Combinatorial Synthesis and Ionic Conductivity of Amorphous Oxynitrides in a Pseudo-ternary $\text{Li}_3\text{PO}_4\text{-Li}_4\text{SiO}_4\text{-LiAlO}_2$ System

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ABSTRACT

A combinatorial synthesis system consisting of co-sputtering multiple radio frequency (RF) cathodes was developed to investigate the presence of new amorphous solid electrolytes in a pseudo-ternary $\text{Li}_3\text{PO}_4\text{-Li}_4\text{SiO}_4\text{-LiAlO}_2$ system. Oxynitride solid-electrolyte films were synthesized under an N_2 atmosphere by reactive RF sputtering with cathodes made of different materials, such as Li_3PO_4 , Li_4SiO_4 , and LiAlO_2 installed at different positions in the chamber. The formation of amorphous films with no grains and a continuous atomic distribution was confirmed using scanning electron microscopy and energy-dispersive X-ray spectroscopy. In a single synthesis, we fabricated an oxynitride solid-electrolyte film, in which the composition range of the components was approximately one-eighth that in the corresponding pseudo-ternary system. The highest Li-ion conductivity of $3.1 \times 10^{-6} \text{ S cm}^{-1}$ was obtained for the LiPSiAlON film with a composition ratio of $\text{LiPON} : \text{LiSiON} : \text{LiAlON} = 48.5 : 33.9 : 17.6$. The different bonding states of O and N in the LiPSiAlON film doped with P, Si, and Al were examined using X-ray photoemission spectroscopy. The ionic conductivity was improved by the mixed anion effect. The combinatorial synthesis enables the efficient optimization of the chemical composition and facilitates the development of highly conductive amorphous solid electrolytes.

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Keywords : Thin Film, Solid Electrolyte, Combinatorial Synthesis, Lithium Batteries

1. Introduction

All-solid-state thin-film secondary Li batteries (TFBs) are viable for use as auxiliary power sources in small devices, such as wireless sensors and smart devices. TFBs, which are mainly fabricated by physical vapor deposition, consist of a cathode, solid electrolyte, metal anode, and current collectors arranged in a layer.^{1,2} Generally, a solid electrolyte layer is deposited on the cathode layer at room temperature to suppress undesirable chemical reactions that generate an ionically resistive interphase.³ Amorphous solid-electrolyte layers have a uniform morphology with no grain boundaries, which suppresses the short circuit between the cathode and anode layers. Due to this advantage, amorphous materials have been used as solid electrolytes in this study. Amorphous Li phosphorus oxynitride (LiPON) has been widely used for the fabrication of solid electrolyte layers owing to its relatively high Li ionic conductivity ($\sim 10^{-6} \text{ S/cm}$ at 25°C) and superior electrochemical stability,⁴ compared to other amorphous materials, such as Li_3PO_4 , Li_2SiO_3 , Li_4SiO_4 , and Li-Si-V-O glass.^{5–7} However, the ionic conductivity of LiPON is much lower than those of crystalline solid electrolytes composed of perovskite- and garnet-type oxides,⁸ which limits the high-power

operation of TFBs. To improve the apparent ionic conductivity, it is necessary to decrease the thickness of the solid electrolyte layer and increase the electrochemical reaction area. To address this technical challenge associated with TFB fabrication, it is important to develop amorphous electrolytes with higher Li ionic conductivities. Tatsumisago et al. reported that the Li ionic conductivities of amorphous Li phosphate can be improved by adding Li silicate because of the mixed anion effect.⁹ Although the mixed anion effect has been proposed by other research groups,^{10–18} the synthetic conditions and equipment are different in each report. Therefore, it is difficult to discuss the detailed mechanism of the mixed anion effect and the corresponding optimal chemical composition in a unified manner.

Combinatorial synthesis is an efficient method for accessing material libraries. It is an experimental method for efficiently synthesizing multiple varieties of materials using the same synthetic route. The technology of combinatorial synthesis was proposed in the 1960s by Merrifield¹⁹ (solid-phase peptide synthesis). The application of this technology for the development of suitable materials begun in the 1990s.²⁰ In particular, it has led to the discovery of new active substances,²¹ which has had an impact on the pharmaceutical industry. Beal et al.²² developed a perovskite-type solid electrolyte ($\text{Li}_{3-x}\text{La}_{2/3-x}\text{TiO}_3$, $x = 0.11$) through a combinatorial evaporation synthesis method using an E-beam or a Knudsen cell.

Radio Frequency (RF) sputtering is one of the most suitable methods for synthesizing electronically insulating oxide thin films.²³ When an ionized gas with high energies of $> 10 \text{ eV}$ collides with the

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target material, the species of the target material simultaneously scatter from the surface and deposits onto the opposing substrate. This allows for a highly reproducible and fast deposition of materials with high melting points, and the chemical composition of the deposited films is relatively close to that of the target material, compared to vapor deposition and electron beam evaporation. However, there have been no reports on the combinatorial synthesis of solid electrolyte materials using RF sputtering. Vacuum film deposition via combinatorial synthesis methods using RF sputtering can be achieved through judicious equipment design and the incorporation of unique sputtering technologies. In this study, we developed a combinatorial synthesis system for the simultaneous deposition of multiple materials using RF sputtering with different targets. Oxynitride solid-electrolyte films were fabricated in pseudo-binary LiPON-LiSiON, LiSiON-LiAlON, and LiPON-LiAlON systems, and pseudo-ternary LiPON-LiSiON-LiAlON systems, and their structures and Li ionic conductivities were investigated.

2. Materials and Methods

Oxynitride solid electrolyte films were fabricated using a combinatorial reactive RF system (QAM-4ST, ULVAC), as shown in Fig. 1. The system is equipped with four sputtering cathodes and a substrate holder in the process chamber for the simultaneous deposition of materials. All the sputtering cathodes were positioned outwards relative to the center of the substrate. Each sputtering target set to the cathode was tilted at an angle of 30° to the center. The distance between the center of the target and the substrate changed from 150 to 215 mm, depending on the substrate position. When the substrate was rotated during deposition, the deposited film had a uniform thickness distribution of less than $\pm 5\%$ within the substrate with a diameter of 101.6 mm.

In contrast, an atomic distribution was observed in the film deposited with the fixed substrate. To operate the multiple RF cathodes simultaneously, it is essential to suppress the interference of the RF circuits, including the matching box between the RF cathodes, because the interference causes the application of a non-uniform power balance to each RF cathode and finally leads to a mismatch between the incident and reflected waves. The RF frequency is typically shifted by several kHz to suppress interference. However, the effective output remains unclear because the reflected wave cannot be completely suppressed. In our system, all the power supplies are connected to the phase shifter in the RF cathodes, enabling control of the phase of the output transmitted from the RF power supply. It is configured such that the power balance applied by the phase difference of each RF power supply can be controlled. Additionally, such a configuration ensures alignment of the power balance from the matching box to the sputtering target, special design of the distance, and phase adjustment. As a result, the simultaneous deposition of stable films is possible with multiple RF cathodes.

The process chamber was evacuated to a pressure of below 1×10^{-4} Pa using a turbo molecular pump and a rotary pump. The oxynitride solid electrolyte films were fabricated using different cathodes under an N_2 atmosphere. Li_3PO_4 , Li_4SiO_4 , $LiAlO_2$ pellets were used as the targets and the films were deposited on glass substrates (diameter 101.6 mm, Eagle XG Corning). Pt and Ti films of 100 and 200 nm thicknesses, respectively, were deposited as lower electrodes on the substrate surface. The solid electrolyte films were deposited on the metal electrode film at an N_2 pressure of 0.3 Pa and power output of 100 or 200 W. Two or three reagent materials were simultaneously deposited on the substrate using different RF cathodes. The positions of the targets and substrates were fixed during deposition. This introduced a gradual slope in the chemical composition and thickness of each solid-electrolyte film. After the deposition of the solid-electrolyte films, Pt upper electrode

Figure 1. Schematics of RF sputtering system for combinatorial synthesis. a) overall view, b) cross-sectional view, and c) top view.

films with diameters of 5 mm were deposited in an X-pattern onto the films.

The film thickness of the solid electrolyte films was measured using a profilometer (DEKTA-XT Bruker) and an ellipsometer (ESM-1AT ULVAC). The deposition rate of each film was calculated based on the film thickness and duration of deposition. The film surface conditions and composition distributions were measured using scanning electron microscopy (SEM, SU8220, Hitachi High-tech) and energy dispersive X-ray (EDX, Xflash5060FQ, Bruker) analysis. Structural investigations of the films were performed using Raman spectroscopy (inVia, RENISHAW) and X-ray diffraction (XRD, Smartlab, Rigaku) and X-ray photoelectron spectroscopy (XPS, VersaProbe III, ULVAC-PHI). XPS spectra were recorded for the Li 1s, P 2p, Si 2p, O 1s, and N 1s transitions. The X-ray source was Al $K\alpha$ (1486.6 eV), and

the beam diameter was 100 μm (100 W, 20 kV). The signal extraction angle, path energy, and step size were 45°, 55 eV, and 0.10 eV, respectively.

The electrochemical properties of the films were investigated via AC impedance spectroscopy between the upper and lower Pt electrodes using an electrochemical measuring instrument (IM6 Zahner). An AC voltage of 10 mV was applied in the frequency range of 0.1 Hz to 1 MHz at room temperature. The ionic conductivities were calculated using the electrode area (25 mm²), film thickness, and resistance determined using impedance spectroscopy. The film thicknesses of LiPSiON, LiSiAlON, LiPAION, and LiPSiAlON were estimated from the deposition rates of the LiPON, LiSiON, and LiAlON single films determined from the thicknesses at each position on the substrate.

3. Results and Discussion

3.1 Combinatorial synthesis of Li conductive films in pseudo-binary systems

LiPON and LiAlON single films were deposited on a fixed Pt/Ti substrate for 2 h to investigate the position dependence of the film thickness. The Li₃PO₄ and LiAlO₂ targets were set on cathodes 1 and 2, as shown in Fig. 1, and were deposited under an N₂ atmosphere at 200 and 100 W, respectively. The film thicknesses were measured at 15 positions with an interval of 6.25 mm for each sample. Figure 2 shows the position dependence of the thicknesses of the LiPON and LiAlON single films deposited on the Pt/Ti substrate. The deposited films had the largest thickness at the position nearest to the sputtering cathode. The thickness of the LiPON film at position 1 was 341 nm, which corresponded to a deposition rate of 2.84 nm min⁻¹. The film thickness gradually decreased to 46 nm at position 15 as the distance from the target increased. The thickness of the LiAlON film at position 1 was 34 nm, which gradually increased to 100 nm at position 15 as the distance from the target decreased. The deposition rate of the LiAlON film was 0.830 nm min⁻¹ at position 15, which was much lower than that of the LiPON film. The proportion of each material can be changed by changing the power of each cathode. From the thicknesses of the LiPON and LiAlON films observed at each position, we estimated the composition ratio of LiPON to LiAlON in the LiPON-LiAlON film fabricated via simultaneous deposition

Figure 2. Position dependence of thicknesses of LiPON and LiAlON single films deposited on Pt/Ti substrate for 120 min and estimated composition ratio of LiPON to LiAlON in LiPAION film fabricated by simultaneous deposition.

using multiple cathodes. The estimated composition ratio in the LiPON-LiAlON film is shown in Fig. 2. The ratios of LiPON to LiAlON were 91.0 and 31.6 % at positions 1 and 15, respectively. A gradual decrease in the ratio was observed from position 1 to 15, which indicated the formation of the LiPON-LiAlON film with a continuous atomic distribution. This result demonstrates the feasibility of combinatorial synthesis of the LiPON-LiAlON film with a continuous compositional distribution.

With the same positions of the substrate and targets, the LiPAION film was synthesized by the simultaneous deposition of the LiPON and LiAlON targets. Figure 3 shows the Raman spectra of the LiPAION films with different ratios of LiPON to LiAlON. Three major peaks were observed at approximately 800, 960, and 1020 cm⁻¹, which were attributed to P-N=P, PO₄³⁻, and P₂O_{7-x}N_xⁿ⁻, respectively. The PO₄³⁻ peak was observed at all the measurement points, which is consistent with the existence of LiPON at all the positions, as shown in Fig. 2.

Although the LiPON content decreased gradually from position 1 to 15, position 6 exhibited the lowest intensity of the PO₄³⁻ peak. This result indicates that the introduction of LiAlON alters the chemical bonding between P and O. Figure 4 depicts the SEM and EDX images of the LiPON-LiAlON film collected in the region between positions 8 and 9. The SEM image shows no significant changes in the contrast, which indicates a very smooth surface with no grain boundaries. The EDX analyses detected O, P, and Al signals, and all the elements were uniformly distributed in the film without segregation. This result indicates the formation of an amorphous LiPAION film with a continuous atomic distribution.

Figure 5 shows the room-temperature Li ionic conductivities of the LiPAION films with different compositions. The ionic conductivities were calculated from the estimated thicknesses and resistance values of the first semicircles in the Nyquist plots, shown in the insets in Fig. 5. The film compositions at each position were estimated from the deposition rates of the LiPON and LiAlON single films on the Pt/Ti substrate (Fig. 2).

Figure 3. Raman spectra of LiPAION films with different ratios of LiPON to LiAlON fabricated at different positions on Pt/Ti substrate. The measurement positions are shown in Fig. 2.

Figure 4. SEM-EDX images of the LiPON-LiAlON film between positions 8 and 9.

Figure 5. Ionic conductivity changes of the LiPON-LiAlON films depending on the film composition. The film compositions were estimated by their deposition rates at each position on the substrate. Insets depict the Nyquist plots of the films with the LiPON/LiAlON ratios of 91.0, 81.3, and 31.6 %. Ionic conductivities of end-member single films are presented for comparison.

The ionic conductivities of the LiPON and LiAlON single films ($5.0 \times 10^{-7} \text{ S cm}^{-1}$ and $1.0 \times 10^{-9} \text{ S cm}^{-1}$, respectively) were also plotted for comparison. The conductivity showed no significant change when the ratio of LiPON to LiAlON was in the range of 100 to 86.8 %. When the ratio decreased from 86.8 to 81.3 %, the ionic conductivity increased slightly to $7.3 \times 10^{-7} \text{ S cm}^{-1}$. In the Raman spectra shown in Fig. 3, the PO_4^{3-} peak had the lowest intensity with the largest peak width at the position with a LiPON content of 81.3 %. Upon reducing the LiPON content to 31.6 %, the ionic conductivity decreased to $2.4 \times 10^{-7} \text{ S cm}^{-1}$ owing to the higher

proportion of the poorly conductive LiAlON phase. Randomizing the binding state of PO_4^{3-} facilitated the Li ionic conduction in the amorphous LiPAION film. The change in the local structures around the Li ions was inferred to be a consequence of the mixed anion effect. According to a previous report,²⁴ amorphous solid electrolytes contain stable sites where the potential energy of the Li ions is low because of the surrounding atoms and their bonding states, and the Li ions are conducted via the pathways with the lowest activation energies from one stable site to another. The configurational freedom of the diffusion pathways in amorphous solid electrolytes formed by multiple ortho-oxoanions, such as MO_x^- ($\text{M} = \text{P}, \text{Si}, \text{and B}$), is significantly higher than that of those comprising a single type of ortho-oxoanions. Therefore, it is probable that diffusion occurs at lower energies in the presence of multiple ortho-oxoanions. Although certain experimental results support the feasibility of using different types of anions for improving the ionic conductivity, a guiding principle for mixing different types of anions for this purpose has not been established.

The LiPSiON and LiSiAlON films were fabricated using the same method as that used for the LiPAION film (all the films were deposited at a power of 100 W), and their ionic conductivities were investigated. Figure 6 shows the ionic conductivities of the LiPSiON and LiSiAlON films with different compositions. The chemical compositions were estimated based on the deposition rates of each target at different positions on the substrate. In the LiPON-LiSiON system, the ionic conductivity exceeded $10^{-6} \text{ S cm}^{-1}$ when the LiPON to LiSiON ratio ranged from 20.9 to 92.9 %. Lower ionic conductivities were observed for the end components, LiPON ($5.0 \times 10^{-7} \text{ S cm}^{-1}$) and LiSiON ($6.2 \times 10^{-7} \text{ S cm}^{-1}$). The results at positions 1 and 15 showed that mixing small amounts of content increased ionic conductivity. This observation is consistent with a previous report.¹⁷ In the LiSiON-LiAlON system, the composition ratio of LiSiON to LiAlON changed from 11.2 to 73.0 %. In contrast to the LiPAION and LiPSiON films, the ionic conductivities were lower than that of the LiSiON single film. According to our experimental results, the ionic conductivities of the LiPON-based solid electrolytes can be changed by randomizing the binding state of each element through the mixing of multiple anion species.

3.2 Combinatorial synthesis in a pseudo-ternary $\text{Li}_3\text{PO}_4\text{-Li}_4\text{SiO}_4\text{-LiAlO}_2$ system

To examine the effect of mixing three anionic species on the Li conductivity, we synthesized LiPSiAlON films based on a pseudo-ternary system using two different targets, LiSiON and LiPON-

Figure 6. Li ionic conductivities of (a) LiPON-LiSiON and (b) LiSiON-LiAlON films with different chemical compositions. Ionic conductivities of end-member single films are also depicted for comparison.

Figure 7. Variation of Li ionic conductivity with chemical compositions of LiAlON-LiSiON film. Ionic conductivities of end-member single films are also depicted for comparison.

Figure 8. Electrode positions and photograph of a LiPON-LiSiON-LiAlON film with different composition ratios.

system showed no significant effect of Al doping. The LiPON : LiSiON : LiAlON ratio of the LiPSiAlON film was analyzed to 49.2 : 39.3 : 11.5 from XPS peak fitting. This value is consistent with the calculated composition of 44.6 : 42.7 : 12.7 using the deposition rates of the single films synthesized with each target. Thus, the film compositions of the combinatorially synthesized films were estimated from the deposition rates in this study.

To efficiently investigate LiPSiAlON films with a wider compositional range, we fabricated a LiPSiAlON film by simultaneous sputtering under an N_2 atmosphere using three cathode targets: Li_3PO_4 , Li_4SiO_4 , and LiAlO_2 . Figure 8a shows the setting positions of the substrate and three cathode targets in the chamber and a photograph of the LiPSiAlON film. A total of 127 positions were selected to investigate the compositions and ionic conductivities of the LiPSiAlON film. According to Fig. 8b, different color distributions were observed depending on the position due to the interference of light induced by the differences in film thickness and refractive index. The composition ratios in the LiPSiAlON films were estimated from the deposition rates of the LiPON, LiSiON, and LiAlON single films. The film thicknesses and composition ratios corresponding to all the positions are listed in Table S1 (Supplementary Information). The contents of LiPON, LiSiON, and LiAlON were 28.8 to 57.5 %, 14.7 to 49.2 %, and 17.0 to 48.2 %, respectively. Figure 9 shows the XRD patterns of the LiPON : LiSiON : LiAlON films with different LiPON : LiSiON : LiAlON ratios of 31.4 : 49.2 : 19.4, 57.2 : 17.5 : 25.3, and 43.4 : 15.0 : 41.6. All XRD patterns showed the 111 diffraction peaks of the Pt

Figure 9. XRD patterns of LiPSiAlON films in ternary LiPON-LiSiON-LiAlON system at position 106, 114, and 118.

Figure 10. Ionic conductivities of LiPSiAlON films in ternary LiPON-LiSiON-LiAlON system.

substrate at around 40° and very broad peaks between 15° and 30° . The broad peaks confirmed that the amorphous LiPON : LiSiON : LiAlON films were formed regardless of the film composition.

Figure 10 illustrates the dependence of the ionic conductivity of the LiPSiAlON film on the film position. The ionic conductivity gradually changes with the position depending on the film composition. Compared with the films obtained by combinatorial synthesis using two materials, the measurable range changed from linear to areal, and the maximum value ($3.1 \times 10^{-6} \text{ S cm}^{-1}$) of the ionic conductivity corresponded to position 111 where the LiPON : LiSiON : LiAlON ratio was 53.1 : 28.7 : 18.2.

Figure 11 shows the X-ray photoelectron spectra of the LiPSiAlON film collected at position 111, where the film showed the highest ionic conductivity. The binding energies of the Li 1s and P 2p orbitals were 55.3 and 133.1 eV, respectively, which were not significantly different from the corresponding values for the LiPON film. In contrast, the Si 2p peak shifted from 102.5 eV for the LiSiON film to 101.7 eV for the LiPSiAlON film. The binding energy of Si was decreased upon doping with P and Al. The O 1s peak of the LiPSiAlON film was observed at 531.4 eV, which was slightly different from those observed for LiPON (531.2 eV) and LiSiON (531.8 eV). Furthermore, two N 1s peaks were observed at 398.2 and 397.2 eV, corresponding to LiSiON and LiPON, respectively. These results suggest that the O and N atoms in the LiPSiAlON film had intermediate binding conditions to those in the

Figure 11. Li 1s, P 2p, Si 2p, Al 2p, O 1s, and N 1s X-ray photoelectron spectra of the LiPSiAlON film. The spectra obtained for the LiPON and LiSiON films are also shown for comparison.

LiPON and LiSiON films. It is postulated that the intermediate conditions affect the diffusion pathways of the Li ions. From the quantitative analyses of the XPS peaks, the chemical formulas for the LiPON, LiSiON, and LiPSiAlON species were estimated to be $\text{Li}_{1.90}\text{PO}_{3.01}\text{N}_{0.61}$, $\text{Li}_{2.12}\text{SiO}_{4.34}\text{N}_{0.13}$, and $\text{Li}_{1.88}\text{P}_{0.51}\text{Si}_{0.42}\text{Al}_{0.07}\text{O}_{3.46}\text{N}_{0.36}$, respectively. All the materials showed a decrease in Li composition compared to the target. Notably, LiPSiAlON, with the highest ionic conductivity, had the lowest Li content. The ionic conductivity is generally proportional to the product of the carrier concentration and mobility. Therefore, the high ionic conductivity observed in films with low Li contents should be associated with the improved mobility induced by the mixed anion effect. However, there are no clear design guidelines for optimizing the mixed anion effect to achieve high Li-ion conduction. The combinatorial synthesis method is advantageous for efficiently synthesizing films and identifying trends in the mixed anion effect in glassy solid electrolytes. The ionic conductivity of the LiPSiAlON film was further improved by increasing the carrier concentration of Li.

4. Conclusion

An efficient material search method was successfully developed using combinatorial synthesis in conjunction with the co-sputtering method to develop amorphous oxynitride solid electrolytes. In the pseudo-ternary $\text{Li}_3\text{PO}_4\text{-Li}_4\text{SiO}_4\text{-LiAlO}_2$ system, a high ionic conductivity of $3.1 \times 10^{-6} \text{ S cm}^{-1}$ was obtained for the LiPSiAlON film with a LiPON : LiSiON : LiAlON ratio of 48.5 : 33.9 : 17.6. The high ionic conductivity was associated with the randomization of the binding state of each element by mixing multiple cation and anion species. The proposed system is advantageous for the efficient development of glassy solid electrolytes with high ionic conductivity which can potentially be applied in TFBs.

Acknowledgments

This work was partially supported by the Grant-in-Aid for Scientific Research on Innovative Areas [19H05785].

CRediT Authorship Contribution Statement

Shunsuke Sasaki: Conceptualization (Lead), Data curation (Lead), Formal analysis (Lead), Investigation (Lead), Methodology (Lead), Resources (Lead), Software (Equal), Supervision (Equal), Validation (Lead), Visualization (Lead), Writing – original draft (Lead)

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Data Availability Statement

The data that support the findings of this study are openly available under the terms of the designated Creative Commons License in J-STAGE Data listed in D1 of References.

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

Funding

Japan Society for the Promotion of Science: 19H05785

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