# Intact sea-island nanostructures of solid-state electrolytes snapshotted with a femtosecond X-ray laser

All-solid-state batteries are promising as next-generation batteries for electric vehicles, so applications and fundamental research have been intensively active in both industry and academia in recent years. Solid electrolytes can replace the conventional liquid electrolytes, which are highly reactive and flammable; thus, solid electrolytes can improve the safety, lifetime, and energy density of batteries. Glass-ceramics, which have an amorphous phase and one or more crystalline phases, have attracted significant interest as a solid electrolyte material. In particular, sulfide glass-ceramics have achieved ionic conductivity at room temperature equivalent to or higher than that of liquid electrolytes [1]. Knowledge of the relationship between the structural information of sulfide glass-ceramics and its battery performances will accelerate further improvement of solid electrolytes towards widely practical use. So far, various methods such as Raman spectroscopy, nuclear magnetic resonance, transmission electron microscopy (TEM), and molecular dynamics simulation have provided new insights into the structure of sulfide glass-ceramics. Among them, high-resolution TEM is a powerful tool that enables direct observation of the sea-island (amorphous-crystal) structure of sulfide glass-ceramics with nanometer spatial resolution and *in situ* measurement [2]. However, imaging intact nanostructure is still challenging because the crystal grains become amorphous during the observation owing to electron beam damage.

In the current study [3], we visualized the structure of an intact sulfide glass-ceramic electrolyte particle using pulsed coherent X-ray solution scattering (PCXSS). Additionally, we suggested an image processing method that makes use of morphological operations to obtain crystal images and the volume ratio of the amorphous to crystalline phases from the two-dimensional projection image produced via PCXSS (Fig. 1). PCXSS is a coherent diffractive imaging technique based on the X-ray free-electron laser (XFEL) and micro-liquid enclosure array (MLEA). Since XFEL pulses are extremely short (in the femtosecond range), it is possible to collect diffraction data from samples before radiation damage sets in. MLEA integrates many small solution wells into a single device and makes it possible to hold specimens in a vacuum environment with control over parameters such as temperature and solvent.

PCXSS measurements of $(Li_2S)_{70}$–$(P_2S_5)_{30}$ glass-ceramic particles were carried out at SACLA **BL2** EH3. The incident XFELs with a photon energy of 4 keV were focused to ~1 μm on the sample using total reflection mirrors. Immediately prior to the PCXSS measurement, the particles dispersed in a heptane solvent were enclosed in the MLEA (Fig. 2) using a semiautomated assembly system. Heptane solvent prevented the deliquescence of sulfide glass-ceramics and enhanced the slight image contrast between the amorphous and crystalline phases, as previously described [3]. Figure 3(a) shows a single-shot X-ray laser diffraction pattern from a glass-ceramic particle. The diffraction pattern reached the edge of the detector with a good signal-to-noise ratio, though the presence of the solvent generally reduces diffracted intensities from the sample. The maximum spatial frequency was 0.105 $nm^{-1}$. Figure 3(b) is a projection image reconstructed by applying the phasing method to the diffraction pattern (Fig. 3(a)). The spatial resolution was 14.5 nm, as evaluated by the phase retrieval transfer function. The particle size was approximately 300 nm, and there were many bright spots all throughout the

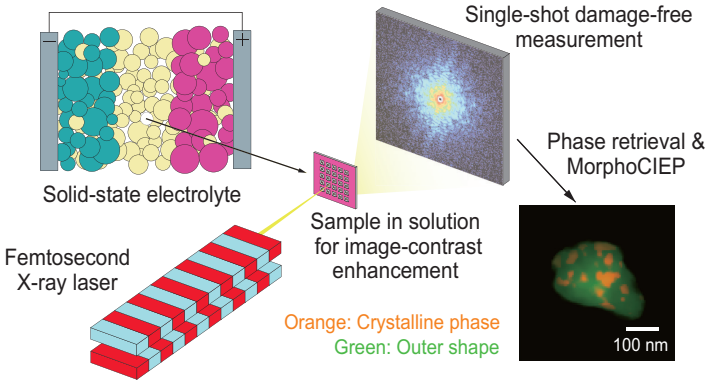


Fig. 1. Schematic of a femtosecond X-ray laser and cutting-edge image-processing technique that reveal intact sea-island nanostructures of fragile solid-state electrolytes for batteries. [3]

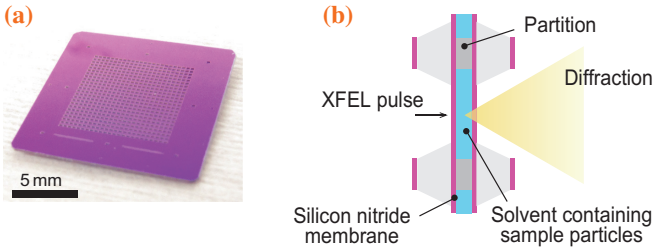


Fig. 2. **(a)** Photograph of an MLEA. The MLEA comprises 576 micro-liquid enclosures. **(b)** Schematic of the cross-section of an MLEA chip. The micro-liquid enclosures are separated from each other by epoxy grid partitions. [3]

particle. Because the outer shape of the particle is smooth, these bright spots can be attributed to crystal grains with higher electron densities rather than to the roughness of the particle surfaces.

We applied a newly developed image processing technique, morphological crystal-image-extraction processing (MorphoCIEP), to the reconstructed image in Fig. 3(b) to quantitatively extract the outer shape and crystal images. Figure 3(c) shows the superposition of the crystal (orange) and outer shape (green) images. The extracted crystal image clarified the sea-island nanostructures. MorphoCIEP consists of several steps, including high-pass filtering (HPF), rotational morphological processing (RMF) [4], and interpolation processing. HPF and RMF act complementarily in the reciprocal and real spaces to effectively emphasize crystal grains. Parameters in each image processing step can be optimized by repeatedly performing the process while feeding back the output results. The sizes of the crystal grains were approximately 10–50 nm, which is consistent with observations of the TEM images. There were 23 crystal grains in total, and they covered the entire particle, from the edge to the center. Furthermore, the volume ratio of amorphous to crystalline phases in the particles was determined to be approximately 2.5:1 using the intensity values of the extracted images and known electron densities of amorphous and crystalline phases of $(Li_2S)_{70}$–$(P_2S_5)_{30}$. The proportion and distribution of crystalline grains in the particles are related to the lithium-ion conductivity, which is essential to battery performance.

The quantitative morphological information obtained via PCXSS with MorphoCIEP will guide the optimization of various properties of solid electrolytes, including thermal stability, moisture resistance, potential window, interface resistance, and ionic conductivity. In future work, we aim to perform *in situ* temperature-controlled PCXSS measurements to observe the dynamics of structural changes during the annealing process in the synthesis of sulfide solid-state electrolytes. The studied sulfide solid-state electrolyte is a kind of metastable material. With the progress of materials informatics [5], metastable materials have been found to be innovative materials with unprecedented functions. However, as the name implies, the low thermodynamic stability of metastable materials makes it difficult to fully analyze their structures by conventional measurement methods. PCXSS with MorphoCIEP has the potential to contribute to the development of reliable, safer, and higher-performance batteries and advanced metastable materials for realizing a sustainable society.

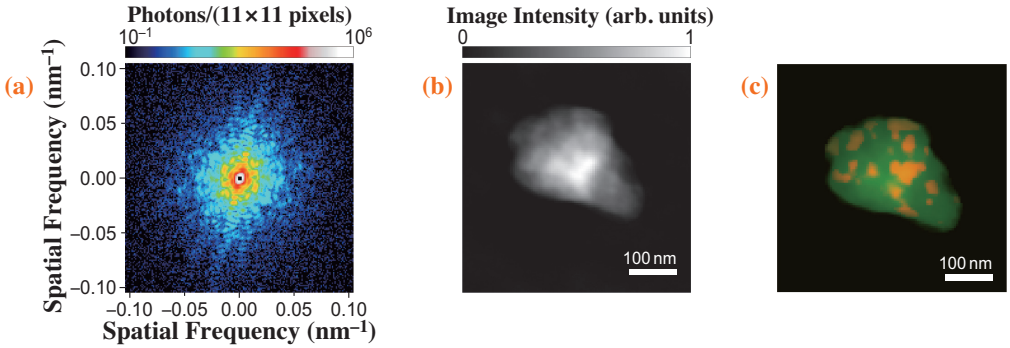


Fig. 3. **(a)** Measured diffraction pattern from a glass-ceramic particle. **(b)** Reconstructed image obtained via phase retrieval. **(c)** Superposition of crystal (orange) and outer-shape (green) images after applying MorphoCIEP to the reconstructed image in Fig. 3(b). [3]

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**References**

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