

A computational investigation of oxygen reduction reaction mechanisms on Si- and Al-doped graphene: A comparative study

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ABSTRACT

In this letter, the mechanisms of the oxygen reduction reaction (ORR) on Si- and Al-doped graphene have been investigated to understand the effect of doped graphene on the ORR and predict details of ORR pathways. Density functional theory (DFT) calculations were used to achieve the true mechanism pathways of ORR on the surfaces. Also, free energy diagrams for the ORR were constructed to provide the stability of possible intermediates in the electrochemical reaction pathways. At first stage, the adsorption of O₂ molecule on both surfaces was studied with two possible configurations: atop (most stable) and bridge with the E_{ads} of -60.6 and -72.4 kcal/mol, while for bridge site they were about -48.9 and -60.4 kcal/mol, respectively. Then, the most stable configuration (atop) was selected and the pathways formed after the adsorption of four atomic hydrogen to O₂ molecule for both surfaces. These mechanisms were similar in both Si- and Al-doped graphene but there was a little difference in the obtained intermediates formed in each surface. In each pathway, the O₂ dissociation reaction was neglected because it was unlikely to occur due to the high activation energy (> 45 kcal/mol). The results of this study show an easy and economic way to obtain Si- and Al-doped graphene as a non-metal catalyst for ORR at the cathode electrode in fuel cells. Copyright © 2015 VBRI Press.

Keywords: Oxidation reduction; reaction mechanism; Si-doped graphene; Al-doped graphene; DFT.



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Introduction

Proton exchange membrane fuel cells (PEMFCs) are known as highly sources of clean energy in electronics and automobile industries due to producing high power energy products [1]. They convert the chemical energy into the electric energy without any pollution and their performance definitely depends on the oxygen reduction reaction (ORR) at the cathode [2]. However, the slow kinetic which occurs at the cathode electrode is one of the main problems in improving fuel cell efficiency. In the past decades, important efforts have been done to apply new electrocatalysts for ORRs based on noble metal catalysts such as Pt [3,4]. However, the high cost of the Pt catalyst hinders the large-scale commercialization of fuel cells.

Recently, great efforts have been devoted to develop alternative ORR electrocatalysts for the cathode of PEMFCs, such as platinum alloys [5], platinum nanoclusters [6], or non-platinum catalysts [7].

Graphene is a carbon based material which has shown great chemical and physical outstanding properties, such as high surface to volume ratio, excellent conductivity, ease of functionalization and high thermal conductivity [8]. Doping of pristine graphene with guest atoms such as B [9], N [10, 11], Si [12,13] and Pd [14] can significantly modify its physical and chemical properties [15]. For instance, Zhao et al. [16] suggested that Si-doped graphene has shown high catalytic activity for CO oxidation. Also, in another work, Jiang et al. [17] demonstrated that the low cost Al-doped graphene is an effective catalyst for CO oxidation at room temperature. In another investigation Zhang et al. [18] studied the ORR mechanisms on N-doped graphene. Results showed that the nitrogen doping introduces asymmetry spin density and atomic charge density, making it possible for N-graphene to show high electrocatalytic activities for the ORR.

Despite efforts ongoing theoretical studies of ORR mechanisms on different metal-doped graphene, as we discussed above, few theoretical studies of ORR

mechanisms on Si- or Al-doped graphene have been conducted to date. The purpose of the current study is to investigate ORR mechanisms on Si- and Al-doped graphene, as a low-cost and economic catalyst at the cathode electrode in fuel cells, using density functional theory (DFT) calculations to provide information regarding the stability of possible intermediates within the electrochemical reaction pathways. We compare O₂ adsorption and reactivity results to demonstrate the effect of Si- and Al-doped graphene on the catalytic activity.

The elementary catalytic reaction steps and reaction pathways for ORR on Si- and Al-doped graphene were also studied which are keys of understanding electrocatalytic reactions on the fuel cells cathode. The obtained results indicated that Si- and Al-doped graphene have increased the interaction of the surface with O₂ molecule which concluded in two different pathways.

Computational details

We performed all-electron DFT calculations by 6-31G* basis set, as implemented in the GAMESS package [19]. Because the M06-2X density functional has been known as a reliable method to study non-covalent interactions, so, we preferred to apply this method for our calculations [20]. The adsorption energy (E_{ads}) of adsorbate was calculated by M06-2X/6-31G* method, based on the equation of $E_{\text{ads}}(A) = E_{A/M} - E_M - E_A$, where $E_{A/M}$, E_M and E_A are the total energies of the adsorbate-substrate system, the substrate, and the energy of the adsorbate in the gas phase, respectively. Negative adsorption energy shows that the adsorption is stable, exothermic and vice versa. Free energies of formed intermediates in different pathways were calculated based on a computational hydrogen electrode (CHE) model which defines that the chemical potential of a proton/electron ($H^+ + e^-$) in solution is equal to half of the chemical potential of a gas-phase H₂ [21].

Results and discussion

Geometric and electronic properties of Si- and Al-doped graphene

As is well-known, the introduction of Si or Al atom into sp^2 -hybridized carbon framework of graphene seems generally effective in modulating its electrical property and chemical reactivity [16-17]. The optimized geometry for the Si- and Al-doped graphene is shown in Fig. 1. It is clear that the geometric structure of Si- and Al-doped graphene is significantly distorted, where the Si/Al impurity projects out of the surface due to its larger size than C atoms and its preference to sp^3 hybridization. The optimized Si-C bond length is about 1.7 Å, which is larger than C-C bond in pristine graphene (1.4 Å). Similarly, this is happened for Al-doped graphene with the Al-C bond length of about 1.8 Å. On the other hand, Mulliken charge density calculations indicates that in the optimized Si- and Al-doped graphene, the amount of about 0.6 and 0.4 electrons are transferred from Si and Al atoms to C atoms of the graphene sheet, respectively. Therefore, we conclude that Si and Al dopants can improve the electronic structure of graphene sheet via

charge transfer and chemical reactivity through sp^3 hybridization.

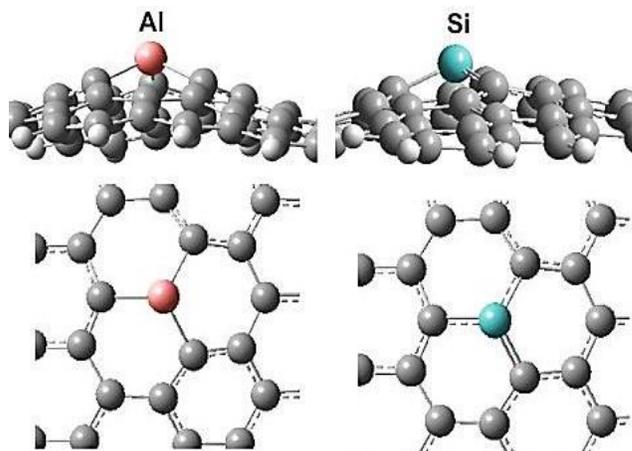


Fig. 1. Top and side view of the geometric structures for Si- and Al-doped graphene.

Adsorption of O₂ molecule on Si- and Al-doped graphene

To better understand the catalytic activity of Si- and Al-doped graphene toward O₂ molecule, the adsorption of a single O₂ molecule on the graphene surface is studied. Two adsorption sites are considered for O₂ adsorption according to Fig. 2 : (I) atop (S1, A1) and (II) bridge (S2, A2) sites. The calculated bond lengths in both Si- and Al-doped graphene, before and after O₂ adsorption, are listed in Table 1.

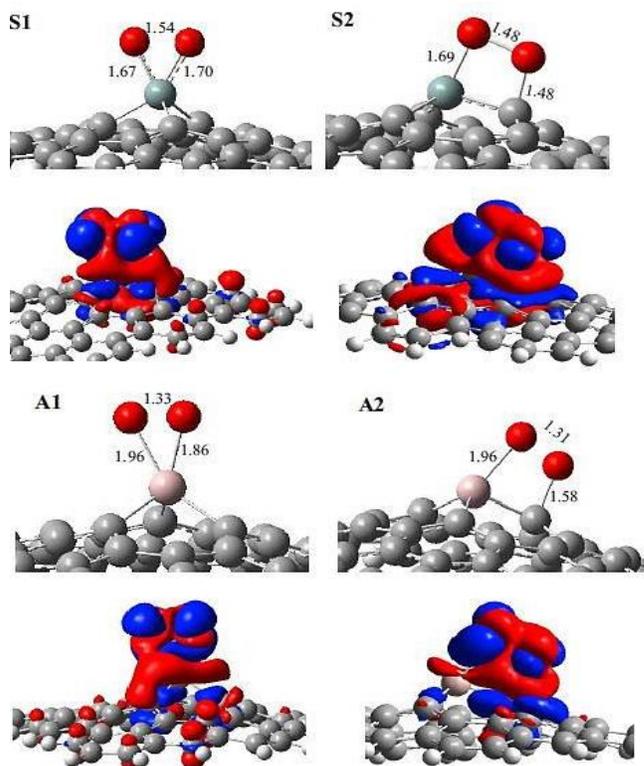


Fig. 2. Optimized structures and corresponding electron density difference maps of O₂ adsorption on Si (S1, S2) and Al (A1, A2) doped graphene.

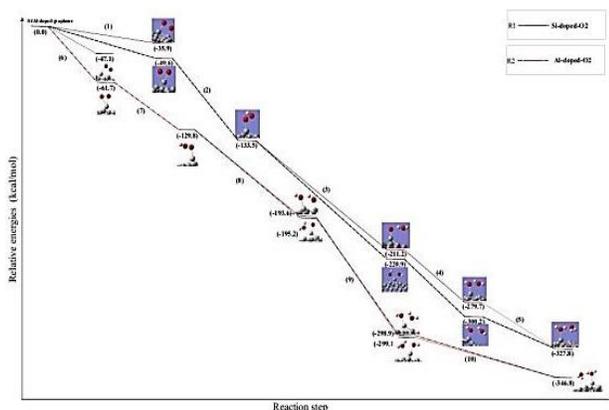


Fig. 3. Comparative reaction pathways of ORR on the Si and Al-doped graphene.

After adsorption of O_2 , the bond lengths of Si-C and Al-C are increased to about 1.9 Å. Like Tang et al. [22] work, the most favorable configuration of O_2 adsorption on Si- and Al- graphene is atop site with the E_{ads} of -60.6 and -72.4 kcal/mol, while for bridge site they are -48.9 and -60.4 kcal/mol, respectively. Meanwhile, comparing these structures with pristine graphene demonstrates that Si- and Al-doping on graphene significantly enhance the adsorption energies. In these structures a net charge about 0.8 and 0.5 electrons is transferred from the Si- and Al-doped graphene to the $2\pi^*$ orbital of O_2 , respectively, which results in the elongation of the O-O bond of the adsorbed O_2 from 1.2 to 1.6 and 1.5 Å. Noticeably, the elongation of the O-O bond length in atop site increases the activity of the adsorption site for ORR. These results are supported by electron density difference maps, which are presented in Fig. 2. The pronounced charge density redistribution indicates a significant interaction between the O_2 molecule and Si-/Al-doped graphene surface.

Table 1. Calculated bond lengths and adsorption energies for Si-/Al-doped graphene and different configurations of adsorbed O_2 on the Si/Al-doped graphene surface.

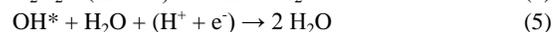
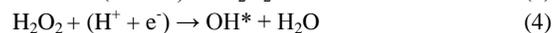
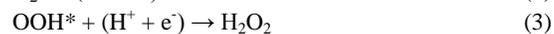
system	Si-doped graphene				Al-doped graphene			
	Si-C (Å)	Si-O (Å)	O-O (Å)	E_{ads} (kcal/mol)	Al-C (Å)	Al-O (Å)	O-O (Å)	E_{ads} (kcal/mol)
Si-/Al-doped graphene	1.72				1.83			
Atop (S1, A1)	1.90	1.71	1.55	-60.6	1.94	1.86	1.34	-72.4
Bridge (S2, A2)	1.79	1.70	1.48	-48.9	1.86	1.97	1.31	-60.4

ORR mechanisms on Si- and Al-doped graphene

In the next stage, ORR mechanisms are studied theoretically for both Si- and Al-doped graphene. Based on the previous investigations [2-3], the following two general pathways are suggested (denoted as R1 and R2 pathways): (I) O_2 is reduced to H_2O through the formation of H_2O_2 (R1); (II) O_2 is reduced to H_2O without the formation of H_2O_2 intermediate (R2). However, according to other studies [23], ORR activities are directly dependant to material microstructure. The active sites are more likely to locate at the higher positive charge density or positive spin density areas. Further, the number of dopants in cluster or defects strongly affects the ORR mechanism on graphene. For example, Chen et al. [2] have investigated the ORR mechanism on Pt (111) and Pd (111) surfaces. They have

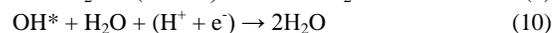
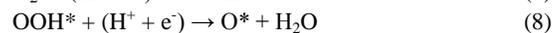
found that ORR mechanism on the Pd (111) surface in the presence of hydrated protons involved the dissociation mechanism of O_2 molecule, while on the Pt (111) surface it involved the dissociation mechanism of O_2 molecule and OOH species.

Fig. 3 compares ORR mechanisms between Si- and Al-doped graphene. It is clear that the atop configuration has the most negative E_{ads} against bridge site, so it is chosen as an active configuration for the rest of reactions. Both mentioned pathways (R1 and R2) are performed on Si- and Al-doped graphene and noticeably the pathway in which Si- or Al-doped graphene has chosen was different from each other. In each pathway the O_2 dissociation reaction is neglected because it is unlikely to occur due to the high activation energy (> 45 kcal/mol). For Si-doped graphene, the pathway R1 includes a four electron route as the following reaction steps:



At first step, the atop configuration proceeds to oxygen reduction through the O_2 activation and then upon H adsorption the OOH* species has been formed. After the adsorption of second hydrogen on the OOH* species, two intermediates have formed: $O^* + H_2O$ and H_2O_2 with relative free energies of about -211.2 and -220.9 kcal/mol, respectively. However, the dissociation of H_2O_2 into two separate OH with activation energies larger than 40kcal/mol is very hard which hinders this reaction under fuel cell conditions. Due to the weak interaction between H_2O_2 intermediate and the surface, this relatively high energy barrier is completely favorable. In the next step, third H-atom is added to both previous intermediates and results in the formation of $OH^* + H_2O$ species with the free energies of about -279.7 and -300.2 kcal/mol respectively. So, the reaction should proceed through the formation of H_2O_2 intermediate which has the most negative free energy. Finally, with the adsorption of last H-atom, according to Eq. (5), two H_2O molecules have been formed with the free energy of about -327.8kcal/mol. As with the ORR mechanism over N-doped carbon nanotubes [7], the formation of final product ($2H_2O$) is the rate determination step in R1 mechanism. Moreover, compared to the defective graphene-supported Pt nanoparticles [4, 24], our results demonstrate that Si-doped graphene is more favorable for oxygen reduction process.

Similarly, after applying both R1 and R2 mechanisms on Al-doped graphene, it prefers to proceeds via pathway R2 which have been demonstrated as the following reaction steps:



At first step, the cooperated O_2 in the atop configuration, with adsorption energy of about -72.4 kcal/mol, is activated via Eq. (6) and then, upon adsorption of H atom, the OOH^* species is formed. Afterward, with addition of second H atom to OOH^* species, two intermediates $OH^* + OH^*$ and $O^* + H_2O$ have established with relative free energies of about -193.6 and -195.2 kcal/mol, respectively.

As it is clear in **Fig. 3**, this mechanism will proceed through the formation of $O^* + H_2O$ intermediates which results in the formation of $OH^* + H_2O$ species with two different energies of about -298.9 and -299.1 kcal/mol, respectively. Although the OH^* species with higher free energy should be chosen to continue the rest of reactions, but due to the same structures the mechanism proceed via the intermediate with lowest (more negative) free energy. Finally, with addition of the last H atom, this intermediate result in the formation of two H_2O molecules with free energy of about -346.8kcal/mol. Overall, the formation of water molecule in Eq. (9) is the rate determination step.

Additional views of **Fig. 3** indicate that the significant enhancement of ORR relative free energies on Al-doped graphene are achieved and the H_2O molecules which obtained in the Al-doped graphene have the higher free energy compared with the Si-doped graphene. So, it can serve as an ORR electrocatalyst, in contrast of other expensive metal catalysts and we expect that graphene embedded with the low-cost metal Al, may be an active catalyst for the ORR.

Conclusion

The current study has demonstrated theoretically that Si- and Al-doped graphene as a catalyst, may be used to enhance the catalytic activity of graphene. Our purpose was to investigate ORR mechanisms on Si- and Al-doped graphene using density functional theory (DFT) calculations to provide information regarding the stability of possible intermediates within the electrochemical reaction pathways. We compare O_2 adsorption and reactivity results to demonstrate the effect of Si- and Al-doped graphene on the catalytic activity. The elementary catalytic reaction steps and reaction pathways for ORR on Si- and Al-doped graphene were also studies which are keys of understanding electrocatalytic reactions on the fuel cells cathode. It was clear from relative free energy plot that Si-doped graphene has proceeded via pathway R1 in which O_2 is adsorbed on the surface through the formation of H_2O_2 intermediate while the Al-doped graphene goes forward via the formation of O^* and H_2O . Comparing the Si-doped versus Al-doped graphene has shown that the Al-doped graphene is a little more activated than Si-doped graphene with -327.8 and -346.8 kcal/mol, respectively. However, both systems were in fine relative free energies and in both mechanisms, the formation of water molecule is found to be the rate determination step. Generally, the lack of such low-cost catalysts made us to study the possibility of using these compounds as a suitable electrocatalysts on the fuel cell cathodes. So, the present study can be useful for future investigations about O_2 adsorption on metal doped graphene surfaces.

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