Exploring the Electrical Properties of Li_5GaO_4 as a Potential Li Battery Electrolyte through Atomistic Simulation

S. Mathushan[1], P. Abiman[1#], P. Iyngaran[1], N. Kuganathan[2]

[1] University of Jaffna, Thirunelvely, Sri Lanka
[2] Imperial College London, UK
#Corresponding Author: abiman@univ.jfn.ac.lk

1. Introduction

In the realm of advanced materials for energy storage, Li_5GaO_4 has garnered attention as a potential candidate for applications in lithium-ion batteries (Li-ion). This compound exhibits unique electrochemical properties that make it a subject of extensive investigation, particularly concerning defects, dopants, and Li-ion migration within its crystal lattice. Utilizing atomistic simulations with the General Utility Lattice Program (GULP) software, this study aims to unravel the intricacies of Li_5GaO_4, shedding light on its behavior at the atomic scale.

The ionic conductivity of Li_5GaO_4 has been noted to exhibit a notable dependency on moisture content. Moreover, Li_5GaO_4 and Li_5AlO_4 have been explored for their ionic conductivity in moist air environments, presenting the prospect of their use as humidity sensors in high-temperature applications. The materials exhibited an exponential increase in ionic conductivity at 500°C with rising moisture content, reaching conductivity levels 2-3 orders of magnitude higher. Li_5AlO_4 and Li_5GaO_4 demonstrated good reproducibility in conductivity changes during wet-dry cycles, indicating stability and suitability as humidity sensors. While they operate at temperatures above 450°C and cover a wide relative humidity range, requiring an oxygen partial pressure for stability, their higher conductivities than other sensor materials make them promising candidates [1]. Notably, Li_5GaO_4 showcases significant promise as a CO_2 captor and enhanced electrical conductivity, unveiling its potential applications in addressing environmental challenges [2].

Li_5GaO_4 holds potential as a solid electrolyte, offering an alternative to liquid electrolytes. The advantages of using solid electrolytes, such as enhanced safety and stability, present an appealing avenue for Li-ion battery technology. However, challenges and problems, such as limited Li-ion conductivity and interface compatibility, need thorough exploration to unlock the full potential of Li_5GaO_4 as a solid electrolyte.

Due to the limited availability of experimental data in existing literature, there is a crucial need for a more comprehensive understanding of Li_5GaO_4 to enhance its efficiency in Li-ion batteries. The predicted formation energy of this compound is negative, [5] and structural stability was ensured with having no imaginary frequencies (often associated with dynamic analyses) during optimization. Exploration of the intrinsic defect energetics, ion migration, and dopant substitution at the atomistic level through computational studies becomes imperative. Remarkably, there is a notable absence of research addressing the defect and diffusion characteristics of Li_5GaO_4. The chosen simulation method, widely employed in examining various oxide materials, including those used in batteries, provides a well-established foundation for this investigation. Subsequent paragraphs, however, are indented.

2. Methodology

The computational framework employed in this study relies on the General Utility Lattice Program (GULP) for classical pair-wise potential simulations. It combines long-range Coulombic interactions with short-range Pauli repulsion and van der Waals attraction forces, utilizing Buckingham potentials for the latter. Structural relaxations are achieved through the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [3]. This algorithm in GULP ensures atomic forces remain below 0.001 eV/Å in relaxed configurations. For modeling point defects and ion migration, the Mott-Littleton method in GULP is adopted to minimize errors. The BFGS algorithm is selected for its efficiency, robustness, and ease of use in solving nonlinear optimization problems. Mott-Littleton Method is chosen for its specialization in defect calculations within crystalline materials, providing accurate and efficient modeling of localized defect effects. Its approach to segregating regions around the defect ensures both accuracy and computational efficiency, making it versatile for a wide range of materials and integrable with other computational techniques. Lithium-ion migration is analyzed at seven interstitial points with equal intervals between neighboring lithium sites. Defect energies along the diffusion path are determined with the midpoint between adjacent oxygen vacancy sites as the calculation center to minimize errors.

Ions are treated as spherical objects with full charge at the diluted limit. Despite the potential overestimation of defect formation enthalpies due to the use of full charge with spherical ions at a diluted limit, these simulations are still valuable for understanding qualitative trends and relative defect behaviors in materials [7].. The crystal is divided into Region I and Region II, with different approaches for encapsulating ions due to varying stress

levels. In Region I, where substantial forces are present, specific ion encapsulation is required, while in Region II, where stresses are milder, quasi-continuum techniques are utilized to stabilize ions. The core-shell technique is employed to model ion polarization, building upon previous research on migratory paths and activation energies.

The GULP code, based on the classical born model description, serves as the foundation for bulk and defective structure calculations [4], incorporating total long-range Coulombic interactions and van der Waals interactions through Buckingham potentials to account for short-range repelling interactions between electrons. The VESTA program was utilized to visualize the optimized structure of the Li_5GaO_4 compound.
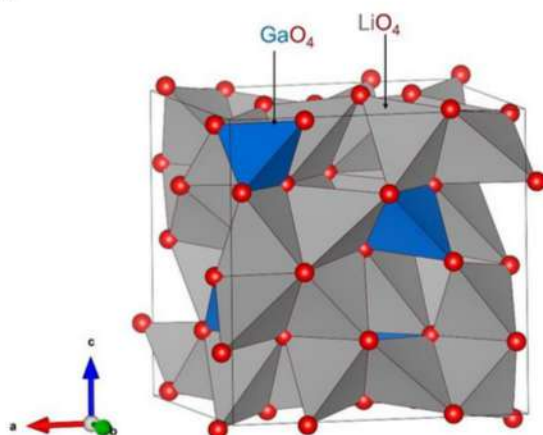
3. Results and Discussion

Fig. 1. The crystal structure of Li_5GaO_4

Li_5GaO_4 exhibits a polar orthorhombic structure within the *Pbca* space group. This investigation provides an in-depth analysis of the crystal structure, comprising Li, Ga, and O with lattice parameters in the x, y, and z directions specified as a= 9.09 Å, b=9.20 Å and c=9.17 Å [5]. The angles α, β, and γ are all set at 90 degrees. Each Ga and Li-ion are intricately coordinated with four O ions, forming $[GaO_4]$ tetrahedra and $[LiO_4]$ tetrahedra. The crystal structure presents itself as a layered arrangement comprising edge-sharing LiO_4 and GaO_4 tetrahedra.
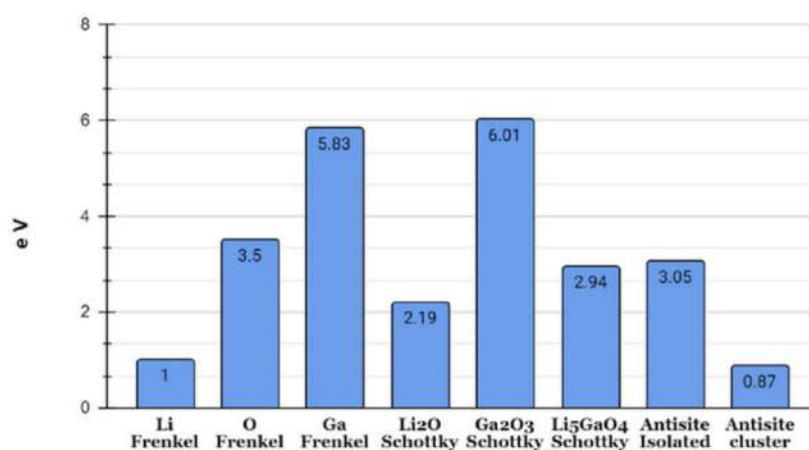

Fig. 2. Energetics of intrinsic defect processes calculated in orthorhombic Li_5GaO_4

In the context of its application in lithium-ion batteries, defect energies of Li_5GaO_4 are crucial in assessing its suitability as an electrode material. The calculated defect energies, encompassing Frenkel and Schottky defects, offer valuable insights into the material's stability and potential performance within a battery environment.

Frenkel defects, which involve the displacement of ions from their regular lattice sites, exhibit varying energies within Li_5GaO_4. Specifically, for Li atoms, the Frenkel Energy per Defect is calculated to be 1.00 eV. These energies range from 0.995 eV to 5.83 eV for Li, Ga, and O ions, suggesting that Frenkel defects, particularly those involving Li ions, are energetically feasible. Notably, Li experiences the lowest energy barrier for displacement.

The Schottky defect in Li_5GaO_4 is found to have an energy of 2.94 eV, while in the reference Li_2O, it measures 2.19 eV for Li vacancies. This indicates that creating Li vacancies in Li_5GaO_4 through the Schottky process may require higher energy compared to Li_2O. Additionally, the Ga_2O_3 Schottky defect exhibits an energy barrier of 6.01 eV for gallium vacancies, suggesting a higher energy requirement.

Considering anti-site defects, the cluster defect involving Li and Ga has a lower energy of 0.87 eV compared to the isolated defect (3.05 eV). This suggests that the formation of anti-site cluster defects is more favorable and likely to occur than isolated anti-site defects in Li_5GaO_4.

These calculated defect energies, along with the low Frenkel energies for Li, suggest that Li_5GaO_4 holds promise as a material for lithium-ion batteries. The favorable Li ion Frenkel defect energy, lower anti-site cluster defect energy, and moderate Schottky defect energy collectively indicate enhanced performance and stability as a potential Li-ion battery electrode material.

Understanding Li-ion diffusion is pivotal in optimizing electrode materials. This comprehension ensures that these materials can effectively accommodate and facilitate the rapid and efficient transport of lithium ions. Six different local Li hops were identified for vacancy-mediated Li-ion migration. The reported activation energy of 0.055 eV for the migration pathway of a local Li-Li hop indicates that this transition necessitates an energy input of 0.055 eV per Li-ion to proceed. Additionally, the lower activation energy of 0.065 eV for another hop suggests that this alternative pathway is also advantageous in terms of energy demands for the migration of lithium ions within the material.

Moreover, in the realm of monovalent doping, solution enthalpies were predominantly endoergic, indicating an energy-absorbing nature. However, sodium (Na) stands out with a solution energy of -0.92 eV, suggesting a noteworthy exception. The endoergic solution energy of silicon (Si) at 0.28 eV surpasses the higher solution energies of germanium (Ge) and tin (Sn) at the gallium site. This supports the feasibility of aliovalent doping at the Ga site with Si, enhancing lithium vacancies and thereby increasing Li ion conductivity.

Conclusion

In conclusion, comprehensive investigation into the Li_5GaO_4 molecule, guided by meticulous computational calculations, has shed light on the intricate dynamics of intrinsic defects, Li-ion migration, and dopant solutions. Noteworthy among these revelations is the energy-efficient nature of the Li Frenkel defect process and the superior feasibility of the Li-Ga anti-site cluster, boasting an impressive binding energy of -2.18eV. The calculations conducted have unveiled Li-ion migration pathways with a remarkably low activation energy of 0.055 eV, indicating a heightened Li-ion conductivity compared to prevalent materials, thereby warranting further, in-depth examination. The introduction of iso-valent dopants has pointed towards a preference for Na on the Li site, presenting a promising avenue for pioneering Sodium-based research. Additionally, the Aliovalent Doping of Si on Ga, with an unexpectedly low energy value of 0.28eV, beckons for further exploration. Beyond the confines of this study, these findings hold transformative implications for experimental endeavors. The focus will pivot toward unraveling the electronic properties of dopant configurations, employing the potent tool of Density Functional Theory (DFT).

Keywords: Anti-site, Frenkel, Iso-valent, Defect

References

1. R. T. Johnson and R. M. Biefeld, (1979), "Ionic Conductivity of Li5AlO4 And Li5GaO4 In Moist Air Environments: Potential Humidity Sensors,"
2. B. Gao, R. Jalem, and Y. Tateyama, (2022), "Atomistic insight into the dopant impacts at the garnet Li7La3Zr2O12 solid electrolyte grain boundaries," J Mater Chem A Mater.
3. 18. T. Ávalos-Rendón and H. Pfeiffer, "Evidence of CO2 chemisorption at high temperature in lithium Gállate (Li5GaO4)," Chem Lett, vol. 40, no. 5, pp. 504–505, 2011
4. Gale, JD, (1997), *GULP* A computer program for the symmetry-adapted simulation of solids, Journal of the Chemical Society, Faraday Transactions. 1997, 93, 629-37.
5. Stewner, F, Hoppe, R, Die Kristallstruktur von alpha-Li5GaO4, Acta Crystallographica, Section B: Structural Crystallography and Crystal Chemistry (1971) 27, 616-623
6. Anubhav Jain, Shyue Ping Ong, Geoffroy Hautier, Wei Chen, William Davidson Richards, Stephen Dacek, Shreyas Cholia, Dan Gunter, David Skinner, Gerbrand Ceder, Kristin A. Persson, (2013) "Commentary: The Materials Project: A materials genome approach to accelerating materials innovation," APL Mater., vol. 1, 011002.
7. R. W. Grimes, G. Busker, M. A. McCoy, A. Chroneos, J. A. Kilner, and S.-P. Chen, Ber. Bunsengesellschaft Phys. Chem. 101, 1204 (1997).