

LiVOPO₄ as a new cathode materials for Li-ion rechargeable battery

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Abstract

Improvement in the rate properties of orthorhombic LiVOPO₄ was investigated and it was found that making a fine powder of LiVOPO₄ by the mechanical milling pretreatment is effective for increasing the de-intercalation capacity of Li from LiVOPO₄. The electrochemical de-intercalation capacity at high current density can further increase by optimizing the acetylene black amount as a conducting binder. The optimized acetylene black amount was 15 wt.% and intercalation capacity of Li was achieved a value of 100 and 60 mAh g⁻¹ at high rate condition of C/5 (0.4 mA cm⁻²) and 1C (2 mA cm⁻²), respectively.

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1. Introduction

Recently, performance of mobile electronic devices such as mobile phone or laptop computer is drastically improving and so, the demands for battery became sever and sever. Since Li ion battery has an advantage in large power density and cycle stability, this battery is now widely used for the electric source of mobile equipment. The current most important requirement for Li ion rechargeable battery is to decrease cost and increase the power density. In the current battery, LiCoO₂ and graphitic carbon are commonly used for cathode and anode, respectively. However, natural abundant of Co is limited and this element is expensive. Therefore, development of cathode material without containing Co is strongly required. In our previous study, we investigated vanadium phosphate (VOPO₄) phases for the new cathode of Li ion rechargeable battery and it was found that δ-phase VOPO₄ exhibits fairly large capacity of 80 mAh g⁻¹ at 0.4 mA cm⁻² (corresponded to C/5 rate) [1]. At present, great attentions are paid for LiFePO₄ as a candidate material

for alternative cathode. However, comparing with LiFePO₄ [2–4], LiVOPO₄ has an advantage of higher potential (4.0 and 3.7 V versus Li/Li⁺) for charge and discharge and this phosphate is highly interesting from the viewpoint of the alternative cathode [1]. However, the cathode with discharge state is preferable from the viewpoints of practical use, because some part of lithium ion in electrolyte is lost at the initial discharge stage and internal resistance of the battery increase. For lithiated phosphate materials, Li intercalation property of olivine structure of LiCoPO₄ [5,6] and NASICON type structure of Li₃V₂(PO₄)₃ [7–9] are also reported. Since existing of large PO₄-poly anions is expected to stabilize the structure, higher redox potential is expecting on phosphate. Recently, lithiated phase of VOPO₄ also became an interesting material for alternative cathode in Li ion secondary battery. Li_{0.92}VOPO₄ that can be obtained by electrochemical synthesis from LiI and β-VOPO₄ exhibits a capacity of 80 mAh g⁻¹ at the flat potential of 3.95 V versus Li/Li⁺ [10]. However charge and discharge capacity of this system decreased drastically as increasing applied charge/discharge current density. On the other hand, Kerr et al. also presented that the triclinic phase LiVOPO₄ synthesized from ε-VOPO₄ shows the capacity of 100 mAh g⁻¹ up to 100 cycles at C/10 of current rate [11]. In our latest work, orthorhombic phase of LiVOPO₄ that can be synthesized by impregnation method also exhibited fairly good cycle stabil-

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ity for Li de-intercalation and intercalation [12]. Therefore, LiVOPO_4 is also highly interesting from the alternative cathode with discharged state. However, although high potential of 3.85 V is exhibited, capacity for Li de-intercalation decreased with increasing current density. Therefore, improvement in Li intercalation and de-intercalation capacity at high current density is strongly required for LiVOPO_4 . In this study, effects of ball milling and carbon binder contents of orthorhombic phase LiVOPO_4 on Li electrochemical intercalation property were investigated.

2. Experimental

Orthorhombic LiVOPO_4 in this study was prepared by impregnation method according to the procedure reported in our previous work [12]. LiVOPO_4 was synthesized by using LiNO_3 (Wako, 99.9%), NH_4VO_3 (Wako, 99.9%) and $(\text{NH}_4)_2\text{HPO}_4$ (Wako, 99.9%) as the starting reagent. The starting materials at the stoichiometric ratio to LiVOPO_4 were dissolved into deionized water. The resultant solution was stirred at 353 K until light yellowish/orange powder was obtained. The solution was evaporated and the obtained powder was heated for 14 h at 873 K in air. Crystal phase of the obtained LiVOPO_4 was determined by XRD measurement using $\text{Cu K}\alpha$ line (Rint 2500, Rigaku Co. Ltd.). Milling of the powder was carried out by using the planetary ball mill and 1 g of the sample was set into the stainless steel jar (80 ml in volume) with Zr balls ($\text{Ø}5$ mm in diameter). The samples were milled at 200 rpm for 5 h under Argon atmosphere. Electrochemical characterization was carried out by mixing the powders of the active materials of LiVOPO_4 with acetylene black and polytetrafluoroethylene (PTFE) as a binder at the weight ratio of 6:3:1 or pure acetylene black. Then the active materials were pressed onto the stainless steel current collector (SUS 316, 100 mesh) at 81 MPa. Used electrolyte was 1 M LiPF_6 in EC:DMC (1:2 vol%) which is supported by UBE Kosan Co. Ltd., and the Li metal sheet (1 mm thickness) was always used for the counter electrode. Unless otherwise noted, the charge and discharge property of the prepared LiVOPO_4 was measured in the potential range from 3.0 to 4.5 V versus Li/Li^+ by applying a constant current (mainly 0.04 mA cm^{-2} , C/50) with the computer controlled dc source (BTS2004, Nagano Co. Ltd.). The average particle size of the sample powder was estimated by using the laser scattering particle size distribution analyzer (Horiba Co. Ltd., LA-920). The morphology of the obtained particles was observed by using the scanning electron microscope (Hitachi, S-2400).

3. Results and discussion

Fig. 1 shows the initial charge–discharge curve of as-prepared LiVOPO_4 and that after ball mill pretreatment at 0.04 mA cm^{-2} (1/50C). As shown in Fig. 1, at low current

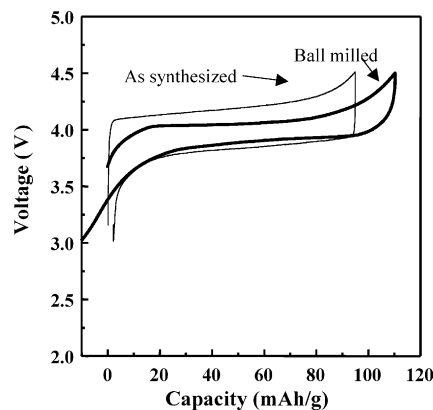


Fig. 1. Charge discharge curves for as-synthesised LiVOPO_4 and ball milled LiVOPO_4 (current density: 0.04 mA cm^{-2} (C/50), potential window: 3.0 ~ 4.5 V).

density, orthorhombic LiVOPO_4 prepared by impregnation method is highly attractive as the alternative cathode for Li ion rechargeable battery. This is because LiVOPO_4 exhibits high discharge potential of 3.85 V and reasonably large capacity of 90 mAh g^{-1} . However, Li intercalation capacity of as-prepared LiVOPO_4 drastically decreased with increasing current density for charge and discharge. Therefore, the most important issues which should be overcome for LiVOPO_4 is the improvement in rate property. The low rate property may be assigned to low electrical conductivity in LiVOPO_4 . In this study, effects of particle size on the rate property were studied first. In Fig. 1, initial charge and discharge curve of LiVOPO_4 after ball milling treatment was also superimposed. It is reported that the rate property for Li intercalation could be improved by decreasing the particle size [13]. By reducing the particle size of LiVOPO_4 , it is seen that the initial Li de-intercalation capacity is slightly increased and also discharge potential was slightly improved, however, potential for charge slightly decreased. As a result, potential required for charge and discharge became close. It is considered that the smaller in LiVOPO_4 particle size leads to the easier in Li ion diffusion resulting in the improved capacity of Li de-intercalation and the decreased Li intercalation potential. Therefore, application of ball milling treatment for LiVOPO_4 is effective for improving the cathodic performance of LiVOPO_4 .

Fig. 2 shows SEM micrograph of (a) as-synthesis LiVOPO_4 and (b) ball milled one. It is obvious that the particle size of LiVOPO_4 became much smaller after ball milling treatment. As-synthesized LiVOPO_4 powder consists of a large particle of which particle size is around $5.0 \mu\text{m}$, in addition, particle is highly aggregated and dense. Therefore, it seems like that diffusivity of Li in as-synthesized LiVOPO_4 is not easy. In contrast, although there are some large particles observed, large part of LiVOPO_4 particle became smaller than $1 \mu\text{m}$ in size after ball milling treatment and the particle is not so aggregated. In agreement with SEM observation, it is also noted that BET surface areas of as-synthesis and ball milled LiVOPO_4 were 0.1 and $12.1 \text{ m}^2 \text{ g}^{-1}$, respectively.

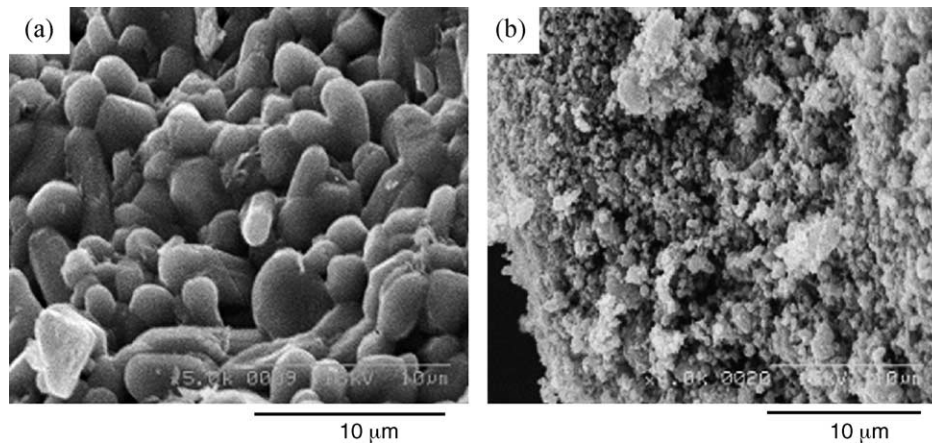


Fig. 2. SEM micrographs of (a) as-synthesised LiVOPO₄ and (b) ball milled LiVOPO₄.

Therefore, although the particle distribution is not even, particle size of LiVOPO₄ was successfully reduced by ball milling treatment.

Fig. 3 shows the capacity of Li intercalation into LiVOPO₄ as a function of current density. As shown in Fig. 3, intercalation capacity drastically decreased with increasing current density in case of the as-synthesized LiVOPO₄. On the other hand, capacity for Li intercalation at each current density is much increased by ball milling of LiVOPO₄. In particular, increase at high current density is significant. At 0.4 mA cm⁻² (C/5) of practically used current density, capacity was sustained to be 40 mAh g⁻¹. The improvement in capacity at high current density was explained by improved diffusivity of Li into LiVOPO₄ bulk by decreasing the particle size. Although the capacity at high current density much increased by ball milling treatment, the capacity is still much smaller than that of LiCoO₂. Therefore, further improvement in Li intercalation capacity is required.

Carbon binder has an important role for achieving a superior cathodic performance. In LiFePO₄ study, it was reported

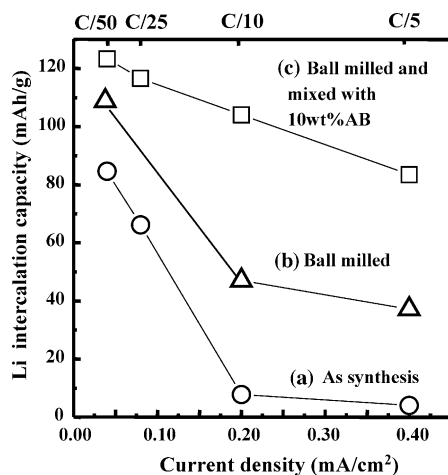


Fig. 3. Li intercalation capacity of (a) as-synthesis LiVOPO₄, (b) ball milled LiVOPO₄, and (c) ball milled and mixed with 10 wt.% acetylene black as a function of current density (binder amount: 40 wt.%).

that LiFePO₄ cathodic performance improved greatly by optimizing the carbon content [14,15]. In particular, as discussed, LiVOPO₄ exhibits a low electrical conductivity. Therefore, it is expected that capacity at high current density could increase by optimizing the amount of carbon binder. In case of δ-VOPO₄, optimizing carbon binder is highly effective for increasing the capacity at high current density. In this study, optimizing the amount of acetylene black as a carbon binder was studied for further improving the capacity at high current density. Effect of 10 wt.% acetylene black mixing on the capacity of Li intercalation of LiVOPO₄ at high current density was also shown in Fig. 3. It is seen that mixing 10 wt.% acetylene black is highly effective for increasing the capacity. At low current density of 0.04 mA cm⁻² (C/50), discharge capacity of 123 mAh g⁻¹ is achieved and even at 0.4 mA cm⁻², discharge capacity is still sustained a value of 80 mAh g⁻¹. Therefore, reasonably large capacity at high current density can be sustained by optimizing the amount of acetylene black as binder.

Fig. 4 shows the capacity for Li intercalation into LiVOPO₄ as a function of acetylene black. Since only small

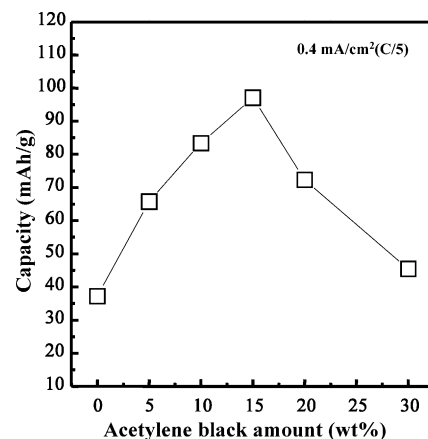


Fig. 4. Effect of mixed acetylene carbon black mixed on first reversible capacity in LiVOPO₄ (current density: 0.4 mA cm⁻² (C/5), potential window: 4.5 ~ 3.0 V).

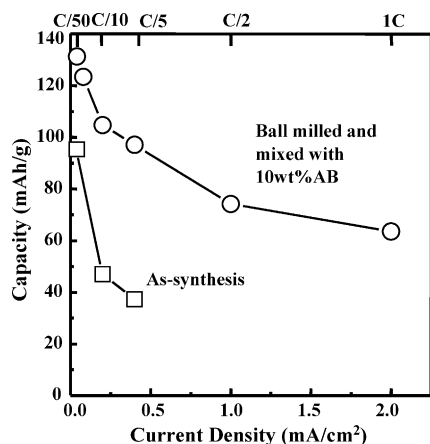


Fig. 5. Initial Li intercalation capacity of as-synthesized LiVOPO_4 and LiVOPO_4 mixed with 15 wt.% ACB as a function of current density (binder amount: 40 wt.%).

Li intercalation is occurred into acetylene black, excess amount of acetylene black is not desired. As expected, Li intercalation capacity increase with increasing amount of acetylene black and the largest capacity is achieved when 15 wt.% acetylene black was mixed with the sample. At this composition, capacity of Li intercalation into LiVOPO_4 is as high as 100 mAh g^{-1} at 0.4 mA cm^{-2} . Therefore, it is seen that the optimum amount of acetylene black binder for LiVOPO_4 exists around 15 wt.%.

Fig. 5 shows the Li intercalation capacity into LiVOPO_4 sample mixed with 15 wt.% binder as a function of current density. Although capacity decreased with increasing current density, capacity at high current density is much improved by optimizing acetylene black amount and reasonably large capacity of 60 mAh g^{-1} was sustained at current density of 2.0 mA cm^{-2} . This capacity is slightly smaller than that of LiCoO_2 . Therefore, reasonably large capacity of LiVOPO_4 at high current density can be achieved by applying ball milling treatment and optimizing the amount of binder. It is also noted that the stable capacity is sustained not only at 0.4 but also at 2.0 mA cm^{-2} , while small decrease in capacity is observed at initial few cycles. After 100 cycles, the capacity of 50 mAh g^{-1} is stably sustained at 2.0 mA cm^{-2} . Therefore, it can be said that LiVOPO_4 has high cycle stability at high current density. Consequently, orthorhombic phase of LiVOPO_4 is highly promising as alternative cathode materials for Li ion rechargeable battery, since the potential for discharge (3.9 V versus Li/Li^+) is almost the same with that of LiCoO_2 .

4. Conclusion

Capacity of the electrochemical intercalation of Li of LiVOPO_4 decreased drastically as increasing current density for charge and discharge. However, by ball milling and optimizing the amount of binder, LiVOPO_4 exhibited a sufficient capacity, i.e. the capacities of 130 and 60 mAh g^{-1} at 0.04 mA cm^{-2} (C/50 rate) and 2 mA cm^{-2} (1C rate), respectively. Since the theoretical density of this LiVOPO_4 is 3.34 g cm^{-3} , this LiVOPO_4 also exhibits the large volumetric capacity of 435 mAh cm^{-3} . Therefore, this study revealed that orthorhombic LiVOPO_4 with fine powder could be another promising candidate for the alternative cathode of Li ion rechargeable battery.

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