Redox Mechanism of $Li_3V_2(PO_4)_3$ Lithium-Ion Battery Cathode

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Abstract

The redox mechanism of the V species in $Li_3V_2(PO_4)_3$ cathode of lithium ion battery has been analyzed by the *in-situ* XAFS technique. It was found that the charging process is composed of three successive one-electron oxidation steps in a sequence of V(III,III), V(III,IV), V(IV,IV), and V(IV,V), whereas the discharging process was not the reverse steps. The generated charge unbalance in the final form of the charging process causes the intervalence electron transfer between the V(IV) and V(V) sites, and it explains the potential reduction at the initial stage of the discharging process and the two-electron reduction from V(V,IV) to V(III,IV) during the discharging process.

1. Introduction

Many compounds containing lithium ion have been examined as the cathode material of lithium ion rechargeable battery (LIB). Phosphates are favorable in the stable utilization as the cathode material because of their rigid crystal structure at the delithiated state. Although lithium iron phosphate is utilized as a practical active material, its effective discharging voltage of 3.4 V is unfortunately low due to the redox potential of Fe^{3+}/Fe^{2+}. A substitution of the transition metal element is effective to increase the cell voltage, and thus lithium vanadium phosphate ($Li_3V_2(PO_4)_3$) is one of potential cathode materials with its high operating voltage [1]. There are three different sites occupied by lithium ion in the crystal structure, and the charging potential depends on the site at which the lithium ion is dissociated. The charging and discharging processes under 4.5 V are reversible, where two of three lithium ions participate in the electrochemical reaction [2]. However, when all lithium ions are extracted at the charging process to 4.8 V, the initial voltage at the next discharging process quickly drops to about 4.2 V and thus the discharging curve is apparently different from the charging curve. It means that the third delithiation process is not reversible, and thus the redox reactions of $Li_3V_2(PO_4)_3$ is not fully understood. Yin *et al.* has reported the crystal structure and the oxidation state of vanadium species for the chemically prepared $Li_xV_2(PO_4)_3$ ($x = 3.0$, 2.5, 2.0, 1.0, and 0.0) by means of the powder X-ray and neutron diffraction techniques [2]. It has been proposed that the vanadium ion in $V_2(PO_4)_3$ takes a random oxidation state of +4 or +5 independent at their two lattice sites and that the lithium ion in $LiV_2(PO_4)_3$ partly occupies both of two different sites in $Li_2V_2(PO_4)_3$ during the discharging process. These considerations require the complicated movement for the Li and V ions during the charging/discharging processes. In addition, the reported crystal is not electrochemically prepared state. Therefore, the detail redox mechanism of the electrode reaction of $Li_3V_2(PO_4)_3$ is still unclear to understand the potential drop and the low voltage at the beginning of the discharging process. In this study, we have analyzed the chemical state of the vanadium species in the $Li_3V_2(PO_4)_3$ cathode during the charging and discharging processes by the *in-situ* XAFS measurements.

2. Experimental

A carbon-containing lithium vanadium phosphate ($Li_3V_2(PO_4)_3$) was synthesized by a solid phase method [3]. As the vanadium source, vanadium(V) oxide was used with oxialic acid as the reducing agent. Ammonium dihydrogen phosphate and lithium carbonate were dissolved into deionized water, and the solution was dried in air at 80 ºC after adding a conductive carbon material. The obtained powder was heated at 800 ºC under 5 vol% H_2/Ar gas flow. The prepared material was characterized by the X-ray diffraction as $Li_3V_2(PO_4)_3$. The carbon content was determined by the thermogravimetric analysis.

The cathode material was prepared by mixing the synthesized carbon-containing $Li_3V_2(PO_4)_3$ powder and polyvinylidene difluoride at the weight ratio of 9:1 in *N*-methylpyrrolidone as a dispersion medium. The mixture was spread on an aluminum foil to the thickness of 100 μm, dried at 80 ºC in vacuum, and then pressed with the roll press. A current collector tab was ultrasonically welded to the cathode sheet. The LIB cell for *in-situ* XAFS measurements was assembled from the cathode sheet, an Li foil as the anode, two separator sheets, and 1 mol dm^{-3} $LiPF_6$ electrolyte solution in a 3:7 (v/v) mixture of ethylene carbonate and ethyl methyl carbonate. Aluminum-coated laminate films were used as the outer shell of the battery cell. The *in-situ* XAFS measurements for the $Li_3V_2(PO_4)_3$ battery cell were carried out at BL-3 of Ritsumeikan SR Center after three aging cycles. The charging and discharging rate was 0.25 C for the *in-situ* experiment, and the cut-off voltage was set from 3.0 to 4.8 V vs. Li^+/Li. The vanadium K-edge XANES spectra were collected in the transmission mode. The scanning time of one spectrum was 3 min.

3. Results and discussion

The measured charging curve is shown in Fig. 1 for the prepared $Li_3V_2(PO_4)_3$ battery cell. Three voltage plateaus were clearly observed at 3.7, 4.1, and 4.6 V, and their charging capacities were almost identical, indicating that one lithium ion was extracted at each charging plateaus voltage. On the other hand, the discharging curve shown in Fig. 2 was not apparently in accordance with the charging curve. It is concluded that the discharging process consists of two redox steps of 4.2 – 3.7 V and 3.7 – 3.4 V based on the shape of the discharging curve. The former voltage almost corresponds to the second plateau voltage during the charging process, and the latter is in agreement with the first charging step. The third lithium ion was extracted at around 4.6 V in the charging process terminated at 4.8 V to form $V_2(PO_4)_3$, whereas the initial voltage at the next discharging process was dropped to less than 4.5 V. Such voltage loss strongly suggests the chemical state conversion in the $V_2(PO_4)_3$ state.

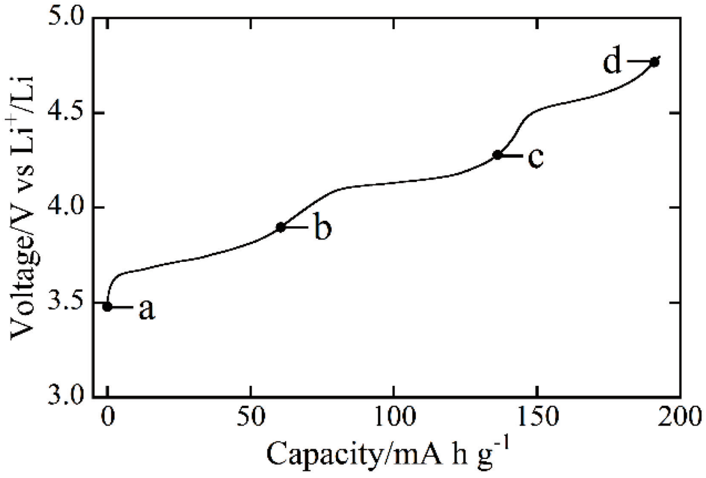

Fig. 1 Charging curve of $Li_3V_2(PO_4)_3$ LIB during the *in-situ* XAFS measurement

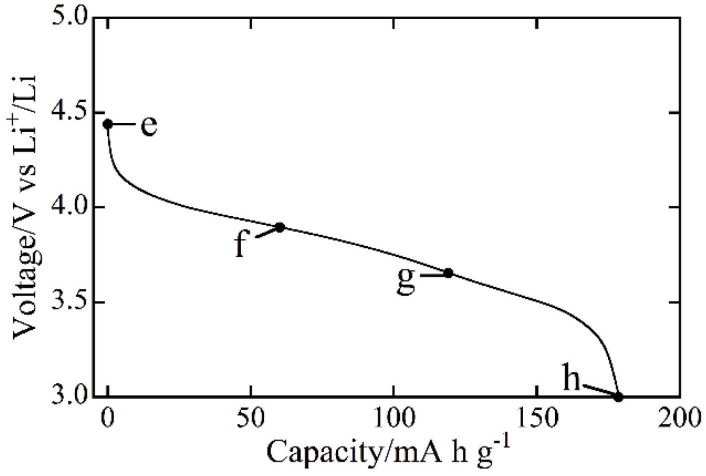

Fig. 2 Discharging curve of $Li_3V_2(PO_4)_3$ LIB during the *in-situ* XAFS measurement

Figure 3 shows the XANES change during the charging process. The three step observed in the spectral change corresponds to each of three delithiation steps during the charging process. The initial oxidation state of two vanadium centers was +3, and it was oxidized to the average oxidation state of +3.5 at the first step (see Fig. 3(A)). It means that one of two V atoms is oxidized to V(VI). This valence shift is reasonable in considering the dissociation of one lithium(I) ion from $Li_3V_2(PO_4)_3$. As shown in Fig. 3(B), the higher shift of the absorption edge energy was observed at the second plateaus, however the intensity of the pre-edge peak observed at around 5468 eV was not changed, indicating the V oxidation state of +4, because it is know that the V(V) state shows more intense pre-edge peak. The V(IV,IV) state is thus formed after the second delithiation. The pre-edge peak energy showed the slight higher shift through the first and second delithiation processes. At the third plateaus in the charging process, the pre-edge peak intensity was developed as shown in Fig. 3(C), although the edge energy was almost unchanged. The final feature of the XANES spectrum was interpreted by the mixture of the V(IV) and V(V) states and was in agreement with the composition of $V_2(PO_4)_3$. The present *in-situ* XAFS study revealed that the valence state of the V center was changed in a sequence of V(III,III), V(III,IV), V(IV,IV), and V(IV,V) during the charging process accompanying the dissociation of totally three lithium(I) ion and the elimination of three electrons from two V(III) ions.

The XANES spectral change during the discharging process is shown in Fig. 4. The decrease of the pre-edge peak intensity and the lower energy shift of the absorption edge were simultaneously observed in Fig. 4(D) and (E). This result clearly demonstrated that these changes were not reverse processes of the second and third delithiation in the charging

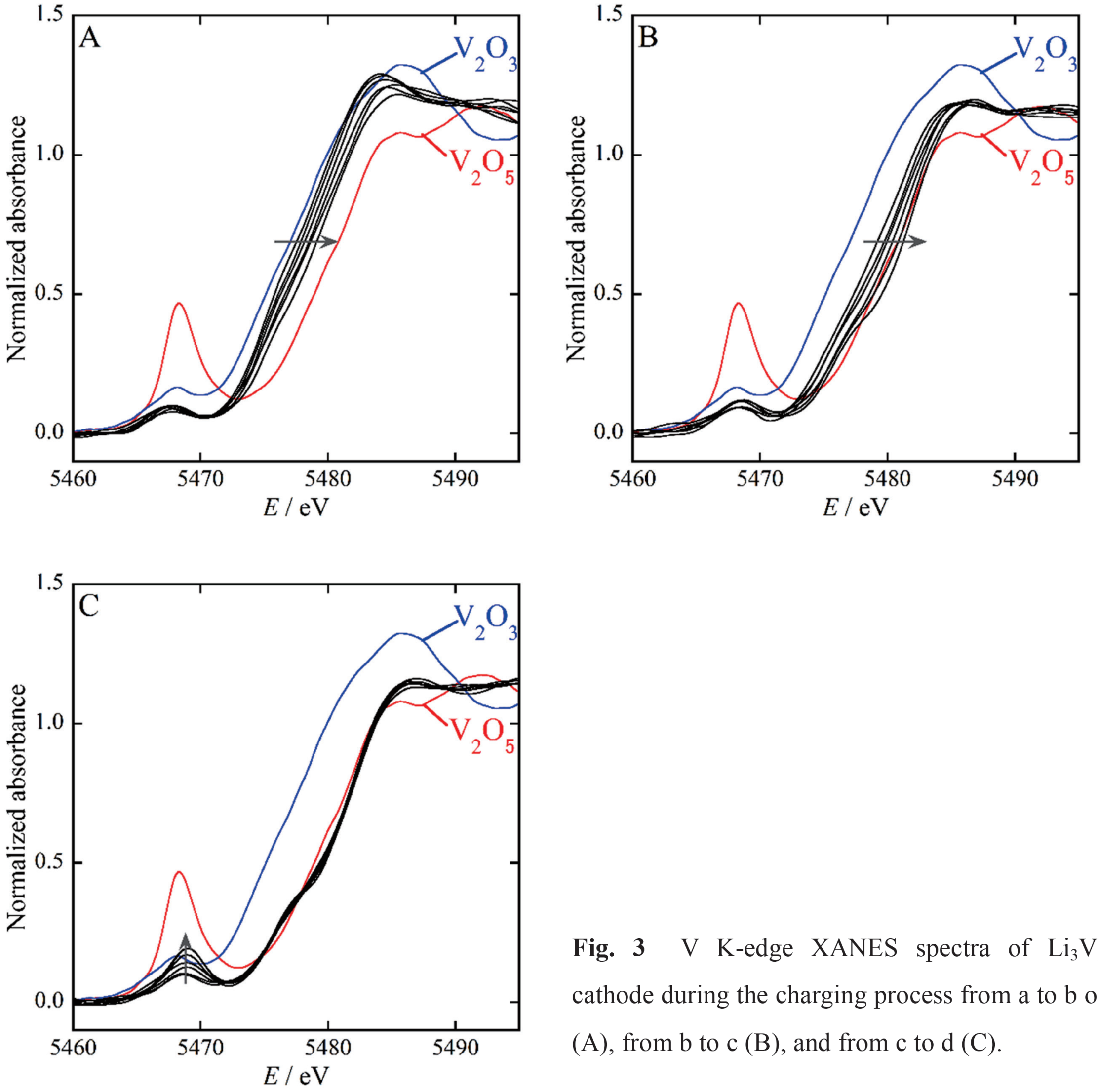

Fig. 3 V K-edge XANES spectra of $Li_3V_2(PO_4)_3$ cathode during the charging process from a to b of Fig. 1 (A), from b to c (B), and from c to d (C).

process shown in Fig. 3(B) and (C). During the discharging process at the voltage range from 4.2 V to 3.7 V, it was considered that the oxidation state of the V center was changed from (IV,V) to (III,IV), because the XANES spectrum at 3.7 V was in good agreement with that after the first delithiation in the charging process. The spectral change shown in Fig. 4(D) and (E) implies that the V(V) species exists through the discharging step from $V_2(PO_4)_3$ to $Li_2V_2(PO_4)_3$, and the V(V) species disappears at the final point (Fig. 2(g)) of the two-electron reduction step. The last step of the discharging process (Fig. 4(F)) was a reverse process of the first step in the charging process, indicating that the initial V(III,III) state was regenerated after the charging/discharging cycle.

The present *in-situ* XAFS investigation for the charging and discharging processes of the $Li_3V_2(PO_4)_3$ cathode clarified the changes of the oxidation state for the V center, that is, the V ions occupied at two different sites are oxidized in a sequence of V(III,III), V(III,IV), V(IV,IV), and V(IV,V) during the charging process, whereas the V ions are reduced from

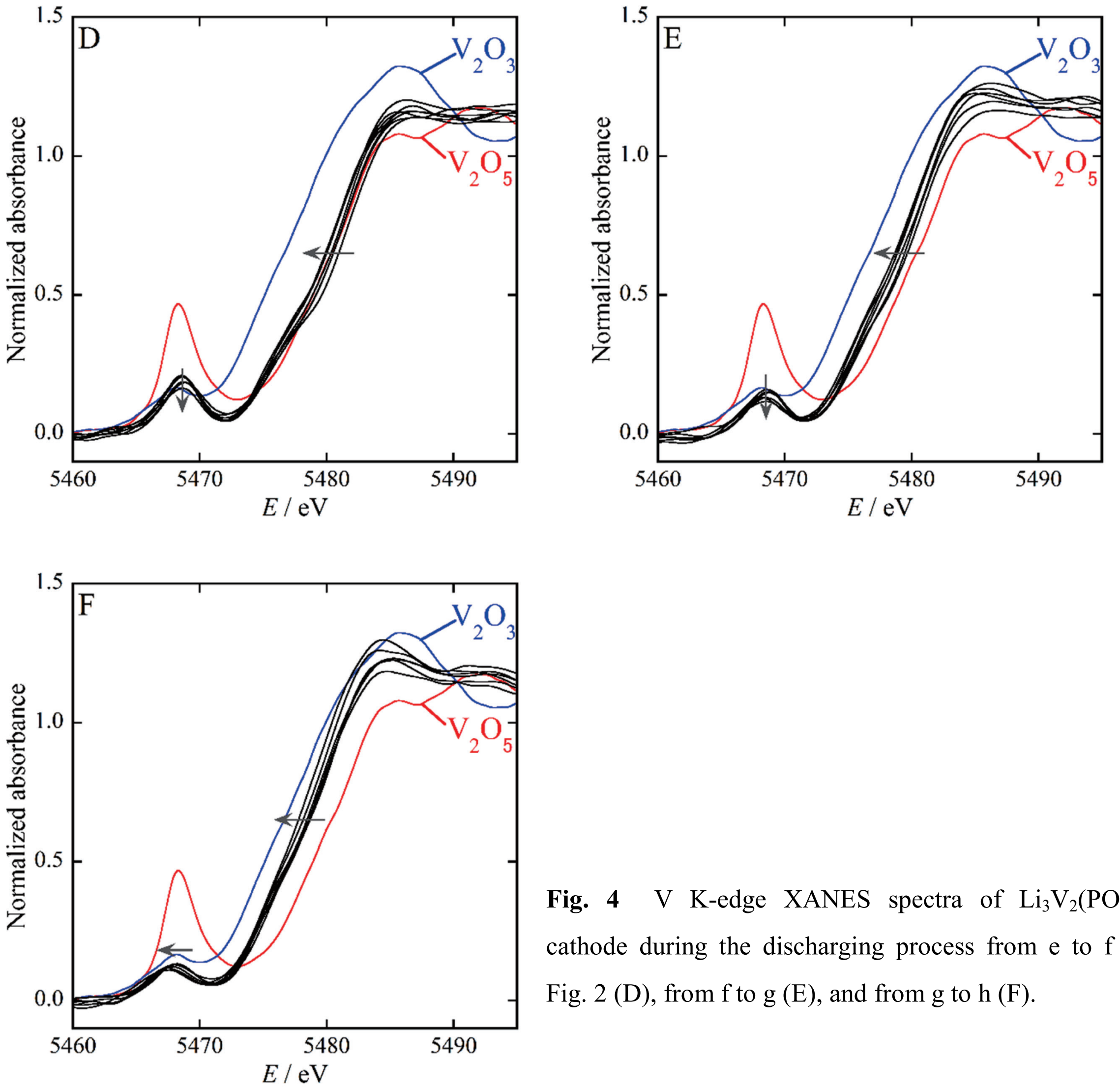

Fig. 4 V K-edge XANES spectra of $Li_3V_2(PO_4)_3$ cathode during the discharging process from e to f of Fig. 2 (D), from f to g (E), and from g to h (F).

(V,IV) to (III,III) via (III,IV) during the discharging process. The reduction processes are not simple backward reactions of the oxidation processes, and the state of V(IV,IV) is not observed during the discharging process. The voltage drop at the fully charged state of V(IV,V) indicates the electronic modification proceeded at the beginning of the discharging process. We have proposed the redox mechanisms for the cathode reactions of $Li_3V_2(PO_4)_3$ as shown in Fig. 5. The first oxidation is considered to proceed at the V(III) site (V(B) site), because there are two close Li ions around the V(B) site. It is much favorable than at the V(A) site, which has only one close Li ion. The first oxidation forms the V(III,IV) state, and one Li ion exists close to both the V sites. The asymmetric occupation of the phosphate ions around two V sites promotes the prior oxidation at the remaining V(III) site (V(A) site), and the V(IV,IV) state is then produced at the second plateaus voltage. The final oxidation occurs at the V(B) site, because there is a remaining Li ion beside it. A series of the oxidation processes finally generates the V(IV) and V(V) ion at the V(A) and V(B) site, respectively. It is considered that this state is unstable because of the unbalanced charge separation between the positive V ions and the negative phosphate ions. The intervalence electron transfer between the V(IV) and V(V) sites can relax such the charge separation, and thus the potential reduction

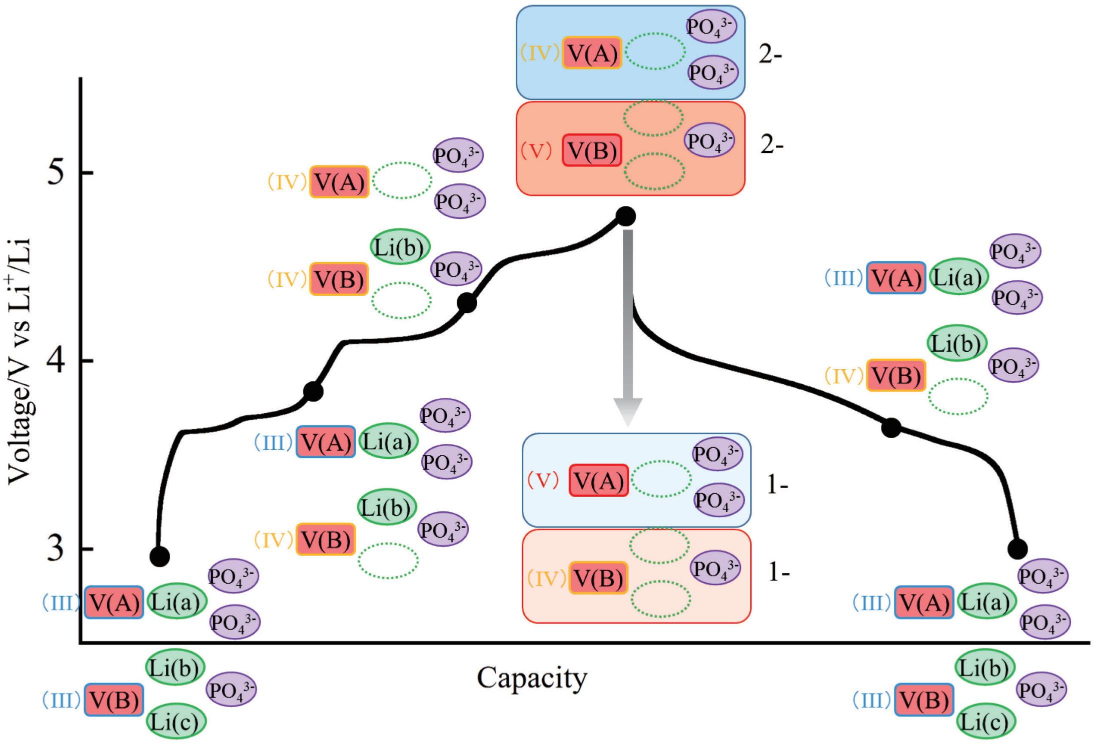

Fig. 5 Redox mechanism of the $Li_3V_2(PO_4)_3$ species during the charging and discharging processes. The vanadium ion, lithium ion, and phosphate ion are schematically shown to explain their relative location. The labels (A) and (B) for vanadium ion and (a), (b), and (c) for lithium ion mean the distinguishable site in the crystal structure.

occurs at the initial stage of the discharging process. The discharging process at 4.2–3.7 V regenerates the V(III,IV) state, which is identical to that formed at the first charging process, that is, the V(III) ion at the V(A) site and the V(IV) ion at the V(B) site. It means that the V(A) site is reduced from V(V) to V(III) during the discharging process at 4.2–3.7 V. The available capacity is in accordance with the two-electron reduction process. The final one-electron reduction occurs at the V(IV) ion (V(B) site) to regenerate the V(III,III) state. This step is the backward of the first oxidation step in the charging process, and thus the discharging voltage is almost consistent with the corresponding charging voltage.

5. Conclusion

The chemical state of the vanadium species has revealed for the $Li_3V_2(PO_4)_3$ cathode during the charging and discharging processes in the LIB by means of the *in-situ* XAFS technique. It was found that the charging process is composed of three successive one-electron oxidation steps in a sequence of V(III,III), V(III,IV), V(IV,IV), and V(IV,V). The unbalanced charge formed at the end of the charging process causes the intervalence electron transfer between the V(IV) and V(V) sites and thus the potential reduction at the initial stage of the discharging process. The two-electron reduction from V(V,IV) to V(III,IV) and the succeeding one-electron reduction to V(III,III) occur during the discharging process. The proposed mechanism reasonably explains the observed asymmetrical charging/discharging curves.

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