

Improved Rate Capability of Li/Li₃V₂(PO₄)₃ Cell for Advanced Lithium Secondary Battery

Hyun-He Lim,[†] A-Ra Cho,[†] Nagarajan Sivakumar,^{†,§} Woo-Seong Kim,[‡] Won-Sub Yoon,[§] and Yun-Sung Lee^{†,*}

[†]Faculty of Applied Chemical Engineering, Chonnam National University, Gwang-ju 500-757, Korea

*E-mail: leeys@chonnam.ac.kr

[‡]Daejung EM Co. LTD., Incheon 405-820, Korea

[§]School of Advanced Materials Engineering, Kookmin University, Seoul 136-702, Korea

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Lithium vanadium phosphate, Li₃V₂(PO₄)₃ was prepared by a simple solid state route. It was found that making a fine powder of Li₃V₂(PO₄)₃ by the mechanical milling is very effective for increasing the insertion/extraction of lithium from Li₃V₂(PO₄)₃ structure. In charge/discharge test, the ball-milled Li₃V₂(PO₄)₃ sample exhibited a higher initial discharge capacity of 174 mAh/g in the voltage range of 3.0-4.8 V, compared with pure Li₃V₂(PO₄)₃ sample (152 mAh/g). Furthermore, the ball-milled Li₃V₂(PO₄)₃ presented not only higher cycle retention rate after 50 cycles, but also better rate capability compared with pure sample in the whole region (0.1-7 C).

Key Words : Lithium vanadium phosphate, Ball milling, Solid state route, Lithium-ion batteries

Introduction

Portable electronic devices are likely to continue to rely on lithium ion batteries. In recent decades, lithium transition metal phosphates such as Li₃M₂(PO₄)₃ (M = Fe, V) have been extensively studied as cathodes for Li-ion batteries, due to their better thermal stabilities than the oxidative unstable lithium transition metal oxides, such as LiCoO₂.¹⁻³ In general, NASICON-like phosphates have enhanced electronic conductivity and are also more stable even when alkali-to-metal ratios are larger than one.⁴ In the phosphate structure, V³⁺/V⁴⁺ is one of the most important transition metals with functional redox potential. Framework materials based on the phosphate polyanion, such as Li₃V₂(PO₄)₃, has better thermal stability, good ion mobility, and a high reversible capacity. This material has an especially large theoretical capacity (197 mAh/g) and higher operating voltage, making it a promising candidate for high power-density and large-scale batteries.⁵⁻⁸

Li₃V₂(PO₄)₃ as cathodes in lithium ion batteries has been studied previously and its electrochemical properties have been reported.^{5,7,9-12} It contains three independent lithium sites with a theoretical capacity of 197 mAh/g, and three lithium ions are completely extracted at the voltage of 4.8 V.⁸ However, its intrinsic low electronic and ionic conductivities hinder its electrochemical performance. Zhu *et al.*¹³ synthesized Li₃V₂(PO₄)₃ by carbothermal solid state reactions, the resulting sample exhibited an initial discharge capacity of 119 mAh/g. Moreover, Fu *et al.*⁷ reported that Li₃V₂(PO₄)₃ prepared by a solid state method using hydrogen or carbon as the reducing agent exhibits an initial capacity of 146.3 mAh/g at 1 C rate. However, it presented abrupt capacity decline in the early stage and showed only 83% cycle retention rate at 1 C rate until 10 cycles. Further-

more, many research groups have tried to adopt carbon coating process improving electric conductivity of Li₃V₂(PO₄)₃ material.¹⁴⁻¹⁶ In this study, we report the improved battery performance of carbon free Li₃V₂(PO₄)₃ material using simple ball milling, which showed a similar improved electrochemical properties compared with various carbon coated Li₃V₂(PO₄)₃ materials.

Experimental

As-prepared Li₃V₂(PO₄)₃ was prepared using the conventional solid-state method. High purity LiCO₃ (Wako, Japan), V₂O₅ (Sigma-Aldrich, USA), and (NH₄)₂HPO₄ (Sigma-Aldrich, USA) were used. The starting materials were thoroughly ground in an agate mortar and precalcined at 300 °C for 4 h. The resultant compound was ground thoroughly again and sintered at 900 °C for 8 h under an Ar atmosphere using a tubular furnace to obtain the pure Li₃V₂(PO₄)₃ samples. The as-prepared samples were milled by using the planetary ball mill with Zr balls at 230 rpm for 12 h. Crystallographic phases of the samples were determined by x-ray diffraction (XRD, Rint 1000, Rigaku, Japan) data were collected over 2θ ranging from 10 to 80° at 0.01° intervals. X-ray photoelectron spectroscopic (XPS, VG Inc. MultiLab 2000, UK) analysis of the Li₃V₂(PO₄)₃ samples was undertaken with monochromatic AlKα radiation (hν = 1486.6 eV). The collected high resolution XPS spectra were analyzed by an XPS peak-fitting program. Surface morphologies of the samples were studied using a scanning electron microscope (FE-SEM, S4700, Hitachi, Japan).

The electrochemical charge/discharge performances of the samples were evaluated in a CR2032 coin-type cell with a cathode made of 20 mg of the active material, 3 mg of Ketjen black and 3 mg of conductive binder (TAB). The test

cell comprised the cathode and a lithium metal anode separated by a porous polypropylene film (Celgard 3401, USA) and an electrolyte of 1M LiPF_6 in EC:DMC = 1:1 (Techno Semichem Co., Ltd., Korea). This composite was pressed on a 200 mm² stainless steel mesh, which was used as the current collector, under a pressure of 300 kg/cm² and dried at 160 °C for 4 h in a vacuum oven. The cells were assembled in a glove box under an argon atmosphere. The charge/discharge current density was 0.1 mA/cm² and the cut-off voltage was controlled in the range of 3.0 to 4.8 V. Cyclic voltammetry (CV) were performed using a Bio-Logic electrochemical work station (SP-150, Biologic, France) with a three electrode cell configuration. In the three electrode configuration, metallic lithium served as the counter and reference electrodes.

Results and Discussion

XRD patterns of as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples are shown in Figure 1. All the diffraction patterns indexed well to monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ with the space group of $P2_1/n$. Moreover, the diffraction peaks show a single-phase without any impurities, such as Li_2O and Li_3VO_4 .⁶ Both materials were prepared in an inert Ar atmosphere and thus it was significant to identify the oxidation state of V in the samples. Figure 1(c) shows the experimental values and the fitted curves of the x-ray photoelectron spectroscopy (XPS) for V 2p in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The V 2p core level fits to a single peak with a binding energy (BE) of 516.4 eV, which is well matched with that observed in V_2O_5 (516.9 eV),¹⁷ confirming that the oxidation state of V is +5 in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

Figure 2 shows SEM images of as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ materials, respectively. It is evident that the particle size of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ became smaller after ball milling. As-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powders consists of a large particle size of about 3 to 5 μm, mixed with very small particles of about 200–300 nm. Moreover, the particles are highly aggregated and dense. As a result, it seems like that diffusivity of Li is not easy in as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample. In the case of milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powder large part

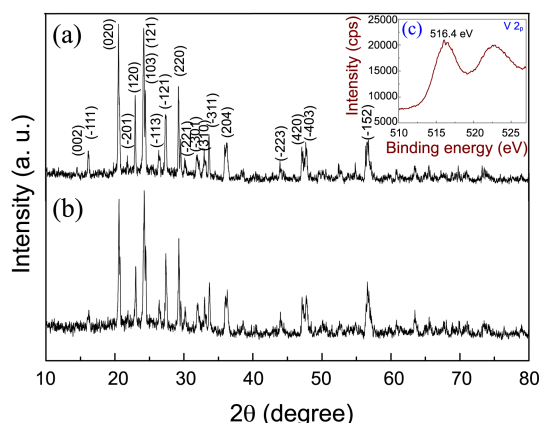


Figure 1. Powder XRD patterns of (a) as-prepared and (b) milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and (c) XPS core level of V 2p from $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

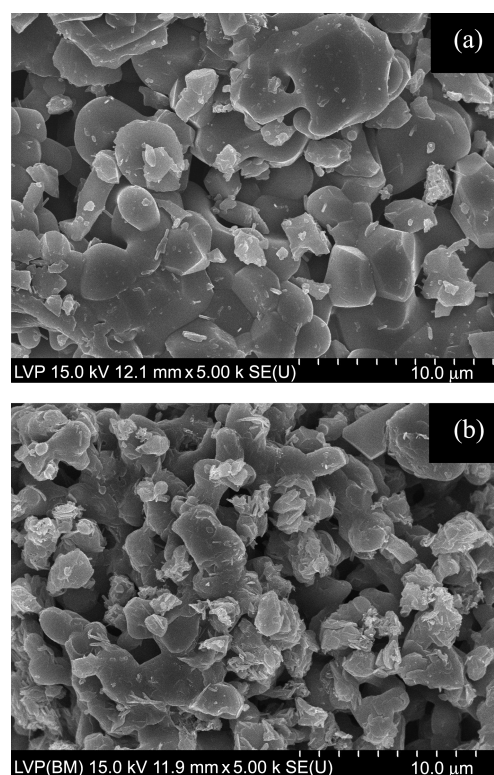


Figure 2. SEM images of (a) as-prepared and (b) milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles became smaller about 1 to 3 μm size, after ball milling treatment and the particles are not so aggregated.

Figure 3(a) shows the initial charge/discharge curves of

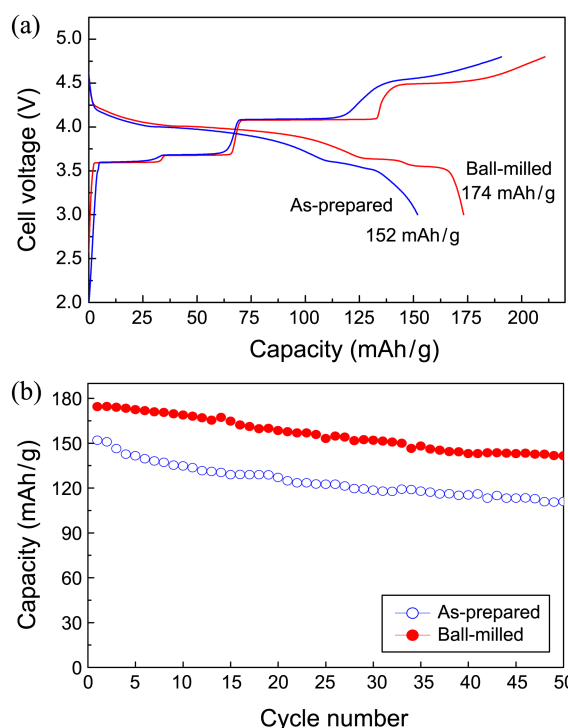


Figure 3. (a) Charge/discharge curves of as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, and (b) cyclic performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples.

the $\text{Li}/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cells, performed at a current density of $0.1 \text{ mA}/\text{cm}^2$ between 3.0 and 4.8 V. The curve of the milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ exhibits four charge plateaus (3.60, 3.67, 4.10 and 4.55 V) and three discharge plateaus (4.04, 3.64 and 3.56 V) during electrochemical cycling. In this study, effects of particle size on the rate property were investigated. The initial discharge capacities were found to increase from 152 mAh/g for as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ to 174 mAh/g for the milled sample, indicating that the milling is very effective in improving electrochemical properties, such as low polarization and good electron and ion transport during cycling. Choi *et al.*¹⁸ have reported that the rate property for Li intercalation could be improved by reducing the particle size. By reducing the particle size of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, it is seen that the initial Li de-intercalation capacity is slightly increased and also discharge potential was slightly enhanced, though, potential for charge slightly decreased. Therefore, the smaller particle size in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ leads to the easier in Li ion diffusion resulting in the improved capacity of Li de-intercalation and the decreased Li intercalation potential. As a result, the effect of ball milling for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ is effective for improving the charge/discharge properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The cycle performances of the samples are shown in Figure 3(b). Although both the as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cells present commonly good cycleabilities, the cycle retention rate of the milled sample was 81.2% and as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ sample was 73.1% after 50 cycles. This indication is quite interesting result, which presented its improved cycle retention after a ball-milling process because many cathode materials with enlarged surface area by milling could exhibit a poor cycleability due to the structural collapse against electrolyte reaction. It might be a main reason of the characteristic structural stability for NASICON type $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ material.

To investigate the extraction and insertion processes of the third lithium ion in the as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples, CV profiles have been taken in the voltage range of 3.0 to 4.8 V is shown in the Figure 4. The as-prepared $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ powder showed four oxidation and one reduction peaks in the CV curve. The oxidation peak at 4.57 V is the extraction of the third Li^+ ion, associated with phase transition from $\text{LiV}_2(\text{PO}_4)_3$ to $\text{V}_2(\text{PO}_4)_3$. Although the corresponding reduction peak does not appear in the CV curves, it

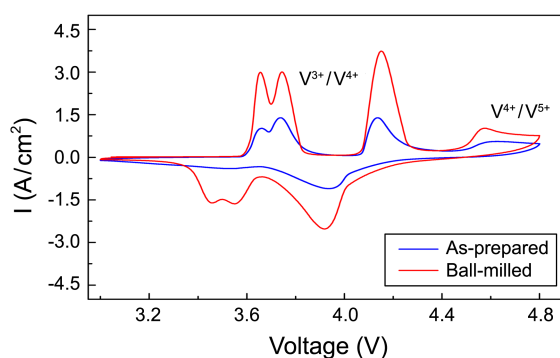


Figure 4. Cyclic voltammetry of as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples.

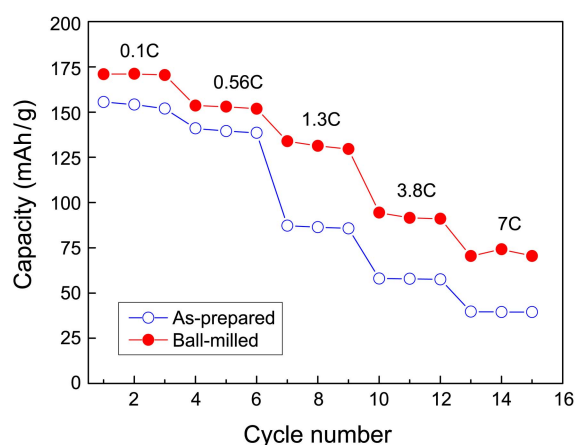


Figure 5. Rate capability performances of as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

agrees with the fact that the initial reinsertion of Li^+ in $\text{V}_2(\text{PO}_4)_3$ forms a solid solution of two phases.⁵ It also shows that there are three more oxidation peaks at 3.64, 3.72 and 4.13 V during the positive scan, which correspond to lithium extraction at the following stoichiometric ranges: $x = 0.0$ to 0.50 , 0.50 to 1.0 , and 1.0 to 2.0 in $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$, respectively.¹⁹ The two Li^+ ions extraction is also associated with the $\text{V}^{3+}/\text{V}^{4+}$ redox couple. Throughout the negative scan, however there is apparent difference that can observe between as-prepared and milled samples. The reduction peak at 3.58 V exists for the as-prepared sample even though the peak intensity is very weak. But, in the case of milled sample, there are likewise two clear reduction peaks at 3.58 and 3.94 V owing to the insertion of the Li ions. The reason for enhancing the reduction peak at 3.58 V in milled sample could be due to reduction of particle size which increases the specific surface area. From the result, it can be suggested that, milling is favorable for enhancing the rate capacity through improved Li^+ diffusion kinetics. More detail study is undergoing using XANES and *in-situ* XRD investigation.

Figure 5 shows the rate capability studies for as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples. Different current densities from 0.1 to 7 C have been used at room temperature. At 0.1 C, the discharge capacities exhibited for as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ are 152 and 174 mAh/g, respectively. The current densities increased up to 7 C with the discharge capacity of 39 and 71 mAh/g obtained for as-prepared and milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ samples, respectively. With this results, the milled $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ play a significant role in enhancing battery performance of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ material through improving the kinetics of the lithium oxidation/reduction reaction on the electrode by enlarging the contact area of the particles.

Conclusion

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode material was effectively synthesized by a simple solid state route followed by ball milling. The homogeneity and crystallinity of the synthesized powders were examined by X-ray diffraction analysis and particle

size by SEM analysis. The fitted curve of XPS data for V 2p showed evidence of the V^{5+} ion existing in the $Li_3V_2(PO_4)_3$ sample. The milled $Li_3V_2(PO_4)_3$ sample exhibited a better electrochemical performance of 174 mAh/g at room temperature compared with the as-prepared $Li_3V_2(PO_4)_3$ sample (152 mAh/g). It was concluded that milling is a very effective tool to improve Li^+ diffusion kinetics in $Li_3V_2(PO_4)_3$. Hence, this study exposed that monoclinic $Li_3V_2(PO_4)_3$ with the fine powder could be additional promising candidate for the alternative cathode of lithium secondary battery.

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