A DFT Study of the Oxygen Reduction Reaction Mechanism on Be Doped Graphene

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Abstract

Graphene despite its high surface area has very limited activity towards the oxygen reduction reaction (ORR), demonstrating selectivity towards the unfavorable two-electron mechanism. We have employed the spin polarized density functional theory (DFT) method to investigate the effect of the heteroatom p-type beryllium (Be) dopant on the oxygen reduction reaction activity of graphene. The preferred doping sites, active sites and reaction mechanism available on the doped graphene surfaces were investigated with increasing Be concentrations of 0.03 ML, 0.06 ML and 0.09 ML. Our results reveal that oxygen does not bind strongly to bare graphene, and Be at the lattice sites provides site for the oxygen adsorption and ORR. Oxygen binds dissociatively on the doped surfaces preferentially in the order 0.06 ML > 0.09 ML > 0.03 ML. From this studies introduction of Be impurities in a single honeycomb ring of graphene has significant impact on the binding and adsorbate-adsorbent interactions which leads to dissociative adsorption of oxygen, favouring the 4e- ORR pathway. The reaction is kinetically favoured most on the surface with a stronger O* binding and weaker OH* binding. Overall, the 0.03 ML and 0.06 ML doped surfaces are the most active facets for the ORR showing exergonic reaction energies at 0 V.

Introduction

The global interest in electrochemical energy technologies, such as fuel cell and battery technologies, is rising. This is towards attaining energy sustainability and to reduce the global carbon economy. Traditional solid-oxide fuel cells (SOFCs) have the highest performance and durability but operate at temperatures above 600 °C. Lowering the operating temperature is critical. However, the energy-conversion efficiency of the low-temperature SOFC is mainly limited by the slow kinetics of the oxygen reduction reaction (ORR) at the cathode.[1, 2]

Pt and its alloys are effective cathodes,[3] however, due to the high cost, low abundance and poor durability of the Pt-based catalysts, alternative low-cost efficient metal and carbon-based cathodes have been of interest worldwide in recent years. For instance, the interest in carbon sheets like graphene is due to their low cost, environmental friendliness, outstanding activity and stability.[4]

Heteroatom-doped graphene cathodes have attracted considerable interest in very recent years, owing to its excellent ability to fine-tune the physicochemical properties and catalytic activity of graphene. For example, materials like p-type doped graphene (e.g., boron), n-typed doped graphene (e.g., nitrogen, phosphorus) and halogen doped graphene have received significant attention. This includes their ternary and quaternary doped compounds [5, 6, 15, 7–14] which have shown high catalytic activity and selectivity towards the ORR.

The ORR is reported to occur along two possible pathways; via the 2-electron pathway which could lead to hydrogen peroxide formation or via 4-electron pathway which will directly transform into water. Understanding the detailed mechanisms have focused on other heteroatom doped graphene and not boron. Using both experiment and density functional theory calculations, the detailed mechanisms on

doped graphene has been studied i.e., nitrogen,[16] phosphorus,[17, 18] boron,[19] boron and nitrogen,[20] nitrogen, sulfur and phosphorus,[10] MnN₄ [21] and FeN₄. [22]

To the best of our knowledge, although p-type heteroatom doped graphene are efficient, work on p-type dopants have focused only on boron (B). However, no work systematic studies have been conducted on the effect of beryllium dopant on graphene. Thus, we have conducted for the first time, a comprehensive study of the Be-doped graphene, to understand the impact of Be doping on surface active sites, adsorption modes of adsorbates and the detailed reaction mechanism of the oxygen reduction reaction. In this study, graphene has been doped with beryllium at varying monolayer concentrations of 0.03 ML, 0.06 ML and 0.09 ML. This work provides a basis for the study of binary, ternary and quaternary Be-doped systems and their efficiencies as a cathodic fuel cell material.

Computational Details

All calculations were carried out using the spin-polarized density functional theory (DFT) method where periodic boundary conditions were applied as implemented within the Quantum-Espresso suite of programs. [23] This performs fully self-consistent DFT calculations to solve the Kohn-Sham equations. [24] The generalized gradient approximated exchange correlation functional of Perdew, Burke, and Ernzerhof [25] as well as the ultra-soft Vanderbilt pseudopotentials were used. The Grimme's D2 correction was implemented for dispersion corrections. The plane wave basis set was employed with a kinetic energy cutoff of 40 Ry, as obtained from convergence test. The Fermi-surface effects were treated by the smearing technique of Fermi-Dirac, using a smearing parameter of 0.003 Ry. An energy convergence threshold defining self-consistency of the electron density was set to 10^{-6} eV and a beta defining mixing factor for self-consistency of 0.2.

A p(3x3) supercell of graphene was employed in all adsorption studies which is made up of 32 carbon atoms, whereby adsorbates were more than 6 Å apart. Also, a vacuum region of 20 Å perpendicular to each surface was introduced to avoid interactions between periodic units. The Monkhorst-Pack k-point Brillouin Zone sampling method was implemented, [26] with k-point sampling grids of (7 x 7 x 1) for the unit cell and (3 x 3 x 1) for the p(3 x 3) supercell. The graphics of the atomic structures have been prepared with the XCrysDen software. [27] Transition states were searched using the CI-NEB method, where structures at the saddle point are characterized by a single imaginary frequency.

Results And Discussions

The resulting C-C bond of pure graphene has been reported to be 1.43 Å using density functional theory. [7] Our calculated C-C bond is seen to be 1.42 Å, in good agreement with previous studies. In Fig. 1, Be impurities were introduced at three (3) unique doping sites, i.e. (D) lattice point, where carbon at the lattice site is replaced with impurity, site (E) where Be bridges two carbon atoms and site (F) where there is bridge doping and carbon vacancy at the neighboring lattice site.

In Fig. 1, three (3) surface oxygen adsorption sites (A, B and C) were considered for the adsorption of the O₂ molecule. The molecules were adsorbed at three unique sites on the surface, i.e., hollow (A), bridge (B) and top (C) sites.

a. Oxygen Adsorption on Bare Graphene

Molecular oxygen was first adsorbed onto clean graphene at the surface adsorption sites i.e., (A), (B) and (C) as indicated in Fig. 1. The binding energies are calculated as shown below:

$$E_{ads} = (E_{G+O_2}) - (E_G + E_{O_2}) \quad (1)$$

Where E_{ads} is the adsorption energy indicating the binding strength and stability of products relative to reactants. E_{G+O_2} is the energy of adsorbed system, E_G is the energy of isolated graphene and E_{O_2} is the energy of isolated oxygen molecule.

Upon geometry optimization, oxygen adsorption on graphene is thermodynamically unfavoured, with a distance of 3.64 Å from graphene and a binding energy of 0.96 eV. Super-oxo (O²⁻) species is formed on pure graphene. This being a diatomic oxygen molecular species accounts for pure graphene promoting oxygen transformation through the two-electron pathway (H₂O₂ intermediate) and not the 4-electron pathway. We observed that the O-O bond is polarized resulting in bond activation from 0.91 Å in isolated oxygen molecule to about 1.25 Å in the adsorbed state. (See Table 1).

Table 1
The binding energies and sites of oxygen species on bare graphene

Surface	Ads Site	E _{ads} / eV	d(C-O)/Å	d(O-O)/Å	O ₂ species	Δq/e ⁻
-	Gaseous	-	-	0.91	molecular	0
a	hollow	0.94	3.64	1.25	superoxo	0.22
b	bridge	0.96	3.33	1.25	superoxo	0.22
c	top	0.96	3.31	1.25	superoxo	0.22

b. Be-doped Graphene

On doping at the three investigated sites i.e., D, E and F (see Fig. 1), and upon optimization, the ground state structures were obtained (see Fig. 2). The preferred dopant site was investigated, where the defect formation energies were calculated with the formula below;

$$E_{def} = \left(\frac{(E_{doped} + nEC) - (EG + nEBe)}{n} \right) \quad (2)$$

Where E_{doped} is the energy of the Be-doped surface, E_C is the energy of carbon atom in gas phase, E_G is the energy of isolated graphene, E_{Be} is the energy of beryllium atom in gas phase and n is the number of dopants i.e., 1, 2 and 3 for 0.03 ML, 0.06 ML and 0.09 ML doping respectively.

At 0.03 ML Be doped graphene concentration, it is observed that the dopant prefers the point defective site (D) over the interstitial site (E) (Fig. 2). The bridge site doping with vacancy i.e., structure (F) optimizes to (D). For structure (F), beryllium atom moves from the bridge site to the vacant lattice site after optimizing.

Beryllium binds at the point lattice site more favorable with a defect formation energy of 7.68 eV for D and F, and binds least at the interstitial site with a defect formation energy of 8.66 eV at the bridge (E) site. In structure E, around the defective point, graphene C-C bond shrinks from an inter-nuclear distance of 1.42 Å to about 1.34 Å and C-Be interaction bond is at 1.33 Å. In structure D and F, the C-Be bond is weaker at 1.56 Å and C-C shrinks less to 1.38 Å. The structural distortions are due to the higher radius of the impurity causing strain in the material. Beryllium doping of graphene is an endothermic process requiring energy at both the lattice and interstitial sites.

c. Oxygen Adsorption on Be-doped Graphene

Beryllium absorbs at the point defective site, more Be is introduced into the point lattice sites of graphene, to produce higher concentrations of 0.06 ML and 0.09 ML. Subsequently, oxygen adsorption studies were carried out on 0.03 ML, 0.06 ML and 0.09 ML doped graphene sheets on different sites (see Table 2).

Table 2: Preferred O_2 adsorption modes and sites on Be-doped graphene, O_2 strength of interaction and extent of activation, adsorption energies, bond distances, oxygen species realized and surface coordination numbers

At 0.03 ML Be doping, the preferred binding of O_2 was investigated at the hollow, bridge and top sites using **Eq. 1**. It was observed that the oxygen binds most strongly when absorbed at the top site of Be (see Fig. 3). At the hollow site, the oxygen molecule moved from the hollow position to the top site of Be, where oxygen is absorbed at the edge with a binding energy of 1.27 eV. On the bridge site, oxygen aligns to surface carbon atoms, with a binding energy of 2.16 eV. However, at the top site, oxygen binds most strongly leading to oxygen decomposition onto the bridge carbon atoms of beryllium. At the top Be site the interatomic distances were measured at 1.59 (O-O bond) and 1.40 Å (O-C bond) indicative of oxygen decomposition onto the surface (see Table 2). The most active site and preferred binding site for oxygen on doped graphene at 0.03 ML concentration is seen to be the top site. Dissociation of the oxygen species is indicative of favourable transformation via the 4-electron pathway.

At the dopant concentration of 0.06 ML, the binding energy of O_2 were investigated on two surfaces, an

Conc	Surface	Site	O ₂ Ads Site	E _{ads} / eV	d _(Be-o) / Å	d _(C-O) / Å	d _(O-O) / Å	O ₂ Species	Δq/ e ⁻	η
0.03 ML	a	hollow	Be-top	1.27	1.57	2.64	1.30	superoxo	0.23	1
	b	bridge	Be-top	2.16	2.36	1.95	1.27	superoxo	0.22	0
	c	top	Be-top	0.68	2.38	1.40	1.59	dissociated	0.28	2
0.06 ML	a	iso	Be-top	-1.63	2.68	1.39	1.34	peroxo	0.24	0
	b	adj	Be-top	-7.62	1.50	1.30	2.91	dissociated	0.27	4
0.09 ML	a	iso	Be-top	0.98	1.58	1.42	1.47	peroxo	0.27	2
	b	adj	Be-top	-1.63	1.47	1.31	3.29	dissociated	0.30	4

isolated defective surface (a) and a conjugated defective surface (b) as depicted in Fig. 4. Increasing Be concentration generally increases the binding strength of oxygen on graphene. The binding of oxygen on the conjugated defective surface is preferred as oxygen is decomposed, while an activated per-oxo-like species is formed on the isolated defective surface. At the conjugated defective site, the binding energy is -7.62 eV with a binding coordination number of 4. In the isolated case, a binding energy of -1.63 eV is obtained.

Be dopant concentration in graphene lattice was increased to 0.09 ML (see Fig. 5), in the isolated (a) and conjugated (b) defective cases. From Table 2, oxygen prefers to adsorb at the conjugated defective surface with a binding energy of -1.63 eV over the isolated defective surface with energy of 0.98 eV. Activated per-oxo-like species is obtained on the isolated defective surface while on the conjugated defective surface (where binding is preferred) a decomposed oxygen molecule is seen.

These results indicate that on 0.03 ML, 0.06 ML and 0.09 ML Be-doped graphene, oxygen is activated to dissociation into atomic oxygen which will favour transformation via the 4-electron pathway and not the 2-electron pathway as seen on pure graphene. Be impurities oriented in an isolated fashion are generally less efficient for molecular oxygen binding as compared to the conjugated defects. The oxygen adsorbed at the conjugated defective site favors decomposition, which in turn favors the 4-electron pathway. This also reduces the possibility of reduction via the 2-electron pathway which is undesirable and competitively leads to hydrogen peroxide formation. From this studies introduction of Be impurities in a single honeycomb ring of graphene has more impact on the binding efficiency of doped graphene.

d. ORR Reaction Mechanisms on Be-doped Graphene

On the most active Be-doped surfaces at 0.03 ML top site, 0.06 ML conjugated and 0.09 ML conjugated defective surfaces the ORR was studied and compared. In the oxygen reduction reaction, two elementary

steps were considered for the complete reduction of dissociated oxygen in to water i.e., equations 3 and 4.

Barriers for proton transfer to adsorbates from solution are expected to be quite small. Hence for electrochemical processes, the reaction pathway is analyzed, taking into account the hydrogen electrode potential as utilized by Peterson et al.[28] Each reaction step involves an electrochemical proton electron transfer, and the free energy change of each step is determined as a function of the applied electrical potential known as the computational hydrogen electrode (CHE) model.

In the CHE, the chemical potential of a proton electron pairs, $\mu(H^+) + \mu(e^-)$ is equal to half of the chemical potential of gaseous hydrogen ($1/2 \mu(H_2)$) at a potential of 0 V using equations 5 and 6 below (see Table 4).

$$1. O^* + (H^+ + e^-) \rightarrow OH^*; \Delta G_1 = \mu(OH^*) - \mu(O^*) - \mu(H^+) - \mu(e^-); \Delta G_1 = \mu(OH^*) - \mu(O^*) - \mu_{1/2}(H_2) (5)$$

$$2. OH^* + (H^+ + e^-) \rightarrow H_2O^*; \Delta G_2 = \mu(H_2O^*) - \mu(OH^*) - \mu(H^+) - \mu(e^-); \Delta G_2 = \mu(H_2O^*) - \mu(O^*) - \mu_{1/2}(H_2) (6)$$

The chemical potentials (reaction energies) of each adsorbed species were calculated by standard DFT techniques as the free energy of formation from the elements, isolated surface, oxygen gas and hydrogen gas using Eqs. 7 and 8. (See Table 3). The reaction energies of adsorbed systems are calculated relative to the reactant molecules (i.e., energy of isolated O_2 , H_2 and doped graphene) where;

$$\Delta E = (E_{\text{products}}) - (E_{\text{reactants}}) (7)$$

Where E_{products} is the energy of the intermediate and $E_{\text{reactants}}$ is the energy of reactants i.e., energy of isolated O_2 , H_2 and doped graphene.

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S (8)$$

However, entropy contributions were considered at 298 K and at 0 K. ΔZPE is the change in ground state zero-point vibrational energy. The change in free energy (ΔG_n) of each step will change with a simple linear function of applied potential (U).

$$\Delta G_n(U) = \Delta G_n(U = 0) + neU (9)$$

Where n is the number of proton-electron pairs transferred relative to CO_2 and e is the number of elementary positive charges transferred. For the 0.09 ML, the reaction is endogenic at 0 V, using Eq. 9, the energetics were obtained at -0.40 V, where the reaction is exergonic at 298 K.

Table 3
Formation Energies for the of Intermediates on Be-doped Graphene in the ORR

Adsorbed Species	T/ K	0.03 ML		0.06 ML		0.09 ML	
		$\Delta G/ \text{eV}$	$\Delta E/ \text{eV}$	$\Delta G/ \text{eV}$	$\Delta E/ \text{eV}$	$\Delta G/ \text{eV}$	$\Delta E/ \text{eV}$
2O*	0	0.29	0.68	-8.01	-7.62	-2.02	-1.63
	298	0.89		-7.42		-1.42	
O*	0	0.15	0.34	-4.00	-3.81	-1.01	-0.82
	298	0.45		-3.71		-0.71	
O*/ H*	0	-4.54	-4.15	-5.73	-5.34	-0.87	-0.48
	298	-3.69		-4.88		-0.02	
OH*	0	-3.26	-3.12	-5.25	-5.11	-5.25	-5.11
	298	-2.41		-4.40		-4.40	
OH*/ H*	0	-2.70	-2.56	-3.85	-3.71	-5.80	-5.66
	298	-1.03		-2.18		-4.13	
H ₂ O*	0	-4.18	-3.88	-6.43	-6.13	-5.01	-4.71
	298	-2.51		-4.76		-3.34	

Table 4: Formation Energies for the Electrochemical Reaction on Be-doped Graphene in the ORR at 0 V

Adsorbed Species	0.03 ML	0.06 ML	0.09 ML	0.09 ML
	@ 0 V	@ 0 V	@ 0 V	@ -0.40 V
O*→ OH* (ΔG_1)	-2.86	-0.69	-3.69	-4.09
OH*→ H ₂ O* (ΔG_2)	-0.10	-0.36	0.79	-0.01

From the energy profile diagram for the electrochemical reaction of O₂ on Be-doped graphene in the ORR, Fig. 6, the reaction is feasible on both 0.03 ML and 0.06 ML surfaces at 0 V and feasible on the 0.09 ML surface at a higher voltage of -0.40 V.

We also considered hydrogenation of oxygen with a surface hydrogen. The transition states for the hydrogenation of the adsorbed O atom at the preferred defective sites and the hydrogenation of the hydroxyl into water are both explored using the Climbing Image-Nudged Elastic Band method. Transition state energies are calculated as;

$$E_a = E_{TS} - E_{IS} \quad (10)$$

where E_{TS} is the absolute energy of the transition state and ΔE_{IS} is the absolute energy of the intermediate state leading to product formation.

Considering the thermodynamics of the co-adsorbed states (see Table 3), some elementary steps like OH formation from adsorbed O^* and H^* is endothermic on the 0.03 ML and 0.06 ML doped surfaces. However, transformation on the 0.03 ML and 0.06 ML surfaces is thermodynamically feasible for OH hydrogenation into water but on the 0.09 ML surface that elementary step is endothermic.

From the reaction energy profile diagram in Fig. 7, kinetically, OH^* formation is most feasible in the order 0.06 ML (1.62 eV) > 0.03 ML (1.84 eV) > 0.09 ML (1.69 eV). The subsequent step i.e., water formation is most favoured on 0.03 ML (0.59 eV) > 0.06 ML (2.53 eV) > 0.09 ML (1.95 eV) surfaces. Strong binding of intermediate species e.g., O^* and OH^* at active sites have been reported to control the reaction kinetics on transition metals where strong binding increases the barrier for ORR reactions by reducing surface activity.

Our results show that stronger binding of O^* is consistent with lower barrier for OH formation. The O^* binding strength shows the order 0.06 ML > 0.09 ML > 0.03 ML and the reverse trend is seen for the O^* hydrogenation barriers i.e., 0.03 ML > 0.09 ML > 0.06 ML with energies of 1.8 eV > 1.7 eV > 1.6 eV respectively. This indicates that strong binding of atomic oxygen on Be-doped graphene does not impede its hydrogenation as expected. Oxygen is rather hydrogenated easily as the hydrogenation product formed i.e., OH^* species, is not a leaving group. However, OH^* hydrogenation leads to the formation of water, which is a leaving group, hence the strong OH^* binding energies are consistent with higher energy barriers. On both 0.06 ML and 0.09 ML, OH^* interactions are greater compared to the 0.03 ML surface, hence hydrogenation and leaving of OH^* is challenging on those surfaces. The hydrogenation of OH^* is challenging and the rate determining step in the ORR process on both 0.06 ML and 0.09 ML surfaces. On the 0.03 ML surface however, the hydrogenation of the O^* species is the rate limiting step.

Overall, the 0.03 ML surface favours the ORR reaction kinetically due to the rate limiting barrier of 1.84 eV for the hydrogenation of O^* compared to 2.5 eV and 1.9 eV on 0.06 ML and 0.09 ML surfaces respectively for the hydrogenation of OH^* . Although substantial charge transfer to the O_2 molecule is desirable to favour the O_2 dissociation and the 4-electron pathway, additionally, surfaces that can preferentially bind O^* strongly and OH^* weakly will be kinetically suitable for the ORR. The Be point doped graphene at dilute concentrations like 0.03 ML is the most promising candidate that can be explored further for fuel cell applications at more dilute concentrations as well as the 0.06 ML surface.

Conclusion

Using spin-polarized DFT calculations, the effect of p-type beryllium dopant was seen to impact on the surface reactivity of graphene. Beryllium binds at the point lattice site of graphene more favorably than at the interstitial site. The presence of Be at the lattice site of graphene tuned the selectivity of graphene towards the 4-electron ORR pathway by causing oxygen dissociation. Through the 4-electron pathway,

two steps are encountered for the O* hydrogenation and the OH* hydrogenation into water. The reaction is seen to be challenging on the 0.09 ML Be-doped graphene. The ORR is exergonic on the 0.03 ML and 0.06 ML surfaces at 0 V. Hence doping at low Be concentrations could be desirable. This work provides a basis for exploring more dilute Be doped materials and Be based ternary compounds as cathodic material for the ORR.

Declarations

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Code availability: Quantum Espresso is an opensource code available at <https://www.quantum-espresso.org/>

Author's contributions: Data was collected by Mr. Kenneth Limbey and Mr. Destiny Konadu. Manuscript was drafted by Dr. Caroline Rosemyya Kwawu and revised by Dr. Albert Aniagyei. Research concept was developed and supervised by Prof. Richard Tia and Prof. Evans Adei.

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Figures

Figure 1

The binding sites of O₂ adsorbates i.e., A (hollow), B (bridge) and C (top), and the doping sites of Beryllium i.e., D (lattice site), E (Interstice site) and F (interstice with lattice vacancy).

Figure 2

Initial (Top) and Optimized (down) structures of Be-doped Graphene at 0.03 ML

Figure 3

Guess (left) and optimized (right) structures of oxygen adsorbed at the hollow, bridge and top sites of 0.03 ML Be-doped Graphene

Figure 4

Guess (left) and optimized (right) structures of oxygen adsorbed on isolated and concentrated 0.06 ML Be-doped Graphene

Figure 5

Guess (left) and optimized (right) structures of oxygen adsorbed on isolated and concentrated 0.09 ML Be-doped Graphene

Figure 6

Energy Profile Diagram for the Electrochemical Reaction of O₂ on Be-doped Graphene in the ORR

Figure 7

Reaction Profile Diagram for the ORR on Be-doped Graphene at 0 K