

AI-Assisted Exploration of Superionic Glass-Type Li<sup>+</sup> Conductors with Aromatic Structures

Kan Hatakeyama-Sato, Toshiki Tezuka, Momoka Umeki, and Kenichi Oyaizu\*

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**ABSTRACT:** It has long remained challenging to predict the properties of complex chemical systems, such as polymer-based materials and their composites. We have constructed the largest database of lithium-conducting solid polymer electrolytes (10<sup>4</sup> entries) and employed a transfer-learned graph neural network to accurately predict their conductivity (mean absolute error of less than 1 on a logarithmic scale). The bias-free prediction by the network helped us to find superionic conductors composed of charge-transfer complexes of aromatic polymers (ionic conductivity of around 10<sup>−3</sup> S/cm at room temperature). The glassy design was contrary to the traditional concept of rubbery polymer electrolytes, but it was found to be appropriate to achieve fast, decoupled motion of ionic species from polymer chains and to enhance thermal and mechanical stability. The unbiased suggestions generated by machine learning models can help researches to discover unexpected chemical phenomena, which could also induce a paradigm shift of energy-related functional materials.

A key to discovering attractive materials by artificial intelligence (AI) lies in its potentially high predictive performance; however, it is exceptionally difficult to predict the properties of most natural, complex systems. The properties that can be predicted by AI have been commonly limited to simple ones, such as fundamental characteristics of ceramics and small molecules, because AI is trained only by simulation-based databases.<sup>1–4</sup> Development of experiment-oriented AI is highly demanded to cope with the most practical cases, including polymer-based materials, the responses of which cannot be predicted accurately by simulations due to the astronomically high number of possible interactions.<sup>5,6</sup>

Li<sup>+</sup>-conducting polymers, promising components for solid-state lithium batteries and energy-related devices,<sup>7–11</sup> are one of the most important targets for machine learning and materials science (Figure 1). The polymers offer high processability and appropriate binding properties in solid-state batteries, but insufficient conductivity and mechanical stability impedes their worldwide commercialization.<sup>7,8</sup> A striking approach is needed to break through the limitation of Li<sup>+</sup> conduction through the polymeric matrix.<sup>8</sup> Molecular dynamics simulations can estimate the Li<sup>+</sup> diffusivity quasi-quantitatively.<sup>5,12,13</sup> Still, the overall conductivity cannot be fully calculated with current computing power because of the complicated interactions, including orbital coupling and domain effects.<sup>5</sup> Furthermore, most Li<sup>+</sup> conductors, and most polymeric materials, are composed with additives such as plasticizers and inorganic materials to improve their performances, but this increased complexity would result in a huge computational cost.<sup>7,8</sup> Although there have been few informatics studies of the composites, accurate prediction is required in order to shorten the length of time-consuming experiments.<sup>1,3,14,15</sup>

In the present work, we constructed what is currently the largest machine learnable database of Li<sup>+</sup>-conducting polymers,

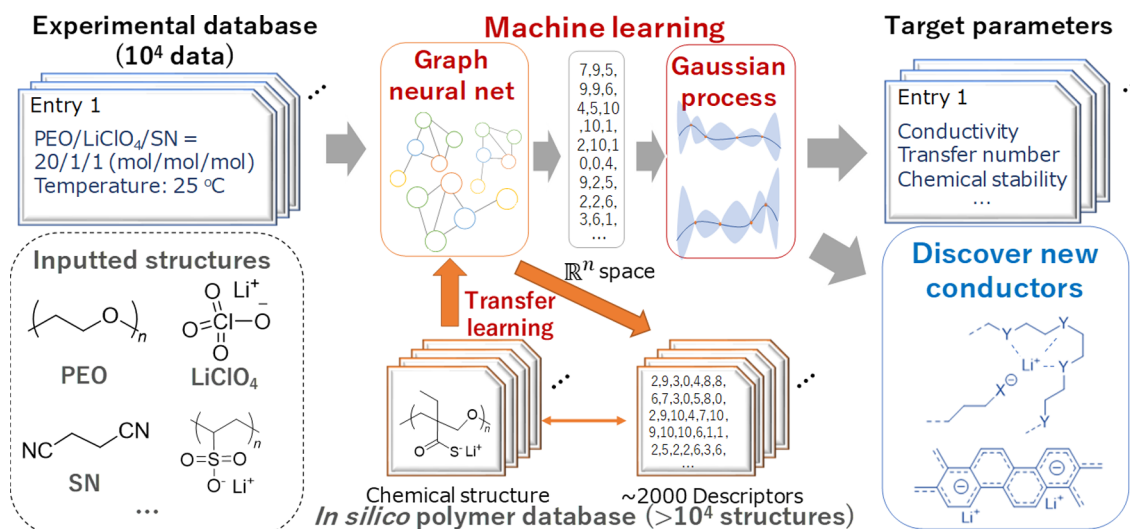
containing comprehensive information about relationships between the chemical structures and conductivity (10<sup>4</sup> entries including temperature dependence). The database covers most of the basic chemical structures reported as solid polymer electrolytes (Figures S1 and S2). Ether, phosphazene, methacrylate, siloxane, aluminate, and borate ester were typical polymer backbones. Bis(trifluoromethanesulfonyl)imide (TFSI<sup>−</sup>), tetrafluoroborate (BF<sub>4</sub><sup>−</sup>), trifluoromethanesulfonate (CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>), hexafluorophosphate (PF<sub>6</sub><sup>−</sup>), and their derivatives were the representative anions.<sup>7,8</sup> The database contains most types of conductors, including polyanions (single-ion-conducting polymers), mixtures of monomeric salts and matrix polymers, plasticized or gelled materials, and inorganic composites. Li<sup>+</sup>-conducting liquid electrolytes with various solvents and salts (about 3000 conductivity data points) were also added to the database to allow AI to recognize a wider range of chemicals and conductivity.

We trained a learning model by teaching it the relationships among the chemical structures, composition ratio, and measured temperatures as the input (X) and ionic conductivity as the output (Y). Types of primary polymer structures (e.g., normal or copolymerized/grafted) were treated as bit flags (0 or 1). On the other hand, intermediate properties, such as crystallinity and domain size, were not inputted because the parameters depend on X (Figure S3). Process and hysteresis information may affect the performance,<sup>3</sup> but sufficient information was not given in most publications. The factors were treated as uncertainty by a probabilistic model (*vide infra*).

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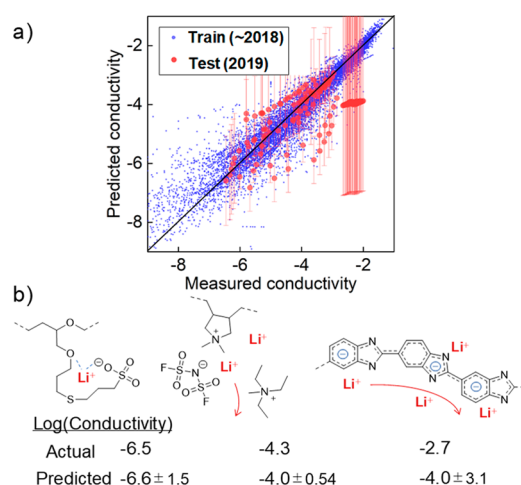




**Figure 1.** Scheme for predicting properties of the solid polymer electrolytes by AI. Conductivity was predicted in this study.

Probabilistic models, represented by a Gaussian process, are suitable for solving the uncertainty problems because the models consider the probability distribution of inputs ( $X$ ) and outputs ( $Y$ ).<sup>16</sup> Further, the models can predict values with confidence intervals: the error bars are qualitative criteria for the reliability of the prediction, which are valid even for the extrapolative cases. The key to using probabilistic models was to express the chemicals features (i.e., numeric arrays inputted to the Gaussian process) with low-dimensional vectors because of the exceptionally high calculation cost.<sup>16</sup> To extract only essential information automatically, we used a gated graph neural network.<sup>17</sup> With the randomly generated *de novo* polymer and monomeric compound database, the network was pretrained to predict their 2000 molecular descriptors (e.g., number of nitrogen atoms and polarizability, etc.) with only 32-dimensional vectors (i.e., floating-point arrays, such as (0.55, -0.12, ..., 1.23), Figures S4–S17). The pretraining processes, namely transfer learning, were necessary to recognize the important features of a variety of chemical structures.

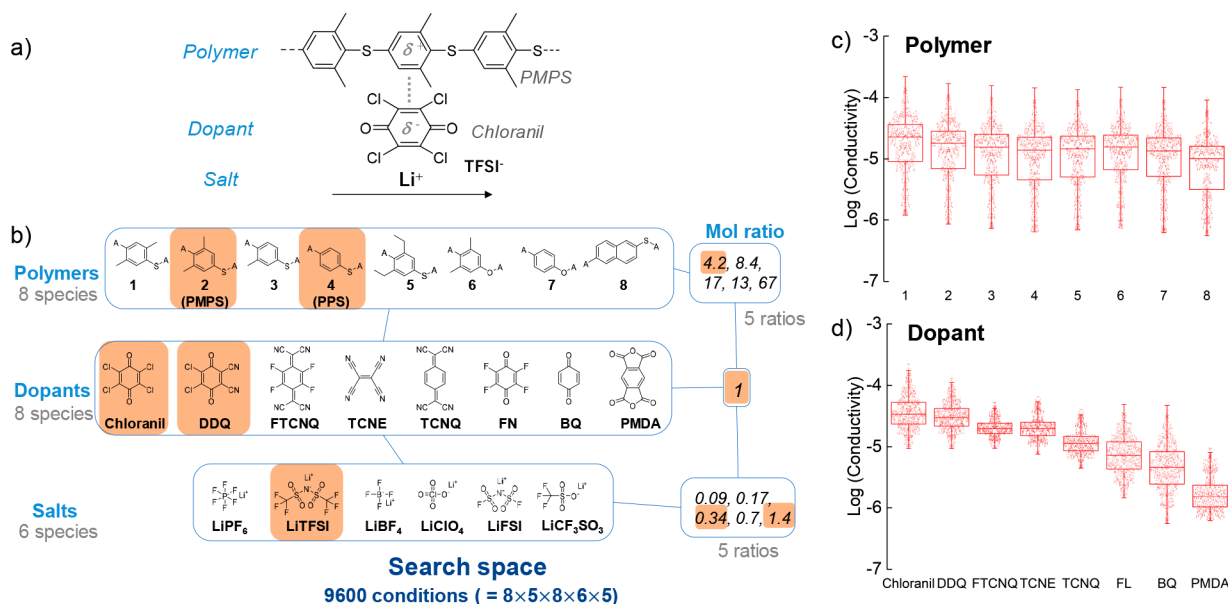
The relationship between the composite information and its conductivity was trained by a Gaussian process model (Figure 2; comparisons with other machine learning approaches are shown in Figure S8). AI was trained with conductors reported up to 2018, and then the conductivity values of representative conductors reported in early 2019 (about 150 cases, not trained by AI) were predicted. Accurate prediction was achieved for most conductors. For instance, the experimental and predicted values almost coincided for traditional-type polyethers and aliphatic polymer electrolytes plasticized with ionic liquids (Figure 2b).<sup>14,18</sup> The mean absolute error of logarithmic conductivity for all test samples was less than 1, meaning that the predicted conductivity was generally on the same the order of magnitude as the experimental results. The small prediction errors suggested that the effects of process information were not as large as previously thought.<sup>4</sup> Furthermore, 92% of the predicted plots existed within the range of  $1.96\sigma$  error bars, supporting the reliability of the probabilistic model; considering the Gaussian distribution, the score should be 95% (Figure S18). Such accurate predictions may not be achieved even by well-experienced researchers because of the wide variety of chemical structures.



**Figure 2.** Prediction of ionic conductivity. (a) Relationship between the experimentally observed and predicted conductivity (log scale, original units of S/cm). Conductors reported up to 2018 were trained, and samples from early 2019 were used for prediction. Training data contained solid-state conductors, plasticized/gelled ones, and liquids.  $R^2$  scores were 0.90 and 0.16 for training and test datasets, respectively. The test score becomes 0.37 when polybenzimidazole electrolytes (measured conductivity of around  $-2$ ) are excluded. (b) Example structures and room-temperature conductivity of recently reported polymer-based conductors.<sup>14,18,19</sup> For test data,  $1\sigma$  error bars are shown.

The large error bars for several test data (experimental conductivity of around  $10^{-2}$  S/cm) were attributed to the introduction of unconventional conductors, consisting of conjugated polybenzimidazole and ionic liquid (Figure 2).<sup>19</sup> Electrolytes are normally designed to have flexible ether chains to solvate  $\text{Li}^+$ ,<sup>7,8</sup> whereas the conjugated main chains were newly selected in the study to suppress the excessive  $\text{Li}^+$ –polymer interactions.<sup>19</sup> The unfamiliarity of chemical structures can be quantified by the length of error bars.

To explore new polymeric conductors, the trained AI was used to predict the conductivity of miscellaneous chemicals. One of the most interesting results indicated by AI was that charge-transfer complexes of polyphenylene sulfide (PPS) derivatives and aromatic oxidants<sup>20–23</sup> could facilitate transport



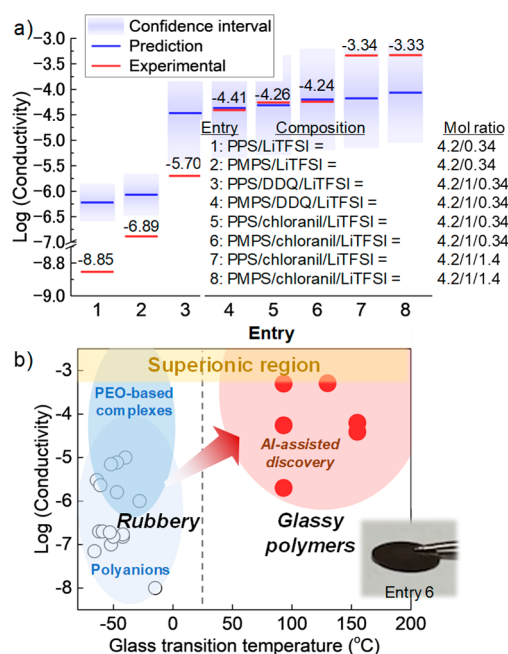
**Figure 3.** Screening of chemical structures for new electrolytes. (a) Example structure of a charge-transfer complex to transport lithium ions. (b) Search space for screening chemicals. Conditions marked in red were experimentally studied. (c, d) Predicted effects of polymers and dopants for conductivity. The concept of a charge-transfer complex was preliminarily proposed in a patent by Zimmerman et al., although the details have remained unknown (no scientific papers).<sup>23</sup>

lithium ions ( $>10^{-4}$  S/cm) (Figure 3). The prediction was impressive because PPS has been known as an insulating engineering plastic, not a conductor. Further, the concept of charge-transfer complexes has been pursued for electron (super)conductors, not for electrolytes.<sup>21,22,24</sup>

In the *in silico* database, the electrolyte composition was optimized by changing the types of polymers, dopants, salts, and their ratios (in total 9600 candidates, Figures 3 and S19). Dimethyl-substituted PPS (PMPS)<sup>25</sup> was extracted as a highly conductive yet facily processable polymer (i.e., soluble in solvents during electrolyte preparation, in contrast to PPS). Chloranil and LiTFSI were also selected as promising dopant and salt, respectively. The lengths of error bars (ca. 2) were smaller than those with the polybenzimidazole-based composite (ca. 3), suggesting that the conductor had similarities with the training dataset that were still hidden to humans (Figure 4).

Experimentally, the PMPS and PPS electrolytes exhibited a superionic conductivity around  $10^{-3}$  S/cm maximum and a potentially high  $\text{Li}^+$  transfer number ( $>0.7$ ) at room temperature (Figures 4a and S20). The presented performance was  $10^1$ – $10^6$  times higher than that for the previous polymer electrolytes with single-ion conduction (Figure 4b and Table S1).<sup>7</sup> The doped electrolytes had a wide potential window to be used in lithium-ion batteries ( $>4$  V, Figures S21 and S22).<sup>8</sup> Despite the large thickness of the prototype electrolytes (about 400  $\mu\text{m}$ ), sufficiently fast charge/discharge at a rate of 1 C was preliminarily achieved with a cathode of  $\text{LiFePO}_4$  and an anode of  $\text{Li}_2\text{TiO}_3$ , which gave rise to high-power solid-state batteries (current density of 1.5  $\text{mA}/\text{cm}^2$ ;  $x$  C corresponds to the rate of charging/discharging batteries in  $1/x$  hours, Figure S22).

Most importantly, the glassy property of the complexes (glass transition temperature of  $>150$   $^\circ\text{C}$  for PMPS) was contrary to the common strategy of using solid polymer electrolytes, because much lower transition temperatures ( $\ll 0$   $^\circ\text{C}$ ) have been pursued traditionally (Figures 4b and S23).<sup>8</sup>



**Figure 4.** Predicted and experimental conductivity of polythioether/dopant/LiTFSI composites at room temperature. (a) Conductivity and electrolyte conditions. 0.5 $\sigma$  error bars are shown. (b) Comparison of the charge-transfer complex electrolytes with the traditional polymers. Single-ion-conducting electrolytes without inorganic additives or liquids were plotted.<sup>7</sup>

The conventional electrolytes suffered from low mechanical stability, especially with heated conditions (e.g., poly(ethylene oxide) (PEO)-based electrolytes melt around 60  $^\circ\text{C}$ ), because of the flexible polymer chains, the segmental motion of which was, however, still insufficient for superionic properties (normally  $10^{-6}$ – $10^{-4}$  S/cm at room temperature).<sup>7,8</sup> Stiff plastics, such as polyacrylonitrile, were also examined preliminarily but suffered from low conductivity due to the



small diffusivity of ions ( $<10^{-6}$  S/cm, Table S1).<sup>26</sup> In contrast, the glass-type, charge-transfer complex conductors offer both high conductivity and robustness with a wide temperature range. Permittivity analyses indicated the decoupled motion of charge carriers, free from the polymer matrix, and about  $10^2$  times higher dissociation degree of salts (compared to PEO-based electrolytes,<sup>27</sup> Figure S24). The polarized structures of charge-transfer complexes<sup>24</sup> certainly played an important role in dissociating ions. On the surfaces of the complex domains, where electrostatic interactions become smaller than in bulk, the ions can move more freely, leading to higher conductivity (a more detailed comparison is shown in Table S2). The processes may have some common factors with other decoupled systems, such as polymer-in-salt electrolytes.<sup>7,28</sup> The presented electrolytes have the potential to surpass the performances of recently reported superionic inorganic electrolytes ( $10^{-2}$  S/cm),<sup>29</sup> which still suffer problems of insufficient processability and stability (i.e., often degrade under ambient conditions).<sup>8,30</sup>

Despite the unfamiliar electrolyte design, the AI-based prediction was basically consistent with the series of experiments (mean absolute error of  $<0.8$ ). As forecasted by AI, the glass-type PMPS gave higher conductivity than a partially crystalline polymer, PPS (Figure 4a), although the previous, human-based report had emphasized the importance of crystalline structures for conduction.<sup>23</sup> The successful predictions will be utilized to further explore improved conductors and to reveal their transport properties.

In summary, this study represents an experiment-oriented, machine learning approach to find attractive composites consisting of ordinary chemicals. The AI-based screening yielded highly conducting glass-type polymer complexes (around  $10^{-3}$  S/cm), the chemical design of which was contrary to the common sense of rubbery polymer electrolytes but paved a way to superionic properties. Unbiased predictions by experiment-oriented AI will help researchers explore unexpected chemical systems more efficiently. Revealing the detailed conduction processes and pursuing the enhanced electrolyte properties, including higher ionic conductivity, stability, processability, and binding properties to connect solid particles tightly, utilizing machine learning techniques, will be our next challenge.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.9b11442>.

Preparation of  $\text{Li}^+$  conductor database, machine learning, and preparation and measurements of solid polymer electrolytes, including Figures S1–S24 and Tables S1 and S2 (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Kenichi Oyaizu — Waseda University, Tokyo, Japan;  
orcid.org/0000-0002-8425-1063; Email: [oyaizu@waseda.jp](mailto:oyaizu@waseda.jp)

### Other Authors

Kan Hatakeyama-Sato — Waseda University, Tokyo, Japan; orcid.org/0000-0003-1959-5430  
Toshiki Tezuka — Waseda University, Tokyo, Japan

Momoka Umeki — Waseda University, Tokyo, Japan

Complete contact information is available at:

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## Notes

The authors declare no competing financial interest.

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