

Cite this: *J. Mater. Chem. A*, 2025, **13**, 8816Received 25th November 2024  
Accepted 14th February 2025

DOI: 10.1039/d4ta08352k

rsc.li/materials-a

Pseudo-lithium vacancies in hydrogen rich  $\text{Li}_3\text{OCl}^\dagger$ Benjamin A. D. Williamson, \* Kristoffer Eggestad  and Sverre M. Selbach 

The antiperovskite  $\text{Li}_3\text{OCl}$  is reported as a superionic conductor, however, reproducibility has been poor due to its hygroscopic nature, suggesting that reports are in fact on  $\text{Li}_{3-x}\text{OH}_x\text{Cl}$ . Most experimental and computational studies in the literature focus on pure  $\text{Li}_3\text{OCl}$  however, and do not take into account the role of hydrogen in the material. Here, we develop a full defect model of H-doped  $\text{Li}_3\text{OCl}$ , showing that the nominal Schottky disorder diminishes with hydrogen incorporation. Additionally, H helps to facilitate Li-ion mobility in  $\text{Li}_3\text{OCl}$  by firstly introducing rotatable OH species as well as forming  $\text{H}_{\text{Li}}$  which relaxes off site to form what we define as a “pseudo- $\text{V}_{\text{Li}}$ ” enhancing the ionic conductivity in line with experimentally observed values. Intentional hydrogen doping of hygroscopic materials constitute an underexplored strategy for enhancing ionic transport properties.

## 1. Introduction

Electrochemical energy storage has become an increasingly vital component of modern society ever present in both portable electronics and transportation, as well as becoming important in the realisation of a full renewable energy grid. The dominating type of rechargeable battery rely on Li-ions which intercalate into an anode upon charging, typically graphitic,<sup>1</sup> migrate back to a cathode (for example:  $\text{LiCoO}_2$ ,<sup>2</sup>  $\text{LiFePO}_4$  (ref. 3 and 4) (LFP), or  $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$  (NMC)<sup>5</sup>) upon discharging, and a liquid/polymer electrolyte such as LiTFSI.<sup>6</sup> These electrolytes typically possess desirable conductivities<sup>7</sup> of the order of  $10^{-2}$   $\text{S cm}^{-1}$ . However, they present significant safety risks due to their flammable nature. Further disadvantages are formation of potentially rate limiting solid-electrolyte interphases, simultaneous anion diffusion,<sup>8</sup> lower operating voltages,<sup>9</sup> and (dendrite formation causing incompatibility with Li-metal anodes with  $\sim 10\times$  the capacity of current graphitic anodes<sup>10</sup>).<sup>11</sup> The use of a solid-state electrolyte (SSE) is therefore desirable as it fixes many of these problems simultaneously.

Current solid electrolyte materials include *e.g.* the Li-rich garnets such as  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO),<sup>12–14</sup> the Argyrodites  $\text{Li}_6\text{MS}_5\text{X}$  ( $\text{M} = \text{S, Se, X} = \text{Cl, Br, I}$ ),<sup>15–17</sup>  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$  (LGPS),<sup>18–20</sup> as well as  $\text{Li}_x\text{P}_y\text{O}_z\text{N}$  (LiPON).<sup>21,22</sup> Unfortunately, these materials possess a tradeoff between stability and conductivity. LiPON, for example, possesses excellent electrochemical stability and resistance towards dendrite formation,<sup>23</sup> (yet poor/mediocre conductivities of the order of  $10^{-6}$   $\text{S cm}^{-1}$  are typically observed<sup>21</sup>), making it suitable for small scale devices or as a protective layer in conventional lithium battery cells.<sup>24</sup> Whilst

a lower conductivity would intuitively be expected in the solid state compared to the liquid state, competitively high conductivities ( $>10^{-3}$   $\text{S cm}^{-1}$ ) are observed for some solid state materials.<sup>25</sup> However, some expected issues do arise with respect to stability and synthesis of these materials.<sup>8,26</sup>

Within the past decade, Li-rich anti-perovskites, such as  $\text{Li}_3\text{OCl}$  have gained a lot of interest due to their initial high reported ionic conductivities at ambient conditions ( $10^{-3}$   $\text{S cm}^{-1}$ ) as reported by Zhao and Daemen.<sup>27</sup> Subsequent experimental and density functional theory (DFT) studies, however, have placed the conductivity to be much lower with a higher migration barrier ( $\sim 0.6$  eV and  $10^{-6}$   $\text{S cm}^{-1}$  (ref. 28 and 29)). Both nominally  $\text{Li}_3\text{OCl}$  and  $\text{Li}_3\text{OBr}$  have been shown to possess wide electrochemical stability windows even if they are metastable and not in a global ground state. This has been attributed to not possessing additional cations that may be reduced by Li-metal, yet may form  $\text{Li}_2\text{O}$  and  $\text{LiCl/Br}$  at the anode.<sup>30</sup> Additional antiperovskite ionic conductor compositions have been reported including,  $\text{Na}_3\text{OCl/Br}$ ,<sup>31,32</sup>  $\text{Na}_3\text{SI}^{33}$  and  $\text{Na}_3\text{HS}$ <sup>34</sup> to name a few.

Despite promising electrochemical stability and sometimes promising ionic conductivities,  $\text{Li}_3\text{OCl}$  is a hygroscopic and air sensitive material.<sup>29</sup> This has raised numerous questions on the legitimacy of  $\text{Li}_3\text{OCl}$  as the true composition, with consensus trending towards the fact that  $\text{Li}_3\text{OCl}$  being a hydrated form ( $\text{Li}_{3-x}\text{OH}_x\text{Cl}$ ) or even  $\text{Li}_2\text{OHCl}$ .<sup>29,35</sup> In a critical review by Rettenwander and coworkers,<sup>35</sup> they point out the fact that typical syntheses of  $\text{Li}_3\text{OCl}$  uses  $\text{LiH}$ ,  $\text{H}_2\text{O}$ , or  $\text{LiOH}$  within the synthesis, thus it is inevitable that H/OH will be present in “ $\text{Li}_3\text{OCl}$ ”. All may not be lost, however, after several experimental and computational studies show that a hydrated composition may be to the advantage of the ionic conductivity, as rotatable OH units enhance the mobility of Li-species in the bulk and at grain boundaries.<sup>36–38</sup> Ultimately this may come at a cost, as the conductivity has been shown to be highly

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ta08352k>



correlated with the proton and lithium vacancy concentration,<sup>36</sup> and controlling the amount of hydrogen in a hygroscopic material is difficult at best.<sup>35</sup> Whilst computational studies exist on the intrinsic defects of Li<sub>3</sub>OCl,<sup>30,33,39–42</sup> including a full defect model by Squires *et al.*,<sup>43</sup> hydrogen has not previously been included in these. Squires *et al.* show that purely undoped Li<sub>3</sub>OCl is an extended Schottky disordered material ( $[V_{\text{Li}} + V_{\text{Cl}} + \text{O}_{\text{Cl}}]$ ), similar to what is seen in previously calculated models  $[V_{\text{Li}} + V_{\text{Cl}}]$ ,<sup>43</sup> which Mouta *et al.* showed to enhance the ionic conductivity of Li<sub>3</sub>OCl.<sup>42</sup> Squires also showed that undoped Li<sub>3</sub>OCl could expect equilibrium ionic conductivities of  $\sim 10^{-10}$  S cm<sup>-1</sup>, significantly below experimental observations.<sup>29</sup>

Here, we present full intrinsic and extrinsic (H) defect models for metastable Li<sub>3</sub>OCl, calculated with the hybrid functional HSE06. Using the quasi-harmonic approximation (QHA), the chemical potential stability region of Li<sub>3</sub>OCl is shown to exist from  $\sim 750$  K and shows that when undoped, Li<sub>3</sub>OCl displays two types of Schottky disorder: full disorder under Li-rich conditions, and Li<sub>2</sub>O disorder under Li-poor conditions. Hydrogen is shown to incorporate very easily, in line with the hygroscopic nature of Li<sub>3</sub>OCl, and suppresses these Schottky defect clusters. Additionally, lithium substituted hydrogen is likely to relax offsite to form OH groups and induce a “pseudo- $V_{\text{Li}}$ ”. Accounting for this defect in a conductivity model reproduces experimentally observed values.

## 2. Computational methods

*Ab initio* calculations were performed using DFT implemented within the plane-wave periodic code, VASP.<sup>44–47</sup> The projector-augmented wave method (PAW)<sup>48,49</sup> was used to describe the interaction between the core electrons and the valence electrons. All electrons were treated explicitly for Li, while for O, Cl, and H the standard pseudopotentials supplied with VASP were used. The hybrid functional HSE06 (Heyd–Scuseria–Ernzerhof)<sup>50</sup> was used in order to address the self-interaction error thus allowing for an accurate description of the band gap and electronic properties of Li<sub>3</sub>OCl.

Hybrid functionals have consistently displayed improved geometry and electronic properties of semiconductors.<sup>13,51–53</sup> The band gap calculated herein is  $\sim 6.6$  eV which aligns well with previous HSE06 studies ( $\sim 6.4$ – $6.6$  eV).<sup>43,53,54</sup> To date, however, there is no experimental band gap with which to compare.

Determination of the bulk electronic and structural properties were performed on the cubic form (5 atom primitive cell) of Li<sub>3</sub>OCl (space group:  $Pm\bar{3}m$ ). To this end, a full geometric relaxation using a  $\Gamma$ -centred  $k$ -point grid of  $6 \times 6 \times 6$  and a plane wave energy cutoff of 500 eV was carried until the largest force on any atom was below the force criterion of 0.01 eV Å<sup>-1</sup>. The intrinsic defects were simulated using a  $3 \times 3 \times 3$  supercell expansion of the conventional cell containing 135 atoms. Spin-polarised geometry relaxations (to the same convergence criteria as the conventional cell) of each defect cell and its respective charge states were performed using a  $\Gamma$ -centred  $2 \times 2 \times 2$   $k$ -point mesh and 500 eV plane wave energy cutoff. A  $\Gamma$ -centred  $k$ -point  $2 \times 2 \times 2$  mesh was chosen in order to capture

the  $M$ -point in the 1st Brillouin zone, which is the valence band maximum (VBM) and conduction band minimum (CBM) (ESI Fig. S1†), which was not captured in a Monkhorst–Pack  $2 \times 2 \times 2$  grid. The bulk electronic and structural properties are given in the ESI (Sections ESI 2 and ESI 1).†

### 2.1. Defect formalism

Eqn (1) describes the enthalpy of formation of a defect in charge state  $q$ :

$$\Delta H_{\text{f}}(D, q) = (E^{D,q} - E^{\text{H}}) + \sum_i n_i (\mu_i + \Delta \mu_i) + q(E_{\text{Fermi}} + \epsilon_{\text{VBM}}^{\text{H}} + \Delta E^{\text{Pot}}) + q^2 E_{\text{corr}}^{\text{IC}} + E_{\text{corr}}^{\text{BF}} \quad (1)$$

Where  $E^{\text{H}}$  is the total energy of the host supercell,  $E^{D,q}$  is the total energy of the defective supercell in charge state  $q$ . Chemical potentials denoted by  $\mu_i$  of each atomic species,  $i$  (Li(s), Cl<sub>2</sub>(g), O<sub>2</sub>(g), H<sub>2</sub>(g)), are added to or removed from an external reservoir<sup>55</sup> by an amount  $n$ . In this work, the Fermi level ranges from the valence band maximum (VBM) at 0 eV (where  $\epsilon_{\text{VBM}}^{\text{H}}$  denotes the eigenvalue of the VBM in the host material) to the conduction band minimum (CBM) which occurs at 6.38 eV. The potential of the defect supercell bar the immediate vicinity of the defect is averaged and aligned to the host supercell and is described by  $\Delta E^{\text{Pot}}$ .<sup>56</sup>

To account for the finite size effects of the defect supercells, two post-processing corrections are applied,  $E_{\text{corr}}^{\text{IC}}$  and  $E_{\text{corr}}^{\text{BF}}$ . The first correction term corresponds to the image-charge correction which minimises the long ranged nature of the Coulomb interaction<sup>57,58</sup> of the charged defect and its periodic images. The implementation used herein uses a formalism based upon the Lany and Zunger correction<sup>56</sup> with a ‘non-cubic’ adaptation as implemented by Hine and Murphy.<sup>58,59</sup> Lastly a band-filling correction is applied to shallow and resonant defects to account for the high carrier concentrations present in supercell calculations so as to regain the ‘dilute limit’.<sup>56,60</sup>

### 2.2. Equilibrium concentrations

Equilibrium concentrations of defects in both Li<sub>3</sub>OCl can be calculated self-consistently as implemented in the code SC-FERMI.<sup>61</sup> By determining the Fermi energy self-consistently the concentration of a defect  $D$  in charge state  $q$  can be evaluated through:

$$[D, q] = N_D g_{D,q} \exp\left(\frac{-\Delta H(D, q)}{kT}\right) \quad (2)$$

where  $N_D$ ,  $g_{D,q}$  and  $\Delta H(D, q)$  are the number of sites on which the defect can form, the degeneracy of the defect state and the enthalpy of formation of the defect as calculated in eqn (1) respectively. Given a constraint of overall charge neutrality, the electron and hole concentrations can be determined from eqn (3) and (4):

$$n_0 = \int_{E_g}^{\infty} f_e(E) \rho(E) dE \quad (3)$$



$$p_0 = \int_{-\infty}^0 f_h(E)\rho(E)dE \quad (4)$$

where  $\rho(E)$  is the density of states (DOS),  $E_g$  is the band gap and  $f_e$  is the Fermi-Dirac distribution function given by  $f_e = \left[ \exp\left(\frac{|E_F - E|}{kT}\right) + 1 \right]^{-1}$  and  $f_h = 1 - f_e(E)$ . This approach has successfully been applied to  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (ref. 13) (LLZO) and elsewhere.<sup>51,62</sup>

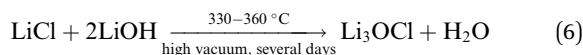
## 3. Results

### 3.1. Defining a chemical potential stability region for metastable $\text{Li}_3\text{OCl}$

Determination of the formation energies of defects in materials requires knowledge of the individual elemental chemical potentials (eqn (1)) which are typically constrained by the thermodynamic stability of the host material relative to competing phases. As  $\text{Li}_3\text{OCl}$  is metastable and not globally stable, calculating the chemical potentials requires either prior experimental knowledge about phase stability,<sup>43</sup> or calculation of host and competing phases at finite temperatures.<sup>63</sup> As the structure and composition of  $\text{Li}_3\text{OCl}$  is not widely acknowledged, the latter is chosen in this instance, however it is important to note that studies exist showing  $\text{Li}_3\text{OCl}$  to possess kinetic stability relative to  $\text{LiCl}$  and  $\text{Li}_2\text{O}$ ,<sup>30,64</sup> proposed to be due to the sluggish anion transport in  $\text{Li}_3\text{OCl}$ .<sup>65</sup> In this study, the chemical potential limits analysis program (CPLAP<sup>66</sup>) is combined with the quasi-harmonic approximation (QHA) to determine the temperature dependent stability region of  $\text{Li}_3\text{OCl}$  and thus unveil suitable chemical potentials without *a priori* knowledge. This approach, whilst not widely used due to its increased computational expense, has shown recent success in determining the stability of  $\text{Na}_2\text{Ti}_3\text{O}_7$ .<sup>63</sup> From our results,  $\text{Li}_3\text{OCl}$  becomes the dominant phase at 750 K/476.85 °C (HSE06 functional), which agrees well with the expected experimental synthesis temperature from nominally non-hydrogen containing precursors,  $\text{Li}_2\text{O}$  and  $\text{LiCl}$  at (773 K/500 °C):<sup>35</sup>



Typically, however,  $\text{Li}_3\text{OCl}$  is often formed *via* a solid state synthesis from a combination of  $\text{LiCl}$  and  $\text{LiOH}$  at lower temperatures:<sup>27</sup>



An overview of the common synthesis routes is given in ESI Section 6† together with their calculated Gibbs free energy of reaction ( $\Delta G_{\text{reac}}$ ). Rettenwander and coworkers<sup>35</sup> showed that  $\text{LiCl}$  is still present after following the synthesis outlined in eqn (6) suggesting that  $\text{Li}_3\text{OCl}$  is Cl-poor. This indicates that  $\text{OH}^-$  is likely present in the samples due to an excess of  $\text{LiOH}$ .<sup>35</sup>

Nevertheless, a calculated stability region can be formed and is given in Fig. 1. What is seen is a very narrow region (straight line)

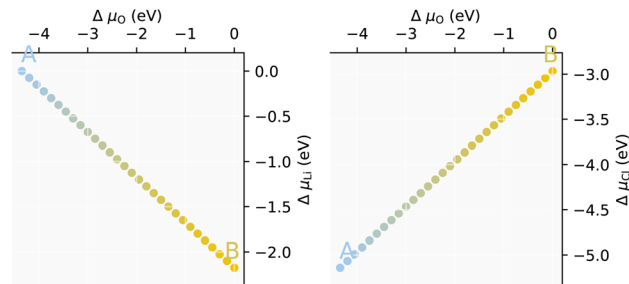


Fig. 1 The chemical potential limits of Li and Cl as a function of O chemical potential as calculated using HSE06 within the QHA formalism at 750 K. The chemical potential stability region is a thin area and is traversed by the coloured dots along  $\mu_{\text{O}}$  from point A to point B.

between Li-rich/anion-poor ( $\mu_{\text{Li}} = -2.17$  eV,  $\mu_{\text{O}} = 0$  eV,  $\mu_{\text{Cl}} = -2.97$  eV) designated point A, and Li-poor/anion-rich ( $\mu_{\text{Li}} = 0$  eV,  $\mu_{\text{O}} = -4.35$  eV,  $\mu_{\text{Cl}} = -5.14$  eV) designated point B. Whilst the results obtained from this method are somewhat strict, a larger region may be realised due to anion partial pressures. Anhydrous  $\text{Li}_3\text{OCl}$  can therefore be said to be stable over a more modest range of  $\mu_{\text{Li}}$  than the larger  $\mu_{\text{O}}$  and  $\mu_{\text{Cl}}$ , anion deficiency or substitution in  $\text{Li}_3\text{OCl}$  is much more tolerated compared to Li deficiency, which could lead to thermodynamic instability towards other phases.

At point A,  $\text{Li}_3\text{OCl}$  is calculated to be in equilibrium with  $\text{Li}_2\text{O}$ ,  $\text{Li}$ , and  $\text{LiCl}$ . At point B,  $\text{Li}_3\text{OCl}$  is in equilibrium with  $\text{LiCl}$ ,  $\text{Li}_2\text{O}$ , and  $\text{O}_2$ .

### 3.2. Defect thermodynamics

The thermodynamic transition levels as calculated with the HSE06 functional for  $\text{Li}_3\text{OCl}$  are plotted in Fig. 2 showing both intrinsic (upper panels (a) and (b)) and extrinsic hydrogen defects (lower panels (c) and (d)) at anion-poor/Li-rich conditions (point A, in Fig. 1) and anion-rich/Li-poor conditions (point B in Fig. 1) respectively. Additionally, the equilibrium concentrations of the dominant defects ( $\geq 1 \times 10^8$  cm<sup>-3</sup>) are given in Fig. 3 as a function of oxygen chemical potential ( $\mu_{\text{O}}$ ) as one travels from point A to point B. Even though hydrogen incorporation is typically unavoidable in  $\text{Li}_3\text{OCl}$  we will still refer to it as “doping” for the case of simplicity in this work.

**3.2.1 Intrinsic defects.** The intrinsic defects of  $\text{Li}_3\text{OCl}$  are given in Fig. 2(a) and (b) for Li-rich and Li-poor conditions respectively. Equilibrium concentrations when undoped and under H-doping are given in Fig. 3(a) and (b) respectively. Under both regimes, lithium vacancies ( $V_{\text{Li}}$ ) are the dominating defect possessing a formation energy of  $\sim 1.02$  eV at the Fermi level ( $E_{\text{F}} \sim 3.71$  eV and  $\sim 1.37$  eV for Li-rich and Li-poor conditions respectively when undoped). If we compare the Fermi level calculated at  $\mu_{\text{O}} = -1.08$  and  $-1.34$  eV corresponding to the “experimentally accessible” oxygen chemical potentials of Li-rich and Li-poor conditions set out in the work by Squires *et al.*<sup>43</sup> we obtain formation energies of 2.05 eV and 1.89 eV respectively in good agreement with their values of  $\sim 2.20$  eV and  $\sim 1.90$  eV. A thermodynamic determination of the “experimentally accessible” region of oxygen chemical potentials is given in ESI Section 5.† Upon H-doping,  $E_{\text{F}}$  increases in energy to  $\sim 4.12$  eV and  $\sim 1.72$  eV for Li-rich and Li-poor conditions



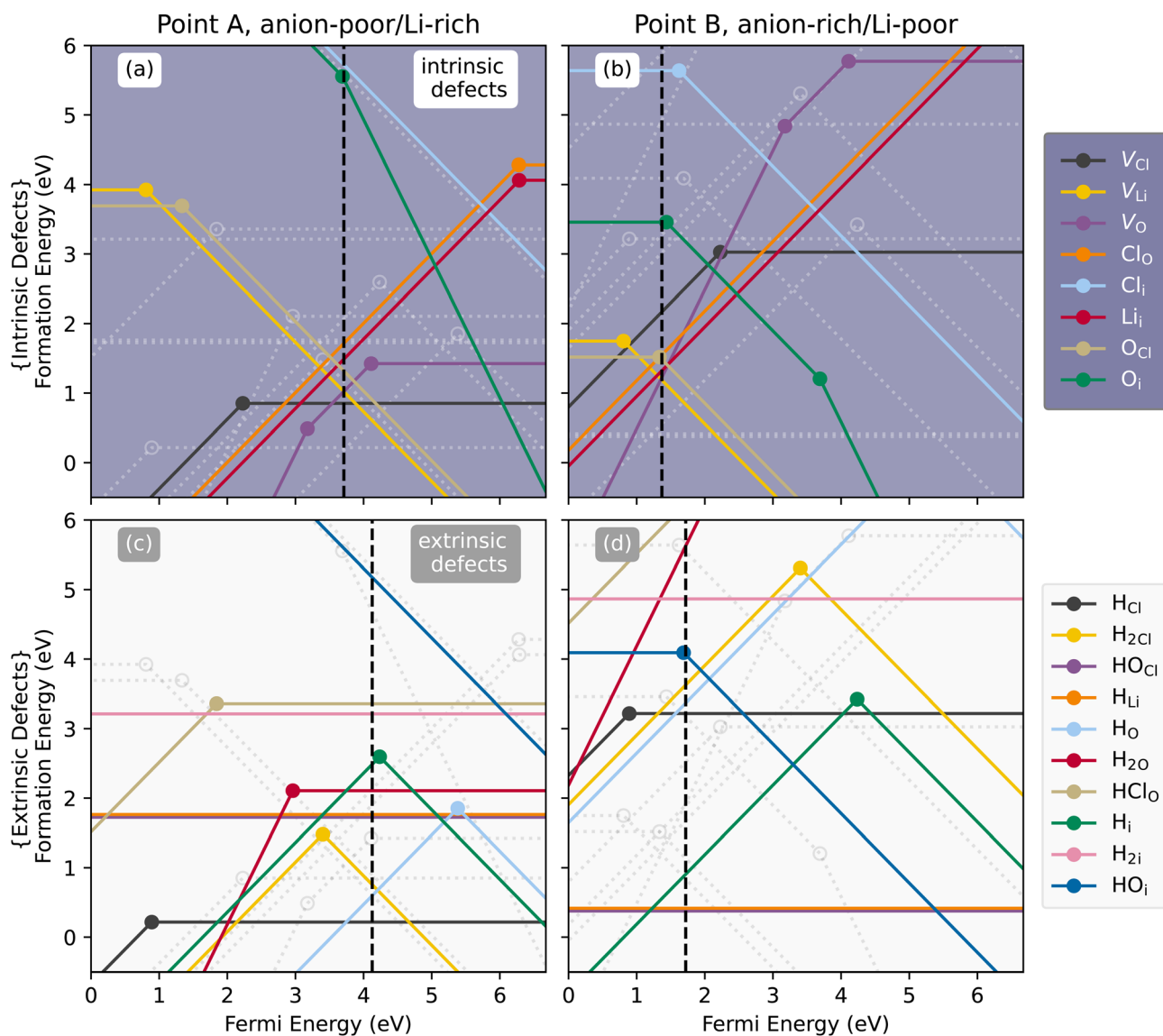
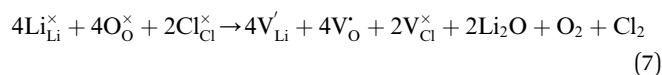


Fig. 2 The thermodynamic transition levels for (a) and (b) intrinsic defects and (c) and (d) extrinsic H defects for the chemical potentials at points A (O-poor) and B (O-rich) respectively at 750 K, 1 atm. In each example the dashed vertical line represents the equilibrium Fermi level ( $E_F$ ) and the corresponding extrinsic and intrinsic defects are shown by the faded dotted lines for reference.

respectively. Pushing  $E_F$  higher in energy, such as through doping<sup>43</sup> results in an ease in the formation of  $V_{Li}$ , increasing the concentration and therefore the ionic conductivity.

**3.2.2 Li-rich/anion-poor conditions, point A.** The dominant intrinsic defects are seen to be  $V_{Li}$ ,  $V_{Cl}$ , and  $V_O$ , indicative of full Schottky disorder. This is partially in agreement with previous literature findings<sup>30,39,42,43</sup> where three types of Schottky disorder are predicted, either “LiCl” partial Schottky: ( $V_{Li} + V_{Cl}$ ),  $Li_2O$  partial Schottky: ( $2V_{Li} + V_O$ ) or in the case of Squires *et al.*: ( $V_{Li} + V_{Cl} + O_{Cl}$ ) (under Li-rich conditions).<sup>39,42,43</sup> Contrary to Squires *et al.*, however, in this work, both antisite defects,  $O_{Cl}$  and  $Cl_O$ , whilst forming in modest quantities, ( $\sim 10^{12}$ – $10^{13}$   $cm^{-3}$ ) are not expected to dominate the defect landscape of  $Li_3OCl$ . It is important to note that,  $O_{Cl}$  does increase to concentrations

$\geq 10^{16}$   $cm^{-3}$  upon H-doping, as seen in Fig. 3(b) simultaneously reducing  $[V_O]$ , thus it could be said that the modified Schottky defect as calculated by Squires *et al.*<sup>43</sup> is somewhat valid. The full Schottky defect calculated in this work is interesting in that  $V_{Cl}$  and  $V_O$  exist in the neutral ( $q = 0$ ) and partially ionised ( $q = 1+$ ) charge states respectively. Charge neutrality of the defect cluster is consequently caused by  $V_{Li}$  and  $V_O$  and can be defined in Kröger-Vink form as:



Partial charge densities are provided in ESI Fig. S5–S7† for  $V_{Li}$ ,  $V_O$ , and  $V_{Cl}$  and their corresponding charge states,





at  $E_F$  under point B of around 0.42 and 0.37 eV respectively. As both defects are neutral ( $q = 0$ ), they aren't expected to be charge compensated by any intrinsic or otherwise H-related species. The equilibrium concentrations of  $[H_{Li}]$  and  $[HO_{Cl}]$  are fairly high  $\sim 1 \times 10^{20} \text{ cm}^{-3}$  and  $\sim 2 \times 10^{20} \text{ cm}^{-3}$  respectively. It is important to note, that whilst "equilibrium concentrations" are stated, we are constrained by the formation of  $Li_3OCl$  and it is highly likely that in reality excess H will make its way into the structure increasing H defect concentrations, or form additional  $Li_{3-x}OH_xCl$  phases or  $Li_2OHCl$ . Upon H doping under Li-poor conditions,  $E_F$  again, shifts towards the conduction band minimum (CBM) from 1.37 eV to 1.7 eV resulting in a lower effective formation energy of  $V_{Li}$  from  $\sim 1.18$  eV to  $\sim 0.84$  eV. As at point A, it is expected that  $[V_{Li}]$  rises from  $\sim 6 \times 10^{14} \text{ cm}^{-3}$  when undoped to  $\sim 1.4 \times 10^{17} \text{ cm}^{-3}$ .

Fig. 4(a) and (b) show the relaxed defect supercells of  $HO_{Cl}$  (at  $q = 0$ ), and  $H_{Li}$  (at  $q = 0$ ) respectively.  $HO_{Cl}$ , warps the structure shifting adjacent Li away from its preferred site (Wyckoff: 3c) towards the neutral cluster. As this defect is nominally neutral, the displacement arises due to the smaller  $OH^-$  radii (110 pm) compared to  $Cl^-$  radii (181 pm) and may aid in improving Li-ion transport by increasing "accessible space" and weakening the Li–O bonds. In  $H_{Li}$  (Fig. 4(b)), H shifts off its Li site (3c) towards an adjacent O forming a neutral OH. This defect can therefore be seen as a "pseudo- $V_{Li}$ " or as suggested by Song *et al.*<sup>67</sup> a Frenkel-type defect as any moving Li into this space technically becomes an interstitial. Experimentally, Schwering *et al.*<sup>68</sup> suggested  $H_{Li}$  as the dominant defect, remarking also that  $H_{Li}$  provides rotatable OH that facilitates Li transport. Work carried out by Eilbracht *et al.*<sup>69</sup> using single crystal data on  $Li_2OHCl$  also suggest Li site occupation. Similar evaluations of the role of rotatable OH groups have been suggested in the literature.<sup>36,67,70</sup> Dawson *et al.*<sup>36</sup> using molecular dynamics simulations (MD) combined with  $^2H$  NMR spectroscopy, observe that both highly rotatable OH groups exist alongside fixed OH groups. Further investigation shows that OH rotations are more free when O is coordinated to fewer lithiums.

## 4. Discussion

In this study, we have performed hybrid functional charged defect calculations on H-doped  $Li_3OCl$ . This is in order to determine the influence of hydrogen on intrinsic defect

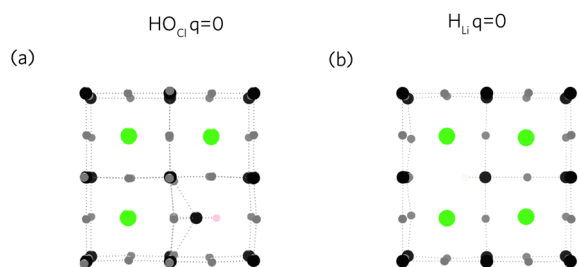


Fig. 4 Relaxed defect structures of (a)  $HO_{Cl}$  ( $q = 0$ ), and (b)  $H_{Li}$  ( $q = 0$ ). In each example, lithium is coloured grey, chlorine is green, oxygen is black and hydrogen is pink. In (b),  $H_{Li}$  relaxes towards O forming a neutral OH species and forming a pseudo- $V_{Li}$ .

chemistry of  $Li_3OCl$  and its influence on structure and ionic conductivity. In this model we have considered all vacancies, interstitials, antisites and varying H-related extrinsic species such as singular H,  $H_2$ , OH and HCl. A self-consistent model such as this is highly important for getting a holistic overview of the mechanisms for ionic conductivity as well unravelling the thermodynamics of  $Li_3OCl$  as given in experimental and computational studies in previous literature.<sup>30,33,36,39–42,67,70</sup>

Taking undoped  $Li_3OCl$ , we find that across the range of synthesis conditions, (Li-poor to Li-rich),  $V_{Li}$  is the dominant charge carrying defect whilst  $Li_i$  exists in much lower concentrations, thus ruling out an interstitial or interstitialcy mechanism within  $Li_3OCl$  consistent with other reports,<sup>30,42,43,71</sup> despite the lower migration energy barrier of 0.17 eV (compared to 0.34 eV for  $V_{Li}$ ).<sup>30</sup> Under the most Li-rich/anion-poor conditions, the full Schottky defect exists, ( $V_{Li} + V_O + V_{Cl}$ ), however with  $V_{Cl}$  existing in the neutral charge state. This is somewhat contrary to previous reports of  $Li_3OCl$  being  $LiCl$  ( $[V_{Li} + V_{Cl}]$ ) Schottky disordered.<sup>30,40,43,72,73</sup> It is important to note, however, that with the exception of the work in ref. 43, the other studies only consider neutral defects and assume full charge neutrality from  $V_{Li}$  and  $V_{Cl}$ , yet we find that the positive compensating defect for  $V_{Li}$  are oxygen vacancies ( $V_O$ ). This changes to a  $Li_2O$  Schottky defect ( $V_{Li} + V_O$ ) under Li-poor conditions. Equally, whilst antisites are expected to form in small quantities ( $\sim 10^{12}$ – $10^{13} \text{ cm}^{-3}$ ) in undoped  $Li_3OCl$ , our results do not point towards significant anion disorder.<sup>18</sup> Consensus in the literature is that anion disorder is beneficial to increasing the conductivity of Li-ion solid electrolytes. This is attributed to significant anion disorder opening up percolating three-dimensional pathways previously inaccessible to anion ordered systems.<sup>15</sup> In a paper by Li *et al.*<sup>74</sup> they stated that due to the size mismatch between O and Cl, anion antisite defects would cause a strong structural distortion and an electrostatic penalty for mobile lithium defects thus reducing the conductivity.

The inconsistency between this work and previous calculations is likely down to both the choice of functional, as well as from the calculation of the chemical potential stability region for  $Li_3OCl$  of which the defect formation energies are highly sensitive to. Hybrid functionals typically give a much better description of electron localisation for defects, as well as favourable description of the band gap of a material relative to experiment.<sup>12,52,75,76</sup> Both of these are crucial when determining charged defect calculations in order to correctly describe the thermodynamic defect quantities of solid electrolytes.<sup>12,13,18,43</sup> In this work, the chemical potential region was determined "temperature-dependently" through calculating the free energies of competing phases using QHA (Section 3.3.1), which has shown success previously in  $Na_2Ti_3O_7$ .<sup>63</sup> Confidence in this result arises from the fact that  $Li_3OCl$  becomes "stable" around  $\sim 750$  K, in excellent agreement with the experimental synthesis temperature (without H) of  $\sim 773$  K.<sup>35</sup>

The unfortunate reality of  $Li_3OCl$  is that it is highly unlikely to be purely  $Li_3OCl$ , but a hydrated form  $Li_{3-x}OH_xCl$ .<sup>35,36</sup> Even when attempting to create dehydrated forms of  $Li_3OCl$ , Li *et al.*<sup>77</sup> acknowledged that some form of OH is observable from FTIR. This work shows that hydrogen defects are omnipresent in the



structure of  $\text{Li}_3\text{OCl}$  and high defect concentrations of at least  $\geq 10^{20} \text{ cm}^{-3}$  are to be expected. Our results indicate a baseline equilibrium which is likely to be higher based on both synthesis conditions and local atmosphere indeed forming  $\text{Li}_2\text{OHCl}$ . Nevertheless, our results do not rule out the formation of cubic anti-perovskite  $\text{Li}_3\text{OCl}$  without forming full  $\text{Li}_2\text{OHCl}$  compositions. Dawson *et al.* showed that hydrogen does not diffuse in  $\text{Li}_3\text{OCl}$  due to the large jump distances of 3.91 Å.<sup>36</sup>

Under Li-rich conditions, it is expected that neutral  $\text{H}_{\text{Cl}}$  forms as the dominant defect which pushes  $E_{\text{F}}$  higher in energy towards the CBM thereby reducing the formation energy of  $\text{V}_{\text{Li}}$  within the crystal structure. Additionally in work carried out by Gao *et al.*,<sup>37,78</sup> they showed that in  $\text{M}_3\text{HCh}$  ( $\text{M} = \text{Li}, \text{Na}; \text{Ch} = \text{S}, \text{Se}, \text{Te}$ ), that the influence of  $\text{H}^-$  reduced the energy barrier of migration due to its large polarizability, thus a similar effect may be present here with  $\text{H}_{\text{Cl}}$ . At the same time, H-incorporation suppresses the Schottky disorder as seen in purely undoped  $\text{Li}_3\text{OCl}$ . This is also the case under Li-poor conditions, whereby the  $\text{Li}_2\text{O}$  Schottky disorder is cancelled by the neutral hydrogen defects:  $\text{H}_{\text{Li}}$  and  $\text{OH}_{\text{Cl}}$ .  $\text{H}_{\text{Li}}$  is seen to relax off its nominal Li site towards an adjacent oxygen forming an “ $\text{OH}_{\text{O}}$ ” which can also be seen as a “pseudo- $\text{V}_{\text{Li}}$ ”. Work by Schwering *et al.*<sup>68</sup> on  $\text{Li}_3\text{OCl}$  and Eilbracht *et al.*<sup>69</sup> on  $\text{Li}_2\text{OHCl}$  agree with this conclusion. This “pseudo- $\text{V}_{\text{Li}}$ ” can also be seen as a Frenkel defect, where the mobile Li becomes effectively an interstitial upon rotation of the OH species.<sup>67</sup> Additionally,  $\text{OH}_{\text{Cl}}$ , whilst neutral, acts to distort the structure slightly due to its smaller radii compared to Cl which may also aid Li mobility.

Squires *et al.*<sup>43</sup> calculated the conductivity of  $\text{Li}_3\text{OCl}$  within their full defect model through:

$$\sigma = \frac{Cq^2}{kT} D^* \quad (11)$$

where  $C$  is the concentration of mobile ions,  $q$  is the charge of those ions,  $k$  the Boltzmann constant,  $T$  the temperature and the self-diffusion coefficient is given by  $D^*$  and takes into account the attempt frequency ( $1 \times 10^{13} \text{ Hz}$ ), the hop distance (2.67 Å (ref. 43)) and the migration barrier,  $E_{\text{m}}$  (0.34 eV (ref. 30)).<sup>43</sup> In their work they showed that undoped  $\text{Li}_3\text{OCl}$  expects values of  $\sim 10^{-10} \text{ S cm}^{-1}$  far off the values present in experiment ( $\sim 10^{-6} - 10^{-2} \text{ S cm}^{-1}$ ).<sup>29</sup>

Fig. 5 displays the ionic conductivity as a function of  $\mu_{\text{O}}$  calculated with the same strategy using our defect model for undoped and H-doped  $\text{Li}_3\text{OCl}$ . Our results align well with Squires *et al.*<sup>43</sup> where low conductivities of  $\sim 10^{-10} \text{ S cm}^{-1}$  are observed. Upon incorporation of hydrogen, the  $\text{V}_{\text{Li}}$  conductivity increases from  $\sim 3.75 \times 10^{-11} \text{ S cm}^{-1}$  under Li-poor conditions to  $\sim 3.35 \times 10^{-10} \text{ S cm}^{-1}$  under Li-rich conditions. By including the “pseudo- $\text{V}_{\text{Li}}$ ” into our model, before considering potential enhancements to the mobility due to OH rotations the ionic conductivity of H-doped  $\text{Li}_3\text{OCl}$  lie in the region of  $\sim 10^{-6} \text{ S cm}^{-1}$  in better agreement with experiment. Work by Dawson *et al.*<sup>36</sup> showed that lower concentrations of H within  $\text{Li}_3\text{OCl}$  resulted in lower migration energy barriers  $\sim 0.30 \text{ eV}$  whilst Song *et al.*<sup>67</sup> predicted values of  $\sim 0.24/0.26 \text{ eV}$ . Whilst  $\text{OH}_{\text{Cl}}$  has an increased Li-coordination to  $\text{H}_{\text{Li}}$ , it is likely that

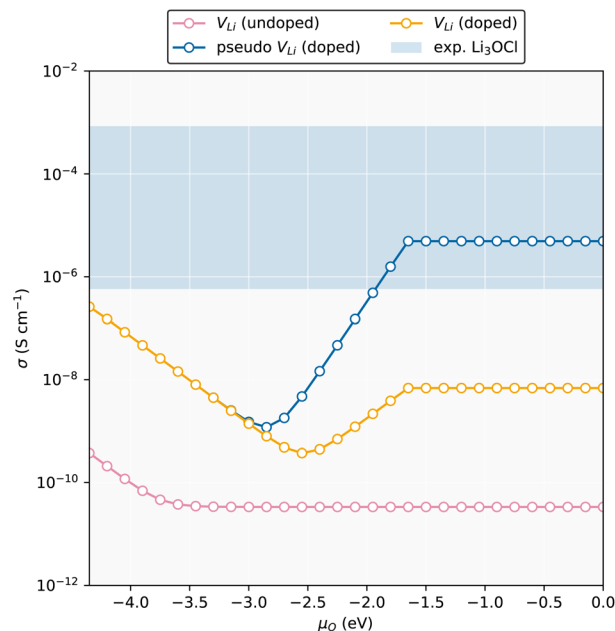


Fig. 5 Room temperature ionic conductivity as a function of oxygen chemical potential taking into account the sum of  $\text{V}_{\text{Li}}$  and  $\text{Li}_i$ . Included is also the “pseudo- $\text{V}_{\text{Li}}$ ” whereby  $\text{H}_{\text{Li}}$  is treated as a  $\text{V}_{\text{Li}}$  using the same migration barrier. The blue shaded region corresponds to experimental conductivities taken from ref. 27 and 79.

$\text{OH}_{\text{Cl}}$  may lower the barrier for migration in a similar way that Br does in  $\text{Li}_3\text{OCl}_{1-n}\text{Br}_n$ .<sup>80</sup>

## 5. Conclusions

In this work we illustrate the need for consideration of hydrogen as both a compositional changing opportunistic dopant, as well as a strategy for enhancing the ionic conductivity, not only in  $\text{Li}_3\text{OCl}$  but other hygroscopic solid electrolytes as well. A full defect model combined with a temperature dependent defined chemical potential stability region is necessary in order to outline doping strategies, killer defects, as well as structural changes in a given material. Our results highlight that, when undoped,  $\text{Li}_3\text{OCl}$  can expect a degree of Schottky disorder, both full and  $\text{Li}_2\text{O}$ -Schottky, in line with other computational predictions. Such a disorder, particularly anion disorder, can give rise to favourable ionic mobility of Li-species within the structure, similar to that in other solid electrolytes. Upon inevitable hydrogen incorporation, the Schottky disorder disappears, instead favouring the formation of neutral H species such as  $\text{OH}_{\text{Cl}}$  and  $\text{H}_{\text{Li}}$ .  $\text{H}_{\text{Li}}$  is shown to relax off site towards an adjacent oxygen forming an effective ( $\text{OH}_{\text{O}} + \text{V}_{\text{Li}}$ ) defect pair, or a “pseudo- $\text{V}_{\text{Li}}$ ”. Considering only purely  $\text{V}_{\text{Li}}$  results in low ionic conductivities, however, upon consideration of a “pseudo- $\text{V}_{\text{Li}}$ ”, our calculated ionic conductivities are more in line with experimentally observed values. Whilst  $\text{Li}_3\text{OCl}$  remains a controversial and challenging material, our results show that H may be a source of enhancement in  $\text{Li}_3\text{OCl}$ , increasing both the ionic mobility due to OH rotations, as well as increasing the effective carrier concentration.



## Data availability

The data for this article have been included as part of the ESI.†

## Author contributions

BADW provided the idea for this study and performed the calculations and analysis, with help from KE. BADW wrote the manuscript, and all authors contributed to the reviewing and editing of the final manuscript and have given approval to the final version of the manuscript. SMS provided funding for this project.

## Conflicts of interest

There are no conflicts of interest in this work.

## Acknowledgements

This work was supported by the Research Council of Norway through Projects no. 275810 and 302506. Computational resources were provided by UNINETT Sigma2 through Projects NN9264K and ntnu243. B.A.D.W would like to acknowledge Nora S. Løndal and Caren R. Zeiger for useful discussions.

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