Supplementary materials for the manuscript

Stability and ionic mobility in argyrodite-related lithium-ion solid electrolytes

Chen Haomin, Chen Maohua and Stefan Adams

1. Program calculating critical reaction from inputted formation energies

The windows command line version of program and its source code is zipped and stored in another supplementary material "critical_reaction_v0.1-cmd.zip". To use the program, unzip the file and execute file "critical_reaction_v0.1.exe" from command line by:

```
> critical_reaction_v0.1.exe sample.txt
```

where "sample.txt" can be replaced by any other text file containing correctly formatted input. Results will be displayed in the console output.

To get instructions on how to prepare sample input:

```
> critical_reaction_v0.1.exe –h
```

To generate a sample input file (which is also included as "sample.txt" by default):

```
> critical_reaction_v0.1.exe –s
```

Binaries on other platforms can be compiled from "critical_reaction_v0.1.c" if properly linking to GLPK libraries (version 4.55 or above). Or you may write to us for binaries on Linux platforms.

2. Scaling formulas for conversion of site energy barriers to predicted activation energies

Table S1 Scaling formulas used in calculating activation energies for mobile cations in various systems.

System	Scaling formula
Default	$E = 0.5 \times E_{unscaled}$
Li-O	$E = 0.479 \times E_{unscaled}$
Li-S	$E = 0.535 \times E_{unscaled}$
Cu-S	$E = 0.516 \times E_{unscaled}$
Na-S	$E = 0.415 \times E_{unscaled}^{2/3}$

3. Structural stability

The following tables provide detailed results of the structural stability calculations dicussed in the manuscript.

Table S2 Structural stability of $Li_{12-m-x}M^{m+}S_{6-x}X_x$ (in units of eV/atom) as shown in Fig. 2.

x	0	1	2
M=Si, X=Cl, argyrodite	-0.022	-0.013	-0.102
M=Si, X=Br, argyrodite	-0.022	-0.001	-0.067
M=Si, X=I, argyrodite	-0.022	0.002	-0.048
M=Ge, X=Cl, argyrodite	-0.029	-0.023	-0.115
M=Ge, X=Br, argyrodite	-0.029	-0.011	-0.076
M=Ge, X=I, argyrodite	-0.029	-0.006	-0.052
M=Sn, X=Cl, argyrodite	-0.058	-0.043	-0.143
M=Sn, X=Br, argyrodite	-0.058	-0.035	-0.093
M=Sn, X=I, argyrodite	-0.058	-0.030	-0.058
M=Si, X=Cl, $NaHg_2$	-0.074	-0.056	-0.008
M=Si, X=Br, $NaHg_2$	-0.074	-0.047	-0.008
M=Si, X=I, $NaHg_2$	-0.074	-0.060	-0.035
M=Ge, X=Cl, $NaHg_2$	-0.078	-0.062	-0.014

M=Ge, X=Br, $NaHg_2$	-0.078	-0.046	-0.013
M=Ge, X=I, $NaHg_2$	-0.078	-0.064	-0.036
M=Sn, X=Cl, $NaHg_2$	-0.067	-0.082	-0.029
M=Sn, X=Br, $NaHg_2$	-0.067	-0.066	-0.024
M=Sn, X=I, $NaHg_2$	-0.067	-0.084	-0.032
M=P, X=Cl, argyrodite	-0.026	-0.026	-0.032
M=P, X=Br, argyrodite	-0.026	-0.030	-0.031
M=P, X=I, argyrodite	-0.026	-0.018	-0.043
M=As, X=Cl, argyrodite	-0.038	-0.037	-0.047
M=As, X=Br, argyrodite	-0.038	-0.035	-0.036
M=As, X=I, argyrodite	-0.038	-0.022	-0.044
M=P, X=Cl, NaHg2	-0.072	-0.033	-0.033
M=P, X=Br, NaHg2	-0.072	-0.031	-0.032
M=P, X=I, NaHg2	-0.072	-0.041	-0.044
M=As, X=Cl, NaHg2	-0.077	-0.042	-0.043
M=As, X=Br, NaHg2	-0.077	-0.041	-0.038
M=As, X=I, NaHg2	-0.077	-0.047	-0.044

Table S3 Structural stability of $A_{7-x}PS_{6-x}X_x$ (in units of eV/atom) as shown in Fig. 10.

x	0	1	2
A=Li, X=Cl, argyrodite	-0.026	-0.026	-0.032
A=Li, X=Br, argyrodite	-0.026	-0.030	-0.031
A=Li, X=I, argyrodite	-0.026	-0.018	-0.043
A=Na, X=Cl, argyrodite	-0.028	-0.043	-0.051
A=Na, X=Br, argyrodite	-0.028	-0.047	-0.056
A=Na, X=I, argyrodite	-0.028	-0.039	-0.046
A=Cu, X=Cl, argyrodite	-0.053	-0.018	-0.013
A=Cu, X=Br, argyrodite	-0.053	-0.021	-0.017
A=Cu, X=I, argyrodite	-0.053	-0.028	-0.051
A=Li, X=Cl, $NaHg_2$	-0.072	-0.033	-0.033
A=Li, X=Br, $NaHg_2$	-0.072	-0.031	-0.032
A=Li, X=I, $NaHg_2$	-0.072	-0.041	-0.044
A=Na, X=Cl, $NaHg_2$	-0.057	-0.024	-0.042
A=Na, X=Br, $NaHg_2$	-0.057	-0.020	-0.037
A=Na, X=I, $NaHg_2$	-0.057	-0.021	-0.032
A=Cu, X=Cl, $NaHg_2$	-0.101	-0.068	-0.023
A=Cu, X=Br, $NaHg_2$	-0.101	-0.076	-0.041
A=Cu, X=I, $NaHg_2$	-0.101	-0.084	-0.079

Table S4 Structural stability of $Li_{7-x}PY_{6-x}X_x$ (in units of eV/atom) as shown in Fig. 14.

x	0	1	2
Y=O, X=Cl, argyrodite		-0.009	
Y=O, X=Br, argyrodite		0.006	
Y=S, X=Cl, argyrodite	-0.026	-0.026	-0.032
Y=S, X=Br, argyrodite	-0.026	-0.030	-0.031
Y=S, X=I, argyrodite	-0.026	-0.018	-0.043
Y=Se, X=Cl, argyrodite	-0.031	-0.043	-0.040
Y=Se, X=Br, argyrodite	-0.031	-0.037	-0.032
Y=Se, X=I, argyrodite	-0.031	-0.039	-0.041
Y=Te, X=Cl, argyrodite	-0.087	-0.103	-0.103
Y=Te, X=Br, argyrodite	-0.087	-0.089	-0.093
Y=Te, X=I, argyrodite	-0.087	-0.093	-0.095
Y=S, X=Cl, $NaHg_2$	-0.072	-0.033	-0.033

Y=S, X=Br, $NaHg_2$	-0.072	-0.031	-0.032
Y=S, X=I, $NaHg_2$	-0.072	-0.041	-0.044
Y=Se, X=Cl, $NaHg_2$	-0.067	-0.043	-0.042
Y=Se, X=Br, $NaHg_2$	-0.067	-0.036	-0.035
Y=Se, X=I, $NaHg_2$	-0.067	-0.039	-0.041
Y=Te, X=Cl, $NaHg_2$	-0.103	-0.116	-0.116
Y=Te, X=Br, $NaHg_2$	-0.103	-0.104	-0.105
Y=Te, X=I, $NaHg_2$	-0.103	-0.096	-0.107

Table S5 Structural stability of $Li_{12-m-x}M^{m+}S_{6-x}X_x$ (in units of eV/atom) as a function of degree of anion site-inversion as shown in Fig. 3, 11 and 15.

	0%	25%	50%	75%	100%
Li_6PS_5Cl	-0.081	-0.026	-0.032	-0.047	-0.265
Li_6PS_5Br	-0.049	-0.030	-0.030	-0.051	-0.278
Li_6PS_5I	-0.020	-0.018	-0.034	-0.059	-0.314
Li_6AsS_5Cl	-0.088	-0.037	-0.040	-0.057	-0.276
Li_6AsS_5Br	-0.055	-0.036	-0.035	-0.056	-0.282
Li_6AsS_5I	-0.025	-0.022	-0.035	-0.059	-0.302
Li_7SiS_5Cl	-0.013	-0.021	-0.023	-0.018	-0.013
Li_7SiS_5Br	-0.001	-0.011	-0.020	-0.015	-0.010
Li_7SiS_5I	0.002	-0.011	-0.018	-0.016	-0.013
Li_7GeS_5Cl	-0.023	-0.031	-0.036	-0.026	-0.024
Li_7GeS_5Br	-0.011	-0.021	-0.025	-0.025	-0.015
Li_7GeS_5I	-0.006	-0.019	-0.024	-0.023	-0.019
Li_7SnS_5Cl	-0.054	-0.059	-0.046	-0.051	-0.043
Li_7SnS_5Br	-0.038	-0.045	-0.035	-0.039	-0.037
Li_7SnS_5I	-0.030	-0.041	-0.043	-0.041	-0.031
Na_6PS_5Cl	-0.110	-0.043	-0.054	-0.063	-0.253
Na_6PS_5Br	-0.082	-0.060	-0.047	-0.058	-0.268
Na_6PS_5I	-0.049	-0.039	-0.044	-0.075	-0.299
Cu_6PS_5Cl	-0.032	-0.018	-0.033	-0.047	-0.324
Cu_6PS_5Br	-0.021	-0.027	-0.030	-0.040	-0.332
Cu_6PS_5I	-0.028	-0.028	-0.039	-0.051	-0.346
Li_6PSe_5Cl	-0.118	-0.043	-0.043	-0.055	-0.260
Li_6PSe_5Br	-0.088	-0.049	-0.037	-0.050	-0.267
Li_6PSe_5I	-0.055	-0.039	-0.051	-0.051	-0.289
Li_6PTe_5Cl	-0.234	-0.103	-0.104	-0.116	-0.289
Li_6PTe_5Br	-0.196	-0.089	-0.097	-0.110	-0.289
Li_6PTe_5I	-0.159	-0.093	-0.099	-0.106	-0.303
Li_6PO_5Cl	-0.009	-0.388	-0.621	-0.933	-0.457
Li_6PO_5Br	0.006	-0.315	-0.322	-0.993	-1.327

Table S6 Structural stability of Li_6PS_5Br four-fold supercell (in units of eV/atom) as a function of degree of anion site-inversion as shown by open triangles in Fig. 3(a).

Site-inversion	Dissociation energy
0.00%	-0.049
6.25%	-0.017
12.50%	-0.021
18.75%	-0.019
25.00%	-0.023
31.25%	-0.022
37.50%	-0.026
43.75%	-0.027

50.00%	-0.031
56.25%	-0.031
62.50%	-0.034
68.75%	-0.032
75.00%	-0.034
81.25%	-0.037
87.50%	-0.032
93.75%	-0.030
100.00%	-0.279

4. Hydrolysis stability

Table S7 Hydrolysis stability of $Li_{12-m-x}M^{m+}S_{2-x}X_x$ (in units of eV/atom) as shown in Fig. 4.

	Li_7MS_6	Li_6MS_5Cl	Li_6MS_5Br	Li_6MS_5I	$Li_5MS_4Cl_2$	$Li_5MS_4Br_2$	$Li_5MS_4I_2$
M=P	-0.324	-0.303	-0.306	-0.295	-0.284	-0.283	-0.295
M=As	-0.166	-0.131	-0.130	-0.116	-0.101	-0.090	-0.098
M=Si	-0.292	-0.262	-0.250	-0.246	-0.326	-0.290	-0.272
M=Ge	-0.161	-0.123	-0.111	-0.106	-0.178	-0.139	-0.116
M=Sn	-0.198	-0.152	-0.144	-0.139	-0.216	-0.166	-0.131

Table S8 Hydrolysis stability of $A_{7-x}PS_{6-x}X_x$ (in units of eV/atom) as shown in Fig. 12.

	A_7PS_6	A_6PS_5Cl	A_6PS_5Br	A_6PS_5I	$A_5PS_4Cl_2$	$A_5PS_4Br_2$	$A_5PS_4I_2$
A=Li	-0.324	-0.303	-0.306	-0.295	-0.284	-0.283	-0.295
A=Na	-0.142	-0.165	-0.169	-0.161	-0.182	-0.187	-0.177
A=Cu	-0.053	-0.018	-0.021	-0.028	-0.013	-0.017	-0.051

Table S9 Hydrolysis stability of $Li_{7-x}PY_{6-x}X_x$ (in units of eV/atom) as shown in Fig. 16.

	Li_7PY_6	Li_6PY_5Cl	Li_6PY_5Br	Li_6PY_5I	$Li_5PY_4Cl_2$	$Li_5PY_4Br_2$	$Li_5PY_4I_2$
Y=S	-0.324	-0.303	-0.306	-0.295	-0.284	-0.283	-0.295
Y=Se	-0.322	-0.316	-0.311	-0.313	-0.293	-0.285	-0.294
Y=Te	-0.590	-0.553	-0.540	-0.543	-0.492	-0.483	-0.485
Y=O		-0.106	-0.092				

5. Activation energy

Table S10 Activation energy for Li^+ migration in $Li_{12-m-x}M^{m+}S_{2-x}X_x$ (in units of eV) as shown in Fig. 5.

x	0	1	2
M=Si, X=Cl, argyrodite	0.318	0.243	0.602
M=Si, X=Br, argyrodite	0.318	0.256	0.714
M=Si, X=I, argyrodite	0.318	0.441	0.827
M=Ge, X=Cl, argyrodite	0.287	0.233	0.597
M=Ge, X=Br, argyrodite	0.287	0.265	0.720
M=Ge, X=I, argyrodite	0.287	0.334	0.853
M=Sn, X=Cl, argyrodite	0.393	0.243	0.548
M=Sn, X=Br, argyrodite	0.393	0.243	0.736
M=Sn, X=I, argyrodite	0.393	0.286	0.891
M=P, X=Cl, argyrodite	0.302	0.366	0.484
M=P, X=Br, argyrodite	0.302	0.425	0.607
M=P, X=I, argyrodite	0.302	0.527	0.821

M=As, X=Cl, argyrodite	0.340	0.201	0.548
M=As, X=Br, argyrodite	0.340	0.236	0.522
M=As, X=I, argyrodite	0.340	0.457	0.773
M=Si, X=Cl, $NaHg_2$	0.209	0.408	0.409
M=Si, X=Br, $NaHg_2$	0.209	0.393	0.559
M=Si, X=I, $NaHg_2$	0.209	0.495	0.671
M=Ge, X=Cl, $NaHg_2$	0.220	0.473	0.404
M=Ge, X=Br, $NaHg_2$	0.220	0.393	0.500
M=Ge, X=I, $NaHg_2$	0.220	0.499	0.645
M=Sn, X=Cl, $NaHg_2$	0.366	0.601	0.361
M=Sn, X=Br, $NaHg_2$	0.366	0.542	0.393
M=Sn, X=I, $NaHg_2$	0.366	0.564	0.607
M=P, X=Cl, $NaHg_2$	0.260	0.227	0.511
M=P, X=Br, $NaHg_2$	0.260	0.238	0.586
M=P, X=I, $NaHg_2$	0.260	0.291	0.693
M=As, X=Cl, $NaHg_2$	0.222	0.286	0.532
M=As, X=Br, $NaHg_2$	0.222	0.318	0.570
M=As, X=I, $NaHg_2$	0.222	0.334	0.559

Table S11 Activation energy for mobile cation A^+ migration in $A_{7-x}PS_{6-x}X_x$ (in units of eV) as shown in Fig. 13.

x	0	1	2
A=Li, X=Cl, argyrodite	0.302	0.366	0.484
A=Li, X=Br, argyrodite	0.302	0.425	0.607
A=Li, X=I, argyrodite	0.302	0.527	0.821
A=Na, X=Cl, argyrodite	0.326	0.246	0.341
A=Na, X=Br, argyrodite	0.326	0.267	0.344
A=Na, X=I, argyrodite	0.326	0.300	0.402
A=Cu, X=Cl, argyrodite	0.302	0.441	0.529
A=Cu, X=Br, argyrodite	0.302	0.446	0.555
A=Cu, X=I, argyrodite	0.302	0.446	0.581
A=Li, X=Cl, $NaHg_2$	0.260	0.227	0.511
A=Li, X=Br, $NaHg_2$	0.260	0.238	0.586
A=Li, X=I, $NaHg_2$	0.260	0.291	0.693
A=Na, X=Cl, $NaHg_2$	0.356	0.263	0.410
A=Na, X=Br, $NaHg_2$	0.356	0.303	0.427
A=Na, X=I, $NaHg_2$	0.356	0.341	0.480
A=Cu, X=Cl, $NaHg_2$	0.242	0.177	0.286
A=Cu, X=Br, $NaHg_2$	0.242	0.198	0.322
A=Cu, X=I, $NaHg_2$	0.242	0.234	0.400

Table S12 Activation energy for Li^+ migration in $Li_{7-x}PY_{6-x}X_x$ (in units of eV) as shown in Fig. 17.

x	0	1	2
Y=O, X=Cl		0.529	
Y=O, X=Br		0.611	
Y=S, X=Cl	0.302	0.366	0.484
Y=S, X=Br	0.302	0.425	0.607
Y=S, X=I	0.302	0.527	0.821
Y=Se, X=Cl, argyrodite	0.438	0.178	0.478
Y=Se, X=Br, argyrodite	0.438	0.208	0.438

Y=Se, X=I, argyrodite	0.438	0.288	0.493
Y=Te, X=Cl, argyrodite	0.533	0.233	0.493
Y=Te, X=Br, argyrodite	0.533	0.208	0.448
Y=Te, X=I, argyrodite	0.533	0.233	0.628
M=P, X=Cl, $NaHg_2$	0.260	0.227	0.511
M=P, X=Br, $NaHg_2$	0.260	0.238	0.586
M=P, X=I, $NaHg_2$	0.260	0.291	0.693
Y=Se, X=Cl, $NaHg_2$	0.378	0.368	0.432
Y=Se, X=Br, $NaHg_2$	0.378	0.352	0.613
Y=Se, X=I, $NaHg_2$	0.378	0.337	0.471
Y=Te, X=Cl, $NaHg_2$	0.533	0.828	0.346
Y=Te, X=Br, $NaHg_2$	0.533	0.863	0.477
Y=Te, X=I, $NaHg_2$	0.533	0.818	0.624

Table S13 Activation energy for Li^+ migration in Li_6PS_5Br four-fold supercell (in units of eV) as a function of degree of anion site-inversion as shown in Fig. 6.

Site-inversion	1D	2D	3D
0.00%	0.431	0.431	0.431
6.25%	0.490	0.500	0.500
12.50%	0.554	0.554	0.570
18.75%	0.463	0.580	0.580
25.00%	0.527	0.613	0.623
31.25%	0.543	0.570	0.580
37.50%	0.516	0.554	0.559
43.75%	0.484	0.511	0.570
50.00%	0.409	0.441	0.447
56.25%	0.447	0.516	0.591
62.50%	0.490	0.564	0.570
68.75%	0.538	0.554	0.580
75.00%	0.548	0.602	0.623
81.25%	0.554	0.575	0.602
87.50%	0.607	0.607	0.639
93.75%	0.548	0.570	0.591
100.00%	0.415	0.415	0.415