

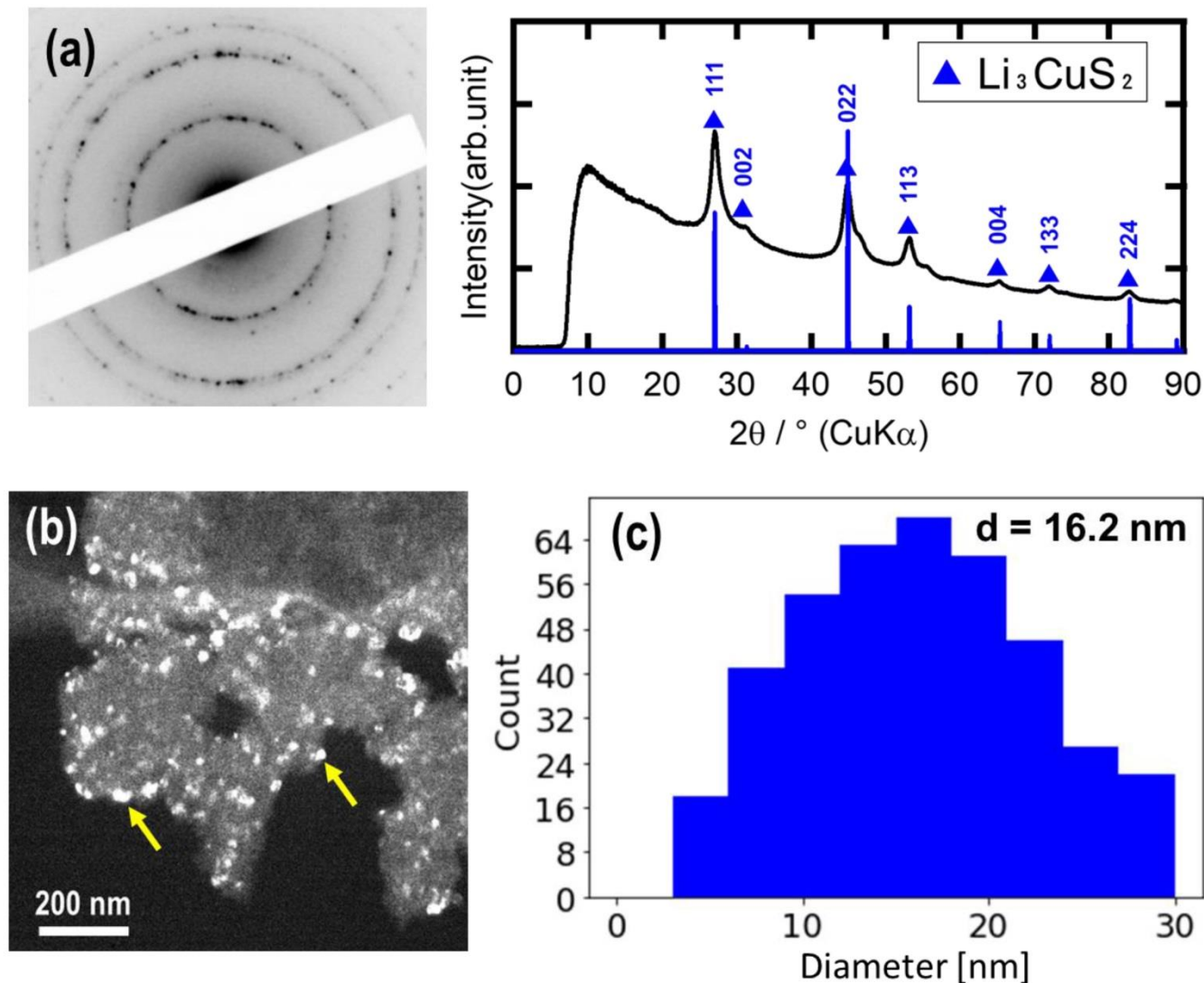
## Microstructure and Charge-discharge Properties of a $\text{Li}_3\text{CuS}_2$ active material for All-Solid-State Batteries

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Owing to excellent charge-discharge characteristics and high energy density, lithium-ion batteries are widely used in energy storage for electronic devices. However, there is a serious safety risk because a flammable organic electrolyte is commonly used. To resolve safety concerns, all-solid-state batteries with incombustible inorganic solid electrolytes have recently attracted attention because of their high safety and reliability [1, 2]. The feature of all-solid-state batteries is that since a lot of active materials can be introduced into the electrode layer, further increase in energy density can be expected. Hence, for their practical applications, it is important to develop electrode active materials with high capacity. Among many electrode active materials,  $\text{Li}_2\text{S}$  is a promising candidate for the positive electrode material owing to high theoretical capacity (1167 mAh g<sup>-1</sup>). However, because  $\text{Li}_2\text{S}$  itself is an insulator, it is necessary to construct an electronic and ionic conduction path. Kawasaki et al. have recently synthesized a  $\text{Li}_3\text{CuS}_2$  positive-electrode active material by the partial substitution of  $\text{Cu}^+$  with the  $\text{Li}^+$  in the antifluorite-type  $\text{Li}_2\text{S}$  [3]. Activation of  $\text{Li}_2\text{S}$  by Cu substitution can achieve the electronic and ionic conduction.  $\text{Li}_3\text{CuS}_2$  exhibits a high theoretical capacity (~540 mAh g<sup>-1</sup>). In addition, they demonstrated that the sulfide-based all-solid-state cell using the composite electrode comprising of  $\text{Li}_3\text{CuS}_2$  and  $\text{Li}_3\text{PS}_4$  (LPS) glass exhibited high charge-discharge cycle performance and operated without a conductive additive. It is thus important to clarify the charge-discharge mechanism of  $\text{Li}_3\text{CuS}_2$ . In this study, the microstructure and morphology of the  $\text{Li}_3\text{CuS}_2$ -LPS positive electrode composites were investigated mainly by a transmission electron microscope (TEM). Fig. 1 shows the ex-situ TEM observation results of the pristine  $\text{Li}_3\text{CuS}_2$ -LPS composite before charge and discharge. Debye-Scherrer rings were clearly observed in the electron diffraction pattern. Based on the analysis of the corresponding intensity profile (Fig. 1(a)), each diffraction peak is consistent with the simulated XRD pattern of the antifluorite-type  $\text{Li}_3\text{CuS}_2$ . To examine the size and spatial distribution of crystallites, the hollow-corn dark-field (HCDF) imaging technique was utilized. The HCDF image can visualize crystallites as a bright contrast, as indicated by the arrows in Fig. 1(b). Fig. 1(c) shows the crystallite size distribution obtained from several HCDF images. Each bright contrast region was recognized as a crystallite by supervised machine learning and then counted. Based on the crystallite size distribution, the average particle diameter ( $d$ ) of pristine  $\text{Li}_3\text{CuS}_2$  was approximately 16.2 nm. In the presentation, microstructural changes after charge-discharge cycles and charge-discharge mechanism of  $\text{Li}_3\text{CuS}_2$  will be discussed.

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**Figure 1.** Ex-situ TEM observation results of the pristine  $\text{Li}_3\text{CuS}_2$ -LPS composite before charge and discharge. (a) The electron diffraction pattern and the corresponding intensity profile. (b) HCDF image. (c)  $\text{Li}_3\text{CuS}_2$  crystallite size distribution.

#### References

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