2</sub>O<sub>5</sub> in **Fig. S4b**, pattern 21<sup>st</sup>). Some new reflections appear at 3.8°, 5.7°, 7.0°, 7.6°, 8.84°, 11.4°, 11.65°, 13.5°, 14.94°, and

15.99° when the composition is  $\text{Mg}_{0.143}\text{V}_2\text{O}_5$ , with a capacity of 42 mAh g<sup>-1</sup>. The intensities of these new reflections increase, while those from the  $\text{Mg}_{0.14}\text{V}_2\text{O}_5$  phase decrease and do not disappear completely at the end of discharge (See **Fig. S5**). Therefore, in the composition range of  $\text{Mg}_{0.143}\text{V}_2\text{O}_5$  to  $\text{Mg}_{0.49}\text{V}_2\text{O}_5$  (Mg in total 0.49 at 0.01V), a two-phase transition between  $\text{Mg}_{0.14}\text{V}_2\text{O}_5$  and a new phase with higher Mg-content occurs (**Region II**). The appearing phase also has an orthorhombic structure with a space group  $Pmn2_1$  as the pristine  $\text{V}_2\text{O}_5$ , but with different lattice parameters. This two-phase transition process was not finished at the end of discharge at 0.01 V due to the limited capacity of 144 mAh g<sup>-1</sup> in the cell configuration. For the Mg-rich phase ( $\text{Mg}_x\text{V}_2\text{O}_5$ ),  $x$  was estimated as 0.6 with lattice parameters of  $a=12.503$  Å,  $b=4.181$  Å, and  $c=3.523$  Å, according to the Rietveld refinement and the corresponding electrochemical profile (see the Rietveld refinement based on pattern 70<sup>th</sup> in **Fig. S4c**). In the very beginning of the 1<sup>st</sup> charge process, the intensities of the reflections from the Mg-rich  $\text{Mg}_x\text{V}_2\text{O}_5$  phase slightly increase, which might be a delay of the structural response, because of the slow  $\text{Mg}^{2+}$  diffusion inside the electrode materials. Then, the intensities of the Mg-rich  $\text{Mg}_x\text{V}_2\text{O}_5$  phase gradually decrease, while those intensities of the phase with lower Mg content grow up. The positions of the reflections remain at slightly lower 2theta values than that for the initial state. This small unit cell expansion indicates either some residual Mg in the host structure or an irreversible transformation, for example, due to a minor oxygen loss. However, the reflections from the Mg-rich  $\text{Mg}_x\text{V}_2\text{O}_5$  phase still exist at the end of the 1<sup>st</sup> charge (see **Fig. S4d**), which might be correlated to the small irreversible capacity. For the second discharge, the evolution of the reflections is very much resembling what is observed for the first discharge, suggesting that the same mechanism remains active during the second and successive cycles. In contrast, the reflections return back to the initial positions of pristine  $\text{V}_2\text{O}_5$  and a single phase is obtained at the end of the 2<sup>nd</sup> charged state at 1.4 V (not reach 1.6 V due to the limited beamtime), indicating the high reversibility of the  $\text{V}_2\text{O}_5$  material during Mg insertion/extraction (see **Fig. S4e**). Note that the ratio of V and O is constantly 2:5 in the chemical formula,  $\text{Mg}_x\text{V}_2\text{O}_5$ , in spite of the existence of minor  $\text{V}^{3+}$  and minor residual from the surfactant symmetric triblock copolymer P123 (confirmed by XPS), as well as the possible dissolution of V ions into the solvent or decomposition of  $\text{V}_2\text{O}_5$ .



**Figure 5** The structural parameters and phases ratios from chosen diffraction patterns with Rietveld refinement during the first two cycles for  $V_2O_5$

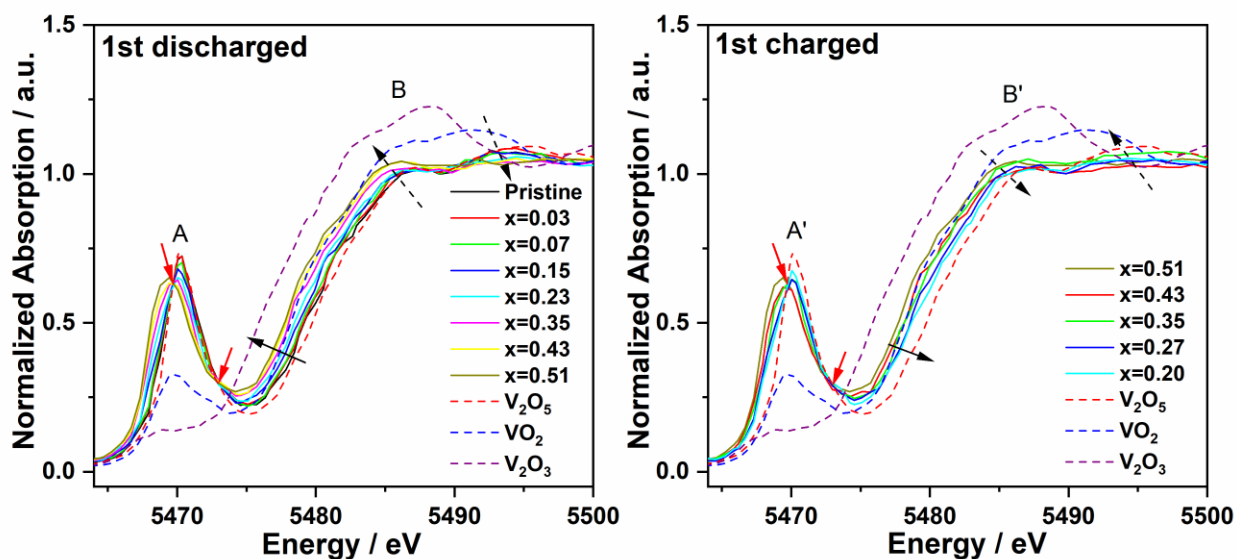
The structural parameters and phases ratios are displayed in **Fig. 5**. At the beginning of the first discharge, the phase  $V_2O_5$  accommodates Mg-ions via a solid solution mechanism up to a limiting stoichiometry of  $Mg_{0.14}V_2O_5$  accompanied by an increase of lattice parameters  $a$  and  $c$  and a decrease of lattice parameter  $b$ . After that, magnesium uptake goes through a two-phase region with the decrease of the  $Mg_{0.14}V_2O_5$  amount and an increase of Mg-rich  $Mg_{0.6}V_2O_5$  phase with constant cell parameters for both phases. The phase ratio of  $Mg_{0.14}V_2O_5$ : $Mg_{0.6}V_2O_5$  is 13:87 at the end of 1<sup>st</sup> discharge. In the 1<sup>st</sup> charge process, the material exhibits first a two-phase transition and then a solid solution together with a two-phase transition (the decrease of  $a$  and  $c$ , the increase of  $b$ ). In the second cycle, the material shows the same behavior as observed in the first discharge-charge process, except the slightly different phase contribution of both phases at the end of 2<sup>nd</sup> discharge ( $Mg_{0.14}V_2O_5$ : $Mg_{0.6}V_2O_5$ =15:85) and a very short region close to the end

of the 2<sup>nd</sup> charge. The V<sub>2</sub>O<sub>5</sub> material returns back to its original structure at the end of the 2<sup>nd</sup> charge. However, in our case, the crystal structure for Mg-rich Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> does not display the same result as reported for the structures of MgV<sub>2</sub>O<sub>5</sub> and Mg<sub>0.2</sub>V<sub>2</sub>O<sub>5</sub>, where MgV<sub>2</sub>O<sub>5</sub> crystallizes in orthorhombic structure with a space group of *Cmcm* and Mg<sub>0.2</sub>V<sub>2</sub>O<sub>5</sub> has the same structure as the parent V<sub>2</sub>O<sub>5</sub> with similar lattice parameters<sup>57-58</sup>. In addition, first-principles calculations, in which a  $\delta$ -phase (space group: *Cmcm*) presuppose a better mobility for Mg diffusion<sup>59</sup>, are not supported by our experimental results either. Meanwhile, first-principles calculations also illustrate that an  $\varepsilon$ -phase<sup>59</sup>, with a specific ordering of Mg-ions at half magnesiated  $\alpha$ -V<sub>2</sub>O<sub>5</sub> host, is the most stable configuration in the  $\alpha$  host and is somehow in agreement with our result, like Li-ordering is discovered in Li-V<sub>2</sub>O<sub>5</sub> system<sup>32, 59</sup>, as well as has Li-ions at alternate locations along with a-axis<sup>60</sup>. Recently, Xiao et al.<sup>61</sup> reported that V<sub>2</sub>O<sub>5</sub> goes through a phase-transition of  $\alpha$ -phase into  $\varepsilon$ -phase and then  $\delta$ -phase in turn upon Mg insertion ( $0 \rightarrow 0.5 \rightarrow 1$ ) using first-principles calculations. In the Li-V<sub>2</sub>O<sub>5</sub> system, it is well known that a topotactic reaction is observed during lithium insertion into V<sub>2</sub>O<sub>5</sub> ( $0 < x < 1$ )<sup>62</sup>, where “topotactic” is used to describe that the basic structure of the positive electrode material is maintained during the reaction. The structure of  $\varepsilon$ -Li<sub>0.46</sub>V<sub>2</sub>O<sub>5</sub> ( $a=11.417$  Å,  $b= 3.565$  Å, and  $c=4.508$  Å) has been identified and is very close to that of  $\alpha$ -V<sub>2</sub>O<sub>5</sub><sup>60</sup>. The newly observed Mg<sub>0.6</sub>V<sub>2</sub>O<sub>5</sub> phase ( $a=12.503$  Å,  $b=4.181$  Å, and  $c=3.523$  Å) can also be called  $\varepsilon$ -Mg<sub>0.6</sub>V<sub>2</sub>O<sub>5</sub> phase since the basic structure of the pristine V<sub>2</sub>O<sub>5</sub> material is maintained, although the differences in the lattice parameters are more pronounced. However, an increase of the interplanar spacing and a decrease of lattice parameter  $a$  were observed during the lithiation of  $\alpha$ -V<sub>2</sub>O<sub>5</sub><sup>60</sup>, different from a decrease of the interplanar distance and an increase of lattice parameter  $a$  as obtained during magnesiation of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> (**Region I** in **Fig. 4**). This is attributed to the larger charge and smaller radii of Mg<sup>2+</sup> in the host structure V<sub>2</sub>O<sub>5</sub>, compressing the layer and extending the  $a$  direction.

In order to probe the electronic and structural environments of V-ions during the electrochemical process, *in operando* X-ray absorption spectroscopy was performed on the V<sub>2</sub>O<sub>5</sub> cathode material in an *in operando* coin cell. For the V K-edge, XAS spectra of V<sub>2</sub>O<sub>5</sub>, VO<sub>2</sub>, and V<sub>2</sub>O<sub>3</sub>, where the V-ions exist in +5, +4, and +3 oxidation states, respectively, are used as standard materials. The edge position of XAS spectra measured at different electrochemical potentials is compared with reference spectra, where the  $x$  values of Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> were determined from the charge and capacity in the electrochemical data recorded by EC lab software for each spectrum.



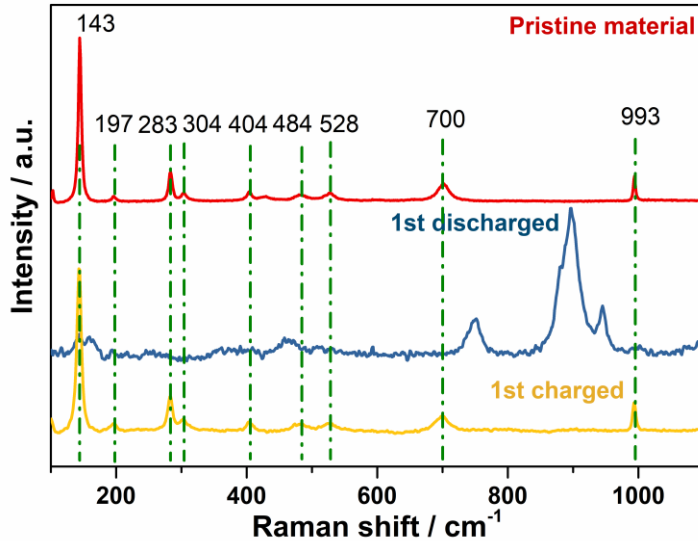
As demonstrated in **Fig. 6**, in terms of V K-edge, the edge position of the XAS spectrum, corresponding to the initial state, is slightly lower than that of  $\text{V}_2\text{O}_5$  reference. Therefore, the oxidation state of V can be confirmed to be mainly +5 in the initial state, which is in agreement with the XPS result for pristine  $\text{V}_2\text{O}_5$  (**Fig. 8**). In addition, an intense pre-edge peak on XANES data for V K-edge of pristine  $\text{V}_2\text{O}_5$  is observed, which is attributed to the transitions between the 1s and bound p-hybridized d-states<sup>63-64</sup> when the centrosymmetric character of V site is lost. This is because the crystal structure of  $\text{V}_2\text{O}_5$  is orthorhombic, made of  $[\text{VO}_5]$  square pyramids layers by sharing edges and corners, and the V-ions are five-fold coordinated by oxygens in a distorted tetragonal pyramid.



**Figure 6** *In operando* X-ray absorption near edge spectroscopy (XANES) for V K-edge during the first discharge-charge process; the isosbestic points are indicated by red arrows.

During the discharging process, the edge position of the V K-edge progressively shifts to lower energy, indicating the reduction of vanadium ions, which attributes to the increase of inserted  $\text{Mg}^{2+}$  ions into  $\text{V}_2\text{O}_5$ . This is consistent with the electrochemical data (see **Fig. S6**) and XPS result in **Fig. 8**. The edge position of the V K-edge for the electrode discharged to 0.01 V ( $x=0.51$  in  $\text{Mg}_x\text{V}_2\text{O}_5$ ) is almost in the middle between that of standard  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ , where a similar result was observed for bilayered  $\text{V}_2\text{O}_5$  after Mg-ion insertion<sup>65</sup>. The pre-edge peak (A in **Fig. 6**) also gradually shifts to lower energy and becomes broad, while the pre-edge peak intensity progressively reduces, suggesting the vanadium ions' reduction and the deformation of the local V environments during  $\text{Mg}^{2+}$  insertion. The broadness of the pre-edge peak is attributed to co-

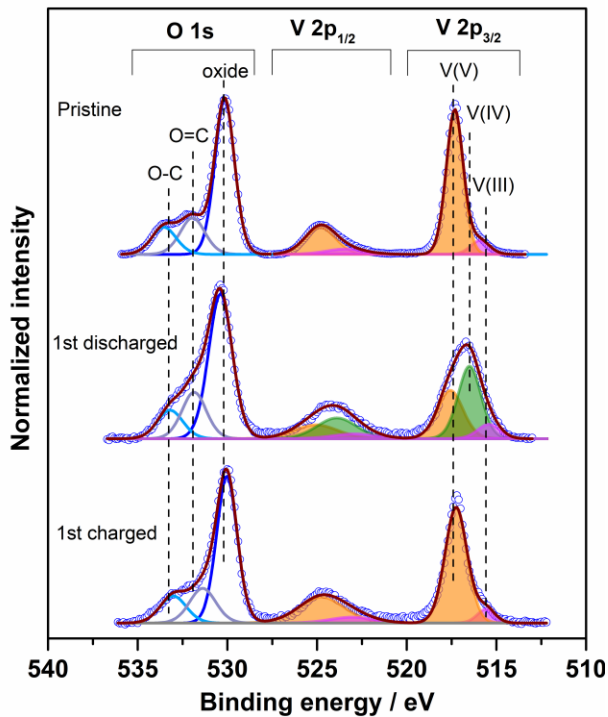
existence of distorted tetragonal pyramid and centrosymmetric  $\text{VO}_6$  octahedral. The edge resonance (B and B' in **Fig. 6**) displays significant changes in both shape and intensity, which is associated with the energy absorption by core electrons<sup>64, 66</sup>. For the discharging process, the shape changes from two broad peaks to a single broad peak (peak B in **Fig. 6**) and the intensity of one peak at around 5486 eV slightly increases while the other one at around 5493 eV slightly decreases. Moreover, two distinct isosbestic points<sup>67</sup> (red arrows in **Fig. 6**) are detected at both high and low energy for discharge and charge processes, indicating the two-phase along with the Mg ions insertion into and extraction from  $\text{V}_2\text{O}_5$ . For the charging process, the edge position of V K-edge shows a reversible behavior with a shift to higher energy, indicating the oxidation of V in the material. The pre-edge peak and edge resonance (A' and B' in **Fig. 6**) also display reversible behavior compared with that of the discharging process. However, unfortunately, the recording of the charging process is not complete due to a beam loss during the experiment at the beamline.



**Figure 7** Raman spectrum of pristine  $\text{V}_2\text{O}_5$ , 1<sup>st</sup> discharged  $\text{V}_2\text{O}_5$ , and 1<sup>st</sup> charged  $\text{V}_2\text{O}_5$

To study the local structure of the samples, Raman scattering was carried out as shown in **Fig. 7**. As known in the pristine orthorhombic  $\text{V}_2\text{O}_5$ , oxygen atoms occupy four types of sites in a  $[\text{VO}_5]$  slab, denoted as O(1)–O(4). The stretching mode of the V–O(1) bond is located at  $993\text{ cm}^{-1}$  while its bending vibrations are located at  $404$  and  $283\text{ cm}^{-1}$ . Raman peaks at  $484\text{ cm}^{-1}$  and  $700\text{ cm}^{-1}$  are attributed to the V–O(2) bending vibration and the V–O(3) stretching vibration, respectively. The peaks at  $528$  and  $304\text{ cm}^{-1}$  are assigned to the V–O(4) bond stretching and

bending vibrations, respectively. The peaks at lower wavenumbers, 143 and 197  $\text{cm}^{-1}$  are because of a weak van der Waals interaction between neighboring  $[\text{VO}_5]$  slabs. These results are highly consistent with previous work<sup>28, 68</sup>. After  $\text{Mg}^{2+}$  is inserted, significant changes can be obtained and some peaks from  $\text{V}_2\text{O}_5$  become weak such as 993 and 143  $\text{cm}^{-1}$ , while those at 700, 528, 304, and 283  $\text{cm}^{-1}$  completely disappear. Meanwhile, some broad new peaks appear at 159, 246, 360, 460, 509, 751, 896, and 945  $\text{cm}^{-1}$ . Similarly, significant changes via *in operando* Raman study are also obtained for  $\text{V}_2\text{O}_5$  during Li-insertion in the range of  $0 < x < 1.0$  ( $\text{Li}_x\text{V}_2\text{O}_5$ )<sup>68</sup>. Therefore, these new peaks might be attributed to the new phase of  $\epsilon\text{-Mg}_{0.6}\text{V}_2\text{O}_5$ , where the broad peaks are probably ascribed to the disordered local structure in the  $\epsilon\text{-Mg}_{0.6}\text{V}_2\text{O}_5$  phase. A broad peak centered at 900  $\text{cm}^{-1}$  is also obtained for  $\text{Mg}_{0.5}\text{V}_2\text{O}_5$  in Gershinsky's work<sup>28</sup>. It can be deduced that  $\text{Mg}^{2+}$  ions are inserted into the interlayer of  $\text{V}_2\text{O}_5$  crystals and bonded with oxygen atoms ( $[\text{MgO}_6]$  octahedra) in the  $\text{V}_2\text{O}_5$  structure to form the Mg-rich  $\text{Mg}_x\text{V}_2\text{O}_5$  phase. After charging, new peaks observed in the discharged state disappear and those peaks from  $\text{V}_2\text{O}_5$  return back to the initial state. These results indicate that the  $\text{Mg}^{2+}$  insertion leads to the formation of  $\text{Mg}_{0.6}\text{V}_2\text{O}_5$  phase and Mg extraction returns the Mg-rich material to initial  $\text{V}_2\text{O}_5$  structure as derived from *in operando* synchrotron diffraction.



**Figure 8** V 2p and O1s X-ray photoelectron spectra of pristine V<sub>2</sub>O<sub>5</sub>, 1<sup>st</sup> discharged V<sub>2</sub>O<sub>5</sub>, and 1<sup>st</sup> charged V<sub>2</sub>O<sub>5</sub>

X-ray photoelectron spectroscopy (XPS) was utilized to look into the surface chemistry and surface elemental composition of pristine V<sub>2</sub>O<sub>5</sub>, 1<sup>st</sup> discharged V<sub>2</sub>O<sub>5</sub>, and 1<sup>st</sup> charged V<sub>2</sub>O<sub>5</sub> (XPS survey spectra of three materials see **Fig. S7**). According to **Fig. 8**, the V 2p spectrum of pristine V<sub>2</sub>O<sub>5</sub> can be fitted with two doublets: a main one with V 2p<sub>3/2</sub> at 517.2 eV and a second one with weak intensity at 515.7 eV<sup>69</sup>, which indicates that V exists mainly in the oxidation state +5 with a minor contribution of vanadium in +3. It can be seen that the O 1s spectrum of pristine V<sub>2</sub>O<sub>5</sub> can be fitted with 3 peaks at 533.6 eV, 532.0 eV, and 530.1 eV, which correspond to the O-C and O=C, as well as V-O groups<sup>70-72</sup>. O=C and O-C could be attributed to the residual surfactant symmetric triblock copolymer P123 during synthesis while the minor V(III) could be assigned to the reduction of residual surfactant P123 during the annealing at 400 °C. The V 2p spectrum in the discharged state could be fitted with 3.6 at% V(IV) at 516.7 eV, 2.6 at% V(V) at 517.3 eV, and 0.7 at% V(III) at 515.7 eV, while the V 2p spectrum of charged state displays two V 2p<sub>3/2</sub> components at 517.3 eV and 515.7 eV, returning back to the spectrum of pristine V<sub>2</sub>O<sub>5</sub>, with 5.9 at% V(V) and 0.6 at% V(III). Therefore, ~60 % of V(V) was reduced to V(IV) during the electrochemical discharge and then again fully oxidized upon electrochemical charging, which is consistent with the electrochemical data (x=0.62 in Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub>).

#### 4. Conclusion

In conclusion, the orthorhombic V<sub>2</sub>O<sub>5</sub> nanowires were successfully synthesized via a hydrothermal approach. In the V<sub>2</sub>O<sub>5</sub> | Mg(ClO<sub>4</sub>)<sub>2</sub>/AN | Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> cell configuration, the V<sub>2</sub>O<sub>5</sub> nanowires obtain an initial discharge/charge capacity of 103 mAh g<sup>-1</sup>/110 mAh g<sup>-1</sup> and the highest discharge capacity of 130 mAh g<sup>-1</sup> in the 6<sup>th</sup> cycle at a C/20 rate. The reversibility of the magnesium insertion/extraction in the V<sub>2</sub>O<sub>5</sub> is clarified through *in operando* synchrotron diffraction and *in operando* XAS together with *ex situ* Raman and XPS. *In operando* synchrotron diffraction and *ex situ* Raman revealed the formation of a new phase of Mg-rich Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> during Mg insertion and the recovery of V<sub>2</sub>O<sub>5</sub> during Mg extraction. *In operando* XAS and *ex situ* XPS confirmed the reduction/oxidation of vanadium during the Mg insertion/extraction. It is the first time that the structural evolution and charge compensation mechanisms of Mg insertion into V<sub>2</sub>O<sub>5</sub> in an electrochemical cell configuration are elucidated through *in operando* synchrotron

diffraction and *in operando* XAS. This will pave the way to study the mechanism of electrode materials not only within the Mg-based batteries but also within other various different challenging systems.

## Acknowledgments

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## Additional information

Supplementary Information is available free of charge on the ACS Publications website at DOI.

Fig. S1-S7.

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