Supporting Information

First-Principles Study on Ultrafast Li-ion Diffusion in Halospinel $Li_2Sc_{2/3}Cl_4$ Through Multichannels Designed by Aliovalent Doping

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Table S1. Type of sharing for each site of halospinel.

Site	8a	16c	16d	48f
8a	None	Face	Corner	Corner / Edge
16c	Face	Edge	Corner / Edge	Corner / Face
16d	Corner	Corner / Edge	Edge	Face
48f	Corner / Edge	Corner / Face	Face	Corner / Edge

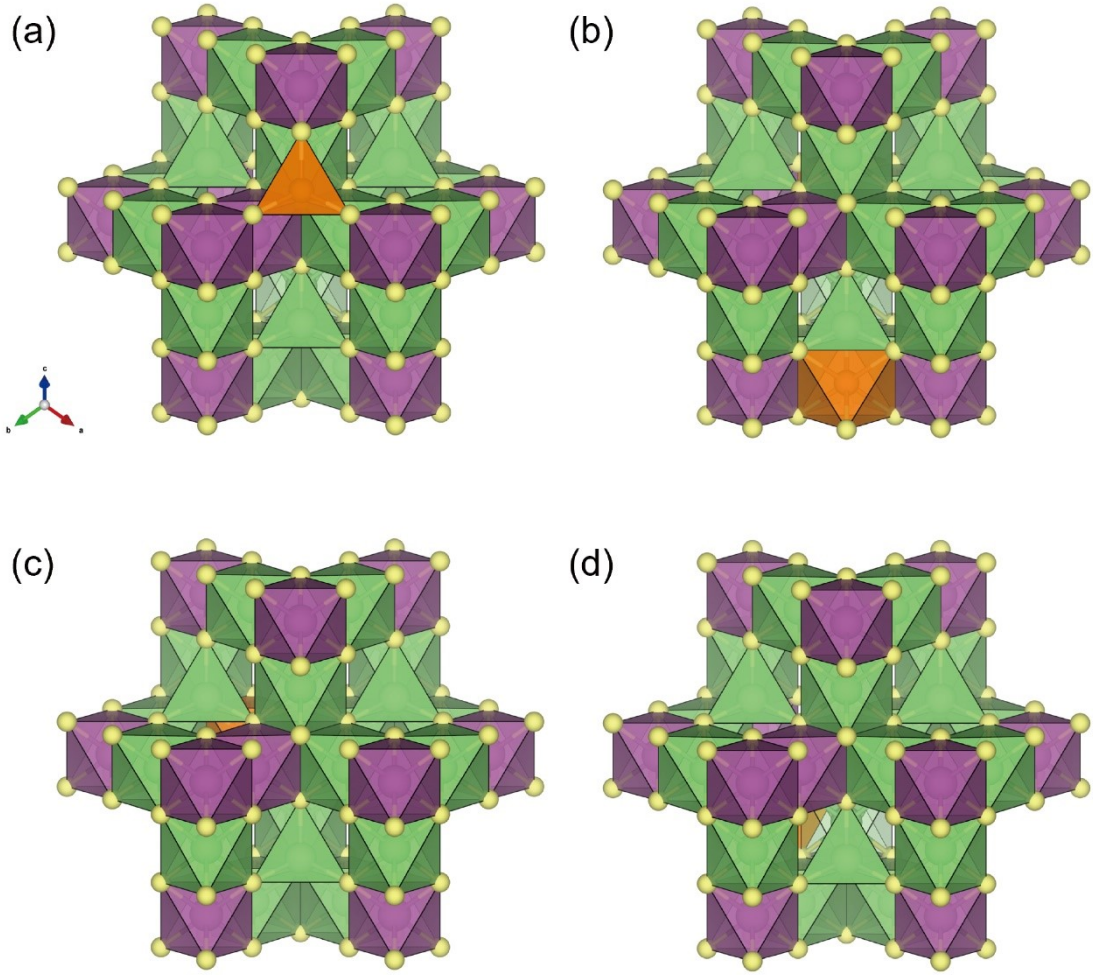
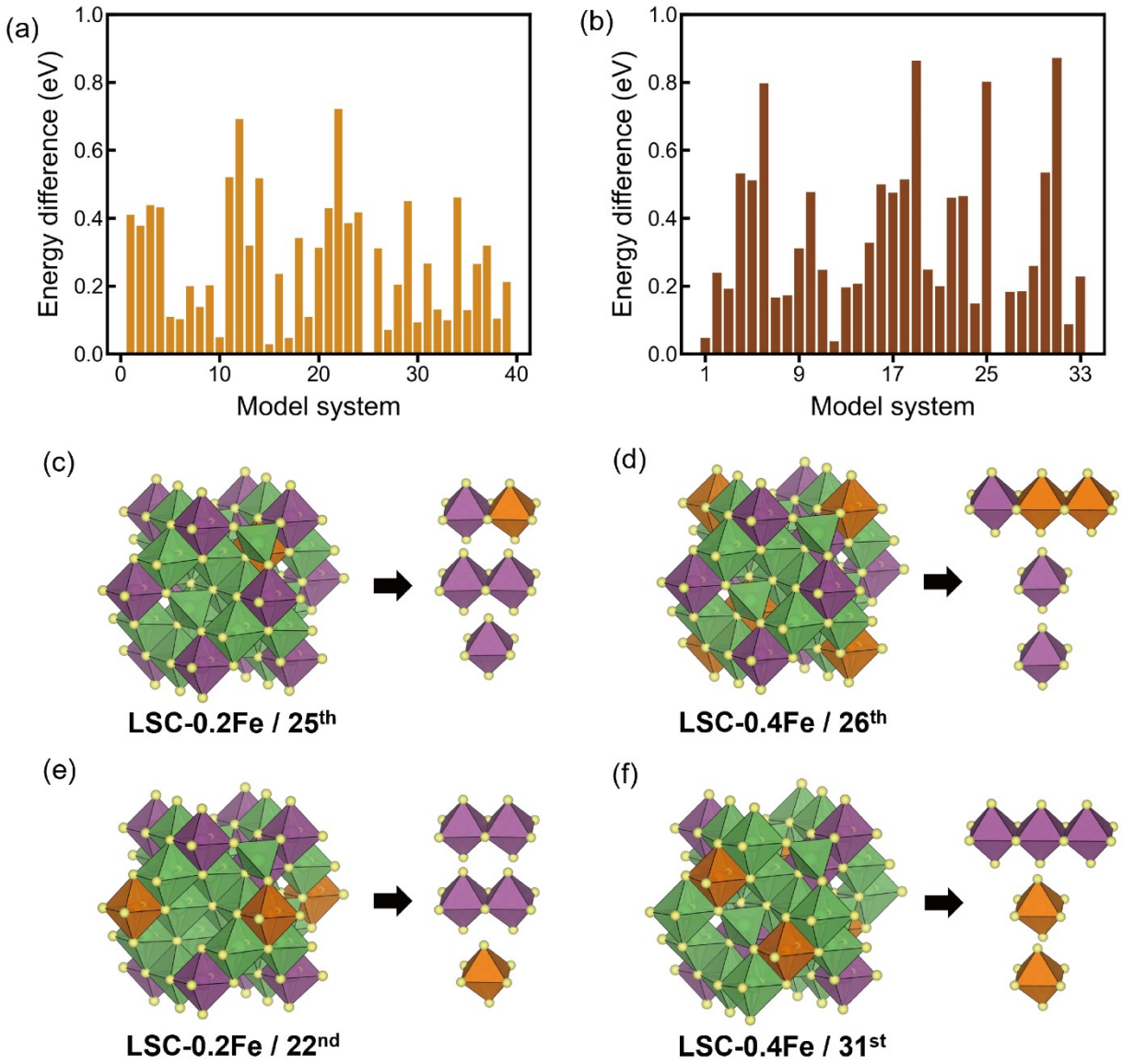


Figure S1. The structure of LSC-0.2Fe with Fe doping at (a) 8a, (b) 16c, (c) 16d, and (d) 48f sites, respectively.

Table S2. The doping energy of LSC-0.2Fe with several doping sites obtained by DFT calculations. Each energy corresponds to Fig. S1(a-d).

Site	8a	16c	16d	48f
Doping energy (eV)	5.267	4.729	2.632	4.469



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2 **Fig. S2.** DFT energy differences relative to the energy of the most thermodynamically stable structure for (a) LSC-
3 0.2Fe and (b) LSC-0.4Fe; the most stable structure and its cation polyhedron distribution for (c) LSC-0.2Fe and (d)
4 LSC-0.4Fe; the most unstable structure and its cation polyhedron distribution for (e) LSC-0.2Fe and (f) LSC-0.4Fe.

5

Table S3. The doping energy of halospinel with doping Fe^{3+} ($Li_{17}Sc_4FeCl_{32}$) and Fe^{2+} ($Li_{18}Sc_4FeCl_{32}$), respectively. In both cases, Fe was doped at the 16d site which is the most thermodynamically stable one.

LSC-0.2Fe	Formal charge				Doping Energy (eV)
	Li	Sc	Fe	Cl	
$Li_{17}Sc_4FeCl_{32}$	+1	+3	+3	-1	5.589
$Li_{18}Sc_4FeCl_{32}$	+1	+3	+2	-1	2.632

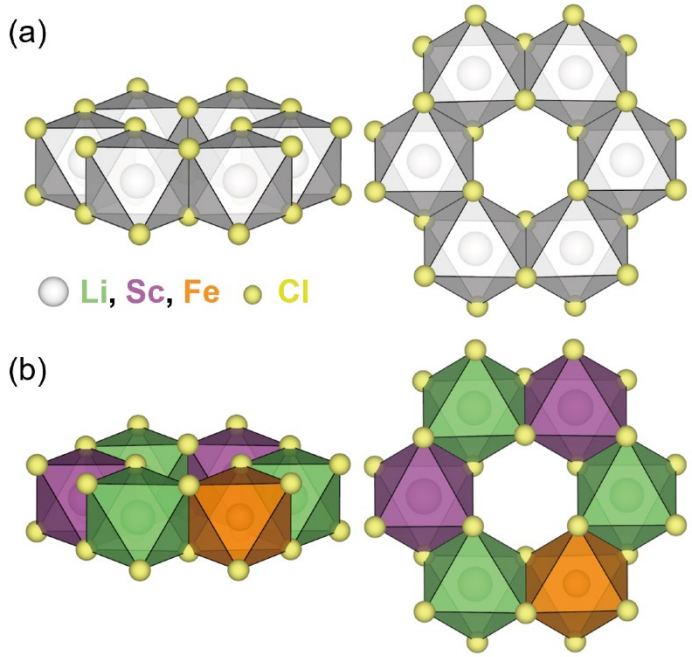

Fig. S3 (a) Schematic of the gate. (b) Gate considered in our study. The octahedral site can be occupied in the center of the gate, which is here called the 'gate site'.

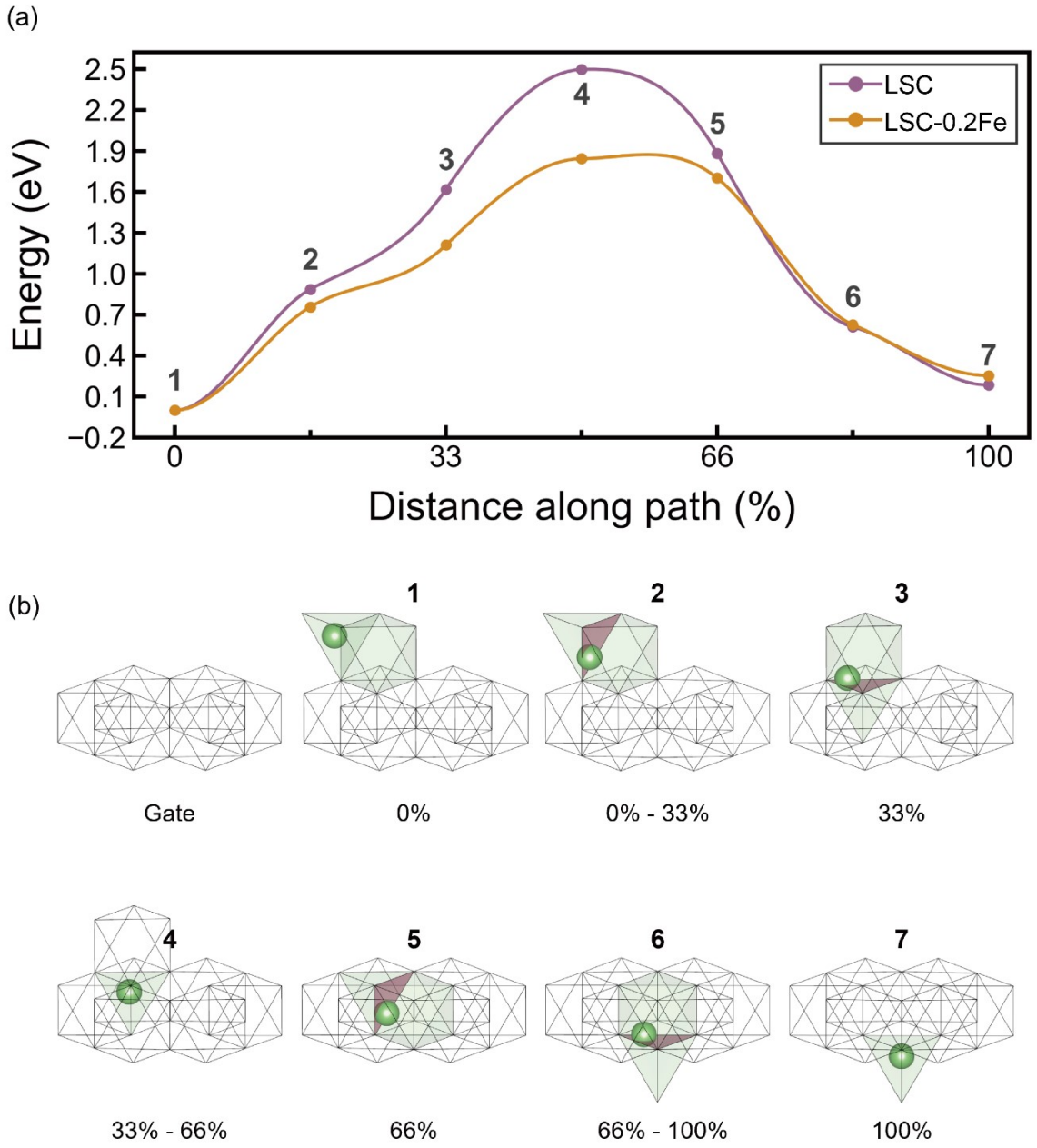

Fig. S4 Li^+ migration pathway through the gate site. (a) Energy profile of the migrating Li^+ along the path and (b) image of migration. It is one of the tetrahedral-to-tetrahedral (8a-to-8a site) pathways but was not considered significant because the migration occurs through face sharing and accordingly has a high energy barrier.

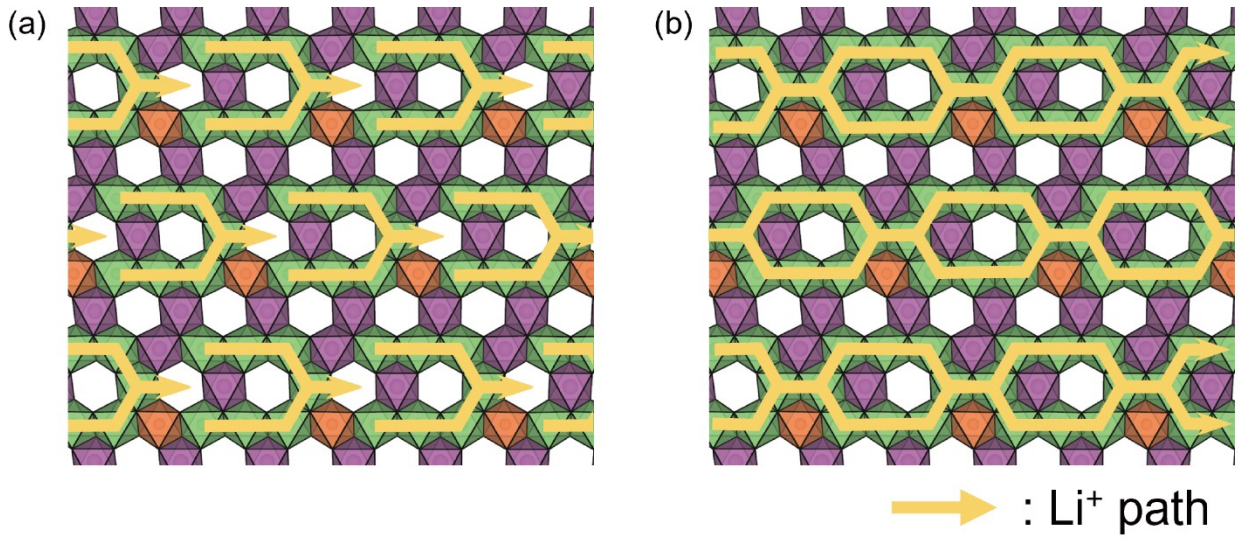

Fig. S5. Formation of a new connection on the $(11\bar{1})$ plane during the migration of Li^+ through the gate, as illustrated in Fig. 3: (a) 1st and (b) 5th images, respectively.

Table S4. Li-Cl distances($d_{Li^+-Cl^-}$), bader charges (Q), and the estimated electrostatic interactions ($Q_{Li^+}Q_{Cl^-}/d_{Li-Cl}$) of the atoms shown in Fig. 5(b), for each model system.

Model system	$d_{Li^+-Cl^-}$ (Å)	$Q_{Cl^-}(e)$ [a]	$Q_{Li^+}(e)$ [b]	$Q_{Li^+}Q_{Cl^-}/d_{Li-Cl}$ [c]
LSC	2.649	-0.752	0.887	-0.252
LSC-0.2Fe	2.518	-0.762	0.886	-0.268

The approximation of electrostatic energy was calculated on the 4th image of migration in Fig. S4.

[a] The average value of three Cl close to Li among Cl constituting $[FeCl_6]^{4-}$ octahedron.

[b] The Li^+ passing through the gate

[c] A higher negative value indicates a stronger attraction.

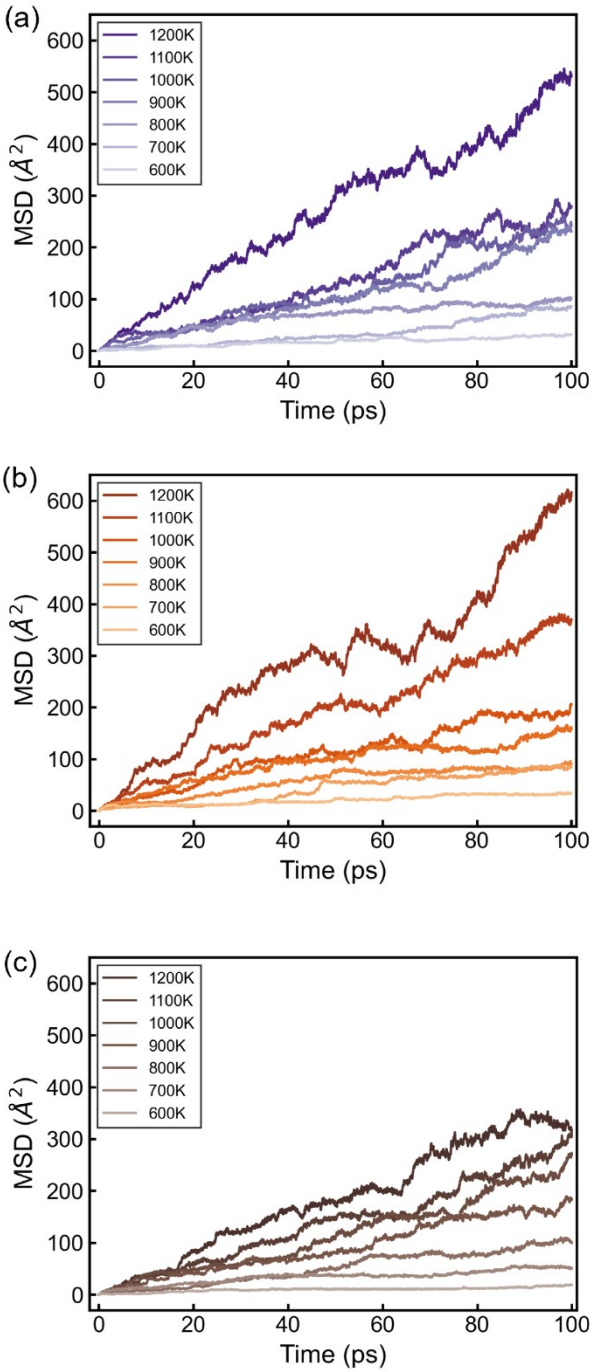

Fig. S6 Mean-square displacement (MSD) plots of Li^+ for (a) LSC, (b) LSC-0.2Fe, and (c) LSC-0.4Fe.

Table. S5. The distance between the initial and final positions for considerable Li^+ hopping in this work. The distance was measured in the most stable LSC-0.2Fe.

Model system	Tet – Tet	Tet – Oct	Oct – Oct	
Initial – Final	8a – 8a	8a – 16c[a]	16c[a] -16d	16d – 16d
Distance (Å)	4.50	2.25	3.68	3.68

[a] The gate site notated in Fig. S3.

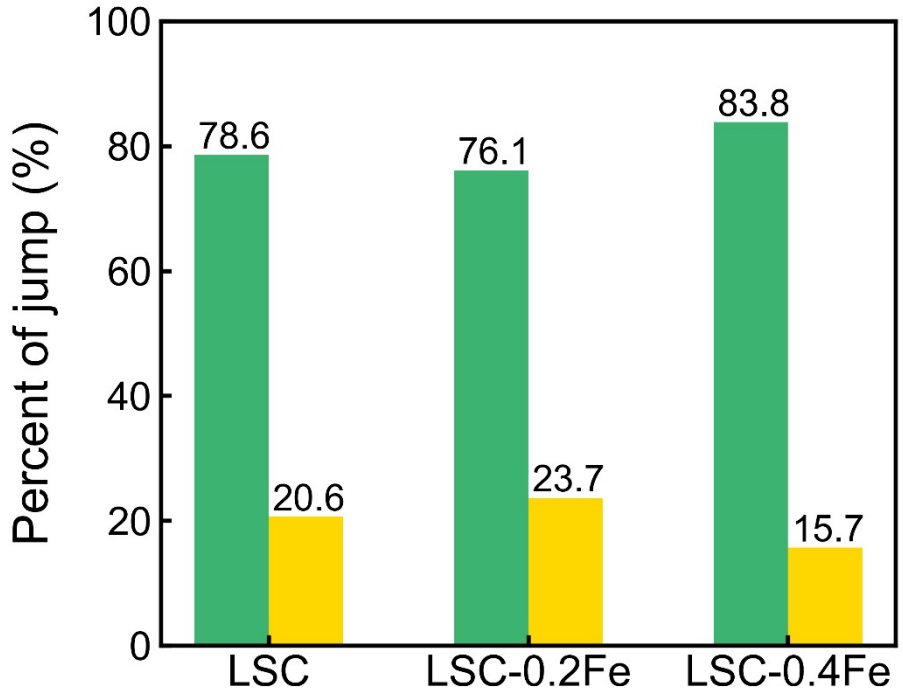

Fig. S7. The total collective motion of Li+ (green) and collective motion paired only octahedron to octahedron hopping (yellow). The data are from the AIMD simulation at 1000K.

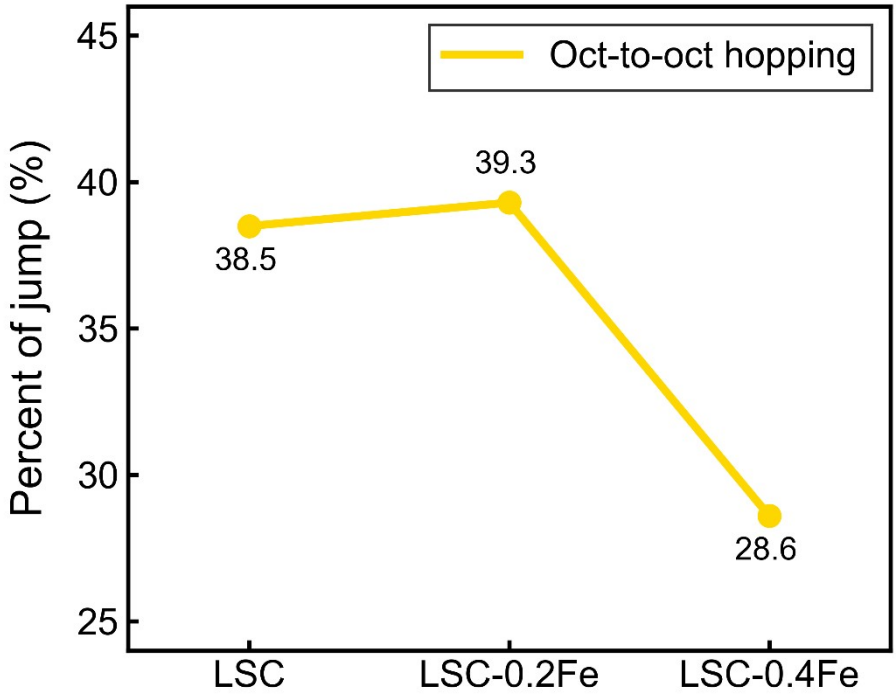

Fig. S8. The ratio of Octahedral – Octahedral site hopping for single Li^+, among the considered type of hopping listed in Table. S5. The data are from the AIMD simulation at 800K.