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XAFS Study of Conductive Sodium Phospho-Vanadate Glass as a Cathode Active Material for Na-ion Batteries with Large Capacity

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Rechargeable lithium-ion battery (LIB) is widely applied as a battery for smartphones, laptop type personal computers because of the high capacity. Because of the difficulty to use of Li, post-lithium-ion batteries have been extensively developed. In particular, sodium-ion battery (SIB) is one of the strong candidates. As for the development of cathode active materials for SIB, $30Na_2O{\cdot}40FeO{\cdot}30P_2O_5$ glass showed an initial discharge capacity when it was used as a cathode active material of SIB. Therefore, the amorphous vanadate including glass has a high potential for a cathode active material for SIB with high performance.

During the development of vanadate glass as a new cathode material for the secondary battery, it was reported that the introduction of P_2O_5 up to 10 mol% into vanadate glass systems enhanced chemical durability by keeping the electrical conductivity which will lead to the recyclability of electrode for secondary batteries. In this study, a relationship between the local structure and chemical bonding properties of sodium phospho-vanadate glasses was investigated using X-ray absorption fine structure (XAFS). The charge-discharge capacity of a new SIB glasses was evaluated as a new cathode active material at a lower cost.

Homogeneous vanadate glasses with the composition of $x Na_2O{\cdot}10P_2O_5 \cdot (90-x)V_2O_5$ ($5 \leq x \leq 45$ mol%, abbreviated as xNPV) were prepared by a melt-quenching method in air and melted in an electric muffle furnace at 1200°C for 1 h. Vanadium K-edge X-ray absorption spectra (XANES / EXAFS) were measured in transmission mode by using BL-12C at KEK-PF. For the measurement, a pellet with a diameter of 1 cm was prepared by pressing the mixture composed of a 5 mg sample and 95 mg boron nitride pressed at 5 kN. The obtained spectra were analyzed by Athena package.

XANES spectra of xNPV glasses with 5, 25 and 45 mol% of Na_2O content before and after heat-treatment at 450°C for 100 min are shown in Fig. 1. A pre-edge peak for V_2O_5 was observed at 5468 eV, while that of xNPV glasses shifted to smaller energy with increasing the intensity of the normalized absorbance. After crystallization of the xNPV glasses, all the near-edge pre-peaks are very similar to each other. In particular, XANES spectra of 5NPV glass after the heat treatment (Fig. 1(B) green) is similar to that of V_2O_5 (Fig. 1(B) black dotted line), showing that the crystalline phase of V_2O_5 is precipitated. The enlarged sections of Fig. 1 with the rising absorption show a clear difference between VO_2 and V_2O_5 behavior. The curves of 25NPV and 45NPV glasses in Fig. 1(B) are close to that of VO_2 while that of 5NVP is close to that of V_2O_5. XANES spectra of heat-treated xNPV samples containing 25 and 45 mol% of Na_2O are shifted toward a smaller energy region by decreasing its intensity at the pre-edge peak and becomes closer to that of VO_2 in the profile. This indicates that the heat-treatment of xNPV samples with 25 and 45 mol% of Na_2O resulted in the precipitation of VO_2 together with V_2O_5.

The Fourier transform (FT)-EXAFS curves of three xNPV glasses show the difference from V_2O_5 and VO_2 crystal. The short V=O double bonds are present which is different from the majority of V-O bonds of the glasses seen at the peaks at 1.3 Å. The shortest V-V peak is not detected in the FT curves of the glasses. After crystallization, the structural units of all xNPV glasses change clearly. The peak at 2.8 Åin the 5NPV sample increases its resemblance with V_2O_5 and the same can be confirmed from their X-ray diffraction patterns [1].

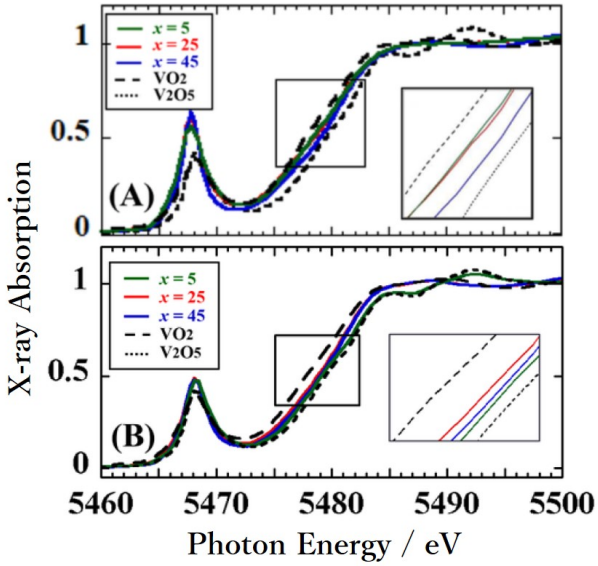

Fig. 1, XANES spectra of V_2O_5 (dotted line), VO_2 (dashed line) and xNPV glass (solid lines) with x of 5 (green), 25 (red) and 45(blue) (A) before and (B) after heat treatment at 450°C for 100 min. Insets show the expanded views.

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