

Vanadyl phosphates of VOPO₄ as a cathode of Li-ion rechargeable batteries

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Abstract

Seven phases of VOPO₄ were synthesized and their Li intercalation properties were investigated. Li can be reversibly intercalated into all phases of VOPO₄ and potential plateaus for Li intercalation and de-intercalation exist at 3.7 and 3.9 V, respectively, except for the β- and ε-phases. β- and ε-phases of VOPO₄ exhibit slightly higher flat potentials of 3.9 and 4.1 V. The capacity for Li intercalation is strongly affected by the crystal structure of VOPO₄ and the Li intercalation capacity increases with increasing average valence of V. Among the VOPO₄ crystal phases, it was found that the δ-phase exhibits the largest reversible capacity of ca. 130 mAh/g. The capacity for Li de-intercalation in δ-phase VOPO₄ hardly decreased over 35 charge and discharge cycles. On the other hand, the Li intercalation capacity in δ-phase VOPO₄ decreased with increasing current density for charge and discharge and temperature. However, even at a current density of 0.4 mA/cm², corresponding to C/5, fairly large capacity of ca. 60 mAh/g was sustained, and at a operating temperature or 323 K, a capacity of 110 mAh/g was exhibited at 0.04 mA/cm².

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1. Introduction

Li-ion rechargeable batteries have advantages of high power density and good reversibility compared to other types of rechargeable batteries. Use of transition metal oxides such as LiCoO₂ and LiMn₂O₄ leads to a high operating voltage that is suitable for various portable electronic devices. However, it is well known that limited availability of Co increases the cost of LiCoO₂, the main cathode for the commercial Li-ion rechargeable battery. Therefore, Mn-based oxides such as LiMn₂O₄ attract much interest as alternative new cathode materials with low cost. However, the chemical stability of Mn-based oxides is not sufficient for this application. In particular, Mn dissolution at high temperature is problematic for the application of these Mn-based oxides as the cathode. Therefore, development of alternative host materials for cathodes is being studied extensively, at present.

Among the various compounds containing Li, metal phosphates have been attracting much interest as new cathode

materials for Li-ion rechargeable batteries [1–4]. This is because metal phosphates are generally more stable than oxides and some of them have unique layered and/or tunnel structures. Among the metal phosphates, olivine phase LiFePO₄ [1] or LiCoPO₄ [2] have been reported as good candidates for new cathode materials in Li-ion rechargeable batteries. Recently, Dupre et al. reported the electrochemical intercalation and de-intercalation of Li into VOPO₄ with various structures and demonstrated a high potential plateau of 3.76 V for Li intercalation in this compound [5]. On the other hand, Kerr et al. also reported a high Li intercalation potential in α-LiVOPO₄ that was electrochemically synthesized from ε-type VOPO₄ [6]. In addition, Li₃V₂(PO₄)₃ is also being considered as a new cathode for commercial cells. Therefore, Li intercalation properties of vanadium phosphate are highly interesting from the new cathode material point of view. However, the Li intercalation property into vanadium phosphate has not been studied systematically.

Li intercalation into VOPO₄ with different crystal structures was examined under the same conditions in this study, since the theoretical capacity of VOPO₄ is as high as 166 mAh/g and it has a high potential for intercalation and de-intercalation of Li. It is well known that one type

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Table 1
Average valence number of V in synthesized VOPO₄ and initial reversible capacity in this study and reported one

| Phase | Discharge potential (V) | V ⁴⁺ content (mol%) | Average valence of V | Reversible capacity (mAh/g) | Remarks |
|-----------------|-------------------------|--------------------------------|----------------------|-----------------------------|-----------|
| α _I | 3.7 | 4.5 | 4.95 | 85.3 | C/50 |
| | 3.7 | | | 55 | C/20 [5] |
| α _{II} | 3.7 | 6.5 | 4.94 | 77.5 | C/50 |
| | 3.7 | | | 135.0 | C/50 [11] |
| β | 3.9 | 11.4 | 4.89 | 16.7 | C/50 |
| | 3.9 | | | 3.5 | C/50 [10] |
| δ | 3.7 | 4.8 | 4.95 | 118.4 | C/50 |
| | 3.7 | | | 130.0 | C/50 [11] |
| ε | 3.8 | 1.4 | 4.99 | 77.5 | C/50 |
| | 3.8 | | | 106.0 | C/50 [6] |
| ω | 3.7 | 5.3 | 4.95 | 85.7 | C/50 |
| γ | 3.7 | 4.4 | 4.96 | 95.2 | C/50 |
| | 3.7 | | | 60.0 | C/50 [11] |

of VOPO₄ have an open tunnel structure, and that there are seven different types of crystal structures that differ in the connection and arrangement of VO₆ octahedral and PO₄ tetrahedral units [7–9,13]. The Li intercalation properties of some phases have already reported. However, as summarized in Table 1, the observed Li intercalation capacities are much smaller than that of the theoretical values. In addition, the cycle stability is not high [5,6,10,11]. Since various preparation methods have been reported for VOPO₄ [7,8,12–14], there is a possibility that VOPO₄ with larger capacity and better cycle stability can be obtained by changing the preparation method and crystal structure. For this study, VOPO₄ with seven different crystal phases were synthesized and their electrochemical performance as the cathode in Li-ion rechargeable batteries were investigated.

2. Experimental

All vanadyl phosphates (VOPO₄) in this study were prepared according to the procedures reported in the literature [8,9,12,13]. β-VOPO₄ was synthesized by a conventional solid-state reaction from stoichiometric amounts of NH₄H₂PO₄ and V₂O₅. Powders were mixed by using an Al₂O₃ mortar and pestle. The mixture was calcined at 973 K in an oxygen stream for 3 h. Finally, the mixture was calcined again at 973 K for 5 h in order to achieve a uniform composition. The γ-phase was obtained by firing the precursor powder mix at 973 K for 14 h in air. Differing calcination procedures result in different phases. The rest of the VOPO₄ phases were prepared from the following three precursors: VOPO₄·2H₂O, VOHPO₄·0.5H₂O and VPO₄·H₂O that were obtained according to the references [8,13]. α_I- and α_{II}-phases of VOPO₄ were obtained by the

calcination of VOPO₄·2H₂O at 773 and 973 K for 14 h in air. The δ-phase was obtained by the calcination of VOHPO₄·0.5H₂O at 773 K in air for 14 h, and the ω-phase was obtained by calcination of the same precursor at 773 K in a N₂ stream for 3 h followed by calcination at 873 K in an O₂ stream for 14 h. The ε-phase was obtained by the calcination of the VPO₄·H₂O precursor at 773 K in an O₂ stream for 6 h [13].

The crystal phase of the VOPO₄ samples was determined by X-ray diffraction (XRD) measurement using the Cu Kα line (Rint 2500, Rigaku Co. Ltd.). The average valence number of vanadium ion was estimated with an electron spin resonance (ESR) measurement (ESP 380E, Bruker), because ESR analysis is highly sensitive to V⁴⁺. All ESR measurements were performed at room temperature under air, and tetramethylpiperidine-1-oxyl (TEMPO) was used as the standard sample for estimating the amount of V⁴⁺. The amount of V⁴⁺ was estimated by the double integral of the ESR spectra [15] and the average valence number of V was obtained by averaging the amount of estimated V⁴⁺ and V⁵⁺, which was obtained by subtracting the V⁴⁺ amount from the total amount of V. Electrochemical Li intercalation characterization was measured by applying a constant current, generally, 0.04 mA/cm², which corresponds to C/50. The VOPO₄ powder was mixed with acetylene black (AB) and polytetrafluoroethylene (PTFE) as a binder with a weight ratio of VOPO₄:AB:PTFE = 60:30:10. The electrolyte used was 1 M LiPF₆ dissolved in ethylene carbonate (EC) mixed with dimethyl carbonate (DMC) at EC:DMC = 1:2 vol.% (UBE Kosan Co. Ltd.) and a Li metal sheet (1 mm thickness) was used as the counter electrode. The charge and discharge properties of the VOPO₄ samples were measured in the potential range of 3.2–4.3 V by using a computer-controlled battery tester (BTS2400, Nagano Co. Ltd.).

3. Results and discussion

Powder X-ray diffraction patterns of crystalline VOPO₄ obtained in this study are shown in Fig. 1. The X-ray

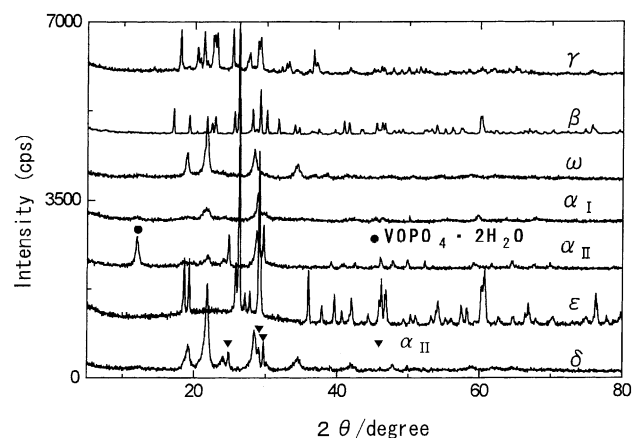


Fig. 1. XRD patterns of synthesized VOPO₄.

diffraction patterns of the VOPO_4 samples were almost consistent with those reported in the literature [7,13,16] and JCPDS data (Card nos. 27-0947, 27-0948, 47-0950, 37-0809). Therefore, single phases of α_{I} -, β -, γ -, ω - and ε - VOPO_4 were successfully obtained in this study. In the case of the α_{II} -phase, X-ray diffraction peaks from $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ were also observed, indicating that a small amount of sample was hydrated. However, the intensities of the diffraction peaks from $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ were weak, and so the content of such hydrated species is small. Benabdelouahad et al. [8] reported that some VOPO_4 phases are easily hydrated. Some weak diffraction peaks, which could be identified as α_{II} -phase, were also observed in the δ -phase product. It is estimated that the amount of α_{II} -phase is not large. The diffraction patterns of the δ - and ω -phases resemble each other due to their similar layered structure. According to the JCPDS files (Nos. 47-0951 and 37-0809), the difference in the diffraction patterns is that there are two characteristic diffraction peaks (0 1 2) and (2 0 0) around the main peak for δ -phase, but only one (1 1 2) for ω -phase.

Fig. 2 shows the initial charge and discharge curves of the VOPO_4 samples at room temperature. All VOPO_4 phases exhibit Li intercalation and de-intercalation in the potential window from 3.2 to 4.3 V. It was seen that the capacity of the electrochemical Li intercalation in VOPO_4 is strongly dependent on the crystal structure and δ -, ε -, α_{I} -, γ - and ω -type VOPO_4 exhibits fairly large capacity, above 100 mAh/g. On the other hand, VOPO_4 with β - and α_{II} -

phase structures exhibit small capacities. In particular, the Li intercalation and de-intercalation capacity of the β -phase is less than 50 mAh/g. The poor cathodic characteristics of β -phase have already been reported by Gaubicher et al. [10]. From the data shown in Fig. 2, it was seen that the initial Li intercalation capacity increases in the following order: $\beta \ll \alpha_{\text{II}} < \gamma < \omega < \alpha_{\text{I}} < \varepsilon < \delta$. As for the potential, all VOPO_4 exhibits a high potential plateau of about 3.7 V, making them suitable for use as cathodes for Li-ion rechargeable batteries. It is interesting that the plateau potential is also dependent on the crystal structure. In particular, the plateau potential of β -phase for de-intercalation is the highest (3.9 V) of all the VOPO_4 phases. Considering the small Li de-intercalation capacity and the high potential, it seems that V^{4+} in β - VOPO_4 is fairly stable in the lattice and not easily oxidized. The reduction from V^{5+} to V^{4+} is essential for the intercalation of Li. On the other hand, δ -phase VOPO_4 exhibited the largest capacity (124 mAh/g) for Li intercalation among the seven VOPO_4 phases and the ratio of Li intercalated to that of V achieved is 0.75. This large capacity might be related to the open structure of δ -phase crystal structure.

Since Li intercalation into VOPO_4 occurs by reducing V^{5+} to V^{4+} to form LiVOPO_4 , the capacity should be related to the average valence of V in VOPO_4 . The average valence of V in the various VOPO_4 crystal phases was estimated by ESR measurement. Table 1 summarizes the estimated V^{4+} amount and the average valence number of V in various VOPO_4 crystal phases. It is well known that the valence number of V in VOPO_4 varies with the crystal structure and synthesis conditions. In practice, the estimated valence number of V in VOPO_4 changes with the crystal phase as shown in Table 1. Notably, the β -phase, which exhibits a small capacity for Li intercalation, contains a fairly large amount of V^{4+} . Therefore, one reason for the small capacity in β -phase could be assigned to the low average valence number of vanadium cations in the lattice. In contrast, the average valence number of V in ε -, δ -, β -, α_{I} -, γ - and ω -type VOPO_4 is close to +5. Therefore, the large capacity for Li intercalation in ε -, δ -, α_{I} -, γ - and ω -type VOPO_4 could be associated with a high valence number of V. However, the difference in valence number of V in the ε -, δ -, α_{I} -, γ - and ω -phases is not large, while the difference in the Li intercalation capacity is large as shown in Fig. 2. Therefore, the stability of VOPO_4 lattice as well as the diffusivity of Li ion in the lattice are other important factors for determining the capacity for the electrochemical Li intercalation.

Fig. 3 shows cycling data for the various phases of VOPO_4 . In accordance with the report by Dupre et al. [5], the Li intercalation capacity gradually decreases with cycle number in the case of the γ -phase. This suggests that the chemical stability of the γ -phase is not high and the crystal structure may decompose during Li intercalation and de-intercalation. On the other hand, the δ -, ω -, α_{I} - and α_{II} -phases exhibit a stable capacity for Li intercalation over 30 cycles. The reason why the capacity of the ω -phase

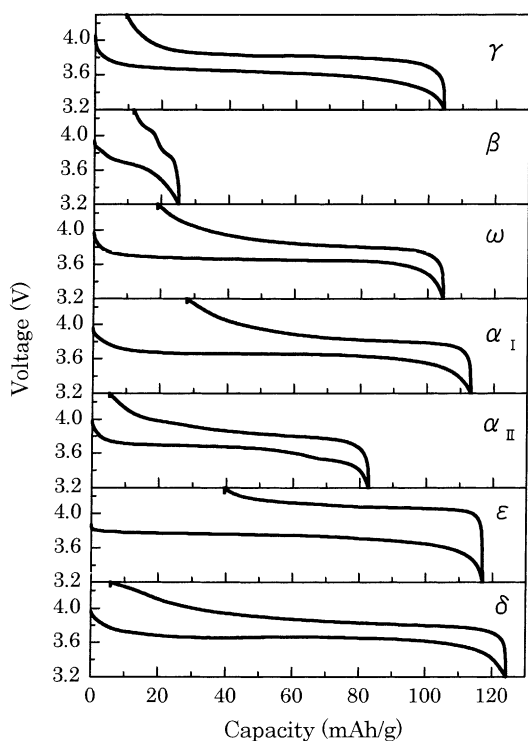


Fig. 2. Initial charge–discharge curves for VOPO_4 with different crystal phases. Measurement was performed at the constant current density of 0.04 mA/cm² and potential windows of 3.2–4.3 V.

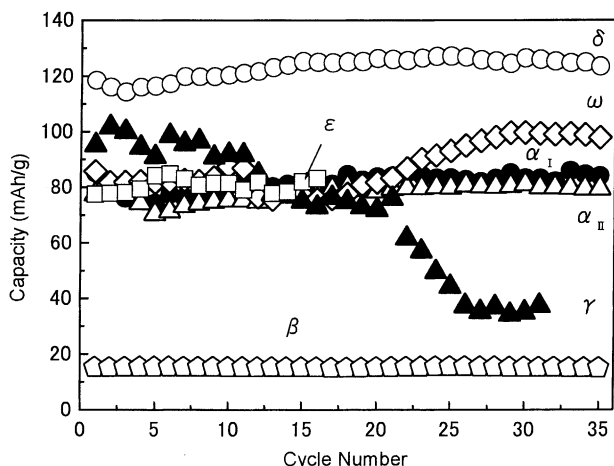


Fig. 3. Li de-intercalation capacity for α_I - (\bullet), α_{II} - (Δ), β - (\blacklozenge), δ - (\circ), ϵ - (\square), γ - (\blacktriangle) and ω -VOPO₄ (\diamond) with different crystal phases as a function of cycle number. Current density: 0.04 mA/cm²; potential window: 3.2–4.3 V.

gradually increases with cycle number was not clear at present. However, there are two possibilities: one is that the inter-planar distance of VOPO₄ layer expands during repeating intercalation and de-intercalation resulting in improved Li diffusivity. The second is that the phase converts from ω - to δ -phase during cycling because of the similarity in crystal structures. This is now under investigation. The cycling stability of these phases is acceptable. In particular, a decrease in Li intercalation capacity was hardly observed for δ -phase VOPO₄. Although it was reported that capacity for Li intercalation drastically decreased in β - and ϵ -phase VOPO₄ [6,10], good cycle stability for the electrochemical Li intercalation was observed for the samples prepared in this study. The differences in cycle stability of β - and ϵ -phases between the present study and previous reports may be related to the post treatment of the sample, because these phases are rather hygroscopic. It appears that δ -phase VOPO₄ is the most suitable as the cathode of Li-ion rechargeable battery due to its good cycling stability. In the

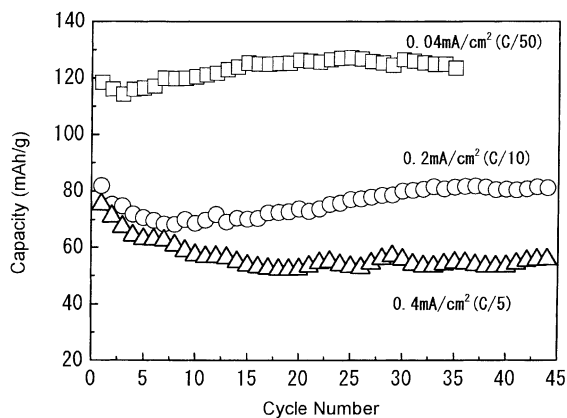


Fig. 4. Effects of the current density on the Li de-intercalation capacity of δ -VOPO₄. Potential window: 3.2–4.3 V.

following part, electrochemical Li intercalation and de-intercalation in this phase was studied in detail.

Fig. 4 shows the Li de-intercalation capacity as a function of cycle number for δ -phase VOPO₄ at different current densities. Although a large Li intercalation capacity ($\text{Li}/\text{V} = 0.75$) is obtained at low current density, it decreases monotonically upon increasing the current density. At 0.4 mA/cm² (C/5), the initial capacity for Li de-intercalation is 60% of that at 0.4 mA/cm². The decrease in Li intercalation capacity can be assigned to the low conductivity of VOPO₄. Therefore, decreasing the particle size could be effective for improving the capacity at high current density. The cycle stability is also strongly affected by the current density. As discussed before, the Li intercalation capacity hardly decreases 0.04 mA/cm², but slightly decreases at 0.2 mA/cm². At 0.4 mA/cm², a decrease in Li intercalation capacity became more obvious and the capacity decreases from 80 to 60 mAh/g. Improvement in the cathodic performance at high current density is very important for VOPO₄ cathodes. Considering the low electrical conductivity of VOPO₄, improvement of Li intercalation capacity could be achieved by decreasing the particle size. This is now under investigation.

Another important subject for the cathode of Li-ion battery are chemical stability over a wide operating temperature range. Fig. 5 shows the charge and discharge curves of δ -phase VOPO₄ at various temperatures at 0.04 mA/cm² (C/50). Since EC-DMC is used for the electrolyte in this study, the capacity for Li intercalation is greatly decreased at 283 K. Because the melting point of EC is 310 K, the decrease in Li intercalation capacity at 283 K may be caused by the increased viscosity of the organic electrolyte and the decreased Li-ion conductivity. In contrast, a decrease in the capacity is not large at higher temperatures up to 323 K. Furthermore, the potential plateau of the Li intercalation is almost the same as that at room temperature. Since the electrical conductivity increases with increasing temperature,

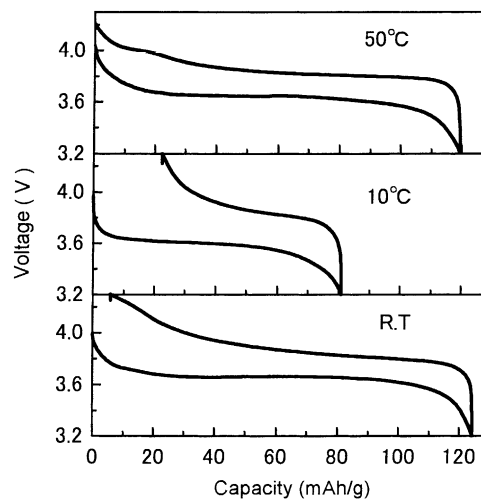


Fig. 5. Initial charge–discharge curves of δ -phase VOPO₄ at the different operating temperatures. Potential window: 3.2–4.3 V.

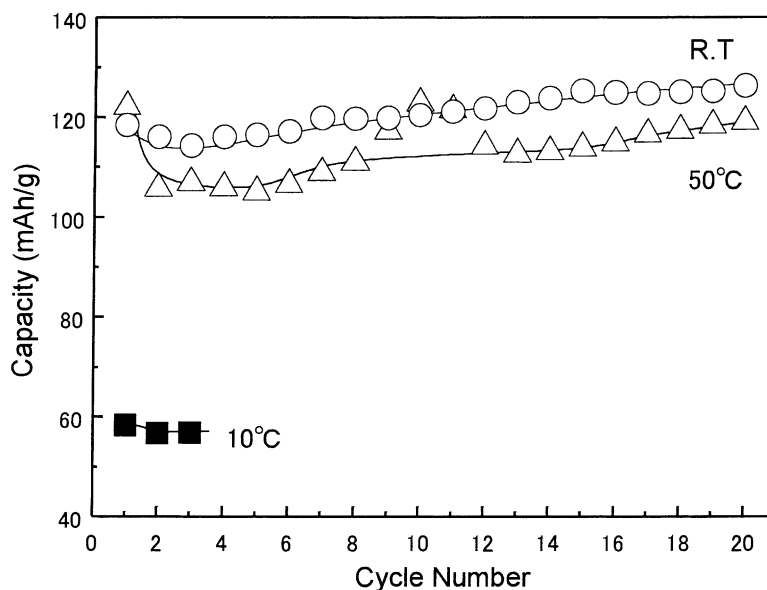


Fig. 6. Effects to Li de-intercalation stability in δ -VOPO₄ at different operating temperatures. Potential window: 3.2–4.3 V.

the reversibility between intercalation and de-intercalation improves with an increase in the operating temperature. The Coulombic efficiency is also improved by increasing the temperature up to 323 K. Fig. 6 shows the effects of temperature on the cycle stability of δ -phase VOPO₄ at 0.04 mA/cm² (C/50). Although the capacity for Li intercalation slightly decreased at initial few cycles, fairly stable capacity was exhibited over 20 cycles even at 323 K. An unusual increase in the capacity was also observed from cycle numbers 10 to 14 at 323 K. The reason for this deviation is not clear at present. However, the low boiling points of DMC (363 K) may be related to the anomalous performance at 323 K. Considering the cycling dependence of the Li intercalation capacity between 14 and 20 cycles, a stable capacity of ca. 110 mAh/g is expected for later cycles. The δ -phase VOPO₄ stably inserts and de-inserts Li into and from lattice at temperature up to 323 K.

4. Conclusions

The cathodic performance of VOPO₄ phases has not previously been systematically investigated. This study shows that the capacity for Li intercalation is strongly dependent on the crystal structure. The capacity for Li intercalation increases in the order: $\delta > \varepsilon > \alpha_I > \omega > \gamma > \alpha_{II} \gg \beta$. In particular, it was found that δ -phase VOPO₄ exhibits a fairly large capacity and high flat discharge potential of 3.7 V. The δ -phase VOPO₄ also exhibits good cycling stability; after 30 cycles, a capacity of 130 mAh/g is still sustained. A fairly high Li intercalation capacity of ca. 60 mAh/g is also exhibited for β -phase VOPO₄ at a high current density of 0.4 mA/cm², but the cycling stability decreased slightly. Since the electrical

conductivity of VOPO₄ increases with higher temperature, the reversibility of the Li intercalation and de-intercalation was improved by increasing the operating temperature, resulting in improved Coulombic efficiency. Consequently, it can be concluded that δ -phase VOPO₄ is promising as a cathode material for Li-ion rechargeable batteries.

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