

Lithium diffusion coefficient in amorphous lithium phosphate thin films measured by secondary ion mass spectroscopy with isotope exchange methods



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ABSTRACT

Lithium diffusion coefficients in amorphous lithium phosphate (a-Li₃PO₄) thin films were determined by secondary ion mass spectroscopy (SIMS), using ⁷Li and ⁶Li stable isotopes. The diffusion couples were prepared by an ion-exchange method using liquid electrolyte and a mask method based on thin-film deposition. The tracer diffusion coefficient, D_{Li}^* , was evaluated by analyzing the isotope profiles obtained by SIMS in the temperature range of 25–160 °C. The diffusion coefficient of a-Li₃PO₄ was 6.0×10^{-13} cm²/s at 25 °C, while the activation energy was 0.58 eV, as measured for the samples prepared by using the ion-exchange method. The conductivity diffusion coefficient, D_{σ} , was calculated from the thin film ionic conductivity, which was determined by impedance spectroscopy. The correlation factor, H_R , was 0.55 ± 0.20 in the measured temperature range, which indicated the cooperative motion of lithium ions in lithium phosphate glasses.

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1. Introduction

The determination of the diffusion coefficient of lithium ions in solids is critical for understanding the ionic transport mechanism in solid-state lithium batteries. However, owing to the absence of suitable radioactive isotopes, only a few experimental studies have been reported on the lithium self-diffusion coefficient in battery materials [1–5]. Here, we present a new method to study the lithium diffusion coefficient in a thin film of a lithium ion conductor. Amorphous lithium phosphate (a-Li₃PO₄) is widely used in thin-film batteries as a solid electrolyte with wide electrochemical window [6,7] and negligible interface resistance [8,9]. Thin-film solid-state batteries have shown excellent cycle stability and high operating voltages [6,8].

The radioactive isotope of lithium, ⁸Li, has a very short half-life of 0.84 s. Nevertheless, measurements of ⁸Li tracer diffusion coefficient (D_{Li}^*) were performed in β-LiGa [10] and amorphous Li₃₋₄V_{0.6}Si_{0.4}O₄ thin films [11,12] by using ⁸Li beam generated by a radioactive ion accelerator facility. On the other hand, the stable isotopes, i.e., ⁶Li and ⁷Li, can also be used for evaluating D_{Li}^* . Takai et al. measured the D_{Li}^* value in Li₄Ti₅O₁₂, Li_{2+2x}Zn_{1-x}GeO₄, La_{2/3-x}Li_{3x}TiO₃, and LiMn₂O₄ by neutron radiography [3,13–15]. However, this method requires large-scale facilities as a neutron source. Secondary ion mass spectroscopy

(SIMS) is capable of measuring the accurate isotope ratio of lithium (⁶Li and ⁷Li) as well as distinguishing the isotopes.

Lithium diffusion measurements using SIMS analysis were early reported by Coles and Long for single crystal LiF in 1974 [1]. Okumura et al. reported the chemical diffusion coefficient (\bar{D}_{Li}) in Li_xMn₂O₄ thin films by using SIMS depth measurements [16]. Recently, Rahn et al. reported the diffusion coefficient in single crystal LiNbO₃ [17,18]. A similar method, i.e., laser ablation inductively coupled plasma mass spectrometry, has been applied to lithium tracer diffusion measurements in LiAlSi₂O₆ [4] and Li₂O-SiO₂ glasses [5]. SIMS analysis was also utilized to measure the diffusion of lithium in a thin film of a Li-W-O coating layer by Hayashi et al. [19].

In the present study, D_{Li}^* was determined in a thin-film solid electrolyte by adopting ion-exchange and SIMS techniques. We prepared the diffusion couples by using two different kinds of processes, namely, ion-exchange and mask methods. The combination of the two techniques and SIMS measurements was applied to a-Li₃PO₄ thin films to determine D_{Li}^* .

2. Experimental

Polycrystalline lithium phosphate (Li₃PO₄) with ⁶Li isotope was synthesized by solid-state reaction. Lithium-6 carbonate (⁶Li₂CO₃, 95% ⁶Li, 5% ⁷Li, Cambridge Isotope Laboratories) and NH₄H₂PO₄ (Wako Pure Chemical) were mixed and calcined at 700 °C for 6 h. The sample was

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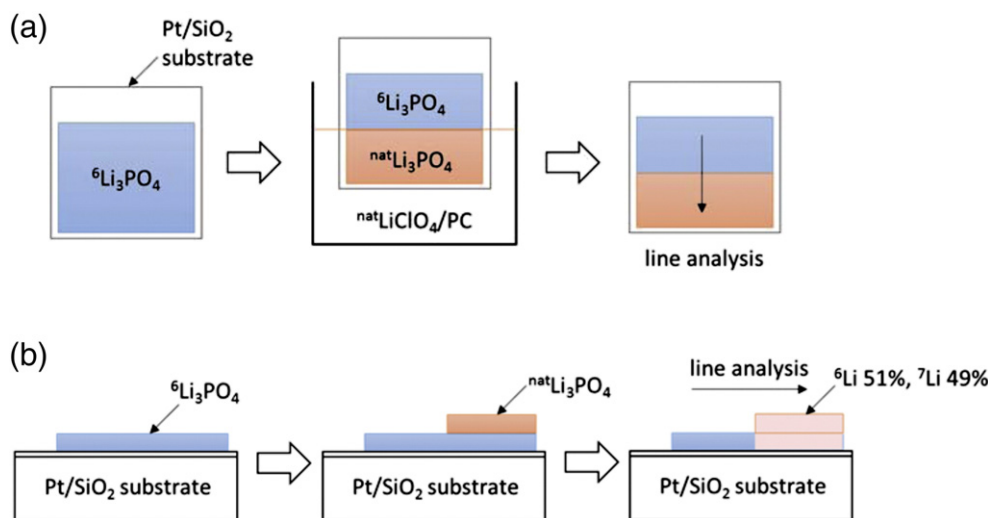


Fig. 1. Schematic diagram of sample preparation methods: (a) ion-exchange method using ${}^{\text{nat}}\text{LiClO}_4/\text{PC}$ electrolyte and (b) mask method. The surface concentration of ${}^6\text{Li}$ and ${}^7\text{Li}$ was measured by secondary ion mass spectroscopy line analysis.

crushed in an agate mortar, pressed under the uniaxial pressure of 178 MPa, and sintered at 750 °C for 12 h. The ${}^6\text{Li}_3\text{PO}_4$ target was 23.7 mm in diameter and 4.4 mm in thickness, and had a density of 1.92 g/cm³. The relative density was 81% of the theoretical density of ${}^6\text{Li}_3\text{PO}_4$ (2.37 g/cm³). X-ray diffraction (XRD) analysis was conducted to confirm the crystal structure of $\gamma\text{-Li}_3\text{PO}_4$ (PDF#01-074-0358).

Thin films of $\alpha\text{-}{}^6\text{Li}_3\text{PO}_4$ were prepared by pulsed laser deposition (PLD) [6,8,20]. The PLD system consisted of a main vacuum chamber (PLAD-221, AOV Co., Ltd.) and an ArF excimer laser (COMPexPro 205, Coherent). The vacuum chamber was evacuated to 1×10^{-4} Pa; then, high-purity oxygen was introduced, and the pressure was maintained at 0.2 Pa. The ArF excimer laser ($\lambda = 193$ nm) was focused onto the surface of the ${}^6\text{Li}_3\text{PO}_4$ target with pulse energy of 150 mJ, pulse frequency of 10 Hz, and laser fluence of 0.85 J/cm². Thin films of $\alpha\text{-Li}_3\text{PO}_4$ were grown on Pt (200 nm) coated SiO₂ glass substrates at room temperature. The deposition rate was 500 nm/h. The thicknesses of the thin films, measured by a surface profilometer, were controlled to be ~450 nm. Morphology of the thin films was observed by a field emission scanning electron microscope (FE-SEM, SU6600, Hitachi). The operating voltage was 15.0 kV. For cross-section view, the substrate was cut and the fracture surface was observed. Surface roughness of the film was measured by a laser microscope (VK-9710, Keyence) and the surface profilometer (SE-3500, Kosaka Lab.).

Two different types of diffusion couples were prepared by using two different techniques, as shown in Fig. 1. The first method (Fig. 1(a)) is called “ion-exchange method”. The $\alpha\text{-}{}^6\text{Li}_3\text{PO}_4$ thin film was immersed in a solution of 1 mol/L lithium perchlorate (${}^{\text{nat}}\text{LiClO}_4$) in propylene carbonate (PC), which has a natural isotope composition (92.4% ${}^7\text{Li}$, 7.6% ${}^6\text{Li}$). When the sample was immersed in the solution for 10 h at room temperature, ${}^6\text{Li}$ in the film contacting the solution was completely exchanged with ${}^{\text{nat}}\text{Li}$. A glass beaker cell sealed with grease (Demnum grease L-65, Daikin Industries, Ltd.) was used for ion exchange. The beaker cell was airtight to avoid evaporation of the solvent. After ion exchange, the sample was washed with dimethyl carbonate, and dried in an Ar-filled glove box. Then, the sample was cut into several pieces. Each of the samples was annealed at different temperatures and times. The isotope profiles of ${}^6\text{Li}$ and ${}^7\text{Li}$ were measured by SIMS, and the D_{Li}^* values were obtained by fitting the isotope profiles with the diffusion equation. Fig. 1(b) shows the second procedure, named “mask method”, where an $\alpha\text{-}{}^{\text{nat}}\text{Li}_3\text{PO}_4$ thin film was deposited on a section of the $\alpha\text{-}{}^6\text{Li}_3\text{PO}_4$ film by using a metal mask. The thicknesses of the ${}^6\text{Li}$ and the ${}^{\text{nat}}\text{Li}$ films were ~400 nm. Initially, these films contain 95% and 7.6% of ${}^6\text{Li}$, respectively. After sufficient time had passed, the average isotope composition, 51% of ${}^6\text{Li}$ and 49% of ${}^7\text{Li}$, was obtained

owing to mutual diffusion. Due to variation of the film thickness, the experimental results show $51 \pm 5\%$ of ${}^6\text{Li}$. Then, the samples were annealed at different temperatures for the SIMS measurements.

The analysis of the diffusion profiles was performed by using the double-focusing magnetic sector SIMS (IMS-7f, CAMECA) available at Tohoku University. The line profile analysis was conducted by using a Cs^+ primary ion beam operating at 15 keV and 1 nA. The spot size of Cs^+ ion beam was 1 μm . The minimum distance between two points was set to 13 μm for line analysis. Mapping was measured in a range of $200 \times 200 \mu\text{m}^2$ with 2 μm spatial resolution. As the ${}^6\text{Li}$ and ${}^7\text{Li}$ isotopes have the same chemical properties, ionization and detection efficiencies remain nearly constant. The quantitative isotope ratios were directly calculated from the counting rates of the ${}^6\text{Li}$ and ${}^7\text{Li}$ isotopes.

The ionic conductivity of thin films was measured by impedance spectroscopy. The $\alpha\text{-}{}^6\text{Li}_3\text{PO}_4$ films were deposited on interdigitated array Pt electrodes (ALS Co., Ltd.). The intervals between Pt electrodes were 2 μm . The length was 2.4 mm, and the number of repetitions

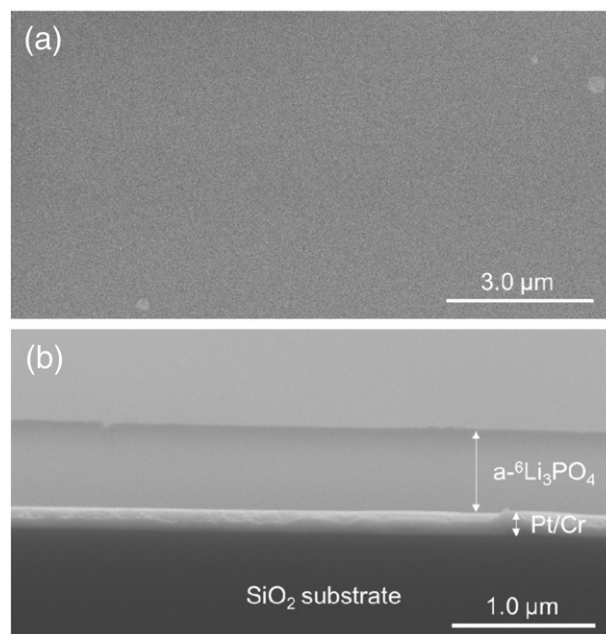


Fig. 2. Morphology of an $\alpha\text{-}{}^6\text{Li}_3\text{PO}_4$ thin film observed by FE-SEM; (a) surface and (b) cross-section. The thin film was deposited on a Pt/Cr/SiO₂ substrate.

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