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RESEARCH ARTICLE

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Structural and electronic properties of fluorine-doped lithium oxide as a solid electrolyte interphase for lithium air batteries

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Abstract

In Lithium-Air Batteries (LABs), the solid electrolyte interphase (SEI) layer plays a crucial role as a protective barrier and regulates the transport of lithium ions, preventing deterioration of the electrode and electrolyte during undesired reactions. The SEI layer acts as a barrier between the lithium anode and electrolyte, enhancing the stability and efficiency of LABs during charge/discharge cycles. In this study, the effectiveness of a composite SEI layer consisting of Li_2O and LiF was investigated. Fluorine-Doped Lithium Oxide was proposed, and the dynamical stability of this configuration was verified using Density Functional Theory and analysis of the phonon spectrum, leveraging its quantum mechanical accuracy for this purpose. The study of the electronic properties of the structure revealed a noteworthy decrease in the band gap. This decrease in the band gap is particularly significant as it contributes to the improved performance of lithium-air batteries. Furthermore, additional investigations were conducted to examine the effects of doping other halogen atoms, including chlorine and bromine, and increasing the concentration of fluorine. In the meticulous process of sublattice doping, careful consideration of electronegativity, ionic radius, and experimental doping probability is crucial. However, improper selection rendered such structures unstable, posing challenges in achieving stable configurations for practical applications. According to the results, doping one fluorine in each unit cell does not lead to instability.

Keywords: Lithium air batteries; Solid electrolyte interphase; Band gap; Phonon spectrum; Fluorine-doped lithium oxide

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1. Introduction

Rechargeable lithium-air batteries have the potential to be used in long-distance electric vehicles as well as other energy storage applications due to their high energy density [1]. They fall under the broad classification of next-generation lithium-based batteries [2-3]. The basic principle of a lithium-air battery relies on the reaction of Lithium metal and Oxygen in the ambient air resulting in lithium oxide $\mathbf{Li_2O}$ as the discharge product. $\mathbf{Li_2O}$ gets converted back into lithium metal and oxygen is released through the charging process respectively. The following cycles will continue this process [4]. Since oxygen from the air is used as one of the reactants in lithium-air batteries, which eliminates the need to store one of the reactants inside, these batteries have the potential to have very high energy densities. This characteristic facilitates a significantly higher level of energy storage compared to what is achievable with conventional lithium-ion batteries.

The key components of a lithium-air battery typically include Anode, cathode, and electrolyte. Typically, metallic lithium or lithium compounds are used as the anode in lithium-air batteries. It acts as a lithium-ion source while the battery is being discharged. Despite low electrode potential and high theoretical capacity, lithium metal anodes have several limitations that prevent their use in rechargeable batteries. The formation of lithium dendrites during cycling is one of the most significant challenges with lithium metal anodes [5-7]. Dendrite needle-like structures that grow on the surface of the lithium electrode can pierce the separator and cause short circuits, poor battery performance, and safety risks. Side reactions and electrolyte decomposition, volume changes and mechanical stress, limited coulombic efficiency, and safety concerns are other challenges that associated with lithium metal anodes. To decrease these difficulties, several strategies are being used and reported. In lithium-based battery systems, an essential component called the solid-electrolyte interphase (SEI) develops at the area where the electrolyte and lithium metal anode meet. It is an electrochemically produced layer that performs as a passivation layer, preventing additional interactions of the reactive lithium metal with the electrolyte [8]. In general, the SEI layer is composed of both inorganic and organic materials, such as lithium carbonate ($\mathbf{Li_2CO_3}$), lithium oxide ($\mathbf{Li_2O}$), lithium alkyl carbonates, lithium fluoride ($\mathbf{LiF}$), and other decomposition products [9- 11]. In comparison to $\mathbf{Li_2CO_3}$ and due to acceptable mechanical stability and lithium ionic conductivity of $\mathbf{Li_2O}$ and good electrochemical stability of $\mathbf{LiF}$, a composite of $\mathbf{Li_2O}$ and $\mathbf{LiF}$ is more promising as SEI. Rezaee et al [12] reported that Lithium oxide with fluorine doping is a novel material for solid electrolyte interphase applications and investigated its physical characteristics using Molecular dynamic simulations in detail. However, to best of our knowledge, there is not any study on the validation and stability of the structure and its electronic properties. Therefore, to introduce this structure as the proper material for SEI applications it is important to prove its dynamic stability and investigate the electronic properties in Quantum Mechanics [13]. Quantum Mechanics is a fundamental theory in physics and describes the energies and behaviour of materials in the smallest scales. It offers a framework to understand the behaviour of particles, atoms, molecules, and electrons in atoms.

In the current study, the validity, and electronic properties of $\boldsymbol{Li_{(2-x)}O_{(1-x)}F_x}$ were investigated. Density Functional Theory (DFT) was employed for this purpose, leveraging its quantum mechanical accuracy to offer a more nuanced representation of electronic stability. Furthermore, the study emphasized the observed decrease in the band gap as a clear indication of lower resistance—an essential characteristic for the Solid Electrolyte Interface (SEI) in effectively mitigating undesired side reactions. The dynamic stability of the structure was tested by the Phonon spectrum [14]. The term "phonon spectrum" refers to the energy range of quantized vibrational modes in a material. A phonon's energy is quantized and is frequency dependent. The range of energy values of these vibrational modes have been expressed by the phonon spectrum. For extensive consideration, the acceptable concentration of fluorine and the doping effect of other halogen materials was checked too. Electronic behaviours and properties of SEI as a lithium anode protection layer play an important role in LAB's performance. To this end, the Efficacy of doping Florin in $\boldsymbol{Li_2O}$ structure was investigated and was compared with pure $\boldsymbol{Li_2O}$. All modeling and analysis have been done under Quantum Mechanics Methods that provide a close agreement with the experimental results.

2. Computational details

The geometrical, electronic, and phonon calculations were performed using the Density Functional Theory (DFT) methods [15] implemented in Quantum ESPRESSO Package [16]. The Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [17] type parameterization has been applied to represent the electrons' interchange and correlation interaction energy. Electronic structure calculations and geometry optimizations including lattice constant and atomic positions are done based on an iterative solution of the Kohn-Sham equation [18] and ultrasoft Pseudopotentials by minimizing the total energy. To attain a balance between computational accuracy and efficiency in energy and force calculations, convergent thresholds of 10^6 Ry and 0.001 Ry/Bohr, respectively, were employed. These specific values have proven effective in ensuring the convergence of energy calculations to a sufficiently accurate result and stabilizing forces to reach equilibrium, thus optimizing the reliability of computational outcomes while preserving computational efficiency. Throughout the investigation, periodic boundary conditions were used. For Band Gap energies, both valence band maximum (VBM) and conduction band minimum (CBM) were extracted.

3. Results and discussion

3.1. Perfect Li_2O

As a foundation, all the structures studied in this study have been developed using antifluorite unit cells of Li_2O [19]. As shown in Figure1-a and under ambient pressure and temperature, Li_2O has 12 basic atoms, a cubic cell, space group of Fm3m. The structure is optimized and gets to its minimized energy with lattice parameters, total energy, force, and stress per atom at 4.6 Å [20], -249.48 Ry, 0.000003 Ry/Bohr, 0.4 kbar respectively.

The phonon spectrum, energy band diagram, and Partial Density of states for Li_2O were displayed in Figure 1-b-c. It is evident that the phonon dispersion does not exhibit any imaginary mode, which indicates the system's inherent dynamical stability. This finding confirms that the Pristine Li_2O represents a local minimum. The band gap of the structure was 5.2ev and the PDOS of the system represented the distribution of available energy states and atomic orbitals. There was good conformity with Previous studies [21-22].

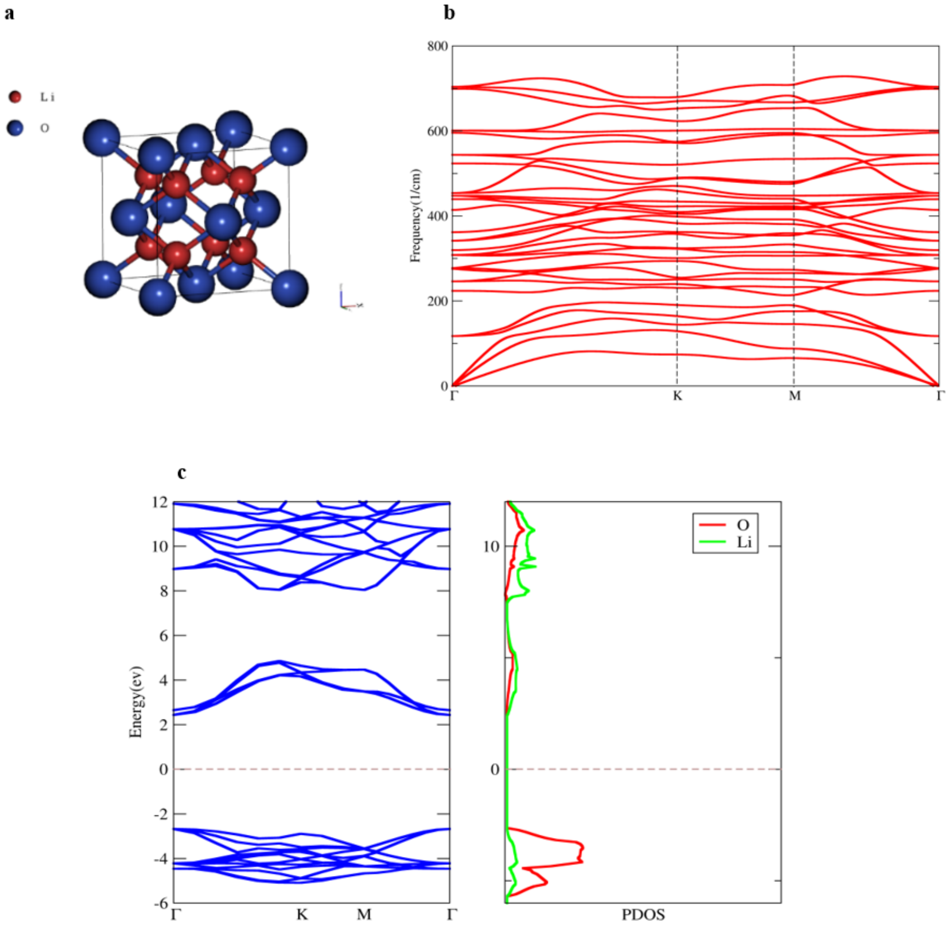

Fig.1 a- Configuration, b- Phonon spectrum, c- Band structure and PDOS, of the antifluorite unit cell of Li_2O

3.2. Fluorine doped Li_2O

3.2.1 A single atom

To modify and improve the structure fluorine was doped in an oxygen site. fluorine has a single negative charge and the destruction of local electrostatic charge conservation leads to the formation of metastable microstates within the system [23]. In the meticulous process of doping within the sublattice, careful consideration of electronegativity, ionic radius, and experimental doping probability is crucial. With an electronegativity of 4.193, fluorine competes with oxygen (3.610) for O-sites, utilizing its heightened electronegativity to attract lithium electrons and form robust ionic bonds, contributing significantly to the stability of the $Li_{(2-x)}O_{(1-x)}F_x$ structure. Additionally, the proximity of the ionic radii of $F^{-\ (1.285)}$ and $O^{(2-)}$ (1.350 Å) enhances the precision of the doping process, ensuring a seamless integration of fluorine into the sublattice. This nuanced interplay highlights the importance of a comprehensive approach in doping strategies, where both electronegativity and ionic radius are carefully balanced to maximize the effectiveness of fluorine in modifying the compound's structure [12].

Therefore, a Lithium atom was deleted and the system reached its balance local electrostatic charge. The defective $\mathrm{Li}_{(2-x)}\mathrm{O}_{(1-x)}\mathrm{F}_x$ structure ($x = \frac{\text{number of doped} - \text{F}}{\text{number of O in perfect crystal}}$ [24]) was created and optimized to minimize energy. Afterward and due to validity, the configuration phonon calculation was used and vibrational frequencies were calculated and plotted.

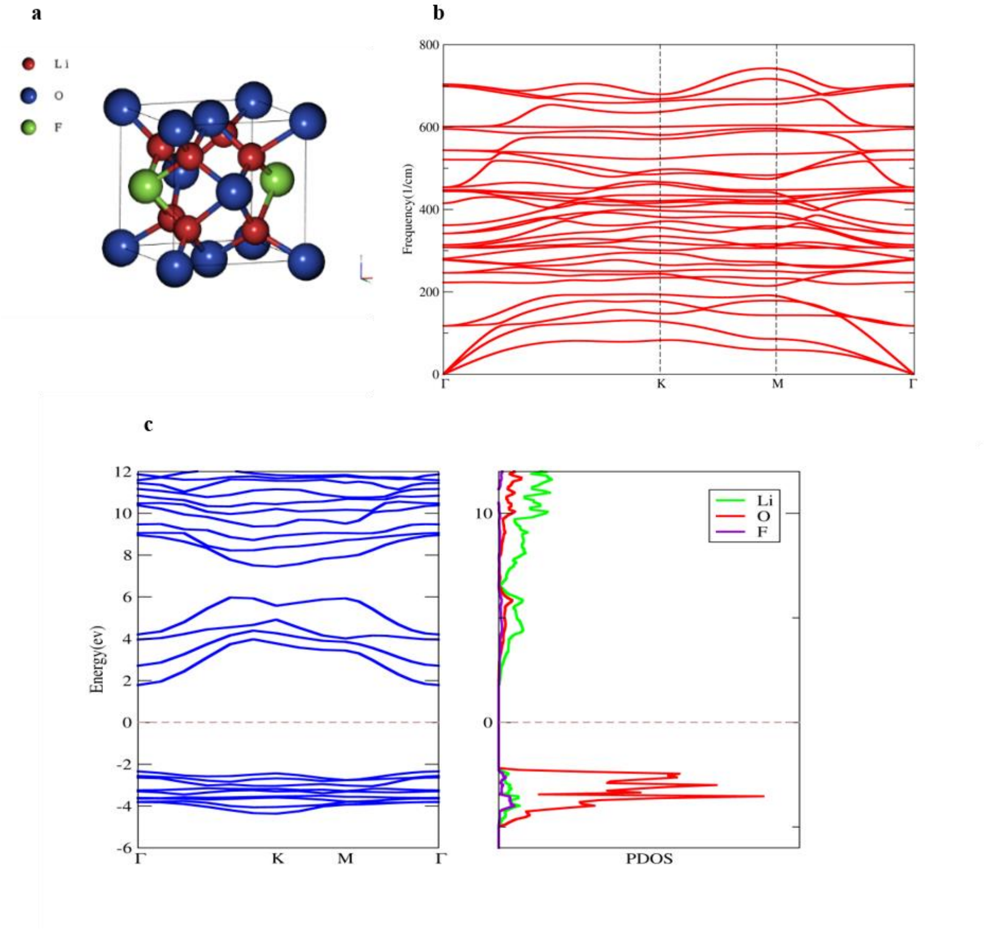

Fig. 2 a- Configuration, b- Phonon spectrum, c- Band structure and PDOS, of Fluorine doped Li_2O

Figure 2a-b displays the doping structure and its phonon spectrum. The phonon spectrum includes both positive and negative frequencies, representing the real and imaginary components of the vibrations, respectively. Negative frequencies indicate unstable or imaginary modes, whereas positive frequencies correlate to observable vibrations of the lattice in a material. Negative frequencies represent energetically unfavourable structures and are derived mathematically so the physically observable positive frequencies are the primary focus of the phonon spectrum analysis. Due to all real modes, the structure as shown in Figure2-b is stable.

From the PDOS, one can observe the contributions of specific atomic orbitals or groups, where a high density of states indicates a greater probability of finding electrons at those energy levels.

3-2-2 Two atoms

In this section, the effect of doping of another fluorine in structure was investigated. The configuration was shown in Figure 3-a. As can be seen from Figure 3-b, the phonon spectrum encompasses both positive (real) and negative (imaginary) frequencies. Because of imaginary frequencies, this formation is dynamically unstable. This is because of the high electronegativity of fluorine [25]. Fluorine is the most electronegative element, meaning it has a strong affinity for electrons. When a single fluorine atom is doped into $\mathrm{Li_2O}$, it can replace an oxygen atom and form a stable $\mathrm{Li_{(2-x)}O_{(1-x)}F_x}$compound. The electronegativity of fluorine allows it to effectively attract and bond with the surrounding atoms, maintaining the structural integrity and charge balance of the compound. However, when two fluorine atoms are introduced, the high electronegativity of fluorine can lead to an excessive electron transfer. This disrupts the charge balance within the crystal structure of $\mathrm{Li_2O}$.

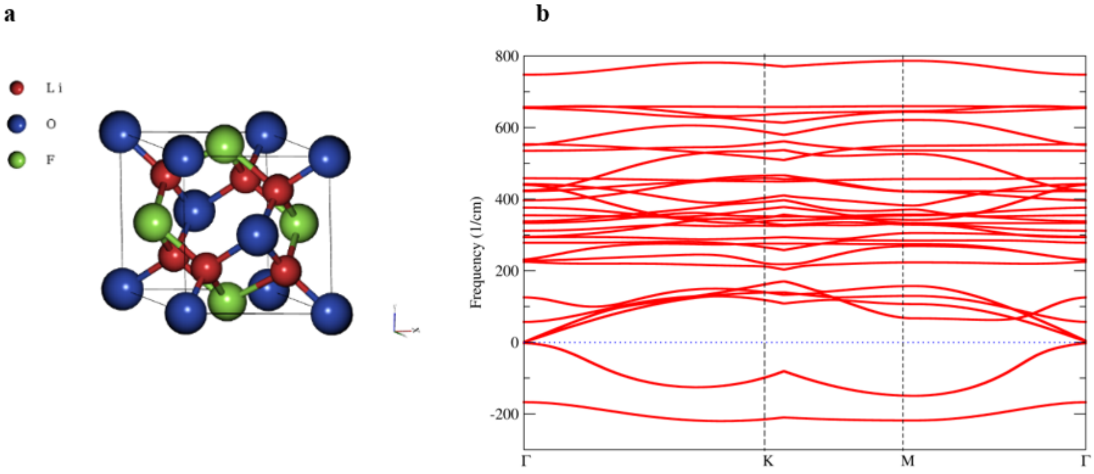

Fig. 3 a- Configuration, b- Phonon spectrum, of 2Fluorine doped $\mathrm{Li_2O}$

The study was continued and the effect of enlarging the system to two single cells where each cell has a single fluorine was tested. Figure 4 shows two cell configurations and related phonon spectrums. Due to the real frequencies of this diagram, this structure is dynamically stable. In summary, just one Fluorine can be doped in each unit cell of $\mathrm{Li_2O}$.

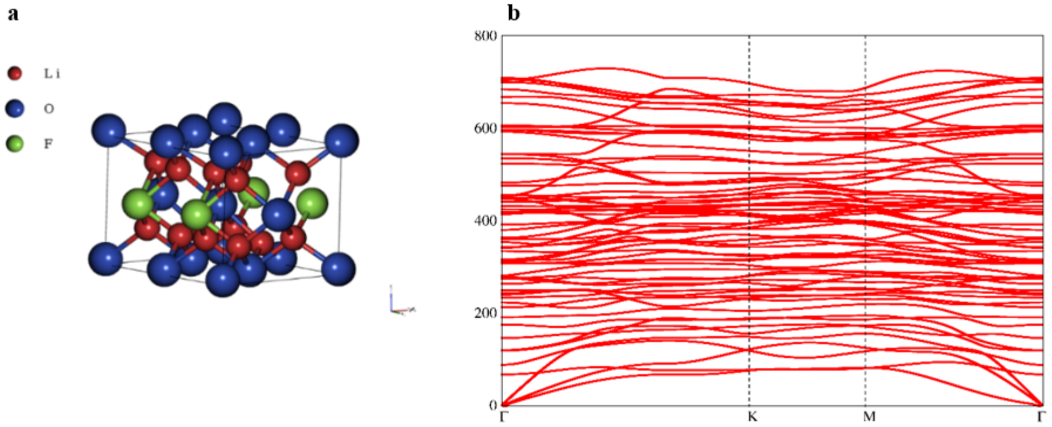

Fig. 4 a- Configuration, b- Phonon spectrum, 1Fluorine dopped in each unit cell of Li2O

3-3 Chlorine/ Bromine doped Li_2O

In this section effect of doping other elements was investigated. To this end, Chlorine and Bromine were introduced into the structure as a dopant. The configuration of doped structures was displayed in Figure 5 and Figure 6 respectively. As shown in the figure and referring to their phonon spectrums these systems were not stable.
Electronegativity quantifies an atom's capability to attract shared electrons within a chemical bond. When incorporating a foreign atom into a crystal lattice through doping, it is crucial to consider the disparity in electronegativity between the dopant atom and the host atoms. A significant electronegativity difference can cause an uneven distribution of electron density, which may result in imbalances in charge and instabilities in the structure. On the Pauling scale, oxygen has a greater electronegativity value than chlorine (around 3.44 vs. 3.16). It means that in a chemical bond, oxygen has a greater inclination to shared electrons and doping halogens except for fluorine which has similar electronegativity with oxygen, can lead to uneven distribution of electron density and disrupt the charge balance within the crystal lattice.

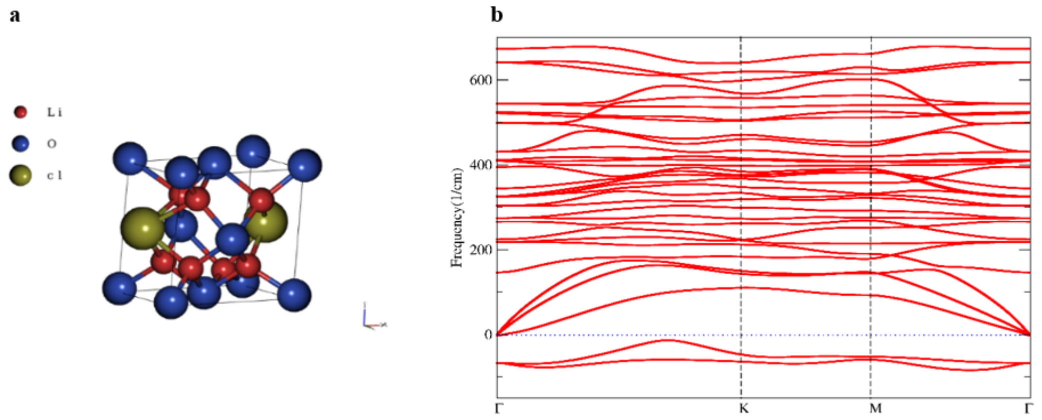

Fig. 5 a- Configuration, b- Phonon spectrum, of Cholerine doped Li_2O

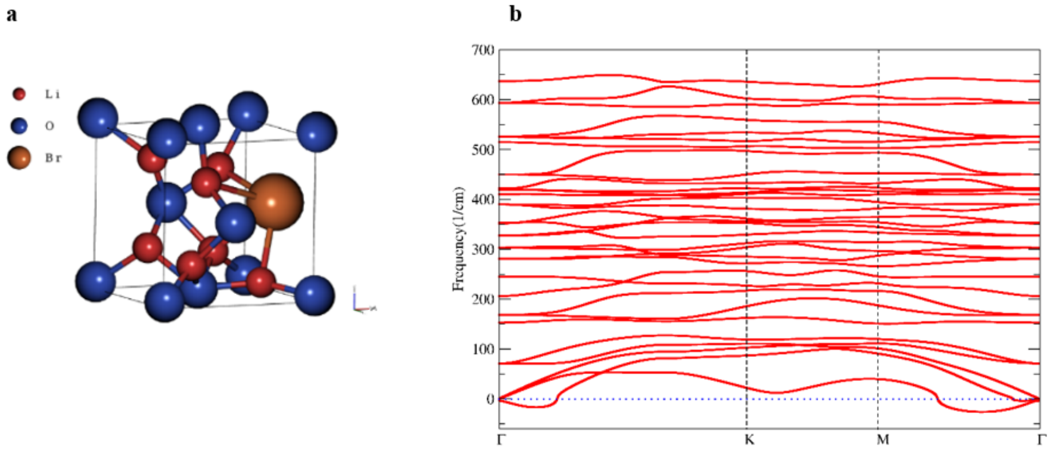

Fig. 6 a- Configuration, b- Phonon spectrum, of Cholerine doped Li_2O

The ramifications of introducing heteroatoms into the pristine structure of Li_2O were compiled in Table 1. Considering the ionic radii and electronegativity associated with heteroatoms, the strategic incorporation of one fluorine in each unit cell is recommended, as it imparts heightened stability. This doping mechanism precipitates a reduction in the band gap of the solid electrolyte interface (SIE), thereby amplifying the performance of Li-air batteries.

Table 1. Stability of configuration based on doped type

Doped type	**Stability**	**Doped type**	**Stability**
No doped	Yes	2 Fluorine doped in 2 unit cell	Yes
1 Fluorine doped in 1 unit cell	Yes	1 Chlorine doped in 1 unit cell	No
2 Fluorine doped in 1 unit cell	No	1 Bromine doped in 1 unit cell	No

3. Conclusion

Utilizing solid-electrolyte interphase (SEI) layers as protective coatings on the lithium anode is an effective strategy to maintain coulombic efficiency and extend the cycle life of Lithium-Air Batteries (LABs). In this study, the effectiveness of $\mathrm{Li_{(2-x)}O_{(1-x)}F_x}$ as a novel solid-electrolyte interphase (SEI) was examined. The stability and reliability of this configuration were confirmed through analysis of the phonon spectrum and DFT calculations. The low resistance of SEI plays a critical role in minimizing unwanted side reactions, ensuring the stability of the electrode-electrolyte interface, enhancing the transport of charges, and reducing ohmic polarization. Therefore, analysing and optimizing the electronic properties of the layer is essential for achieving these objectives. To investigate the electronic properties, the band energies of $\mathrm{Li_{(2-x)}O_{(1-x)}F_x}$ were calculated. The introduction of fluorine (F) dopants in the oxygen (O) site of the $\mathrm{Li_2O}$ structure resulted in a decrease in the band energies, indicating a lower resistance of the SEI layer. This decrease in resistance contributes to improved performance and stability of battery systems. Additionally, the effects of chlorine and bromine halogens as dopants were examined. However, due to their lower electronegativity compared to oxygen, these configurations were found to be dynamically unstable. Based on the findings, it is suggested to consider doping one fluorine atom in each unit cell as a viable approach. This strategy offers potential benefits in terms of enhancing the performance and stability of the battery system.

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