

Li⁺ interstitials as the charge carriers in superionic lithium-rich anti-perovskites [Electronic Supplementary Information]

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Here, we deduce an analytical expression for the ratio between the number of interstitials and vacancies in LiCl-deficient Li₃OCl and use data obtained from atomistic modelling to calculate this ratio at 550 K as a function of the degree of LiCl deficiency. We also discuss briefly some technical details regarding the atomistic modelling and provide the numerical data obtained from them.

Atomistic Modelling

The general aspects of the computational methods and the interionic potentials parameters used have already been described in a previous paper¹, in which we show that our model reproduces structural, thermal, dielectric and vibrational properties remarkably well.

All defect, supercell and (stoichiometric) bulk calculations performed used the rational function optimizer (RFO) as minimizer. All calculated final gradient norms were lower than $2 \cdot 10^{-4} \text{ eV}/\text{\AA}$. In supercell calculations, we introduced random small “noises” in all initial fractional coordinates and lattice parameters to avoid symmetry constraints during optimization process.

Several initial positions were tested for interstitials. However, all final positions corresponded either to the so-called “dumbbell” configuration^{1,2} or to the bound state between the interstitial and the oxygen impurity. This latter configuration was achieved whenever the interstitial was initially placed in the cavity comprised by the eight OLi₆ octahedra around the oxygen impurity or in a dumbbell configuration inside any of the eight unit cells around the oxygen impurity, while all remaining final configurations corresponded to the “dumbbell” one.

Supercell and Defect Calculations Data

Non-stoichiometric crystal's Gibbs energy in each picture can be obtained from defect and (stoichiometric) bulk energies from the following expressions.

(a) LiCl deficiency picture (Li⁺ and Cl⁻ vacancies)

$$G(\text{Li}_{3-\delta}\text{OCl}_{1-\delta}) = G(\text{Li}_3\text{OCl}) + \delta \cdot G(v'_{\text{Li}} + v'_{\text{Cl}})$$

(b) Li₂O excess picture (O²⁻ in A-site + interstitial Li⁺ + reduction of one unit formula)

$$G(\text{Li}_{3-\delta}\text{OCl}_{1-\delta}) = \left(1 - \frac{\delta}{2}\right) \cdot G(\text{Li}_3\text{OCl}) + \frac{\delta}{2} \cdot G(O'_{\text{Cl}} + \text{Li}_i)$$

The calculated values are shown in Table S1. Both equations have a linear behaviour in relation to the deficiency degree, shown in Fig. 2.

The lattice Gibbs energies can also be obtained from supercell calculations. In picture (a), only one lithium vacancy and one chlorine vacancy were created, so that the unit formula in a supercell with N unit cells can be written as:

Table S1 Gibbs energy of terms required in pictures (a) and (b).

Picture	Term	G/eV
(a)	v'_{Li}	5.374
	v'_{Cl}	5.286
	$v'_{\text{Li}} + v'_{\text{Cl}}$ (unbound)	10.661
	$v'_{\text{Li}} + v'_{\text{Cl}}$ (bound)	10.263
(b)	Li_3OCl	-39.239
	O'_{Cl}	-15.624
	Li_i	-2.354
	$O'_{\text{Cl}} + \text{Li}_i$ (unbound)	-17.978
	$O'_{\text{Cl}} + \text{Li}_i$ (bound)	-19.592

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$$Li_{3N-1}O_NCl_{N-1} = N \cdot Li_{3-\frac{1}{N}}OCl_{1-\frac{1}{N}} = N \cdot Li_{3-\delta}OCl_{1-\delta},$$

so that the deficiency degree is given by:

$$\delta = 1/N.$$

Thus, the lattice Gibbs energy is

$$G(Li_{3-\delta}OCl_{1-\delta}) = \frac{1}{N}G(Li_{3N-1}O_NCl_{N-1}).$$

Table S2 shows the lattice Gibbs energy in picture (a) for all deficiency degrees considered. All values correspond to the lowest energy configuration (bound state). In picture (b), only one lithium interstitial and one oxygen impurity were created, so that the unit formula in a supercell with N unit cells can be written as:

$$Li_{3N+1}O_{N+1}Cl_{N-1} = Li_{3(N+1)-2}O_{(N+1)}Cl_{(N+1)-2} = (N+1) \cdot Li_{3-\frac{2}{N+1}}OCl_{1-\frac{2}{N+1}} = (N+1) \cdot Li_{3-\delta}OCl_{1-\delta},$$

so that the deficiency degree is given by:

$$\delta = \frac{2}{N+1}.$$

Thus, the lattice Gibbs energy is

$$G(Li_{3-\delta}OCl_{1-\delta}) = \frac{1}{N+1}G(Li_{3N+1}O_{N+1}Cl_{N-1}).$$

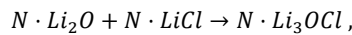
Table S3 shows the lattice Gibbs energy in picture (b) for all deficiency degrees considered. All values correspond to the lowest energy configuration (bound state).

Table S2 Lattice Gibbs energies in picture (a).				Table S3 Lattice Gibbs energies in picture (b).			
δ (%)	Supercell dimensions	Supercell energy /eV	Lattice energy /eV	δ (%)	Supercell dimensions	Supercell energy /eV	Lattice energy /eV
12.50	2 X 2 X 2	-303.589	-37.949	22.22	2 X 2 X 2	-333.602	-37.067
6.25	2 X 2 X 4	-617.547	-38.597	11.76	2 X 2 X 4	-647.464	-38.086
3.70	3 X 3 X 3	-1049.116	-38.856	7.14	3 X 3 X 3	-1079.038	-38.537
1.56	4 X 4 X 4	-2500.963	-39.078	3.08	4 X 4 X 4	-2530.869	-38.936

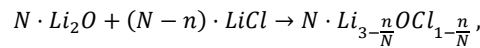
Statistical Physics Analysis

In this section we calculate the ratio between the number of interstitials and vacancies in Li_3OCl from a statistical physics analysis.

A regular synthesis reaction of Li_3OCl in which N "molecules" of Li_2O and N "molecules" of $LiCl$ are involved can be stated as follows:



whereas the synthesis reaction of $LiCl$ -deficient Li_3OCl , i.e., $Li_{3-\delta}OCl_{1-\delta}$, can be stated as follows:



in which n is difference between the number of Li_2O "molecules" and $LiCl$ "molecules" involved in the reaction. This can be put in a more usual form:



in which we define

$$\delta \equiv n/N$$

as the degree of $LiCl$ deficiency, i.e., the amount of $LiCl$ that is absent in relation to the amount that would be used in a regular (non- $LiCl$ -deficient) synthesis.

In a picture in which both Li^+ interstitials and vacancies may be present, there is a direct correspondence between n (which can also be considered as the number of LiCl “molecules” absent in relation to what this number was supposed to be in a non-deficient synthesis) and the number of Li^+ interstitials (n_i) and vacancies (n_v). For each vacancy, there is 1 LiCl “molecule” absent, whereas for each interstitial, there are 2 LiCl “molecules” absent, so that the total number of LiCl “molecules” absent is given by the sum of both contributions:

$$n = 2n_i + n_v .$$

This constraint equation relating the number of interstitials and the number of vacancies for a given number of LiCl “molecules” absent can also be written as:

$$\delta = 2\eta_i + \eta_v ,$$

in which we define η_i and η_v as the concentration of Li^+ interstitials and vacancies, respectively:

$$\eta_i = \frac{n_i}{N} ;$$

$$\eta_v = \frac{n_v}{N} .$$

It is also important to note that, in this picture, the number of unit cells (and, consequently, the number of A-sites, N_A) is reduced in relation to the number in a non-deficient sample, due to the presence of interstitials (see Figure 1), so that the number of A-sites is:

$$N_A = N - n_i ,$$

since the presence of each interstitial correspond to the absence of 1 unit cell. Vacancies, on the other side, do not lead to reduction in the number of unit cells. So, there is not a term in this equation related to the number of vacancies.

Now, if we want to determine the relation between the number of interstitials and vacancies in equilibrium, we must calculate the Gibbs energy of the LiCl-deficient crystal and minimize it in relation to the number of interstitials and vacancies. The Gibbs energy is given by the sum of the Gibbs energy of the perfect crystal, G_0 , and the change in crystal's Gibbs energy due to the presence of the defects, G_d :

$$G = G_0 + G_d .$$

The change in Gibbs energy can be written as:

$$G_d = H_d - TS_d ,$$

in which H_d and S_d are, respectively, the enthalpy and entropy of formation of defects (change in crystal's enthalpy and entropy associated to the formation of the defects), and T is the absolute temperature. The entropy of formation of defects has two sources: one configurational, S_d^{conf} , (due to the many forms of placing the defects along the crystal) and one vibrational, S_d^{vib} , (change in crystal's entropy due to the change in vibrational modes caused by the presence of defects). Thus, we can write:

$$G_d = H_d - TS_d^{vib} - TS_d^{conf} .$$

The first two terms can be obtained by atomistic simulations, since they are able to calculate the change in Gibbs energy associated with a single compound defect (as, for instance, the pair $v'_{Li} - v_{Cl}$ or the pair $O'_{Cl} - Li_i$ plus the removing of a unit formula from the crystal). However, these simulations do not include the configurational term in the calculation of entropy (since the focus is on a single compound defect), and this must be calculated from a statistical physics analysis, using an adequate model. Therefore, the crystal's Gibbs energy can be expressed as:

$$G = G_0 + n_i g_i + n_v g_v - TS_d^{conf} ,$$

in which g_v is the Gibbs energy of formation of one bound pair $v'_{Li} - v_{Cl}$, and g_i is the Gibbs energy of formation of one bound pair $O'_{Cl} - Li_i$ plus the removing of a unit formula from the crystal. Note that the Gibbs energy of formation of a single compound defect does not include the configurational contribution. Also note that the number of the first and second kinds of compound defects in the equation above equals the number of lithium interstitials and vacancies, respectively. Then, the thermodynamic equilibrium requirement is:

$$\frac{\partial G}{\partial n_i} = 0 \Rightarrow \frac{g_i}{T} = \frac{\partial S_d^{conf}}{\partial n_i} ;$$

$$\frac{\partial G}{\partial n_v} = 0 \Rightarrow \frac{g_v}{T} = \frac{\partial S_d^{conf}}{\partial n_v}.$$

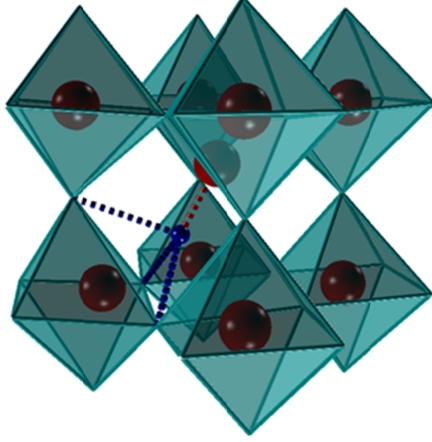


Fig. S1 One of the eight symmetry equivalent positions corresponding to the bound state between the lithium interstitial and the oxygen impurity. Blue and red spheres represent lithium and oxygen ions, respectively. The oxygen impurity lies in the A-site cavity, whereas the lithium interstitial is in front of the face of one of the eight octahedra closest to the impurity. Lithium ions in the octahedra corners and chlorine ions were omitted for simplicity. Dashed lines are merely guides to the eye.

These two equations are related to each other by the constraint $n = 2n_i + n_v$. Here, g_i and g_v were considered constant, since we showed that Gibbs energies of the compound defects are independent of the concentration of charge carriers.

Next, we need to calculate the configurational entropy according to our model. This is done by computing the number of states, Ω , i.e., the number of different ways of placing the defects along the crystal, once the configurational entropy is given by

$$S_d^{conf} = k_B \ln(\Omega),$$

in which k_B is Boltzmann's constant. First, we calculate the number of different ways of placing the n_v associated pairs $v_{Li}^i - v_{Cl}^i$. In fact, we just need to focus on placing the n_v chlorine vacancies along the N_A positions available, once each lithium vacancy is associated to a chlorine vacancy and must be in one of the $z_v=12$ positions closest to it. Thus,

$$\Omega_v = \frac{1}{n_v!} (N_A) \cdot z_v \cdot (N_A - 1) \cdot z_v \cdot (N_A - 2) \cdot z_v \cdot \dots \cdot (N_A - n_v + 1) \cdot z_v$$

$$\Omega_v = \frac{(z_v)^{n_v} N_A!}{n_v! (N_A - n_v)!}.$$

The term $n_v!$ arises from the fact that the pairs are indistinguishable and exchanging them does not lead to a distinct microstate. Following, we calculate the number of different ways of placing the n_i associated pairs $Li_i^i - O_{Cl}^i$. Similar to the previous case, we just need to focus on placing the n_i oxygen impurities along the remaining $N_A - n_v$ positions available, once each lithium interstitial is associated to an oxygen impurity and must be in one of the $z_i=8$ positions closest to it (see Fig. S1). Thus,

$$\Omega_i = \frac{1}{n_i!} (N_A - n_v) \cdot z_i \cdot (N_A - n_v - 1) \cdot z_i \cdot (N_A - n_v - 2) \cdot z_i \cdot \dots \cdot (N_A - n_v - n_i + 1) \cdot z_i$$

$$\Omega_i = \frac{(z_i)^{n_i} (N_A - n_v)!}{n_i! (N_A - n_v - n_i)!},$$

in which the term $n_i!$ has the same origin as in the previous case.

Therefore, the configurational entropy is

$$S_d^{conf} = k_B \ln(\Omega) = k_B \ln(\Omega_v \Omega_i) = k_B \ln \left[\frac{(z_v)^{n_v} (z_i)^{n_i} N_A!}{n_v! n_i! (N_A - n_v - n_i)!} \right]$$

$$S_d^{conf} = k_B [n_v \ln z_v + n_i \ln z_i + N_A \ln N_A - n_v \ln n_v - n_i \ln n_i - (N_A - n_v - n_i) \ln (N_A - n_v - n_i)],$$

in which Stirling's approximation ($\ln x! \approx x \ln x - x$) was used. Though, the number of A-sites in the crystal, as aforementioned, is a function of the number of interstitials and this dependence must be explicitly written, since derivatives will be taken next:

$$S_d^{conf} = k_B [n_v \ln z_v + n_i \ln z_i + (N - n_i) \ln (N - n_i) - n_v \ln n_v - n_i \ln n_i - (N - n_v - 2n_i) \ln (N - n_v - 2n_i)].$$

Now we derivate this configurational entropy in relation to the number of vacancies and interstitials:

$$\frac{\partial S_d^{conf}}{\partial n_i} = k_B \ln \left[\frac{z_i (N - n_v - 2n_i)^2}{(N - n_i) n_i} \right];$$

$$\frac{\partial S_d^{conf}}{\partial n_v} = k_B \ln \left[\frac{z_v (N - n_v - 2n_i)}{n_v} \right].$$

This gives the following relations for thermodynamic equilibrium:

$$\frac{g_i}{T} = k_B \ln \left[\frac{z_i(N - n_v - 2n_i)^2}{(N - n_i)n_i} \right] \Rightarrow \frac{(N - n_i)n_i}{(N - n_v - 2n_i)^2} = z_i \exp\left(-\frac{g_i}{k_B T}\right);$$

$$\frac{g_v}{T} = k_B \ln \left[\frac{z_v(N - n_v - 2n_i)}{n_v} \right] \Rightarrow \frac{n_v}{(N - n_v - 2n_i)} = z_v \exp\left(-\frac{g_v}{k_B T}\right).$$

The term $(N - n_v - 2n_i)$ can be eliminated, leading to:

$$\frac{(N - n_i)n_i}{n_v^2} = \frac{z_i}{z_v^2} \exp\left[-\frac{(g_i - 2g_v)}{k_B T}\right],$$

which can also be written it in terms of concentrations:

$$\frac{(1 - \eta_i)\eta_i}{\eta_v^2} = \frac{z_i}{z_v^2} \exp\left[-\frac{(g_i - 2g_v)}{k_B T}\right].$$

We can now perform a variables change and write both variables as a function of the ratio η between the number of interstitials and vacancies:

$$\eta_i = \frac{\eta\delta}{1 + 2\eta};$$

$$\eta_v = \frac{\delta}{1 + 2\eta},$$

so that we can rewrite the equation as

$$(1 - \eta\delta)\eta = \frac{\delta z_i}{z_v^2} \exp\left[-\frac{(g_i - 2g_v)}{k_B T}\right].$$

This can be easily solved for η and the solution is:

$$\eta = \frac{\eta_i}{\eta_v} = \frac{n_i}{n_v} = \frac{\sqrt{1 + 4\alpha\delta(2 - \delta)} - 1}{2(2 - \delta)},$$

with α defined as

$$\alpha \equiv \frac{z_i}{z_v^2} \exp\left(\frac{2g_v - g_i}{k_B T}\right).$$

As discussed previously, $z_i = 8$ and $z_v = 12$. Also, as we defined g_v as the Gibbs energy of formation of one bound pair $v'_{Li} - v_{Cl}$, and g_i as the Gibbs energy of formation of one bound pair $O'_{Cl} - Li_i$ plus the removing of a unit formula from the crystal, according to Table S1, their values are 10.263 and 19.647 eV, respectively. Thus, at $T = 550$ K, we have

$$\alpha = 6.167 \times 10^6.$$

Since $\alpha \gg 1$, our result can be approximated with excellent accuracy as:

$$\frac{n_i}{n_v} = \sqrt{\frac{\alpha\delta}{2 - \delta}} = 3.042 \times 10^3 \sqrt{\frac{\delta}{2 - \delta}}.$$

Notes and references

- 1 R. Mouta, M. Á. B. Melo, E. M. Diniz and C. W. A. Paschoal, Chem. Mater., 2014, 26, 7137–7144.
- 2 A. Emly, E. Kioupakis and A. Van der Ven, Chem. Mater., 2013, 25, 4663–4670.