

Beyond lithium-ion batteries: A computational study on Na-S and Na-O batteries

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Abstract. The first principle pseudopotential calculations based on the Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) within density functional theory (DFT) has been utilized to investigate the stabilities of insoluble discharge products of oxygen and sulphur in the Na-O and Na-S batteries. Their structural, mechanical and electronic properties were determined. The lattice parameters were well reproduced and agree with the available experimental data. The heats of formation predict that all structures are generally stable and Na₂S has the lowest value. The elastic constants suggest that all the structures are mechanically stable which in good agreement with the calculated phonon dispersions.

1. Introduction.

Lithium-air batteries are potentially viable ultrahigh energy density chemical power sources, which could potentially offer specific energy up to 3000 Wh/kg being rechargeable [1]. Although their implementation holds the greatest promise in a number of applications ranging from portable electronics to electric vehicles (EV), there are also impressive challenges in developments of cathode materials and electrolyte system of these batteries. Li-air batteries has a number of difficult problems to overcome, the biggest shortfall exhibited with these systems is the formation of lithium dendrite which raises safety issues [2].

It has been suggested to replace the metallic lithium anode by sodium and operate the sodium-air cell, which could enable the development of a new generation of high specific energy rechargeable batteries. The theoretical specific energy of the sodium-air cell, assuming Na₂O as one of the discharge product and including the weight of oxygen, is 1690 Wh/kg, about four times that of state-of-the-art lithium-ion batteries. The surface tension of the liquid sodium anode is expected to prevent the formation of sodium dendrites on charge. Any sodium dendrites that might be formed would be absorbed into the liquid phase [3].

In the current work we present a comparative study on stability, structural and electronic properties of discharge products of sulphur and oxygen in Na-O and Na-S batteries.



2. Structures.

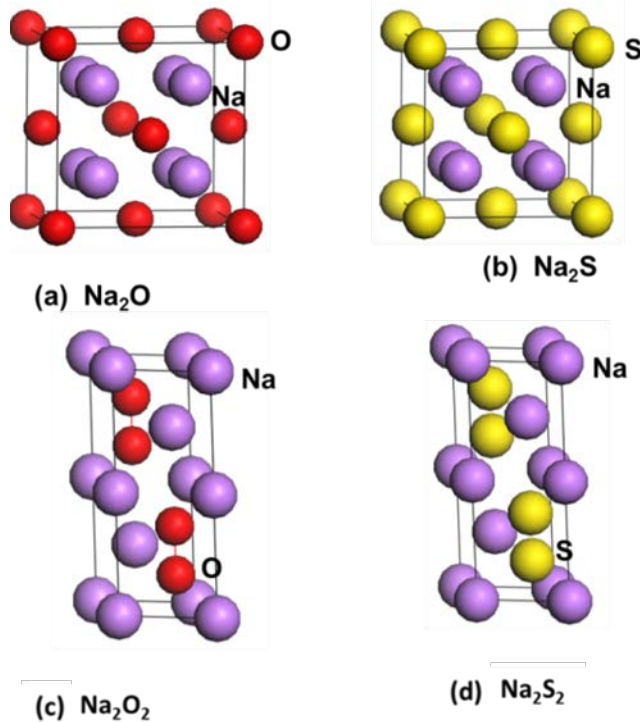


Figure 1: Crystal structures of Na₂S, Na₂O, Na₂O₂ and Na₂S₂, the red atom represent O, yellow atom is S and purple atom is Na.

Figure 1 shows the crystal structures of Na₂S, Na₂O, Na₂O₂ and Na₂S₂ to be studied in this work. Na₂S and Na₂O both have a cubic anti-fluorite structure with Fm-3m symmetry whereas Na₂O₂ and Na₂S₂ show a hexagonal structure with symmetry P₆₃/mmc. There is no much study performed on Na₂O₂ and Na₂S₂ both computationally and experimentally. Na₂O₂ and Na₂S₂ systems were generated from existing Li₂O₂ by replacing lithium with sodium and oxygen with sulphur using VASP total energy package [4]

3. Methodology.

The calculations were carried out using *ab initio* density functional theory (DFT) formalism as implemented in the VASP total energy package [4] with the projector augmented wave (PAW) [5]. 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) [6] was chosen. The Brillouin zone integrations were performed for suitably large sets of *k* points according to Monkhorst and Pack [7]. The phonon dispersion spectra were evaluated using PHONON code [8] as implemented by Materials Design within their MedeA software, VASP code [4]. *k*-point mesh of 8x8x8 was used. Optimization of structural parameters (atomic positions and lattice parameters) was achieved by minimization of forces and stress tensors.

The heat of formation can be estimated by

$$\Delta H_f = E_c - \sum_i x_i E_i \quad (2-21)$$

where E_c is the calculated total energy of the compound, E_i is the calculated total energy of element *i* in the compound.

4. Results and Discussions.

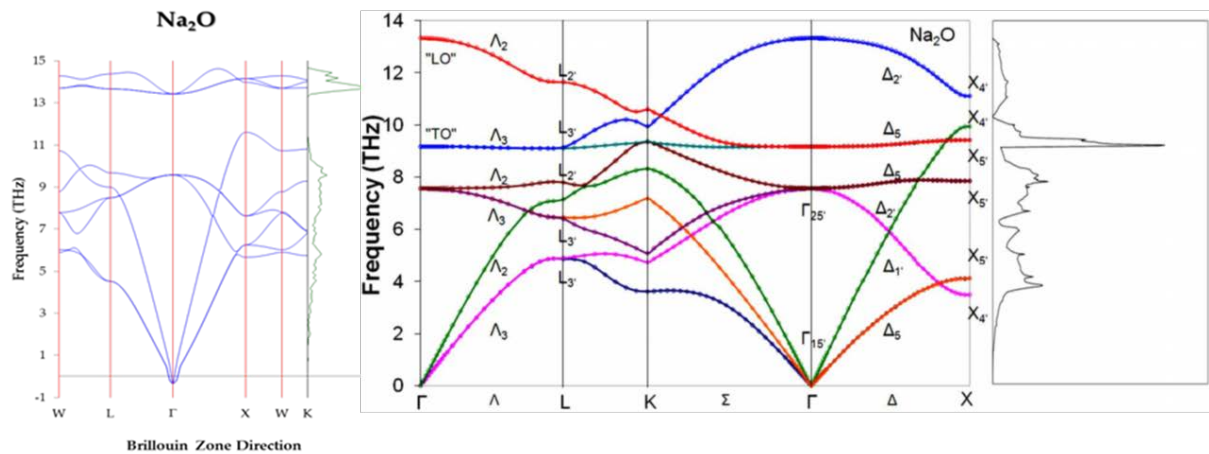
4.1. Structural Properties.

Table 1: The equilibrium lattice parameters and heats of formation (ΔH_f) of the Na_2O , Na_2S , Na_2O_2 and Na_2S_2 structures.

Structure	Lattice Parameters (\AA)		ΔH_f (KJ/mol)		Volume (\AA^3)
	VASP	Exp	VASP	Exp	
Na_2O	a=5.12	5.49 [9]	-318.25		134.29
Na_2S	a= 6.55	6.52 [10]	-298.13		281.50
Na_2O_2	a=5.26 c=4.45		-145.08		107.06
Na_2S_2	a=7.66 c=5.3		-148.11		274.26

There is good agreement between the experimental and calculated lattice constants, especially for Na_2S and Na_2O agrees within 7%. The observed values of heats of formation (ΔH) suggest that all structures are generally stable which is in good agreement with calculated phonon dispersions. Na_2O has the lowest heat of formation.

4.2. Phonon Dispersions Calculations.



This work

Literature [11]

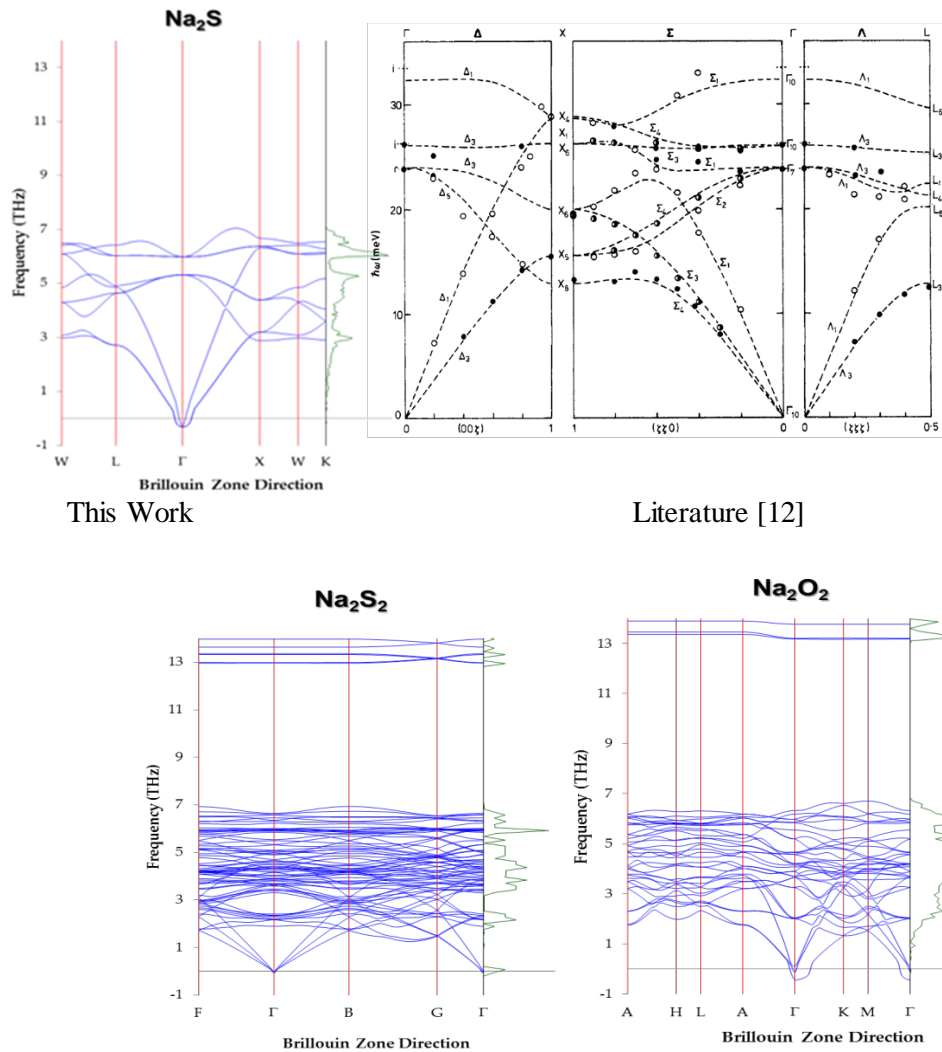


Figure 2: Phonon dispersion curves of Na_2S , Na_2O , Na_2O_2 and Na_2S_2 structures.

The phonon dispersion calculations show that all the structures are stable due absence or minimum soft modes observed in the along gamma point of the Brillouin zone and is in good agreement with the calculated elastic properties.

The phonon dispersion Na_2S and Na_2O compares well with some of work done with DFT and experiment, whereas for Na_2O_2 and Na_2S_2 there is no much work on phonon dispersions.

4.3. Elastic Properties.

Table 2: The elastic constants (GPa) for Na₂O, Na₂S, Na₂O₂ and Na₂S₂ structures.

	Na ₂ O		Na ₂ S		Na ₂ O ₂	Na ₂ S ₂
	VASP	Exp [13]	VASP	Exp [10]	VASP	VASP
C_{11}	127.59	114.00	51.61		220.40	59.35
C_{12}	75.87	34.71	16.25		147.98	16.78
C_{13}					101.21	12.14
C_{33}					263.25	59.88
C_{44}	26.67	27.40	14.56		79.57	9.99

The accurate calculation of elasticity is essential for gaining an insight into the mechanical stability and elastic properties of solids. The mechanical stability criteria of cubic systems as outlined elsewhere [14] [15] [16] are given as follows:

$$C_{44} > 0, \quad C_{11} > C_{44}, \quad C_{11} + 2C_{12} > 0 \quad (1)$$

where C_{11} , C_{12} and C_{44} are the only three independent elastic constants. The corresponding mechanical stability criterion for hexagonal crystal reads as

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

Na₂O, Na₂S, Na₂O₂ and Na₂S₂, are positive, thus satisfying mechanical stability criteria set in equations (1) and (2).

Which means suggest that Na₂O, Na₂S, Na₂O₂ and Na₂S₂ are mechanically stable.

Conclusion.

Heats of formations suggest that all structures (Na₂O, Na₂S, Na₂O₂ and Na₂S₂) are stable because of negative values of heats of formation. The calculated values of lattice parameters and elastic constants are in reasonable agreement with the available experimental values for both Na₂O and Na₂S. The elastic constants suggest mechanical stability for cubic systems Na₂O and Na₂S and hexagonal systems Na₂O₂ and Na₂S₂ since their necessary mechanical stability conditions are satisfied. The phonon dispersions calculations show that all structures are stable which is further confirmed by positive elastic properties values and is in good agreement with some work done in literature.

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