

N-Doped CNT: Distribution Electron on Different Ratio N/C for Oxygen Reduction Reaction

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ABSTRACT

Carbon nanotubes (CNTs) have the advantage to improve electrochemical fuel cell reactions by increasing the dispersion of nanoparticles as well as having high strength in mechanical and electrical properties. Therefore, this study presents the comparison of nitrogen doped CNT and other doping heteroatom on CNT as a catalyst support for application in the Direct Liquid Fuel Cell (DLFC). The doping ratio in CNT was conducted to determine the effect of the oxygen reduction reaction. In addition, the effect of CNT diameter in oxygen adsorption also has been tested. The models and calculations were done using density functional theory (DFT). The result showed that the ratio of N/C is decreases as the diameter of CNT decreases. The value is even dropped as the unit cell is increased to 1x1x2. The band gap value of CNT before doping is higher compared to after nitrogen doping. While increasing the diameter of doped CNT has increased the mulliken charge distribution and thus make the model more stable. In the adsorption energy of molecule oxygen, the 1x1x2 unit cell of CNT and large diameter show a remarkable and stable compared to in 1x1x1 unit cell and small diameter of CNT. Thus, the adsorption energy of the oxygen molecule shows a more stable value in the low doping ratio and high CNT diameter compared to a high doping ratio and a small diameter of the CNT. This result shows the potential of the CNT in helping to improve electrochemical reaction in DLFC.

Keywords: Surface reaction; CNT; electrochemical reaction; oxygen adsorption

INTRODUCTION

High energy demand is fueled by the need to generate energy that is inexpensive, available and sustainable energy. Fuel cells promise energy generation that can meet these needs Lie et al. (2015). The fuel cell is one of the alternative energy that produces electricity from chemical without combustion. Direct Methanol Fuel Cell (DMFC) use methanol as the fuel chemical. The methanol oxidized at anode chamber to produce carbon dioxide, electrons, and protons. The completed oxygen reduction reaction at the cathode side producing water as well as electricity. Sluggish oxygen reduction reaction still occurs despite using platinum as a catalyst mention by Sui et al. (2017). Platinum currently the best material for oxygen reduction reaction in fuel cell because it has high selectivity compared to other materials but platinum also can oxidize the methanol and bring mix potential at the cathode side. The present of methanol at the cathode side due to the methanol crossover from anode to cathode side lead to reduce the performance of DMFC. In addition, using the platinum catalyst will increase the cost of material and hinder the commercialization of DMFC. Finding new materials that have a lower cost but high reactivity in oxygen reduction reaction is the best solution. Li et al.

(2015) and Karim et al. (2013) studies several materials to replace platinum such as cobalt, iron, macrocycle, transition metal oxide, and many other materials.

The research using carbon materials as electrocatalyst for oxygen reduction reaction is increasing rapidly (Wang et al. 2018). The advantages of using this carbon material not only the carbon is low cost but the production of this material are also easy to find from a variety of sources [6]. For example, Lie et al. (2015) used the urea material to produce electrocatalyst for the oxygen reduction reaction. The carbon material concentrations such as graphene and carbon nanotubes (CNT) without any other metal mixtures are studied but need to doped with nitrogen to activate the oxygen reduction reaction (Rivera et al. 2018 and Rocha et al. 2016) and called as N-doped CNT or N-doped graphene.

In many N-doped CNT studies, the percentage of nitrogen in the material is very important to evaluate the activity of the oxygen reduction reaction. The higher the value of this nitrogen element will increase the activity of the oxygen reduction reaction. However, it appears that no researcher has so far been able to produce a percentage of nitrogen elements in materials more than 10%. Under the nitrogen percentage (or atomic present), there are different types of nitrogen bonding in doped nitrogen such as

pyridinic, pyrrolic, and graphitic analyzed by XPS. Liu et al. (2015) have done analysis and conclude that only pyridinic and graphitic sites contribute to the reactivity of the oxygen reduction reaction. The study also showed that the oxygen molecules are adsorbed on carbon sites near nitrogen and the ratio of nitrogen to carbon is very important (Zhang et al. 2014; Kattel and Wang 2014; Zhang and Xia 2011).

The prediction active site for oxygen reduction reactions is very important. Oxygen reduction reaction occurs when the molecule oxygen adsorbed on specific atomic catalyst on the catalyst surface. Then there is the decomposition of oxygen and the formation of water. Unlike the platinum or other metals, the oxygen molecules can absorb on one platinum atom and one or two other platinum atoms. Like in this study, the coverage of oxygen plays an important role in determining the position adsorption and thus the value of oxygen adsorption energy. The absorption energy of one oxygen molecules as opposed to adsorption of oxygen molecules with some oxygen molecules does not look much different. For example, the oxygen adsorption at site namely as atom Pt1, the probabilities for other oxygen to absorb on the other site may occur. In other words, the oxygen molecule tends to adsorb at any site or atom at the surface of platinum atoms. In contrast to N-doped nitrogen in which depends on the nitrogen atom preset at the surface catalyst, the value of the nitrogen percentage decreases leads to a decrease in the adsorption. Thus in this study, the adsorption of oxygen is calculated from the theoretical aspect of the CNT after doping with nitrogen with different ratio and diameter.

COMPUTATIONAL METHOD

The program Materials Studio DMol3 (version 5.5) from Accelrys is used in this study. Density functional theory (DFT) calculations were carried out with the PBE functional. Effective potential with relativistic effect-accounted DFT semi-core DSPP and effective core potential (ECP) were applied for optimization of the doped CNT structure. DNPs, double numerical plus polarization function basis sets, were employed for all the calculations. The Brillouin-zone sampling was set to 1x1x8. The spin unrestricted method was used for all open shell systems. The SCF criterion used was 10^{-6} Hartree for the total energy. All structures were

fully optimized without any symmetry constraints, with a convergence criterion of $0.004 \text{ Ha } \text{\AA}^{-1}$ for the forces, 0.005 \AA for the displacement and $2 \times 10^{-5} \text{ Ha}$ for the energy change. The adsorption energy is calculated as $E_{\text{ads}} = E_{\text{substrate+adsorbate}} - E_{\text{substrate}} - E_{\text{adsorbate}}$, where $E_{\text{substrate+adsorbate}}$, $E_{\text{substrate}}$, and $E_{\text{adsorbate}}$ refer to the total energies of a substrate and adsorbate, a substrate and a gas phase adsorbate, respectively.

Figure 1 shows the top and side view of CNT. There are two unit cells namely as 1x1x1 and 1x1x2 of the CNT and five different diameters of CNT are calculated in this study. The diameter of CNT is being investigated is 8.14 Å, 9.49 Å, 10.85 Å, 12.20 Å, and 13.56 Å. The N-doped CNT of graphitic and pyridinic is being considered as shown in Figure 2. A model from graphitic N-doped CNT namely as N1 and four models from pyridinic N-doped CNT is developed. The four models of pyridinic N-doped CNT has a different value of nitrogen atom with N2, N3, N4, and N5 referring to the increasing value of nitrogen-doped from 1 to 4 atom nitrogen, respectively. The stability of the adsorption oxygen on both unit cells is being compared. The labeling of number atom nitrogen and carbon in each model has been presented in Figure 2.

RESULT AND DISCUSSION

RATIO N/C

Figure 3 shows the trend of ratio N/C in N-doped CNT for graphitic (N1) and pyridinic (N4 and N5). Figure 3a shows the trend of ratio N/C for 1x1x1 unit cell N-doped CNT. The CNT with a diameter of 8.14 Å has increasing value of N/C ratio from 0.0141 in N1 increasing to 0.0606 in N5. The other diameters of N-doped CNT also showing this increasing value of N/C from N1 to N5 model. But the as the number of carbon atom increasing as increasing the diameter of CNT, the ratio value of N/C is decreasing in trend from CNT having 8.14 Å to 13.56 Å in diameter. CNT having a diameter of 13.56 Å has a value of N/C ratio 0.0084, 0.0259 and 0.0351 for N1, N4, and N5, respectively. Figure 3b shows the same trend of the N/C ratio but for 1x1x2 unit cell of N-doped CNT. The value of the N/C ratio decreases almost half from 1x1x1 unit cell.

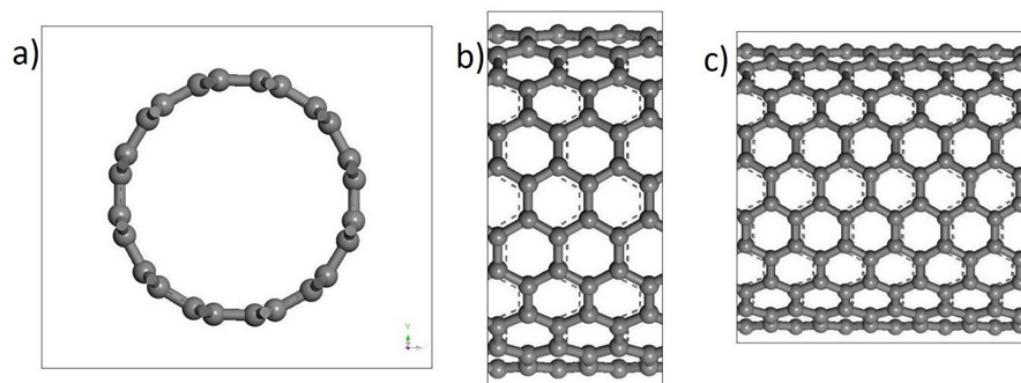


FIGURE 1. CNT a) top view; side view of b) 1x1x1 and c) 1x1x2 unit cell CNT

BAND GAP ENERGY VALUE OF CNT AND N5-DOPED CNT

Figure 4 shows the band gap energy value of CNT and N5-doped CNT. CNT in 1x1x1 unit cell has semiconductor properties with value of bandgap energy decreasing with increasing diameter of CNT as shown in Figure 4a. The N-doped CNT in graphitic (N1) and pyridinic with the model of N2, N3 and N4 have metallic properties showing no bandgap energy value in all diameter of N-doped CNT. But after doping with four nitrogen atom in CNT (N5), the N-doped having semiconductor properties with decreasing value of bandgap energy as shown in Figure 4a. In Figure 4a, the value of bandgap energy of CNT is higher than N5 shows in CNT having a diameter of 8.14 Å and 9.49 Å and almost same in the diameter of 10.85 Å. As the increasing diameter of CNT for 12.20 Å and 13.56 Å, the value of band gap energy increases after doping with four nitrogen atoms in N5. Doping one nitrogen atom in CNT as for N1 and N2 model has turned the semiconductor properties of CNT to metallic properties. Same goes as doping with two and three nitrogen atom for N3 and N4, respectively. While doping with four nitrogen atoms in the N5 model has maintained the semiconductor properties of CNT but for the N-doped CNT which having a diameter of 8.14 Å and 9.49 Å has reduced the value of bandgap energy. In contrast for the N-doped CNT with a diameter of 12.20 Å and 13.56 Å, doping four nitrogen atoms has increased the value of bandgap energy compared to CNT only.

Figure 4b shows the bandgap energy value for CNT and N5-doped CNT for 1x1x2 unit cell. The CNT has shown semiconductor properties with decreasing value of bandgap energy as the value of diameter CNT increases. The CNT has a diameter of 8.14 Å and 13.56 Å has 0.276 eV and 0.083 eV of bandgap energy, respectively. While after doping with 1, 2 and 3 nitrogen atoms in CNT has changes the semiconductor properties of CNT to metallic properties same as in 1x1x1 unit cell. The trend a little bit different for four nitrogen-doped CNT in N5 model compared in 1x1x1 unit cell. All of the N5 models have turned into semiconductor properties

like CNT but as the diameter of N5 increases, the value of band gap energy decreases less than the value in CNT or before doping. The 1x1x2 unit cell in each N5 model may have stabilized the doping of four nitrogen atoms into CNT. Both CNT in 1x1x1 and 1x1x2 unit cells have almost the same value in the bandgap. However, the bandgap of CNT in 1x1x1 unit cell is decreased a little after doping with nitrogen atoms. The bandgap value is further decreasing in 1x1x2 CNT unit cell after doping with nitrogen atoms. However, both CNT with and without doping in 1x1x1 and 1x1x2 unit cells is further decreasing in bandgap value as the diameter increase. However, the deviation of bandgap decrease as the diameter increases in CNT after doping less significantly than CNT after doping. In comparison with the CNT after doping between 1x1x1 and 1x1x2 unit cell, the 1x1x2 showed much less deviation in the bandgap. This result showed that the doping is more stable in 1x1x2 unit cells as the reduction in bandgap value is become stable as the diameter size of CNT increases.

DISTRIBUTION OF MULLIKEN CHARGE IN N-DOPED CNT

Figure 5 showed the example distribution charge in each atom in N-doped CNT. Figure 6 shows the distribution Mulliken charge on the nitrogen atom in graphitic N1-doped CNT for both 1x1x1 and 1x1x2 unit cell. The value of Mulliken charge for 1x1x1 is higher than for 1x1x2 for all diameter of N1-doped CNT. But as the diameter of N1-doped CNT increases, the value of Mulliken charge of nitrogen atom increases. For 1x1x1 unit cell, N1-doped CNT with diameter of 8.14 and 13.56 has Mulliken charge on the nitrogen atom is -0.401e and -0.410e, respectively. While for 1x1x2 has Mulliken charge on the nitrogen atom is -0.394e and -0.406e for diameter 8.14 and 13.56, respectively. The value of Mulliken charge in 1x1x1 unit cell is higher than in the 1x1x2 unit cell due to the charge confinement in 1x1x1 is larger than in the 1x1x2 unit cell. The size unit cell 1x1x1 is shorter than 1x1x2, thus giving effect in Mulliken charge larger than in 1x1x2 unit cell.

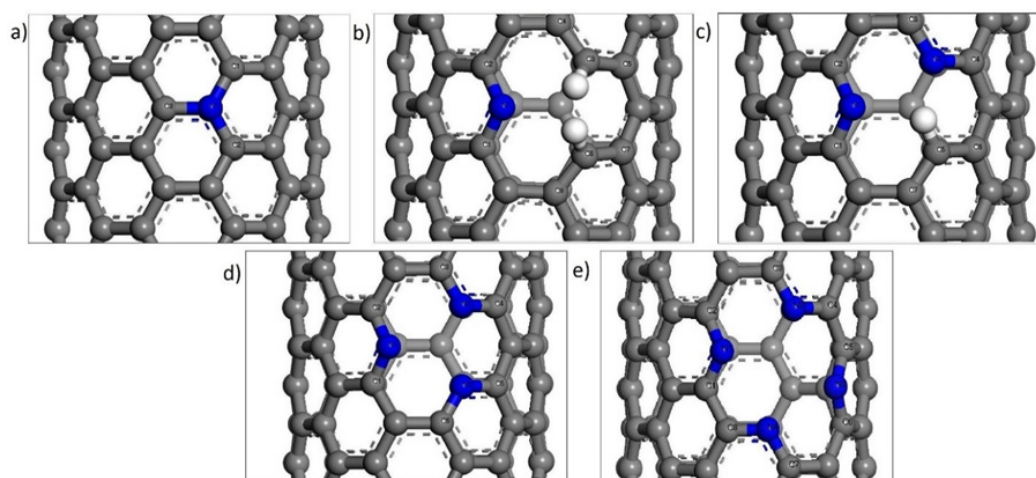


FIGURE 2. Different N-doped CNT a) graphitic, N1; b) pyridinic, N2; c) pyridinic, N3; d) pyridinic, N4; e) pyridinic, N5. Atom carbon, nitrogen and hydrogen labelling as in grey, blue and white colour, respectively

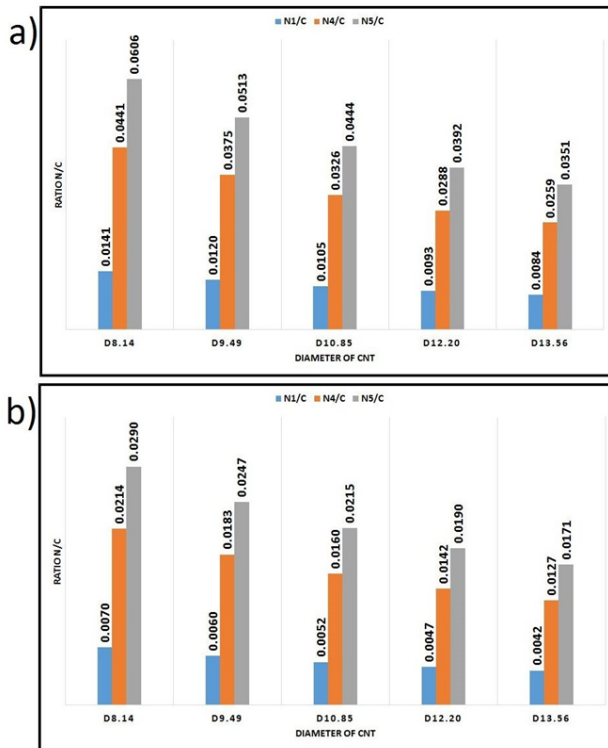


FIGURE 3. Trend of ratio N/C to CNT diameter in N-doped CNT after optimization in a) 1x1x1 and b) 1x1x2 unit cell

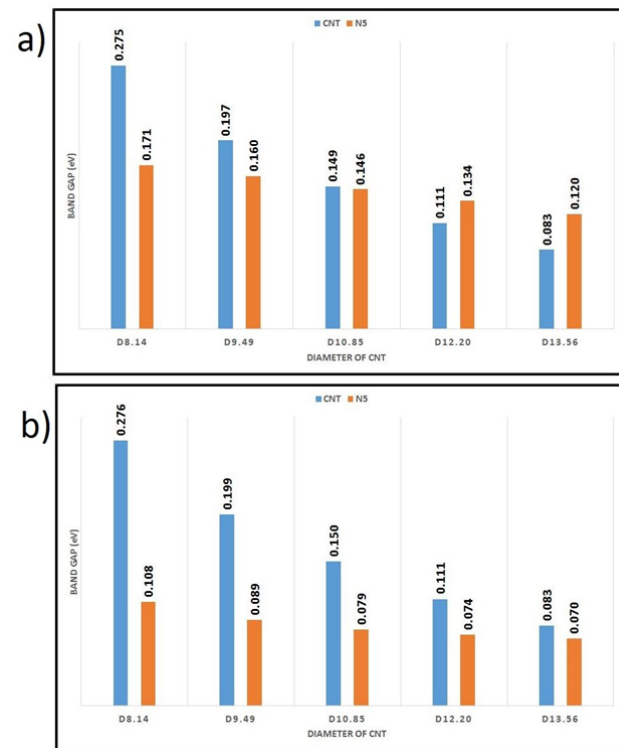


FIGURE 4. Band gap energy value for CNT and N5-doped CNT in a) 1x1x1 and b) 1x1x2 unit cell

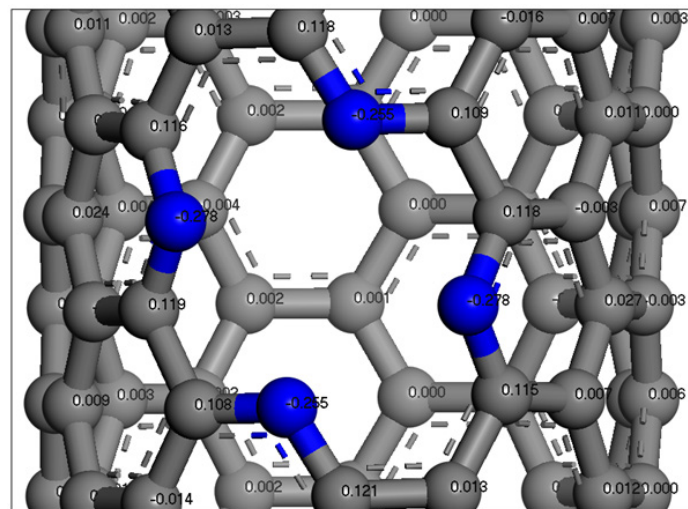


FIGURE 5. Example of the distribution Mulliken charge on nitrogen atom

Figure 7 shows the distribution Mulliken charge on carbon atoms in graphitic N1-doped CNT with different diameter of CNT and unit cells. In Figure 7a shows that the distribution of Mulliken charge of carbon atoms on the 1x1x1 unit cell of N1-doped CNT trying to get a uniform distribution as the diameter of CNT increases. The value of Mulliken charge on 8.14 Å diameter of N1-doped CNT is 0.171e, 0.158e and 0.158e. The changes of Mulliken charge on 13.56 Å N1-doped CNT become 0.165e, 0.162e and 0.162e. This is to believe that if the diameter of CNT increases the value of Mulliken charge will be maintain

become 0.163e. While for 1x1x2 unit cell as shown in Figure 7b, the trend quite different from 1x1x1 unit cell, the value of Mulliken charge reduced from diameter 8.14 to 9.49 and maintaining the same for 10.85. Then the value of Mulliken charge is uniformly distributed well in CNT with diameter of 12.20.

It seems that the Mulliken charge has optimized at CNT having a diameter of 12.20. The 1x1x1 unit cell may have a strain effect between atoms after doping one nitrogen atom comparing to 1x1x2 unit cell. In the 1x1x2 unit cell has less strain effect because the change of distribution atoms after

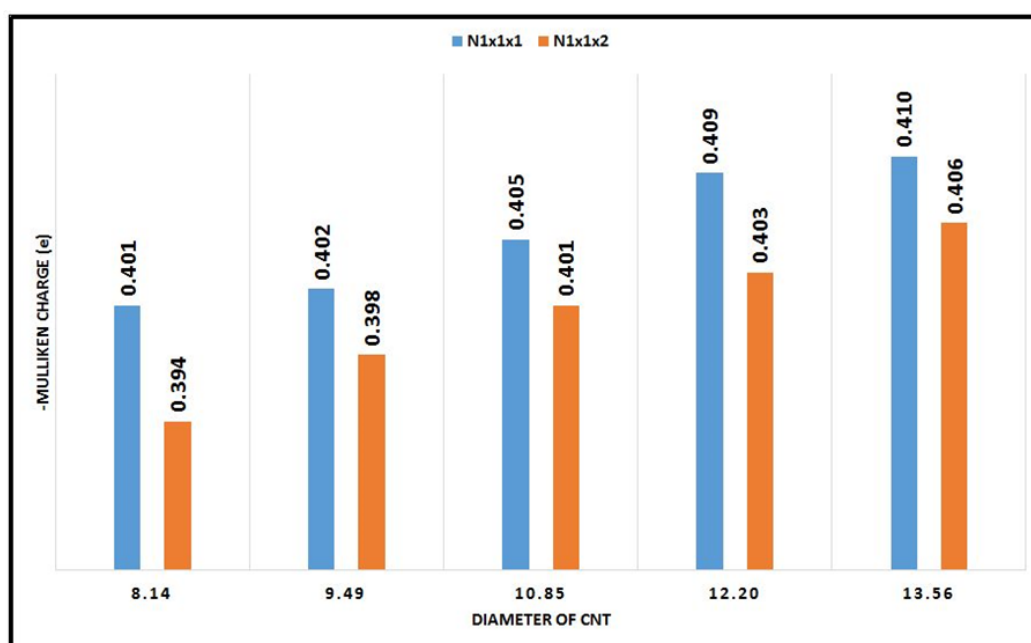


FIGURE 6. Distribution Mulliken charge on nitrogen atom in graphitic N1-doped CNT with different diameter of CNT and unit cell of 1x1x1 and 1x1x2

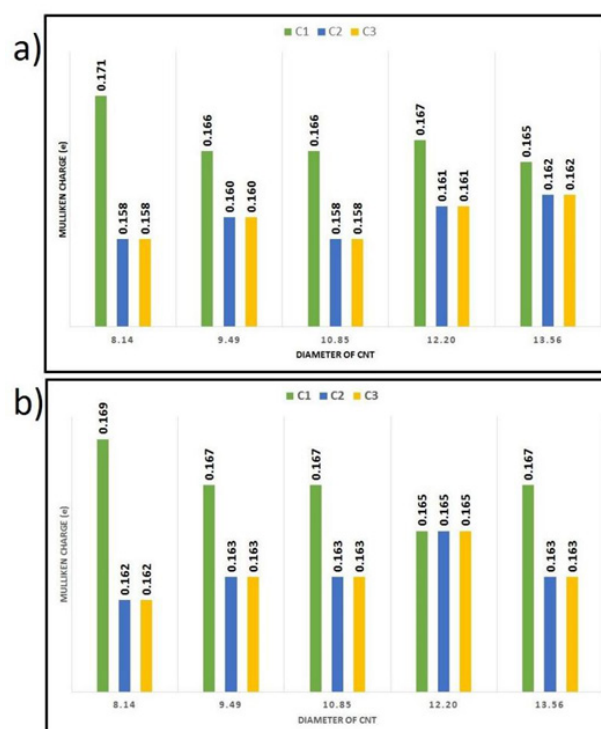


FIGURE 7. Distribution mulliken charge on carbon atoms in graphitic N1-doped CNT with different diameter of CNT and unit cell of a) 1x1x1 and b) 1x1x2

doping is larger for the next unit cell in 1x1x2 compared in 1x1x1.

ADSORPTION OF OXYGEN MOLECULE ON CNT SURFACE

Figure 8 showed the example of adsorption oxygen molecule in the surface N-doped CNT. Table 1 showed

the adsorption energy of oxygen molecule on the CNT at 1x1x1 and 1x1x2 unit cell. From the Table 1a showed that the adsorption energy of oxygen molecule using a 1x1x1 unit cell of CNT. The value of adsorption energy of N1, N4 and N5 using 8.14 Å diameter of CNT is 0.18 eV, 0.43 eV, and 1.03 eV, respectively. The N5 showed the highest adsorption energy compared to other models. In contrast in

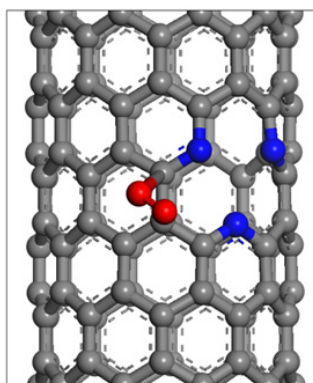


FIGURE 8. Example of the adsorption molecule on surface N-doped CNT

TABLE 1. Adsorption Energy of oxygen molecule on CNT a) 1x1x1 unit cell and b) 1x1x2 unit cell

1. 1x1x1 unit cell of CNT		
Diameter (Å)	Model CNT	Adsorption Energy (eV)
8.14	N1	0.18
8.14	N4	0.43
8.14	N5	1.03
13.56	N1	0.72
13.56	N4	-
13.56	N5	1.38
2. 1x1x2 unit cell of CNT		
Diameter (Å)	Model CNT	Adsorption Energy (eV)
8.14	N1	1.24
8.14	N4	-
8.14	N5	1.49
13.56	N1	1.73
13.56	N4	0.45
13.56	N5	1.73

this unit cell, the diameter of CNT at 13.56 Å has adsorption energy of 0.72 eV and 1.38 eV for N1 and N5, respectively. There is no adsorption energy value for N4 due to unstable adsorption configuration. As the diameter of CNT and number of nitrogen atom increases, the adsorption energy also increases.

Table 1b showed the adsorption energy of oxygen molecule on the 1x1x2 unit cell of CNT. From the table, the adsorption energy of CNT with a diameter of 8.14 Å is 1.24 eV and 1.49 eV for N1 and N5, respectively. While increasing the diameter of CNT to 13.56 Å has increased the adsorption energy to 1.73 eV, 0.45 eV and 1.73 eV for N1, N4 and N5, respectively. The adsorption energy is increased from 1x1x1 unit cell to 1x1x2 unit cell. CNT in the 1x1x2 unit cell may have a stable structure compared to 1x1x1 unit cell.

The N4 CNT model may show unstable adsorption as the model has no adsorption energy in diameter 8.14 Å (in 1x1x2 unit cell) and 13.56 Å (in 1x1x1 unit cell). In addition to that, the N4 CNT in 8.14 Å (in 1x1x1 unit cell) and 13.56 Å (in 1x1x2 unit cell) has same adsorption energy value.

This also give the implication that the doping nitrogen in N4 model is not suitable for CNT.

CONCLUSION

The doping ratio in CNT was conducted to determine the effect of the oxygen reduction reaction. In addition, the effect of CNT diameter in oxygen adsorption also has been tested. The result showed that the ratio of N/C decreases as the diameter of CNT decreases. The value is even dropped as the unit cell is increased to 1x1x2. The bandgap value of CNT before doping is higher compared to after nitrogen doping. However, in 1x1x1 unit cell, the decrease in band gap value is more significant than in the 1x1x2 unit cell. While increasing the diameter of doped CNT has increased the Mulliken charge distribution and thus make the model more stable. In the adsorption energy of molecule oxygen, the 1x1x2 unit cell of CNT and large diameter show a remarkable and stable compared to in 1x1x1 unit cell and small diameter of CNT. Thus, the adsorption energy of the

oxygen molecule shows a more stable value in the low doping ratio and high CNT diameter compared to a high doping ratio and a small diameter of the CNT. This result shows the potential of the CNT in helping to improve the electrochemical reaction in DLFC.

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DECLARATION OF COMPETING INTEREST

None.

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