

Material Search of Oxide-Based Lithium Ionic Conductors for Next-Generation All-solid-state Lithium Battery

Kota Suzuki^{1, 2)} Ryoji Kanno¹⁾

1) Institute of Innovation Research, Tokyo Institute of Technology, Yokohama, Japan

E-mail: suzuki.k.bf@m.titech.ac.jp, kanno@echem.titech.ac.jp

2) School of Materials and Chemical Technology, Tokyo Institute of Technology, Yokohama, Japan

ABSTRACT: New material search approaches along the unique two guidelines were conducted to discover the oxide-based lithium ionic conductors for next-generation all-solid-state lithium batteries. A machine learning model was developed, which predicts the ionic conductivity of materials from chemical composition information alone. This model indicated the high ionic conductivity in the $\text{Li}_2\text{O-SiO}_2\text{-MoO}_3$ system. Systematic synthesis and evaluation revealed the new LISICON phases with the composition of $\text{Li}_{4-2x}\text{Mo}_x\text{Si}_{1-x}\text{O}_4$. The material search in the ternary LISICON system (Li-M-M'-M''-O) indicated that the compositional complexity could enhance the ionic conducting properties. In addition to the classical concept (e.g., bottleneck size, polarizability, carrier density), the complexity could be a good indicator for ionic conductor exploration. Finally, in the $\text{Li}_4\text{GeO}_4\text{-Li}_3\text{VO}_4\text{-Li}_5\text{GaO}_4$ system, the highest ionic conductivity ($1.5 \times 10^{-4} \text{ S cm}^{-1}$ at 298 K) of the LISICON family was discovered.

KEY WORDS: solid electrolyte, lithium conducting oxides, material search, machine learning, all-solid-state lithium battery

1. INTRODUCTION

All-solid-state lithium batteries (ASBs) with highly safe characteristics are expected to replace conventional lithium-ion batteries, especially for electric vehicle, because high stability is one of the most critical requirements for EV use. Recently, sulfide based ASBs are supposed to be the closest to social implementation for their high discharge performance [1, 2]. This favorable performance as EV batteries is attributable to the high ionic conductivity ($> 10^{-2} \text{ S cm}^{-1}$) of sulfide-based solid electrolytes. Nevertheless, hygroscopic properties of the sulfides exist as issues to be solved for the higher reliability of the battery system.

Oxide-based solid electrolytes are expected to be applied into the next generation ASBs while their ionic conductivities are still lower than sulfides ($\sim 10^{-3} \text{ S cm}^{-1}$). However, the development history for sulfide ASBs clearly indicates that high-ionic conductivities are indispensable for large-scale battery fabrication [3]. Since the material search for lithium-conducting oxides has a more extended history than sulfides, most crystalline systems were near the completion of exploration; therefore, there is little room for further investigation in the known crystal systems. To find a new research field, we have examined the feasibility of the machine learning method [4] to discover new attractive candidates and introduced the concept of compositional complexity [5, 6] in

the known crystalline phase. Eventually, we demonstrated that both directions could be the promising approach for the oxide materials search.

This study conducted further material explorations for lithium conducting oxide along two guidelines: (i) conductivity prediction by machine learning [7] and (ii) lattice size regulation in the ternary LISICON system [8]. As the guideline (i), a machine learning model was developed that predicts the ionic conductivity of a material from its chemical composition alone. As shown in Fig. 1, the developed model predicted a relatively high ionic conductivity ($> 10^{-4} \text{ S cm}^{-1}$) for pseudo-ternary phases of $\text{Li}_2\text{O-SiO}_2\text{-MoO}_3$. Along the chemical formula of $\text{Li}_{4-2x}\text{Mo}_x\text{Si}_{1-x}\text{O}_4$ (i.e., the $\text{Li}_4\text{SiO}_4\text{-Li}_2\text{MoO}_4$ tie line), the relationship between the obtained phases and ionic conductivity was investigated.

The effectiveness of this multi-component strategy (guideline (ii)) was verified by systematic experiments using $\text{Li}_4\text{GeO}_4\text{-Li}_3\text{PO}_4\text{-Li}_3\text{VO}_4$ [5] and $\text{Li}_4\text{GeO}_4\text{-Li}_4\text{SiO}_4\text{-Li}_3\text{VO}_4$ [6] systems; an additional cation (V and Si, respectively) was doped into the known binary systems (Li-Ge-P-O and Li-Ge-V-O, respectively). The additional cation could lead to improvements in ionic conductivity. A relationship between the average ionic radius and ion-conducting properties in a two-component LISICON system (Li-M-M'-O) has been established [9], while the counterpart of ternary LISICON systems (Li-M-M'-M''-O) is still unclear.

Therefore, solid solutions in the quasi-ternary $\text{Li}_4\text{GeO}_4\text{-Li}_3\text{PO}_4\text{-Li}_4\text{SiO}_4$ and $\text{Li}_4\text{GeO}_4\text{-Li}_3\text{VO}_4\text{-Li}_5\text{GaO}_4$ systems were systematically investigated as smaller and larger frameworks, respectively. Finally, this research discovered some novel lithium-conducting oxides through the two guidelines. Also, the possibilities and remaining issues of the newly introduced approaches were clarified.

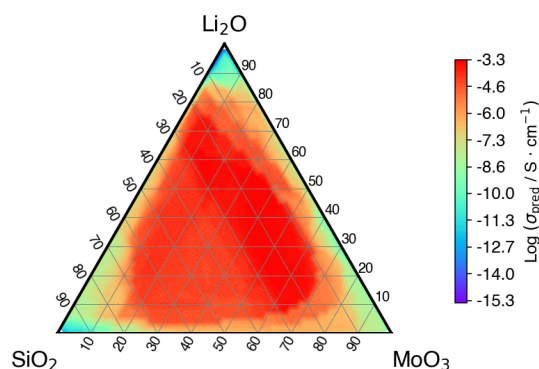


Fig.1 Predicted ionic conductivity for a $\text{Li}_2\text{O-SiO}_2\text{-MoO}_3$ pseudo-ternary system using a Random Forest model.

2. METHODOLOGY

2.1. Experimental

Synthesis and phase identification

Lithium-containing oxides were fabricated by a solid-state reaction using the mixtures of the starting materials (>99% purity). The precursors were weighed in stoichiometric ratios and pre-milled for 15 min using an agate mortar and pestle in an Ar-filled glovebox, followed by ball milling at 380–1000 rpm for 4–24 h. Ceramic pellets were obtained by pressing the powders at 20–30 MPa, followed by sintering at 973–1173 K in the air.

The crystalline phases of the samples were identified by X-ray diffraction (XRD). The XRD patterns were indexed using PDXL software. Samples were scanned over a diffraction angle (2θ) range of $15^\circ\text{--}60^\circ$ with a step width of 0.01° .

Electrochemical measurements

The prepared pellets were coated on both sides with Au paste or powder and heated in an Ar atmosphere to evaporate the residual organic solvents. The pellets were maintained at the desired temperature for 30 minutes before the experiments. Alternating current (AC) impedance measurements were conducted in the frequency range of 0.1 Hz to 3 MHz at an amplitude of 20–50 mV in the temperature range 298–373 K in an environmental test chamber.

2.2. Computational

Prediction of ionic conductivity by machine learning

The collected information on chemical compositions and ionic conductivities of 256 lithium-based solid electrolyte materials from previous reports was used as a machine-learning dataset to predict the ionic conductivity. Regression-based learning was carried out using the descriptors obtained from the chemical composition [10], where the objective variable was the ionic conductivity at room temperature (approximately 300 K).

The 'Random Forest' machine learning algorithm was selected, and the function implemented in 'scikit-learn' was used. Forty-one physical properties and intrinsic values (e.g., ionic radius [11], electronegativity [12], polarizability [13]), which can be derived from the chemical composition of each material, were used to generate the descriptors. Finally, 820 descriptors were obtained by a conversion process (i.e., the mean, variance, standard deviation, etc.) using each chemical composition. The details of the descriptors are summarized elsewhere [7].

3. RESULTS AND DISCUSSION

3.1 Material search using conductivity prediction by machine learning

Fig. 2 shows a plot of the ionic conductivities predicted by the 'Random Forest' algorithm compared to actual data. The training and test data plots are aligned on the diagonal line, indicating that the developed prediction model has relatively good accuracy. In contrast, the root mean squared errors (RMSEs) for the training and test data were $\text{RMSE}_{\text{train}} = 1.064$ and $\text{RMSE}_{\text{test}} = 1.648$, respectively. In other words, the predictive accuracy of the test data was slightly inferior to that of the training data. However, the results suggest that the region with lower accuracy corresponds to low ionic conductivity ($< 10^{-15} \text{ S cm}^{-1}$). Also, according to the importance analysis of the descriptors, the effective ion volume and polarizability are highly critical values for the machine learning process. The control of bottleneck size and lattice size, as well as the introduction of elements with high polarizability, are thought to be key general design guidelines for ionic conductors. These results imply that the developed prediction system could make meaningful predictions based on solid-state chemistry principles, especially for highly conductive compositions ($> 10^{-10} \text{ S cm}^{-1}$). Therefore, a material search was conducted in the $\text{Li}_2\text{O-SiO}_2\text{-MoO}_3$ system pseudo-ternary phase diagram (Fig. 1) since a high ionic conductivity had been predicted.

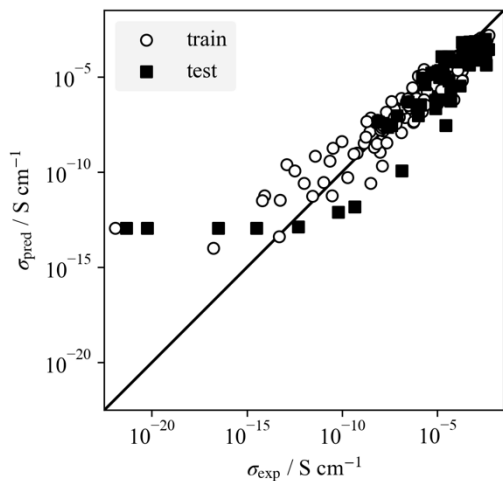


Fig. 2 Plot of experimental (σ_{exp}) vs. predicted conductivity (σ_{pred}) values in a Random Forest regression model on compositional descriptors. The unfilled circles and the filled squares represent the training and the test data, respectively.

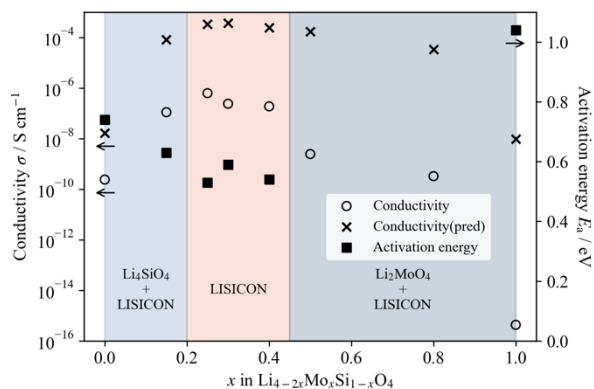


Fig. 3 Relationship between x in $\text{Li}_{4-2x}\text{Mo}_x\text{Si}_{1-x}\text{O}_4$ and ionic conductivity, activation energy, and identified phases. Unfilled circle markers, which belong to the left axis, represent the conductivity, while filled square markers, which correspond to the right axis, represent the activation energy. Cross markers also indicate predicted conductivities.

Phase identification results and ionic conductive properties of $\text{Li}_{4-2x}\text{Mo}_x\text{Si}_{1-x}\text{O}_4$ are summarized in Fig. 3. The introduction of Mo into the Li_4SiO_4 increased the extremely low ion conductivity of Li_4SiO_4 ($x = 0$, $2.4 \times 10^{-10} \text{ S cm}^{-1}$) by approximately three orders of magnitude while decreasing the activation energy for lithium-ion conduction. In addition, the Mo introduction contributed to the LISICON phase formation. The ionic conductivity was particularly high in the LISICON single-phase region and showed the highest value of the synthesized samples

($2.6 \cdot 10^{-7} \text{ S cm}^{-1}$) at $x = 0.3$. Furthermore, the conductivity decreased for compositions with a high Mo content ($x > 0.5$). As a result, the $\text{Li}_{4-2x}\text{Mo}_x\text{Si}_{1-x}\text{O}_4$ system exhibited high ionic conductivity in the region where the LISICON single phase was formed. The machine learning prediction could imply this experimentally confirmed conductivity trend since the intermediate region on the Li_4SiO_4 - Li_2MoO_4 tie line exhibit high ionic conductivity compared to the compositions around the end members. Therefore, the developed prediction model can be used as an initial guideline for material exploration within the phase diagram. However, the experimentally obtained ionic conductivity did not achieve the predicted values for overall compositions. These results suggest room for improvement in the predictive accuracy and reliability of the machine learning model developed in this study.

3.2 Lattice size regulation in the ternary LISICON system

Phase formation region of the crystalline LISICON in the quasi-ternary Li_4GeO_4 - Li_3PO_4 - Li_4SiO_4 and Li_4GeO_4 - Li_3VO_4 - Li_5GaO_4 systems were investigated. The former system showed a wide LISICON single-phase formation region (region (i) in Fig. 4), which is comparable to the reported two systems (Li_4GeO_4 - Li_3PO_4 - Li_3VO_4 [5] and Li_4GeO_4 - Li_4SiO_4 - Li_3VO_4 [6]. On the other hand, the Li_4GeO_4 - Li_3VO_4 - Li_5GaO_4 system showed only a limited solid solution range. This result indicated that the relatively large cation of Ga^{3+} is not easy to be incorporated into the LISICON crystal structure under the examined experimental conditions.

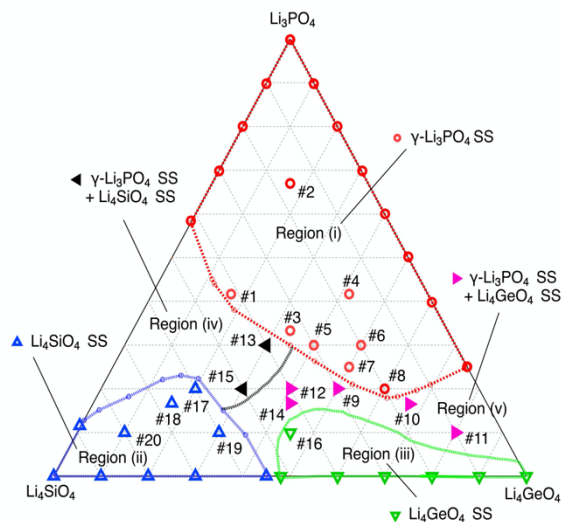


Fig. 4 Identified phases of the Li-Ge-P-Si-O system. Data represented by the sample codes (such as #1 and #2) indicate the samples identified in this study.

Fig.5 shows plots of the ionic conductivities and activation energy (E_a) values for the binary and ternary systems of LISICON-structured lithium conductors as functions of their average ionic radii. The compositions featuring components with larger ionic radii exhibit enhanced ion-conducting properties in both systems. Furthermore, comparing binary and ternary systems at the comparable average ionic radii indicates that the ternary systems have slightly higher ionic conductive properties. This trend implies that the complexity of the framework components is an additional significant factor in determining the ionic conductivity, in addition to their ionic radii.

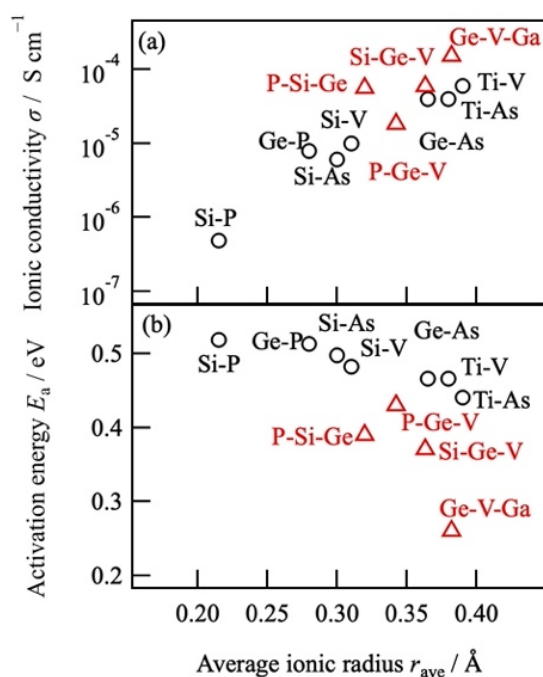


Fig. 5 Lithium ionic conductivities (a) and activation energies (b) of LISICON-type Li-M-M'-M''-O and $\text{Li}_{3.5}\text{M}_{0.5}\text{M}'_{0.5}\text{O}_4$ systems with different cationic radii at room temperature as functions of the average ionic radius.

The hypothesis is particularly evident in the E_a and average ionic radius correlation. The ternary materials exhibit remarkably lower E_a values than those of binary materials. Significantly, the Li-Ge-V-Ga-O ternary system shows an E_a value of <0.30 eV. In addition, the relatively modest doping of the aliovalent cations (4%) leads to a significant improvement in ionic conductivity (from 10^{-5} to $10^{-4} \text{ S cm}^{-1}$) with the lowest E_a . This result suggests that along with the amounts and/or ionic radii of specific elements, the number of cations incorporated into the LISICON framework may be crucial in realizing the high ion conductive properties. Therefore, introducing an additional cation (e.g., quaternary

system; Li-M-M'-M''-M'''-O) and compositional optimization may reasonably facilitate the development of solid electrolytes.

4. CONCLUSION

Novel material search approaches were conducted along with the proposed two guidelines, and some new materials were discovered. A machine learning model was developed, which predicts the ionic conductivity of materials from chemical composition information. This model figured out the conductivity trend depending on the chemical composition in the $\text{Li}_{4-2x}\text{Mo}_x\text{Si}_{1-x}\text{O}_4$ system. Although the absolute values of the prediction differed from the experimental data, further training data augmentation and trial of the various machine learning algorithms could reduce this deviation.

The material search in the ternary LISICON system (Li-M-M'-M''-O) revealed that the compositional complexity could enhance the ion-conducting properties. This concept can be a good indicator for ionic conductor exploration in addition to the classical concept (e.g., bottleneck size, polarizability, carrier density). At the same time, it indicates the value of exploring the complex compositions in crystal structures that have already been examined experimentally and theoretically. Although this research did not lead to the discovery of practical lithium superionic conducting oxides, it is necessary to continue investigating new search methods for discovering new materials.

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