Structural Transformation of LiVOPO$_4$ to Li$_3$V$_2$(PO$_4$)$_3$ with Enhanced Capacity

H. T. Kuo, N. C. Bagkar,$^1$ R. S. Liu,$^{*,3}$ C. H. Shen,$^3$ D. S. Shy,$^3$ X. K. Xing,$^3$ J.-F. Lee,$^8$ and J. M. Chen$^8$

Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, SYnergy Scien Tech Corporation, Science Tech-based Industrial Park, Hsinchu 300, Taiwan, and National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

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In the present investigation, we report the transformation of α-LiVOPO$_4$ to α-Li$_3$V$_2$(PO$_4$)$_3$, leading to an enhancement of capacity. The α-LiVOPO$_4$ sample was synthesized by a sol–gel method, followed by sintering at 550–650 °C in a flow of 5% H$_2$/Ar. The structural transformation of a triclinic α-LiVOPO$_4$ structure to a monoclinic α-Li$_3$V$_2$(PO$_4$)$_3$ structure was observed at higher sintering temperatures (700–800 °C in a flow of 5% H$_2$/Ar). The α-Li$_3$V$_2$(PO$_4$)$_3$ phase was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, thermal gravimetric analysis, and X-ray absorption near edge spectrum (XANES) techniques. The valence shift of vanadium ions from +4 to +3 states was observed using in situ XANES experiments at V K-edge. The structural transformation is ascertained by the shape changes in pre-edge and near edge area of X-ray absorption spectrum. It was observed that the capacity was enhanced from 140 mAh/g to 164 mAh/g via structural transformation process of LiVOPO$_4$ to Li$_3$V$_2$(PO$_4$)$_3$.

1. Introduction

During the past decade, the research on cathode materials in lithium-ion batteries has focused mainly on lithium transition metal oxides that operate between 3.0–4.0 V, which finds application in powering electronic equipments such as cellular phone, bluetooth, and laptop computers. At present, layered LiCoO$_2$ is used commercially as 4.0 V cathode materials in rechargeable lithium-ion batteries. However, there are some limitations of these materials related to the transport of electrons and lithium ions within the lattice, structural stability and safety issues. An ideal cathode material should have large capacity, good framework stability, low activation energy, good electronic conductivity, and high redox potential versus Li/Li$^+$ potential that can be beneficial for energy consumption. Recently, the phosphate-based compounds, such as LiFePO$_4$, LiCoPO$_4$, Li$_3$V$_2$(PO$_4$)$_3$, and LiVOPO$_4$ have been extensively used as the cathode materials for lithium ion batteries. The structural framework of these phosphate compounds made them useful cathode material, which limits the likelihood of oxygen liberation and combustion. The intrinsic stability of such a scaffold structure derives from its strong covalent P–O bonding and the large PO$_4^{3–}$ anions are expected to possess higher redox potential. Among the phosphate-based cathode materials, LiFePO$_4$ has attracted much attention as an alternative cathode material. In comparison with LiFePO$_4$, LiVOPO$_4$ has an advantage of higher potential (4.0 V versus Li/Li$^+$) for charging/discharging and triclinic phase of LiVOPO$_4$ synthesized from α-LiVOPO$_4$ shows the capacity of 100 mAh/g up to 100 cycles at C/10 rate. However, the capacity for Li deintercalation is decreased with increasing current density although higher potential of 4.0 V is exhibited. Therefore, improvement in Li intercalation and deintercalation capacity is strongly desired for LiVOPO$_4$. The capacity as well as cycle stability of electrochemical Li intercalation into LiVOPO$_4$ could be improved by optimizing the preparation conditions. The syntheses of LiVOPO$_4$ by hydro-thermal and solid state reaction have been reported.

On the other hand, Li$_3$V$_2$(PO$_4$)$_3$ is also considered as a promising material because of its higher theoretical capacity (197 mAh/g) as a cathode material in lithium ion batteries. Accordingly, Li$_3$V$_2$(PO$_4$)$_3$ can be synthesized directly from reactant materials by chemical method. In this paper, we report the sol–gel method to prepare the α-LiVOPO$_4$ and investigate the process of structural transformation from α-LiVOPO$_4$ to α-Li$_3$V$_2$(PO$_4$)$_3$ at higher sintering temperatures. The results are particularly interesting, since there are not many reports on the structural transformation of the triclinic structure of α-LiVOPO$_4$ into the monoclinic structure of α-Li$_3$V$_2$(PO$_4$)$_3$ by sintering at 550–900 °C in a flow of 5% H$_2$/Ar reducing atmosphere. The objective of the present investigation is to attribute this novel method of transformation to the enhancement in the capacity of α-LiVOPO$_4$ sample. The physical, electrical, and electrochemical characteristics of α-Li$_3$V$_2$(PO$_4$)$_3$ sample are investigated.

2. Experimental Section

2.1. Synthesis of Cathode Materials. V$_2$O$_5$·nH$_2$O hydrogel was prepared as follows: 35 wt % H$_2$O$_2$ solution was slowly added to V$_2$O$_5$ with vigorous stirring in an ice bath until a clear orange solution was formed. A stoichiometric mixture of NH$_4$H$_2$PO$_4$ and LiF was added to the above V$_2$O$_5$·nH$_2$O hydrogels, stirred at room temperature for 8 h, and finally dried at 100 °C in the oven. The product was ground in the mortar for 5 min and heated at 300 °C in a tube furnace in a flow of 5% H$_2$/Ar gas for 4 h. After slowly cooling to room temperature, the samples were ground again for 5 min and heated from 550 to 900 °C for 2 h in a flow of 5% H$_2$/Ar gas.

2.2. Preparation of Cathode Films and Coin Cells. Cathode was made by mixing 80 wt % active material, 10 wt % conductor (Carbon, Super P), and 10 wt % binder (polyvinylidene fluoride, PVDF) in N-methyl-2-pyrrolidinone (NMP). The mixture slurry was stirred in ambient conditions for 2 h, followed by coating on to an aluminum foil as the electronic collector.
The prepared cathode was heated for 4 h at 70 °C in an oven and then cold pressed by rollers with 0.04 µm thicknesses. It was further dried in a vacuum at 110 °C for at least 12 h to remove the trace NMP and absorbed water in the electrode lamella. The cathode lamella was cut into circular disk with a diameter of 1 cm. The loading amount of the active materials was 10–20 mg/cm². The cell consisted of a cathode and a lithium metal anode separated by a porous polyethylene film. The coin cell was assembled in the glovebox filled with the Argon gas (<5 ppm H₂O and O₂). The electrolyte was consisted of 1 M solution of LiPF₆ in a mixture of ethylene carbonate (DC) and dimethyl carbonate (DMC) in the volume ratio of 1:1. The electrochemical testing of coin cells was performed automatically with a Maccor battery cycling system.

2.3. Characterization. X-ray diffraction (XRD) was performed on a PANalytical X’Pert PRO diffractometer operating in transmission mode with Cu Kα radiation (λ = 1.5418 Å). X-ray profile was measured between 20 and 70° (2θ angle) using a step size of 0.02° with a counting time of 30 s per step. Rietveld refinement was performed using the general structure analysis system (GSAS) program to obtain the parameters of crystal structure. Scanning electron microscopy (SEM) was performed on Hitachi S-2400 equipped with a thermal emission gun. The microstructure and selected area electron diffraction (SAED) pattern of sample were obtained by using a transmission electron microscopy (TEM) apparatus on a JEOl 100CX. Thermogravimetric analysis–differential thermal analysis (TGA-DTA) was performed on a TA Instrument 5100 in a heating rate of 5 °C/min from room temperature to 1000 °C in a flow of 5% H₂/Ar gas. The V K-edge of X-ray absorption experiments were carried out at a BL17C Wiggler beam line of the National Synchrotron Radiation Research Center (NSRRC) in Hsin-Chu, Taiwan. The electron storage ring was operated at energy of 1.5 GeV with a beam current of 300 mA. A Si(111) double-crystal monochromator was employed for energy selection with a resolution (ΔE/ΔE) around 2 × 10⁻⁴. The data was recorded at room temperature in transmission mode using gas-filled ionization chambers. The ion chambers used for measuring the incident (I₀) and transmitted (It) beam intensities were filled with a mixture of N₂ and H₂ gases and a mixture of N₂ and Ar gases, respectively. Energy calibration was carried out by using the first inflection point of the V K-edge (5486 eV) absorption spectrum of V metal foil as a reference. Reference spectra were simultaneously collected for each in situ spectrum by using V metal foils. After background subtraction, the X-ray absorption near edge structure (XANES) spectra was normalized with respect to the edge jump. The V L-edge X-ray absorption measurements were performed at a 6 m high-energy spherical grating monochromator (HSGM) beam line of the NSRRC in Taiwan. The absorption spectra of V L₂,₃-edge were recorded in the X-ray sample current-yield (SC) mode in an ultrahigh vacuum chamber (10⁻⁹ Torr) at the 6 m HSGM. The incident photon flux (I₀) was monitored simultaneously by using a Ni mesh located after the exit slit of the monochromatic beam. All the absorption measurements were normalized to I₀. Infrared spectroscopy was carried out with a Perkin-Elmer System 2000 infrared (IR) spectrometer equipped with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. The measurement scheme was a single reflection mode and the p-polarized light was incident at 85° from the surface normal with a grazing angle accessory (FT-85, Spectra-Tech, Shelton, CT). The light path, detector, and sample chambers were purged with dry nitrogen. A total of 1024 scans of both the sample and the reference (bare Au) were collected at 4 cm⁻¹ resolution for signal averaging. 7Li magic angle spinning nuclear magnetic resonance (7Li MAS NMR) spectra were acquired at a Larmor frequency of 194.3 MHz on a Varian Infinityplus-500 spectrometer. The static 7Li was measured as a function of temperature from 233 to 393 K using a double-tuned static probe. 7Li chemical shifts were externally referenced to a 1 M aqueous solution of LiCl at 0 ppm.

3. Results and Discussion

The XRD profiles of the α-LiVOPO₄ sample sintered at different temperatures are shown in the Figure 1. The XRD profile from 600 °C indicated the crystallization of α-LiVOPO₄ with the presence of small amount of α-Li₃V₂(PO₄)₃ phase, which is identified as triclinic system with a P₁ space group (ICSD: 20345). As the temperature was further increased to 800 °C, the α-LiVOPO₄ transformed completely to α-Li₃V₂(PO₄)₃ which is identified as monoclinic system with a P2₁/n space group (ICSD: 69–345). The XRD results showed the process of transformation at higher temperature in reducing atmosphere. The possible chemical reaction can be given as shown in Eq. [1]:

\[
3\text{LiVOPO}_4 \rightarrow \text{Li}_3\text{V}_2(\text{PO}_4)_3 + \text{VO}_2 + 1/2\text{O}_2 \quad (1)
\]

The VO₂ may be formed as amorphous phase hence could not be detected in XRD patterns shown in Figure 1.

Figure 2 shows the SEM of α-LiVOPO₄ and α-Li₃V₂(PO₄)₃ phases. It was observed that the shape of particle is like a rockstone as displayed in Figure 2a and microstructure image is enlarged as shown in Figure 2b. As the temperature was increased to 700–900 °C, the morphology of the particle was changed as displayed in Figure 2c, and the microstructure image is enlarged as shown in Figure 2d. The formation of erosive cavity framework between the bigger crystallites can be seen from the figure. The larger crystals with erodelike structure have advantages of large specific area and fast transport of lithium ions, which can afford enough active sites for lithium ions to simultaneously intercalate into them. The porous structure has thin pore wall which can reduce the diffusion path of the lithium ions.

The crystalline nature of α-LiVOPO₄ and α-Li₃V₂(PO₄)₃ samples was analyzed by using the SAED pattern techniques. The electron diffraction pattern is shown in Figure 3a,c.
3b,d is the simulated pattern obtained by using the CaRIne v3.1 software for α-LiVOPO₄ and α-Li₃V₂(PO₄)₃, respectively. The splitting can be observed in the diffraction spots which further spread away from the incident electron beam (labeled as *). A small difference in the position of spots is observed as a result of the difference in the lattice parameters of α-LiVOPO₄ and α-Li₃V₂(PO₄)₃ phases. The SAED is typically for the triclinic crystal system (α = β = γ = 90°, α ≠ b ≠ c) and monoclinic crystal system (α = γ = 90° ≠ β, a ≠ b ≠ c) as shown in Figure 3, panels a, b, c, and d, respectively. The zone axis is identified as [111] for α-LiVOPO₄ and [112] for α-Li₃V₂(PO₄)₃ by using eq 2 listed below:

\[ R \times d = L \times \lambda \]  

where \( R \) is the distance between the diffraction spot and incident electron beam, \( d \) is the spacing value of diffraction spot from JCPDS database, \( L \) (60 cm) is the length of camera from TEM machine, and \( \lambda \) (0.037 Å) is the wavelength of electron beam from TEM machine. The agreement between experimental and calculated TEM images confirms the structure of α-LiVOPO₄ and α-Li₃V₂(PO₄)₃.

The TGA-DTA curves of the dry-gel precursor are given in Figure 4. The five distinctive regions, labeled as a–e, were observed in the temperature range of 30–1000 °C. Below 200 °C (in region a), a small amount of weight loss was observed due to the loss of water molecules. In region b (300–500 °C), the sharp peak at around 367 °C and broad peak between 400–500 °C with rapid mass loss can be attributed to the decomposition of NH₄H₂PO₄ and LiF. A small peak in region c was observed with a smooth mass loss at around 529–650 °C, which can be attributed to the formation of α-LiVOPO₄.

As the temperature was increased to 700–900 °C (region d), there was a little mass loss with a broad peak which may be as a result of the process of structural transformation of α-Li₁₋₃V₂(PO₄)₃ from α-LiVOPO₄. Further increase in temperature to 1000 °C (region e) may result in the decomposition of α-Li₃V₂(PO₄)₃.

The XANES spectra at V K-edge for a series of samples sintered at different temperatures along with the reference materials such as V₂O₃, VO₂, and V₂O₅ in different oxidation states are shown in Figure 5. To compare quantitatively the intensity of absorption features in various compounds, the experimental V K-edge spectra were normalized using standard edge step normalization procedure. All the XANES spectra were reduced by background subtraction and normalized with respect to the edge jump. The absolute zero point of energy is taken with respect to the first point of inflection of the vanadium metal derivative spectrum (called \( E₀ \)), which corresponds to the excitation of an inner shell electron to an empty state just above the Fermi edge of the V metal. For each spectrum, the vanadium foil was scanned to correct for energy shift to obtain energy calibrated spectra in a consistent fashion. The pre-edge peak (labeled A in the inset) at around 5455 eV in Figure 5a is related to the 1s to 3d transition, which is electric dipole forbidden. It is well known that this transition is dipole forbidden (symmetry forbidden) but gains intensity through the allowed electric quadrupole transition. The pre-edge peak intensity is a clear fingerprint of the symmetry change and is used to evaluate qualitatively the alteration of the vanadium local symmetry. It has been reported that the intensity of the pre-edge absorption increases as the site symmetry of the transition metal decreases.
from a centrosymmetric to a noncentrosymmetric environment. In most of the studies, the vanadium oxidation state is determined through the position of the absorption near edge (labeled B in the inset), which shifts to higher energies with an increasing valence state. The \( \alpha \)-LiVOPO\(_4\) samples formed at low sintering temperature (600 \(^\circ\)C) exhibits the triclinic crystal system in a lower symmetry unit with a noncentrosymmetric environment around the vanadium site, which showed a sharp pre-edge peak. On the other hand, \( \alpha \)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) sample formed at high temperature (700–800 \(^\circ\)C) has transformed into the phase of monoclinic crystal system in a higher symmetry unit which showed a smooth pre-edge peak. As the temperature is increased, \( \alpha \)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) is transformed from \( \alpha \)-LiVOPO\(_4\), and the valence state of vanadium metal is shifted from +4 (high energy) to +3 (low energy). The details are shown in the inset as labeled B in Figure 5a. The edge energy corresponds to \( \alpha \)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) indicating that the vanadium ion is reduced to a trivalent cation. In addition, the decrease of the pre-edge peak intensity was also observed. For a better understanding and clarity of the edge features, we have shown only a smaller energy range for the XANES. Figure 5b shows the second derivative function of the V \( K\)-edge for each sample with different sintering temperature. The zero crossing of the main absorption features, which represents the inflection point energy, was found to be from 5468.51 to 5467.18 eV for 600 and 800 \(^\circ\)C, respectively. Due to the structure transformation results, the curve shape of second derivative function for the V \( K\)-edge at around 600 \(^\circ\)C has the similar shape, whereas at around 700–800 \(^\circ\)C the shape of second derivative function is changed. Figure 5b also shows that the zero crossing of the main absorption features, which suggests that the local structure is significantly altered by different sintering temperatures. The shape of secondary derivative has changed from 600 to 800 \(^\circ\)C as the temperature is increased. This is also particularly
The XAS spectra at V L-edge together with the reference materials in different valence state of vanadium are shown in Figure 6. The main spectra features of the L edge for V metal originate from dipole transitions of the core V 2p level to the empty V 3d states, and are separated into two broad multiple structures by the core-hole spin–orbit interaction. Both line shape and transition energy at the absorption edge can be used as a fingerprint to determine the chemical state and the local symmetry of the absorbing atom. The spectra contain two major features due to the absorption at the V L III (2p3/2 to 3d) and L II (2p1/2 to 3d) edges. The line shape of the V L -edge is determined by the relative magnitude of the electron–electron interaction versus the bandwidth, i.e., the splitting and the intensity ratio between them are determined by the interplay of crystal-field effects and electronic interactions. The chemical shift is caused by the change in the electrostatic energy at the V site, which is driven by varying the valence states in the compounds. The absorption peak was shifted from higher energy (+4 state for V in α-LiVOPO₄ phase) to lower energy (+3 state for V in α-Li₁V₂(PO₄)₃ phase) as the sintering temperature was increased from 600 to 800 °C as shown by the dash line in the L II part. For the L III part in Figure 6, the peak shape was changed as the sintering temperature increased from 600 to 800 °C shown by the dash rectangle in the L III part. It means that different crystal systems (triclinic versus monoclinic) have different crystal-field effects and electronic interactions around the vanadium metal ion.

The infrared spectra as the function of sintering temperature are shown in the Figure 7. The assignment of the spectra for the PO₄ groups seems to be easier in the higher frequency region because the stretching vibrations of the PO₄ units and the V dO are the only expected modes in R-LiVOPO₄ at around of 900 cm⁻¹. The vibration modes of the α-Li₁V₂(PO₄)₃ can be assigned to PO₄ tetrahedral internal and external modes, as well as to lattice modes including the motion of metallic and Li⁺ ions in their octahedral cages. The internal modes of the phosphate ions...
of Figure 8. The crystal parameters obtained after refinement are summarized in Table 1. The cell parameters $a = 8.6075(3)$ Å, $b = 12.0449(5)$ Å, and $c = 8.5993(3)$ Å are in good agreement with previously reported values for $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$.

The temperature dependence of the $^7$Li MAS NMR line width for the transformed samples is shown in Figure 9. The $^7$Li MAS NMR line width measurements as a function of temperature were useful in determining the status of the motional narrowing process of the lithium cations. It shows one-dimensional (1D) variable-temperature study from 233 to 393 K, with the sample temperature corrected to include the heating effects of spinning at 15 kHz. The chemical shift has a linear dependence on temperature, showing Curie−Weiss behavior. Thus the possibility of contributions from diamagnetic and Van Vleck susceptibilities can be ruled out, which both give rise to temperature-independent NMR shifts. These materials are electronically insulating, and therefore, the possibility of a Knight shift can be ignored. The variable temperature NMR measurements thereby confirmed that the origin of the large chemical shifts was from hyperfine couplings of the Li nucleus with unpaired electron density, as described above. The intensity ratio of the three resonances, after performing spectral deconvolution of the full span of spinning sidebands was approximately 1:1:1, as predicted from the crystal structure.

Figure 10 shows the electrochemistry of $\alpha$-LiVOPO$_4$ and $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ samples at room temperature. The cell was cycled between 2.0 to 4.8 V. Figure 10a shows the galvanic profiles of $\alpha$-LiVOPO$_4$ and $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ samples at 0.1 C (0.031 and 0.022 mA/g, respectively). In $\alpha$-LiVOPO$_4$ system, the charging curve at around 3.25 and 3.85 V with small flat plateau was observed because of the existence of small amount of $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ phase. A typical flat plateau was also observed at around 4.3 V resulting from the $V^{4+}/V^{5+}$ redox couple of $\alpha$-LiVOPO$_4$. In $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ system, a flat plateau was observed at around 3.55–3.65 V with a small jump and at 4.2 and 4.6 V. The discharge capacities of $\alpha$-LiVOPO$_4$ and $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ samples at 0.1 C (0.031 and 0.022 mA/g, respectively) discharge rate were found to be 140 and 164 mAh/
g, respectively. For \(\alpha\)-LiVOPO\(_4\) sample, the discharging curve at around 2.4–2.0 V with a several flat plateau were observed because of the existence of \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) phase.\(^{32}\) This phenomena displayed the coexistence of \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) as an active cathode material. The enhanced electrochemical performance of \(\alpha\)-LiVOPO\(_4\) is mainly caused by the trace amount of transformed \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) phase (higher specific capacity than \(\alpha\)-LiVOPO\(_4\)). Thus, the coexistence of \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) is also an improvement for the charge and discharge properties of \(\alpha\)-LiVOPO\(_4\). During the structural transformation from \(\alpha\)-LiVOPO\(_4\) to \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\), the capacity was increased from 140 to 164 mAh/g. For structure-transformed \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\), we have calculated the actual number of lithium for the intercalation-de-intercalation process, which is around 2.7 and 2.5, respectively. The reversible capacity is around 93%. The suitable discharge mechanism can be described as follows:

**Cathode:**

\[
\begin{align*}
\text{V}_2(\text{PO}_4)_3 + \text{Li}^+ + e^- & \rightarrow \text{Li}_1\text{V}_2(\text{PO}_4)_3 \\
\text{Li}_1\text{V}_2(\text{PO}_4)_3 + \text{Li}^+ + e^- & \rightarrow \text{Li}_2\text{V}_2(\text{PO}_4)_3 \\
\text{Li}_2\text{V}_2(\text{PO}_4)_3 + \text{Li}^+ + e^- & \rightarrow \text{Li}_3\text{V}_2(\text{PO}_4)_3
\end{align*}
\]

**Anode:**

\[
\text{Li}_3\text{C}_{66} \rightarrow \text{C}_6 + 3\text{Li}^+ + 3e^-
\]

Figure 10b shows the cycle stability of \(\alpha\)-LiVOPO\(_4\) and \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) samples during the discharge cycles at 0.2 C (0.062 and 0.045 mAh/g, respectively). The stability of \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) was retained 85% even after 30 cycles, whereas the capacity was reduced from 144 to 123 mAh/g. For \(\alpha\)-LiVOPO\(_4\) sample, the stability was retained 86% even after 30 cycles, whereas the capacity was reduced from 104 to 90 mAh/g. Thus the electrochemical performance was improved through the structure transformation from \(\alpha\)-LiVOPO\(_4\) to \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\).

XAS is used to study the structural and electronic modification occurring around the V center atom during the charging process of \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) sample, which are assembled as the cathode material of coin cell. We have recorded in situ mode of XAS at the V K-edge for \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\)/C during the charging process in order to determine the electronic modifications occurred during the charging process of \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\). The room-temperature in situ XAS of \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) at different voltage is shown in Figure 11. It is generally assumed that the pre-edge and near edge (normalized absorbance value is 0.5) features are sufficient to determine the oxidation state of V.\(^{33}\) Hence the pre-edge and near edge features were compared for \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) at different voltage as shown in Figure 11a,b. The V pre-edge peak around 5465 eV corresponds to the 1s–3d transitions, which is electric dipole forbidden but quadrupole allowed.\(^{34}\) A weak absorption at this energy was due to the mixing of V 3d orbital with 4p orbital (3d–4p mixing) of the surrounded oxygen atoms which split the 3d orbital into \(t_2g\) and \(e_g\) states. The observed splitting of the 3d state can be assigned...
to the VO₆ octahedral crystal field splitting of the t₂g and e₈ energy level in the α-Liⱽ₂V₂(PO₄)₃ structure. The pre-edge feature of α-Liⱽ₂V₂(PO₄)₃ during charging process was compared with that of standard V₂O₅, VO₂, and V₂O₅ samples. The pre-edge before charging clearly showed that the oxidation state of V in α-Liⱽ₂V₂(PO₄)₃/C have shifted from higher to lower energy. It indicates that the oxidation of V has occurred in α-Liⱽ₂V₂(PO₄)₃ during the lithium ion extraction from the α-Liⱽ₂V₂(PO₄)₃ structure, which is in line with our assumption of extraction of Li⁺ from the crystal structure. The near-edge peak at around 5475 eV (normalized absorbance value is 0.5) as shown in Figure 11b, also shifted to higher values due to the fact that the electrons are more strongly bound to the V⁴⁺,⁵⁺ nucleus than V⁺⁺ which leads to a shift of corresponding transition toward high energy.

4. Conclusions

The compound α-Liⱽ₂V₂(PO₄)₃ was obtained through a structure transformation process during the sintering of precursor containing α-LiVOPO₄ at 600–800 °C in a flow of 5% H₂/Ar gas. The obtained sample α-Liⱽ₂V₂(PO₄)₃ exhibited a better electrochemical performance than α-LiVOPO₄. Accompanying the structural change from α-LiVOPO₄ (triclinic structure) to α-Liⱽ₂V₂(PO₄)₃ (monoclinic structure), the morphology has transformed from rock-stone to erode-like shape. It was observed that the valence state as well as the environment of vanadium element has also been changed. The first discharge capacity of obtained α-Liⱽ₂V₂(PO₄)₃ could reach to a value of 164 mAh/g at 0.1 C (0.031 and 0.022 mA/g, respectively), and capacity retained rate was 85% after 30 cycles.

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