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# Prediction of Ground State Configurations and Electrochemical Properties of Li<sub>3</sub>InCl<sub>6</sub> doped with F, Br and Ga

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# **Prediction of Ground State Configurations and**

# Electrochemical Properties of Li<sub>3</sub>InCl<sub>6</sub> doped with F, Br and Ga

Zheng-Yu Lu(鲁征宇)<sup>1</sup>, Le-Tian Chen(陈乐添)<sup>1</sup>, Xu Hu(胡绪)<sup>1</sup>, Su-Ya Chen(陈素雅)<sup>1</sup>, Xu Zhang(张旭)<sup>2\*</sup> and Zhen Zhou(周震)<sup>1,2</sup>

 <sup>1</sup> Department of Materials Science and Engineering, Nankai University, Tianjin 300350, China
<sup>2</sup> Interdisciplinary Research Center for Sustainable Energy Science and Engineering (IRC4SE<sup>2</sup>), School of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China

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\*Xu Zhang. Email: zzuzhangxu@zzu.edu.cn

### Abstract

Compared with conventional solid-state electrolytes, halide solid-state electrolytes have several advantages such as a wider electrochemical window, better compatibility with oxide cathode materials, improved air stability, and easier preparation conditions making them conductive to industrial production. We focused on a typical halide solid-state electrolyte, Li<sub>3</sub>InCl<sub>6</sub> and predicted the most stable structure after doping with Br, F, and Ga by using the Alloy Theoretic Automated Toolkit based on first-principles calculations, and verified the accuracy of the prediction model. To investigate the potential of three equivalently doped ground state configurations of Li<sub>3</sub>InCl<sub>6</sub> as solid-state electrolytes for all-solid-state lithium-ion batteries, their specific properties such as crystal structure, band gap, convex packing energy, electrochemical stability window, and lithium-ion conductivity were computationally analyzed using first-principles calculations. After a comprehensive evaluation, it was determined that the F-doped ground state configuration Li<sub>3</sub>InCl<sub>2.5</sub>F<sub>3.5</sub> exhibits better thermal stability, wider electrochemical stability window, and better lithium ion conductivity (1.80 mS cm<sup>-1</sup> at room temperature). Therefore, Li<sub>3</sub>InCl<sub>2.5</sub>F<sub>3.5</sub> has the potential to be used in the field of all-solid-state lithium-ion batteries as a new type of halide electrolyte.

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# Introduction

After decades of development, lithium-ion batteries consisting of graphite as the anode, transition metal oxides as the cathode, and liquid organic electrolyte have reached the upper limit of energy density (about 350 Wh kg<sup>-1</sup>).<sup>[1]</sup> However, some issues related to the cycle life and safety of traditional lithium-ion batteries make it difficult to meet the increasing demand for future applications. The safety threat associated with the leakage and flammability of liquid organic

electrolytes cannot be ignored. The improved safety, wider electrochemical window, and longer cycle life of solid-state electrolytes (SSE) make all-solid-state lithium batteries (ASSLB) the most promising contender for the next generation of batteries.<sup>[2,3]</sup>

SSE mainly includes several types of polymers, oxides, sulfides, and halides. The ionic conductivity of polymer SSEs is greatly affected by temperature, which makes it difficult to work stably in a wide temperature range.<sup>[4]</sup> Oxide SSEs exhibit good electrochemical stability, however, their poor mechanical properties due to the rigid structure lead to insufficient contact between the electrode and electrolyte, resulting in a large interfacial impedance.<sup>[5]</sup> Sulfide SSEs possess high ionic conductivity but they are less stable in the presence of air and humidity.<sup>[6]</sup>

Halide SSEs offer several advantages, including a wider electrochemical window, better compatibility with oxide cathode materials, greater stability in the presence of water and air, and easier preparation conditions conducive to industrial production. The halide SSEs can be represented in the form of Li-M-X, where M is a metal element and X is a halogen. The categorization of halide SSEs is based on the classification of the metal element M, which can be grouped as follows: (1) M belonging to group IIIA, (2) M belonging to group IIIB, and (3) M being a divalent metallic element such as Ti, V, Fe, Co, and Ni. Asano et al.<sup>[7]</sup> reported novel halide SSE materials, Li<sub>3</sub>YBr<sub>6</sub> and Li<sub>3</sub>YCl<sub>6</sub>, which exhibit high ionic conductivity while also possessing satisfactory electrochemical and thermal stability as well as mechanical properties suitable for large-scale fabrication.

Doping with different elements has shown promising results in the field of discovering novel SSE materials. On the one hand, doping can improve the ionic conductivity of SSE creating vacancy defects and broadening ion transport channels. On the other hand, doping can regulate the composition of SSE, reduce interfacial resistance and improve chemical stability, thus effectively solving the SEI problem. For example, doping with Mo,<sup>[8]</sup> Fe,<sup>[9,10]</sup> Zn,<sup>[11]</sup> and Mn<sup>[12]</sup> can effectively improve the ionic conductivity of Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> and form a metallic phase at the interface to reduce the interfacial resistance; doping with O,<sup>[11,13]</sup> Cl,<sup>[14,15]</sup> Br,<sup>[11,16]</sup> and I<sup>[17,18]</sup> can also improve the ionic conductivity of SSE.

However, the wide range of available doping concentrations means that researchers are constantly searching for efficient ways to determine the optimal doping concentration. While the traditional trial-and-error experimental method obviously requires a significant amount of time and may lead to inaccurate data, computational simulations based on Density Functional Theory (DFT) can make a big difference. Software for ground state configuration search have been successfully developed, such as Alloy Theoretic Automated Toolkit (ATAT)<sup>[19-23]</sup> which uses the total energy calculated by the Vienna Ab-initio Simulation Package (VASP)<sup>[24]</sup> program to determine the most stable phase for each component. The ATAT program employs the Cluster Expansion (CE)<sup>[25-28]</sup> method through the embedded MIT Ab-initio Phase Stability (MAPS)<sup>[23]</sup> program to generate various candidate structures with doping concentration ranging from 0 to 100%, and the energy of each cluster and structure is then evaluated and compared by linked first-principles calculations. The CE method has a significant advantage in terms of rapid convergence, enabling the use of relatively compact clusters to determine the energies of crystalline phases through the structure inversion method while still achieving sufficient accuracy.<sup>[29]</sup>

Li et al.<sup>[30]</sup> successfully synthesized a halide SSE material, Li<sub>3</sub>InCl<sub>6</sub>, exhibiting high ionic conductivity (up to  $1.49 \times 10^{-3}$  S cm<sup>-1</sup> at 298 K), as well as stability to air and humidity. Since Br and F are congeners of Cl with the same valences, and Ga for the same reason, we have chosen F,

Br and Ga as doping elements. In this work, we predict the ground state configurations of Li<sub>3</sub>InCl<sub>6</sub> after equivalent doping of F, Br, and Ga using ATAT and evaluate the accuracy of the adopted CE model. The potential of the predicted ground state configuration to be applied to all-solid-state lithium-ion batteries is also explored through DFT calculations and modules in the Python materials genomics (Pymatgen)<sup>[31]</sup> program.

# **Computational Methods**

For DFT calculations, we use VASP with the projector augmented wave (PAW)<sup>[32]</sup> method to describe the interaction between ions and electrons and the Perdew-Burke-Ernzerhof (PBE)<sup>[33]</sup> functions are employed for exchange-correlation (XC). In order to balance the computational accuracy and efficiency, we use the default value of the cutoff energy during the ground state structure search process. Moreover, for further structure optimization and property calculation, we apply a cutoff energy of 450 eV. The k-points in the Brillouin zone are selected using Monkhorst-Pack method.<sup>[34]</sup> To ensure the uniform accuracy of k-points throughout the search process, we set KPPRA (K-Point Per Reciprocal Atom) to 1000 in the input file vasp.wrap of ATAT, allowing the package to automatically generate a suitable k-point grid. During the process of searching the structure, along with the expansion of the cell, the precision of the K-point is sufficient. For the further calculation, we adopt the K-point density recommended by VASPKIT.<sup>[35]</sup> The pseudopotential recommended by VASP is chosen for the calculation after completing the structural relaxation.

Through the Materials Project (MP) REST (Representational State Transfer) API (Application Programming Interface),<sup>[36]</sup> we use Pymatgen program to access the MP database and perform phase diagrams, the energy above hull ( $E_{hull}$ ) and electrochemical stability window calculations. We construct phase diagrams based on the Gibbs free energy of all components within the ground state structure. The Gibbs free energy of a substance is defined as

$$G = H - TS = E + PV - TS \tag{1}$$

where H and S represent enthalpy and entropy respectively. To approximate G for the condensed phase at 0 K, we assume G to be equal to E. The total  $E_{hull}$  is defined as the difference between the linear combination of the internal energy of a compound in the phase diagram and the surrounding steady-state components, which is generally zero for them. A higher  $E_{hull}$  value reflects lower thermal stability of the structure. We construct the phase diagram based on the grand potential of all components within the ground state structure. The grand potential of lithium is defined as

$$\phi = G - \mu_{Li} N_{Li} = E + PV - TS - \mu_{Li} N_{Li}$$
(2)

where  $N_{Li}$  means the number of lithium atoms and  $\mu_{Li}$  represents the chemical potential of lithium in the environment. In this work,  $\mu_{Li}$  is defined as

$$\mu_{Li} = \mu_{Li}^0 - e\varphi \tag{3}$$

a function of voltage. The grand potential phase diagram of lithium enables us to determine the thermal stability of the doped ground state configuration at different voltages, as well as the electrochemical stability window of the structure. The construction of the phase diagram above is realized through the Phase Diagram module<sup>[37]</sup> of Pymatgen.

The conductivity of lithium ions is a key property that determines whether a material can be used as SSE. To calculate the conductivity of lithium ions for the three doped ground-state configurations, we use Ab initio molecular dynamics (AIMD) method, performed by using the Nosé-Hoover thermostatic conditions at 600 K, 900 K, 1200 K and 1500 K with a time step of 2 fs for a total simulation time of 60 ps. First, we calculate the root mean square displacement (RMSD) of the lithium ion as

$$RMSD = \left\langle \left[ r_m \left( t + t_0 \right) - r_m \left( t_0 \right) \right]^2 \right\rangle = \frac{1}{N} \sum_m \left[ r_m \left( t + t_0 \right) - r_m \left( t_0 \right) \right]^2$$

The calculation of RMSD is performed through the Diffusion Analyzer module of Pymatgen. The self-diffusion coefficient of lithium ions is calculated as

$$D = \lim_{t \to \infty} \frac{\left\langle r^2(t) \right\rangle}{2dt}$$

Then we could obtain the conductivity of lithium ions by the Nernst-Einstein equation as

$$\sigma = \frac{Nq^2D}{k_BT} \tag{6}$$

(4)

(5)

According to Arrhenius equation, we could express the conductivity as a function of temperature, using several constants parameters. Finally we get the equation:

$$\ln\left(\sigma T\right) = \frac{K}{T} + A \tag{7}$$

which indicates that  $\ln(\sigma T)$  is proportional to the inverse of T. Due to the low conductivity at room temperature, the direct calculation of RMSD is not accurate. By the equation above, we could use the conductivity at high temperature to obtain the conductivity and the activation energy of lithium ions transport at room temperature.

# **Results and Discussion**

Prediction of the ground state configurations

Fig.1 shows the crystal structure of Li<sub>3</sub>InCl<sub>6</sub> with space group c2/m. The crystal lattice of Li<sub>3</sub>InCl<sub>6</sub> is composed of Cl<sup>-</sup> ions arranged in six-coordinated octahedral sites, with In<sup>3+</sup> and Li<sup>+</sup> occupying these sites and sharing common edges. After structural relaxation calculations, the lattice constants of Li<sub>3</sub>InCl<sub>6</sub> obtained agree well with the experimental values (a = b = 6.364 Å, c = 6.368 Å,  $\alpha = \beta = 100.197^{\circ}$ ,  $\gamma = 119.630^{\circ}$ ).<sup>[30]</sup>



Fig. 1. Schematic diagram of the crystal structure of Li<sub>3</sub>InCl<sub>6</sub> (a) ball-stick (b) polyhedral. The blue, purple and green balls represent Cl, In and Li respectively.

We successfully predict the ground state configurations of Li<sub>3</sub>InCl<sub>6</sub> doped with F, Br, and Ga

using ATAT. Fig.2 illustrates the relationship between the energy of the doped structure and the doping concentration. To verify the accuracy of the CE model, we compare the energy values obtained from first-principles calculations to those predicted by the CE model. As shown in the Fig.3, there is not much difference between the predicted and calculated energy values for the three doping strategies. To better visualize the relationship between predicted and calculated energy values for various configurations, a linear fitting has been performed, as shown in Fig.4. We verify the accuracy of the CE model for all three doping strategies and found that it falls within the ideal range. Therefore, the ground state configurations predicted by ATAT are accurate and can be used for subsequent property studies.



Fig.2. The relationship between configuration energy and doping concentration predicted by ATAT: (a) doping F (b) doping Br (c) doping Ga.





Fig.3. The difference between the energy calculated by DFT and predicted by CE model: doping (a) F (b) Br (c) Ga.



Fig.4. Linear fitting of the energy calculated by DFT and predicted by CE model: doping (a) F (b) Br (c) Ga.

#### Electrochemical properties of the ground state configurations

The ground state configurations of Li<sub>3</sub>InCl<sub>6</sub> doped with F, Br and Ga are obtained by prediction as Li<sub>3</sub>InCl<sub>2.5</sub>F<sub>3.5</sub>, Li<sub>3</sub>InCl<sub>0.33</sub>Br<sub>5.67</sub> and Li<sub>3</sub>In<sub>0.83</sub>Ga<sub>0.17</sub>Cl<sub>6</sub>, respectively. Their structures are shown in Fig.5, which have been expanded for comparison. Comparison with the original structure of Li<sub>3</sub>InCl<sub>6</sub> reveals that the lattice of all three doped ground-state configurations is distorted and the symmetry is weakened, however the cations are still located on the six-coordinated co-sided octahedral sites composed of anions, indicating that the overall transport mechanisms and pathways of lithium ions have not been significantly altered.



Fig.5. Ground state structure of Li<sub>3</sub>InCl<sub>6</sub> doped: (a) Li<sub>3</sub>InCl<sub>0.33</sub>Br<sub>5.67</sub> (b) Li<sub>3</sub>InCl<sub>2.5</sub>F<sub>3.5</sub> (c) Li<sub>3</sub>In<sub>0.83</sub>Ga<sub>0.17</sub>Cl<sub>6</sub>. (The blue, purple, green, brown, yellow, and red balls represent Cl, In, Li, Br, F, and Ga respectively.)

To investigate their potential applications in ASSLB, we calculate the electronic structures of both the original structure of Li<sub>3</sub>InCl<sub>6</sub> and the three doped ground state configurations. Fig.6 shows the diagrams of band structure and density of states for each of the configurations. The band gap of the four configurations are obtained by analyzing the energy band structure, as shown in Table 1. It can be found that doping with Br significantly reduces the band gap and the insulation making it unsuitable for use as an SSE in ASSLB. Conversely, doping with F and Ga does not significantly alter the band gap and improves the insulation performance, suggesting their potential suitability for use in ASSLB.



Fig.6. The diagram of band structure and density of states of Li<sub>3</sub>InCl<sub>6</sub> pristine structure and doped structure: (a) Li<sub>3</sub>InCl<sub>6</sub> (b) Li<sub>3</sub>InCl<sub>0.33</sub>Br<sub>5.67</sub> (c) Li<sub>3</sub>InCl<sub>2.5</sub>F<sub>3.5</sub> (d) Li<sub>3</sub>In<sub>0.83</sub>Ga<sub>0.17</sub>Cl<sub>6</sub>

Table 1. Band gap and Ehull of Li3InCl6 pristine structure and doped structure.							
	VBM	CBM	Band gap (eV)	$E_{hull}$			
	(eV)	(eV)		(eV/atom)			
Li <sub>3</sub> InCl <sub>6</sub>	0.48	3.84	3.36	0.055			
Li3InClo.33Br5.67	0.12	2.46	2.34	0.055			
Li <sub>3</sub> InCl <sub>2.5</sub> F <sub>3.5</sub>	-0.04	3.46	3.50	0.053			
Li3In0.83Ga0.17Cl6	0.48	3.79	3.31	0.061			

The  $E_{hull}$  of the original structure of  $Li_3InCl_6$  and the three doped ground state structures is calculated by the PhaseDiagram module of Pymatgen, as shown in Table 1. It can be seen that the stability of the structure doped with Br and F does not differ significantly from that of the original

structure, however the thermal stability becomes worse after doping with Ga.

Then we calculate lithium grand potential phase diagrams of the above four structures by Pymatgen to explore the thermal stability of the doped ground state configurations at different voltages, and the resulting electrochemical stability windows of the materials are obtained as shown in Fig.7 and Table 2. It can be seen that the width of the electrochemical stability window is reduced for all three doped structures. However, it is significantly wider than many current sulfide and oxide SEs such as LGPS (1.72-2.29 V) and Li<sub>3</sub>PS<sub>4</sub> (1.71-2.31 V).<sup>[38,39]</sup>



Fig.7. The electrochemical stability windows of the four configurations: (a)  $Li_3InCl_6$  (b)  $Li_3InCl_{0.33}Br_{5.67}$  (c)  $Li_3InCl_{2.5}F_{3.5}$  (d)  $Li_3In_{0.83}Ga_{0.17}Cl_6$ .

$\overline{\mathcal{A}}$	Electrochemical stability	Electrochemical stability	
	range (V)	width (V)	
Li3InCl6	$2.28 \sim 4.42$	2.14	
Li <sub>3</sub> InCl <sub>0.33</sub> Br <sub>5.67</sub>	$2.17 \sim 3.14$	0.97	
Li <sub>3</sub> InCl <sub>2.5</sub> F <sub>3.5</sub>	$2.94 \sim 4.43$	1.49	
Li3In0.83Ga0.17Cl6	$2.32 \sim 4.25$	1.93	

Table 2. The electrochemical stability window range and width of four configurations.

Finally, to investigate the lithium ion conductivity of the three doped configurations, we utilize the Diffusion Analyzer module of Pymatgen. We perform AIMD calculations at 600 K, 900 K, 1200 K and 1500 K and calculate the ionic conductivity at the corresponding temperatures from the obtained RMSD data. To obtain the ionic conductivity at room temperature, we employ Arrhenius equation to plot  $\ln(\sigma T)$  against 1000/T and fit a straight line for extrapolation, as shown in Fig. 8 and Table 3.



Fig.8. Lithium ion conductivity vs. temperature for three doped configurations (Black, red and blue represent doped Br, F, Ga respectively).

	600 K	900 K	1200 K	1500 K	300 K
	(mS cm <sup>-1</sup> )				
Li <sub>3</sub> InCl <sub>0.33</sub> Br <sub>5.67</sub>	_	297.63	549.00	720.19	0.79
Li3InCl <sub>2.5</sub> F <sub>3.5</sub>	237.91	1153.56	1351.92	3140.43	2.01
Li3In0.83Ga0.17Cl6	127.10	693.06	1063.61	2120.74	0.64

Table 3. Lithium ion conductivity of three doped configurations at different temperatures.

The ionic conductivities of Li<sub>3</sub>InCl<sub>6</sub> synthesized by Li et al.<sup>[30]</sup> using mechanical and annealing methods are 0.84 and 1.49 mS cm<sup>-1</sup>, respectively, which shows that Li<sub>3</sub>InCl<sub>2.5</sub>F<sub>3.5</sub> obtained by F-doping exhibits good potential as a new halide SSE using in ASSLB. Interestingly, a report has demonstrated that F-doped Li<sub>3</sub>InCl<sub>6</sub> (Li<sub>3</sub>InCl<sub>5.8</sub>F<sub>0.2</sub>) solid electrolyte shows significant potential in ASSLB.<sup>[40]</sup>

#### Conclusions

We utilize DFT calculations and software programs, such as ATAT and Pymatgen to investigate the potential application of the ground state configuration of the ternary metal halide electrolyte Li<sub>3</sub>InCl<sub>6</sub>, after equivalent doping with Br, F and Ga, as an SSE in ASSLBs. Our calculations successfully predict the ground state configuration of the doped structures and the accuracy of the predicted results is scientifically evaluated using the adopted CE model, demonstrating good accuracy. Three ground state configurations after doping are obtained which are identified as Li<sub>3</sub>InCl<sub>0.33</sub>Br<sub>5.67</sub>, Li<sub>3</sub>InCl<sub>2.5</sub>F<sub>3.5</sub>, and Li<sub>3</sub>In<sub>0.83</sub>Ga<sub>0.17</sub>Cl<sub>6</sub>. A comprehensive analysis of the crystal structure, band gap, energy above hull, electrochemical stability window and lithium ion conductivity is performed to evaluate their capability as SSE for ASSLB. The calculation results show that  $Li_3InCl_{2.5}F_{3.5}$  possesses superior thermal stability, wider electrochemical stability window and better lithium ion conductivity (up to 2.01 mS cm<sup>-1</sup> at room temperature). Our findings not only provide a prediction of a novel halide SSE for use in ASSLBs, but also offer a systematic approach to the design of SSE materials and a novel research model that could contribute to the advancement of the field.

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