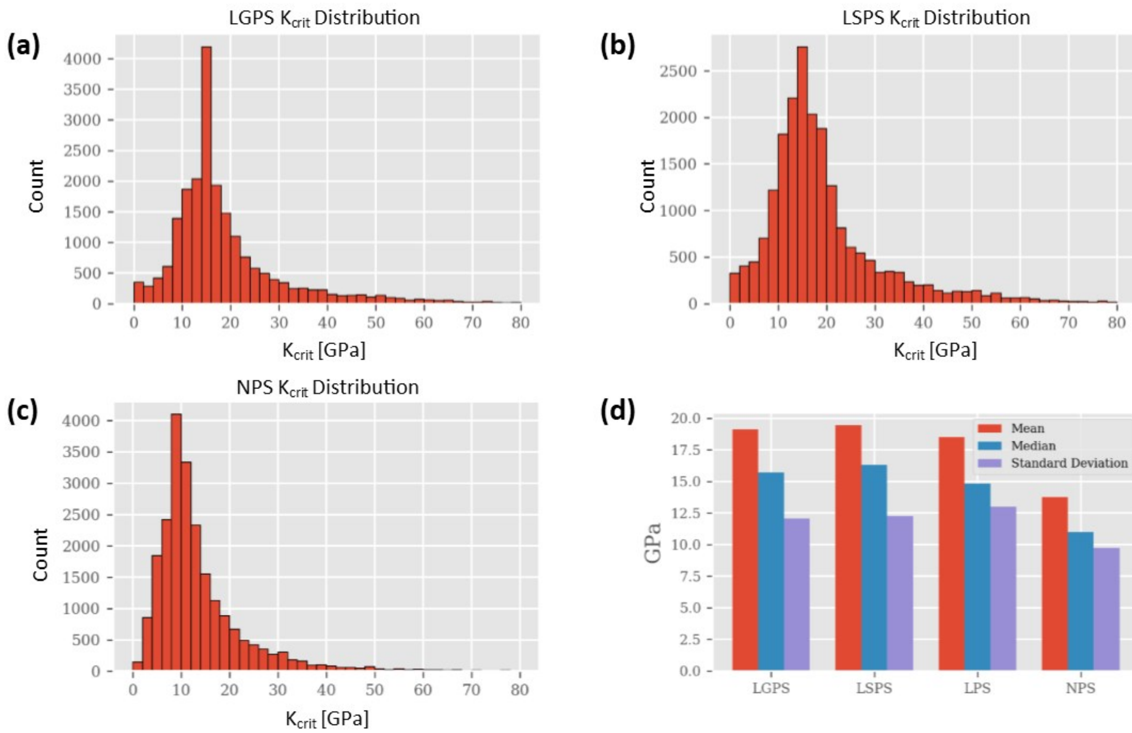
Supplementary Information for "Solid-Electrolyte-Interphase Design in Constrained Ensemble for Solid-State Batteries"

William Fitzhugh[a,*], Xi Chen[a,*], Yichao Wang[a], Luhan Ye[a], Xin Li[a,1]

[a] John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States



Supplementary Figure 1. Statistical behavior of interface K_{crit} at 4V. (a-c) The distribution of K_{crit} for binary pseudo-phases where one of the interfacing materials is LGPS, LSPS, NPS, respectively. **(d)** Statistical figures of merit for each four SSE distributions.

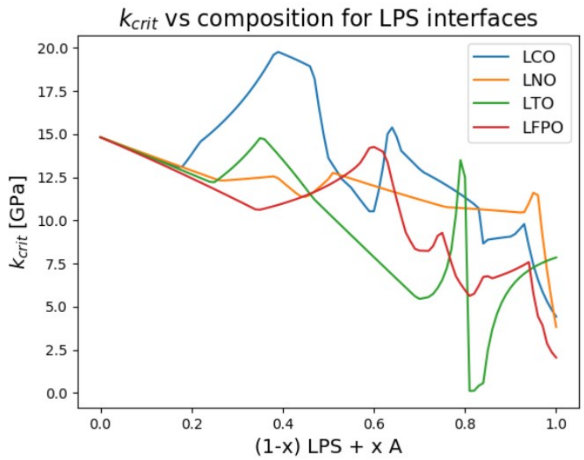
---

1. Corresponding author.

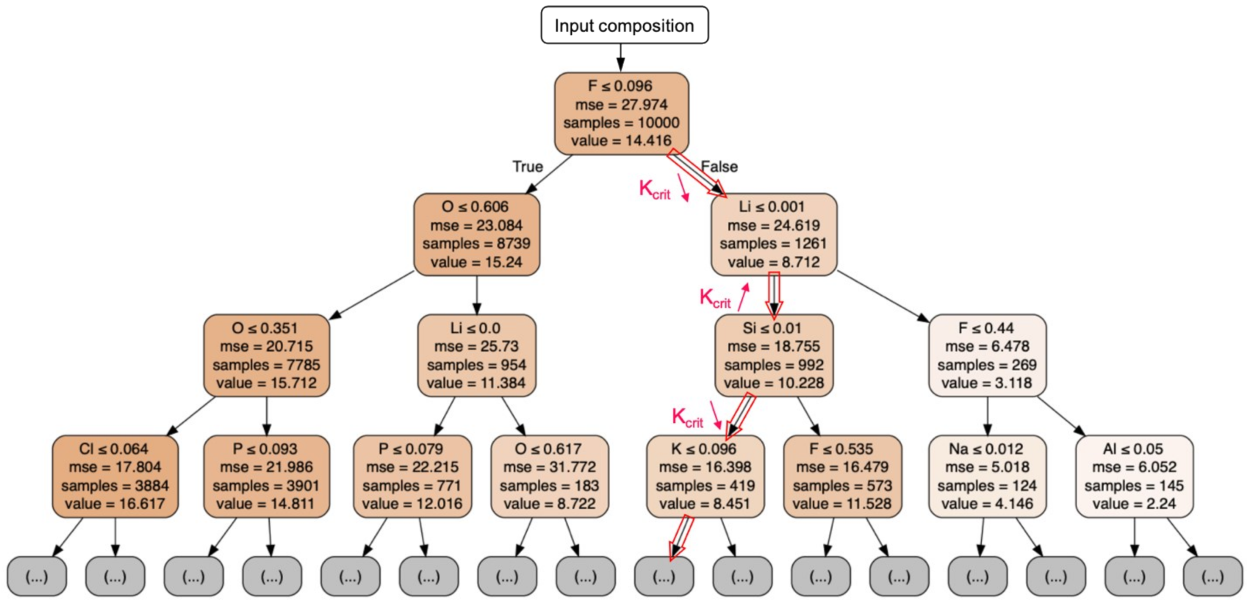
*. Equal contribution.

E-mail address: lixin@seas.harvard.edu (Xin Li).

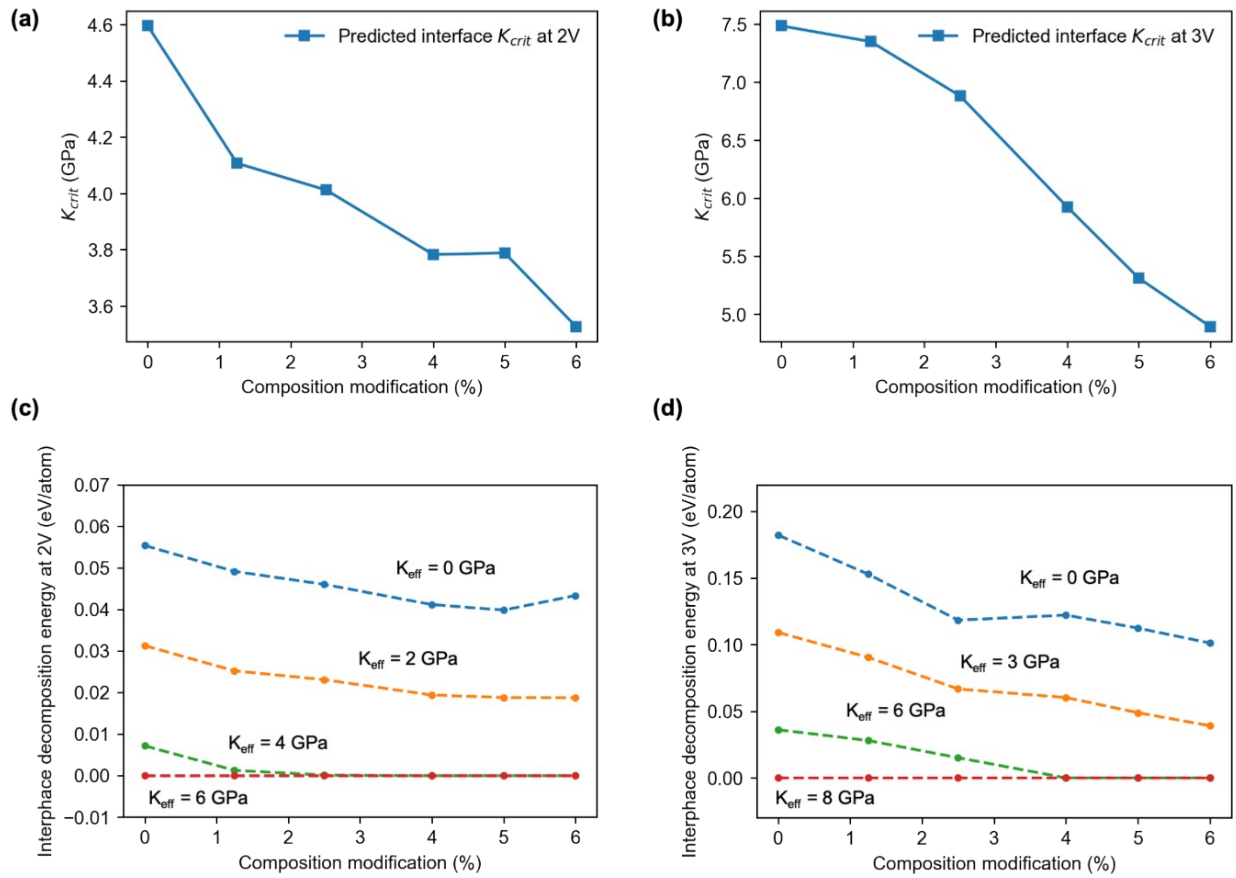
Phone: (617) 496-3075



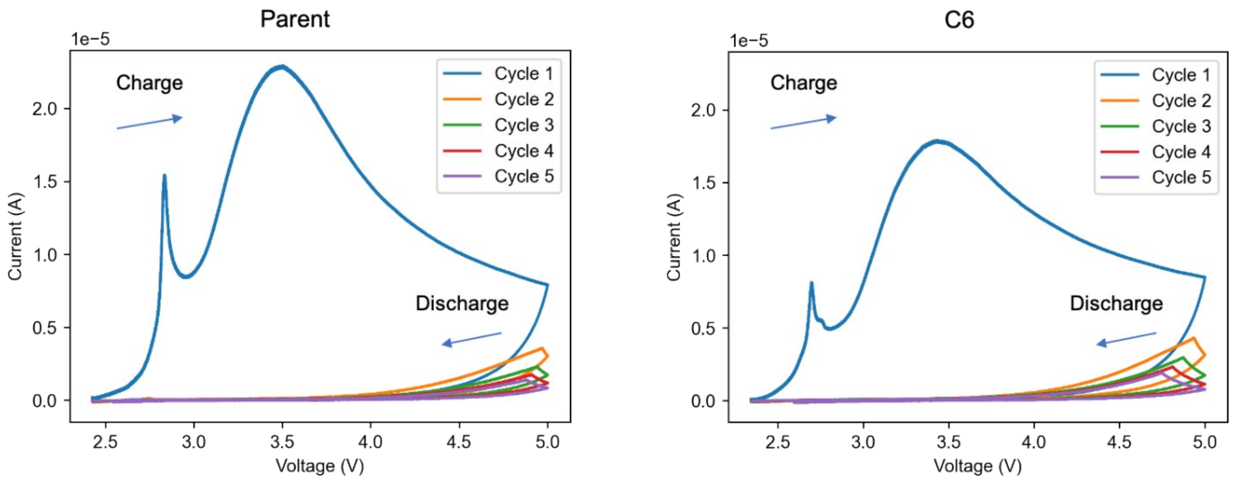
Supplementary Figure 2. Oscillatory nature of K_{crit}. Four one dimensional slices of the K_{crit} vs composition manifold show the oscillatory nature of K_{crit}. In practice, optimizing the composition to minimize K_{crit} is non-trivial as this oscillatory nature is compounded in the 117 degree of freedom (number of elements minus one) composition space.



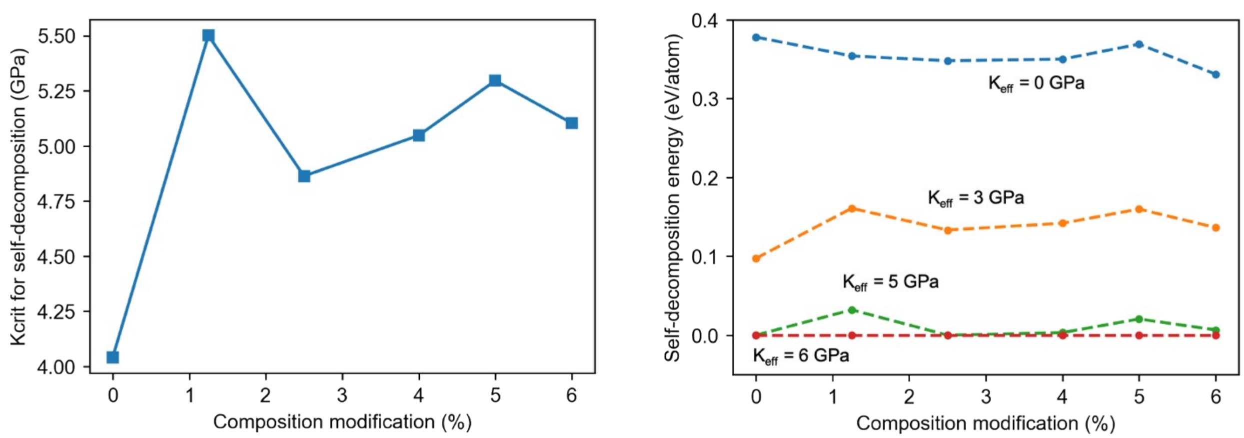
Supplementary Figure 3. Structure and mechanism of decision trees. The figure shows one of the 50 members of the decision tree ensemble. The decision tree is formed by a hierarchy of nodes, with the composition as input features and K_{crit} as output. Each node has a criterion to determine how the information flows through the tree. An example of information flow is illustrated with red arrows and if the specific flow is with a K_{crit} increase ($K_{crit}\uparrow$) or decrease ($K_{crit}\downarrow$). Apart from the decision criteria, other information that helps to balance the tree and regularize training are also shown in each node. At the beginning, criteria are randomly initialized. Both the feature and threshold of each criterion will be updated during training to minimize errors. Those nodes with darker [lighter] node background correspond to features with higher [lower] predicted value of K_{crit} for the given input. The precise value of the coloring represents the average value of all instances below that node. While each node corresponds to the evaluation of a single element, each element may be evaluated many times throughout the tree. Thus, each tree represents an approximate mapping of the K_{crit} manifold. The ensemble then performs a weighted average of the predicted manifolds for the final value.



Supplementary Figure 4. Interface decomposition energy and K_{crit} at 2V and 3V with composition modification. (a, b) Predicted K_{crit} of coating materials at the interface to LGPS electrolyte at 2V (a) and 3V (b) versus the parent (0%) and modified glass coatings (1.25, 2.5, 4, 5, 6%). **(c, d)** Predicted interface decomposition energy to LGPS at 2V (c) and 3V (d) versus the parent (0%) and modified glass coatings (1.25, 2.5, 4, 5, 6%) at different K_{eff}.



Supplementary Figure 5. CV test for the parent glass (left) and modified child glass C6 (right) for the first 5 cycles. The charge curve lies above the discharge curve for each cycle.



Supplementary Figure 6. Predicted K_{crit} for self-decomposition energy (left) and predicted self-decomposition energy at different K_{eff} (right) at 3.5V for the parent glass and 5 modified child glasses.

Table 1. Results from decision tree optimization of known sulfide glass SSE's. Each child allows various levels of composition change from the parent compound as indicated by the constraint. A 95% constraint allows for up to 5% change in each element's fractional composition. All compositions are normalized to 1 atom per formula unit. The constraint is in some cases approximate, as changing the composition of one element will affect the composition of other elements, resulting in, for example, the final amount of changes slightly exceeding 5% (10%) in the 95% (90%) constraint group. The predicted K_{crit} is at the 4V interface to LSPS sulfide electrolyte.

Parent Glass			Child A (C 5) (95% Constraint)		Child B (C 10) (90% Constraint)		Child C (C 100) (0% Constraint)	
Formula	Conductivity/ mS cm^{-1} (ref)	K_{crit} /GPa	Formula	K_{crit}/ GPa	Formula	K_{crit}/ GPa	Formula	K_{crit}/ GPa
$Li_{0.364}P_{0.110}S_{0.388}I_{0.138}$	1.7 [1]	16.07	$Li_{0.324}O_{0.04}F$-$_{0.042}P_{0.098}S_{0.346}Cl_{0.026}I_{0.123}$	12.07	$Li_{0.306}O_{0.014}F$-$_{0.090}P_{0.093}S_{0.324}Cl_{0.002}Br_{0.03}Sb_{0.024}I_{0.115}$	6.89	$Li_{0.141}O_{0.375}F_{0.282}P_{0.01}S_{0.14}I_{0.053}$	2.05
$Li_{0.338}B_{0.169}S_{0.351}I_{0.143}$	0.2 [2]	15.7	$Li_{0.335}B_{0.135}O_{0.019}F_{0.047}S_{0.322}Cl_{0.002}I_{0.142}$	11.23	$Li_{0.322}B_{0.069}F_{0.102}P_{0.015}S_{0.275}Br_{0.042}Sb_{0.038}I_{0.136}$	5.46	$Li_{0.113}B_{0.010}O_{0.323}F_{0.282}S_{0.138}Cl_{0.010}I_{0.048}Bi_{0.076}$	1.90
$Li_{0.431}Si_{0.092}S_{0.323}I_{0.154}$	0.04 [3]	17.74	$Li_{0.369}O_{0.033}F_{0.041}Si_{0.067}P_{0.039}S_{0.274}Cl_{0.044}I_{0.132}$	12.45	$Li_{0.406}F_{0.103}Si_{0.004}P_{0.015}S_{0.273}Cl_{0.001}Sb_{0.053}I_{0.145}$	5.49	$Li_{0.149}O_{0.336}F_{0.321}S_{0.140}I_{0.053}$	2.19
$Li_{0.423}O_{0.013}Si_{0.118}P_{0.003}S_{0.443}$	0.12 [4]	17.4	$Li_{0.362}O_{0.033}F_{0.043}Si_{0.068}P_{0.003}S_{0.394}Cl_{0.046}Br_{0.045}Pb_{0.006}$	11.78	$Li_{0.376}O_{0.093}F_{0.082}Si_{0.019}P_{0.003}S_{0.355}Cl_{0.059}K_{0.001}Sb_{0.012}$	7.51	$Li_{0.123}O_{0.288}F_{0.281}P_{0.001}S_{0.149}Cl_{0.008}Ti_{0.150}$	2.11
$Li_{0.333}S_{0.500}Ge_{0.167}$	0.15-0.5 [5,6]	15.57	$Li_{0.300}O_{0.033}F_{0.043}S_{0.449}Cl_{0.025}Ge_{0.150}$	10.75	$Li_{0.312}O_{0.002}F_{0.090}S_{0.398}Cl_{0.008}Ge_{0.111}Br_{0.040}Sb_{0.013}I_{0.022}Pb_{0.004}$	5.93	$Li_{0.078}O_{0.348}F_{0.285}P_{0.017}S_{0.117}Ge_{0.009}Bi_{0.145}$	1.56
$Li_{0.333}Si_{0.167}S_{0.500}$	0.27 [4]	15.2	$Li_{0.275}O_{0.035}F_{0.041}Si_{0.140}S_{0.413}Cl_{0.042}Br_{0.012}Pb_{0.041}$	11.22	$Li_{0.266}O_{0.065}F_{0.068}Si_{0.125}S_{0.399}Cl_{0.064}Br_{0.005}Sb_{0.009}$	8.66	$Li_{0.083}O_{0.367}F_{0.375}P_{0.018}S_{0.124}Cl_{0.033}$	1.86
$Li_{0.400}Si_{0.133}S_{0.467}$	1.0 [7]	16.51	$Li_{0.341}O_{0.049}F_{0.043}Si_{0.133}S_{0.398}Cl_{0.025}Br_{0.004}Pb_{0.004}$	11.66	$Li_{0.338}O_{0.065}F_{0.072}Si_{0.063}S_{0.394}Cl_{0.068}$	9.49	$Li_{0.147}O_{0.365}F_{0.301}S_{0.177}Cl_{0.010}$	2.21
$Li_{0.370}Si_{0.130}S_{0.389}Cl_{0.111}$	0.05 [8]	13.57	$Li_{0.334}O_{0.048}F_{0.021}Si_{0.081}S_{0.415}Cl_{0.100}$	10.47	$Li_{0.287}O_{0.096}F_{0.083}Si_{0.132}P_{0.011}S_{0.305}Cl_{0.086}$	8.98	$Li_{0.070}O_{0.188}F_{0.317}Si_{0.025}S_{0.074}Cl_{0.021}Br_{0.306}$	2.27
$Li_{0.406}O_{0.061}Si_{0.130}S_{0.403}$	0.1 [1]	15.24	$Li_{0.297}O_{0.092}F_{0.039}Si_{0.125}S_{0.349}Cl_{0.037}Br_{0.025}Pb_{0.036}$	10.68	$Li_{0.332}O_{0.093}F_{0.069}Si_{0.030}S_{0.330}Cl_{0.061}K_{0.001}Zn_{0.044}Br_{0.040}$	8.86	$Li_{0.223}O_{0.040}F_{0.445}Si_{0.070}S_{0.222}$	1.90
$Li_{0.425}O_{0.013}Si_{0.121}S_{0.441}$	0.3 [9]	16.62	$Li_{0.355}O_{0.055}F_{0.040}Si_{0.127}S_{0.399}Cl_{0.025}$	11.82	$Li_{0.364}O_{0.078}F_{0.077}Si_{0.023}S_{0.378}Cl_{0.080}$	9.00	$Li_{0.129}N_{0.156}O_{0.257}F_{0.291}Si_{0.006}P_{0.010}S_{0.131}Cl_{0.020}$	1.81

Table 2. Results of the predicted K_{crit} at the 4V interface to LGPS sulfide electrolyte. The K_{crit} shows a similar decreasing trend from parent to child A, to B and to C.

Parent Glass			Child A (C 5) (95% Constraint)		Child B (C 10) (90% Constraint)		Child C (C 100) (0% Constraint)	
Formula	**Conductivity/ mS cm^{-1} (ref)**	**K_{crit} /GPa**	**Formula**	**K_{crit}/ GPa**	**Formula**	**K_{crit}/ GPa**	**Formula**	**K_{crit}/ GPa**
$Li_{0.364}P_{0.110}S_{0.388}I_{0.138}$	1.7 [1]	13.31	$Li_{0.280}O_{0.021}F_{0.042}P_{0.085}S_{0.417}Cl_{0.048}I_{0.106}$	7.60	$Li_{0.319}O_{0.021}F_{0.105}P_{0.010}S_{0.387}Cl_{0.099}K_{0.018}I_{0.040}$	3.88	$Li_{0.128}C_{0.011}N_{0.115}F_{0.508}P_{0.022}S_{0.137}K_{0.030}I_{0.049}$	1.36
$Li_{0.338}B_{0.169}S_{0.351}I_{0.143}$	0.2 [2]	12.62	$Li_{0.345}B_{0.119}O_{0.008}F_{0.037}P_{0.037}S_{0.308}I_{0.146}$	9.23	$Li_{0.316}B_{0.177}N_{0.008}F_{0.092}S_{0.274}I_{0.133}$	6.89	$Li_{0.100}B_{0.050}O_{0.199}F_{0.466}S_{0.104}Ni_{0.038}I_{0.042}$	2.83
$Li_{0.431}Si_{0.092}S_{0.323}I_{0.154}$	0.04 [3]	12.77	$Li_{0.417}O_{0.013}F_{0.029}Si_{0.120}S_{0.272}I_{0.149}$	7.75	$Li_{0.337}N_{0.035}O_{0.080}F_{0.079}P_{0.080}S_{0.252}I_{0.138}$	5.50	$Li_{0.137}N_{0.010}O_{0.220}F_{0.461}P_{0.020}S_{0.103}I_{0.049}$	2.13
$Li_{0.423}O_{0.013}Si_{0.118}P_{0.003}S_{0.443}$	0.12 [4]	13.35	$Li_{0.451}O_{0.010}F_{0.054}Si_{0.078}S_{0.408}$	8.58	$Li_{0.348}N_{0.065}F_{0.094}S_{0.394}Cl_{0.075}K_{0.006}$	4.71	$Li_{0.117}O_{0.247}F_{0.453}Si_{0.040}P_{0.019}S_{0.123}$	2.10
$Li_{0.333}S_{0.500}Ge_{0.167}$	0.15-0.5 [5,6]	14.54	$Li_{0.272}Ni_{0.034}O_{0.030}F_{0.042}P_{0.021}S_{0.444}Cl_{0.042}Ge_{0.115}$	9.25	$Li_{0.294}O_{0.052}F_{0.091}P_{0.040}S_{0.406}Ge_{0.117}$	6.77	$Li_{0.051}N_{0.267}O_{0.520}F_{0.054}P_{0.098}Ge_{0.010}$	2.05
$Li_{0.333}Si_{0.167}S_{0.500}$	0.27 [4]	13.56	$Li_{0.314}O_{0.031}F_{0.048}Si_{0.148}S_{0.459}$	8.90	$Li_{0.299}O_{0.001}F_{0.091}Si_{0.206}S_{0.403}$	6.02	$Li_{0.088}O_{0.257}F_{0.453}Si_{0.050}S_{0.132}$	2.09
$Li_{0.400}Si_{0.133}S_{0.467}$	1.0 [7]	13.68	$Li_{0.387}O_{0.010}F_{0.049}Si_{0.083}P_{0.035}S_{0.435}$	8.68	$Li_{0.416}O_{0.009}F_{0.105}Si_{0.103}S_{0.367}$	5.74	$Li_{0.106}O_{0.257}F_{0.454}Si_{0.040}P_{0.020}S_{0.124}$	2.10
$Li_{0.370}Si_{0.130}S_{0.389}Cl_{0.111}$	0.05 [8]	9.61	$Li_{0.359}O_{0.013}F_{0.050}Si_{0.089}P_{0.033}S_{0.349}Cl_{0.108}$	6.26	$Li_{0.330}O_{0.017}F_{0.096}Si_{0.115}P_{0.016}S_{0.327}Cl_{0.099}$	4.18	$H_{0.011}Li_{0.125}N_{0.012}O_{0.011}F_{0.579}P_{0.026}S_{0.131}Cl_{0.037}Ni_{0.025}Br_{0.043}$	1.80
$Li_{0.406}O_{0.061}Si_{0.130}S_{0.403}$	0.1 [1]	13.45	$Li_{0.376}O_{0.068}F_{0.051}Si_{0.081}P_{0.035}S_{0.355}Cl_{0.034}$	7.63	$H_{0.003}Li_{0.288}O_{0.068}F_{0.067}Si_{0.180}P_{0.078}S_{0.219}Cl_{0.096}$	4.62	$Li_{0.329}F_{0.516}Si_{0.070}P_{0.021}S_{0.065}$	1.04
$Li_{0.425}O_{0.013}Si_{0.121}S_{0.441}$	0.3 [9]	13.35	$Li_{0.458}O_{0.010}F_{0.054}Si_{0.071}S_{0.407}$	8.59	$Li_{0.390}F_{0.103}Si_{0.023}S_{0.376}Cl_{0.105}Ge_{0.003}$	4.15	$Li_{0.118}O_{0.247}F_{0.453}Si_{0.040}P_{0.019}S_{0.122}$	2.10

References

1. Mercier, R., Malugani, J. P., Fahys, B. & Robert, G. Superionic conduction in Li2S - P2S5 - LiI - glasses. *Solid State Ionics* **5**, 663–666 (1981).

2. Aotani, N., Iwamoto, K., Takada, K. & Kondo, S. Synthesis and electrochemical properties of lithium ion conductive glass, Li3PO4Li2SSiS2. *Solid State Ionics* **68**, 35–39 (1994).

3. Ribes, M., Barrau, B. & Souquet, J. L. Sulfide glasses: Glass forming region, structure and ionic conduction of glasses in Na2SXS2 (XSi; Ge), Na2SP2S5 and Li2SGeS2 systems. *J. Non. Cryst. Solids* **38**–**39**, 271–276 (1980).

4. Kennedy, J., Sahami, S., Shea, S. & Zhang, Z. Preparation and conductivity measurements of SiS2□Li2S glasses doped with LiBr and LiCl. *Solid State Ionics* **18**–**19**, 368–371 (1986).

5. Morimoto, H., Yamashita, H., Tatsumisago, M. & Minami, T. Mechanochemical Synthesis of New Amorphous Materials of 60Li2S·40SiS2 with High Lithium Ion Conductivity. *J. Am. Ceram. Soc.* **82**, 1352–1354 (2004).

6. Pradel, A. & Ribes, M. Electrical properties of lithium conductive silicon sulfide glasses prepared by twin roller quenching. *Solid State Ionics* **18**–**19**, 351–355 (1986).

7. Hirai, K., Tatsumisago, M. & Minami, T. Thermal and electrical properties of rapidly quenched glasses in the systems Li2S-SiS2-LixMOy (LixMOy = Li4SiO4, Li2SO4). *Solid State Ionics* **78**, 269–273 (1995).

8. Tatsumisago, M. & Hayashi, A. Superionic glasses and glass–ceramics in the Li2S–P2S5 system for all-solid-state lithium secondary batteries. *Solid State Ionics* **225**, 342–345 (2012).

9. Sakuda, A., Hayashi, A. & Tatsumisago, M. Sulfide Solid Electrolyte with Favorable Mechanical Property for All-Solid-State Lithium Battery. *Sci. Rep.* **3**, 2261 (2013).