First principle studies on stability of reactive products of Li-O and Li-S batteries

Cliffton Masedi* and Phuti Ngoepe

1Materials Modelling Centre, University of Limpopo, Private Bag X1160, Sovenga, South Africa

Abstract. We investigated the phase stabilities of insoluble discharge products of oxygen and sulphur (Li$_2$O, Li$_2$S, Li$_2$O$_2$ and Li$_2$S$_2$ structures) formed in Li-O and Li-S batteries using density functional theory within the generalized gradient approximation. Their structural, electronic and mechanical properties were determined to show their stability trend. The lattice parameters were well reproduced and agree to within 1% with the available experimental data. We have found good correlation between the heats of formation, density of states, elastic constant and phonon dispersion curves. The heats of formation predict Li$_2$O to be the most stable structure whereas Li$_2$S$_2$ is the least stable. Our phonon dispersion calculations show that Li$_2$O, Li$_2$S and Li$_2$O$_2$ structures are mechanically stable consistent with the elastic constants. The Li$_2$S$_2$ structure display soft modes associated mainly with sulphur atoms vibrations in the a-b plane, suggesting that the structure is unstable.

1. Introduction

Lithium-air batteries are potentially viable ultrahigh energy density chemical power sources, which could potentially offer specific energies of up to 300 Wh/kg being rechargeable. The modern state of art and the challenges in the field of Li-air batteries are considered [1]. For all redox couples enabling for rechargeable batteries, Li/S couple has almost the highest specific-energy of 2600 Wh/kg, because the theoretical capacity of sulfur is the highest (1672 Ma/g) among all the possible solid compounds known for primary and rechargeable cathodes [2] [3]. In addition to the high capacity, elemental sulfur also has advantages of natural abundance, low cost and low toxicity, which are all the important factors for the next generation of lithium batteries.

However, the realization of Li/S battery has a number of difficult problems to overcome. Typically, the biggest shortfall exhibited by these systems is a difficulty to sustain long cycle life. In order to improve the electrochemical rechargeability of the sulfur electrodes, several research activities have been carried out to develop a denser and firmer cathode for stabilizing the morphology of the carbon matrix [4] and to use organosulfur compounds [5] or sulfur-composite compounds for alleviating the dissoluble loss of sulfur in liquid electrolytes. So far some success of achieving reasonably good life span of 50 cycles has been reported [6]. However, cycle capability still remains the bottleneck for the realization of the Li/S cell. A

* Corresponding author: cliffton.masedi@ul.ac.za

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solution is the formation of Li/S-O2 hybrid cell, whose overall specific capacity is limited by the maximum deposition of the insoluble discharge products (i.e., Li2O, Li2S, Li2O2 and Li2S2) of oxygen and sulphur. In this work we will focus mainly on the insoluble discharge products (i.e., Li2O, Li2S, Li2O2 and Li2S2) of oxygen and sulphur to determine structural, electronic, mechanical and vibrational properties using ab-initio method.

2. Methodology

The calculations were carried out using ab initio density functional theory (DFT) formalism as implemented in the VASP total energy package [12] with the projector augmented wave (PAW) [13]. An energy cutoff of 500 eV was used, as it was sufficient to converge the total energy of all the systems. For the exchange-correlation functional, the generalized gradient approximation of Perdew and Wang (GGA-PBE) [14] was chosen. The Brillouin zone integrations were performed for suitably large sets of k points according to Monkhorst and Pack [15]. The phonon dispersion spectra were evaluated using PHONON code [16] as implemented in the MedeA software, VASP code [12]. k-point mesh of 8x8x8 was used as it was enough to converge the total energy of the systems. Optimization of structural parameters (atomic positions and lattice parameters) was achieved by minimization of forces and stress tensors. The phonon dispersions and phonon densities states for the structures were calculated in the framework of the direct method [16], for which the force constants were derived by a supercell approach.

3. Results and Discussion

3.1 Heats of formation

Table 1: The equilibrium lattice parameters and heats of formation (ΔHf) of the Li2O, Li2S, Li2O2 and Li2S2 structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice Parameters (Å)</th>
<th>ΔHf (KJ/mol)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2O</td>
<td>a=3.16 c=7.69</td>
<td>-277.16</td>
<td>66.57</td>
</tr>
<tr>
<td>Li2S2</td>
<td>a= 4.13 c=10.52</td>
<td>-40.25</td>
<td>155.50</td>
</tr>
<tr>
<td>Li2O</td>
<td>a=4.63</td>
<td>-541.57</td>
<td>99.42</td>
</tr>
<tr>
<td>Li2S</td>
<td>a=5.72</td>
<td>-378.02</td>
<td>187.15</td>
</tr>
</tbody>
</table>

The formation energy (ΔHf), of the intermetallic phases is computed according to the relation [15,16]

\[ \Delta H_f = E_{LiS/O} - [(1-x)E_{LiSolid} + x E_{S/OSolid}] \]  

where \( E_{LiS/O} \), \( E_{LiSolid} \) and \( E_{S/OSolid} \) are the total energies of an intermetallic, elemental Li and S/O in their respective ground-state crystal structures, while \( x \) and \( 1-x \) refers to the fractional concentrations of the constituent elements.
In Table 1, the calculated lattice parameters and the heats of formation ($\Delta H_f$) of the Li$_2$O, Li$_2$S, Li$_2$O$_2$ and Li$_2$S$_2$ structures are presented. Our DFT results are in good agreement with the available experimental data. In particular, the lattice parameters agree to within 1% with the available experimental values.

### 3.2 Elastic constants

Table 2: The elastic constants (GPa) for Li$_2$O, Li$_2$S, Li$_2$O$_2$ and Li$_2$S$_2$ structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Li$_2$O</th>
<th>Li$_2$S</th>
<th>Li$_2$O$_2$</th>
<th>Li$_2$S$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VASP</td>
<td>Exp</td>
<td>VASP</td>
<td>Exp</td>
<td>VASP</td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>200.60</td>
<td>217.00</td>
<td>82.14</td>
<td>83.90</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>19.39</td>
<td>25.00</td>
<td>18.43</td>
<td>18.10</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>-0.13</td>
<td>21.50</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>158.50</td>
<td></td>
<td>358.10</td>
<td>36.63</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>0.65</td>
<td>68.00</td>
<td>34.19</td>
<td>32.20</td>
</tr>
</tbody>
</table>

The accurate calculation of elasticity is essential for gaining an insight into the mechanical stability and elastic properties of solids. For the cubic, tetragonal and orthorhombic crystals, there are three ($C_{11}$, $C_{12}$, $C_{44}$), six ($C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, $C_{44}$, $C_{66}$) and thirteen ($C_{11}$, $C_{22}$, $C_{33}$, $C_{12}$, $C_{13}$, $C_{23}$, $C_{44}$, $C_{44}$, $C_{55}$, $C_{66}$, $C_{15}$, $C_{25}$, $C_{35}$, $C_{46}$) independent elastic constants. Applying two kinds of strains ($\varepsilon_1$ and $\varepsilon_2$) can give stresses relating to these three elastic coefficients, yielding an efficient method for obtaining elastic constants for the cubic system. This method has been successfully used to study the elastic properties of a range of materials including metallic systems [17]. The mechanical stability criteria of cubic systems as outlined elsewhere [18] are given as follows:

$$C_{44} > 0, \quad C_{11} > |C_{12}|, \quad C_{11} + 2C_{12} > 0,$$

(2)

where $C_{11}$, $C_{12}$ and $C_{44}$ are the only three independent elastic constants. Based on three independent single crystal elastic constants of a cubic crystal, $C_{11}$, $C_{12}$, $C_{44}$, the elastic moduli are determined using the following expressions:

$$B = \left( C_{11} + \frac{2C_{12}}{3} \right), \quad C' = \frac{C_{11} - C_{12}}{2}, \quad A = \frac{2C_{44} + C_{12}}{C_{11}}$$

(3)

where $B$ is the bulk modulus, $C'$ tetragonal shear modulus and anisotropic factor $A$. It is acknowledged that the bulk modulus $B$ is a measure of resistance to volume change by applied pressure, whereas the elastic anisotropy $A$ has an important implication in engineering science since it is highly correlated with the possibility of inducing micro-cracks in materials [19]. If the material is completely isotropic, the value of $A$ will be 1, while values smaller or larger than 1 measure the degree of elastic anisotropy. The positive $C'$ indicates the mechanical stability of the crystal, otherwise unstable.

The corresponding mechanical stability criterion for hexagonal crystal reads as

$$C_{11} > 0, \quad C_{11} - C_{12} > 0, \quad C_{44} > 0, \quad (C_{11} - C_{12}) C_{33} - 2C_{13} > 0$$

(4)

We calculated the elastic constants of Li$_2$O, Li$_2$S, Li$_2$O$_2$ and Li$_2$S$_2$ structures, as compiled in Table 2. All the elastic constants and shear moduli of the four structures, Li$_2$O, Li$_2$S, Li$_2$O$_2$ and Li$_2$S$_2$, are positive, thus satisfying mechanical stability criteria set in equations (2) and (4). For a cubic material, it is well known that $B$, $C'$ and $C_{44}$ must be positive for a structure
to remain mechanically stable. More importantly, we note a good agreement in our predicted heats of formation and the elastic constants which is consistent with phase stability trend.

### 3.3 Phonon dispersions

The stability of the structures with respect to the phonon dispersion calculations is shown in figure 1 and 2. Our phonon dispersion calculations shows that indeed Li$_2$O, Li$_2$S and Li$_2$O$_2$ structures are stable since there are no soft modes in the negative frequency observed in the phonon dispersion curve. Li$_2$S$_2$ structure is unstable since there are soft modes observed in the phonon dispersion curve.

The soft modes are observed along F, B, G and Γ brillouin zone directions which are due to the high vibrations of the sulphur atoms as observed on the phonon density of states due possible low temperature. However, the observed imaginary phonon modes may disappear at minimal increase in temperature and pressure. Of the four systems, the Li$_2$O, Li$_2$S and Li$_2$O$_2$ structures are highly mechanically stable while the Li$_2$S$_2$ is mechanical unstable, consistent with heats of formation. The soft modes are also due to a negative C13 value observed on elastic constant table.

![Phonon dispersion spectra](image)
3.3 Phonon dispersions

The stability of the structures with respect to the phonon dispersion calculations is shown in figure 2 and 3. Our phonon dispersion calculations show that indeed Li$_2$O, Li$_2$S and Li$_2$O$_2$ structures are stable since there are no soft modes in the negative frequency observed in the phonon dispersion curve. Li$_2$S$_2$ structure is unstable since there are soft modes observed in the phonon dispersion curve. The soft modes are observed along F, B, G and Γ Brillouin zone directions which are due to the high vibrations of the sulphur atoms as observed on the phonon density of states. However, the observed imaginary phonon modes may disappear at minimal increase in temperature and pressure. Of the four systems, the Li$_2$O, Li$_2$S and Li$_2$O$_2$ structures are highly mechanically stable while the Li$_2$S$_2$ is mechanically unstable, consistent with the heats of formation. The soft modes are also due to a negative C$_{13}$ value observed on the elastic constant table.

3.4 Density of states

In figure 3 we show the superimposed density of states (DOS) plots of Li$_2$O, Li$_2$S, Li$_2$O$_2$ and Li$_2$S$_2$ structures. There is a clear distinction between the plots for the Li$_2$O, Li$_2$S, Li$_2$O$_2$ and Li$_2$S$_2$ structures especially in the optical and acoustic modes. However, their density of states behaviour at E$_f$ is significant and can be used to correlate their stability. It is also known from literature that the DOS of structures of the same composition can be used to mimic the stability trend with respect to their behaviour at the E$_f$. The structure with the highest and lowest density of density at E$_f$ is considered the least and most stable, respectively [20]. Furthermore we can determine whether our structures are metal, semi-conductors or insulators by measuring their band gaps respectively. From figure 4 we measured the band gaps of all the discharge products to confirm whether they are metal, semi-conductors or insulators. Li$_2$O and Li$_2$S have the band gaps of 5 and 3.5 eV which is good agreement with [21] respectively hence they are called semi-conductors, whereas Li$_2$O$_2$ and Li$_2$S$_2$ have the band gaps of 2.2 and 2.0 eV hence they are preferably called insulators.
Figure 3: The total and partial density of states (DOS) for the Li$_2$O and Li$_2$S structures.
Figure 4: The total and partial density of states (DOS) for the Li$_2$O and Li$_2$S structures.

(c) Li$_2$O$_2$

(d) Li$_2$S$_2$

Figure 4: The total and partial density of states (DOS) for the Li$_2$O$_2$ and Li$_2$S$_2$ structures.
4 Summary and Conclusion

The equilibrium lattice parameters and the heats of formation for the Li₂O, Li₂S, Li₂O₂ and Li₂S₂ structures were found to be in good agreement with the available experimental values. The heats of formations confirm that Li₂O is most stable structure while Li₂S₂ structure is the least stable. The phonon dispersion curves of the Li₂O, Li₂S and Li₂O₂ have no soft modes hence are all stable which is in consistent with heats of formation and elastic constant.

The phonon dispersion curve of the Li₂S₂ structure showed the availability of the soft modes along F, B, G and Γ directions which are due to the high vibrations of the sulphur atoms as observed on the phonon density of states. Therefore we confirmed the instability of Li₂S₂ using heats of formation, elastic constants and phonon dispersions. We also calculated the density of states to confirm that Li₂O and Li₂S are insulators whereas Li₂O₂ and Li₂S₂ are semi-conductors. This stability of this discharge products are very important factor the next generation beyond lithium–ion battery materials.

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References