Improvement of High Rate Performances for Ti-Doped Li$_3$V$_2$(PO$_4$)$_3$ Cathode Materials

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ABSTRACT
Ti-doped lithium vanadium(III) phosphate cathode materials, Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$, were prepared by a solid state reaction. The Ti-doped samples exhibited that the γ-phase is stabilized at room temperature by substituting Ti for V sites at more than $x = 0.10$. The discharge capacity of the doped samples at a 60°C rate was found to be much higher than that for the non doped sample. This improved performance found for the doped cathodes was attributed to the increase in ionic conductivity given by the transition of α- to γ-phase via Ti substitution.

Keywords: Li$_3$V$_2$(PO$_4$)$_3$, Ti Doping, Ionic Conductivity, Carbon Coating

1. Introduction
Lithium vanadium(III) phosphate, Li$_3$V$_2$(PO$_4$)$_3$, has three independent lithium sites in the low-temperature form, where all the three type lithium ions located on these sites can take part in redox reaction. Therefore, this material is capable to keep a large number of Li ions in electrical conductivity (especially ionic conductivity) of materials. Titanium used here has been known to be one of the promising elements as an additive stuff for the improvement of electrical conductivity. The Ti-doped samples exhibited that the ionic conductivity is improved by substituting Zr for V sites in Li$_3$V$_2$(PO$_4$)$_3$ changed from α-phase to γ-phase via Ti substitution. Furthermore, Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$ samples without carbon-coating. After heating the mixture of the starting materials at 300°C as described above, the Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$ precursors obtained were mixed with polystyrene by using the ball mill with toluene as a mixing solvent for 2 h and then calcined at 880°C for 12 h in an Ar + 5% H$_2$ atmosphere in a tubular furnace to obtain the Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$ samples without carbon-coating. After heating the mixture of the starting materials at 300°C as described above, the Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$ precursors obtained were mixed with polystyrene by using the ball mill with toluene as a mixing solvent for 2 h and then calcined at 880°C for 12 h in an Ar + 5% H$_2$ atmosphere in a tubular furnace to obtain the carbon-coated Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$/C samples.

2. Experimental
Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$ (x = 0.0, 0.025, 0.050, 0.10, 0.20) samples were prepared as follows. Stoichiometric amounts of Li$_2$CO$_3$, V$_2$O$_5$, NH$_4$H$_2$PO$_4$, and TiO$_2$ were mixed by the ball-milling with toluene as a mixing solvent for 4 h. The mixture was heated at 300°C for 6 h in an Ar atmosphere in a tubular furnace and then cooled to room temperature. The prepared Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$ precursors were reground by the ball-milling for 2 h, followed by heating at 880°C for 12 h in an Ar + 5% H$_2$ atmosphere in a tubular furnace to obtain the Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$ samples without carbon-coating. After heating the mixture of the starting materials at 300°C as described above, the Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$ precursors obtained were mixed with polystyrene by using the ball mill with toluene as a mixing solvent for 2 h and then calcined at 880°C for 12 h in an Ar + 5% H$_2$ atmosphere in a tubular furnace to prepare the carbon-coated Li$_{3-2x}$(V$_1$–Ti$_x$)$_2$(PO$_4$)$_3$/C samples.

A LCR meter (NF Co., ZM2375) was used in the temperature range from 20 to 200°C under an Ar atmosphere. The conductivity was determined by the complex impedance diagrams obtained using alternating currents with frequencies between 0.02 and 5.5 MHz.

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The DSC curves of the non-doped sample, two characteristic peaks, were clearly observed at around 110 and 180°C (exothermic) and at 120 and 185°C (endothermic) and indicated the temperature dependent phase transitions from monoclinic to orthorhombic. However, no reversible transitions were seen for the Ti-substituted samples ($x \geq 0.025$). Referring to our previous work,\textsuperscript{5} two reversible phase transitions observed are considered to be due to the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ phases transitions, respectively. On the other hand, from the XRD patterns of Li$_3$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3/C$ ($x = 0, 0.025, 0.050, 0.10$, 0.20) (Fig. 1), it was confirmed that all samples consist of a single phase. Making the comparison of the XRD pattern from ICSD date, the minor peak characteristic of orthorhombic Li$_3$(Ti)$_2$(PO$_4$)$_3$ at 24° emerged with increasing Ti more than $x = 0.10$, while the minor peak characteristic of monoclinic Li$_3$V$_2$(PO$_4$)$_3/C$ at 37° faded with increasing Ti more than $x = 0.10$. These results suggest that the Li$_3$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3/C$ samples with the Ti substitution ratios above $x = 0.10$ stabilize in the orthorhombic $\gamma$-phase at room temperature.

The variations in the temperature dependence of the conductivity for non carbon-coated Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3$ are illustrated in Fig. 2. When taking notice of the region where the high temperature phase (i.e., $\gamma$-phase) is stable, the Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3$ ($x = 0.10$, 0.20) samples are apparent to have a linear dependence of log $\sigma$ versus $1/T$ and also to show almost the same slope as that of the $\gamma$-phase of Li$_3$V$_2$(PO$_4$)$_3$ ($x = 0$), also indicating the stabilization of the $\gamma$-phase at room temperature,\textsuperscript{5} though, in the regions where the low and middle temperature phases are stable, the details of conductivity behavior remained unknown at present because of lack of enough data points. On the other hand, Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3$ ($x = 0.025, 0.050$) do not exhibit the same tendency as Li$_3$V$_2$(PO$_4$)$_3$ ($x = 0$) at the high temperature region. Such findings are consistent with those of Fig. 1.

Figure 3 shows the charge/discharge curves of Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3/C$ at 0.2 C in the voltage range between 2.0 and 4.8 V. For Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3/C$ ($x = 0$, 0.025, 0.050), the discharge capacities at 3.0 V are found to be about 160 mAh g$^{-1}$, whereas about 150 mAh g$^{-1}$ for the samples with $x = 0.10$ and 0.20. The charge curves apparently exhibit four plateaus (3.60, 3.68, 4.08, and 4.63 V) that imply the phase transitions based on 3Li delivery, in contrast, the discharge ones are of wavelike curves. It is clear from such discharge curves that 3Li migration scarcely reflects on the appearance of plateau; the discharge curves for Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3/C$ show a solid solution behavior.\textsuperscript{8,9} The sample with $x = 0.2$ shows another plateau at 2.5 V both in charge and discharge processes, indicating a redox couple of Ti$^{4+}$/Ti$^{3+}$ and higher discharge capacity about 30 mAh g$^{-1}$.

The rate performances of Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3/C$ were examined in the range from 0.2 to 60 C. As can be seen from Fig. 4, the discharge capacity are apparent to be markedly decreased in the range from 0.2 to 3 C, while the capacity are dropped gradually below the theoretical capacity of 2Li delivery (132 mAh g$^{-1}$) over 5 C.\textsuperscript{10} In this range, Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3/C$ ($x = 0.20$) showed comparatively higher discharge capacity than other samples because a redox reaction of Ti$^{3+}$/Ti$^{4+}$ was confirmed between 2.0 and 2.5 V. When the amount of dopant Ti exceeds a constant amount about $x = 0.2$, two orthorhombic phases of Li$_3$V$_2$(PO$_4$)$_3$ and Li$_3$Ti$_2$(PO$_4$)$_3$
coexist in the cathode product. At 60°C, the discharge capacity of Li$_3$V$_2$(PO$_4$)$_3$/C ($x = 0$) is considerably lower than that of Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3$/C, indicating importance of high ionic conductivity of γ-phase to high capacity achievement. Here, for Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3$/C ($x = 0.025$), the capacity could not be measured at 60°C. In addition, from the charge/discharge performances at 0.2 C measured again after 50 cycles at 60°C, the decrease in the capacity are hardly observed, indicating that a robust crystal lattice of Li$_{3-2x}$(V$_{1-x}$Ti$_x$)$_2$(PO$_4$)$_3$/C is evident.

4. Conclusions

Temperature dependent conductivity measurements for Li$_3$V$_2$(PO$_4$)$_3$ without carbon-coating exhibited the phase transition from α- to γ-phase at room temperature by substituting Ti for V sites. The discharge capacity at 60°C of the Ti-substituted samples was found to be much larger than the non-substituted ones, indicating that the high ionic conductivity of the γ-phase at room temperature plays a crucial role for the electrochemical performance in these cathode materials.

References