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Li-rich channels as the material gene for facile lithium diffusion in halide solid electrolytes

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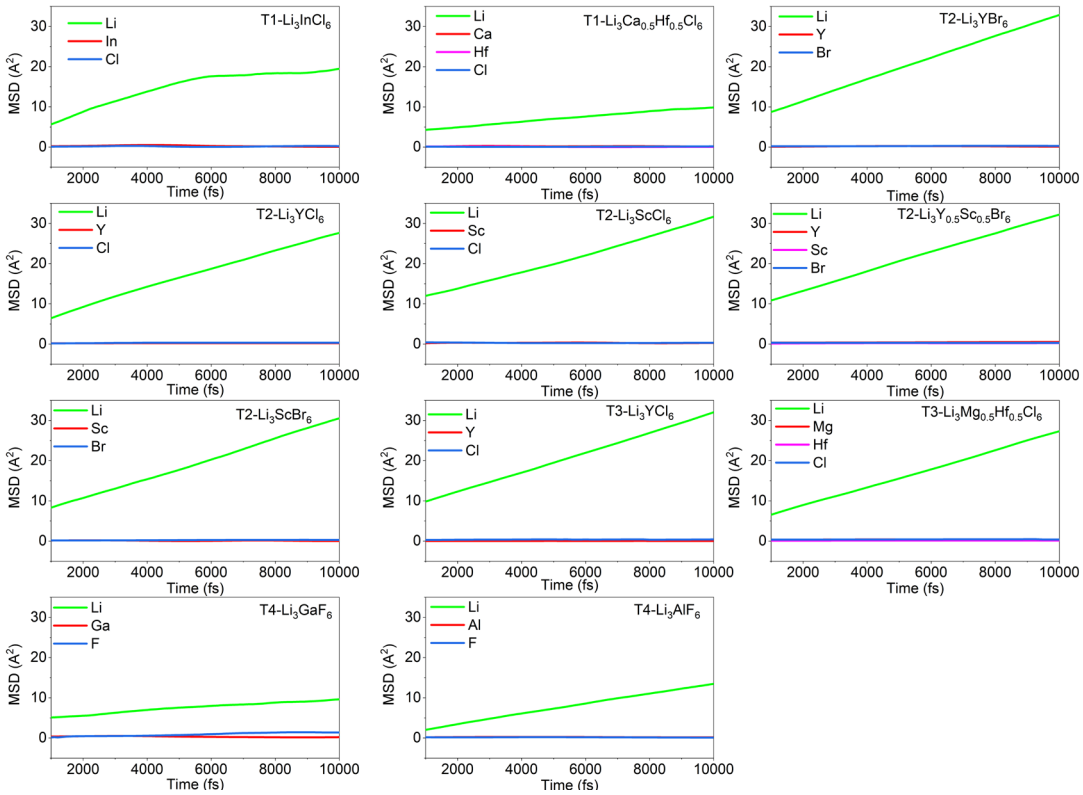

Figure S1. MSD for Li, M and X ions in the halide compounds at 1200 K.

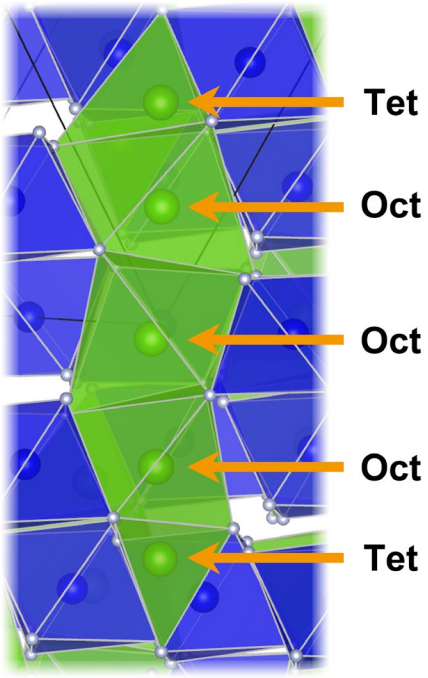

Figure S2. The direct Oct-Oct channels in T4-Li_3AlF_6.

Table S1. Energy above hull (E_{hull}, meV/atom) for T1 compounds.

T1-Li_3MX_6	E_{hull}	T1-$Li_3M^{I}_{0.5}M^{II}_{0.5}Cl_6$	E_{hull}	T1-$Li_3M^{I}_{0.5}M^{II}_{0.5}Cl_6$	E_{hull}
Li_3AlBr_6	47	$Li_3Sc_{0.5}Y_{0.5}Cl_6$	25	$Li_3Mg_{0.5}Ge_{0.5}Cl_6$	91
Li_3AlCl_6	53	$Li_3Sc_{0.5}Al_{0.5}Cl_6$	42	$Li_3Mg_{0.5}Sn_{0.5}Cl_6$	48
Li_3AlF_6	51	$Li_3Sc_{0.5}Ga_{0.5}Cl_6$	59	$Li_3Mg_{0.5}Ti_{0.5}Cl_6$	62
Li_3GaBr_6	99	$Li_3Sc_{0.5}In_{0.5}Cl_6$	40	$Li_3Mg_{0.5}Zr_{0.5}Cl_6$	25
Li_3GaCl_6	87	$Li_3Y_{0.5}Al_{0.5}Cl_6$	35	$Li_3Mg_{0.5}Hf_{0.5}Cl_6$	31
Li_3GaF_6	54	$Li_3Y_{0.5}Ga_{0.5}Cl_6$	52	$Li_3Ca_{0.5}Ge_{0.5}Cl_6$	84
Li_3InBr_6	50	$Li_3Y_{0.5}In_{0.5}Cl_6$	33	$Li_3Ca_{0.5}Sn_{0.5}Cl_6$	40
Li_3InCl_6	0	$Li_3Al_{0.5}Ga_{0.5}Cl_6$	70	$Li_3Ca_{0.5}Ti_{0.5}Cl_6$	46
Li_3InF_6	84	$Li_3Al_{0.5}In_{0.5}Cl_6$	51	$Li_3Ca_{0.5}Zr_{0.5}Cl_6$	18
Li_3ScBr_6	7	$Li_3Ga_{0.5}In_{0.5}Cl_6$	68	$Li_3Ca_{0.5}Hf_{0.5}Cl_6$	23
Li_3ScCl_6	32			$Li_3Sr_{0.5}Ge_{0.5}Cl_6$	87
Li_3ScF_6	82			$Li_3Sr_{0.5}Sn_{0.5}Cl_6$	42
Li_3YBr_6	23			$Li_3Sr_{0.5}Ti_{0.5}Cl_6$	49
Li_3YCl_6	18			$Li_3Sr_{0.5}Zr_{0.5}Cl_6$	20
Li_3YF_6	99			$Li_3Sr_{0.5}Hf_{0.5}Cl_6$	26
				$Li_3Zn_{0.5}Ge_{0.5}Cl_6$	111
				$Li_3Zn_{0.5}Sn_{0.5}Cl_6$	67
				$Li_3Zn_{0.5}Ti_{0.5}Cl_6$	72
				$Li_3Zn_{0.5}Zr_{0.5}Cl_6$	46
				$Li_3Zn_{0.5}Hf_{0.5}Cl_6$	32

Table S2. Energy above hull (E_{hull}, meV/atom) for T2 compounds.

T2-Li_3MX_6	E_{hull}	T2-$Li_3M^{I}_{0.5}M^{II}_{0.5}Br_6$	E_{hull}	T2-$Li_3M^{I}_{0.5}M^{II}_{0.5}Br_6$	E_{hull}
Li_3AlBr_6	17	$Li_3Sc_{0.5}Y_{0.5}Br_6$	25	$Li_3Mg_{0.5}Ge_{0.5}Br_6$	80
Li_3AlCl_6	24	$Li_3Sc_{0.5}Al_{0.5}Br_6$	42	$Li_3Mg_{0.5}Sn_{0.5}Br_6$	42
Li_3AlF_6	41	$Li_3Sc_{0.5}Ga_{0.5}Br_6$	59	$Li_3Mg_{0.5}Ti_{0.5}Br_6$	45
Li_3GaBr_6	70	$Li_3Sc_{0.5}In_{0.5}Br_6$	40	$Li_3Mg_{0.5}Zr_{0.5}Br_6$	11
Li_3GaCl_6	59	$Li_3Y_{0.5}Al_{0.5}Br_6$	35	$Li_3Mg_{0.5}Hf_{0.5}Br_6$	14
Li_3GaF_6	48	$Li_3Y_{0.5}Ga_{0.5}Br_6$	52	$Li_3Ca_{0.5}Ge_{0.5}Br_6$	81
Li_3InBr_6	29	$Li_3Y_{0.5}In_{0.5}Br_6$	33	$Li_3Ca_{0.5}Sn_{0.5}Br_6$	43
Li_3InCl_6	0	$Li_3Al_{0.5}Ga_{0.5}Br_6$	70	$Li_3Ca_{0.5}Ti_{0.5}Br_6$	47
Li_3InF_6	100	$Li_3Al_{0.5}In_{0.5}Br_6$	51	$Li_3Ca_{0.5}Zr_{0.5}Br_6$	11
Li_3ScBr_6	0	$Li_3Ga_{0.5}In_{0.5}Br_6$	68	$Li_3Ca_{0.5}Hf_{0.5}Br_6$	15
Li_3ScCl_6	19			$Li_3Sr_{0.5}Ge_{0.5}Br_6$	94
Li_3ScF_6	94			$Li_3Sr_{0.5}Sn_{0.5}Br_6$	55
Li_3YBr_6	0			$Li_3Sr_{0.5}Ti_{0.5}Br_6$	60
Li_3YCl_6	16			$Li_3Sr_{0.5}Zr_{0.5}Br_6$	23
Li_3YF_6	132			$Li_3Sr_{0.5}Hf_{0.5}Br_6$	27
				$Li_3Zn_{0.5}Ge_{0.5}Br_6$	97
				$Li_3Zn_{0.5}Sn_{0.5}Br_6$	60
				$Li_3Zn_{0.5}Ti_{0.5}Br_6$	62
				$Li_3Zn_{0.5}Zr_{0.5}Br_6$	29
				$Li_3Zn_{0.5}Hf_{0.5}Br_6$	39

Table S3. Energy above hull (E_{hull}, meV/atom) for T3 compounds.

T3-Li_3MX_6	E_{hull}	T3-$Li_3M^{I}_{0.5}M^{II}_{0.5}Cl_6$	E_{hull}	T3-$Li_3M^{I}_{0.5}M^{II}_{0.5}Cl_6$	E_{hull}
Li_3AlBr_6	45	$Li_3Sc_{0.5}Y_{0.5}Cl_6$	25	$Li_3Mg_{0.5}Ge_{0.5}Cl_6$	81
Li_3AlCl_6	52	$Li_3Sc_{0.5}Al_{0.5}Cl_6$	42	$Li_3Mg_{0.5}Sn_{0.5}Cl_6$	36
Li_3AlF_6	69	$Li_3Sc_{0.5}Ga_{0.5}Cl_6$	59	$Li_3Mg_{0.5}Ti_{0.5}Cl_6$	43
Li_3GaBr_6	97	$Li_3Sc_{0.5}In_{0.5}Cl_6$	40	$Li_3Mg_{0.5}Zr_{0.5}Cl_6$	16
Li_3GaCl_6	86	$Li_3Y_{0.5}Al_{0.5}Cl_6$	35	$Li_3Mg_{0.5}Hf_{0.5}Cl_6$	21
Li_3GaF_6	217	$Li_3Y_{0.5}Ga_{0.5}Cl_6$	52	$Li_3Ca_{0.5}Ge_{0.5}Cl_6$	86
Li_3InBr_6	46	$Li_3Y_{0.5}In_{0.5}Cl_6$	33	$Li_3Ca_{0.5}Sn_{0.5}Cl_6$	38
Li_3InCl_6	0	$Li_3Al_{0.5}Ga_{0.5}Cl_6$	70	$Li_3Ca_{0.5}Ti_{0.5}Cl_6$	48
Li_3InF_6	0	$Li_3Al_{0.5}In_{0.5}Cl_6$	51	$Li_3Ca_{0.5}Zr_{0.5}Cl_6$	18
Li_3ScBr_6	60	$Li_3Ga_{0.5}In_{0.5}Cl_6$	68	$Li_3Ca_{0.5}Hf_{0.5}Cl_6$	23
Li_3ScCl_6	5			$Li_3Sr_{0.5}Ge_{0.5}Cl_6$	99
Li_3ScF_6	33			$Li_3Sr_{0.5}Sn_{0.5}Cl_6$	51
Li_3YBr_6	14			$Li_3Sr_{0.5}Ti_{0.5}Cl_6$	60
Li_3YCl_6	23			$Li_3Sr_{0.5}Zr_{0.5}Cl_6$	31
Li_3YF_6	152			$Li_3Sr_{0.5}Hf_{0.5}Cl_6$	35
				$Li_3Zn_{0.5}Ge_{0.5}Cl_6$	99
				$Li_3Zn_{0.5}Sn_{0.5}Cl_6$	54
				$Li_3Zn_{0.5}Ti_{0.5}Cl_6$	61
				$Li_3Zn_{0.5}Zr_{0.5}Cl_6$	34
				$Li_3Zn_{0.5}Hf_{0.5}Cl_6$	51

Table S4. Energy above hull (E_{hull}, meV/atom) for T4 compounds.

T4-Li_3MX_6	E_{hull}	T4-$Li_3M^{I}_{0.5}M^{II}_{0.5}F_6$	E_{hull}	T4-$Li_3M^{I}_{0.5}M^{II}_{0.5}F_6$	E_{hull}
Li_3AlBr_6	50	$Li_3Sc_{0.5}Y_{0.5}F_6$	25	$Li_3Mg_{0.5}Ge_{0.5}F_6$	76
Li_3AlCl_6	140	$Li_3Sc_{0.5}Al_{0.5}F_6$	42	$Li_3Mg_{0.5}Sn_{0.5}F_6$	78
Li_3AlF_6	0	$Li_3Sc_{0.5}Ga_{0.5}F_6$	59	$Li_3Mg_{0.5}Ti_{0.5}F_6$	64
Li_3GaBr_6	/	$Li_3Sc_{0.5}In_{0.5}F_6$	40	$Li_3Mg_{0.5}Zr_{0.5}F_6$	56
Li_3GaCl_6	180	$Li_3Y_{0.5}Al_{0.5}F_6$	35	$Li_3Mg_{0.5}Hf_{0.5}F_6$	41
Li_3GaF_6	18	$Li_3Y_{0.5}Ga_{0.5}F_6$	52	$Li_3Ca_{0.5}Ge_{0.5}F_6$	105
Li_3InBr_6	/	$Li_3Y_{0.5}In_{0.5}F_6$	33	$Li_3Ca_{0.5}Sn_{0.5}F_6$	104
Li_3InCl_6	109	$Li_3Al_{0.5}Ga_{0.5}F_6$	70	$Li_3Ca_{0.5}Ti_{0.5}F_6$	85
Li_3InF_6	73	$Li_3Al_{0.5}In_{0.5}F_6$	51	$Li_3Ca_{0.5}Zr_{0.5}F_6$	84
Li_3ScBr_6	172	$Li_3Ga_{0.5}In_{0.5}F_6$	68	$Li_3Ca_{0.5}Hf_{0.5}F_6$	99
Li_3ScCl_6	137			$Li_3Sr_{0.5}Ge_{0.5}F_6$	119
Li_3ScF_6	64			$Li_3Sr_{0.5}Sn_{0.5}F_6$	122
Li_3YBr_6	/			$Li_3Sr_{0.5}Ti_{0.5}F_6$	111
Li_3YCl_6	132			$Li_3Sr_{0.5}Zr_{0.5}F_6$	/
Li_3YF_6	5			$Li_3Sr_{0.5}Hf_{0.5}F_6$	/
				$Li_3Zn_{0.5}Ge_{0.5}F_6$	80
				$Li_3Zn_{0.5}Sn_{0.5}F_6$	82
				$Li_3Zn_{0.5}Ti_{0.5}F_6$	69
				$Li_3Zn_{0.5}Zr_{0.5}F_6$	60
				$Li_3Zn_{0.5}Hf_{0.5}F_6$	45

Table S5. DFT-PBE bandgaps (eV) of the 36 halides that exhibit E_{hull} below 25 meV/atom.

Halide	Bandgap (eV)	Halide	Bandgap (eV)
T2-$Li_3Al_{0.5}In_{0.5}Br_6$	2.74	T1-Li_3InCl_6	3.38
T3-Li_3InCl_6	4.08	T1-Li_3ScBr_6	2.98
T2-$Li_3Sc_{0.5}In_{0.5}Br_6$	4.89	T3-Li_3ScBr_6	3.55
T2-$Li_3Y_{0.5}In_{0.5}Br_6$	3.38	T2-$Li_3Y_{0.5}Sc_{0.5}Br_6$	3.00
T2-Li_3InCl_6	2.95	T2-Li_3ScBr_6	3.72
T2-$Li_3Ca_{0.5}Zr_{0.5}Br_6$	3.72	T1-$Li_3Ca_{0.5}Hf_{0.5}Cl_6$	2.52
T2-$Li_3Mg_{0.5}Zr_{0.5}Br_6$	4.94	T3-$Li_3Hf_{0.5}Mg_{0.5}Cl_6$	2.93
T2-$Li_3Sr_{0.5}Zr_{0.5}Br_6$	3.56	T3-$Li_3Ca_{0.5}Hf_{0.5}Cl_6$	2.92
T2-Li_3AlBr_6	3.15	T1-Li_3YBr_6	2.32
T2-$Li_3Sc_{0.5}Al_{0.5}Br_6$	4.90	T3-Li_3YBr_6	2.31
T2-$Li_3Y_{0.5}Al_{0.5}Br_6$	3.833	T2-Li_3YBr_6	4.24
T2-$Li_3Hf_{0.5}Mg_{0.5}Br_6$	3.52	T2-Li_3ScCl_6	2.54
T2-$Li_3Ca_{0.5}Hf_{0.5}Br_6$	8.20	T1-Li_3YCl_6	2.95
T1-$Li_3Ca_{0.5}Zr_{0.5}Cl_6$	6.51	T2-Li_3YCl_6	3.16
T1-$Li_3Sr_{0.5}Zr_{0.5}Cl_6$	7.61	T3-Li_3YCl_6	5.02
T3-$Li_3Ca_{0.5}Zr_{0.5}Cl_6$	3.92	T4-Li_3GaF_6	3.71
T3-$Li_3Mg_{0.5}Zr_{0.5}Cl_6$	3.18	T4-Li_3AlF_6	2.73
T2-Li_3AlCl_6	5.51	T4-Li_3YF_6	3.15

Table S6. Reaction energy (ΔE_r, meV/atom) at the interface between the cathodes and the 36 halides that exhibit E_{hull} below 25 meV/atom.

	$LiCoO_2$	$LiFePO_4$	$LiMn_2O_4$	$LiMnO_2$	$LiNiO_2$
T2-$Li_3Al_{0.5}In_{0.5}Br_6$	−59	−23	−46	−63	−118
T3-Li_3InCl_6	−65	−14	−52	−64	−121
T2-$Li_3Sc_{0.5}In_{0.5}Br_6$	−14	0	0	−34	−82
T2-$Li_3Y_{0.5}In_{0.5}Br_6$	−58	−23	−46	−63	−118
T2-Li_3InCl_6	−95	−15	−72	−89	−173
T2-$Li_3Ca_{0.5}Zr_{0.5}Br_6$	−54	−29	−21	−79	−127
T2-$Li_3Mg_{0.5}Zr_{0.5}Br_6$	−14	0	0	−34	−82
T2-$Li_3Sr_{0.5}Zr_{0.5}Br_6$	−105	−69	−63	−128	−181
T2-Li_3AlBr_6	−77	−48	−48	−99	−139
T2-$Li_3Sc_{0.5}Al_{0.5}Br_6$	−96	−14	−73	−88	−179
T2-$Li_3Y_{0.5}Al_{0.5}Br_6$	−42	−36	−22	−65	−100
T2-$Li_3Hf_{0.5}Mg_{0.5}Br_6$	−41	−36	−21	−64	−100
T2-$Li_3Ca_{0.5}Hf_{0.5}Br_6$	−87	−10	−65	−81	−168
T1-$Li_3Ca_{0.5}Zr_{0.5}Cl_6$	−65	−38	−35	−87	−126
T1-$Li_3Sr_{0.5}Zr_{0.5}Cl_6$	−76	−48	−48	−99	−138
T3-$Li_3Ca_{0.5}Zr_{0.5}Cl_6$	−16	−6	−6	−23	−24
T3-$Li_3Mg_{0.5}Zr_{0.5}Cl_6$	−30	0	0	−45	−53
T1-Li_3InCl_6	−98	−23	−80	−92	−158
T1-Li_3ScBr_6	−14	0	0	−34	−82

T3-Li_3ScBr_6	−72	−11	−53	−72	−140
T2-$Li_3Y_{0.5}Sc_{0.5}Br_6$	−130	−37	−103	−111	−215
T2-Li_3ScBr_6	−97	−15	−74	−90	−181
T1-$Li_3Ca_{0.5}Hf_{0.5}Cl_6$	−110	−34	−92	−102	−172
T3-$Li_3Hf_{0.5}Mg_{0.5}Cl_6$	−67	−40	−36	−89	−128
T3-$Li_3Ca_{0.5}Hf_{0.5}Cl_6$	−50	−1	−10	−72	−85
T1-Li_3YBr_6	−174	−63	−146	−152	−260
T3-Li_3YBr_6	−43	−23	−38	−49	−97
T2-Li_3YBr_6	−119	−52	−96	−103	−170
T2-Li_3ScCl_6	−60	−26	−47	−64	−120
T1-Li_3YCl_6	−89	−16	−72	−84	−148
T2-Li_3YCl_6	−119	−48	−91	−102	−193
T3-Li_3YCl_6	−111	−33	−92	−103	−194
T4-Li_3GaF_6	−45	−38	−24	−68	−103
T4-Li_3AlF_6	−82	−47	−47	−100	−144
T4-Li_3YF_6	−73	−37	−34	−90	−134
T1-Li_3InCl_6	−65	−38	−35	−87	−126

Table S7. Volume per formula unit ($V_{f.u.}$) for the promising halides.

Halide	$V_{f.u.}$ (Å^3)	Halide	$V_{f.u.}$ (Å^3)	Halide	$V_{f.u.}$ (Å^3)
T1-Li_3InCl_6	225.5	T1-$Li_3Ca_{0.5}Hf_{0.5}Cl_6$	234.4	T2-Li_3YBr_6	275.8
T2-Li_3ScCl_6	217.9	T2-Li_3ScBr_6	263.7	T2-Li_3YCl_6	231.3
T2-$Li_3Y_{0.5}Sc_{0.5}Br_6$	270.8	T3-Li_3YCl_6	258.0	T3-$Li_3Mg_{0.5}Hf_{0.5}Cl_6$	220.2
T4-Li_3AlF_6	100.5	T4-Li_3GaF_6	104.4		