



Li₆PS₅Cl の溶解再析出による P の化学状態解析

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1. 背景と研究目的

All-solid-state batteries based on inorganic solid electrolytes are an attractive proposal to achieve the demands for safe, efficient, and high energy storage. Among inorganic solid electrolytes, sulfide solid electrolytes have high ionic conductivity and favorable mechanical properties (low Young's modulus, small-scale plasticity).^[1] Sulfide electrolytes can be prepared by solution process and the understanding of the reaction mechanism for their formation^[2] and effect of the solvents have taken tremendous attention. Here, we have studied the effect of ethanol solvent for the preparation of the sulfide solid electrolytes.

2. 実験内容

Argyrodite-type sulfide solid electrolyte Li₆PS₅Cl by dissolution-precipitation process was used. The material was firstly prepared by mechanical milling using stoichiometric LiCl, P₂S₅ and Li₂S precursors. Then, the solid electrolyte was dissolved in ethanol. The solvent was removed at 180 ° C under vacuum. The results were also compared with a commercial source of Li₆PS₅Cl. The solid electrolytes were prepared in a closed vessel to prevent undesired reactions and subjected to soft X-ray absorption spectroscopy (XAS) analyses to identify changes of P K-edge. X-ray photoelectron spectroscopy (XPS) measurements were also carried out.

3. 結果および考察

The structure of argyrodite-type sulfide solid electrolytes such as Li₆PS₅Cl is formed by PS₄³⁻ (ortho-thiophosphate) units. Therefore, the change in the P environment is investigated to clarify the effect of the solvent during the solid electrolyte synthesis by solution process. Fig.1 shows the P K-edge spectra of Li₆PS₅Cl pristine and after the dissolution-precipitation process with ethanol. XAS measurements of Li₃PS₄ and Li₃PO₄ were also included as references. The spectra consist of one dominant feature centered at 2148 eV, corresponding to an electron transition of a P 1s core level. The results suggest that no significant structural changes are occurring in the P environment after the dissolution-precipitation process. This also includes the absence of other interaction such as phosphorous-oxygen or decomposition of PS₄ units.

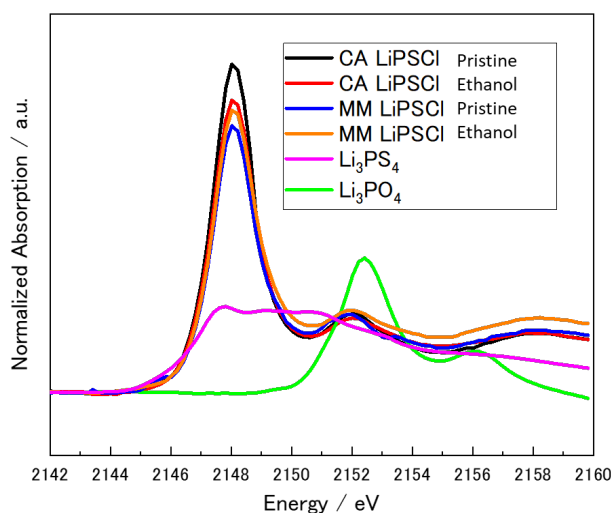


Figure 1. Phosphorus K-edge XANES spectra of sulfide electrolyte. CA: commercial, MM: mechanical milling.

4. 参考文献

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2. Nature Reviews Chemistry 2019, 3 (3), 189-198.