APPLICATION NOTE

B-T-009-R1-en

Evaluation of BET Surface Area and Pore Size Distribution (Denseness) of Sulfide-based Solid Electrolytes in All-Solid-State Batteries under Non-Ambient Conditions using AIRGUARD measurement system

Introduction

In recent years, all-solid-state batteries have attracted attention for their high-power density and safety. Improving ionic conductivity requires solid electrolytes (oxide-based and sulfide-based) with small particle sizes (high specific surface area) and high denseness (non-porosity, defect-free). However, exposure to the atmosphere can cause carbonate precipitation and hydrogen sulfide generation, so it is essential to evaluate the specific surface area and denseness of these battery materials under non-ambient conditions.

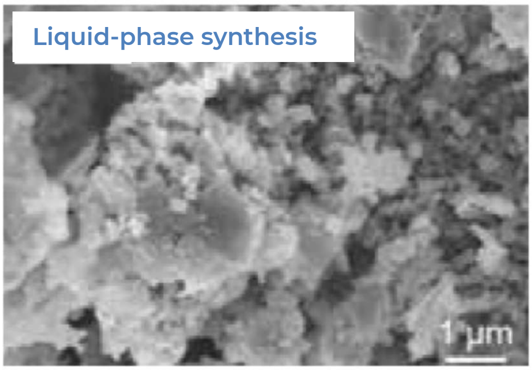

Fig. 1 SEM Images of Li_6PS_5Cl Synthesized by Liquid-Phase and Solid-Phase Methods

Materials & Methods

SEM images of Li_6PS_5Cl solid electrolyte synthesized by liquid-phase and ball-milling solid-phase methods are shown in Fig. 1. The liquid-phase sample consists of aggregated

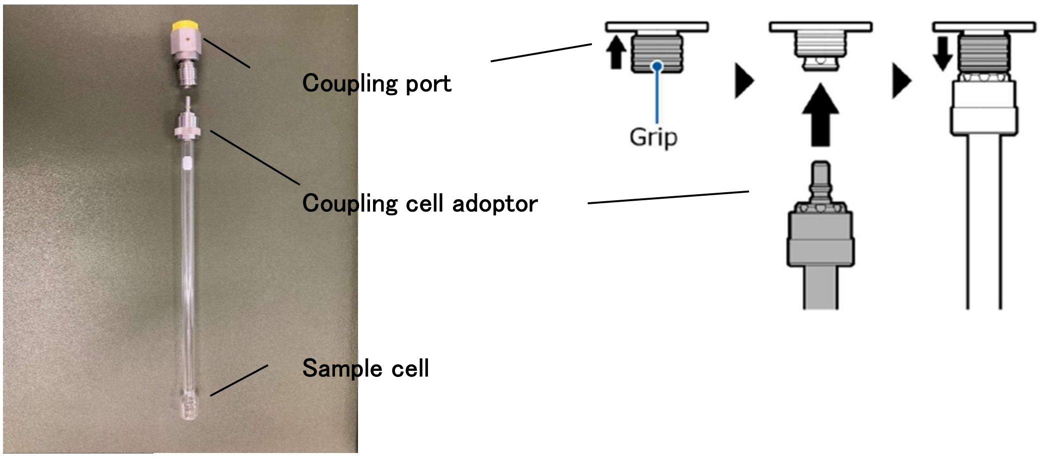

Fig. 2 Adsorption Measurement under Non-Ambient Conditions: AIRGUARD measurement system

particles of several tens of nanometers to sub-micron sized particles, while the solid-phase sample is larger with micron-sized particles. About 0.5g of each sample was weighed in a sample tube inside an argon atmosphere glove box. Using the AIRGUARD measurement system (coupling port and adapter shown in Fig. 2), the samples were pretreated under vacuum at 120°C for 6 h with BELPREP VACⅡ, and N_2 (77.4K) adsorption isotherms were obtained with BELSORP MINI X without atmospheric exposure.

Results & Discussion

The nitrogen gas adsorption isotherms (Fig. 3) of lithium-sulfur solid electrolytes synthesized by liquid-phase and solid-phase methods were type IV and type II, respectively. The BET specific surface areas were 20.6 m²/g and 2.8 m²/g. Pore-size distribution (BJH method, adsorption branch) showed mesopores (2–50 nm) in the liquid-phase sample, but the solid-phase sample was almost non-porous. The mesopores in the liquid-phase sample are presumed to be inter-particle gaps between the nanoparticles. The solid-phase sample had micron-sized particles and was non-porous, resulting in a smaller specific surface area compared to the liquid-phase sample.

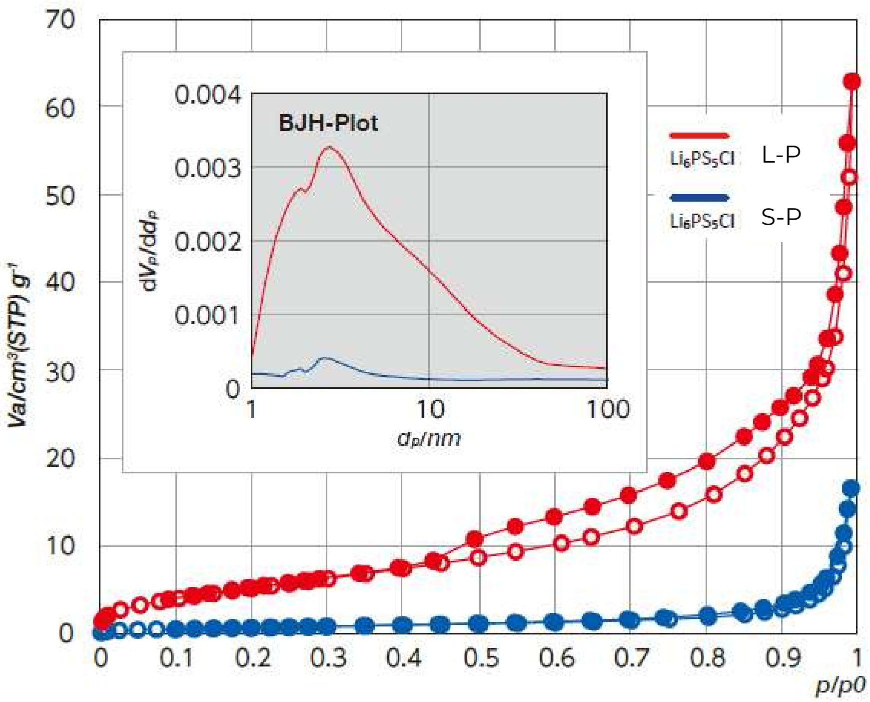

Fig. 3 N_2 (77.4K) Adsorption-Desorption Isotherms and PSD (denseness) Evaluation of Li_6PS_5Cl Synthesized by Liquid-Phase (L-P) and Solid-Phase (S-P) Methods

Summary

By using the AIRGUARD measurement system for adsorption measurements under non-ambient conditions, safe evaluation of adsorption isotherms is feasible. Combined with SEM observation and electrochemical measurements, this is an effective method for understanding the mechanism of ionic conductivity quantitatively.

Samples and SEM images provided by Professor Kiyoharu TADANAGA, Faculty of Engineering, Hokkaido University

(References)

M. Yamamoto et al. ACS Appl. Mater. Interfaces, 13 [32] 38613–38622 (2021)
K. Suzuki et l. Journal of the Ceramic Society of Japan 131 [10] 717-722 (2023)

【Measurement instrument】

BELSORP MINI X
Pore Size Distribution Analyzer: BELSORP MINI X :: Microtrac

AIRGUARD measureement system
new-airguard-measurement-system.pdf