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Electrochemical Characterization, Structural Evolution, and Thermal Stability of LiVOPO_4 over Multiple Lithium Intercalations

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Abstract: α_1 - LiVOPO_4 , β - LiVOPO_4 , and α - LiVOPO_4 are known as multiple lithium intercalation cathode materials. They were characterized by means of half-cell performance, *operando* X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and differential scanning calorimetry (DSC). The *operando* XRD revealed differences in crystal structure evolution during charging/ discharging among the three crystal phases. Although the charge/discharge profiles and the crystal structure evolution behaviors were the same among the three crystal phases in the range of 3.5 - 4.5 V, the profiles and behaviors differed completely in the range of 1.0 - 3.5 V. The thermal stability of each phase of LiVOPO_4 is similar to that of LiFePO_4 in the fully charged state from the results of the DSC profiles.

Keywords: evergreen; Lithium ion battery, Cathode material, LiVOPO_4

1. Introduction

Lithium ion secondary batteries (LIBs) have high energy density, so they are used in a wide range of applications such as smartphones, notebook PCs, and electric vehicles. Battery performance is related to cathode material properties. For example, layered rock salt metal oxide materials such as LiCoO_2 have high energy density, making them suitable for smartphones and notebook PCs, but they could not be expected to have long cycle lives or a high degree of safety because of their low crystal structure stability. Since Co is a limited natural resource, an alternative cathode material to LiCoO_2 is required. Polyanion cathode materials such as LiFePO_4 have high thermal stability and high crystal structure stability because PO_4 has strong covalent bonds that prevent oxygen release¹⁻⁴⁾ and achieved long cycle lives⁵⁻⁶⁾, but its energy density is lower than that of LiCoO_2 , so it is suitable for nonmobile devices that require long cycle lives and a high degree of safety, such as energy storage systems.

Multi-electron phosphate and oxyphosphate materials such as $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ⁷⁻⁸⁾ and LiVOPO_4 ⁹⁻¹⁷⁾ have attracted attention as alternatives to LiFePO_4 due to their higher energy densities. Rui *et al.* reported the characteristics of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as an anode and showed that Li intercalated stepwise between 2.0 V and 1.6 V and was about 130 mAh/g; however, its energy density is too low for it to be useful

as an anode active material¹⁸⁾. Moreover, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ could not be extracted last lithium, and the capacity related to the $\text{V}^{3+}/\text{V}^{4+}$ couples¹⁹⁾. On the other hand, LiVOPO_4 has three types of crystal structure: α_1 - LiVOPO_4 (tetragonal phase)^{9-11, 20-21)}, β - LiVOPO_4 (orthorhombic phase)^{12-14, 22-25)}, and α - LiVOPO_4 (triclinic phase; some reports described the third type as ε - LiVOPO_4)^{15-17, 26-29)}. Good electrochemical performance was found by the use of both the $\text{V}^{3+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$ redox couples. The crystal structure evolution from LiVOPO_4 to Li_2VOPO_4 in relation to α_1 - LiVOPO_4 ⁹⁾, β - LiVOPO_4 ¹²⁻¹³⁾, and α - LiVOPO_4 ¹⁵⁻¹⁶⁾ has been studied, but the discharge voltages were 1.5 V, so it is hard to discuss the possibility of _valence of vanadium becoming less than a trivalent state and generates larger capacity. Although LiVOPO_4 is expected to have high thermal stability because it consists of PO_4 , no report has actually evaluated this.

In our previous study, we succeeded in producing three phases of lithium vanadium oxyphosphate (α_1 - LiVOPO_4 , β - LiVOPO_4 , α - LiVOPO_4) from the same precursor that was synthesized by the hydro-thermal method³⁰⁾. In this study, we used these LiVOPO_4 to reveal the relationship between electrochemical properties and crystal structure evolution in the low-voltage region up to 1.0 V using *operando* XRD and XAFS. We also discussed the thermal stability of LiVOPO_4 .

2. Experimental

Three phases of LiVOPO_4 were prepared by a hydrothermal method and subsequent sintering process as previously reported³⁰. The prepared LiVOPO_4 was mixed with acetylene black at a weight ratio of 92:8, and ball milling was used to downsize the LiVOPO_4 particles and to carbon coat the surface. The crystal structure of each phase was confirmed using powder X-ray diffractometer (Ultima IV, Rigaku) with Cu K α radiation ($\lambda = 0.15418$ nm).

The electrochemical characterization was carried out with Al laminate-type cells assembled in a dry room in which the dew point was -40°C . Electrodes were fabricated by casting the slurry, which was made from the downsized and carbon-coated LiVOPO_4 and PVDF (polyvinylidene fluoride) at a weight ratio 92:8 in NMP (N-Methylpyrrolidone). The active material was around 6 mg/cm^2 on Al foil. The half-cell type of Al laminate cells were used, consisting of the LiVOPO_4 electrode as a cathode, Li metal on Cu as an anode, and a separator (2400, Celgard). As an electrolyte, 1 M of LiPF_6 in a solution of ethylene carbonate (EC) and diethyl carbonate (DEC; volume ratio of EC:DEC=3:7) was used. Charge/discharge testing was performed by a battery charge/discharge system (SM-8, Hokuto Denko) at room temperature.

The crystal structure evolution of LiVOPO_4 during charging and discharging was measured by *operando* X-ray diffraction (XRD) in transmission geometry (Empyrean, Panalytical), using the same configuration of half-cells described above. The charge/discharge rate was C/10 at the voltage range of 4.8 - 1.0 V for the first charge/discharge and for the charge to 3.9 V. XRD patterns were collected every hour. The scan rate of a scan was 360 s, and the 2θ step size was 0.026° in the 2θ range of 10 - 36° .

The vanadium valence of LiVOPO_4 in discharge states was analyzed from the V-K edge X-ray absorption near-edge structure (XANES). *Ex situ* X-ray absorption spectroscopy (XAS) measurements for V-K edge absorption were performed at beamline BL05S1 at the Aichi Synchrotron Radiation Center. The measured electrode samples were extracted from disassembled cells, which had been discharged at target voltage and resealed by an Al laminate in a glove box. The XAS data were collected in quick-scan mode. XANES data were normalized by using Athena developed by Ravel and Newville³¹. Energy was calibrated by using XANES of vanadium thin foil.

The thermal stability of LiVOPO_4 was evaluated by a differential scanning calorimetry (DSC, DSC6220, Hitachi) method at a heating rate of $5^\circ\text{C}/\text{min}$ up to 400°C . Cells at the target voltage were disassembled in a glove box and the electrodes were washed with DEC. Subsequently, punch out with 3 mm of diameter from the electrode. Three sheets of punched-out samples were packed into stainless steel DSC capsules with 4.5 mg of

electrolyte and then hermetically sealed.

3. Results and Discussion

Figure 1 shows the first and second charge/discharge curves of α_1 -, β -, and α - LiVOPO_4 in the voltage range of 1.0 - 4.5 V at a rate of 0.05 C ($1\text{C} = 1.07$ mA/cm^2). The profiles were the same at the first charge, but the discharge profiles and second charge profiles clearly differed among the three phases. The first charge and discharge capacities of α_1 - LiVOPO_4 were 123 mAh/g and 288 mAh/g , respectively. The characteristics of the α_1 - LiVOPO_4 charge/discharge curve correspond to those of previous reports⁹⁻¹⁰. Although the first charge capacity of our α_1 - LiVOPO_4 was lower than those previously published values, the discharge capacity accorded with the discharge capacities considering different cutoff voltages. Discharge capacity from 3.0 - 1.0 V was 165 mAh/g , even though the theoretical capacity of the reaction ($\text{LiVOPO}_4 (\text{V}^{4+}) \leftrightarrow \text{Li}_2\text{VOPO}_4 (\text{V}^{3+})$) is 159 mAh/g . Therefore, it could be expected that the valence of vanadium was decreased to below V^{3+} . On the other hand, charging from 1.0 V requires high voltage to deintercalate Li, which is associated with overpotential¹¹. Therefore, the second charge capacity from 3.0 - 4.5 V was larger than the first. The first charge and discharge capacities of β - LiVOPO_4 were 139 mAh/g and 354 mAh/g , respectively. Three plateau regions appeared in the discharge curve at 3.9, 2.0, and 1.1 V. The first ($\text{V}^{5+}/\text{V}^{4+}$) and second ($\text{V}^{4+}/\text{V}^{3+}$) plateaus corresponded to previous reports^{12-14, 17}. The discharge capacity from 3.0 - 1.0 V was 215 mAh/g . Apparently this is larger than the theoretical capacity, so the valence of vanadium should be decreased to below V^{3+} or the structure change from β - LiVOPO_4 to Li_3PO_4 occurred as Ren *et al.* reported¹⁴; if the valence of vanadium decreased, the reaction at the third plateau could be considered to be a $\text{V}^{3+}/\text{V}^{2+}$ redox couple. The capacity of the second plateau region was 134 mAh/g , which almost matched the first charge capacity. Unlike the case with α_1 - LiVOPO_4 , the $\text{V}^{4+}/\text{V}^{3+}$ discharge did not achieve theoretical capacity. On the other hand, the voltage profile of the second charge was slightly out of shape. The first charge capacity of α - LiVOPO_4 was 99 mAh/g , but the discharge capacity from 4.5 - 1.0 V was 257 mAh/g and the capacity of 3.0 - 1.0V was 158 mAh/g . That is, the theoretical capacity could be achieved in the low-voltage region. This indicates that the lithium intercalate ability differs between high- and low-voltage regions. Furthermore, the voltage profile is relatively the same for charging and discharging. Three distinct plateaus appeared in the range of 2.5 - 1.9 V. This reaction, in which the valence of vanadium is tetravalent and trivalent, has been discussed in detail^{12-13, 15-16}. Hence the reaction of $\text{V}^{3+}/\text{V}^{2+}$ cannot be expected in the region of 1.0 - 4.5 V.

The cycle characteristics were evaluated under the rate of C/20 (first and second cycles) and the C/10 condition. The cycle characteristics of the 2nd, 10th, 20th, and 30th charge/discharge curves are shown in Fig. 2 and indicate that the cycle characteristics were not stable. The capacity in the range of 3.0 - 4.5 V was almost constant, but the

capacity of the low-voltage region decreased as the cycle number increased. This was attributed to the disappearance of $\text{V}^{3+}/\text{V}^{4+}$ reactions. The capacity retention of $\alpha\text{-LiVOPO}_4$ was good compared to the other phases but slightly worse than in previous reports¹⁶⁻¹⁷.

Fig. 1: First and second charge/discharge curves of $\alpha_1\text{-LiVOPO}_4$ (a), $\beta\text{-LiVOPO}_4$ (b), and $\alpha\text{-LiVOPO}_4$ (c) in the range of 4.5–1.0 V at the rate of C/20.

In order to understand the phase evolution of each LiVOPO_4 during charge/discharge, *operando* XRD was performed on an X-ray diffractometer equipped with $\text{Cu-K}\alpha 1$ radiation in transmission geometry, together with the charge/discharge data. The charging and discharging rate was C/10 in the voltage range of 3.5 - 4.8 V for the first charge, 4.8 - 1.0 V for the first discharge, and 1.0 - 3.9 V for the second charge. Every pattern was recorded in the 2θ range of $10\text{--}36^\circ$ every hour, corresponding to $x = 0.1$ in Li_xVOPO_4 . The results are shown in Fig. 3 ($\alpha_1\text{-LiVOPO}_4$), Fig. 4 ($\beta\text{-LiVOPO}_4$), and Fig. 5 ($\alpha\text{-LiVOPO}_4$). Since there was not enough active material on the electrode, sufficient signal intensity could not be detected. We therefore discuss the whether the crystal structure evolution is two-phase or solid-solution behavior, based on changes in the

main peak. If it was two-phase behavior, diffraction peaks from two kinds of crystal phase would be found simultaneously and no diffraction peak shifts would be found. If it was solid-solution behavior, on the other hand, a diffraction peak shift would be found.

Fig. 2: Cycle characteristics of $\alpha_1\text{-LiVOPO}_4$, $\beta\text{-LiVOPO}_4$, and $\alpha\text{-LiVOPO}_4$ in the 4.5–1.0 V range at the rates of C/20 (first and second cycles) and C/10 (a). The 2nd, 10th, 20th, and 30th charge/discharge curves of $\alpha_1\text{-LiVOPO}_4$ (b), $\beta\text{-LiVOPO}_4$ (c), and $\alpha\text{-LiVOPO}_4$ (d).

Variations in the diffraction peaks of $\alpha_1\text{-LiVOPO}_4$

correspond to the results of *ex situ* XRD reported by G. He *et al.*⁹⁾. The final diffraction pattern fully corresponded to the initial diffraction pattern. This suggests that the reaction is highly reversible even though the crystal structure changes dynamically. In the discharge from 4.8 - 1.0 V, the diffraction peak of α_1 -LiVOPO₄ decreases, that of α_1 -Li₂VOPO₄ increases, and that of α_1 -LiVOPO₄ continues to appear distinctly up to 1.5 V. The state of structural change is clearly different between charging and discharging. In discharging, the diffraction peaks of α_1 -LiVOPO₄ and α_1 -Li₂VOPO₄ can be distinguished as two-phase behavior. However, in charging from 1.0 V as the voltage increased, the shape of the peak collapsed, the full width at half maximum widened and gradually shifted to the high-angle side, indicating solid-solution behavior. It can be considered that the difference between Li⁺ intercalation and deintercalation behaviors is associated with the difference in charge/discharge profiles in the low-voltage region. This supports two-phase behavior in low-voltage discharge as G. He *et al.* reported⁹⁾. However, it is solid-solution behavior in charging at low voltage.

Fig. 3: Operando XRD patterns of α_1 -LiVOPO₄ with charge/discharge profiles at C/10 up to 4.8 V (left). An enlarged view of the 25.5–30° region of the first discharge and second charge. The dotted lines indicate the characteristic peak positions of the crystal phases.

Figure 4 shows the results of *operando* XRD for β -LiVOPO₄. There are drastic changes in the XRD patterns as the amount of lithium changes. In the first charge, a peak shift was not found and only diffraction peaks from each phases increase and decrease. This indicates two-phase behavior. In the first discharge, as the black arrows indicate, a diffraction peak shift is found in the latter half of the second plateau (2.1 V). The peak shift started after the LiVOPO₄ peaks disappeared. After the peak shift (corresponding to the end of the second plateau), the peak location was not changed but the intensity started to decrease, and this diffraction peak disappeared at the third plateau. M. M. Ren *et al.* revealed that the crystal structure of discharging β -LiVOPO₄ at 0.01 V changed to Li₂O, V and Li₃PO₄¹⁴⁾. However, we could not find such components, but two new weak peaks appeared at the 2θ region of 26–27°. Due to low crystallinity, we did not know how to attribute the peaks. At least it could be said

that, before Li₂VOPO₄ decomposes to Li₂O, V and Li₃PO₄ at 0.01 V, another crystal phases would exist. In the second charge, although an unknown peak was found at the lower plateau region as indicated by the black dashed arrow, the positions and behaviors of the other diffraction peaks agreed with those in discharging. Thus, unlike the case with α_1 -LiVOPO₄, the phase transition behaviors were the same in charging as in discharging. Therefore, in the charge/discharge curve, the plateau of low voltage appears at the same voltage during charging and discharging.

Fig. 4: Operando XRD patterns of β -LiVOPO₄ with charge/discharge profiles at C/10 up to 4.8 V (left). An enlarged view of the 25.5–30° region of the first discharge and second charge. The dotted lines indicate the characteristic peak positions of the crystal phases.

Fig. 5: Operando XRD patterns of α -LiVOPO₄ with charge/discharge profiles at C/10 up to 4.8 V (left). Enlarged view of the 25.5–30° region of the first discharge and second charge. The dotted lines indicate the characteristic peak positions of the crystal phases.

The results of *operando* XRD for α -LiVOPO₄ are shown in Fig. 5. The capacity of our α -LiVOPO₄ was half of theoretical capacity, so that the diffraction peaks of both VOPO₄ and α -LiVOPO₄ appeared at 4.8 V. Considering the results of our previous study, lithium would perhaps not be deintercalate from large particles,³⁰⁾ and the diffraction peak of α -LiVOPO₄ would be from large particles. As shown in Fig. 1 (c), three peculiar plateaus appeared in the low-voltage region. As shown in Fig. 5, the plateau of 2.4 V (LiVOPO₄ ↔ Li_{1.5}VOPO₄) indicates two-phase behavior, and the plateaus of 2.2 V (Li_{1.5}VOPO₄ ↔ Li_{1.75}VOPO₄) and 2.0 V (Li_{1.75}VOPO₄ ↔

Li₂VOPO₄) indicate solid-solution behavior because peak shifts occurred. These results agreed with that of previous report¹⁵⁾. In charging from 1.0 V, the crystal structure evolution was the same as in discharging. Therefore, α -LiVOPO₄ also exhibits plateaus at the same voltage in charging and discharging. Interestingly, because diffraction peaks of α -LiVOPO₄ clearly disappeared, unlike the case in 4.8 V charging, large particles also contribute to low-voltage charging/discharging.

Fig. 6: Normalized V K-edge XANES spectra of α_1 -LiVOPO₄ (a), (b), β -LiVOPO₄ (c), (d), and α -LiVOPO₄ (e), (f) at various states of OCV compared with various vanadium oxides and vanadium metal. (b), (d), and (f) are enlarged views of the pre-edge peaks.

As mentioned above, the discharge capacities from 3.5 - 1.0 V of α_1 -LiVOPO₄ and β -LiVOPO₄ were larger than the theoretical capacity of LiVOPO₄ (V^{4+}) $\leftrightarrow$ Li₂VOPO₄ (V^{3+}). On the other hand, α -LiVOPO₄ exhibited the theoretical capacity even though the charge capacity from 3.5 - 4.5 V was 99 mAh/g. To explain this capacity from the viewpoint of charge compensation, information on the valence of vanadium at low voltage is needed. *Ex situ* XAFS was performed to investigate the valence of vanadium in the low-voltage region and the results were compared with those of various vanadium oxides and vanadium metal as a standard valence. The results of the normalized XANES spectra are shown in Fig. 6. The pre-edge shape varied and energy shifts were seen, according to OCV changes. The pre-edge peak is due to the 1s $\rightarrow$ 3d transition, which is possible because of the O 2p and V

3d/4p hybrid orbit. The large pre-edge peak is attributable to the distortion of the VO₆ octahedra due to V=O¹²⁻¹³⁾. The pre-edge peak decreased as OCV decreased. This change trend of β -LiVOPO₄ and α -LiVOPO₄ agreed with previous reports¹²⁻¹³⁾. From the results of the XANES absorption edge shift, the valences of vanadium for α_1 -LiVOPO₄ and β -LiVOPO₄ at 1.5 V and for α -LiVOPO₄ at 1.5 V and 1.0 V should be V^{+3} because they corresponded to the absorption edge of V₂O₃. Although it is difficult to determine the valences of vanadium at 1.0 V of α_1 -LiVOPO₄ and β -LiVOPO₄, it can be said that it is sufficiently smaller than at least trivalent. This study revealed the vanadium valence behavior of α_1 -LiVOPO₄ in the low-voltage region using XAFS. G. He *et al.* reported the crystal structure of α_1 -Li₂VOPO₄ using neutron and X-ray diffraction with Rietveld refinement. V-O bonding of α_1 -Li₂VOPO₄ was longer than α_1 -LiVOPO₄, and the summary of bond valance sums of vanadium for the vanadium coordination environment in α_1 -Li₂VOPO₄ was trivalent.⁹⁾ From our XANES results, the trivalent of vanadium was OCV at 1.5 V, and α_1 -LiVOPO₄ must finish changing to α_1 -Li₂VOPO₄ at 1.5 V in discharging. This is supported by our *operando* XRD as shown in Fig. 3, where the crystal structure finished changing around 1.5 V. Additional lithium insertion from 1.5 - 1.0 V suggests that the framework of the crystal structure is not changing; rather, only the valence of vanadium changes.

Fig. 7: DSC profiles of LiVOPO₄, LiFePO₄, and LiCoO₂ with electrolyte at a heating rate of 5°C/min after 4.5 V charge for LiVOPO₄ and LiCoO₂, and 3.8 V for LiFePO₄.

The thermal stability of LiVOPO₄ was investigated using DSC. Figure 7 shows DSC profiles of α_1 -LiVOPO₄, β -LiVOPO₄, α -LiVOPO₄, and LiCoO₂ at 4.5 V charge and LiFePO₄ at 3.8 V charge. The DSC profiles of all LiVOPO₄ had the same shape and were similar to LiFePO₄. All PO₄ tetrahedral corners of LiVOPO₄ are shared with VO₆ octahedra, which is different from the case with LiFePO₄. LiFePO₄ shares one edge of PO₄ tetrahedra with FeO₆ octahedra. However, the difference in crystal structures is not related to thermal stability. Since both LiVOPO₄ and LiFePO₄ are composed of highly thermostable PO₄, there is no oxygen release, so

there is no clear difference in DSC profiles. Figure 8 shows the DSC profiles of LiVOPO_4 at 4.5 V charging and 1.0 V discharging. These profiles differ. It is difficult to discuss a strictly quantitative comparison of the total exothermic reaction enthalpy because the baseline and temperature range for calculating total exothermic enthalpy for each datum cannot always be constant. The exothermic enthalpy values are shown in Fig. 8 as reference values. The exothermic reaction enthalpy of LiVOPO_4 is small enough compared with LiCoO_2 . Although α_1 -, β -, and α - LiVOPO_4 discharged down to 1.0 V have different crystal structures and amounts of Li, they all showed a similar slight exothermic reaction around 90°C. Although we could not determine the reason for the exothermic reaction at 1.0 V of the profile around 90°C, the exothermic reaction enthalpy is around 190 J/g at most, which is considered too low to reduce thermal stability. The high thermal stability of LiVOPO_4 is maintained even in the low-voltage region.

Fig. 8: DSC profiles of LiVOPO_4 at 4.5 V charging and 1.0 V discharging with electrolyte at a heating rate of 5°C/min.

4. Conclusions

α_1 -, β -, and α - LiVOPO_4 have been synthesized from the same precursor, and controlled subsequent sintering temperature. The capacities in the ranges of 3.5 - 4.5 V and 3.5 - 1.0 V differed. The capacity of the high-voltage region is influenced by the particle size, although the capacity of the low-voltage region was close to the theoretical capacity. Moreover, α_1 - and β - LiVOPO_4 exhibited beyond theoretical capacity in discharging to 1.0 V due to the decrease in the vanadium valence to below V^{3+} . This was supported by *ex situ* XANES analysis. *Operando* XRD determined whether the crystal structure evolution was solid-solution behavior or two-phase

behavior during charging/discharging, and the difference in the charge/discharge profiles of α_1 - LiVOPO_4 was associated with crystal structure evolution. The thermal stability of LiVOPO_4 was demonstrated by DSC for the first time. The DSC profiles of LiVOPO_4 in the charging state were similar to that of LiFePO_4 and the total exothermic enthalpy were smaller than that of LiCoO_2 . Although the root cause could not be identified, the DSC profile of LiVOPO_4 at 1.0 V appeared as an exothermic reaction around 90°C. However, it was not so large, and the total exothermic enthalpy from 80 - 350°C was the same as that at 4.5 V charging. Since α_1 -, β -, and α - LiVOPO_4 have high energy densities and high thermal stabilities, we conclude that they can be expected to serve not only as a next-generation polyanion cathode materials to replace LiFePO_4 but also as an anode materials with high thermal stability.

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