Supporting Information

Lithium Ions Diffusion Mechanism on Inorganic Components of Solid-Electrolyte Interphase

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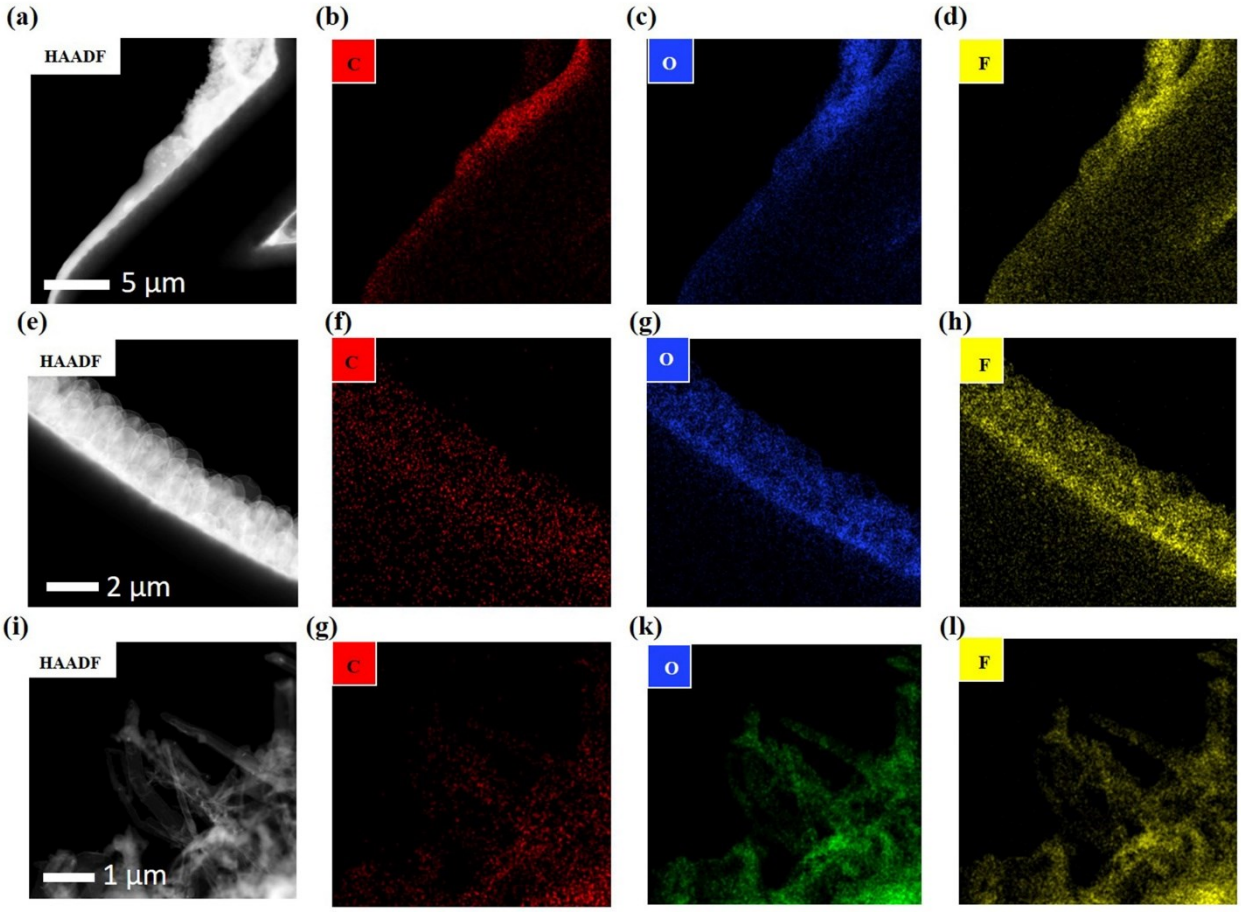

Fig. S1. STEM image of Li deposited and the corresponding elemental mapping images of the C, O, F in SEI formed in (a-d) PEO, (e-h) DOL/DME and (i-l) EC/DEC based electrolyte.

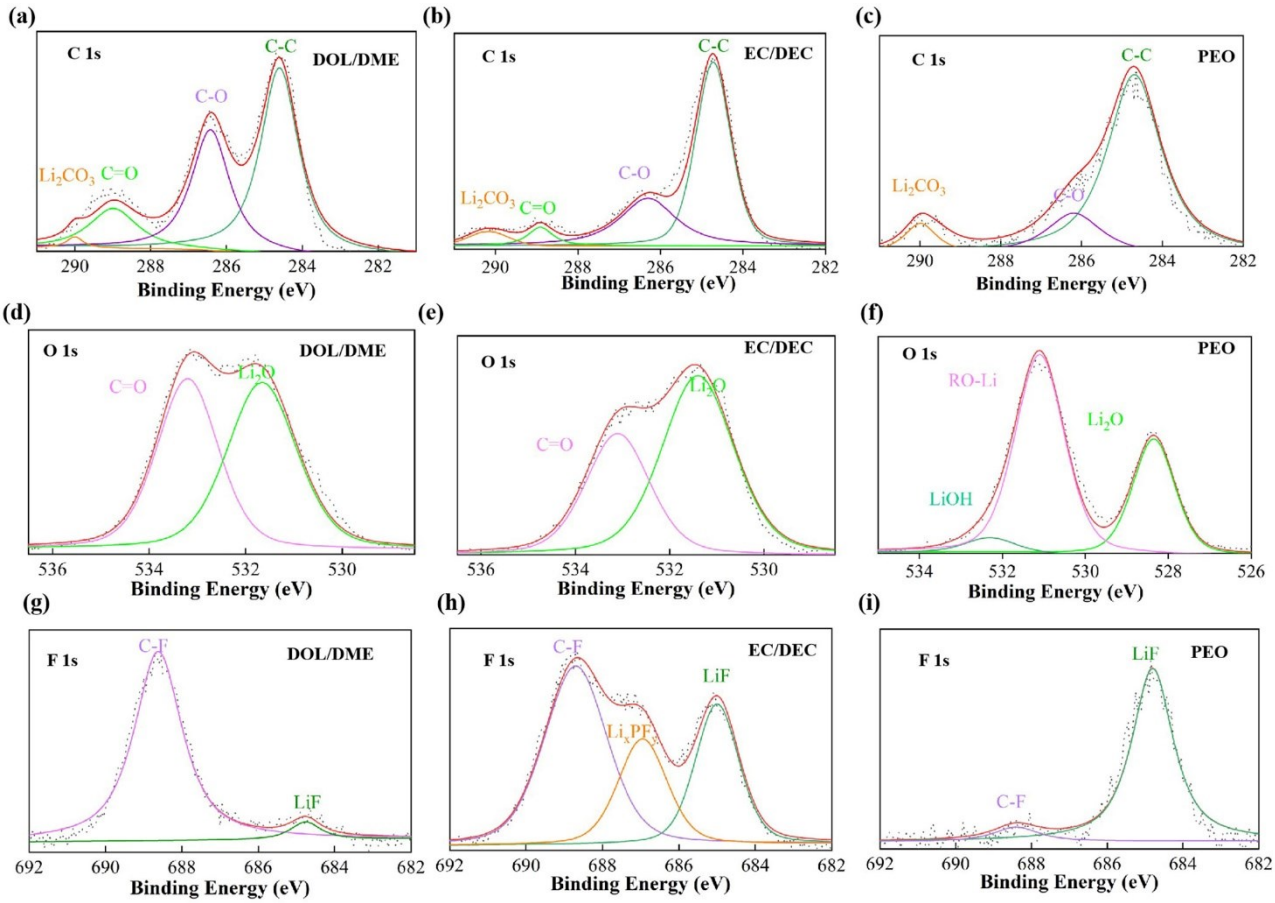

Fig. S2. The C, O and F 1 s XPS spectra of the SEI formed in (a, d, g) DOL/DME, (b, e, h) EC/DEC and (c, f, i) PEO based electrolyte.

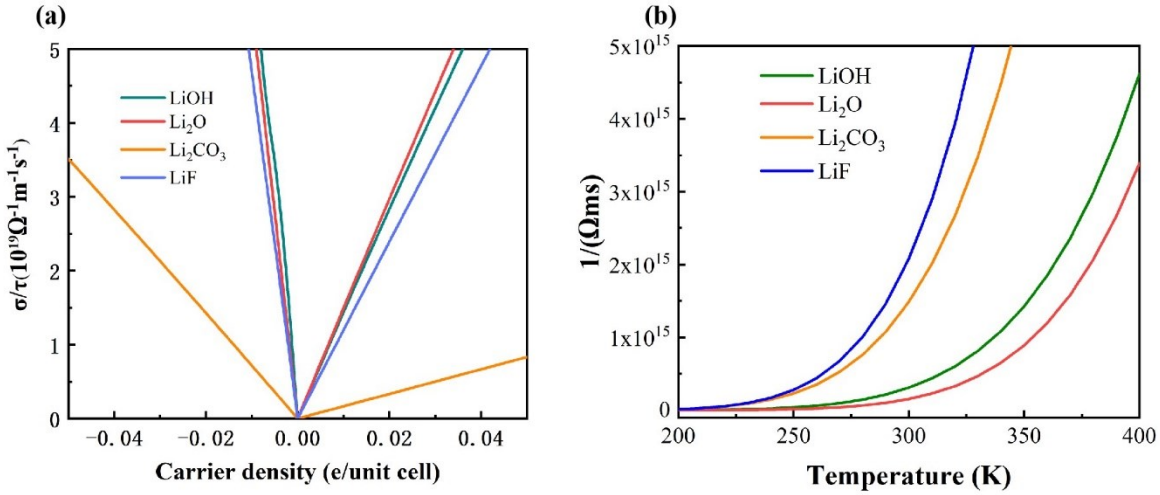

Fig. S3. The (a) σ/τ at 300K and (b) electrical conductivity of LiOH, Li_2O, Li_2CO_3 and LiF. σ is electrical conductivity, τ is relaxation time.

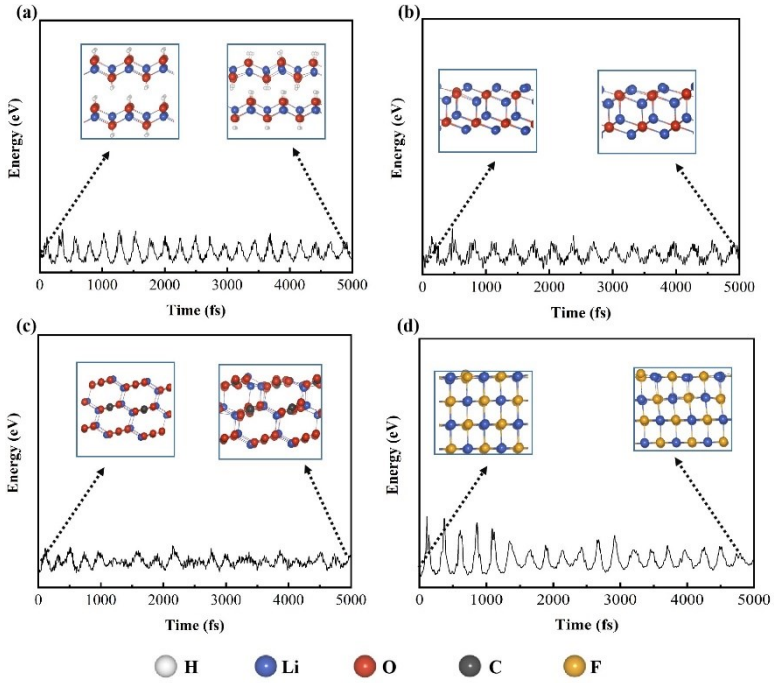

Fig. S4. AIMD simulations of (a) LiOH, (b) Li_2O, (c) Li_2CO_3, (d) LiF and corresponding initial/final structures(inserts).

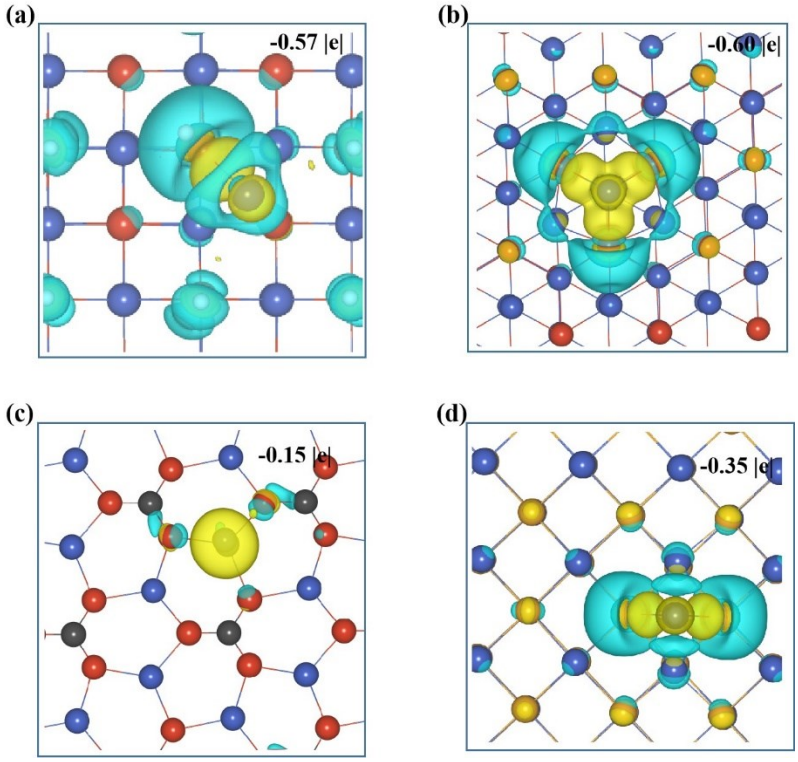

Fig. S5. Top view of charge density difference of a Li atom absorbed on (a) LiOH(001), (b) Li_2O(111), (c) Li_2CO_3(001) and (d) LiF(001) surface at saddle-point configurations. The isosurface value is 0.001 e/Bohr^3. Electron accumulation and depletion are represented by yellow and blue isosurfaces, respectively.

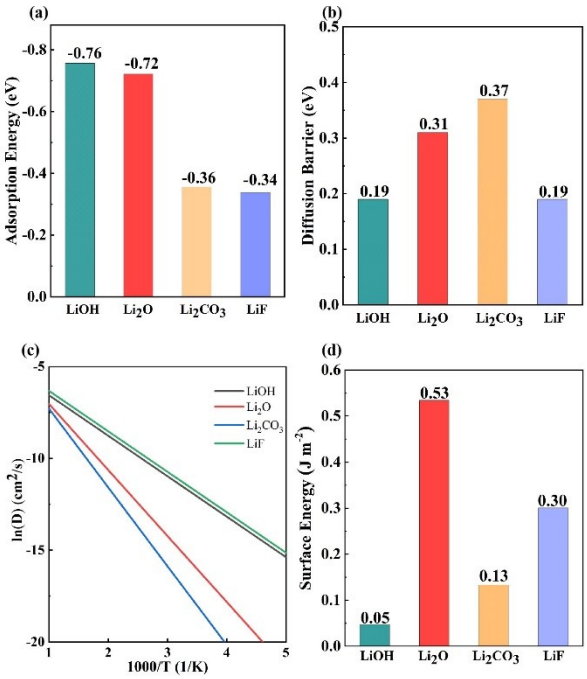

Fig. S6. (a) Adsorption Energy, (b) Diffusion Energy and (c) Arrhenius plot of diffusion coefficient of Li atom on LiOH(001), Li_2O(111), Li_2CO_3(001) and LiF(001) surfaces. (d) Surface Energy of LiOH(001), Li_2O(111), Li_2CO_3(001) and LiF (001).

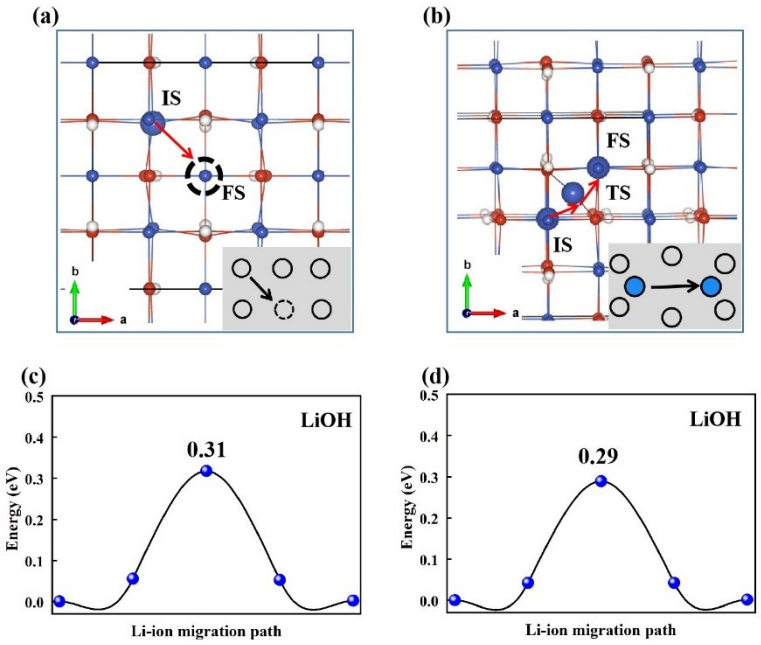

Fig. S7. Migration pathways and potential energy profiles for (a) (c) vacancy diffusion mechanism and (b) (d) direct-hopping diffusion mechanism in LiOH.

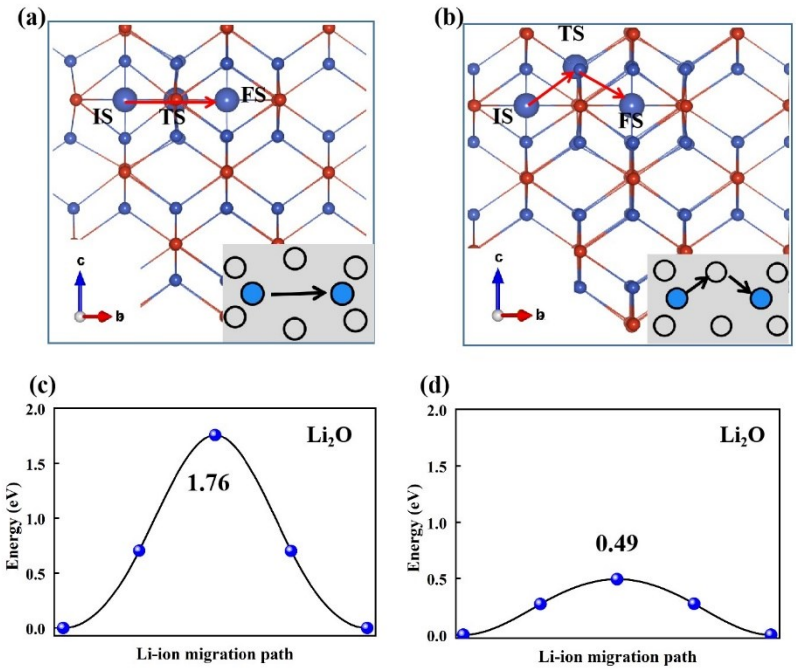

Fig. S8. Migration pathways and potential energy profiles for (a) (c) direct-hopping diffusion mechanism and (b) (d) konock off diffusion mechanism in Li_2O.

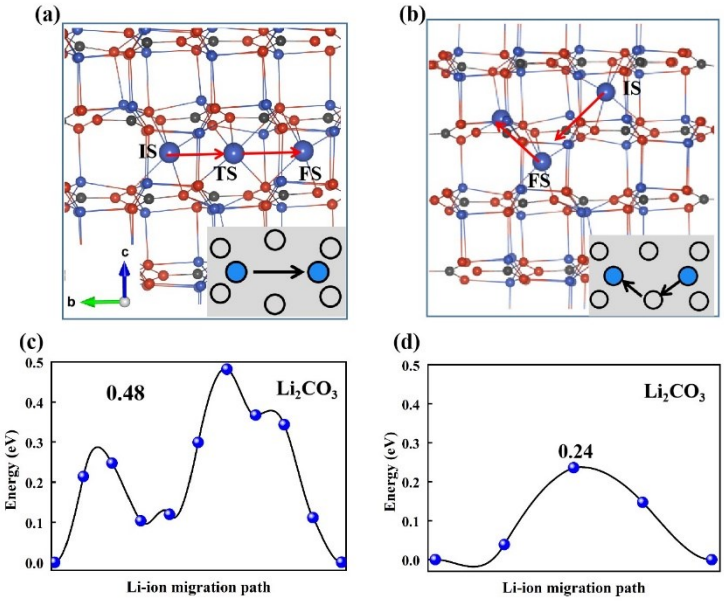

Fig. S9. Migration pathways and potential energy profiles for (a) (c) direct-hopping mechanism and (b) (d) knock-off mechanism in Li_2CO_3.

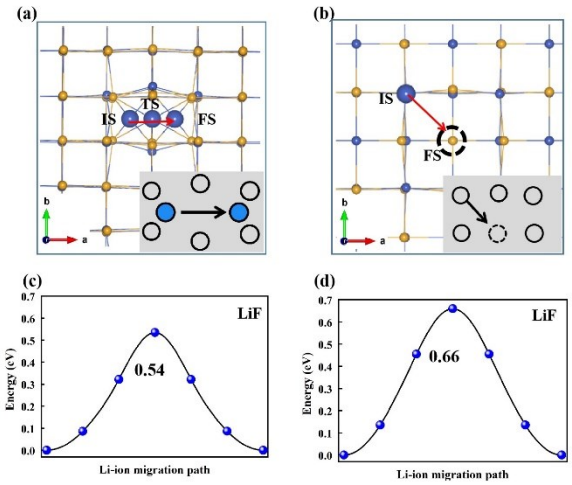

Fig. S10. Migration pathways and potential energy profiles for (a) (c) direct-hopping mechanism and (b) (d) vacancy mechanism in LiF.

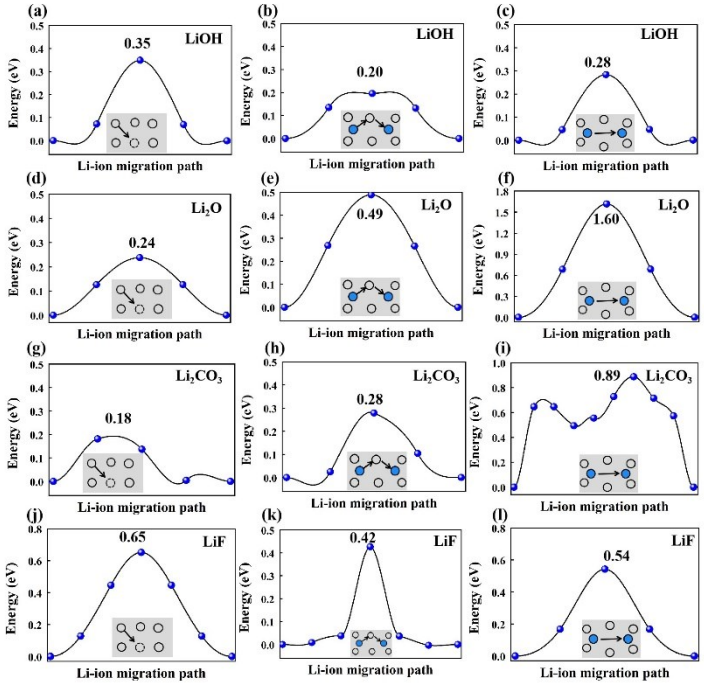

Fig. S11. The migration pathways schematic diagram (inserts) and potential energy profiles of vacancy, knock-off and direct-hopping diffusion mechanisms in (a-c) LiOH, (d-f) Li_2O, (g-i) Li_2CO_3 and (j-l) LiF, respectively. Vacancy and interstitial lithium defects are neutral.

Table. S1. Atomic fraction (%) of the C, O, F in the SEI formed in PEO, DOL/DME and EC/DEC electrolyte analyzed by EDS.

	C	O	F
PEO	7.12	91.45	1.43
DOL/DME	5.05	93.33	1.62
EC/DEC	10.52	84.46	5.02

Table.S2. The mole ratio of Li_2CO_3, Li_2O, LiF, LiOH in the SEI formed in different electrolytes calculated from XPS.

	Li_2CO_3	Li_2O	LiF	LiOH
PEO	1.47	20.92	4.86	1.63
DOL/DME	0.24	15.33	0.49	
EC/DEC	1.44	7.23	5.47	

Table. S3. Calculated Lattice Parameters and Band Gaps for LiOH, Li_2O, Li_2CO_3 and LiF.

structures	lattice parameters (Å)	band gaps (eV)	space group
LiOH	a=b=3.567 c=4.399 α=β=γ=90°	5.481	P4/nmm (No.129)
Li_2O	a=b=c=4.630 α=β=γ=90°	6.262	$Fm\bar{3}m$ (No. 225)
Li_2CO_3	a=8.374 b=5.016 c=6.320 α=90° β=114.094° γ=90°	6.803	C2/c (No. 15)
LiF	a=b=c=4.070 α=β=γ=90°	10.153	$Fm\bar{3}m$ (No. 225)

Table. S4. Calculated surface energies along different orientations. Other theoretical (in parentheses) values obtained from the literature are also presented for comparison.

	N	Surface energies γ (J/m^2)	Surface energies γ ($meV/Å^2$)
LiF(001)	6	0.30(0.29)[1]	18.76
	7	0.30	18.76
LiF(110)	6	0.87	54.10
	7	0.75	46.61
	8	0.74	46.42
	10	0.74	46.42
Li_2O(111)	4	0.53	33.19
	5	0.53(0.54)[2]	33.19(30)[3]
Li_2O(110)	8	0.92	58.03
	10	0.92	58.03(56)[3]
LiOH(001)	6	0.05	3.16
	8	0.05	3.16
LiOH(101)	6	0.30	18.78
	8	0.30	18.78
Li_2CO_3(001)	12	0.13(0.163)[4]	8.33
	14	0.13	8.33

Table. S5. Diffusion Mechanisms, Associated Barriers (Ea), Dimensionality of the diffusion (g), Distance for the lithium ion migration (a), Diffusion Coefficients (D) in inorganic components.

componet	mechanism	Ea (eV)	g	a (×10^{-8}cm)	D (cm^2/s)
LiOH	Surface	0.19	2	2.533	8.602×10^{-6}
LiOH	Vacancy	0.31	2	2.168	6.238×10^{-8}
LiOH	Knock-off	0.20	1	4.499	9.236×10^{-6}
LiOH	Direct-hopping	0.29	2	2.522	1.821×10^{-7}
Li_2O	Surface	0.31	3	3.281	2.142×10^{-7}
Li_2O	Vacancy	0.24	3	2.327	1.591×10^{-6}
Li_2O	Knock-off	0.49	3	3.276	2.104×10^{-10}
Li_2O	Direct-hopping	1.76	3	3.276	1.287×10^{-31}
Li_2CO_3	Surface	0.37	2	5.016	3.322×10^{-8}
Li_2CO_3	Vacancy	0.21	1	2.304	1.649×10^{-6}
Li_2CO_3	Knock-off	0.24	1	4.177	1.709×10^{-6}
Li_2CO_3	Direct-hopping	0.48	1	5.016	2.415×10^{-10}
LiF	Surface	0.19	2	2.860	1.097×10^{-5}
LiF	Vacancy	0.66	3	2.851	2.305×10^{-13}
LiF	Knock-off	0.25	3	3.525	2.486×10^{-6}
LiF	Direct-hopping	0.54	3	2.035	1.187×10^{-11}

References

1 L. Fan, H. L. Zhuang, L. Gao, Y. Lu and L. A. Archer, *J. Mater. Chem. A*, 2017, **5**, 3483–3492.

2 K. Leung and K. L. Jungjohann, *J. Phys. Chem. C*, 2017, **121**, 20188–20196.

3 M. D. Radin, J. F. Rodriguez, F. Tian, D. J. Siegel, *J. Am. Chem. Soc*. 2012, **134**, 1093-1103.

4 Y.-X. Lin, Z. Liu, K. Leung, L.-Q. Chen, P. Lu, Y. Qi, *J. Power Sources* 2016, **309**, 221-230.