Probing adsorption and diffusion mechanisms of sodium-oxides on N-doped graphene for an efficient sodium-oxygen battery: A DFT study

C. Fwalo.[(1)(2)], *A.Kochaev.*[(3)], *and R. E. Mapasha.*[(1)]

(1) Department of Physics, University of Pretoria, Pretoria 002, South Africa.
(2) Department of Physics, Copperbelt University, Kitwe 10101, Zambia.
(3)Department of Physics, Ulyanovsk State University, Ulyanovsk, Russia.

1. Background

The escalating global demand for energy consumption is leading to high dependence on fossil fuels. However, efforts are being put into place to develop energy-storing devices, such as batteries with energy and power densities surpassing those of fossil fuels, linked to the effects of climate change.

Fig. 1: Impact of climate change

2. Research aim and objectives

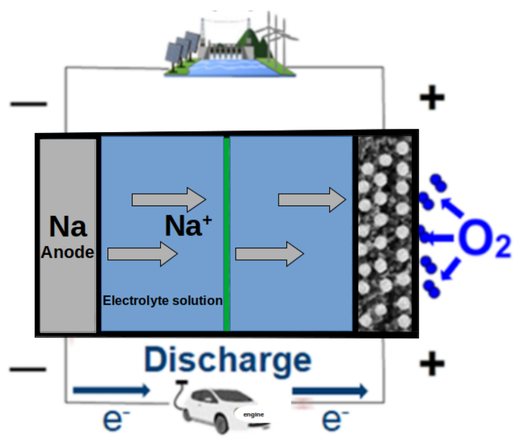


Fig. 2: Discharging

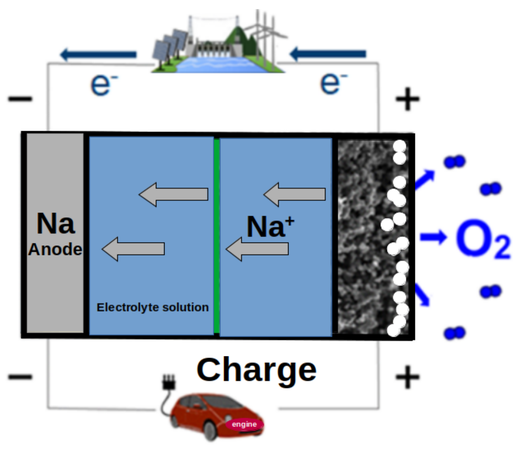


Fig. 3: Charging

Research objectives:

1. To model and generate the nitrogen-doped graphene (NGr) crystal structure.
2. To optimize configurations of sodium-oxides (Na_xO_2, x = 1, 2, 3, and 4) on NGr.
3. To calculate the adsorption energies and charge density distributions.
4. To calculate the Gibbs free energies and diffusion energy barriers.
5. To calculate the density of states (DOS) for analyzing the conductivity.

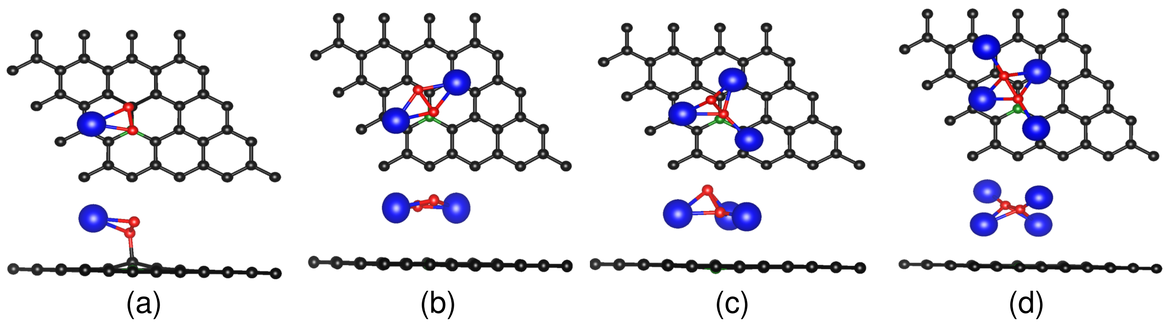
2. Computational Methods

1. $$\hat{H}\Psi(\vec{r}_i, \vec{R}_j) = \tilde{E}\Psi(\vec{r}_i, \vec{R}_j).$$
$$(\hat{T}_e + \hat{T}_N + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN})\Psi(\vec{r}_i, \vec{R}_j) = \tilde{E}\Psi(\vec{r}_i\vec{R}_j) \quad (1)$$
2. DFT in the quantum ESPRESSO code was used for all calculations [1].
3. GGA-PBE functional for the exchange and correlation potential was used [1]. For optimization, a kinetic energy cut-off of 544 eV was used and a K-points grid of 4 x 4 x 1 by adopting the Monkhorst-Pack scheme.
4. The adsorption energies and charge density distributions were calculated using the following formulas: adsorption energy by;
$$E_{ads} = E_{complex} - E_{graphene} - E_{adsorbate} \quad (2)$$

3. Results

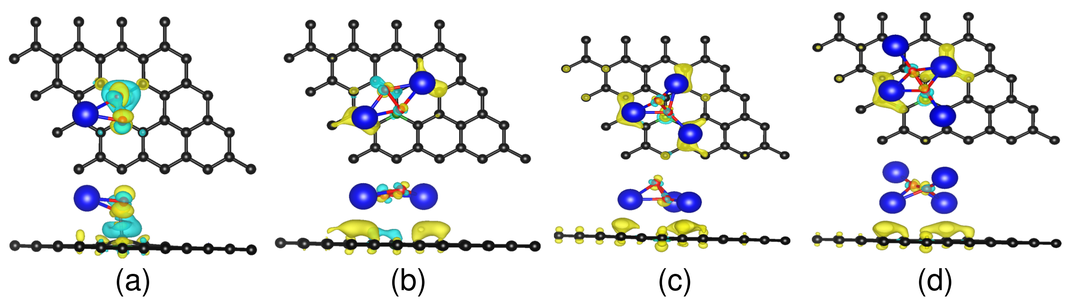
Table. 1: The calculated Adsorption energies for isolated Na, O_2, and various Na_xO_2 on NGr.

System	Adsorption Energy (eV)	Charge Density ($\|e\|$)
Na	-1.56	0.11
O_2	-1.57	-0.31
NaO_2	-1.98	-1.18
Na_2O_2	-2.13	-1.55
Na_3O_2	-2.30	-1.91
Na_4O_2	-2.91	-1.15



(a) (b) (c) (d)

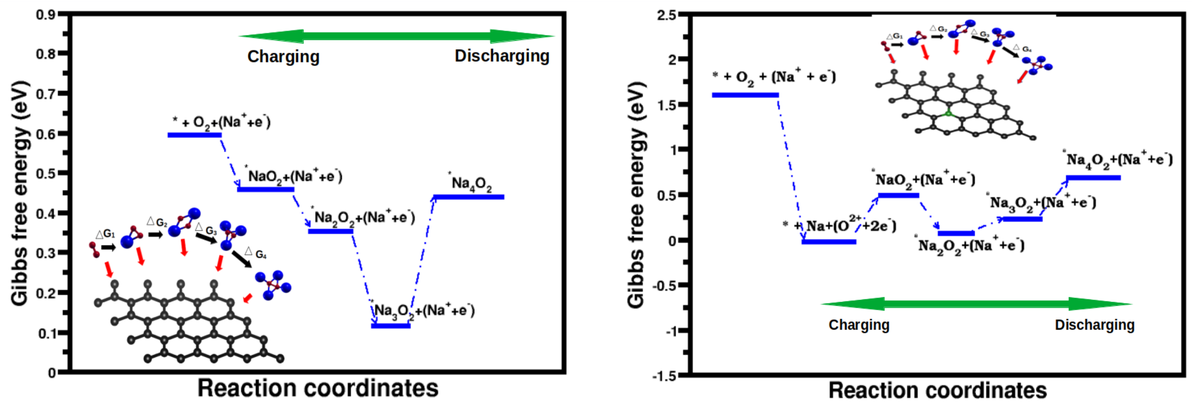
Fig. 4: The optimized configurations of various Na_xO_2 on NGr.



(a) (b) (c) (d)

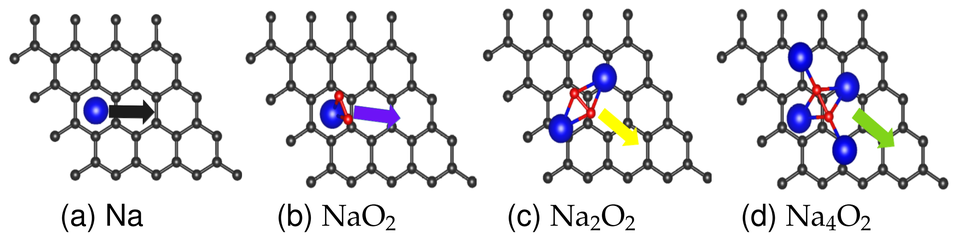
Fig. 5: The charge density distributions in the systems of various Na_xO_2 on NGr.

3. Results conti ...

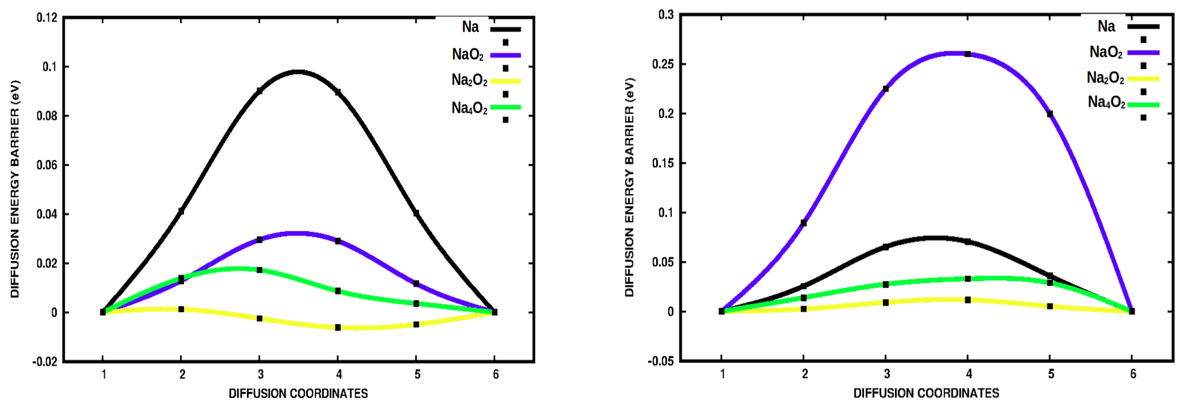


(a) (b)

Fig. 6: Gibbs free energy changes during the formation of the various Na_xO_2.

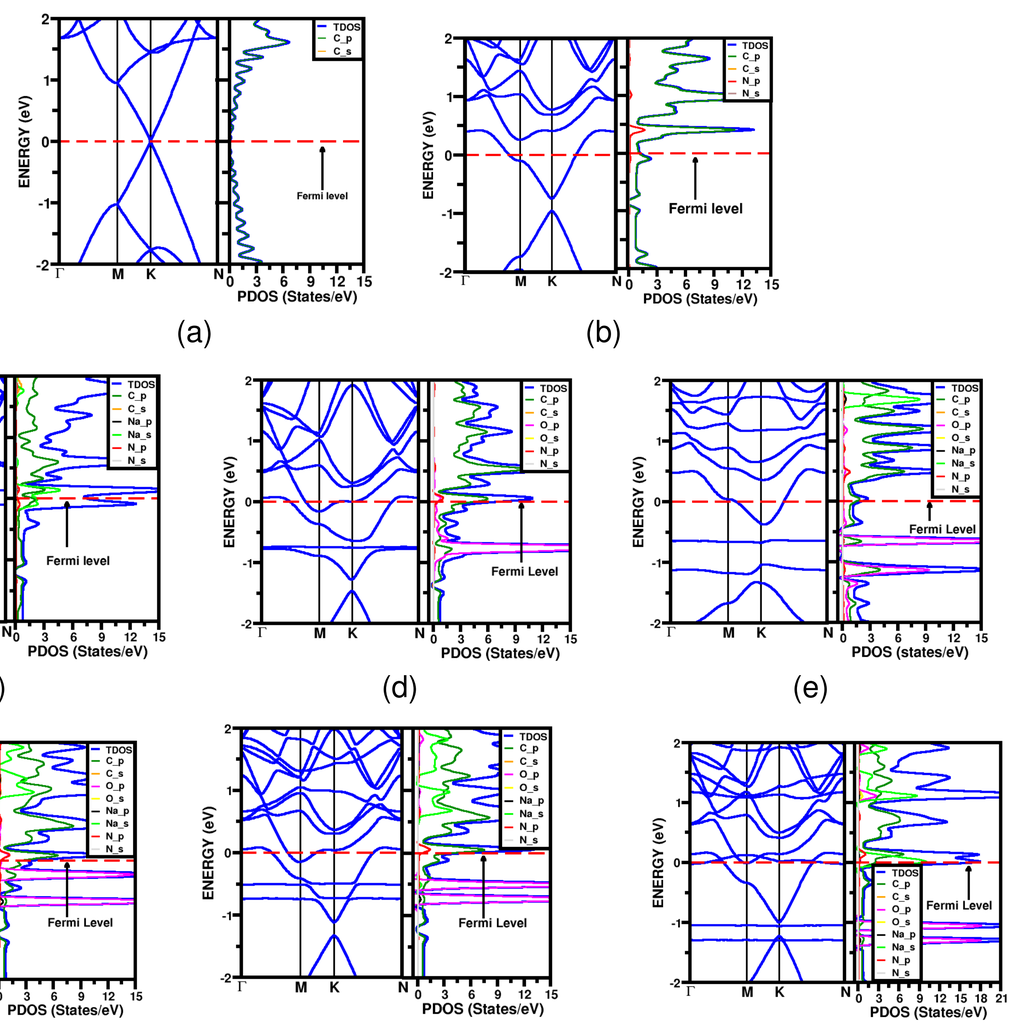


(a) Na (b) NaO_2 (c) Na_2O_2 (d) Na_4O_2



(e) (e)

Fig. 7: Possible diffusion paths and corresponding energy barrier profiles.



(a) (b) (c) (d) (e) (f) (g) (h)

Fig. 8: The density of states (DOS) and band structures for the pristine, Na, O_2, and Na_xO_2 on graphene and NGr.

4. Conclusion

Our findings suggest that NGr:

1. Adsorb various Na_xO_2 strongly, including isolated Na and O_2.
2. Has strong electronic interactions with various Na_xO_2 based on the charge density transferred.
3. has low diffusion energy barriers, suggesting enhanced ion transport.
4. The electronic conductivity was enhanced after adsorbing the final discharge of Na_4O_2.
5. These theoretical properties suggest that NGr has the potential to be used as cathode electrodes for efficient next-generation $Na - O_2$ battery.

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