Ultrafast Cathode Characteristics of Nanocrystalline-Li$_3$V$_2$(PO$_4$)$_3$/Carbon Nanofiber Composites

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Anisotropically grown Li$_3$V$_2$(PO$_4$)$_3$ nanocrystals, which are highly dispersed and directly impregnated on the surface of a carbon nanofiber (CNF), were successfully synthesized via a two-step synthesis process: i) precipitation of nanoplate V$_2$O$_5$ precursors (20–200 nm); ii) transformation of the V$_2$O$_5$ precursor into Li$_3$V$_2$(PO$_4$)$_3$ nanoplates without size change. The direct attachment of the Li$_3$V$_2$(PO$_4$)$_3$ nanocrystals to the carbon surface improves the electronic conductivity and Li$^+$ diffusion of the entire Li$_3$V$_2$(PO$_4$)$_3$/CNF composite, simultaneously producing a mesoporous network (pore size of approximately 10 nm) that acts as an electrolyte reservoir owing to thepillar effect of the impregnated Li$_3$V$_2$(PO$_4$)$_3$ crystals. This ideal Li$_3$V$_2$(PO$_4$)$_3$/CNF nanocomposite enabled a 480°C (7.5 seconds) discharge with 83 mA h g$^{-1}$, and 69% of capacity retention at the slowest discharge rate (1C). Such an ultrafast charge–discharge performance opens the possibility of using Li$_3$V$_2$(PO$_4$)$_3$ as a cathode material for ultrafast lithium ion batteries with a stable cycle performance over 10,000 cycles at a 10C rate, maintaining 85% of the initial capacity.

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In the current society, the storage of electrical energy at high charge and discharge rate is an important technological issue as it enables hybrid and plug-in hybrid electric vehicles and provides a back-up to wind and solar energies.1,2 Rechargeable lithium-ion batteries (LIBs) are considered to be the most advanced energy storage systems; they possess high energy but limited power compared to high-power devices such as supercapacitors.1 To further improve the performance of the LIBs, several electrode materials have been proposed and investigated so far.2–11 Commercial cells utilize the layer-structured LiCoO$_2$ as the positive electrode,3 but the high cost and toxicity of cobalt prohibit its use on a large scale. Spinel-type Li$_5$Mn$_5$O$_{12}$ is one of the alternative materials to cobalt for high-rate use.5 Several reports on such materials for high-rate use have been published; however, the reported discharge performance are limited within 50–150°C. Owing to their easy release of oxygen, LiCoO$_2$ and Li$_5$Mn$_5$O$_{12}$ also have safety issues at overcharged states or high temperatures.3 Thus, to achieve a long-term and safe use of the LIBs, cathode materials other than those including layer-structured or spinel-type materials have received significant attention. Researchers have identified polyanion-type cathode materials—such as phosphate cathode materials like LiFePO$_4$ (LFP)5 and Li$_3$V$_2$(PO$_4$)$_3$ (LVP)—as attractive active materials because of their high thermal stability, high cyclability, and superior safety properties provided by the stable (PO$_4$)$_3^{−}$ unit.8 The presence of a phosphate with a strong P–O covalency stabilizes the antibonding M−O (M = V or Fe) energy level through an M−O–P inductive effect and repulsion between the oxide layers and the destabilization of its crystalline structure after the 3-electron (Li$^+$) extraction, which results in a poor cyclability (<100 cycles). Besides, LVP, when limited to the 2-electron reaction, shows a rather stable cyclability (>1000 cycles) while sacrificing its specific capacity compared to the 3-electron reaction. Thus, using LVP with a 2-electron reaction is a more realistic choice in relation to its application as a cathode material for ultrafast LIBs.

One of the challenges associated with the use of the LVP cathodes is circumventing the limitation of their intrinsically low electronic conductivity ($10^{2}$–$10^{3}$ S cm$^{-1}$).16 Designing nanostructure electrode materials is an effective method for improving the transfer kinetics of Li$^+$.17 An enhancement of the rate capability up to 30C can be achieved by improving the electronic conductivity of LVP within a wide range of diameters, from 10 nm to a few μm, which can be achieved by fine-tuning the thickness of the carbon coating up to 40 nm.18–22 Various organic compounds such as glucose,19 citric acid,19 starch,20 polyethylene glycol,21 and 1,4-dihydropyridine-2-butyne22 are considered as carbon sources for multifunction “nanocomposing” agents. Carbon nanotubes,23 graphene,24,25 and reduced graphene oxides26 are also examined for more effective carbon matrices.

Dowsnizing the particles size (5–100 nm) is one of the most direct approaches, as shortening the path of the Li$^+$ diffusion in LVP nanoparticles definitely enhances the power performance up to a 60C rate. For example, Rui et al. reported LVP nanocrystals (5–8 nm) embedded in an amorphous nanocarbon matrix attached to reduced graphene oxide nanosheets prepared by combination of a sol-gel reaction and high-temperature annealing; the nanocrystals exhibited a capacity of 88 mA h g$^{-1}$ at a 50C rate.27 Wang et al. reported LVP/C nanocomposites synthesized via a sol-gel method based on the composite chelating agents of glycine and beta-cyclodextrin. The pyrolysis products of these chelating agents resulted in the carbon coating on the LVP nanoparticles (approximately 20–40 nm), enabling a high-rate charge–discharge capacity of 88 mA h g$^{-1}$ at 60C.27 The highest C-rate of 100C, however, was achieved with relatively large LVP particles (approximately 1–2 μm).28 Wang et al. reported nitrogen-doped carbon-coated LVP obtained from a facile in-situ fabrication. Surprisingly, this N-doped carbon-coated LVP, with approximately 1–2 μm particles, achieved the highest performance rate (80 mA h g$^{-1}$ at 100C) known to date. This result indicates that the high rate of 100C can be attained even with large LVP particle sizes (>1 μm) thanks to the fast 3D Li$^+$ diffusion, only if the good electron path to LVP is provided from the conductive carbon network. However, to enable ultrafast LVP charge–discharge over 100C, a considerably faster electron path between LVP and carbon is required;
namely, the direct attachment of nanosized LVP on the surface of the conductive carbon matrix is necessary.

To achieve this, we have synthesized nanoplated LVP directly impregnated on the surface of the carbon nanofiber (CNF) via a two-step synthesis. The first step is the in-situ V$_2$O$_3$ nanoimpregnation on the anchor sites of the CNF, deliberately conducted under strong basic conditions (5 M NaOH). The V$_2$O$_3$ nanoimpregnation establishes the ultrafast electron path in nanosized V$_2$O$_3$ (plate-like shape; 20–200 nm). The second step is the in-situ transformation of nanoplated V$_2$O$_3$ into nanoplated LVP on the surface of the CNF without particle size growth and stoichiometric contamination, even in the presence of carbon. Both the in-situ synthesis steps were achieved via our original method, referred to as ultracentrifuging (UC) treatment, and a subsequent instantaneous heat-treatment (post-UC).$^{29-34}$ The UC treatment is a buildup synthetic scheme involving: i) unbundling of the carbon matrix, ii) in-situ sol-gel reaction of the V$_2$O$_3$ precursors on the exposed carbon surface, iii) restructuring of the carbon matrix. We applied this UC treatment to the synthesized V$_2$O$_3$/CNF in order to transform the V$_2$O$_3$ nanocrystals into the LVP precursors on the surface of the CNF. Then, the post-UC treatment effectively and simultaneously completed the crystallization of V$_2$O$_3$. In this study, we will present the optimized LVP/CNF composites exhibiting 80 mAh g$^{-1}$ at 480°C. A detailed evaluation of the structural feature and electrochemical properties of the UC-generated Li$_3$V$_2$(PO$_4$)$_3$/CNF is conducted to investigate its use as an alternative ultrafast cathode material in LIBs.

**Experimental**

Materials.— VCl$_3$ ($>97.0\%$, Sigma-Aldrich Corp.) was used as a source of V$_2$O$_3$. A carbon nanofiber (CNF; received from Mitsubishi Material Corporation) was selected as a carbon matrix to entangle with growing nanoscale V$_2$O$_3$ because of its high electronic conductivity and high specific surface area. 5 M NaOH aq. ($\approx$0.999 at 20°C, Wako Pure Chemicals) was used to drive the sol-gel process via hydration and polycrystallization during the V$_2$O$_3$ precipitation, CH$_3$COOLi ($>98.0\%$, Wako Pure Chemicals) and H$_2$PO$_4$ (85.0%, Wako Pure Chemicals) were used as LVP sources. Ultrapure water (17 MΩ cm) was used as a medium for the entire preparation scheme.

Preparation of the Li$_3$V$_2$(PO$_4$)$_3$/CNF composite under UC treatment.— The two-step process of the Li$_3$V$_2$(PO$_4$)$_3$ nanoplates/CNF is schematically illustrated in Fig. 1.

i) V$_2$O$_3$ nano-impregnation onto the surface of CNF (Fig. 1 i-iii)

First, 0.5512 g of VCl$_3$ was dissolved in 22 mL of ultrapure water. Then, 0.3215 g of the CNF was mixed in the VCl$_3$ solution for 5 min. The UC treatment was conducted for 5 min on the premixed CNF dispersion, while 2 mL of 5 M NaOH aq. was added to the dispersion drop by drop. After the filtration, the resultant precipitate was dried at 80°C for 12 h in vacuo, and then calcinated at 800°C for 30 min under N$_2$ atmosphere to complete the V$_2$O$_3$/CNF synthesis.

ii) In-situ transformation of nano-V$_2$O$_3$ into nano-Li$_3$V$_2$(PO$_4$)$_3$ on the surface of CNF (Fig. 1 iv)

As-prepared V$_2$O$_3$/CNF (0.1433 g), CH$_3$COOLi (0.0928 g), and H$_2$PO$_4$ aq. (0.1588 g) were added to 25 mL of ultrapure water. Then, the UC treatment was performed on the mixed dispersion for 5 min. The LVP/CNF composites were obtained after drying at 80°C for 12 h in vacuo.

The LVP/CNF precursor was reground and sintered at different temperatures ranging from 700°C to 900°C under N$_2$ atmosphere at different holding times, as shown in Fig. 2. The calcination temperature was attained within 3 min, and then the temperature was held for 5 min (Samples A to C in Fig. 2). Sample D was an exception, as it was subjected to a short-duration heating of 3 min at 900°C; subsequently, the heating was immediately turned off to allow natural cooling.

**Figure 1.** Schematic illustration of the concept behind our two-step LVP/CNF fabrication process. First, an ultracentrifugation treatment (UC treatment) is performed to synthesize nanoplated V$_2$O$_3$/CNF composites. i) The nucleation of the V$_2$O$_3$ precursor occurs on the anchor sites of the CNF, which are generated under strong basic conditions (OH$^-$); as a result, nanograins (2–5 nm) of the V$_2$O$_3$ precursor are formed on the anchor sites of the CNF. ii) The nanograins of the V$_2$O$_3$ precursor are anisotropically grown into nanoplates (20–200 nm), owing to the ultracentrifugation at 75000G and the steric hindrance of the CNF. After sintering at 800°C for 30 min (formation of the V$_2$O$_3$ nanocrystals), a second UC treatment is performed to synthesize the LVP nanoplates/CNF composites. iii) After the UC treatment of a mixture of V$_2$O$_3$/CNF, CH$_3$COOLi, and H$_2$PO$_4$, and the subsequent sintering at 900°C without holding time (0 min), iv) the V$_2$O$_3$ nanoplates/CNF composite is transformed into the designated LVP nanoplates/CNF composite without any dimensional change, as confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) results (Figs. 3 and 5).

Physicochemical characterizations of the Li$_3$V$_2$(PO$_4$)$_3$/CNF composite.— The detailed nanostructure features of the composites, such as the LVP particle size distribution and the CNF graphene layer network, were characterized by high-resolution transmission electron microscopy (HRTEM, Hitachi H9500 model). X-ray diffraction (XRD; Rigaku SmartLab) was used to characterize the crystalline structure of V$_2$O$_3$/CNF and LVP/CNF. To examine the stoichiometry of the composites, a thermal analysis was performed under synthetic air atmosphere (20% O$_2$, 80% N$_2$) using a thermogravimetry differential thermal analyzer (TG/DTA, Seiko Instruments TG/DTA6300).

Electrochemical and battery characterizations of Li$_3$V$_2$(PO$_4$)$_3$/CNF composites.— The half-cell was assembled with a Li metal electrode, and a Li$_2$V$_2$(PO$_4$)$_3$/CNF electrode, using 2032 coin-type cell. The composition of the electrolytes was a battery grade mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1.0 M of lithium hexafluorophosphate (LiPF$_6$, Kishida Chemical Co., Ltd) as the electrolyte salt. The Li$_2$V$_2$(PO$_4$)$_3$/CNF electrode was prepared by mixing 90% of the composite and 10% of polyvinylidene difluoride (PVdF) in N-methyl pyrrolidone (NMP). The slurry was coated on a Al foil (current collector) and dried at 80°C in vacuo for 12 h. The electrode density was ca. 0.61 g cm$^{-3}$, calculated from the loading mass of the composite (0.92 mg) on 1.21 cm$^2$ of Cu current collector and the thickness of the Li$_2$V$_2$(PO$_4$)$_3$/CNF electrode (10 ± 1 μm). The charge-discharge tests were performed under a constant current mode (CC-mode) between 2.5 and 4.3 V vs. Li/Li$^+$ at several current densities ranging from 1 to 480 C-rate assuming C-rate being 131 mAh g$^{-1}$. 

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Results and Discussion

Material design and synthetic optimization.— High crystallinity, particle size smaller than 2 μm, and impurity-free phases are essential factors for the ultrafast electrochemical performances of LVP with a reversible capacity higher than 100 mA h g⁻¹ at a rate above 100 C. We identified the optimized calcination conditions that strongly affect these factors in LVP/CNF composites. Fig. 3 (left) shows the XRD patterns of LVP/CNF at different calcination temperatures: (A) 700 °C with a holding time of 5 min; (B) 800 °C, 5 min; (C) 900 °C, 5 min; (D) 900 °C, no holding time (0 min). The temperature profiles of each protocol are shown in Fig. 2. Overall, the XRD patterns of monoclinic LVP[6] (see the inset of Fig. 3, left) were found on the broad peak of the CNF (2θ = 20–30°) in all the XRD patterns of the four composites (A)–(D). Meanwhile, other peaks generated by impurities such as Li₉V₃(P₂O₇)₃(PO₄)₂ were detected in the samples prepared at the lower temperatures of 700 °C (A) and 800 °C (B). Metastable Li₉V₃(P₂O₇)₃(PO₄)₂[37] may be formed by insufficient thermal agitation or convection for the establishment of precise stoichiometric ratio of Li, V, and PO₄ (3:2:3) for the LVP particles. The impurity phase completely disappeared after calcination at the high temperatures of 900 °C. High temperature above 800 °C may provide the LVP particles with enough kinetic energy to allow for a uniform distribution of the resources, preventing the generation of impurities. The heating protocol D, 3 min of rapid heating up to 900 °C without any holding time, driving a fine-tuned control of the stoichiometry of LVP is of particular importance and results in a minimization of the undesirable phenomena that occur during long heating, such as LVP particle growth, agglomeration of the crystal diameter, and any carbon uptake, which would cause the breakage of the conjugation between the CNF and LVP.

The average crystallite sizes of the obtained four samples (A)–(D) of the final LVP/CNF products were calculated from the Scherrer equation with reference to that of the predecessor (V₂O₃/CNF) sample (E). The derived full widths at half-maximum (FWHMs) of the LVP (020) and V₂O₃ (104) peaks have been converted to the apparent average crystallite size, reported in Table I. The order of the calculated...
such a change in the dimensions of the crystallites could be explained by a slight increase in the crystallite dimensions (48 nm) was promoted. The CNF effectively anchors the intermediate a-V2O3 (a nanocrystal size of 32 nm). However, the calcination at a lower temperature (800 °C) and longer holding time (5 min) results in a slight increase of the crystallite size (35 nm). When a higher temperature (900 °C) was held for 5 min, the formation of an unanchored LVP pure phase with a slight increase in the crystallite dimensions (48 nm) was promoted. Such a change in the dimensions of the crystallites could be explained by a possible re-agglomeration of the fractured a-V2O3 before finally being transformed into LVP with sizes in the range of 20–200 nm.

Thermogravimetric analysis (TGA) was performed under synthetic air atmosphere to estimate the residual weight ratio of the CNF to the synthesized LVP crystals in the composites (Fig. 3, right). We firstly checked the thermal behavior of the V2O3/CNF composite (E) under air, and not under N2 as for the synthetic protocol. In the temperature range of 150–400 °C, the thermal curve shows a slight weight increase, equal to approximately 5%, due to the oxidation of V2O3 to V2O5.37 However, the calcination at a lower temperature (800 °C) and longer holding time (5 min) results in a slight increase of the crystallite size (32 nm). When a higher temperature (900 °C) was held for 5 min, the formation of an unanchored LVP pure phase with a slight increase in the crystallite dimensions (48 nm) was promoted. Such a change in the dimensions of the crystallites could be explained by a possible re-agglomeration of the fractured a-V2O3 before finally being transformed into LVP with sizes in the range of 20–200 nm.

The electrochemical performances.— The charge-discharge tests were performed to investigate the electrochemical characteristic of our Li1xV2(P2O7)3(PO4)2/CNF composites (A)-(D) with the good rate capability. The discharge capacity of the half-cell Li/Li1xV2(P2O7)3(PO4)2/CNF at 1 C in the voltage of 2.5–4.3 V. In the charge-discharge curves, three characteristic charge plateaus can be observed at 3.6 V, 3.7 V, and 4.1 V, corresponding with the phase transition of Li1xV2(P2O7)3(PO4)2, from x = 3.0 to 2.5, 2.0, and 1.0, respectively.38 In the case of (A) and (B) which were synthesized at the temperature lower than 800 °C, additional plateau of 3.7 V, which is identical to the impurity Li1xV2(P2O7)3(PO4)2, was observed.39 As the temperature increases to 900 °C (sample (C) and (D)), the plateau of the Li1xV2(P2O7)3(PO4)2 was no longer observed, which is consistent with the results of XRD (Fig. 3). The discharge capacity increases from 93 mA h g−1 to 126 mA h g−1 after the transformation of V2O3 into LVP.

Ultrafast behavior and long-term cyclability.— To investigate the influence of the impurities (Li1xV2(P2O7)3(PO4)2) and the bonding (LVP) on the high-rate performance, charge–discharge tests at variable current densities from 1 C to 480 C were performed, as shown in Fig. 4b. The capacity retentions at 300 °C for the samples (A)–(D) calculated under different conditions are: (A) 88% (700 °C for 5 min), (B) 76% (800 °C for 5 min), (C) 21% (900 °C for 5 min), (D) 81% (900 °C for 0 min). Such an excellent rate capability is ever achieved. This might be due to the optimized nanostructure of the LVP/CNF composites, discussed in the next section (Fig. 5), which helped overcome the
Figure 4. Electrochemical properties of Li insertion–deinsertion for the prepared LVP/CNF composites. (a) Dependence of the charge–discharge profiles on the thermal treatment conditions. Charge–discharge curves at 1C (131 mA g$^{-1}$, corresponding to the current density of ca. 0.069 mA cm$^{-2}$ for the LVP/CNF composites sintered at: (A) 700°C, 5 min; (B) 800°C, 5 min; (C) 900°C, 5 min; (D) 900°C, 0 min. (b) Plots of the discharge capacity for different LVP/CNF samples versus different C rates from 1C to 480C. The tested samples are the same LVP/CNF composites. Charge rates were fixed at 1C. (c) Charge–discharge profiles of the LVP/CNF composite sintered at 900°C for 0 min (sample (D)) at different discharge C-rates from 1C to 480C. (d) Results of the cycle tests for the LVP/CNF composite sintered at 900°C for 0 min (sample (D)). Both the charge and discharge rates were fixed at 10C. The inset shows the charge–discharge profiles at the 1$^{st}$, 2000$^{th}$, 4000$^{th}$, 6000$^{th}$, 8000$^{th}$, and 10000$^{th}$ cycle.

inherent problems of the LVP materials, such as their poor electronic conductivity. The capacity retentions at 480C were: (A) 84% (700°C for 5 min), (B) 57% (800°C for 5 min), (C) 7% (900°C for 5 min), (D) 69% (900°C for 0 min). The capacity retention at 480C decreases with the increase of the calcination temperature. This may be attributed to two possible causes: one is the presence of LVP particles unanchored from the CNF matrix and the other is the crystallite growth of LVP. The exception is sample (D), calcinated at 900°C for 0 min, which shows a capacity retention of 69% at 480°C, higher than that obtained for sample (B) calcinated at 800°C for 5 min. This may be due to the calcination conducted with a holding time of 0 min, which prevents the formation of LVP particles unanchored from the CNF matrix; the provided thermal agitation is large enough to completely convert V$_2$O$_3$ into LVP crystals while maintaining its crystallite size. The LVP/CNF composite in sample (D) retains 85% of the initial capacity even after 10000 cycles at a C-rate of 10C, showing that the LVP/CNF composite is electrochemically stable in a two-electron charge–discharge process (Fig. 4d). The charge–discharge profiles for different cycles ranging from the 1$^{st}$ to 10000$^{th}$ are shown in the inset of Fig. 4d. After every cycle, the discharge capacity gradually decreases and the

Figure 5. HRTEM, SEM, and model images of the synthesized LVP/CNF composites. (a)–(c) and (e) HRTEM images of the LVP nanoparticles and nanoplates; (c) LVP/CNF nanoparticles directly attached on the CNF tubes; (d) schematic illustration of the LVP nanoparticles/CNF composite; (e) clear lattice fringes of the LVP crystal. (f) and (g) SEM images of the LVP nanocomposites; (f) lower magnification SEM image of the composited LVP nanoparticles (>20 nm) highly dispersed within the CNF matrix; (g) most of the LVP nanoparticles are impregnated on the CNF surfaces.
ohmic drop increases, as discussed in other previous reports. Such a degradation may be due to the disappearance of the electron path in the composites resulting from the presence of resistance components such as an accumulated solid electrolyte interphase (SEI) layer on the LVP or CNF surface caused by long-term charge–discharge tests.

**Structural control to nano-sized crystal.—** The nanostructure of the sample (D) 900°C for 0-min hold, which gave the best electrochemical properties at high rate of 480°C among four Li3V2(PO4)3/CNF composites (A)-(D), was observed by HRTEM in order to evaluate its morphology, crystal structure, and the evidence of the attachment between Li3V2(PO4)3 and CNF surface. The high magnification HRTEM images (Fig. 5a and 5b) suggest that the one or two of damaged graphene layers on the CNF surface. In an less magnified image, Li3V2(PO4)3 nanocrystals (<5 nm) can be found embedded within the damaged surface as shown in Fig. 5c. The schematic illustration of Fig. 5c (Fig. 5d) suggests that the Li3V2(PO4)3 nanocrystals are directly attached on the surface of CNF. As shown in SEM images (Fig. 5f and 5g), most Li3V2(PO4)3 nanocrystals have a platelet shape with a 20–200 nm side and thickness, and are well entangled within the CNF matrix. Such a morphology suggests that the electron path between Li3V2(PO4)3 nanocrystals and CNF became shorter, and the lithium diffusion path became shorter as well due to the platelet shape, resulted in the excellent rate performance for the sample (D). Besides, a similar mixed morphology of nanoparticle and platelets for the Li3V2(PO4)3/CNF can be found in the HRTEM images of V2O5/CNF, suggesting that the transformation from V2O5 into Li3V2(PO4)3 proceeds without any changes in its size and dimension. The results of HRTEM observation are well correspond to the postulated synthetic mechanism as illustrated in Fig. 1. As the synthetic reaction proceeds, the 5 nm nanocrystals grow to the larger particles, then merge into the 20–200 nm platelets. The mechanism is under consideration and investigation, as we have not enough strong evidence on our postulation.

N2 adsorption experiments were performed in order to study the pore size distribution within the sample (D). Li3V2(PO4)3/CNF calcinated at 900°C for 0-min hold. Fig. 6 shows the nitrogen adsorption–desorption isotherm curves for the pristine CNF and the sample (D). The shape of both curves is typical IUPAC IV curve, suggesting the meso porous morphology, while the total pore volume of the CNF became 0.7 times smaller after compositing with Li3V2(PO4)3. These isotherm curves were converted into the Barrett-Joyner-Halenda (BJH) pore size distribution, which is presented in the inset of Fig. 6. The pristine CNF possesses 10–40 nm pore distribution attributed to the entangled structure of CNF matrix. The pore distribution became wider (5–40 nm) for the Li3V2(PO4)3/CNF composite, while the intensity of its dVp/dp became smaller than that for the pristine CNF. Such change in the pore distribution by compositing with Li3V2(PO4)3 may be explained by the generation of the 5–10 nm sized Li3V2(PO4)3 nanoparticles on the CNF surface, which fills the pore between the entangled CNF matrix. Still, the wide pore distribution of the Li3V2(PO4)3/CNF composite suggests that the electrolyte reservoir of the CNF matrix are well preserved. Such an electrolyte reservoir may contribute to the fast lithium ion diffusion, and can be additional reason to the nanocrystals and direct attachment on the CNF surface for the ultrafast electrochemical properties for the Li3V2(PO4)3/CNF.

**Conclusions**

Anisotropically grown LVP nanocrystals (20–200 nm), which are highly dispersed and directly impregnated on the surface of a carbon nanofiber (CNF), were successfully synthesized by the combination of a UC treatment and the subsequent short-duration heat-treatment. The first step is the formation of anchor sites on the CNF surface by an ultra-centrifugal force field under strong basic conditions. Simultaneously, nanoplated V2O5 conjugated with the anchor sites of the CNF was produced using an alkaline precipitation method. The second step is the in-situ transformation of the nanoplated V2O5 into the non-plated LVP on the surface of the CNF, without any changes in its conformation or disappearance of the conjugation. Furthermore, the optimization of the thermal conditions suggested that the purity, conjugation, and crystallite size depend on the temperature and time conditions. The XRD measurement shows that high-purity LVP can be produced by calcination at a high temperature of 900°C. On the other hand, in the case of high-temperature calcination, the electron path between carbon and LVP was lost because of the disappearance of the conjugation, resulting in the deterioration of the rate capability. Moreover, the calcination at high temperature promoted the agglomeration of the crystallites; however, short-duration calcination can prevent the agglomeration. Based on these results, we identified the optimized calcination conditions for the high-rate cathode material: high temperature (900°C) without any holding time. From the N2 adsorption results and HRTEM observations, we found that the optimized LVP/CNF composite exhibited hyper-dispersed LVP crystals entangled within the CNF matrix and electrolyte reservoirs contributing to the fast lithium ion diffusion. Owing to the smooth lithium ion diffusion from the electrolyte reservoirs and the good electron path between the LVP crystals and the CNF, the optimized LVP/CNF composite exhibits an excellent rate capability (83 mA h g⁻¹ at 4800C) and an ultra-long cycle-life stability (85% of the initial capacity after 10000 cycles at 10C).

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