Supporting Information: Atomistic insights into the effects of doping and vacancy clustering on Li-ion conduction in the Li_3OCl anti-perovskite solid electrolyte

Matt J. Clarke,[†] James A. Dawson,[‡,¶] Timothy J. Mays,[§] and M. Saiful Islam[*,†]

†*Department of Chemistry, University of Bath, Bath, BA2 7AY*

‡*Chemistry – School of Natural and Environmental Science, Newcastle University, NE1 7RU*

¶*Centre for Energy, Newcastle University, Newcastle upon Tyne, NE1 7RU*

§*Department of Chemical Engineering, University of Bath, Bath, BA2 7AY*

E-mail: M.S.Islam@bath.ac.uk

Table S1: Buckingham potentials parameters used to model doped Li_3OCl

$$\Phi_{ij}(r) = A \cdot \exp\left(\frac{-r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}$$

Li_3OCl parameters				
Interaction	A (eV)	ρ (Å)	C ($eV\,Å^{-6}$)	Ref
Li^+-Li^+	360.53	0.161	0.0	S1
Li^+-O^{2-}	292.30	0.347	0.0	S1
Li^+-Cl^-	421.04	0.334	0.0	S1
$O^{2-}-O^{2-}$	22764.3	0.149	13.19	S1
$O^{2-}-Cl^-$	8286.91	0.259	62.20	S1
Cl^--Cl^-	1227.20	0.321	14.53	S1
Dopant parameters				
Interaction	A (eV)	ρ (Å)	C ($eV\,Å^{-6}$)	Ref
$O^{2-}-Mg^{2+}$	1428.5	0.2945	0.0	S2
$O^{2-}-Ca^{2+}$	1090.4	0.3437	0.0	S2
$O^{2-}-Sr^{2+}$	959.1	0.3721	0.0	S2
$O^{2-}-Ba^{2+}$	905.7	0.3976	0.0	S2
$O^{2-}-Al^{3+}$	1725.0	0.2897	0.0	S3
Cl^--Mg^{2+}	4914.54	0.257	0.0	S4
Cl^--Ca^{2+}	2302.0	0.3402	0.0	S4
Cl^--Sr^{2+}	2191.09	0.3457	0.0	This work, S5
Cl^--Ba^{2+}	2704.55	0.3528	0.0	This work, S6
Cl^--Al^{3+}	1736.12	0.2927	0.0	This work, S7
Li^+-F^-	600.0	0.25	0.0	S8
$O^{2-}-F^-$	198.3	0.1110	73.8	S4
Cl^--F^-	556.83	0.3707	48.8	S4
F^--F^-	2008.6	0.1937	67.5	S4

Dopant–Cl potentials derived in this work were fit to the lattice parameters and formation energies of dopant chloride salts ($SrCl_2$, $BaCl_2$, $AlCl_3$) using GULP.[S9] Lattice parameters were taken from the Materials Project,[S5–S7] whilst lattice energies were taken from the CRC Handbook of Chemistry and Physics.[S10]

Table S2: Core-shell model parameters

$$\Phi_i(r) = k \cdot r_i$$

Li_3OCl parameters			
Species	Y (e)	k (eV Å^{-2})	Ref
Li^+	1.00	–	S1
O^{2-}	-2.183	593.716	S1
Cl^-	-2.485	29.38	S1
Dopant parameters			
Species	Y (e)	k (eV Å^{-2})	Ref
Mg^{2+}	1.585	361.6	S2
Ca^{2+}	3.135	110.2	S2
Sr^{2+}	3.251	71.7	S2
Ba^{2+}	9.203	495.2	S2
Al^{3+}	3.00	–	S3
F^-	-2.390	204.6	S4

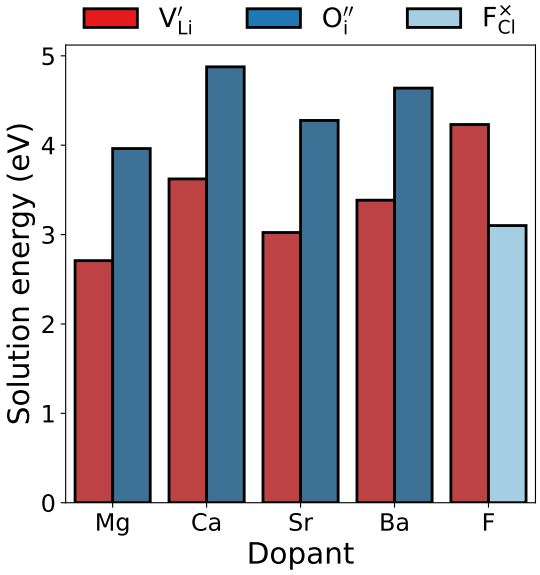

Figure S1: Solution energies for M^{2+}/F^- doping charge compensated by a Li^+ vacancy using oxides as a reference for M^{2+} doping.

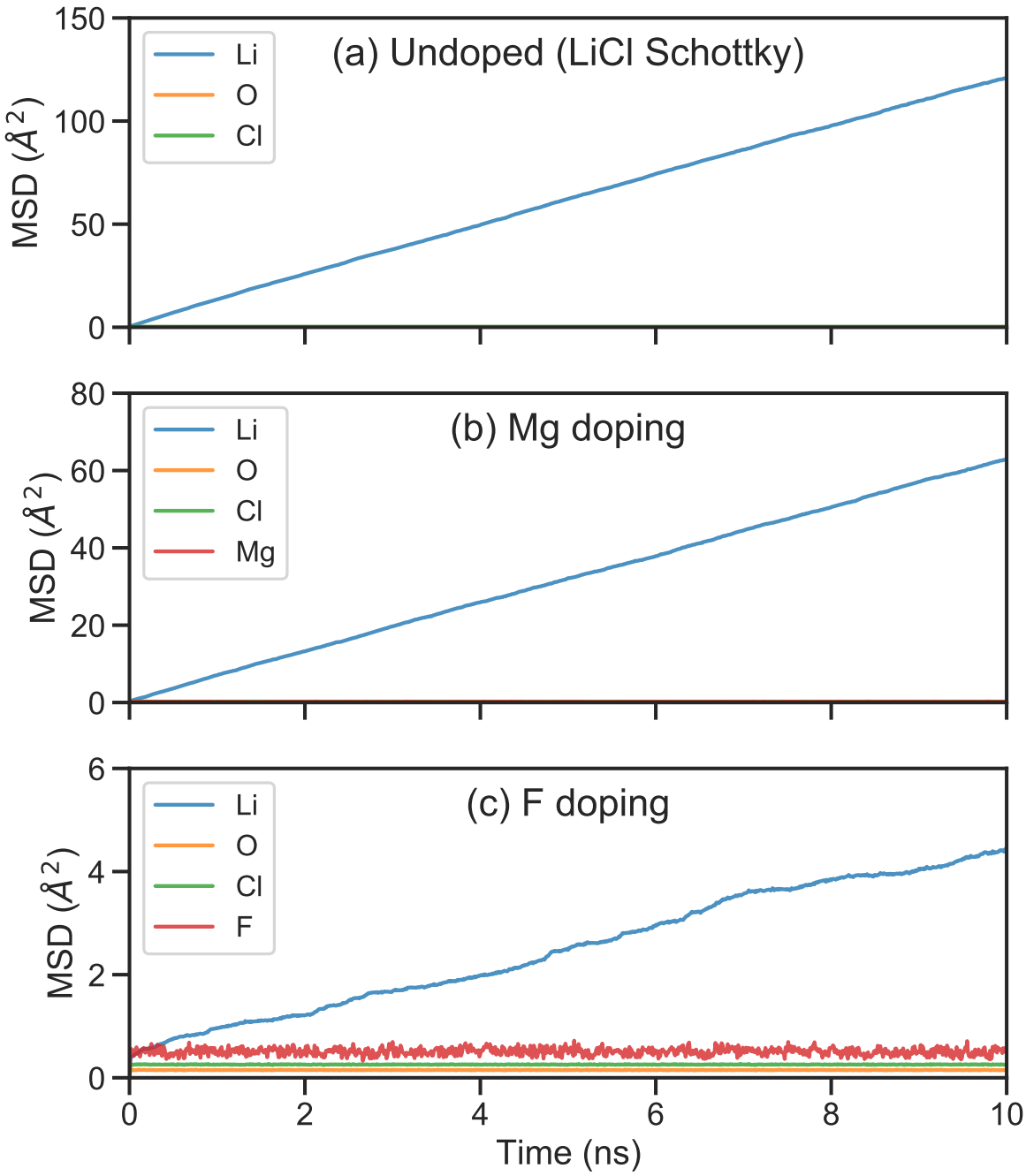

Figure S2: Mean squared displacement (MSD) of each species in Li_3OCl at 800 K with 0.27% Li vacancies. (a) Undoped (LiCl Schottky). (b) Mg doping. (c) F doping.

References

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