Revealing Mechanism Responsible for Structural Reversibility of Single-Crystal VO₂ Nanorods upon Lithiation/Delithiation

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ABSTRACT

A pure phase of VO₂(B) nanorods have been synthesized through an energy-efficient microwave hydrothermal reaction and used as cathode materials of lithium ion batteries, which exhibit promising specific capacity (e.g., 130 mAh g⁻¹ even after 100 charge/discharge cycles) and rate capacity (e.g., ~130 mAh g⁻¹ at a high current of 400 mA g⁻¹). The excellent cyclability originates from the structural reversibility of VO₂(B) upon lithiation/delithiation that is confirmed by the *in situ* high-energy synchrotron X-ray diffraction (HEXRD) and *in situ* x-ray adsorption near-edge spectroscopy (XANES) of the VO₂ nanorods in operating battery cells. The real-time results reveal that discharge forces lithium ions to insert firstly into the tunnels with the largest size along *b* direction followed by the second largest tunnels along *c* direction, which is completely reversible in the charge process.

KEYWORDS: Vanadium dioxide, microwave synthesis, synchrotron characterization, structural reversibility, Li ion battery

1. Introduction

For Lithium ion batteries (LIBs), the layered metal oxides are typically served as the cathode host for the lithium ion insertion during the electrochemical process[1]. Among different metal oxides, there has been great interest in vanadium oxides with the predominately VO_6 octahedra, which normally share corners and/or edges, leading to the formation of layered two-dimensional sheet structures[2]. These vanadium oxides with the typical layered structure allow the reversible incorporation of protons/alkali ions into their lattice and the insertion process always take place with a large free energy of formation, which make them have great potential use as the cathodes for lithium ion batteries[3, 4]. Especially, compared with commercial-used LiCoO_2 cathode, the theoretical discharge capacity of these vanadium oxides are always much higher. Currently, several types of vanadium oxides have been developed for rechargeable lithium ion batteries, including crystalline V_2O_5 [4-7], V_2O_5 xerogel[8, 9], V_6O_{13} [10, 11] , LiV_3O_8 [12, 13], $\text{NH}_4\text{V}_3\text{O}_8$ [14], and $\text{VO}_2(\text{B})$ [15]. And among the family of V_xO_y compounds, monoclinic $\text{VO}_2(\text{B})$ is a promising cathode material for both aqueous and organic lithium ion batteries due to its proper electrode potential and tunnel structure. The crystallographic structure of monoclinic $\text{VO}_2(\text{B})$ ($\text{C2}/m$) is based on an oxygen body-centered (bcc) lattice and made of distorted VO_6 octahedra, in which vanadium ions sit in the octahedral sites and the oxygen octahedral share both corners and edges. Since the edge sharing of octahedral is along the direction of lattice expansion and the lattice of $\text{VO}_2(\text{B})$ consists of perovskite cavities with four capped faces, at the first glance, it is reasonable to expect that the diffusion of lithium ions in $\text{VO}_2(\text{B})$ is only parallel to the $[010]$ crystal orientation, leading to predominant uniaxial expansion of the cavities and structural stability of $\text{VO}_2(\text{B})$ during the electrochemical process[16].

Since monoclinic VO₂(B) was first explored for reversible electrochemical intercalation of Li⁺, due to shorter diffusion lengths in nanostructures, various nanostructured VO₂(B) have been developed as cathode materials, including 0D nanoparticles[17, 18], 1D nanobelts[19], nanorods[20, 21], nanowires[22, 23], nanotubes[24-26]. Recent work demonstrated that the 2D structures or 3D hierarchical nanostructured VO₂(B) and modified VO₂(B) composites could exhibit more improved electrochemical performance[27, 28]. However, though the electrochemical properties of monoclinic VO₂(B) have been significantly improved in the last decades, the underlying lithium insertion/deinsertion mechanism of monoclinic VO₂(B) has yet to be explored. Since, in general, the clarification of a phase transformation and lattice parameters changes is considered to be a key to achieving high battery performance, understanding the phase transformation of these cathode materials is important and could help improve cell design. The phase transitions of the common commercial-used materials like LiFePO₄, LiCoO₂, and LiMn₂O₄ et al. have been widely investigated[29-33], and even for some other vanadium oxides such as crystalline V₂O₅[1, 34], V₂O₅ xerogel[9, 35] et al, the structure change and reaction mechanism during the lithiation/delithiation process are well understood. Thus, the phase transformation and reaction mechanism of monoclinic VO₂(B) during the electrochemical lithium-ion intercalation need to be further ascertained to push this potential material to the market. Herein, we provide new information regarding the lithium insertion/deinsertion mechanism in monoclinic VO₂(B) during the cycling. The single-crystal VO₂(B) nanorods with well-controlled morphology and crystallinity in high uniformity and purity was prepared by an energy-efficient microwave hydrothermal method. The underlying lithium ion insertion/deinsertion mechanism on the structure of single-crystal VO₂(B) nanorods was studied via *in situ* high energy synchrotron X-ray diffraction (HEXRD) and *in situ* X-ray adsorption near-edge spectroscopy (XANES). The diffusion path of lithium ions in VO₂(B) has been clearly identified for the first time and the *in situ* real-time results reveal that discharge forces

lithium ions to insert firstly into the tunnels with the largest size along *b* direction followed by the second largest tunnels along *c* direction, which is completely reversible in the charge process.

2. Experimental

2.1 Synthesis of single-crystal VO₂ nanorods.

Single crystal VO₂ nanorods were synthesized in aqueous solutions with the use of a Monowave 300 microwave reactor (Anton Parr). Vanadium pentoxide (V₂O₅) and citric acid were purchased from Sigma-Aldrich and used without further modification. In a typical process, 13.4 mg of V₂O₅, 19.9 mg of citric acid and 125 μ L of 0.1 M aqueous sulfuric acid (H₂SO₄) solution were sequentially added to 4 mL distilled water in a 10 mL sealed vessel. The mixture was stirred for 12 hours until a light-blue-color solution was obtained. The solution was then transferred to a microwave reaction container. The temperature of the reaction solution was increased from the room temperature to 180 °C in about 30 seconds followed by maintaining the temperature at 180 °C for 3 hours. The reaction changed the color of the reaction solution from light blue to colorless while dark blue solids precipitated at the bottom of the reaction container. The solid product was centrifuged, washed with the distilled water and dried in a vacuum oven.

2.2 Characterization of the synthesized VO₂ nanorods.

TEM images were collected with a transmission electron microscope (JEOL 2100F) operated at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-7500F field emission scanning electron microscope. Synchrotron X-ray diffraction patterns were collected with a high-energy synchrotron X-ray beam at 11-ID-C with a photon energy of 110 keV ($\lambda=0.1174$ Å) at the Advanced Photon Source (APS).

2.3 Electrochemical Characterization.

VO₂ electrodes were prepared by spreading a slurry composed of 80% VO₂ nanorods, 15% carbon black and 5% polyvinylidene difluoride (PVDF, Aldrich, USA) onto a 10- μ m thick Al foil (for battery performance tests) or a carbon paper (for synchrotron XRD measurements). The electrodes were then placed in a vacuum oven and allowed to dry at 90 °C for 24 h. The performance was evaluated by galvanostatically cycling 2032 coin-type half-cells. Each cell was made up of a VO₂ electrode as the working electrode, a lithium foil as the counter electrode, and 1 M LiPF₆/(ethylene carbonate + dimethyl carbonate in 1 : 1 ratio by volume) as the electrolyte. All cells were assembled in an argon-filled glove box and then aged at for 12 h before the electrochemical tests. Galvanostatic charge–discharge measurements were carried out with a MACCOR battery cycler between 2.0–3.6 V at the room temperature. Cyclic voltammetry tests were performed using a Solartron Analytical 1400 system.

2.4 *In-situ* synchrotron HEXRD and XANES experiments.

In-situ time-resolved high-energy synchrotron XRD measurements during cycling were performed at the beamline 11-ID-C of the Advanced Photon Source (APS), Argonne National Laboratory. A high-energy X-ray with beam size of 0.2 mm $\times$ 0.2 mm and wavelength of 0.11748 Å was used to obtain two-dimensional (2D) diffraction patterns in the transmission geometry. X-rays patterned were recorded with a Perkin-Elmer large-area detector placed at 1800 mm from the battery cells. The home-made coin cells were charged/discharged with a constant current between 2.0 V and 3.6 V. The interval between the consequent diffraction patterns was 5 minutes. The obtained 2D diffraction patterns were calibrated by using a standard CeO₂ sample and converted to 1D patterns using Fit2D software. In our XRD data analysis, the general structure analysis software (GSAS)

program was used to fit the observed diffraction patterns. *In situ* XANES measurements of the VO₂ electrode in an operating coin cell were carried out on the beamline 20-BM-B at APS. The XANES measurements were performed at the *K*-edge of vanadium to monitor the change of valence state of V in the single crystalline XANES cathode and the energy calibration was performed using the first derivative point of the XANES spectrum of V (*K*-edge = 5463.76 eV). The reference spectra were collected for each *in situ* spectrum where vanadium metal foil was used in the reference channel. The home-made coin cells were charged/discharged with a constant current between 2.0 V and 3.6 V. The temporal interval for collecting XANES spectrum was 10 minutes. By selecting XANES spectra of V₂O₄ and V₂O₃ as standards, the spectra of Li_xVO₂ in the electrode were determined by linear combination fitting method which is conveniently available in the Athena software package.

3. Results and discussion

Figure 1. Characterization of $\text{VO}_2(\text{B})$ nanorods synthesized from microwave reaction at 180 °C for 3h. (a) XRD pattern recorded with an X-ray of 0.1174 Å in wavelength. (b) TEM images of VO_2 nanorods. (c) Selected electron diffraction pattern and high-resolution TEM image of single VO_2 nanorods.

Due to the unique advantages of microwave nanochemistry, reactions in a microwave reactor enable fast reaction kinetics and hydrothermal conditions to drive slow reactions requiring high temperature and high pressure [36-38]. In a typical synthesis of single crystalline VO₂ nanorods, an aqueous solution containing V₂O₅, citric acid, and sulfuric acid (clear yellow color) is heated in a microwave reactor to 180 °C and maintained at this temperature for three hours. The resulting powders have been characterized with X-ray diffraction (XRD) using a high-energy synchrotron X-ray (with wavelength of 0.1174 Å). The corresponding XRD pattern is presented in Figure 1a, which matches the VO₂(B) with a monoclinic lattice symmetry and space group of *C2/m* (JCPDS card no. 81-2392). The peaks at 1.10°, 1.17°, 1.92°, 2.20°, 2.28°, 2.54°, 3.36° and 3.65° represent reflections of the (001), (200), (110), (002), ($\bar{4}$ 01), (310), ($\bar{6}$ 01) and (020) planes, respectively. Fitting the XRD pattern with the general structure analysis software (GSAS) program gives the lattice parameters of VO₂(B) unit cell: $a=12.085$ Å, $b=3.704$ Å, $c=6.438$ Å, $\alpha=90^\circ$, $\beta=107^\circ$, $\gamma=90^\circ$, and $V=275.589$ Å³. The VO₂ powders are also characterized with scanning electron microscopy (SEM, Figure S1) and transmission electron microscopy (TEM, Figure 1b). The images clearly show that the synthesized VO₂ nanocrystals exhibit rod-like morphology with an average lateral width of ~80 nm. High-resolution TEM images of individual nanorod shows pure and continuous lattice fringes with a spacing of 0.61 nm (consistent with the value of $2\times b$ in a unit cell), indicating that each VO₂ nanorod is single crystalline (right, Figure 1c). The corresponding electron diffraction pattern exhibits a set of reflection spots that can be assigned to the well-defined monoclinic *C2/m* lattice (left, Figure 1c), indicating that the longitudinal axes of VO₂(B) nanorod are along $\langle 001 \rangle$ directions.

Figure 2. Electrochemical characterizations of VO₂ nanorods electrodes: (a) Cyclic voltammograms at different scan rates, (b) Charge-discharge voltage profiles, (c) Cycling performance, and (d) Rate performance of the VO₂ nanorods in half-cells.

The electrochemical activity of the synthesized VO₂(B) nanorods is characterized with cyclic voltammograms (CVs) in the range of 2.0–3.6 V *versus* Li/Li⁺ at varying scan rates. At a scan rate of 0.1 mV s⁻¹, the CV shows a pair of well-resolved redox peaks (i.e., anodic peak at 2.63 V and cathodic peak at 2.50 V) corresponding to the reversible reaction of Equation 1[18, 26]. Increasing the scan rate leads to an enhancement of the current while the symmetric peak profile remains. The peak current density exhibits a linear dependence on the square root of potential scanning rate ($v^{1/2}$), indicating a high reversibility of the reactions of eq. 1 in the range of 2.0-3.6 V (Figure S2).

Such good reaction reversibility is expected to benefit the charge/discharge reversibility of lithium ion batteries when the VO₂(B) nanorods are used as cathodes in coin cells with metallic lithium foils as anodes. Figure 2b and 2c show the typical voltage profile and cycling performance of a cell operated in the range of 2.0–3.6 V and at a current density of 30 mA g⁻¹. The initial discharge capacity is as high as 195 mAh g⁻¹, corresponding to lithiation of VO₂ until the battery voltage drops to 2.0 V. The following first charge capacity can reach 188 mAh g⁻¹, slight lower than the initial discharge capacity. Continuous charge/discharge cycling further decreases the battery capacity, which is considered mainly caused by electrochemical corrosion of lithium anode and formation of SEI layer that usually reduces the electric conductivity of electrodes and slows down interfacial charge transfer [1,2]. The discharge capacity is still larger than 130 mAh g⁻¹ even after 100 discharge/charge cycles while the average Coulombic efficiency remains as high as 99.6%. Such near-unity Coulombic efficiency implies that the crystalline structure of the VO₂ nanorods is highly reversible to efficiently accommodate the insertion and deinsertion of lithium ions. Despite of the commonly observed decrease in capacity, the charge-discharge curves always exhibit stable and wide-range plateaus at 2.55 V. Maintaining a constant discharge/charge voltage is important for reliably powering devices and is necessary to achieve a large extent of Li-ion insertion and deinsertion at this voltage[18, 39, 40]. Figure 2d presents the rate performance of the cell operated at increasing current densities from 30 mA g⁻¹ to 400 mA g⁻¹ for both charged and discharged processes. The capacity gradually decreases from 190 mAh g⁻¹ to 130 mAh g⁻¹ with increasing the rate from 30 mA g⁻¹ to 400 mA g⁻¹ (Table S1 in the supporting information). Even after high rate operation at 400 mA g⁻¹ for multiple discharge/charge cycles, the capacity can be recovered to 153 mAh g⁻¹ once the operation current density is reduced to 100 mA g⁻¹. The results including symmetric CVs, unity Columbic efficiency, and high rate capacity suggest that the single crystalline VO₂ nanorods maintain their structural integrity in the course of battery cell operation

because structural failure of electrode materials usually leads to irreversibility of electrochemical process.

Figure 3. *In-situ* synchrotron HEXRD characterization of the Li/VO₂ coin cells. (a) Contour plot of peak intensities as a function of reaction time. (b) Voltage profile of the coin cell throughout the 1st charge/discharge process. (c) The contour plot of the peak intensities (110) reflection as a function of a

reaction time. The current density was 30 mA g⁻¹. The blue line in the contour plot figure was due to the absence of X-ray beam during the characterization. (d) HEXRD patterns at a number of key times, corresponding to different depth of discharge (DOD). (e) Crystal structure of pristine monoclinic VO₂(B) projected along [010], [100] and [001].

In order to understand how the lithium ion insertion/deinsertion influences the structure of the VO₂(B) nanorods, we have monitored the crystalline structural variation of the VO₂ nanorods in a battery cell using *in situ* synchrotron high-energy X-ray diffraction (HEXRD) in the course of a discharge/charge cycle. The two-dimensional (2D) contour plot of the HEXRD patterns recorded at different discharge/charge stages is shown in Figure 3a and the corresponding voltage profile of the cell is highlighted in Figure 3b. Notably, the evolution of the HEXRD patterns is reversible after a full discharge/charge cycle, correlating well with the electrochemical process. In detail, the evolution profile of HEXRD patterns in the course of discharge is nearly symmetric to that in the course of charge against the pattern at 100% depth of discharge (DOD), highlighted by the white dash line in Figure 3a. Such symmetric evolution profile of HEXRD patterns indicates that the lithiation and delithiation of the single crystalline VO₂ nanorods is completely reversible and both do not change the lattice symmetry and integrity in the VO₂ nanorods. The reversible structural change of the VO₂ nanorods is consistent with the observed reversible electrochemistry of the VO₂-nanorod electrodes highlighted in Figure 2a. More importantly, the reversible structural change of the VO₂ nanorods is well maintained in the course of discharge/charge cycles even after 50 cycles (Figure S3), which indicate the continuous decay of the VO₂ nanorods should not originate the structure failure of VO₂.

When the discharge/charge is performed in the range of 3.6-2.0 V, only the HEXRD peaks of reflections with non-zero value along *b* direction exhibit a stepped change while other peaks are essentially unchanged (Figure 3a and 3c). Changes of the HEXRD patterns in the discharge process are clearly shown in Figure 3d, which highlights the HEXRD patterns at different depth of discharge (DOD). The projections of a pristine monoclinic VO₂(B) crystal along [010], [100] and [001] directions

are shown in Figure 3e. VO₂(B) lattice is made of distorted VO₆ octahedra which share both corners and edges, leading to the formation of tunnels with four different sizes (i.e., 8.2 Å² and 3.4 Å² along *b*, 3.4 Å² along *a*, and 5.0 Å² along *c*). In the discharge process, lithium ions tend to be inserted into the tunnels with the largest size (i.e., the 8.2 Å² tunnel along *b* direction) followed by the second largest tunnels (i.e., the 5.0 Å² tunnels along *c* direction). In the early stage of discharge, the positions of all HEXRD peaks are barely changed, indicating that insertion of Li⁺ ions in the largest tunnels along *b* direction is favorable and does not cause significant expansion of VO₂ lattices. As discharge continues, positions of the (110), (310) and (020) reflections (with non-zero *b*) gradually shift the lower 2θ values although the changes of the (001) and (200) reflections are minor (i.e., the (001) peak maintains unchanged and the (200) peak slightly shifts to the higher 2θ values), indicating that the insertion of Li⁺ ions in the second largest tunnels along *c* direction significantly expands the VO₂ lattices along *b* direction and slightly compresses the lattices along *a* direction. The sudden split of the reflection peaks with non-zero *b* indices indicates a phase transition from the Li-poor Li_xVO₂ phase to the new Li-rich Li_yVO₂ phase. Continuous discharge can completely transform the Li-poor Li_xVO₂ phase to the Li-rich Li_yVO₂ phase, which also adopts the monoclinic lattices with lattice parameters different from the VO₂ nanorods and the Li-poor Li_xVO₂ phase.

According to the crystalline structure of the VO₂ nanorods, the discharge process can be divided into three different stages (Figure 3c). At stage “*I*” of the shallow discharge, a single phase of Li-poor Li_xVO₂ exists. The peak position of the (110) reflections slightly shifts to the lower angles with time, suggesting that the insertion of Li⁺ in VO₂ nanorods does not significantly alter the crystalline lattices of VO₂. At stage “*II*” of the mediate discharge, where the voltage exhibits a plateau, the (110) reflections split into two peaks with the appearance of a peak at a lower angle, which corresponds to a new Li-rich Li_yVO₂ phase. The intensity of the new phase monotonically increases with time while that of the Li-

poor Li_xVO_2 phase continuously decreases to zero, indicating the continuous transformation from the Li-poor phase to the Li-rich phase. It is worthy of pointing out that peak positions of both phases maintain constant, which is consistent with the voltage plateau. At stage “**III**” of deep discharge, only the Li-rich Li_yVO_2 phase exists and the peak position continue to shift to the lower angles with time, indicating that the lattices of Li_yVO_2 can also be slightly expanded to accommodate the insertion of Li ions. Apparently, the processes at stages “**I**” and “**III**” correspond to the single phase solid-solution reaction mechanism, in which only a single phase is involved and its lattice parameters and unit-cell volumes continuously change. Phase transition occurs at stage “**II**”, corresponding to the two-phase reaction mechanism, in which one phase is directly converted to another phase through a first-order process. Such three-stage process can be completely reversed in the charge process (Figure 3c).

The structural reversibility of VO_2 nanorods in discharge/charge cycle implies small volumetric variation of the VO_2 lattice. Figure 4a compares the evolution of lattice parameters a , b and c in VO_2 (including Li_xVO_2 and Li_yVO_2) as a function of depth of discharge (DOD). In the initial shallow discharge process, a and b increase by 0.6% and 0.8%, respectively, at ~50% DOD, while the value of β decreases by ~1 degree. In contrast, c contracts by 0.2% to minimize the volume expansion. Further lithiation leads to the phase transition (Figure 3d), during which a abruptly decreases along with the increase of b (Figure 4a). The value of c first increases followed by a monotonic decrease until the phase transition stops. The variations of lattice parameters indicate the emergence of a new Li-rich Li_yVO_2 phase discussed above. In the region with two phases co-existing, the volume of lattice unit cell of the Li-rich Li_yVO_2 phase experiences a subtle variation while that of the Li-poor Li_xVO_2 phase essentially remains constant. Once the phase transition completes, the Li-poor Li_xVO_2 phase disappears and all lattice parameters become constant until the full lithiation. It is interesting to note that the value of c exhibits a similar evolution profile to the value of β over the course of lithiation. The lattice

parameters c and β have a relationship with the (001) peak, i.e., $d_{(001)} = c \times \sin(\beta)$. As shown in Figure 4a, the evolution profile of the value of c is similar to that of β ($90^\circ < \beta < 180^\circ$). When β decreases, $\sin(\beta)$ increases accordingly. Meanwhile, c decreases, resulting in a almost unchanged value of $c \times \sin(\beta)$. Therefore, $d_{(001)}$ remains almost constant and the (001) peak position remains nearly unchanged over the course of the discharge process (Figure 3a). The evolution of lattice parameters results in an expansion of the unit cell volume from 275.6 Å³ to 292.2 Å³ due to lithiation. Regardless of the value of DOD, lithiation always leads simultaneous lattice contraction and expansion along different crystalline directions, minimizing the possible volume expansion.

The VO₂(B) lattice is composed of distorted VO₆ octahedra, which share both corners and edges to form four types of tunnels with different sizes along different directions (Figure 3e). As highlighted in Figure 4b, lithiation starts with the insertion of Li ions in the largest tunnel parallel to the b direction. Locally, each inserted Li ion occupy the small hexahedral gap (3O1-O4/O2) and coordinate with the five surrounding oxygen. Since every unit cell has four such oxygen hexahedral gaps, it can accommodate up to four Li ions. In the shallow discharge (i.e., DOD < 50%), the minor contraction of c is ascribed to the Coulomb force between the inserted Li⁺ and O2/O4 of the oxygen hexahedral gaps and the slight expansion of a and b is due to the repulsion force between the oxygen (O1) atoms in the a - b plane. At *ca.* 50% DOD, the largest tunnels along b are fully occupied with Li ions. Further lithiation forces the Li⁺ to fill the second largest tunnels along c , leading to a phase transition to form Li-rich Li_{1/2}VO₂ phase (4-b, Figure 4b). Insertion of lithium ion along the [001] direction leads to contraction of a , expansion of b , and relaxation of c back to the value of the original VO₂ lattice. This process continues to fully fill the tunnels along c , reaching 100% of DOD. As shown in Figure 4a, such two-stage lithiation causes the simultaneous lattice contraction and expansion along different directions, which minimizes the overall volumetric lattice expansion to maintain the structural integrity of VO₂ lattice. Since the smaller tunnels

along b and the tunnels along a have sizes of $3.4 \text{ \AA}^2$ and $3.4 \text{ \AA}^2$, respectively, which are too small to accommodate the insertion of more Li^+ without significant structural change.

Figure 4. *In situ* synchrotron HEXRD data analysis: (a) Lattice parameter evolution of Li_xVO_2 during the 1st discharge process, determined from the refinement of the HEXRD patterns shown in Figure 3a. (b) Schematic view of the lithium ion insertion in single crystal VO_2 lattice.

In all, the underlying lithium ion insertion/deinsertion mechanism in the monoclinic $\text{VO}_2(\text{B})$ can be described in three stages as discussed above: Initially, in stage “*I*”, the lithium ions are prone to travel along the b tunnel, the Li-poor Li_xVO_2 formed and experiences a single-phase solid-solution reaction mechanism, which is characteristics of constant lattice parameters evolution. Then in stage “*II*”, the lithium ions continue to travel along the b tunnel but force the former occupied Li^+ to diffuse along other

direction and phase transition occur, leading to the formation of the Li-rich Li_yVO_2 phase. The whole process was undergoing a two-phase reaction, during which the amount of Li-rich Li_yVO_2 phase increases at the expense of the Li-poor Li_xVO_2 phase. Finally, in stage “III”, the formed Li-rich Li_yVO_2 phase experiences another single-phase solid-solution reaction, during which the lattice parameters continuously change without any interruption. And in the following charge process, the Li-rich Li_yVO_2 phase will transfer back again to its original monoclinic $\text{VO}_2(\text{B})$ phase, indicating that the whole charge/discharge process is completely reversibly.

Figure 5. *In situ* synchrotron XANES characterization of the Li/VO₂ coin cells. (a) Normalized XANES spectra (2D contour plot) and voltage profiles of Li/VO₂ coin cells during the first and second discharge/charge process. (b) Typical V K-edge XANES spectra during the first discharge process. (c) Variation of V valence as a function of time in the first and second discharge/charge cycles. (d)

Dependence of intensity of XANES pre-edge and edge resonance (main peak, inset) on composition in the first charge/discharge cycle.

In addition to structural reversibility in the discharge/charge cycle, the oxidation state of V is also reversible, which has been characterized with *in situ* XANES in a coin cell at 20-BM-B, Advanced Photon Source, Argonne National Laboratory. The 2D contour plot of normalized XANES spectra of the V K- edge is presented in Figure 5a. The corresponding voltage profile of the battery cell is also plotted for comparison. It is clear that the evolution of the XANES spectra is reversible as the discharge and charge are alternated. In the course of discharge, the K-edge of V continuously shifts towards the lower binding energy, indicating that the insertion of Li^+ in the VO_2 nanorods decreases the average valence state of V. A new shoulder (highlighted by an arrow) emerges at the fully discharged state, which is consistent with reduction of V(IV) to V(III)[40]. In the charge process, the K-edge of V shifts back to the higher binding energy (supporting information, Figure S4). By using V_2O_3 and VO_2 powders as standards for V^{3+} and V^{4+} , respectively, the valence state of V in the discharge/charge process can be calculated via the linear combination analysis[41]. The variation of valence state of V as a function of time in the first and second discharge/charge cycles is shown in Figure 5c, also highlighting the high reversibility of valence states. In the first discharge process the valence state of V changes from $4+$ to $3.4+$, and it smoothly returns back to $4+$ after the following charge process. The decrease and increase of valence state of V correspond to insertion and desertion of positive charged Li^+ , respectively, to balance the overall charge in the VO_2 nanorods.

The intensity XANES pre-edge peak (labelled with “A” in Figure 5b) and main edge resonance peak (labelled with “B” in Figure 5b) also varies in the course of discharge/charge cycles. Figure 5d shows the intensities of these peaks as a function of Li concentration in lithiated VO_2 in the first discharge/charge cycle, showing linear relationships. The main edge resonance peak is associated with

the energy adsorption by core electrons, showing major changes in both intensity and profile in the course of lithiation: increase in peak intensity and change of peak profile from two overlapped peaks to a single peak (Figure 5b). In the following charge process, the peak intensity decreases and the peak is split into two overlapped peaks, consistent with the original VO₂ before discharge (Supporting information, Figure S4). The results confirm the high reversibility of crystalline and electronic structures of VO₂ upon discharge/charge cycles, which is consistent with our *in situ* synchrotron HEXRD result.

4. Conclusion

In all, single-crystalline monoclinic VO₂(B) with high crystalline purity and uniform morphology were prepared via an energy-efficient microwave-assisted hydrothermal reaction. When used as cathode material of lithium ion batteries, the VO₂(B) nanorods exhibit promising electrochemical performance. When operated between 2.0 V ~ 3.6V, the electrode can deliver an initial discharge capacity as high as 195 mAh g⁻¹ at 30mA g⁻¹ and the retained capacity could be 130 mAh g⁻¹ even after 100 charge/discharge cycles. Meanwhile, the electrode shows a good rate performance (e.g. ~130 mAh g⁻¹ at a high current of 400 mA h⁻¹). The structure evolution and valence evolution of the VO₂(B) electrode during cycling was investigated by *in situ* synchrotron HEXRD and XANES techniques and the lithium insertion/desertion mechanism of this potential material has been clarified for the first time. Our *in situ* real-time results reveal that (i) Both the crystalline structure and the oxidation state of V is reversible during the electrochemical process when the cutoff voltage window is between 2.0 V and 3.6 V; (ii) At the beginning and end of the discharge process, the electrode experiences a single phase solid solution mechanism; while at the voltage plateau, the electrode is undergoing a two phase transition mechanism; (iii) Discharge forces lithium ions to insert firstly into the tunnels with the largest size along b direction

followed by the second largest tunnels along c direction, which is completely reversible in the charge process.

Supporting Information available: SEM images of VO₂(B) nanorods obtained via microwave synthesis at 180 °C for 3h; Calculated $v^{1/2}$ as a function of scan speed, v and t represent the scan speed; *In situ* synchrotron HEXRD characterization of the Li/VO₂ coin cells during the 50th, 51th and 52th cycles; Typical vanadium K-edge XANES spectra during the first charge process; The linear combination fitting result of Li_xVO₂ XANES spectra at 50% DOD; The corresponding current density and capacity of VO₂ nanorods.

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