Exploration of Ternary Thin-Film Lithium Solid Electrolyte Composites Using the Digital Laboratory for Enhanced Lithium-Ion Conductivity

Kazunori Nishio[1,2] Akira Aiba[2,3] Naoto Iihata[2] Shigeru Kobayashi[2], Ryo Nakayama[2], Tomohito Sudare[2], Ryota Shimizu[2,4], Taro Hitosugi[1,2]
[1]*Institute of Science Tokyo, Nagatsuta, Midori, Kanagawa 226-8503 Japan*
[2] *The University of Tokyo, Hongo, Bunkyo, Tokyo 113-0033, Japan*
[3] *Rigaku. Co, Matsubara, Akishima, Tokyo 196-8666, Japan*
[4] *Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan*

Correspondence to: Kazunori Nishio nishio.k.ag@m.titech.ac.jp, nishio.k.foca@m.isct.ac.jp

1. Introduction

Toward high-rate charge and discharge operation of all-solid-state Li batteries, intensive research efforts have focused on the development of novel solid electrolytes. In this context, composites composed of different solid electrolytes have attracted increasing attention as candidates for high Li-ion conductors, and numerous studies on binary mixtures have been reported. In contrast, reports on ternary or higher-order mixtures remain extremely limited, mainly due to the vast exploration space arising from combinations of mixing ratios and synthesis conditions.

Recently, for the ternary Li_3PO_4–Li_2SO_4–Li_3BO_3 system in powder bulk samples, machine-learning-assisted prediction of optimal mixing ratios and synthesis conditions has been proposed to improve exploration efficiency [1–3]. However, manual experiments have inherent limitations in identifying optimal conditions. In this study, we therefore initiated a quantitative exploration of high Li-ion conductors in Li_3PO_4–Li_2SO_4–Li_3BO_3 composites (Fig. 1a) using thin-film samples (Fig. 1b), employing the digital laboratory (dLab) system [4], which integrates machine learning and robotics for automated and autonomous materials exploration (Fig. 1c).

2. The dLab system

The dLab system fabricates thin-film samples using RF magnetron sputtering and integrates a variety of measurement and analysis instruments as physically interconnected modules, enabling multidimensional property acquisition. The measurement results are exported in a unified data format (MaiML [5]) and stored in the cloud. These cloud-based data are then analyzed and fed back into machine learning algorithms, enabling autonomous exploration by robotic systems.

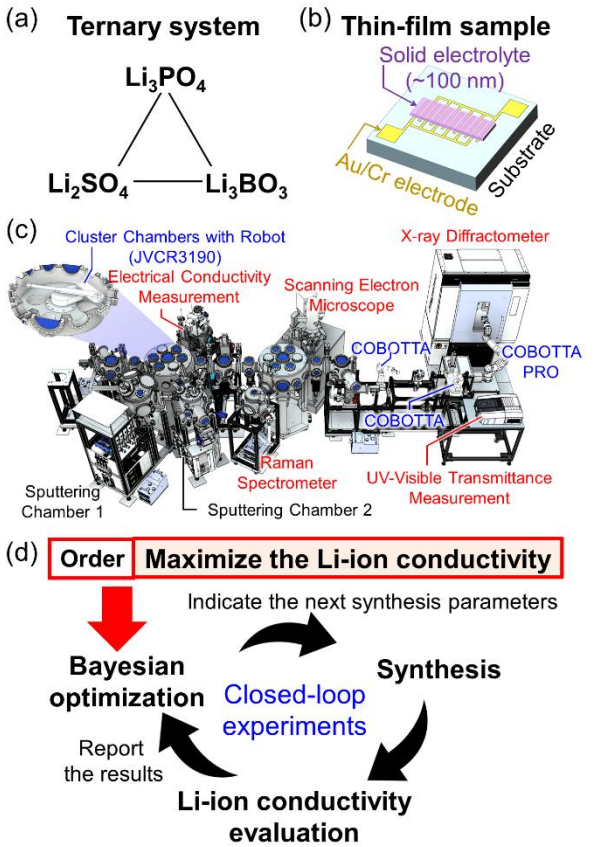

Fig. 1: (a) Li_3PO_4–Li_2SO_4–Li_3BO_3 ternary composite. (b) Schematic illustration of a thin-film sample. (c) Schematic illustration of the dLab system. (d) Closed-loop experimental workflow.

3. Experiments

Li_3PO_4–Li_2SO_4–Li_3BO_3 thin films were deposited by RF magnetron sputtering onto quartz substrates (10 × 10 mm^2, 0.5 mm thickness) patterned with interdigitated 100 nm-thick Au /5 nm-thick Cr electrodes. Sputtering was performed at room temperature in an Ar/O_2 gas mixture (20/0.5 sccm) at a total pressure of 0.5 Pa. The RF power applied to the Li_3PO_4 target was fixed at 80 W, while those for the Li_2SO_4 and Li_3BO_3 targets were independently varied from 0 to 100 W. Post-deposition annealing was subsequently carried out for 1 h under the same

process gas conditions, with the annealing temperature (T_{PA}) varied between 150 and 450°C.

The deposited films were then transferred to an electrical characterization module, where Li-ion conductivity (σ_{Li}) was evaluated by electrochemical impedance spectroscopy. Impedance measurements were conducted at approximately 30°C using an amplitude voltage of 500 mV over a frequency range of 100 mHz–300 kHz.

Closed-loop experiments based on Bayesian optimization were performed to maximize σ_{Li} as the objective function. Gaussian process regression was implemented using the Python package GPy. Three synthesis parameters—the RF powers for Li_2SO_4 and Li_3BO_3, and T_{PA}—were selected as explanatory variables. These parameters were linearly discretized into 51 grids, yielding a search space of 132,651 possible synthesis conditions. A radial basis function kernel with an added white noise term was employed [6], with the variance and initial length scale both set to 1.0. The length scale was sequentially optimized in each experimental cycle by maximizing the logarithmic marginal likelihood using a quasi-Newton method. Expected improvement was adopted as the acquisition function, and its hyperparameter ξ was set to 0.01 to bias the optimization toward exploitation [7].

4. Results and Discussion

Figure 2 shows the measured σ_{Li} obtained from a total of 80 samples. First, when T_{PA} was set to the high-temperature region (approximately 450°C), σ_{Li} exhibited extremely low values on the order of 10^{-8}–10^{-7} S cm^{-1}. This low conductivity was not essentially enhanced even when the RF powers applied to the Li_2SO_4 and Li_3BO_3 targets were varied.

When T_{PA} was reduced to an intermediate temperature range of approximately 300–360°C, the σ_{Li} increased overall to the order of 10^{-6}–10^{-5} S cm^{-1}. However, in this temperature range, the measured values showed relatively large variations (up to approximately two orders of magnitude), and the influence of the RF power conditions became pronounced. In particular, depending on the combination of RF powers for Li_2SO_4 and Li_3BO_3, locally high σ_{Li} was obtained (σ_{Li} = 3.0 × 10^{-5} S cm^{-1} at T_{PA} = 300°C, RF(Li_2SO_4) = 78 W, and RF(Li_3BO_3) = 100 W), whereas other samples still exhibited low conductivity (σ_{Li} = 4.5 × 10^{-7} S cm^{-1} at T_{PA} = 360°C, RF(Li_2SO_4) = 24 W, and RF(Li_3BO_3) = 24W).

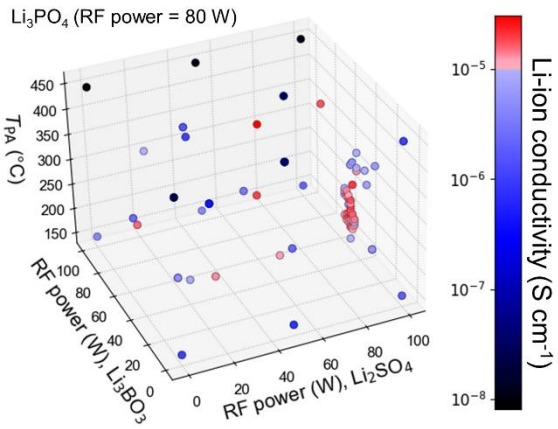

Fig. 2 Li-ion conductivity plotted as a function of the RF powers applied to Li_2SO_4 and Li_3BO_3 targets and the post-deposition annealing temperature (T_{PA}).

Furthermore, when T_{PA} was set to the low-to-intermediate temperature range of approximately 180–240°C, the σ_{Li} reached the order of 10^{-5} S cm^{-1} and exhibited relatively stable high values. In this region, variations in σ_{Li} were suppressed within one order of magnitude even when the RF powers for Li_2SO_4 and Li_3BO_3 were changed. Moreover, a region exhibiting high σ_{Li} was clearly identified around RF powers of approximately 100 W for Li_2SO_4 and 70 W for Li_3BO_3. These results demonstrate that, among the 132,651 possible synthesis conditions in the search space, high σ_{Li} was successfully achieved through 80 automated and autonomous experiments. The obtained conductivity value of 10^{-5} S cm^{-1} is 10^4 times higher than that reported for bulk powder samples (~10^{-9} S cm^{-1} [2]). Additional analyses and detailed discussions will be presented.

References

[1] M. Sumita *et al.*, Bull. Chem. Soc. Jpn. (2019) 92, 1100-1106.
[2] K. Homma *et al.*, J. Phys. Chem. C (2020) 124, 12865-12870.
[3] K. Homma *et al.*, ChemRxiv (2023) DOI: 10.26434/chemrxiv-2023-1hwvm
[4] K. Nishio, T. Hitosugi *et al.*, Digit. Discov. (2025) 4, 1734-1742.
[5] https://www.maiml.org/index_en.html
[6] S. Kobayashi, T. Hitosugi *et al.*, ACS Materials Lett. (2023) 5, 2711-2717.
[7] H. Xu, R. Nakayama, T. Hitosugi *et al.*, STAM Methods, (2023) 3, 2210251.