Exploration of organic superionic glassy conductors by process and materials informatics with lossless graph database

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Abstract

Data-driven material exploration is a ground-breaking research style; however, daily experimental results are difficult to record, analyze, and share. We report a new data platform that losslessly describes the relationships of structures, properties, and processes as graphs in electronic laboratory notebooks. As a model project, organic superionic glassy conductors were explored by recording over 500 different experiments. Automated data analysis revealed the essential factors for a remarkable room temperature ionic conductivity of 10^{-4} – 10^{-3} S/cm and a Li^+ transference number of around 0.8. In contrast to previous materials research, everyone can access all the experimental results, including graphs, raw measurement data, and data processing systems, at a public repository. Direct data sharing will improve scientific communication and accelerate integration of material knowledge.

Main text

Materials informatics is the study of the data-oriented understanding of materials data, represented by structures, properties, mechanisms, and protocols.¹ Artificial intelligence has been used in the field for automated material design, massive data analyses, and accelerated experiments with robots to advance the discovery of materials for energy- and environment-related applications.¹⁻⁵

A long-term challenge in materials informatics and materials science is lossless data sharing by the scientific community.⁶ Although materials and devices are sensitive to their preparation processes, material databases and scientific documents generally do not provide sufficient information.^{1,7,8} Most databases focus on structure–property relations, and ignore or shorten the preparation protocols.^{1,4,6,8} Experimental methods are available in scientific journals, but only specialists can appropriately extract the structure–property–process relationships from the text, and automated text parsing by artificial intelligence is not yet practical.^{7,9} Furthermore, detailed information, including non-representative experimental protocols, lot numbers of reagents, and raw measurement data, is often omitted from articles, which leaves major uncertainties about material data. Researchers may need to improve their communication style to achieve lossless material data sharing.

We propose a new data platform that can explicitly describe the relations among the structures, properties, and processes of materials (Figure 1). Based on the concepts of knowledge graphs or flowcharts,^{7,10} all experimental events are connected as nodes in graphs. Most experimental information can be described losslessly as graphs, the format of which is also compatible with data science.⁷ We demonstrated the system by using it in our superionic organic conductor research that revealed the factors for achieving a remarkable room temperature conductivity of 10^{-4} – 10^{-3} S/cm and a Li^+ transference number of 0.8, practically the highest values of organic solid-state conductors without plasticizers.¹¹⁻¹⁴ All experimental data, including everyday experimental operations and measurements (over 500 records), were recorded in the database, and are available from a public

repository. To our knowledge, this is the first demonstration in experimental materials science of the everything-open research style, which should become the standard for scientific communication to accelerate the integration of materials knowledge.

Figure 1 | Graph-shaped material data storage system. All experimental results were recorded as graph-shaped data, automatically converted into a table database for analysis (see Supplementary Figure 1 for a representative case). Missing values were imputed by machine learning.

Recording daily experiments as graph-shaped data

As the essential components of next-generation secondary batteries,¹²⁻¹⁷ solid-state organic lithium-ion conductors were prepared by mixing aromatic polymers, electron-accepting molecules, and lithium salts (Figure 2a). Several candidates were virtually extracted in our previous machine learning study, the model in which was trained with literature data (>10,000 experimental records).⁴ The model indicated a high room temperature conductivity over 0.1 mS/cm, and we experimentally confirmed some predictions.⁴ However, the model could not input process information, even though

the properties and hierarchical structures of composite materials are changed drastically by different preparation protocols.^{1,7,8} The literature does not provide comprehensive experimental information for each electrolyte, mainly because of the limited space for methodology sections. This is not a problem specific to ionic conductors but has been a general limitation in materials informatics.

Figure 2 | Electrolyte structures and conductivity. **a**, Search space of chemical structures and major operations to prepare electrolytes. **b**, Nyquist plot for a representative electrolyte, PPO/chloranil = 6/4 (mol/mol) with 30 wt % LiFTFSI. Inset: Photograph of the electrolyte layer. **c**, Experimental ionic room temperature conductivities of the electrolytes. The samples were named using the format “XYZMM-NN $\alpha\beta$ ”, which indicates an electrolyte containing MM mol % donor (X = S: PMPS; O:

PPO) versus acceptor (Y = L: chloranil; Q: benzoquinone; D: 2,3-dichloro-5,6-dicyano-*p*-benzoquinone) with NN wt % salt (Z = D: LiTFSI; M: LiFTFSI; N: LiFSI; B: LiBF₄). Symbols α and β indicate operational conditions (α = H: thermal annealing before measurement; L: room temperature, and β = G: cells were kept in a glove box until measurement; O: kept outside). Supplementary Discussion g details the effects of the factors for conductivity.

During electrolyte exploration, we used a graph database as an electronic laboratory notebook in which we recorded the daily experiments (Figure 1, Figure 2b,c). Electronic laboratory notebooks are commercially available, but they are not specially designed for data science, and only available in closed system (e.g., requires payware).¹⁸ In contrast, our management system uses open-format graphs (XML data) and an open-source processing system (Supplementary Figure 1). One graph was designed to contain almost all the information for one experiment, including experiment date, environment, experimenter, protocols, chemical formula, and a link to analytical data.

Although the electrolytes were prepared by simply mixing the components, over 40 small steps and at least 100 variable parameters could be recorded for the conductivity measurements (e.g., heating temperature, duration, and timing; Supplementary Figure 1). For each experiment, experimental protocols were changed slightly to optimize the conditions. These large numbers of steps are usual in materials science, but recording them using conventional frameworks is unmanageable. The protocols are too complex for standard process informatics tools such as experimental design and Bayesian optimization, which typically focus on less than ten variables.^{1,2,6} Only a representative protocol is usually described in the methodology section of scientific articles. In contrast, no data loss would occur in this system because every experimental result is available as graph data on the public repository.

Bridging electronic laboratory notebooks and data science

All experimental results in the project, exceeding 500 records, were recorded in the database. Unsuccessful conductors with poorer performance were also recorded to improve machine learning models, whereas they are often omitted from conventional scientific articles and lost from the community permanently. The graphs were automatically converted into a numerical array by our open-source Python module (Figure 3a). We used a fingerprint algorithm to describe the characteristics of graphs. Fingerprint algorithms were developed to characterize the features of molecules by representing the presence of specific chemical moieties.¹⁹ The availability of specific steps in a protocol were checked in the current algorithm (Figure 3b). Similar operations were automatically grouped by natural language processing (BERT)²⁰ and unsupervised learning (*k*-nearest neighbour, *k*NN). The grouping improved the generality of the fingerprint by addressing orthographical variants (Supplementary Figure 2, Supplementary Table 1). Individual algorithms were designed to parse chemical and measurement data to extract their characteristic features, such as molecular weight, conductivity, crystallinity, and peak position (Supplementary Figure 3).

Figure 3 | Automated feature analysis. **a**, Conversion of process and measurement data into a numerical array. **b**, Fingerprint generation from flowcharts. A binary array expresses specific experimental steps. BERT and k NN automatically group similar steps. **c**, Prediction of ionic conductivity (σ_{ion}) using LightGBM regressor with statistically essential electrolyte parameters extracted by Boruta. **d**, SHAP values during the prediction (explanations of parameters are shown in Supplementary Table 2). **e**, Causal relations estimated by unsupervised machine learning.

Over 50 descriptors, characterizing the features of processes, structures, and analytical data, were automatically generated as a numerical array by parsing the database (Supplementary Figure 4 and Supplementary Figure 5, Supplementary Table 2, Supplementary Data). Conventional materials

informatics usually requires the manual preparation of table databases from experimental results, which is time-consuming and has been a practical bottleneck in material informatics.^{1,7} In contrast, our system automatically converts laboratory notebooks into machine-learnable databases.

Generally, limited research resources do not allow experiments to be conducted with all-inclusive conditions, thereby leading to sparse experimental databases.^{1,6,21} Missing values in the current database were filled by data imputation (Supplementary Figure 5).^{7,21} In other words, the unmeasured data were generated from existing results using a LightGBM regressor, which is a standard decision tree-based ensemble model.^{21,22}

During electrolyte preparation, we milled the electrolytes into microparticles. The diameter measurements were conducted only on a few samples, and the values for the other conductors were estimated by imputation (Supplementary Figure 6). The predicted diameters decreased as the milling time increased, in the same way as for the measured data, indicating successful data imputation. Although the technique is not always accurate,²¹ it can help researchers with objective data analysis and causal exploration.

Data-oriented analysis of electrolytes

Experimentally, various conductors were examined using the polymers poly(*p*-phenylene oxide) (PPO) or poly(2,5-dimethyl-1,4-phenylenesulfide) (PMPS);²³ the electron acceptors chloranil or benzoquinone; the lithium salts lithium bis(trifluoro methanesulfonyl)imide (LiTFSI), lithium (fluorosulfonyl)(trifluoromethanesulfonyl)imide (LiFTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), or lithium tetrafluoroborate (LiBF₄); and different experimental protocols such as mixing and heating conditions (Figure 2a). The conditions were selected based on our previous virtual screening⁴ and on-time data analysis by the current system. Room temperature conductivities varied from almost

insulating to superionic (10^{-11} – 10^{-3} S/cm, Figure 2b and c). The main problems were that the variance was large and the conductivity trend was unclear.

Critical parameters for ionic conductivity (σ_{ion}) were extracted by supervised machine learning. Important descriptors were selected from over 50 descriptors by using the LightGBM regressor and Boruta package,²⁴ which can choose statistically valid parameters based on hypothesis testing (Figure 3c and d). High R^2 scores of σ_{ion} with the randomly split training (>0.9) and testing datasets (>0.6) indicated that the essential factors for conduction were selected adequately (Figure 3c). About 20 descriptors remained after the filtration, the contributions of which were then quantified by SHapley Additive exPlanations (SHAP) values (Figure 3b, Supplementary Figure 7; the scientific significance of parameters are discussed in Supplementary Discussion a).²⁵

We recognized the relations among the composition, conductivity, crystallinity, and NMR peak width (full width at half maximum; FWHM) of the electrolytes from the SHAP analysis (Figure 3d). The detailed causal relationships were analyzed by unsupervised machine learning (Figure 3e).²⁶ The automated causal exploration indicated that adding polymer and acceptor molecules to salts simultaneously reduced the crystallinity, sharpened NMR peaks, and increased σ_{ion} (Supplementary Discussion b). Just by recording the daily exploratory experiments, essential and objective material insights could be extracted by the system.

Revealing superionic conduction

We rationalized the new electrolytes' high conductivity based on materials science. Traditionally, solid-state organic ionic conductors have been designed to contain polar and flexible aliphatic chains, represented by poly(ethylene oxide), for solvation and transportation of ions (Figure 4a).¹² The solidification and overly strong cation-solvent interaction reduced the mobility of molecules,

leading to a typical conductivity of 10^{-6} S/cm and lithium-ion transference number of 0.3, much smaller than liquids or recent inorganic solid conductors, which have conductivities of $>10^{-3}$ S/cm.^{12,16}

An essential feature of our electrolytes is that they consist of only rigid components, namely, aromatic polymers, acceptors, and lithium salts. The highly conductive yet chemically, mechanically, and thermally robust properties of our electrolytes⁴ may not be achieved by other organic or inorganic conductors, which typically suffer from thermal melting, hydrolysis, or large interface resistances.^{12,16} The superionic conduction in the organic glassy media must be understood from both scientific and technological perspectives to advance the practical applications of these materials (e.g., electric vehicles).

The automated causal analysis highlighted the emergence of the amorphous phase after the electrolyte preparation (Figure 4b). The polymers (electron donors) and acceptor molecules form charge-transfer complexes,⁴ inducing electrostatic interactions with lithium salts (Figure 4b, molecular calculations shown in Supplementary Figure 8 and Supplementary Figure 9, and Supplementary Discussion c). As a representative case, electrolytes consisting of PPO/chloranil with different amounts of LiTFSI were examined in detail (maximum conductivity of around 10^{-3} S/cm; Figure 2a). Scanning electron microscopy (SEM) and element mapping showed the uniform distribution of the polymer, acceptor, and salt as microparticles (Supplementary Figure 10). Peak shifts of the aromatic rings of the donor polymer in ^{13}C NMR indicated molecular-level interactions between the complexes and salt (e.g., cation- π interactions;²⁷ Supplementary Figure 11). Simultaneously, the crystal peaks of the salt decreased during differential scanning calorimetry (DSC) and X-ray diffraction (XRD), also indicating the amorphous phase formation (Figure 4c and Supplementary Figure 12–Supplementary Figure 15).

Figure 4 | Characterization of superionic conductors. **a**, Comparison of molecular structures for ionic conductors. **b**, Estimated scheme of ion conduction through the amorphous electrolyte. **c**, DSC curves for the PPO/chloranil = 60/40 (mol/mol) + LiFTFSI electrolytes. **d**, ¹⁹F MAS NMR spectra of the samples. **e**, Temperature dependence of σ_{ion} for the 20 wt % LiFTFSI sample. Inset: DSC for the pristine LiFTFSI salt. **f**, Charge/discharge curves for a solid-state lithium-ion battery containing PPO/benzoquinone = 8/2 with ca. 52 wt % LiFTFSI electrolyte, operated at 50°C.

The addition of the charge-transfer complexes to salts induced unexpected sharpening of solid-state ⁷Li and ¹⁹F NMR peaks (Figure 4d and Supplementary Figure 16–Supplementary Figure 19). Pristine LiFTFSI displayed a broad ¹⁹F magic angle spinning (MAS) NMR peak at -80 ppm and a smaller sharp peak at around -79.5 ppm, attributed to CF₃ groups. After the electrolyte formation, only smaller peaks were visible, and σ_{ion} increased (Figure 4d). Because the peak sharpening indicates the greater atom motion, the high σ_{ion} was explained by the mobile ions in the amorphous phases (Figure 3e and Figure 4b). The fast kinetics was also confirmed by relaxation time T_1 ²⁸ during static NMR measurements (Supplementary Figure 20, Supplementary Discussion d). However, the polymers had

high glass transition temperatures (T_g) over 100°C,^{4,23} and the carbon peaks showed no sharpening (Supplementary Figure 11). The results suggested that the mobile media was the salts themselves, not the polymers or acceptors (Figure 4b).

Although pristine lithium salts have been believed to be almost insulating,¹² our experimental results supported the salt-based conduction model. The temperature dependence of σ_{ion} was fitted by the Vogel-Fulcher-Tammann (VFT) equation, which describes the kinetics of amorphous structures (Figure 4e, Supplementary Figure 21).^{29,30} The fitting yielded a Kauzmann temperature (T_K) of -48°C (Supplementary Figure 12b, Supplementary Discussion e). The value satisfied the empirical relation of amorphous phases, $T_g \cong T_K + 50$,³⁰ where $T_g \cong 0^\circ\text{C}$ –10°C was the experimental glass transition temperature of the salt (Figure 4e).³¹ The agreement demonstrated that the dominant carriers were amorphous salts. Molecular dynamics simulations also showed the advantages of the amorphous phase. Ions were firmly trapped in the crystalline phase, whereas structural vacancies were available in the amorphous phase (Supplementary Figure 22, Supplementary Discussion f).

Although the new electrolytes look dissimilar to conventional ones, they could be regarded as a new type of polymer-in-salt system, in which excess salt is added to polymers (typically over 50 wt % to an aliphatic polymer).^{13,32} In the system, amorphous salt clusters, which emerge after polymer-salt interactions, function as carriers, enabling a conductivity of up to 10⁻⁴ S/cm.¹³ Rubbery polymers are often used, but even high- T_g polymers (e.g., polyacrylonitrile, $T_g \cong 100^\circ\text{C}$) can also become conductors by unexplained mechanisms.^{13,33}

In the current electrolytes, electrostatic interactions of polar charge-transfer complexes and salts should have generated the amorphous clusters, similarly to conventional polymer-in-salt systems. Furthermore, thermal (mainly rotational) motions of anions could transport cations even in the absence of flexible polymer matrices, which is unusual in normal polymeric conductors, but widely observed in ionic liquids, soft crystals, and some polymer-in-salt systems.^{13,34} In our ongoing research, we intend

to reveal more details of the structures and kinetics, including the possible contributions of charge-transfer complexes to salt structures, anion-acceptor exchange reactions,³⁵ and other chemical factors (Supplementary Figure 23 and Supplementary Figure 24, Supplementary Discussion g).

Next, we analyzed the best electrolyte conditions, focusing on the reproducibility of conductivity. A new evaluation score, which was the median minus standard deviation of σ_{ion} for electrolytes with the same composition, was predicted instead of each conductivity (Supplementary Figure 25). The score was low for poorly reproducible conductors with large conductivity variance. The analysis showed the importance of the following factors: a thermally stable PPO polymer; a highly dissociative and asymmetrical LiFTFSI salt; an appropriate donor/acceptor/salt ratio (e.g., donor/acceptor = 6/4 (mol/mol) + 30 wt % salt); sufficient heating during electrolyte formation and premeasurement; and particle milling (Supplementary Discussion h). After the optimization, high room temperature conductivities were obtained with slight variance (e.g., 10^{-4} to 10^{-3} S/cm for electrolyte OLM60-41HG in Figure 2). Thus, the materials informatics tool was suitable for technological optimization tasks.

A solid-state lithium-ion battery was fabricated using a lithium iron phosphatase cathode and a lithium titanate anode. The electrolyte consisted of PPO/benzoquinone = 8/2 with 52 wt % LiFTFSI (maximum $\sigma_{\text{ion}} \cong 1$ mS/cm, OQM78-52 in Figure 2). Benzoquinone was selected because of its potential chemical stability over chloranil (e.g., containing no halogens). The cell operated reversibly at 1.9 V, corresponding to the standard voltage (Figure 4f). Although charge-transfer complexes could become electrically conducting, the composition of electrically insulating salts did not cause short circuits or current leakage (around 10^{-8} S/cm).^{4,36} Even at a large current density of 1.5 mA/cm² (corresponding to 1 C), the charge/discharge reactions proceeded. The impressive performance can be explained by the electrolyte's high Li⁺ transference number (ca. 0.8, estimated from the actual battery

responses; Supplementary Figure 26, Supplementary Discussion i). This high value was also an essential characteristic of the polymer-in-salt system.¹³

Conclusions

We developed a materials science platform for easy data analysis and sharing. Everyday experiments were recorded as graph data in an electronic laboratory notebook, clarifying the relations among structures, properties, and processes. Automated parsing of the graphs and data analysis helped researchers to understand data with broad experimental conditions objectively. The new research style of publishing all raw experimental results with appropriate metadata will pave the way for lossless material data sharing, which is also compatible with big data mining and deep learning.⁷

Scientific and technological aspects of glassy organic superionic conductors were examined using the platform. Semi-automated data analysis helped us reveal the causal relationships in the electrolyte system statistically. The amorphous phases of salts achieved superionic conduction and a high transference number (ca. 0.8) after interacting with polymer charge-transfer complexes. We are now addressing the cyclability problem of the prototype batteries (currently about 30 cycles; Supplementary Figure 26) with our informatics tool, which is highly compatible with composite materials and device development.

Methods

Methods are available in the Supplementary Information.

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Author contributions

K.H. developed the concept and the data analysis system for this work and prepared the manuscript. U.M. and H.A. conducted the electrolyte experiments and measurements. N. K. and G. H. conducted steady state NMR measurements and joined the discussion. K.O. conceived the project and joined the discussion.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

Supplementary Information

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Materials

PPO and chloranil were purchased from Sigma-Aldrich Co. LiFTFSI was purchased from Fujifilm Wako Chemicals Co. LiTFSI was obtained from Kanto Chemical Co. LiFSI, LiBF₄, and benzoquinone were purchased from Tokyo Chemical Industry Co. Other chemicals were obtained from the above companies. All compounds were used as received, and their reagent containers were kept and opened only in a glove box. Detailed information, such as production numbers, is available on the public repository. PMPS was synthesized according to our previous report mentioned in the main manuscript (M_w : 18,000, M_n : 7000).

Electrolyte preparation

a) General information

A typical electrolyte preparation procedure for PPO/chloranil = 60/40 (mol/mol) with 40 wt % LiFTFSI electrolyte (also shown as a flowchart in Supplementary Figure 1) is described here. Methods for the other electrolytes are given in the repository as graph data. All procedures were conducted in an argon-filled glove box (oxygen concentration of less than 10 ppm and dew point of $-80\text{ }^{\circ}\text{C}$). Scrupulously dry conditions were maintained because lithium salts are highly deliquescent.

b) Electrolyte preparation

PPO (211 mg) and chloranil (282 mg) were mixed roughly in a petri dish. The powder was ball-milled (Mini-Mill PULVERISETTE 23, FRITSCH; stainless-steel balls, 10 mm diameter) for 30 min at a frequency of 40 Hz. The mixture was put in a petri dish and heated at 200°C for 65 min to form the charge-transfer complex. The plate was covered with aluminium foil to catch sublimated chloranil, which was collected and returned to the mixture. After mixing the powder with a spatula, the complex was heated at 280°C for 30 min. The product was obtained as a black powder (325 mg). The yield was less than the weight of raw materials ($211 + 282 = 493\text{ mg}$) because the unreacted acceptor had sublimated from the mixture.

LiFTFSI (208 mg) was added to the charge-transfer complex (304 mg) and mixed roughly. The powder was ball-milled at 40 Hz for 60 min, and heated at 150°C for 10 min to melt the salt. After cooling, the mixture was ball-milled at 40 Hz for 75 min, yielding the final product.

c) Impedance measurements

The ionic conductivities of electrolytes were evaluated using solid-state cell equipment (KP-SolidCell, Hohsen; equipped with Macor insulator and PTFE O-ring). Stainless disks (1 cm diameter) were used to sandwich electrolytes. The equipment was dried at 100°C for more than 1 h before it was placed in the glove box. The cell was filled with the electrolyte and sealed with a torque of over 20 Nm. The cell was annealed on a hot plate at 80°C for 4 h and at room temperature for at least 16 h. Impedance measurements were conducted just after removing the cells from the glove box. Several cells were prepared under the same conditions to check the variation in conductivity. Electrolyte thicknesses were measured with a conventional gauge after cell disassembly. Instead of leaving some cells in the glove box, some were sealed with a conventional plastic vacuum bag, kept outside the glove box, and annealed in an incubator (AMF-20N, Asahi Rika Seisakusho Co. Ltd.; the bag was opened just before the measurements).

d) Fabrication of lithium-ion battery

A solid-state lithium-ion cell was prepared in a similar way to the normal cells for impedance measurements. A precoated LiFePO_4 cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode (Piotrek Co.; areal capacity of about 1.5 mAh/cm²) were used instead of stainless disks.

e) Electrolyte abbreviation

The samples were named using the format “XYZMM-NN $\alpha\beta$ ”, and the variables had the following meanings.

X: Donor polymers (S: PMPS, O: PPO)

Y: Acceptor molecules (L: chloranil, Q: benzoquinone, D: DDQ)

Z: Salt molecules (D: LiTFSI, M: LiFTFSI, N: LiFSI, B: LiBF₄)

MM: Formal mole percent of donor with respect to the acceptor

NN: Weight percent of salt in an electrolyte

α : Whether an electrolyte was thermally annealed before electrochemical impedance spectroscopy (EIS) (H: high-temperature thermal annealing (e.g., 80°C), L: only room temperature leaving)

β : Whether annealing was conducted in a glove box or outside (G: glove box, O: outside)

Measurements and data analyses

a) EIS

A photoelectrochemical system (ZAHNER CIMPS, Zahner) was used as a spectrometer for EIS (Supplementary Figure 3a). Samples were measured under open-circuit conditions at frequencies of 10^6 to 1 Hz. The spectra were fitted manually with an RC parallel equivalent circuit. A constant phase element was introduced for a depressed semicircle, and the value of the intercept on the x -axis in the Nyquist plot was extracted for highly conducting samples. Ionic conductivity σ_{ion} was estimated from the measured resistance R ($= 1/\sigma_{\text{ion}} \times \text{electrolyte thickness/area}$). Capacitance C was around 10^{-10} F, corresponding to the relative permittivity of 1–100 of the electrolytes. If a capacitance that was too large or small was obtained, the corresponding semicircle was not attributed to ionic conduction.

b) DSC

Samples were sealed in standard DSC pans in a glove box to avoid air exposure. DSC curves were measured with a differential scanning calorimeter (Q200, TA Instruments) with a typical scan

rate of 20°C/min (Supplementary Figure 3b). The melting temperature and enthalpy of salt components were manually detected and recorded in the database.

c) XRD

XRD measurements were performed with an X-ray diffractometer (SmartLab, Rigaku). In a glove box, samples were sealed in airtight sample holders for the intensive beam method or glass capillaries for the parallel beam method to avoid air exposure (Supplementary Figure 3c). After automatically separating signal peaks from the background, the peak areas were calculated (Supplementary Figure 15).

d) Solid-state NMR

NMR spectrometers were used to obtain solid-state NMR measurements (JNM-ECA400, JEOL). The NMR samples were sealed in airtight sample holders in a glove box to avoid air exposure. During MAS NMR, samples were rotated at 8 kHz. Rotation was stopped during static NMR. Peak position and FWHM of ^7Li and ^{19}F peaks were detected automatically and recorded in the database. The CF_3 fluoride peaks were analyzed for LiTFSI and LiTFSI. In Supplementary Figure 20, an NMR spectrometer with different configuration and lot number was employed. Owing to the shorter dead time, background peaks (i.e., broad components) were more successfully detected in comparison to Supplementary Figure 17 and Supplementary Figure 19. For clearer comparison, the peak positions and FWHM in Supplementary Figure 20 were not used as descriptors for machine learning.

e) Temperature dependence of conductivity

The conductivities of the solid-state cells were measured in a thermostat chamber while the temperature (T) was increased (Supplementary Figure 3e). The temperature dependence was automatically fitted by the VFT equation, $\sigma_{\text{ion}} = \sigma_0 \exp(-B/(T - T_K))$, where σ_0 is the prefactor, B is the activation energy, and T_K is the Kauzmann temperature.

f) Particle size analysis

Electrolytes or charge-transfer complex particles were observed using a conventional optical microscope under atmospheric conditions (Supplementary Figure 3f and Supplementary Figure 6). The particle diameters were automatically calculated from the images, yielding d_{50} and standard deviation. The salts were washed from the electrolytes with water before the measurements.

Computational simulations

a) Workstation

A commercial computer (CPU: AMD Ryzen Threadripper3 3990X with 64 cores; memory: 256 GB; storage: 2 TB SSD and 8 TB HDD) with the Ubuntu 18.04 operating system was used for computational simulations and data processing for materials informatics.

b) Density functional theory calculations

Density functional theory (DFT) calculations were conducted using Gaussian09 (Supplementary Figure 8). Initial structures were preliminarily optimized by the PM6 semi-empirical method. The geometry optimization and main calculations were performed at the B3LYP/6-31+g(d,p) level in vacuo. Stabilization energies were estimated by calculating the differences between the normal solvated structures and the control cases, where salt and solvating molecules were far apart.

c) Molecular dynamics simulation

The molecular dynamics of pristine LiTFSI molecules in the crystal or amorphous phases were calculated by LAMMPS (29 Oct 2020 version) (Supplementary Figure 22). For the crystal phase, public crystallography data were used to place 480 ordered molecules. For the amorphous phase, 128 molecules were placed randomly. The calculation settings were obtained by using Winmostar V8. The atom charges and force fields were generated by the Dreiding and Gasteiger methods. Simulations were conducted with NPT ensembles at 300 K under 1 atm pressure (“pair_style” option of “lj/cut/coul/long 10. 10” and “pair_modify” option of “mix arithmetic”). Periodic boundary conditions were set for all dimensions, and the time step was 2 fs.

Open database and materials informatics

a) General information

All raw experimental data in this project are available at GitHub (<https://github.com/KanHatakeyama/GlassyIonicConductorDatabase>). The measurement data were linked by graph structures as meta information. The data management system is developed as an open-source Python project, FlowMater2 (<https://github.com/KanHatakeyama/FlowMater2>).

b) Preparation of graph-shaped databases

One experiment typically consisted of experimental protocols, material information, and measurement data. Those relationships were expressed in a directed graph explicitly. A diagram was

recorded as a GraphML file, which is an XML-based format for graphs that can be edited with free software, such as yEd graph editor (<https://www.yworks.com/products/yed>).

Experimental procedures were recorded in a graph in a similar way to flowcharts (Supplementary Figure 1a). For one experimental step, one node was introduced, which consisted of a node name and its characteristic features.

For instance, the “Set environment” node in Supplementary Figure 1a had the following features.

type: Indicates that the node was related to an experimental operation.

person: Experimenter.

O2: Oxygen concentration in the glove box.

Dew: Dewpoint in the glove box.

Day: Date of the experiment.

Env: Indicates whether the experiment was conducted in a glove box.

ID: Indication for the data processing system that this node is related to the glove box environment for electrolyte preparation.

In another example, the “Add donor” node, had the following features.

type: Indicates that the node was related to chemical samples.

keyword: A macro command to load further information about PPO, such as molecular weight and production data, from a JSON file where additional data were recorded.

weight: Amount of the sample.

note: User note to improve understanding.

ID: Indication for the data processing system that this node is related to the addition of donor molecules.

In another example, the “Ball mill” node had the following features.

type: Indicates that this node is related to an experimental operation.

frequency: Frequency of ball milling.

time: Milling duration.

The electrolyte information was named “U-1130” for the processing system at the end of the graph. Supplementary Figure 1b shows another graph for an impedance measurement. The data processing system automatically loaded and integrated the electrolyte preparation (Supplementary Figure 1a) and cell fabrication (Supplementary Figure 1c) procedures, making a full experimental graph. Conductivity data measured with different cells were recorded in a JSON file and loaded by the system automatically. Pathways to other measurement data, such as NMR and DSC data, were noted on graph nodes, clarifying the relationships between experimental methods and measurements.

c) Parsing graph data

The graph characteristics were described as fingerprints, which indicated the presence of specific nodes (Figure 3b). For instance, “fingerprint a” in the figure shows the appearance of the “Add” operation in a graph. The corresponding bit is 0 or 1 for the presence or absence of the operation, respectively. The fingerprint algorithm checks the states of the closest neighbouring nodes. The “Cool”

operation neighbouring “Heat” (corresponding to fingerprint c) in Protocol A was distinguished from those in Protocol B because it neighboured an additional node of “Hot plate”. Over 250 checksums were generated from the experimental graph data in the project.

The fingerprint was compressed into a 30-bit array by automatically grouping the similar nodes (e.g., “Heat” and “Hot plate” in Figure 3b). Initially, texts in a node were converted into a 768-dimensional numeric vector by a pretrained model of BERT (bert-base-uncased model available at <https://github.com/google-research/bert>, Supplementary Figure 2). Then, the vectors were automatically categorized into 30 groups by a *k*NN model. The frequently used words in the original nodes were extracted to name the new 30-fingerprint checksums.

Characteristic features of measurement data were manually or automatically extracted using different algorithms, as explained in the Measurements and data analyses section. The molecular weight of a compound (or unit structure in a polymer) was selected as a descriptor to express molecular information. This feature should be enough for this project with several available chemical structures. Numeric values in some nodes with the “ID” keyword (examples shown in Supplementary Figure 1) were also extracted as experimental descriptors. Several new parameters, such as donor and acceptor ratio, were calculated from the information. Major features are summarised in Supplementary Table 2.

c) Conductivity prediction

Graph data were converted into a numerical table after the parsing, allowing conventional data analytics. The LightGBM model was selected for regression. Before regression, missing experimental values were filled using a machine learning-based imputer (https://github.com/KanHatakeyama/gen_model). Conductivity-related variables, such as σ_{ion} and VFT parameters, were removed during the imputation, which was necessary to avoid problem leaking.

The logarithmic experimental ionic conductivity was predicted from the experimental descriptors generated by the system (Figure 3b). Statistical essential descriptors were automatically selected using the Boruta package (https://github.com/scikit-learn-contrib/boruta_py). Then, prediction accuracy was examined with randomly split training (80%) and testing (20%) datasets, using the coefficient of determination, R^2 . Strictly speaking, descriptor selection should be conducted only with the training dataset. However, the whole database was used because the aim of the study was fundamental parameter analysis, not prediction. SHAP values were analyzed for a regression model trained with the entire database. Causal relationships were explored using the CausalNex library (<https://github.com/quantumblacklabs/causalnex>).

In addition to $\log \sigma_{\text{ion}}$, a newly defined score, (median of σ_{ion}) – (standard deviation of σ_{ion}), was predicted for electrolytes prepared under the same experimental conditions (Supplementary Figure 25). The value is an indicator of conductivity and reproducibility.

Supplementary Discussion

Supplementary Discussion a: Significance of essential parameters for σ_{ion}

SHAP values for vital parameters for σ_{ion} were calculated in Figure 3d. The scientific meanings of such variables are given below.

F (static, MAS): FWHM This parameter is the FWHM of a ^{19}F peak during static (MAS) NMR. Narrower peaks indicated higher thermal anion activity, which is essential for transporting lithium ions via thermal motion.

F (Li) (static): δ This parameter is the chemical shift of a ^{19}F (^7Li) peak during static NMR. The value was determined mainly by the type of salt (i.e., LiFTFSI gave the highest performance) and slightly by interactions with charge-transfer complexes.

Process fingerprint (sealing) The full fingerprint name was “temperature-machine-AMF-20N-Measure-EIS|Break-vacuum-pack-Disassemble-cell”. This parameter indicates the processes of sealing a cell with a vacuum pack, thermally annealing it in a constant temperature chamber under atmospheric conditions, breaking the seal, measuring the conductivity, and disassembling the cell. These processes increased conductivity. The most important process was thermal annealing, which improved the interface contacts. Supplementary Discussion g shows that leaving the sealed cell under air should not cause substantial water contamination.

Li (static, MAS): FWHM This parameter is the FWHM of a ^7Li peak during static (MAS) NMR. As discussed in the main manuscript, narrower peaks indicate higher ions mobility. The result that smaller SHAP values indicated higher conductivity was consistent with the physical model.

Thickness This parameter is the thickness of the electrolyte. Smaller SHAP values increased conductivity, whereas σ_{ion} principally should not depend on the thickness. An inhomogeneous electrolyte layer that was too thick may have broken the percolation pathways.

Melting enthalpy This value is the melting enthalpy of salt species during DSC. Smaller SHAP values gave higher conductivity. Because the phase transition from the crystal to amorphous phases decreases the enthalpy, the trend indicates the importance of the amorphous phase for conduction.

Formal donor ratio This parameter is the formal molar ratio of donor molecule in an electrolyte. Smaller SHAP values were favoured for higher conductivity because donor polymers themselves were not ionically conductive, but interacted with salt molecules.

Date difference This parameter is related to the time from electrolyte preparation to measurement. The parameter should be related to the long term stability of the electrolytes. On the other hand, no obvious relation to conductivity was observed currently; further study is needed in the future researches.

Temperature of σ_{ion} This parameter is the temperature during conductivity measurements. Higher temperatures induced greater molecular motion.

d_{50} This parameter indicates the median of electrolyte particle diameters. A smaller diameter should favour dense stacking of electrolytes, although no clear trend was detected with the SHAP values. More experimental results are needed instead of imputed results to improve the trend analysis.

Salt weight ratio This parameter is the weight ratio of salt molecules in an electrolyte. Larger SHAP values resulted in higher conductivity because higher salt concentration increases the number of carriers.

Total heat time This parameter the total duration of heating during electrolyte preparation. Although heating is essential for conductivity, no obvious trend was observed. This indicated the optimal heating conditions (temperature, duration, and timing) were essential for performance.

Donor MW This parameter is the molecular weight of donor polymers. Smaller SHAP values (i.e., use of PPO) contributed to higher performances than low SHAP values (use of PMPS). The effect of

the polymer selection is discussed in the following best electrolyte section (Supplementary Discussion h).

d_{std} This parameter indicates the standard deviation of electrolyte particle diameters. Smaller values favoured higher performance. Physically, smaller particles lead to denser packing and more contacts among electrolyte particles, increasing conductivity.

Supplementary Discussion b: Causal reasoning for electrolyte parameters

According to the SHAP value analysis, the five primary parameters, which were salt ratio, formal donor/acceptor ratio, $\log \sigma_{\text{ion}}$, salt crystallinity, and FWHM of the ^7Li peak (MAS NMR), were selected manually. Causal relationships among the experimental parameters were automatically analyzed by machine learning (Figure 3e). The analysis indicated that salt ratio and formal donor/acceptor ratio were independent variables, and the rest were dependent. The prediction was consistent with the actual experiments because the other three parameters were not directly controllable but depended on experimental conditions.

Higher salt ratio decreased the conductivity, whereas it increased crystallinity and FWHM. As discussed in the main manuscript, amorphous phases with sharp NMR peaks were attributed to ion conduction. The excess salts inhibited the phase transition from the crystal phases with lower conductivity. A higher formal donor/acceptor ratio increased the crystallinity and decreased the conductivity, indicating the important effect of acceptor molecules on the amorphous transition of salts (e.g., formation of the polarised charge-transfer complex and the interaction of polar groups in the acceptors with salts). Our results demonstrate that automated causal exploration can assist objective causal inference and improve our understanding of underlying mechanisms.

Supplementary Discussion c: Molecular interaction analysis by DFT calculations

Molecular-level interactions between LiTFSI and solvating molecules were estimated by simple DFT calculations (Supplementary Figure 8). The model solvents were poly(ethylene glycol) (PEG, trimer), chloranil (two molecules), PPO (trimer), PMPS (trimer), PPO + chloranil, and PMPS + chloranil. The initial geometry for the calculation consisted of the following groups arranged near a LiTFSI lithium atom: PEG oxygen atoms, chloranil carbonyls, and the polymer aromatic rings and heteroatoms.

After structure optimization, the intramolecular distance between lithium and oxygen atoms in the anion increased from 1.8 to 1.9–2.0 Å (Supplementary Figure 9a). The longest length of 2.0 Å was observed with a common solvent, PEG, although other solvents could also work as solvents (distance of ca. 1.9 Å). Mulliken charges were also decreased by the electron-donating effects of the solvents (Supplementary Figure 9b). The original charge of 0.6 was shifted to –0.3 by PEG. The donating effect was smaller with chloranil (ca. 0.2). However, aromatic rings increased the negativity substantially (–0.5 to –0.8).

Stabilization energy was also estimated by calculating the energy difference in cases where the solvents were far from the salt (Supplementary Figure 9c). The stabilization trend almost correlated with the lithium-oxygen distance, as demonstrated by the enormous stabilization energy with PEG (180 kJ/mol) and moderate values with the others (60–100 kJ/mol). Greater stabilization and electron donation effects were observed when both donor and acceptor molecules were present. These moderately strong cation– π and heteroatom interactions induced the phase change of the lithium salt, resulting in higher conductivity.

In the future, further calculations with different molecular geometry and precise methods are needed to understand unexplored issues, such as detailed molecular structures of clusters. An exact

comparison for PPO and PMPS, which displayed similar properties in the current calculation, is also needed to clarify the conduction processes.

Supplementary Discussion d: Relaxation time estimation by solid-state NMR

The relaxation processes of atoms in some electrolytes (OLM60-31, OLM60-40, OQM79-30) and LiFTFSI were investigated by solid-state static NMR. ^7Li peaks of the electrolytes became sharper after increasing the measurement temperatures (25 to 80°C, Supplementary Figure 20a). Similarly, sharp components in the ^{19}F peaks became more significant at elevated temperatures (Supplementary Figure 20b). Thermal activated atomic motions induced the longer spin-spin relaxation time, resulting in the peak sharpening.

FWHM of ^7Li peaks was analyzed as a temperature function (Supplementary Figure 20c). The value was around 3 kHz at room temperature regardless of the samples. The FWHM of the electrolytes decreased to less than 1 kHz by heating. The values converged to about 0.8 kHz at 60–80°C, which was comparable to the conductivity trend (Supplementary Figure 21). In contrast, the FWHM of LiFTFSI was almost constant even at high temperatures, indicating that lithium cations in the salt were trapped firmly.

T_1 relaxation time was estimated by a saturation recovery method. In the case of ^7Li , T_1 of the three electrolytes (0.1–1 s) was much smaller than LiFTFSI (ca. 100 s, Supplementary Figure 20d). The decrease of T_1 along with the heating and the smaller values than LiFTFSI meant the faster lithium atom motions in the electrolytes.

Even with ^{19}F atoms, a shorter relaxation time was observed with the electrolytes (ca. 1 s) than the pure salt (ca. 10 s, Supplementary Figure 20e). The T_1 time of the electrolytes was almost constant at 25–80°C, while the pristine LiFTFSI crystal exhibited a decreasing trend. Active motions of fluorine atoms, such as rotation of CF_3 groups, were available in the amorphous salt phase of the electrolytes even at room temperature, which should be essential to conductivity.

Pulsed-field gradient NMR for estimating the diffusion coefficients of atoms was not possible the fast spin-spin relaxation. The electron spins in the charge-transfer complexes or trace amounts of

metals contaminated during ball milling may have interfered with the measurement, which should be clarified in future work.

Supplementary Discussion e: Temperature dependence of ionic conductivity

Temperature dependencies of σ_{ion} were examined with several electrolytes (Supplementary Figure 21). In most cases, convex upward curves were observed with Arrhenius plots, indicating that the structure changes with heating or amorphous phase conduction. Successful fitting was achieved with OQM80-50, OLM60-40, and OLM60-20 (blue fitting lines), whereas the errors were not negligible for the other conditions (red lines). Some LiTFSI and LiFTFSI electrolytes suffered from unexpected conductivity decrease at higher temperatures, which could not be explained by standard Arrhenius or VFT models. The decrease was attributed to microscopic structure change in the inhomogeneous electrolytes at higher temperatures ($1000/T \cong 3 \text{ K}^{-1}$, corresponding to 60°C). The temperature was higher than the estimated T_g of LiTFSI and LiFTFSI ($0\text{--}10^\circ\text{C}$, Supplementary Figure 12b), where molecular motion occurred actively. No major changes in the diffraction peaks were detected by XRD (Supplementary Figure 13), but structure analyses will elucidate the mechanism in future work.

In contrast to the sulfonyl imide electrolytes, an almost linear fitting line was obtained with a LiBF_4 electrolyte (OLB60-18), which contained a salt that did not display a clear glass transition (Supplementary Figure 12). The amorphous phase, which is key for ionic conduction, was difficult for the symmetrical and compact BF_4 anion to form.

The estimated VFT parameters, apparent activation energy B , Kauzmann temperature T_K , and prefactor σ_0 , were comparable for the successful fitting cases (Supplementary Figure 21c and d). For instance, T_K , ranged from -70°C to -50°C , corresponding to the experimental T_g of $0^\circ\text{C}\text{--}10^\circ\text{C}$ with a general law of $T_g \cong T_K + 50$. The agreement indicated that the thermal motion of salt molecules themselves was essential to conduction and that the polymer and acceptor molecules induced the structure changes and other side effects.

Supplementary Discussion f: Molecular dynamics simulation of LiTFSI

Molecular dynamics simulations were conducted for the crystal and amorphous phases of LiTFSI (Supplementary Figure 22). The salt was selected instead of LiFTFSI because public crystallographic data was available for LiTFSI. The amorphous phase was generated by locating the salt molecules randomly. Conventional calculation settings with a Lennard-Jones potential and Dreiding force field were used, which should be sufficient for the semiquantitative comparison of the different phases. The absolute values of the movement distances or mean square displacement (MSD) of atoms were less important because the interaction parameters were not optimized.

In the crystal phase, the Li, F, and O atoms did not change substantially from their original conformation, even after 200 ns, indicating strong ion trapping (Supplementary Figure 22a). In contrast, the MSD of the atoms increased almost linearly with the calculation time owing to the ion diffusion (Supplementary Figure 22b). MSD of F was higher than those of Li and O because of the smaller electrostatic interaction and greater flexibility of the bonds.

Free volumes can also explain the different mobilities in the phases. The density of the amorphous phase (around 1.97 g/cm^3) was much smaller than that of the crystal phase (around 2.18 g/cm^3). The voids that were formed in the amorphous phase were essential for transporting cations. Higher-accuracy calculations, including the effects of donor and acceptor molecules with more realistic interaction potentials, will provide detailed insights into the conduction processes in future research.

Supplementary Discussion g: Potential factors for conductivity

As discussed in the main manuscript, ionic conduction was attributed to the amorphous phases of the salts. However, pristine salts displayed room temperature conductivities of around 10^{-10} S/cm. LiFTFSI became amorphous after heat treatment (Supplementary Figure 12b), even though it is practically an insulator as a pristine material (Figure 2c, LiFTFSI-HG). Additional components, represented by charge-transfer complexes, were essential for conductivity.

Apart from the polymer and donor molecules, the contribution of trace impurities, such as oxygen, water, and by-products from electrolyte formation, should be considered. Oxygen would help to dope polymers as an oxidant, although the effect would be negligible owing to the low oxygen concentration in the glove box (typically less than 10 ppm, Supplementary Figure 5). We did not detect substantial amounts of by-products with the characterization methods that we used.

Because trace amounts of water would increase conductivity by acting as a solvent, we evaluated the water content in the electrolytes. Karl Fischer titration or the standard drying method was infeasible because of the acceptor molecules' redox capability and tendency to sublime. Therefore, the amount was estimated by ^1H NMR (Supplementary Figure 24). After impedance, water was extracted from the electrolyte and measured by the following procedure. The electrolyte was put into deuterated dimethyl sulfoxide (DMSO- d_6 , 99.9% deuteration, Acros Co.). The concentration of the sample was 10 mg/mL (= 0.0084 g/g_{solvent}). The insoluble components were filtered off; the PMPS electrolytes were mostly insoluble because of thermal cross-linking during electrolyte preparation. The water content in the solvent was measured by conventional solution ^1H NMR.

In the absence of electrolytes, the relative proton peak area of water, initially contained in the solvent, was 0.85 compared with the normalized area of non-deuterated DMSO (Supplementary Figure 24a). By assuming a 99.9% deuteration ratio and solvent density of 1.19 g/cm³, the water content was

converted by a coefficient of 0.0071 wt %/area, that is, the actual water content in the solvent was calculated as $0.85 \times 0.0071 = 0.006$ wt %.

The water content of the SLD67-56 electrolyte was estimated (Supplementary Figure 24b, c). The solid-state cells were kept in a glove box or under atmospheric conditions for 5 days, and the water peak areas were 0.78 and 0.63, respectively. The comparable values indicated that water contamination was not detectable by the current method.

This method's potential water sensitivity was estimated to be around $0.1 \times 0.0071 = 0.00071$ wt %, assuming significant digits of 0.1 for the peak area. The amount corresponds to 0.00071 wt %/ $0.0084 \cong 0.1$ wt % of water in the original electrolyte, indicating that water was not the main matrix for conduction. In the future, more extensive structure analyses will be needed to explain the slight ^7Li and ^{19}F NMR peak shifts after the electrolyte formation and high mobility of ions in the amorphous phases (Supplementary Figure 16 and Supplementary Figure 18).

Supplementary Discussion h: Essential factors for conductivity and reproducibility

The addition of charge-transfer complexes to lithium salts increased the room temperature ionic conductivity from around 10^{-10} to 10^{-8} – 10^{-3} S/cm (Figure 2c). However, the inhomogeneity of the electrolytes led to large variation in conductivity of some electrolytes, even though they were prepared under the same experimental conditions. A new score was defined as the median of σ_{ion} minus standard the deviation of σ_{ion} to discuss the reproducibility (Supplementary Figure 25a). A high score could be achieved only by an electrolyte displaying a high conductivity with sufficient reproducibility.

Similar to the standard σ_{ion} , the reproducibility score was predicted from the medians of explanatory variables (Supplementary Figure 25b). The R^2 values (around 0.5 for both training and testing) became smaller than for the standard case (over 0.8) because of the loss of sample-dependent information (e.g., thickness), but the value was high enough for the following SHAP value analysis

SHAP values indicated that the essential factor for conductivity and reproducibility was sufficient heating (Supplementary Figure 25c and d). Higher scores were observed when a specific heating process (typically, 300°C or 160°C for 30 min) and annealing before measurement were included. The heating was preferred, which induced appropriate molecular interactions among polymer, acceptor, and salt (e.g., LiFTFSI melts at around 110°C). A proper donor/acceptor/salt ratio was also critical to forming percolating pathways in the ion-conducting amorphous phase.

The SHAP analysis indicated the critical effects of component ratio to form conductive pathways in the electrolyte layers. In addition, the authors believe that the selection of molecules is essential. Lower molecular weight of the salt increased the conductivity; this corresponded mainly to using LiFTFSI instead of LiTFSI. The asymmetrical LiFTFSI molecule readily formed the amorphous phase. Similarly, PPO had much higher scores than PMPS (Supplementary Figure 25a). One technical reason could be the difficulty in mixing. Poly(phenylene sulfide) species underwent curing (cross-linking) reactions at high temperatures, which resulted in the formation of solid blocks of the materials.

In contrast, PPO, which is a viscous fluid at high temperatures, was easy to mix with acceptors and salts, enabling greater electrolyte homogeneity. There were no major differences between chloranil and benzoquinone as acceptors, but 2,3-dichloro-5,6-dicyano-*p*-benzoquinone yielded the lowest conductivity and produced a broad ^7Li NMR spectrum (Supplementary Figure 16). Slight differences in molecular-level interactions with salts (e.g., Supplementary Figure 8), also affect the conductivity and reproducibility. We are currently conducting research into these molecular interactions.

According to the scores in Supplementary Figure 25a, one of the best electrolyte conditions was OLM60-41HG, which was a mixture of PPO/chloranil = 60/40 (mol/mol) with about 40 wt % LiTFSI. The electrolyte was milled over 150 min in total, which was also essential for achieving dense packing of the electrolyte particles. Actual room temperature ionic conductivity was as high as 0.3 to 0.8 mS/cm, whereas a non-optimized PMPS-chloranil-LiTFSI (SLD80-57LO) electrolyte suffered from an excessive variation of σ_{ion} (10^{-10} to 10^{-3} S/cm, Figure 2c).

Supplementary Discussion i: Battery analysis

A lithium-ion battery with a LiFePO_4 cathode and a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode was examined with a PPO/benzoquinone = 8/2 with 53 wt % LiTFSI electrolyte. A redox wave was observed at $E_{1/2} \cong 1.9$ V, corresponding to the formal voltage (Supplementary Figure 26a). The areal discharging capacities were 0.34, 0.36, 0.35, and 0.27 mAh/cm² at 0.1, 0.2, 0.5, and 1 C, respectively, compared with the formal capacity of 1.5 mAh/cm² (1 C corresponded to a current of 1.18 mA, Supplementary Figure 26b). The experimental values were smaller than the theoretical value owing to the incomplete ionic conduction throughout electrodes; thus, the electrode fabrication should be optimized in future work.

The ohmic resistance of the cell, R_{DC} , was estimated by extracting the charging plateau voltages, defined as the values at 30% of the experimental charging capacities (Supplementary Figure 26c).

From the slope, the resistance was estimated to be 270 Ω , which was used for the following transference number analysis.

After the rate tests, the cell was repeatedly charged/discharged at 0.05 C (Supplementary Figure 26d). The discharging capacity decreased gradually from 0.36 to 0.20 mAh/cm² over 30 cycles. The side reactions of the electrolyte and electrode caused this decrease. Further analysis is required to understand the capacity decrease and low Coulombic efficiencies (60%–95%) for practical applications.

Because the electrolytes were not highly stable to lithium, the Li⁺ transference number was estimated from the battery results. The estimation was achieved by comparing the DC (charge/discharge) and AC (EIS) resistances of the electrolyte (Supplementary Figure 26e).

The ohmic resistance during the charge/discharge measurements, R_{DC} , should consist mainly of lithium migration resistance R_{Li} and other battery resistances, such as electrode resistance, R_{el} ($R_{DC} = R_{Li} + R_{el}$). The active carrier was only Li⁺ during the charge/discharge of the lithium-ion battery. However, ionic conductivity resistance, R_{ion} , during the ESI measurement consisted of both Li⁺ and anion resistances ($1/R_{ion} = 1/R_{Li} + 1/R_{anion}$). According to the definition, Li⁺ transference t_{Li} is

$$\left(\frac{\text{conductance of Li}^+}{\text{conductance of Li}^+ + \text{conductance of anion}} \right) = \frac{1/R_{Li}}{1/R_{ion}} = \frac{1/(R_{DC} - R_{el})}{1/R_{ion}} = \frac{R_{ion}}{R_{DC} - R_{el}} \text{ (Supplementary Figure 26f).}$$

The overvoltages of plateaus increased linearly along with the higher charging rates because of the ohmic resistance, R_{DC} , of the cell, which was estimated to be 270 Ω . At the same time, R_{ion} was evaluated to be 211 Ω by impedance measurements. Therefore, the estimated transference number t_{Li} was $270/(211 - R_{el}) = 0.78$ with $R_{el} = 0$. Considering $R_{el} > 0$, the actual t_{Li} was more than 0.8.

Supplementary Tables

Supplementary Table 1. Representative process fingerprints and their meanings.^a

ID	Fingerprint ^b	Typical meaning
1	temperature-Heat-mix-with-spatula Petri-dish-Cool-Heat-Refill	Heat the sample and mix with a spatula. Then, cool or heat it.
2	Heat-temperature-300°C-30min-160°C Heat-Cool-Petri-dish-	Heat the sample at typical temperatures of 300 or 160°C for 30 min. Then, cool it.
3	Heat-temperature-200°C-30min-20min Petri-dish-Heat-Stirr-	Heat the sample at a typical temperature of 200°C for 20 or 30 min. Then, heat it.
4	Ball-mill-frequency-50Hz-30min CT-complex-Measure-particle-size	Ball mill the sample with a typical frequency of 50 Hz for 30 min. Then, measure particle size.
5	sample-temperature-CT-complex-Seal Heat-Fill-Ball-mill-and	Prepare a charge-transfer complex and conduct additional steps (e.g., sealing, heating, and ball milling).
6	Ball-mill-frequency-50Hz-60min Cool-Select-cell-Fill-sample	After cooling, ball mill the sample with a typical frequency of 50 Hz for 60 min. Then, fill a cell with it.
7	Weigh-Set-environment- Ball-mill-Set-environment-Fill	Weigh sample, ball milling, etc.
8	sample-Carry-out-from-glove Ball-mill-Weigh-Seal-Measure	Remove a cell from a glove box. Then, measure it.
9	temperature-Measure-machine-AMF-20N-EIS Break-vacuum-pack-Carry-out	Anneal a cell in an incubator (AMF-20N) and open vacuum pack before measurement.
10	Ball-mill-frequency-50Hz-60min Cool-Grind-Ball-mill-Wash	Ball mill the sample with a typical frequency of 50 Hz for 60 min. Then, conduct additional steps (e.g., cooling, grinding, and ball milling).
11	temperature-machine-AMF-20N-Measure-EIS Carry-out-from-glove-box	Remove a cell from a glove box and anneal it in an incubator (AMF-20N).
12	sample-Fill-fill-into-Disassemble Cool-Carry-out-from-glove	Fill an NMR tube with a sample and remove it from the glove box.
13	Ball-mill-frequency-50Hz-30min Mix-Petri-dish-Cool-Carry	Ball mill the sample with a typical frequency of 50 Hz for 30 min. Then, conduct some additional steps
14	Fill-sample-fill-into-tube Carry-out-from-glove-box	Fill an NMR tube with a sample and remove it from the glove box.
15	Measure-Carry-out-from-glove Seal-Ball-mill-Fill-sample	Remove the sample from the glove box, followed by filling and sealing a cell.
16	temperature-Leave-rt-Seal-wrap Seal-glove-box-Carry-out	After sealing, keep the cell in a glove box for some time before removing it.
17	Ball-mill-frequency-50Hz-15min Ball-mill-Select-cell-Fill	Ball mill the sample with a typical frequency of 50 Hz for 15 min. Then, conduct some additional steps
18	Break-vacuum-pack-Transport-to Leave-Cool-Dry-Measure-EIS	Open vacuum pack containing a cell, and measure impedance.
19	Add-Cool-anode-cathode-electrolyte Add-electrolyte-Transport-to-glove	Add cathode, anode, and electrolyte to fabricate a cell.

^a Full data are available in Supplementary Data. ^b The original fingerprints were automatically grouped by BERT and *k*NN models, and frequently used words were extracted. Expression of “AAA|BBB” indicates that a representative step “AAA” neighbours “BBB”.

Supplementary Table 2. Major parameters for analyzing electrolytes.

Parameter	Unit	Explanation
d_{std}	μm	Standard deviation of particle diameters (estimated by optical microscopy)
d_{50}	μm	Median of particle diameters (estimated by optical microscopy)
1st day (Unix)	-	Date of electrolyte preparation (Unix time)
2nd day (Unix)	-	Date of cell fabrication for impedance measurement (Unix time)
Acceptor MW	-	The molecular weight of the acceptor molecule
Acceptor amount	mg	Actual amount of acceptor forming a charge-transfer complex
Acceptor ratio	-	Estimated molar ratio of acceptor in an electrolyte, considering acceptor sublimation
CT complex amount	mg	Actual amount of charge-transfer complex mixed with the salt
Cell ID	-	Solid-state cell equipment ID, which was uniquely numbered in the project (same model number)
DSC melting temperature	$^{\circ}\text{C}$	Melting temperature of salt estimated by DSC
DSC crystallinity	%	Estimated crystallinity of salt, calculated from melting enthalpy (assuming pristine salt exhibited 100% crystallinity)
DSC melting enthalpy	J/g	Melting enthalpy of salt estimated by DSC
Date difference	-	Second day (Unix) minus first day (Unix)
Dew point (1st day)	$^{\circ}\text{C}$	Dew point in the glove box during electrolyte preparation
Dew point (2nd day)	$^{\circ}\text{C}$	Dew point in the glove box during cell fabrication
Donor MW	-	Molecular weight of the donor molecule (polymer)
Donor amount	mg	Actual amount of a donor forming the charge-transfer complex
Donor ratio	-	Estimated molar ratio of a donor in an electrolyte, considering acceptor sublimation
F (MAS): δ	ppm	Chemical shift of ^{19}F peak during solid-state MAS NMR
F (MAS): FWHM	ppm	FWHM of ^{19}F peak during solid-state MAS NMR
F (static): δ	ppm	Chemical shift of ^{19}F peak during solid-state static NMR
F (static): FWHM	ppm	FWHM of ^{19}F peak during solid-state static NMR
Formal donor/acceptor ratio	-	Molar ratio of donor and acceptor molecules, ignoring acceptor sublimation
Formal acceptor ratio	-	Estimated molar ratio of a donor in an electrolyte, ignoring acceptor sublimation
Formal donor ratio	-	Estimated molar ratio of a donor in an electrolyte, ignoring acceptor sublimation

Formal salt ratio	-	Estimated molar ratio of salt in an electrolyte, ignoring acceptor sublimation
Li (MAS): δ	ppm	Chemical shift of ^7Li peak during solid-state MAS NMR
Li (MAS): FWHM	ppm	FWHM of ^7Li peak during solid-state MAS NMR
Li (static): δ	ppm	Chemical shift of ^7Li peak during solid-state static NMR
Li (static): FWHM	ppm	FWHM of ^7Li peak during solid-state static NMR
O ₂ (1st day)	ppm	O ₂ concentration in the glove box during electrolyte preparation
O ₂ (2nd day)	ppm	O ₂ concentration in the glove box during cell fabrication
Salt MW	-	Molecular weight of the salt molecule
Salt amount	mg	Actual amount of salt forming a charge-transfer complex
Salt ratio	-	Estimated molar ratio of salt in an electrolyte, considering acceptor sublimation
Salt weight ratio	-	Actual weight ratio of salt in the electrolyte
Temperature of σ_{ion}	°C	Measurement temperature of σ_{ion}
Thickness	μm	Electrolyte thickness
Total ball milling time	min	Total ball milling time to prepare the electrolyte
Total heating time	min	Total heating time to prepare the electrolyte

Supplementary Figures

a)

Impedance measurement

b)

Cell fabrication procedure

c)

Supplementary Figure 1 | Examples of graph-shaped data, describing experimental procedures.

a, Electrolyte preparation. **b**, Impedance measurement. **c**, Cell fabrication. Corresponding graphml files are available from the public repository.

Supplementary Figure 2 | Scheme for processing fingerprints. First, original experimental text was collected from the graph nodes. The text was vectorized by BERT and grouped by a *k*NN model. Frequently used words were extracted to express each fingerprint (FP1, FP2, ...).

Manual fit by
equivalent circuits
(R or RC parallel)

Calculate σ_{ion}
from resistance R

a)

Manual detection
of melting peaks

Extract **melting point**
and its **enthalpy**
(estimate **crystallinity**
from heat)

b)

Peak-background
separation

Calculate **signal**
peak and
background
areas

c)

Detect peaks
(**peak position**)

Calculate **FWHM**

d)

VFT fit

Extract fitting
parameters
(T_K , B , σ_0)

e)

Supplementary Figure 3 | Schemes to extract descriptors from experimental data. **a**, Impedance spectrum. **b**, DSC. **c**, XRD. **d**, Solid-state ^7Li and ^{19}F NMR. **e**, Temperature dependence of conductivity. **f**, Particle size. **g**, Chemical structures.

Supplementary Figure 4 | Relationships between conductivity and primary fingerprints of experimental steps.

Supplementary Figure 5 | Relationships between conductivity and experimental descriptors (excluding fingerprint). Blue plots show values imputed by a machine learning model.

Supplementary Figure 6 | Particle size estimation. **a**, Optical microscopy and estimated diameter distribution of sample particles. A charge-transfer complex of PMPS/chloranil = 2/1 was processed by a ball mill. **b**, Relationship between the median diameter of particles and total ball milling time during electrolyte preparation. Blue plots show values imputed by a machine learning model. **c**, Plots for the standard deviation of diameter.

Supplementary Figure 7 | Decision plot for the SHAP values. A related figure is shown in Figure 3d.

Supplementary Figure 8 | Optimized geometry of model molecules with LiTFSI, estimated by DFT calculations. a, Pristine salt. **b,** PEG. **c,** Chloranil. **d,** PPO. **e,** PPO/chloranil. **f,** PMPS. **g,** PMPS/chloranil.

a)

b)

c)

Supplementary Figure 9 | Interaction parameters estimated by DFT calculations. a, Average distances of lithium and its neighbouring two oxygen atoms in LiFTFSI. **b,** Mulliken charge of lithium atoms. **c,** Stabilisation energy compared with the cases where the solvents were sufficiently far from the salts.

Supplementary Figure 10 | SEM image and elemental mapping of PPO/chloranil = 6/4 (mol/mol) with 40 wt % LiFTFSI electrolyte.

a)

b)

c)

d)

e)

f)

Supplementary Figure 11 | Solid-state MAS ^{13}C -NMR spectra of samples. **a**, PPO/chloranil = 60/40 (mol/mol) with LiTFSI, charge-transfer complex (donor/acceptor = 80/20), and PPO. **b**, **c**, Enlargement of the spectra in **a**. **d**, Results for PPO/chloranil = 80/20 with LiTFSI. **e**, **f**, Enlargement of the spectra in **d**.

a)

b)

c)

d)

e)

f)

Supplementary Figure 12 | DSC curves of samples. a, Pristine salts. Solid and dashed lines represent the first and second cycles, respectively. **b,** Results for the low-temperature region. LiTFSI electrolytes **c,** with small melting peaks and **d,** with detectable peaks. **e,** LiTFSI electrolytes. **f,** LiBF₄ and LiFSI electrolytes. The scan rate was 20°C/min. Detection of T_g peaks of salts was difficult with electrolytes because of the fluctuating baselines for the polymers.

a)

b)

c)

Supplementary Figure 13 | XRD spectra of samples measured at room temperature. The samples were named using the format “XXX-NNY”, where XXX was the electrolyte measured at NN°C by method Y (I: intense beam; P: parallel beam). **a**, Pristine salts and charge-transfer complex. **b**, LiTFSI electrolytes. **c**, LiFTFSI electrolytes.

a)

b)

c)

d)

Supplementary Figure 14 | Temperature dependence of XRD spectra. **a**, PPO/chloranil = 60/40 with 20 wt % LiTFSI. **b**, PPO/chloranil = 60/40 with 31 wt % LiTFSI. **c**, Pristine LiTFSI. **d**, PPO/chloranil = 80/20 with 24 wt % LiTFSI.

Supplementary Figure 15 | Relationship between salt weight ratio and signal peak areas in XRD spectra. The signals of PPO/chloranil/LiTFSI electrolytes in Supplementary Figure 13b were analyzed.

a)

b)

Supplementary Figure 16 | Solid-state ^7Li MAS NMR spectra of samples. a, LiTFSI electrolytes.

b, LiTFSI electrolytes.

Supplementary Figure 17 | Solid-state ^7Li NMR spectra of samples. NMR tubes did not rotate during the measurements (static measurements).

a)

b)

c)

Supplementary Figure 18 | Solid-state ^{19}F MAS NMR spectra of samples. a, LiTFSI electrolytes. **b,** LiTFSI electrolytes. **c,** LiBF₄ and its electrolyte (no peaks were detected for the electrolyte).

Supplementary Figure 19 | Solid-state ^{19}F NMR spectra of LiFTFSI samples. NMR tubes did not rotate during the measurements (static measurements).

a)

b)

c)

d)

e)

Supplementary Figure 20 | Relaxation time estimation of by solid-state NMR. a, ⁷Li NMR spectra for OLM60-31, OLM60-40, OQM79-30 and LiFTFSI with different temperatures. **b,** ¹⁹F NMR Spectra. **c,** FWHM of ⁷Li peaks. **d,** Arrhenius plots of T_1 relaxation time for ⁷Li. **e,** Arrhenius plots for ¹⁹F. Circle and triangle plots correspond to the broad (ca. -120 ppm) and sharp (ca. -80 ppm) CF₃ peaks, respectively.

a)

b)

c)

d)

Supplementary Figure 21 | Temperature dependence analysis of electrolytes. a, Conductivity versus temperature. Blue plots and solid lines show experimental and VFT fitting results. Fittings with significant errors are shown in red. **b,** Estimated apparent activation energy (B) with successful fittings. **c,** Kauzmann temperature (T_K). **d,** Prefactor (σ_0).

Supplementary Figure 22 | Molecular dynamics simulation of crystalline and amorphous LiFTFSI. a, Molecular structures before/after calculation. Positions of representative lithium atoms are shown in the figures. **b,** MSD of lithium and fluorine atoms in different phases.

Supplementary Figure 23 | Assumed anion exchange reaction induced by the addition of molten salts.

a)

b)

S-61

c)

Supplementary Figure 24 | ^1H NMR spectra of Deuterated DMSO containing electrolytes. a, Pristine DMSO. **b,** DMSO containing the SLD67-56 electrolyte kept in a cell in a glove box. **c,** DMSO containing the SLD67-56 electrolyte kept in a solid-state cell in air for 5 days.

a)

b)

d)

Supplementary Figure 25 | Prediction of conductivity scores instead of $\log \sigma_{\text{ion}}$. The scores were defined as the median of $\log \sigma_{\text{ion}}$ minus its standard deviation. **a**, Scores for each electrolyte. **b**, Predicted and experimental values. **c**, SHAP values for the prediction model. **d**, Decision plot.

a)

b)

c)

d)

e)

f)

Supplementary Figure 26 | Properties of a prototype solid-state lithium-ion battery. **a**, Cyclic voltammogram scanned at 0.5 mV/s. **b**, Charge/discharge curves at different rates. **c**, Plateau voltages during charging. Voltages at 30% of the experimental capacity were plotted. When applied current ΔI increased, overvoltage ΔV increased according to Ohm's law ($\Delta V = \Delta I R_{DC}$). **d**, Charge/discharge curves at 0.05 C with different cycles. **e**, EIS spectrum of the cell after cycling. Blue captions show the measurement frequencies. The first partial semicircle was attributed to ionic conduction. **f**, Equivalent circuits for DC and AC measurements. Only lithium cations moved during the charge/discharge processes of the cell ($R_{anion} = \infty$). All electrochemical measurements were conducted at 50 °C.