One-step Synthesis of LiVPO$_4$F/C Cathode Material with High Performance

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LiVPO$_4$F/C cathode material was synthesized by a novel one-step solid-state reaction method using humic acid as both reduction agent and carbon sources. The SEM image showed that the particles merged with each other to form a porous structure. Electrochemical test showed that the initial discharge capacity of LiVPO$_4$F/C powder was 139 mA h g^{-1} and the capacity was 132 mA h g^{-1} after 30 cycles.

Since the pioneering work on LiFePO$_4$ by Padhi et al.,[1] lithium transition-metal phosphates LiMPO$_4$ (M = Mn, Fe, and V) and lithium transition-metal fluorophosphates LiVPO$_4$F have attracted much attention as potential new cathode materials for lithium ion batteries. Among these compounds, LiFePO$_4$ shows a flat voltage plateau at 3.5 V vs. Li$^+$/Li and a theoretical specific capacity of 170 mA h g^{-1} and, therefore, was previously considered as a candidate cathode material to replace the popularly used LiCoO$_2$. Many attempts have been performed to improve the rate capability of LiFePO$_4$ by minimizing the particle size, cation doping, or conductive coating.[2–8] However, low gravimetric density and low-voltage plate of LiFePO$_4$ limit the performance improvement for applications in lithium ion batteries. Alternately, LiVPO$_4$F is promising for this purpose because it offers the potential of V^{3+}/V^{4+} redox couple at 4.2 V vs. Li$^+$/Li, which is compatible with the system presently used in lithium ion batteries.

By now, the reported methods for synthesizing LiVPO$_4$F are two-step solid-state reaction[9–14] and sol–gel method.[15] The two-step solid-state reaction method is complicated by synthesizing the VPO$_4$ intermediate which is used to react with LiF to produce the final LiVPO$_4$F. Moreover, it is really hard to get LiVPO$_4$F with high purity by two-step solid-state reaction. Though the particle size of the LiVPO$_4$F synthesized by sol–gel method is small and the electrochemical performance is good, the synthesis cost is high and synthesis cycle is long leading to difficult industrialized production.[15] One-step solid-state reaction method is a versatile method for preparing electrode material for lithium ion batteries.[16,17] Its advantages include simple synthetic process, easy scale-up, energy efficient, and environmental friendly. In this work, LiVPO$_4$F was synthesized by a novel one-step solid-state reaction method using humic acid as both reduction agent and carbon sources, and the electrochemical performance was evaluated.

V$_2$O$_5$, NH$_4$H$_2$PO$_4$, LiF, and humic acid (consists of C, H, O, and N elements and the molecular weight is about 300) with a molar ratio of 1:2:2:1 were initially ground in a mortar, then thoroughly mixed by ball milling for 4 h, and calcined at 750 °C for 4 h to yield LiVPO$_4$F/C. To avoid the oxidation of vanadium, the process was carried out under flowing Ar atmosphere.

The crystalline phase was identified with powder X-ray diffraction (XRD, Rint-2000, Rigaku) with Cu Kα radiation. The lattice parameters were refined with peak positions that were calibrated by internal standard of silicon (99.9% pure). The particle size and morphology of the LiVPO$_4$F powders were observed by a scanning electron microscope (JEOL, JSM-5600LV) with an accelerating voltage of 20 kV. The carbon content of samples was determined by a carbon–sulfur analyser (Mlti EA2000).

Electrochemical characterization of the sample was performed using a CR2025 cell. For positive electrode fabrication, the prepared powders were mixed with 10 wt % of carbon black and 10 wt % of poly(vinylidene fluoride) in N-methyl pyrrolidinone until slurry was obtained. Then, the blended slurries were pasted onto an aluminum current collector. The electrode was dried at 120 °C for 10 h in vacuum. The coin cell consisted of the positive electrode, lithium foil negative electrode separated by a porous polypropylene film, and 1 mol L^{-1} LiPF$_6$ in EC:EMC:DMC (1:1:1 in volume) as the electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged over a voltage range of 3.0 to 4.4 V versus Li/Li$^+$ electrode at room temperature. Cyclic voltammograms were tested at a scanning rate of 0.1 mV s^{-1} in the voltage ranges of 3.0–4.9 V.

To synthesize single-phased LiVPO$_4$F material, the one-step solid-state reaction method using humic acid as the reduction agent was adopted. In the heating of humic acid containing the LiVPO$_4$F precursor, hydrogen and carbon are generated by the pyrolysis of humic acid, producing a strong reductive atmosphere for the reduction of V^{5+} to V^{3+}. Figure 1 shows the XRD pattern of the LiVPO$_4$F/C sample. All diffraction peaks are fully indexed as a triclinic structure with a space group (P$\bar{1}$) and the unit parameters ($a = 5.147$, $b = 5.291$, $c = 7.437$ Å, $\alpha = 67.365°$, $\beta = 67.540°$, $\gamma = 81.981°$), and no impurity phase is detected. The XRD result demonstrates that a one-step solid-state route can synthesize single-phased LiVPO$_4$F
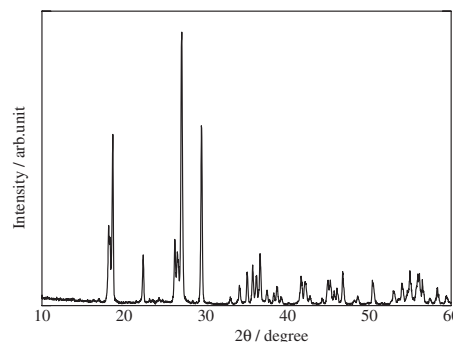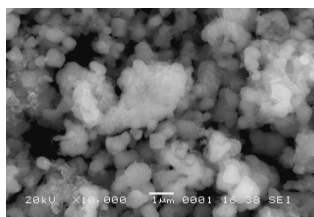

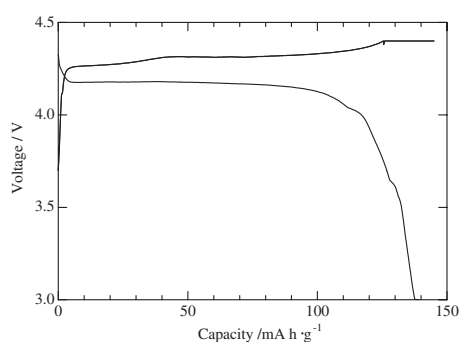**Figure 1.** XRD pattern of LiVPO$_4$F/C.

Figure 2. SEM image of LiVPO$_4$F/C.

Figure 3. First charge–discharge curves of LiVPO$_4$F/C.

Figure 4. Electrochemical cycling performance of LiVPO$_4$F/C.

synthesized by one-step solid-state reaction method. The LiVPO$_4$F/C material exhibits high electrochemical performance with the initial discharge capacities of 139 mA g^{-1} and the capacity is 132 mA h g^{-1} afer 30 cycles.

material using humic acid as the reduction agent. The carbon content of LiVPO$_4$F/C is 5.42 wt % analyzed by a carbon–sulfur analyser. However, no diffraction peaks from carbon is detected in the XRD pattern, indicating that carbon may exist as amorphous form.

Figure 2 shows the SEM image of LiVPO$_4$F/C. In the micrograph, the particles merge with each other to form a porous structure. This microstructure helps the electrolyte to penetrate the cathode materials and improves electronic contact among the LiVPO$_4$F particles. The form of the residual carbon in the micrograph is unclear. It may be covering the surfaces of LiVPO$_4$F particles smoothly and bridging the particles as porous structure.

Figure 3 shows the first charge–discharge curves of LiVPO$_4$F/C cycled between 3.0 and 4.4 V at a current density of 100 mA g^{-1}. As can be seen in Figure 3, the sample clearly exhibits charge and discharge plateaus around the voltage of 4.2 V vs. Li$^+$/Li. These plateaus corresponded to the redox of V^{3+}/V^{4+} that accompanied lithium ion extraction and insertion in LiVPO$_4$F. The initial charge and discharge capacities of LiVPO$_4$F/C are about 145 and 139 mA h g^{-1}, respectively. The columbic efficiency of the initial charge–discharge cycle is about 95.86%.

The electrochemical cycling performance of LiVPO$_4$F/C was evaluated in the Li/LiVPO$_4$F cell configuration in the voltage range of 3.0–4.4 V at room temperature. Figure 4 shows the cyclic charge/discharge profiles for the LiVPO$_4$F sample at a current of 100 mA g^{-1}. As seen in Figure 4, after 30 cycles, the LiVPO$_4$F/C sample exhibits discharge capacities of about 132 mA g^{-1}. Namely, after 30 cycles, the capacity loss is about 5.04%. The above results demonstrate that LiVPO$_4$F/C with high electrochemical performance can be obtained by a simple one-step solid-state method.

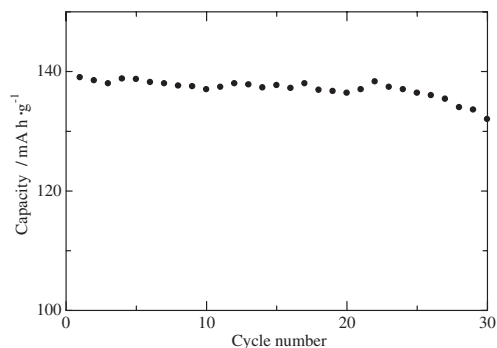In summary, the triclinic structure LiVPO$_4$F/C has been

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