Chemical structure analysis of sulfide-based solid electrolytes by ^{31}P solid-state NMR

Product used：Nuclear Magnetic Resonance Spectrometer (NMR)

Sulfide-based solid electrolyte has been expected as an electrolyte material for the all-solid-state battery, due to its high conductivity and low interface resistance against electrodes. Lithium thiophosphate (LPS) series is a typical sulfide electrolyte, and it is known that its Li^+ conductivity is greatly dependent on the crystallinity and content volume in the secondary phase. ^{31}P solid-state NMR is a powerful measurement method that can quantitatively calculate the crystallinity and the content ratio of secondary phases. Here, an analysis example is introduced, in which structural changes of the sulfide-based solid electrolyte LPS depending on the difference of preparation methods, were analyzed by ^{31}P solid-state NMR.

LPS structural changes depending on the difference of preparation methods - degree of crystallinity and unit structure -

Measurement sample

We have prepared lithium thiophosphate samples with the following four structures ($70Li_2S-30P_2S_5$) and performed structural analysis.

70LPS-g: Mixture of Li_2S and P_2S_5 was obtained with the mix ratio of 7 to 3 by the ball-mill method. Glassy state.

70LPS-gc: 70LPS-g was annealed at high temperature and crystalized.

70LPS-gcg: 70LPS-gc was vitrified (glassy state) again by the ball-mill method.

70LPS-gcgc: 70LPS-gcg was annealed again at high temperature and crystallized.

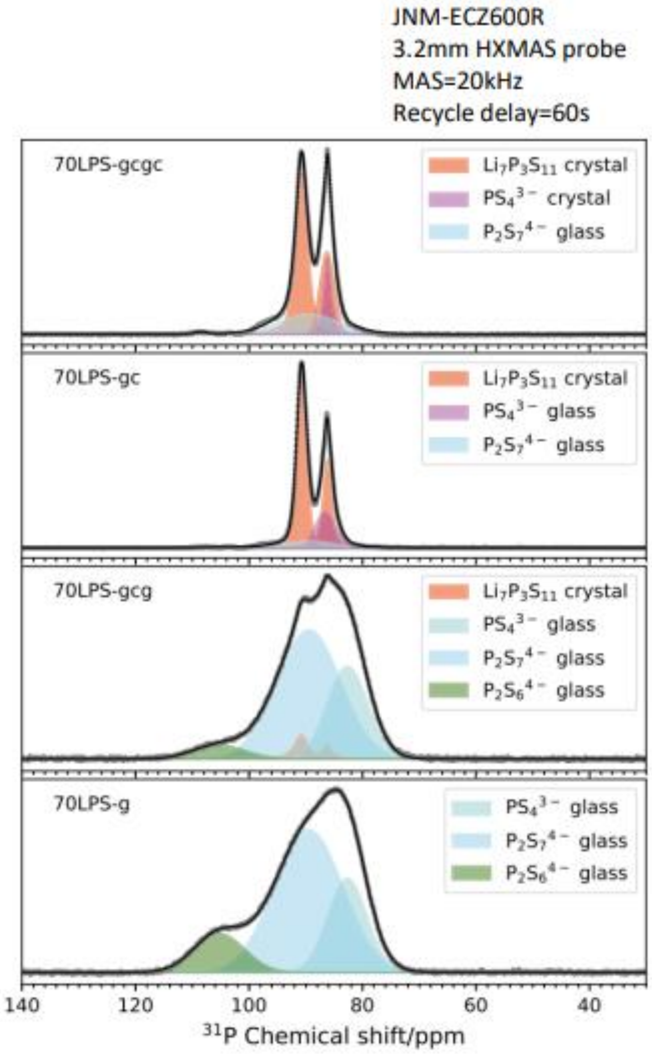
Results and Consideration

^{31}P solid-state NMR spectra of the four samples are shown in the figure on the right. Large differences in line width in the spectra are seen between crystalline samples and glass samples. Since a crystal has uniform bond length and angle, the line width is narrow for exhibiting a linear Lorentz-type spectral shape. But for a glassy state, the bond lengths and angles are distributed, resulting in a thicker line width and a Gaussian-type spectral shape.

The spectrum of 70LPS-g can be separated into three types of Gaussian components, and it is found that the three units are constituted from the chemical shift range; PS_4^{3-}, $P_2S_7^{4-}$, and $P_2S_6^{4-}$. On the other hand, in the spectrum of 70LPS-gcg, which was crystallized once and vitrified again, crystal components of $Li_7P_3S_{11}$, which have a narrow line width, slightly appear, and the area ratio of the three units is found to change. Thus, solid-state NMR elucidates the difference of in chemical structure even in the same glassy state.

$Li_7P_3S_{11}$ crystal consists of two units: PS_4^{3-} unit and $P_2S_7^{4-}$ unit. Since the number of P atoms are two coming from PS_4^{3-} unit, and four coming from $P_2S_7^{4-}$ unit, the area ratio of ^{31}P signal is 1:2. With this as constraint conditions, when peak deconvolution was performed for 70LPS-gc, it was found to have glass components coming from PS_4^{3-}, $P_2S_7^{4-}$ units with a thicker line width and a Gaussian-type spectral shape, other than $Li_7P_3S_{11}$ crystal.

On the other hand, 70LPS-gcgc clearly has a larger PS_4^{3-} component and exhibits a Lorentzian spectral shape with a narrow line width. This result confirms that not only the $Li_7P_3S_{11}$ crystal, but also the PS_4^{3-} single-unit crystal is formed. Despite the low degree of crystallinity, the ionic conductivity of 70LPS-gcgc is 1.7 times higher than that of 70LPS-gc, suggesting that the newly-emerged PS_4^{3-} unit forms a new ion conduction path.


JNM-ECZ600R
3.2mm HXMAS probe
MAS=20kHz
Recycle delay=60s

Reference

K. Uchida, T. Ohkubo, F. Utsuno, K. Yazawa, ACS Appl. Mater. Interfaces. 2021, 13(31), 37071-37081