Enhancement of Capacity via Phase Transformation of $LiVOPO_4$ to $Li_3V_2(PO_4)_3$

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The phosphate-based compounds, such as $LiFePO_4$, $LiCoPO_4$, $Li_3V_2(PO_4)_3$ and $LiVOPO_4$ are recommended as the cathode materials for lithium ion batteries in recent years. At present, great attention has been paid for $LiFePO_4$ as an alternative candidate material. However, in comparison with $LiFePO_4$, $LiVOPO_4$ has an advantage of higher potential (4.0 V versus Li/Li^+) for charging/discharging and triclinic phase of $LiVOPO_4$ synthesized from ε-$VOPO_4$ shows the capacity of 100 $mAhg^{-1}$ up to 100 cycles at C/10 rate. Therefore, $LiVOPO_4$ is also considered as the alternative cathode with discharged state. However, capacity for Li de-intercalation is decreased with increasing current density although higher potential of 4.0 V is exhibited. Therefore, improvement in Li intercalation and de-intercalation capacity is strongly desired for $LiVOPO_4$. The preparation methods of hydro-thermal and solid state reaction[15] have been reported for $LiVOPO_4$, and the capacity as well as cycle stability of electrochemical Li intercalation into $LiVOPO_4$ could be improved by optimizing the preparation method.

In this paper, we report the sol-gel method to prepare the α-$LiVOPO_4$ and investigated the process of phase transformation from α-$LiVOPO_4$ to α-$Li_3V_2(PO_4)_3$. The result is particularly interesting since there are not much reports on the phase transformation of the triclinic structure of α-$LiVOPO_4$ into the monoclinic structure of α-$Li_3V_2(PO_4)_3$ by sintering at 550 ~ 900 °C in 5% H_2/Ar reducing atmosphere.

Figure 1 shows the XANES spectra at V *K*-edge for a series samples with different sintering temperature along with the reference materials such as V_2O_3, VO_2 and V_2O_5 in different oxidation states. For the samples at low sintering temperature (550 ~ 650 °C) are the triclinic crystal system of α-$LiVOPO_4$ in a lower symmetry unit with a noncentrosymmetric environment around the vanadium site which showed a sharp pre-edge peak. On the other hand, the samples at high temperature (700 ~ 800 °C) have transformed to the phase of monoclinic crystal system of α-$Li_3V_2(PO_4)_3$ in a higher symmetry unit which showed a smooth pre-edge peak. The vanadium oxidation state is determined through the position of the absorption edge, which shifts to higher energies with an increasing valence state.

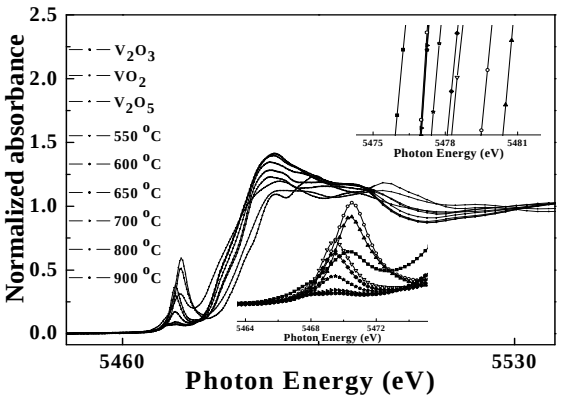

Figure 1. Room temperature of XANES spectrum calibrated and normalized for different temperature series sample at V *K*-edge energy

The XAS spectra at V *L*-edge together with the reference materials in different valence state of vanadium are shown in Fig. 2. The absorption peak is shifted smoothly from higher energy (+4 state for V in α-$LiVOPO_4$ phase) to lower energy (+3 state for V in α-$Li_3V_2(PO_4)_3$ phase) as the sintering temperature is increased from 550 °C to 800 °C as shown by the dash line in the L_{II} part. For the L_{III} part the peak shape is changed as the sintering temperature increased from 550 °C to 800 °C as shown by the dash rectangle in the L_{III} part. It means that different crystal system (triclinic vs. monoclinic) have different crystal-field effects and electronic interactions around the vanadium metal ion.

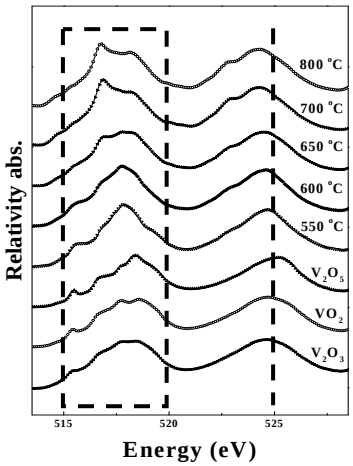

Figure 2. Room temperature of XANES spectrum calibrated and normalized for different temperature series sample at V *L*-edge energy