Supporting Information

Se-doped Li_6PS_5Cl and $Li_{5.5}PS_{4.5}Cl_{1.5}$ with improved ionic conductivity and interfacial compatibility: a high-throughput DFT study

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Table S1. Atomic occupancy in Li_6PS_5Cl and $Li_{5.5}PS_{4.5}Cl_{1.5}$.

Atom	Wyckoff Position	Occupancy (Li_6PS_5Cl)	Occupancy ($Li_{5.5}PS_{4.5}Cl_{1.5}$)
Li_1	*48h*	0.456	0.440
P_1	*4b*	1.000	1.000
Cl_1	*4a*	0.615	0.370
S_1	*4a*	0.385	0.630
Cl_2	*4d*	0.834	0.630
S_2	*4d*	0.166	0.370
S_3	*16e*	0.618	1.000

Table S2. Total energy and lattice parameter of Li_6PS_5Cl obtained from DFT calculations. The most stable structure is indicated in bold.

Structure ID.	Total energy (eV)	Lattice constant (Å)			Degree (°)		
		a	b	c	α	β	γ
1	-215.62	9.91	10.08	10.02	89.92	88.12	89.82
2	-216.05	10.03	9.91	9.89	90.19	89.78	90.45
3	-216.27	9.88	9.95	9.98	89.97	91.54	90.63
4	-216.42	9.97	9.92	9.98	89.89	89.18	90.48
5	-216.25	10.06	9.89	9.99	89.04	89.58	90.36
6	-216.18	10.04	9.97	9.94	89.25	88.69	87.14
7	**-216.87**	**9.98**	**9.96**	**9.92**	**90.77**	**89.53**	**90.68**
8	-216.41	9.92	9.89	9.91	88.94	88.74	89.30
9	-216.03	9.93	9.94	10.09	89.05	88.64	88.02
10	-216.21	9.97	10.05	9.85	89.22	88.99	89.37

Table S3. Total energy and lattice parameter of $Li_{5.5}PS_{4.5}Cl_{1.5}$ obtained from DFT calculations. The most stable structure is indicated in bold.

Structure ID.	Total energy (eV)	Lattice constant (Å)			Degree (°)		
		a	b	c	α	β	γ
1	-203.63	10.18	9.92	9.86	89.46	92.02	89.32
2	-203.45	9.87	10.08	10.21	91.53	89.82	90.64
3	**-203.72**	**9.82**	**10.03**	**10.03**	**90.24**	**88.88**	**89.74**
4	-203.71	10.17	9.79	9.88	89.52	91.99	88.35
5	-203.39	9.99	9.74	10.08	87.64	90.86	90.07
6	-203.34	9.79	10.06	9.88	89.26	89.14	88.83
7	-203.49	9.85	10.02	9.99	89.04	90.19	89.50
8	-202.17	9.88	9.91	9.93	89.55	91.92	91.97
9	-203.15	10.17	9.81	9.86	89.15	90.05	89.07
10	-202.34	9.91	9.92	9.86	90.04	89.20	88.89

Table S4. Total energy of $Li_6PS_{5-x}Se_xCl$ (x = 1 ~ 4) obtained from DFT calculations. The most stable structure for each Se-doped Li_6PS_5Cl is indicated in bold.

Structure ID.	Total energy (eV)			
	Li_6PS_4SeCl	$Li_6PS_3Se_2Cl$	$Li_6PS_2Se_3Cl$	Li_6PS_4SeCl
1	-212.56	-208.15	-204.96	**-201.27**
2	-212.94	-208.99	-204.98	-201.15
3	-212.73	-208.66	-204.91	-201.09
4	212.76	-208.53	-204.95	-200.89
5	-212.83	-208.96	-205.05	-201.09
6	-212.28	-208.59	-204.82	-201.29
7	-212.87	-208.90	-204.88	-201.08
8	-212.82	-208.84	-204.91	-201.12
9	**-213.09**	**-209.05**	**-205.27**	-201.09
10	-212.80	-208.88	-204.92	-201.22

Table S5. Total energy of $Li_{5.5}PS_{4.5-x}Se_xCl_{1.5}$ (x=1 ~ 3) obtained from DFT calculations. The most stable structure for each Se-doped $Li_{5.5}PS_{4.5}Cl_{1.5}$ is indicated in bold.

Structure ID.	Total energy (eV)		
	$Li_6PS_{3.5}SeCl$	$Li_6PS_{2.5}Se_2Cl$	$Li_6PS_{1.5}Se_3Cl$
1	-199.77	-195.97	-192.61
2	-200.18	**-196.63**	-192.61
3	**-200.26**	-196.33	-192.55
4	-200.01	-196.28	-192.36
5	-199.92	-196.12	-192.11
6	-200.02	-196.42	-192.51
7	-199.75	-196.33	-192.17
8	-199.74	-196.12	-192.36
9	-199.76	-196.22	**-192.66**
10	-199.73	-195.81	-191.88

Table S6. Lattice parameter of the most stable $Li_6PS_{5-x}Se_xCl$ (x = 1 ~ 4) structures.

	Li_6PS_4SeCl	$Li_6PS_3Se_2Cl$	$Li_6PS_2Se_3Cl$	Li_6PSSe_4Cl
a (Å)	10.20	10.32	10.67	10.68
b (Å)	10.22	10.66	10.05	10.25
c (Å)	10.27	10.11	10.70	10.92
α (°)	90.14	90.21	92.13	90.30
β (°)	88.18	86.90	90.00	90.30
γ (°)	92.09	90.57	90.00	92.64
V (Å^3)	1069.09	1110.71	1146.05	1193.13

Table S7. The lattice parameter of the most stable $Li_{5.5}PS_{4.5-x}Se_xCl_{1.5}$ (x = 1 ~ 3) structure.

	$Li_{5.5}PS_{3.5}SeCl_{1.5}$	$Li_{5.5}PS_{2.5}Se_2Cl_{1.5}$	$Li_{5.5}PS_{1.5}Se_3Cl_{1.5}$
a (Å)	9.90	9.97	10.11
b (Å)	10.14	10.27	10.34
c (Å)	10.08	10.22	10.39
α (°)	89.95	90.01	89.79
β (°)	89.66	89.62	89.67
γ (°)	90.22	90.24	89.41
V (Å^3)	1012.06	1045.94	1085.29

Table S8. Phase equilibria and reaction energy (ΔE_D) of $Li_6PS_{5-x}Se_xCl$ ($x = 0 \sim 4$) at the interface with $LiCoO_2$ and $Li_{0.5}CoO_2$.

C_{SSE}	$C_{electrode}$	x_m	Phase equilibria at x_m	ΔE_D (meV/atom)
Li_6PS_5Cl	$LiCoO_2$	0.53	LiCl, Li_3PO_4, Co_9S_8, Li_2SO_4, Li_2S	-302.12
	$Li_{0.5}CoO_2$	0.51	Li_2SO_4, Co_9S_8, Li_3PO_4, LiCl, Li_2S	-434.98
Li_6PS_4SeCl	$LiCoO_2$	0.57	Li_2S, Co_9S_8, LiCl, Li_2SO_4, $CoSe_2$, Li_3PO_4	-302.24
	$Li_{0.5}CoO_2$	0.51	Co_9S_8, Li_3PO_4, LiCl, Li_2SO_4, Li_2S, Li_2Se	-434.98
$Li_6PS_3Se_2Cl$	$LiCoO_2$	0.61	Co_9S_8, Li_2S, Li_3PO4, $CoSe_2$, LiCl, Li_2SO_4	-310.77
	$Li_{0.5}CoO_2$	0.53	Li_2SO_4, Li_3PO_4, Co_9S_8, LiCl, Co_3Se_4, Li_2Se	-434.87
$Li_6PS_2Se_3Cl$	$LiCoO_2$	0.62	Li_2S, Co_9S_8, Li_2Se, Li_3PO_4, $CoSe_2$, LiCl	-319.45
	$Li_{0.5}CoO_2$	0.55	LiCl, Co_9S_8, Co_3Se_4, Li_2Se, Li_2SO_4, Li_3PO_4	-433.68
Li_6PSSe_4Cl	$LiCoO_2$	0.62	$CoSe_2$, Li_2S, LiCl, Li_2Se, Co_9S_8, Li_3PO_4	-328.28
	$Li_{0.5}CoO_2$	0.51	Li_2SO_4, Li_3PO_4, Co_9S_8, Co_9Se_8, LiCl, Li_2Se	-432.70

Table S9. Phase equilibria and reaction energy (ΔE_D) of $Li_{5.5}PS_{4.5-x}Se_xCl_{1.5}$ (x = 0 ~ 3) at the interface with $LiCoO_2$ and $Li_{0.5}CoO_2$.

C_{SSE}	$C_{electrode}$	x_m	Phase equilibria at x_m	ΔE_D (meV/atom)
$Li_{5.5}PS_{4.5}Cl_{1.5}$	$LiCoO_2$	0.52	LiCl, Li_2S, Li_2SO_4, Co_9S_8, Li_3PO_4	-308.41
	$Li_{0.5}CoO_2$	0.50	Li_3PO_4, Co_9S_8, Li_2S, LiCl, Li_2SO_4	-443.75
$Li_{5.5}PS_{3.5}SeCl_{1.5}$	$LiCoO_2$	0.56	$CoSe_2$, Co_9S_8, Li_2SO_4, Li_2S, LiCl, Li_3PO_4	-312.97
	$Li_{0.5}CoO_2$	0.52	$CoSe_2$, Li_3PO_4, Li_2Se, Li_2SO_4, Co_9S_8, LiCl	-444.35
$Li_{5.5}PS_{2.5}Se_2Cl_{1.5}$	$LiCoO_2$	0.60	$CoSe_2$, LiCl, Li_2SO_4, Co_9S_8, Li_2S, Li_3PO_4	-322.69
	$Li_{0.5}CoO_2$	0.55	LiCl, Li_3PO_4, $CoSe_2$, Li_2SO_4, Li_2Se, Co_9S_8	-443.70
$Li_{5.5}PS_{1.5}Se_3Cl_{1.5}$	$LiCoO_2$	0.61	$CoSe_2$, Li_3PO_4, Li_2Se, Li_2S, LiCl, Co_9S_8	-332.08
	$Li_{0.5}CoO_2$	0.59	Co_9S_8, LiCl, $CoSe_2$, Li_2SO_4, Li_2Se	-443.10

Table S10. Phase equilibria and reaction energy (ΔE_D) of $Li_6PS_{5-x}Se_xCl$ (x = 0 ~ 4) at the interface with $LiFePO_4$ and $FePO_4$.

C_{SSE}	$C_{electrode}$	x_m	Phase equilibria at x_m	ΔE_D (meV/atom)
Li_6PS_5Cl	$LiFePO_4$	0.39	Li_3PO_4, FePS, $Li_4P_2O_7$, LiCl, FeS_2	-99.75
	$FePO_4$	0.45	LiCl, FeS_2, $Li_4P_2O_7$, FePS, $LiPO_3$	-196.86
Li_6PS_4SeCl	$LiFePO_4$	0.43	FePS, Se, $FeSe_2$, Li_3PO_4, FeS_2, LiCl	-101.73
	$FePO_4$	0.45	$FeSe_2$, LiCl, $LiPO_3$, FeS_2, FePS, $Li_4P_2O_7$	-196.53
$Li_6PS_3Se_2Cl$	$LiFePO_4$	0.43	FeS_2, FePS, $FeSe_2$, LiCl, Li_3PO_4, Se	-107.28
	$FePO_4$	0.45	FeS_2, $FeSe_2$, $Li_4P_2O_7$, FePS, LiCl, $LiPO_3$	-202.34
$Li_6PS_2Se_3Cl$	$LiFePO_4$	0.43	LiCl, FeS_2, FePS, $FeSe_2$, Se, Li_3PO_4	-112.83
	$FePO_4$	0.50	FeS_2, Se, $FeSe_2$, LiCl, $Li_4P_2O_7$, FePS	-208.47
Li_6PSSe_4Cl	$LiFePO_4$	0.43	$FeSe_2$, Li_3PO_4, Se, LiCl, FePS	-118.59
	$FePO_4$	0.50	FePS, FeS_2, LiCl, $FeSe_2$, $Li_4P_2O_7$, Se	-215.19

Table S11. Phase equilibria and reaction energy (ΔE_D) of $Li_{5.5}PS_{4.5-x}Se_xCl_{1.5}$ (x = 0 ~ 3) at the interface with $LiFePO_4$ and $FePO_4$.

C_{SSE}	$C_{electrode}$	x_m	Phase equilibria at x_m	ΔE_D (meV/atom)
$Li_{5.5}PS_{4.5}Cl_{1.5}$	$LiFePO_4$	0.40	$Li_4P_2O_7$, Li_3PO_4, FeS_2, LiCl, FePS	-87.52
	$FePO_4$	0.46	$LiPO_3$, LiCl, FePS, FeS_2, $Li_4P_2O_7$	-177.68
$Li_{5.5}PS_{3.5}SeCl_{1.5}$	$LiFePO_4$	0.45	Se, FePS, LiCl, $Li_4P_2O_7$, FeS_2, Li_3PO_4	-91.61
	$FePO_4$	0.46	$FeSe_2$, FeS_2, $LiPO_3$, $Li_4P_2O_7$, FePS, LiCl	-180.63
$Li_{5.5}PS_{2.5}Se_2Cl_{1.5}$	$LiFePO_4$	0.47	FeS_2, LiCl, FePS, $FeSe_2$, Se, Li_3PO_4	-98.99
	$FePO_4$	0.46	FePS, $Li_4P_2O_7$, LiCl, $LiPO_3$, $FeSe_2$, FeS_2	-187.01
$Li_{5.5}PS_{1.5}Se_3Cl_{1.5}$	$LiFePO_4$	0.47	Li_3PO_4, FePS, $FeSe_2$, Se, LiCl, FeS_2	-105.62
	$FePO_4$	0.46	FeS_2, $FeSe_2$, FePS, $Li_4P_2O_7$, $LiPO_3$, LiCl	-193.51

Figure S1. Crystal structure of (a) - (d) $Li_6PS_{5-x}Se_xCl$ (x = 1 ~ 4) and (e) - (g) $Li_{5.5}PS_{4.5-x}Se_xCl_{1.5}$ (x = 1 ~ 3). The blue, yellow, orange, watchet and purple spheres represent the Li, S, Cl, P and Se atoms, respectively.

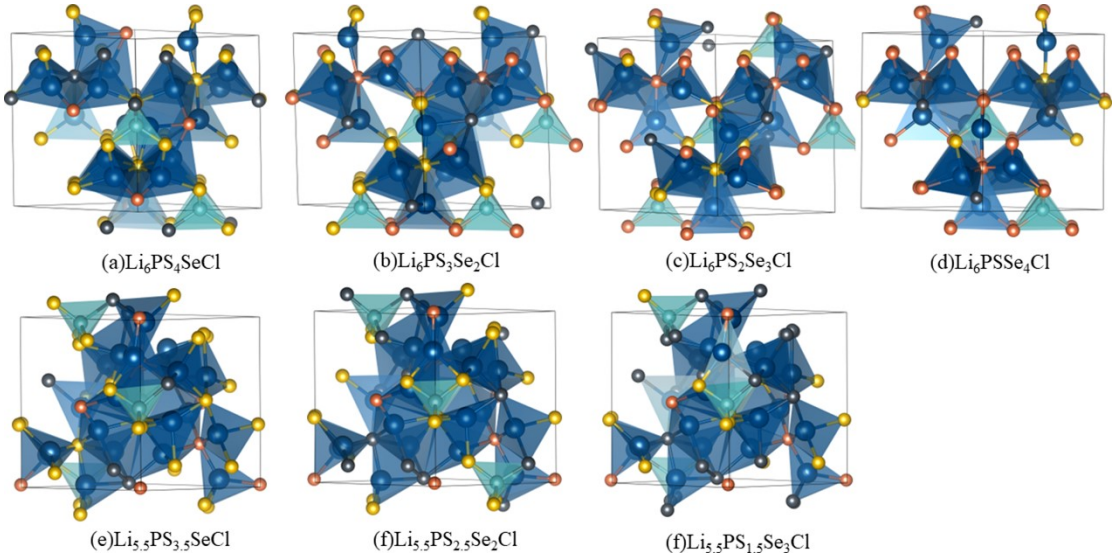

Figure S2. The mean square displacement (MSD) of Li^+ ions in (a) Li_6PS_5Cl, (b) Li_6PS_4SeCl, (c) $Li_6PS_3Se_2Cl$, (d) $Li_6PS_2Se_3Cl$ and (e) Li_6PSSe_4Cl during 120 ps simulation time. (f) Diffusivity and activation energy of $Li_6PS_{5-x}Se_xCl$ (x = 0 ~ 4) deduced from AIMD simulations at elevated temperatures ranging from 500 to 1000 K.

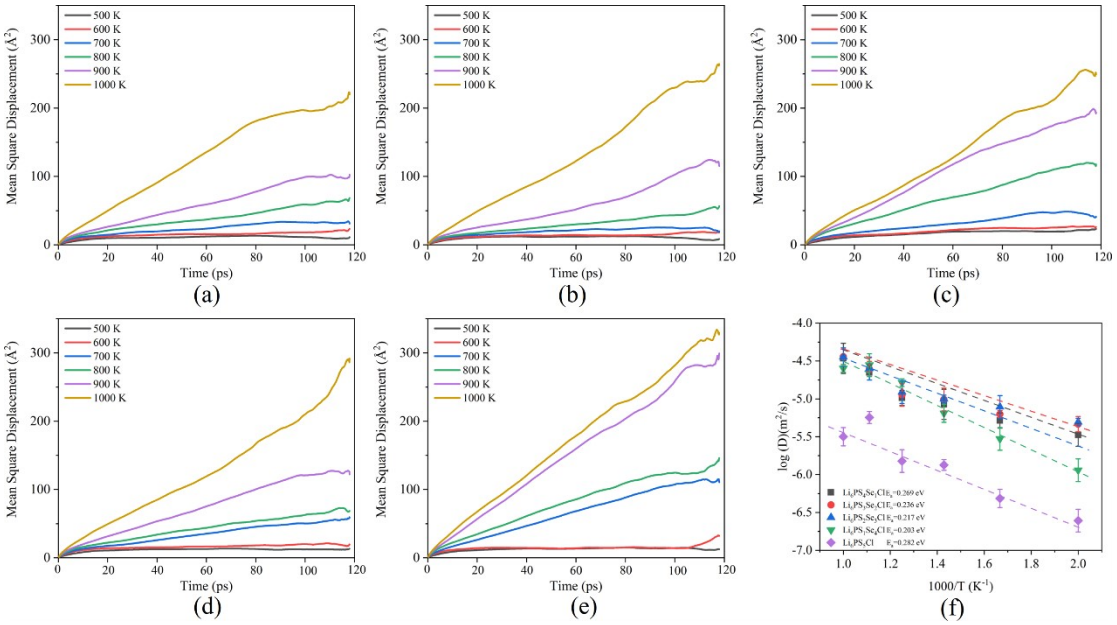

Figure S3. The mean square displacement (MSD) of Li^+ ions in (a) $Li_{5.5}PS_{4.5}Cl_{1.5}$, (b) $Li_{5.5}PS_{3.5}SeCl_{1.5}$, (c) $Li_{5.5}PS_{2.5}Se_2Cl_{1.5}$ and (d) $Li_{5.5}PS_{1.5}Se_3Cl_{1.5}$ during 120 ps simulation time. (e) Diffusivity and activation energy of $Li_{5.5}PS_{4.5-x}Se_xCl_{1.5}$ (x = 0 ~ 3) deduced from AIMD simulations at elevated temperatures ranging from 500 to 1000 K.

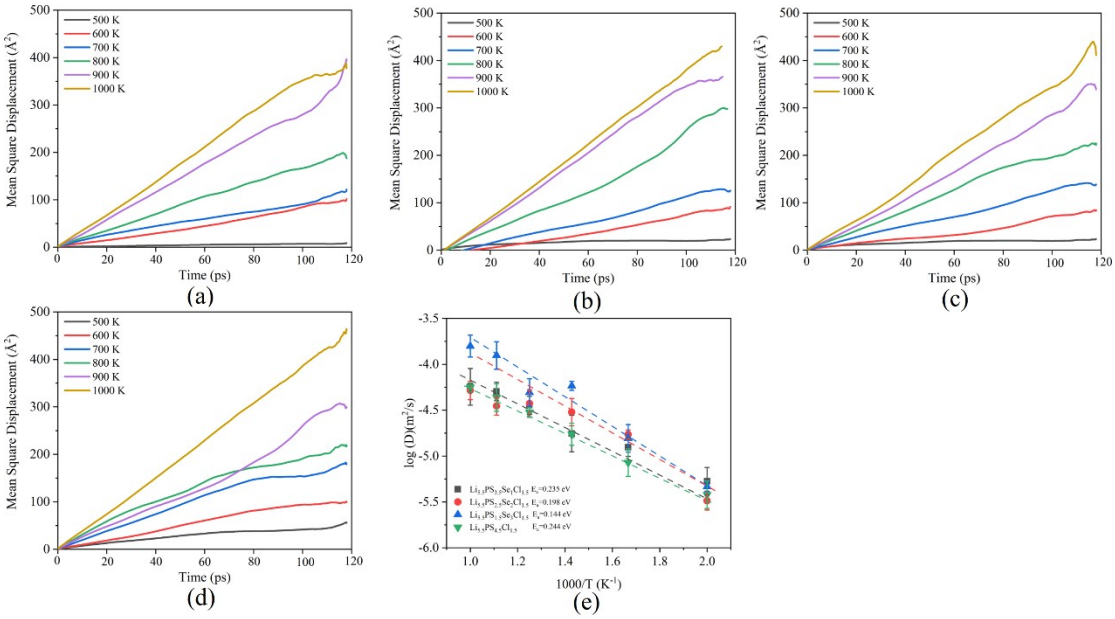

Figure S4. The Li^+ migration pathway of (a) Li_6PS_5Cl and (b) $Li_{5.5}PS_{4.5}Cl_{1.5}$ at 500 K. The blue, green, yellow and red spheres represent the Li, P, S and Cl atoms, respectively. The blue line represents the Li^+ migration pathway during 120 ps simulation time.