

Deterioration Mechanisms during Exposure to Humidity-Controlled Air of Argyrodite Solid Electrolytes for All-solid-state Batteries

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All-solid-state lithium-ion batteries exhibit even higher energy densities owing to their flame retardancy and high thermal stability. Sulfide-based solid electrolytes (SEs) have recently attracted attention due to their high ionic conductivity comparable to that of an organic electrolytic solution [1]. However, their low moisture stability is a common disadvantage. Air exposure causes a significant decrease in their ionic conductivity, together with a toxic H₂S gas generation. This is a major barrier to all-solid-state cells fabrication process cost and its application to electric vehicles. Clarifying their deterioration mechanism during air exposure is necessary to develop sulfide-based SEs with high moisture durability.

As a promising SE for sulfide-based all-solid-state batteries, we focused on the argyrodite. Argyrodite-type crystals Li₆PS₅X (X = Cl, Br or I) have high ionic conductivities of 10⁻²–10⁻³ S cm⁻¹ at room temperature [2, 3]. In particular, Li₆PS₅Cl is reported to have a wide electrochemical window of up to 7.0 V vs. Li/Li⁺ [3]. Furthermore, the all-solid-state cells using Li₆PS₅Cl and positive electrode materials such as Li₂S and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ exhibit high electrochemical performance [4, 5]. Thus, Li₆PS₅Cl is a promising candidate SE for all-solid-state sulfide-based batteries. However, the moisture stability and structural changes it undergoes when exposed to humidified air are still unknown.

In this study, we conducted transmission electron microscope (TEM) observations in investigating the microstructure and morphology of argyrodite Li_{7-a}PS_{6-a}Cl_a (a≈1, D₅₀ = 3.5 μm, Mitsui Mining & Smelting, Japan) to understand its deterioration mechanism during air exposure. Figure 1 shows the electron diffraction pattern and its intensity profile after exposure to moisture at -20°C d.p. for 24 h. Diffraction peaks of Li₂CO₃ and LiCl are detected. These reaction products indicate that Li_{7-a}PS_{6-a}Cl_a reacts with CO₂ and H₂O in the air [6]. Figure 2 shows the corresponding hollow-cone dark-field (HCDF) images. HCDF image (a) and (b) were taken using the Debye-Scherrer rings of Li₂CO₃ and LiCl, respectively. Debye-Scherrer rings, which were used to capture the HCDF images, are indicated by the yellow highlighted areas in the ED patterns. Crystallite size is approximately 20–50 nm, as denoted by the bright contrast. Each reaction product is randomly distributed and deterioration seems to progress from the particle surface. In the presentation, the main factor of the decreased ionic conductivity and the deterioration process were discussed based on the reaction products caused by air exposure [7].

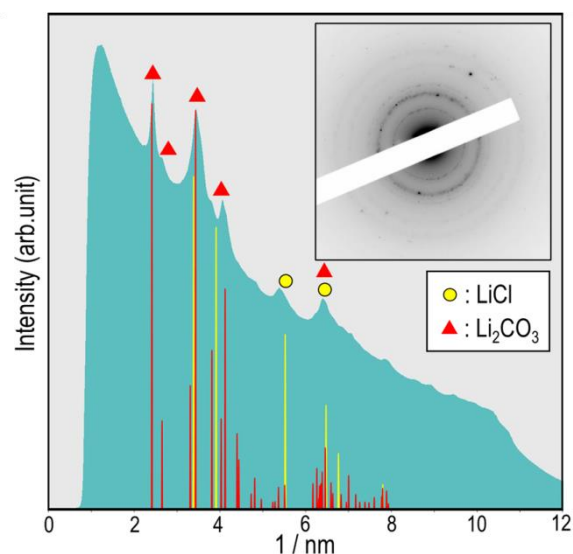


Figure 1. Electron diffraction pattern and its intensity profile for $\text{Li}_{7-a}\text{PS}_{6-a}\text{Cl}_a$ after exposure to moisture of -20°C d.p. for 24 h.

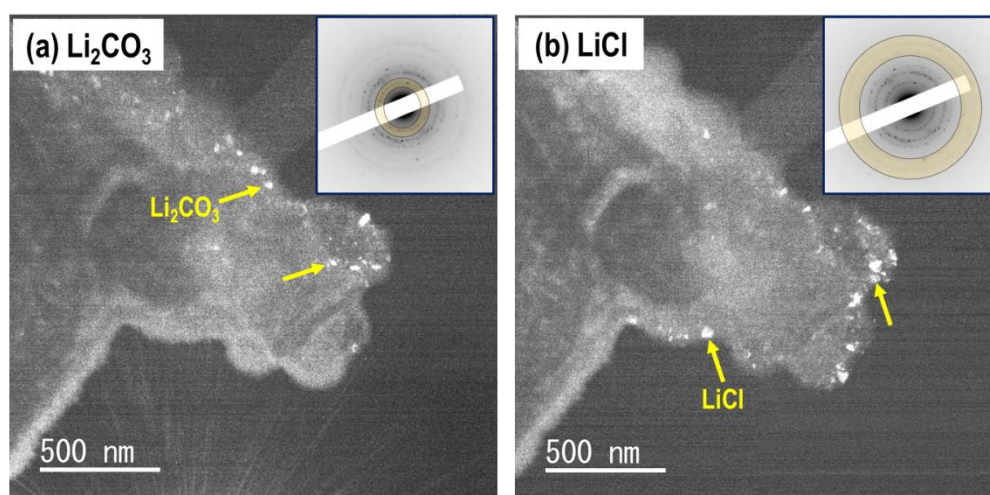


Figure 2. The HCDF images visualizing the size and spatial distribution of Li_2CO_3 , and LiCl nanocrystallites. The images (a) and (b) were taken using the Debye-Scherrer rings of Li_2CO_3 and LiCl , respectively.

References:

- [1] Y. Kato et al., *Nat. Energy* **1** (2016), 16030. doi: 10.1038/nenergy.2016.30
- [2] M. A. Kraft et al., *J. Am. Chem. Soc.* **139**(31) (2017), 10909–10918. doi: 10.1021/jacs.7b06327
- [3] S. Boulineau et al., *Solid State Ionics* **221** (2012), 1–5. doi: 10.1016/j.ssi.2012.06.008
- [4] F. Han et al., *Nano Lett.* **16** (2016), 4521–4527. doi: 10.1021/acs.nanolett.6b01754
- [5] J. Zhang et al., *J. Power Sources* **391** (2018), 73–79. doi: 10.1016/j.jpowsour.2018.04.069
- [6] H. Tsukasaki et al., *J. Power Sources* **524** (2022), 231085. doi: 10.1016/j.jpowsour.2022.231085
- [7] This study is based on results obtained from the project of “Development of Fundamental Technologies for All Solid State Battery applied to Electric Vehicles” (SOLiD-EV, JPNP18003) commissioned by the New Energy and Industrial Technology Development Organization (NEDO).