Improvement of Discharge Capacity of β-$Fe_2(SO_4)_3$-Type $Li_3V_2(PO_4)_3$ by Stabilizing High Temperature Orthorhombic Phase at Room Temperature

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The cathode performance of a lithium ion battery was investigated for β-$Fe_2(SO_4)_3$-type $Li_3V_2(PO_4)_3$ and $Li_3(V_{1-x}Zr_x)_2(PO_4)_3$ (x=0.05, 0.1, 0.15, 0.2). On TG-DTA measurements, $Li_3V_2(PO_4)_3$ exhibited two types of phase transition, while $Li_3(V_{1-x}Zr_x)_2(PO_4)_3$ exhibited no phase transition. Powder X-ray diffraction analysis and conductivity measurements confirmed an evidence for the stabilization of the high temperature phase at room temperature. The discharge capacity of the Zr-substituted $Li_3(V_{1-x}Zr_x)_2(PO_4)_3$ samples became much larger than that of the pure $Li_3V_2(PO_4)_3$ sample.

NASICON-related compounds have been known as good ionic conductors, because of giving open space for the conduction of mobile ions. This feature can also be convenient for cathode materials which need fast ion transport, *e.g.*, $Fe_2(SO_4)_3$ and $Li_3Fe_2(PO_4)_3$ were known to exhibit good cathode performance.[1,2]

$Li_3V_2(PO_4)_3$ crystallizes two modifications of β-$Fe_2(SO_4)_3$-type usually synthesized by a conventional solid state reaction and NASICON-type synthesized by a soft chemistry like an ion-exchange reaction.[3,4] The cathode performance of $Li_3V_2(PO_4)_3$ has been examined for both modifications[1]; the β-$Fe_2(SO_4)_3$-type material has larger discharge capacity than that of the NASICON-type material, but their cycle performance is both poor. The β-$Fe_3(SO_4)_3$-type structure is a NASICON-related structure, where $V_2(PO_4)_3$ frameworks are also built up of PO_4 tetrahedra sharing corners with VO_6 octahedra.

In preliminary experiments, we found that $Li_3V_2(PO_4)_3$ shows two structural phase transitions depending on temperature. Such phase transitions seems to be just the case of $Li_3Sc_2(PO_4)_3$ with the same β-$Fe_3(SO_4)_3$-type crystal structure, the high temperature phase of which is known as an superionic conducting phase.[5] This fact indicates that the high temperature phase of $Li_3V_2(PO_4)_3$ gives good environment for lithium ion diffusion, impling a possibility to improve the cathode performance of $Li_3V_2(PO_4)_3$ by stabilizing the high temperature phase at room temperature. In this study, we have succeeded the stabilization of the high temperature phase of $Li_3V_2(PO_4)_3$ at room temperature by substituting Zr for V sites, and investigated charge/discharge behavior and cycle performance of the stabilized materials.

$Li_3V_2(PO_4)_3$ and $Li_{3-2x}(V_{1-x}Zr_x)_2(PO_4)_3$ was synthesized by a conventional solid-state reaction at 1100 ℃ for 12 h in Ar atmosphere. The completion of the reaction and the phase purity of the products were confirmed by powder X-ray diffraction. The powder X-ray diffraction patterns of $Li_3V_2(PO_4)_3$ and $Li_{3-2x}(V_{1-x}Zr_x)_2(PO_4)_3$ indicated that the samples have a single phase with a monoclinic or an orthorhombic symmetry in the substitution up to x=0.2. Differential thermal analysis (DTA) were conducted between 20 ℃ and 500 ℃ with a heating rate of 5 ℃min^{-1}. The cathode for the electrochemical characterization was fabricated by mixing powders of the sample, acetylen black and PTFE in a weight ratio of 70:25:5 under Ar atmosphere. The cathode properties were measured in a galvanic cell with a nonaqueous electrolyte (1 mol dm^{-3} $LiClO_4$ / PC+DME), a polypropylene separator, and a Li metal anode. Charge/discharge performance was evaluated at a current density of 0.5 $mAcm^{-2}$ in the voltage range between 3.0 and 4.4 V vs. Li/Li^+.

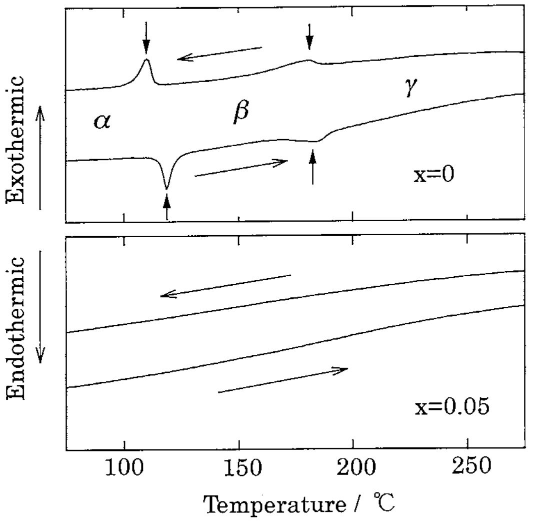

Figure 1. DTA curves of β-$Fe_2(SO_4)_3$ type $Li_3V_2(PO_4)_3$ and $Li_{3-2x}(V_{1-x}Zr_x)_2(PO_4)_3$.

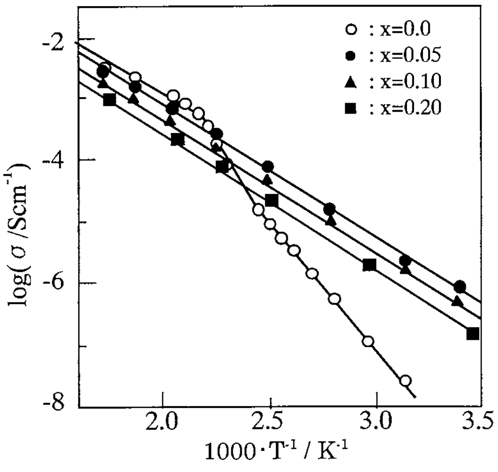

Figure 2. Ionic conductivity of $Li_{3-2x}(V_{1-x}Zr_x)_2(PO_4)_3$.

DTA analysis of $Li_3V_2(PO_4)_3$, as shown in Figure 1, showed three structural modifications, while $Li_{3-2x}(V_{1-x}Zr_x)_2(PO_4)_3$ with Zr substitution ratio beyond x=0.05 did not exhibit any endo- and exo-thermic heat in the range of 20-500 ℃. $Li_3Sc_2(PO_4)_3$ with the same β-$Fe_3(SO_4)_3$-type structure has three structural modifications: low temperature monoclinic α-phase, middle temperature monoclinic β-phase and high temperature orthorhombic γ-phase.[5] The phase transitions are all reversible. In comparison with $Li_3Sc_2(PO_4)_3$, one may assign the same phase relation for $Li_3V_2(PO_4)_3$, as indicated in Figure 1. The conductivity of the samples was evaluated from complex impedance diagrams, and the results are shown in Figure 2. The sample's conductivity was found to be more than 99% ionic conductivity complex impedance and D.C. polarization measurements. For the pure sample, changes of slope can be seen at the temperatures corresponding to the transition points observed in Figure.1. The substituted samples, on the other hand, have a linear dependence of $\log \sigma$ vs. 1000/T and also have almost the same slope as that of the γ-phase of the pure sample. Both the results of DTA and conductivity measurements strongly suggest the stabilization of the γ-phase at room temperature. This is quite similar with our previous studies on $Li_3Sc_2(PO_4)_3$ [6,7]; the γ-phase of $Li_3Sc_2(PO_4)_3$ was successfully stabilized at room temperature by substituting various ions such as Ti, Zr, Nb, Ta, and Mg for Sc sites.

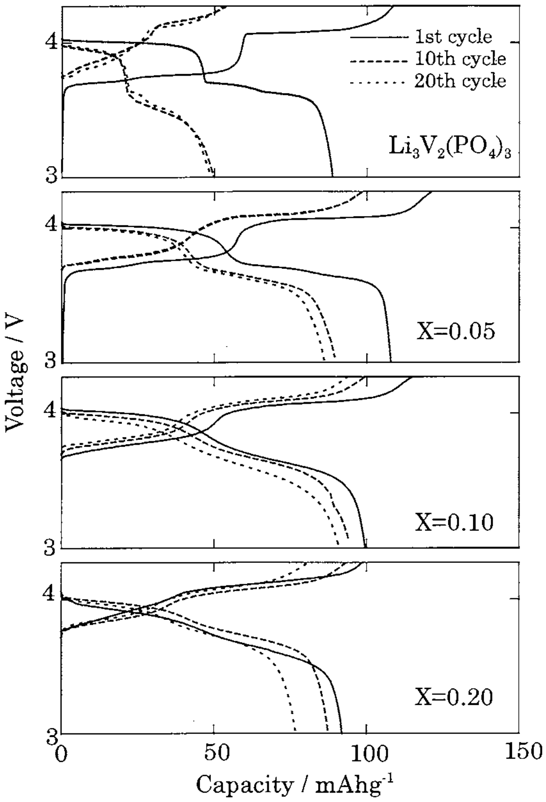

Figure 3. Relationship between cycle number and capacity of $Li_3V_2(PO_4)_3$ and $Li_{3-2x}(V_{1-x}Zr_x)_2(PO_4)_3$.

Figure 3 shows typical charge/discharge curves for pure and Zr-substituted samples. The theoretical capacity of $Li_3V_2(PO_4)_3$ is 131.5 mAhg^{-1}. Discharge curve of the pure sample has two plateau regions with 3.7 and 4.1 V vs. Li/Li$^+$ on charging and with 3.6 and 4.0 V vs. Li/Li$^+$ on discharging, respectively. These charge/discharge behavior is quite similar to that of the previous study.[1] Although the stabilized samples show a somewhat similar charge/discharge performance to those of the pure material, there can be seen two well improved points of the cell performance. One is the enhancement in the discharge capacity, *e.g.*, the sample with x=0.10 has 27% larger discharge capacity than that of the pure sample. Also, one can see that in the substituted samples the two-plateau boundary gradually become ambiguous with increasing the substitution ratio. Such disappearance of the two-plateau boundary could be very effective for the cathode material to give good cycle performance. In fact, the samples with x=0.10 and x=0.20 exhibited a little deterioration in discharge capacity during 20 cycles. The improvement in cell performance observed for the γ-phase stabilized samples should originate from the disordered lithium ion arrangement in the orthorhombic γ-phase. To confirm this, the structure refinement by neutron diffraction is in progress, and the results will be reported elsewhere.

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