



# Computational insights into the effect of carbon structures at the atomic level for non-aqueous sodium-oxygen batteries



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## HIGHLIGHTS

- The effect of atomic carbon structures is investigated for Na–O<sub>2</sub> batteries.
- SV defect has the largest adsorption energy for NaO<sub>2</sub> among samples studied.
- The dangling atoms and the O-attachment are the origin of large adsorption energy.
- Increasing the number of SV defect leads to large capacity and good cyclability.

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## ABSTRACT

Carbon materials have been widely used to form air cathodes for non-aqueous sodium-oxygen (Na–O<sub>2</sub>) batteries due to their large specific surface area, high conductivity and low cost. However, the effect of carbon structures at the atomic level remains poorly understood. In this work, a first-principles study is conducted to investigate how representative carbon structures, including graphite (0001) surface, point defects and fractured edge, influence the discharge and charge processes of non-aqueous Na–O<sub>2</sub> batteries. It is found that the single vacancy (SV) defect has the largest adsorption energy (5.81 eV) to NaO<sub>2</sub> molecule among the structures studied, even larger than that of the NaO<sub>2</sub> molecule on NaO<sub>2</sub> crystal (2.81 eV). Such high adsorption energy is attributed to two factors: the dangling atoms in SV defects decrease the distance from NaO<sub>2</sub> molecules, and the attachment through oxygen atoms increases the electrons transfer. The findings suggest that SV defects can act as the nucleation sites for NaO<sub>2</sub> in the discharge process, and increasing the number of SV defects can facilitate the uniform formation of small-sized particles. The uniformly distributed discharge products lower the possibility for pore clogging, leading to an increased discharge capacity and improved cyclability for non-aqueous Na–O<sub>2</sub> batteries.

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## 1. Introduction

Rechargeable metal-oxygen batteries are considered to be the potential energy storage systems for future electric vehicles (EVs) due to their high theoretical energy densities, which are achieved by the facts that the anode materials are metals and the cathode reactant O<sub>2</sub> is retrieved from ambient air without occupying the cathode volume [1]. Especially, non-aqueous lithium-oxygen (Li–O<sub>2</sub>) batteries have been widely investigated in the past few years [2–6], but varieties of critical issues (e.g., poor electrolyte stability, low energy efficiency, short cycle life and poor power capacity [7,8]) limit their further commercial exploitation, most of

which are related to the high charge overpotential during oxygen evolution reaction (OER) process. One widely applied strategy to decrease the high charge overpotential is developing catalysts, such as carbon-based materials [9–11], noble metals [12,13], metal oxides [14,15] and metal alloys [16,17]. However, some investigated electrocatalysts undesirably promote the decomposition of electrolytes [18,19]. Even worse, the discharge product Li<sub>2</sub>O<sub>2</sub> itself in non-aqueous Li–O<sub>2</sub> batteries was supposed to be the origin of high charge overpotential [20–22].

By contrast, non-aqueous sodium-oxygen (Na–O<sub>2</sub>) batteries exhibit a much lower charge overpotential (<300 mV) than non-aqueous Li–O<sub>2</sub> batteries (typically >1V) do, thus attracting great attention recently [23–26]. In 2010, the rechargeable Na–O<sub>2</sub> batteries were firstly investigated and demonstrated to run for several cycles at 105 °C by Peled *et al.* [27]. After that, Sun *et al.* reported the

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first room temperature Na–O<sub>2</sub> batteries and exhibited up to 20 cycles [28]. Unlike the instability of LiO<sub>2</sub> at room temperature [29,30], NaO<sub>2</sub> is a stable superoxide and found to be the main discharge product in non-aqueous Na–O<sub>2</sub> batteries by both experimental [31,32] and theoretical [22,33] investigations. Therefore, the electrochemical reaction of non-aqueous Na–O<sub>2</sub> batteries can be described as  $\text{Na}^+ + \text{e}^- + \text{O}_2 \leftrightarrow \text{NaO}_2$ , which is kinetically favored as only one electron transfers for a formula unit. More importantly, sodium is the 6th most abundant element in the earth's crust and its amount is more than 1000 times larger than that of lithium [34], suggesting its much lower cost and greater suitability than lithium to be the power source for future EVs.

However, an issue with non-aqueous Na–O<sub>2</sub> batteries is that the discharge product NaO<sub>2</sub> is insoluble to the electrolyte and would deposit in the cathode, leading to the pores clogging and oxygen transports blocking, which significantly limits the discharge capacity and cyclability. Therefore, the design over the porous geometrical structures and surface properties for the cathode material is of great importance to non-aqueous Na–O<sub>2</sub> batteries. In this regard, porous carbon is widely adopted as the air cathode due to its large variety, high specific surface area, good conductivity and low cost. For example, Liu *et al.* investigated graphene nanosheets (GNS) as the air cathode and obtained a high discharge capacity of 8268 mA h g<sup>-1</sup> at a current density of 200 mA g<sup>-1</sup> [35]. Jian *et al.* used a carbon nanotube paper as a binder-free air cathode. Results showed a discharge capacity of 7530 mA h g<sup>-1</sup> at current density of 500 mA g<sup>-1</sup> and a charge overpotential less than 200 mV [36]. Zhao *et al.* founded that the non-aqueous Na–O<sub>2</sub> batteries could be cycled for up to 100 cycles at a limited capacity of 750 mA h g<sup>-1</sup> by pre-depositing a thin NaO<sub>2</sub> layer on vertically aligned carbon nanotubes (VACNTs) network [37]. Although great progress has been made, experiments have so far yielded little mechanistic understanding on the effect of carbon structures at the atomic level in the discharge and charge processes.

In this work, a density functional theory (DFT) based first-principles study is used to investigate the effect of carbon structures at the atomic level on the discharge and charge processes for non-aqueous Na–O<sub>2</sub> batteries. Seven carbon structures, including graphite (0001) surface, SV defect, DV5-8-5 defect, DV555-777 defect, DV5555-6-7777 defect, S-W defect and fractured edge, are considered. Firstly, the adsorption energies of NaO<sub>2</sub> molecules on these carbon structures are calculated. By doing Bader charge analysis, we then build the relationship between electrons transfer and adsorption energies through electrostatic interaction. Thirdly, the investigation of the most favorable carbon structure is presented by comparing several adsorption sites and charge difference plots. Finally, based on the solution mechanism [38,39], the influence of carbon structures at the atomic level on the growing and decomposition processes of product is proposed, and suggestions for the development of high capacity air cathode in non-aqueous Na–O<sub>2</sub> are obtained accordingly.

## 2. Computational methods

All of the calculations were performed using ABINIT [40,41] code. The exchange correlation interaction was implemented within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) type [42], and the core electrons were described by projector augmented wave (PAW) method [43]. The energy cutoff for the plane wave basis expansion was set to be 22 Ha to ensure a good convergence. Periodic boundary condition was used and the vacuum between slabs in z-direction was 15 Å. The force tolerances for self-consistent-field (SCF) cycles and structural optimization were set to be  $4.0 \times 10^{-5}$  Ha/Bohr and  $6 \times 10^{-4}$  Ha/Bohr, respectively.

In this work, all the slab models were presented based on a monolayer graphite (0001) surface. The feasibility of the computational domain has been proved by many previous investigations [44–47]. To make a further validation, we calculated the adsorption of NaO<sub>2</sub> molecule on a triple-layers graphite (0001) surface and that with SV defects, the structures of the built model and optimized structures were shown in Figures S1 and S2. It was found that the energy differences for the monolayer and triple layers were less than 2%. A  $4 \times 4 \times 1$  supercell was prepared for graphite (0001) surface and defective graphite surfaces, and the Brillouin zone was sampled using a  $4 \times 4 \times 1$  k-point Monkhorst-Pack grids. A  $5 \times 5 \times 1$  supercell was also built to test the convergence, and a less than 0.05 eV difference of adsorption energy for NaO<sub>2</sub> molecule was gotten, confirming the rationality of our model. To represent the fractured edge of graphite, the ideal model in the graphite (0001) surface and the selected model in real calculations, including adsorption sites, were presented in Figure S3. In our work, a 9 C atom-wide graphene nanoribbon (GNR) (44 atoms) with armchair edge was used [48]. One edge of GNR was decorated by hydrogen atoms, which were fixed after structure optimization, and the other edge was exposed. The distance between two neighboring nanoribbon was set to be 13.7 Å to ensure the isolation of the edge sites and the k-point mesh for the GNR was set to be  $1 \times 4 \times 1$ .

The adsorption energy of NaO<sub>2</sub> molecule on the model carbon structures was presented by:

$$E_{ad} = E_{carbon} + E_{NaO_2} - E_{NaO_2/carbon} \quad (1)$$

where  $E_{ad}$  is the adsorption energy,  $E_{carbon}$ ,  $E_{NaO_2}$  and  $E_{NaO_2/carbon}$  are the DFT total energies of carbon structures, NaO<sub>2</sub> molecule and NaO<sub>2</sub>-carbon adsorption system, respectively. The Bader charge analysis was implemented by the AIM program [49] in the ABINIT code.

## 3. Results and discussion

NaO<sub>2</sub> is reported to show a crystal structure of  $Pa\bar{3}$  space group between 196 and 223 K, and the O–O bonds arrange disordered above 223 K [50,51]. The optimized structures of pyrite phase and molecular NaO<sub>2</sub> are shown in Fig. 1. The lattice constants of crystal NaO<sub>2</sub> are  $a = b = c = 5.54$  Å, consistently with previous theoretical ( $a = b = c = 5.509$  Å) [52] and experimental ( $a = b = c = 5.460$  Å) [50] investigations. In NaO<sub>2</sub> molecule, the bond lengths of Na–O and O–O are 2.153 and 1.361 Å. The optimized structures of graphite (0001) surface, SV defect, DV5-8-5 (two pentagons and one octagon) defect, DV555-777 (three pentagons and three heptagons) defect, DV5555-6-7777 (four pentagons, one hexagon and

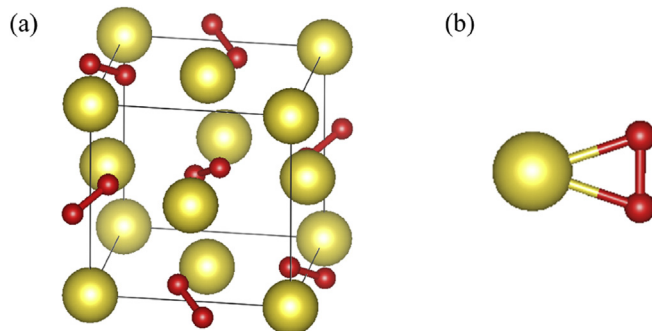


Fig. 1. Optimized structures of (a)  $Pa\bar{3}$  NaO<sub>2</sub> bulk and (b) NaO<sub>2</sub> molecule. The yellow and red balls represent sodium and oxygen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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