Electronic state analysis of $Li_{3+x}V_{1-x}Si_xO_4$

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Currently, organic solvents are used in lithium-ion batteries as the electrolyte. However, attempts to solid electrolyte are proceeding from the viewpoint of safety and durability. The solid electrolyte is mainly oxide system and sulfide system. This time we adopted a highly safe oxide system(LISICON). It is found that the ion conductivity is maximized at x = 4 to 6. It gradually declined before and after that. The reason is that the sites of lithium ion in the lattices and lithium forms a dimer. In this study, we clarified the influence of ionic conductivity by investigating the electronic state of interstitial lithium.

$LiOH \cdot H_2O$, V_2O_5, SiO_2 (Aldrich) was used as a starting material for sample preparation. First, the starting materials were weighed, pulverized with a mortar, and fired at 850 °C. for 5 hours. Thereafter, the sample was crushed again with a mortar and fired under the same condition as the first time. The finished sample was finely pulverized by grinding with a mortar and then used for measurement.

The PES experiment was performed at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University, using a hemispherical electron energy analyzer, SCIENTA SES2002. The measurements were performed at room temperature under ultrahigh vacuum of ~1×10-7 Pa. The XRD experiment was performed at Ritsumeikan University. The radiation source was Cu Ka (λ = 0.15418 nm), scanning speed 4 ° / min, scanning range 3 to 90 °.

Fig. 1 shows the XRD results for each composition. From Fig. 1, it can be seen that there is a change in the case of X = 0.1, 0.3, 0.5 and X = 0.7, 0.9. So it can be seen that the structure is divided into two types within the range of X = 0.1 to 0.9. Fig. 2 shows the PES spector for each composition. Li 1s peak in any composition were seen in around 56 eV. V 2p and Si 2p results was same results with the composition ratio of the chemical formula without x = 0.7.

From the XRD results, We found that X=0.1, 0.3, 0.5 have the same structures as $Li_2Zn[GeO_4]$. Also, X=0.7, 0.9 have the same structure as Li_4SiO_4. From **Fig. 2**, there is one peaks of $Li_{3+x}V_{1-x}Si_xO_4$. From the results of PES and XRD, X=0.1, 0.3, 0.5 have same structure, but their electronic states have changed. Likewise, the same change was seen in X=0.7, 0.9.

In this study, we succeeded in producing LISICON, and performed XRD measurement and PES measurement. We revealed actual spectra with spattering. From XRD and PES results, we revealed that there was a change in the Li 1*s* electronic states with the same crystal structure.

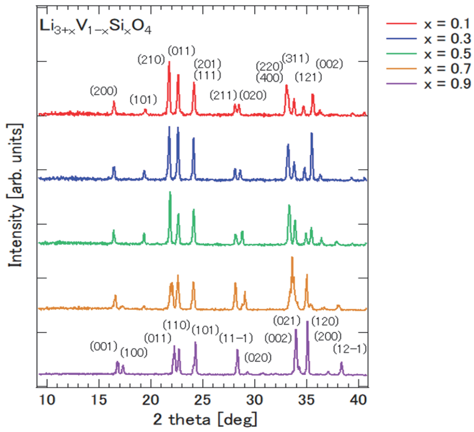

Fig. 1 Results of XRD

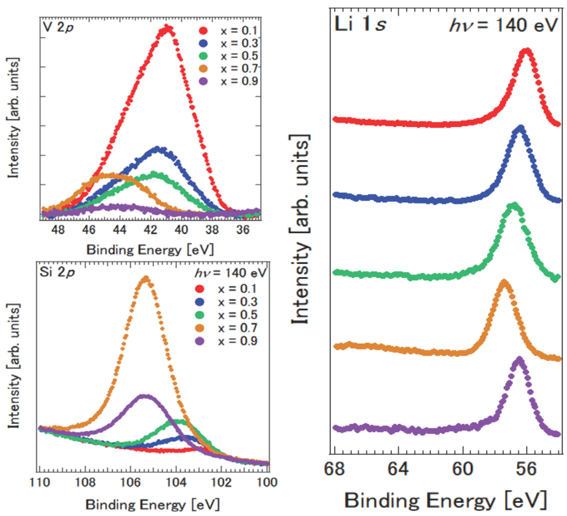

Fig. 2 Results of PES

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