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Hydrogen peroxide adsorption on Fe-filled single-walled carbon nanotubes: a theoretical study

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Abstract

We investigated the adsorption of hydrogen peroxide molecules on Fe-filled single-walled carbon nanotubes (SWNTs) based on density functional theory (DFT) calculations. The adsorption possibilities for the hydrogen peroxide molecule were tested by finding the minimum energy as a function of distance of the molecule from the Fe-filled SWNT. Stable structures were obtained by optimizing the hydrogen peroxide (H₂O₂) as it was adsorbed on to the Fe-filled SWNT. This study may serve as an initial investigation into the possibility of Fe-filled single-walled carbon nanotubes (SWNTs) as catalyst material for the proton exchange membrane fuel cell (PEMFC).

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1], research in the field of CNTs has attracted a great deal of interest. They have fascinating properties that make them potentially useful in nanoscale electronic, spintronic, biomedical applications [2], and in fuel cell technology [3] as catalyst support and hydrogen storage [4, 5]. Moreover, the possible end to fossil fuels has sparked the search for alternative sources of energy, leading to increased attention for hydrogen fuel cell research. One of these fuel cells is the proton exchange membrane fuel cell (PEMFC), which transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy. However, the durability of the PEMFC has been recently recognized as one of the most important issues to be addressed before its commercialization [6–10]. Pt surface area loss due to carbon support corrosion and Pt dissolution/aggregation is considered as one of the major contributors of failure for the PEMFC [7]. Carbon black (Vulcan XC-72), which is the normally used catalyst support for the PEMFC, is known to undergo chemical oxidation to surface oxides, and eventually to CO₂ at the cathode of a fuel cell [11]. It was found by a previous study that Pt accelerated the corrosion rate of carbon black [12]. There is a need to use alternative more stable carbon support. It has been proposed that carbon material with more graphite component (e.g. carbon nanotubes) can be more stable [13]. CNTs

filled with ferromagnets demonstrate very high potential in providing modified magnetic properties, low dimensionality, and small volume which make them possibly useful for many applications [14–19]. In particular, the magnetic and electronic properties of Fe-filled SWNTs were found to differ with varying nanotube diameters [20]. In addition, the SWNTs encapsulating Fe nanowires were found to transform into an arch-like structure when the Fe nanowire is near a Ni(111) surface with spin-polarization [21, 22].

In the PEMFC, the splitting of the hydrogen molecule is relatively easy by using a platinum catalyst, but separating the stronger oxygen molecule is more difficult, and this causes significant energy losses. Separation of the oxygen molecule is necessary to form water or hydrogen peroxide from the reaction with the protons at the cathode. Platinum-decorated single-walled carbon nanotubes (SWNTs) are presently being evaluated as catalyst material for oxygen reduction in PEMFC cathodes [4]. But since platinum is a rare and expensive metal, an alternative material could possibly be found that could also function as the catalyst for oxygen decomposition. In this study, the Fe-filled SWNT is proposed as a cathode material. However, hydrogen peroxide has been found to oxidize semiconducting SWNTs by the active oxygen produced during its decomposition through suspected hole-doping effects. Also, the presence of Fe was found to promote the oxidation of SWNTs in hydrogen peroxide [23]. Moreover, some studies found that the Nafion[®] membrane and membrane electrode assembly (MEA) of PEMFCs become very unstable in the

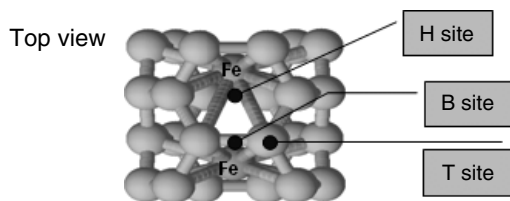


Figure 1. Top view of the supercell of the Fe-filled (3, 3) SWNT. Also shown are the adsorption sites for the hydrogen peroxide molecule.

presence of hydrogen peroxide, which is formed as a by-product [24–26], due to its strong oxidative properties [27–31].

We are looking at the possibility of Fe-filled SWNTs as an alternative material to platinum-decorated SWNTs as catalyst material for oxygen reduction in the cathode of the proton exchange membrane fuel cell (PEMFC). In this study, the effect of hydrogen peroxide adsorption on Fe-filled SWNTs will be investigated through first-principles calculations. The study also aims to compare the adsorption reaction of H_2O_2 on the pristine SWNT with an Fe-filled SWNT.

2. Theoretical model and methods

In this study, the hydrogen peroxide molecule is allowed to approach and be adsorbed on different sites of pristine and Fe-filled SWNTs. A (3, 3) SWNT supercell, having a total of 24 carbon atoms is considered for the pristine SWNT and an additional two Fe atoms for the Fe-filled SWNT. All structures are relaxed and optimized and compared to previous studies [20–22]. A hydrogen peroxide molecule is then placed at different sites of the SWNT: bridge site (B), top site (T), and at the center of the hexagonal plane of the SWNT or hole site (H) as shown in figure 1. In addition, the orientation of the hydrogen peroxide molecule used for this study is shown in figure 2. In this orientation, the two oxygen atoms of hydrogen peroxide approach the SWNT. In all calculations, spin-polarized *ab initio* calculations based on density functional theory (DFT) [32] using plane waves and pseudopotentials are performed and generalized gradient approximation (GGA) [33] is used for the exchange–correlation energy. The electron–ion interaction is described by optimized ultrasoft pseudopotentials. The one-dimensional Brillouin zone is sampled by 35- k points along the nanotube axis. Two methods are used to study the adsorption of H_2O_2 on the Fe-filled SWNT. First, a physisorption study is done. In this case, both the SWNT and H_2O_2 are fixed, with the peroxide molecule placed initially at a distance of 10.0 Å from the adsorption site. The energy difference of the system as a function of the distance of the peroxide molecule as it approaches the SWNT is calculated and the minimum energy is determined. In the second method, the H_2O_2 molecule is relaxed as it is placed near the SWNT adsorption sites at a distance of ~ 1.8 Å and the difference between the optimized energy of the combined system and the sum of the energies of the isolated molecules is considered as the chemisorption energy.

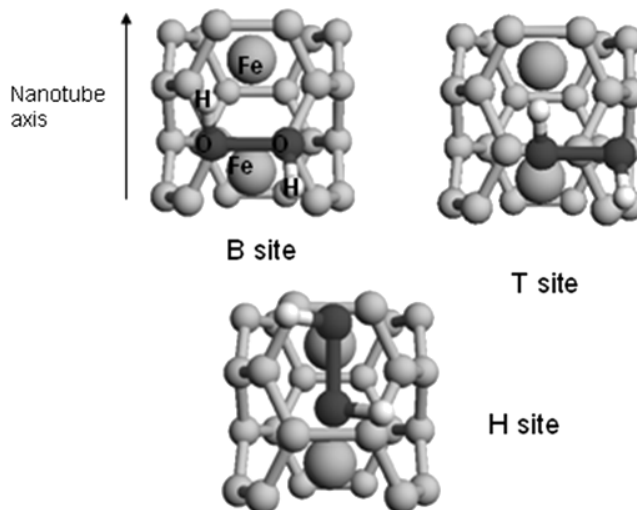


Figure 2. The orientations of the hydrogen peroxide molecule for each adsorption site. The arrow represents the nanotube axis.

3. Results and discussion

The physisorption energy (E_{PE}) is calculated through the energy difference for each of the minimum points using the equation

$$E_{\text{PE}} = E_{\text{f(fixed)}} - E_{\text{Iso_Systems}}, \quad (1)$$

where $E_{\text{f(fixed)}}$ is the total energy of the H_2O_2 and SWNT system in the fixed calculation and $E_{\text{Iso_Systems}}$ is the sum, ($E_{\text{SWNT}} + E_{\text{H}_2\text{O}_2}$), or the energies of the isolated SWNT (pristine or Fe-filled) and H_2O_2 molecule respectively.

The physisorption energies obtained for all cases are small in magnitude (10^{-2} eV) and do not differ from each other by any significant amount. The minimum points were found at a distance of around ~ 4.0 Å from the adsorption sites. Considering that the calculations are of the order of DFT, the energies obtained may be underestimated due to the inability of DFT to describe van der Waals interactions, which play an important role in weak interactions. Therefore, it is difficult to make any conclusion about the stable adsorption sites. Another physisorption study will be done without making the H_2O_2 and SWNT fixed.

For the relaxed system, the fully optimized structures of H_2O_2 as it is placed near the pristine SWNT are shown in figure 3, and for Fe-filled SWNT in figure 4. Distances and magnetization data for the optimized structures are summarized in table 1. In all cases, the hydrogen peroxide molecule dissociates into two OH units and each unit attaches on top of a carbon atom of the SWNT. Similar optimization results were obtained for the T-site and B-site in both pristine and Fe-filled cases. One C–C bond in the unit cell is broken and both carbon atoms have OH units attached (figures 3(a), (b) and 4(a), (b)). However, different results were found for the H-site. In the pristine case, no C–C bond breaking was observed (figure 3(c)) but for the Fe-filled case, two C–C bonds in the unit cell were broken (figure 4(c)). No magnetization was observed for all the pristine cases. However, the oxygen atoms in all Fe-filled cases have magnetic moments while only

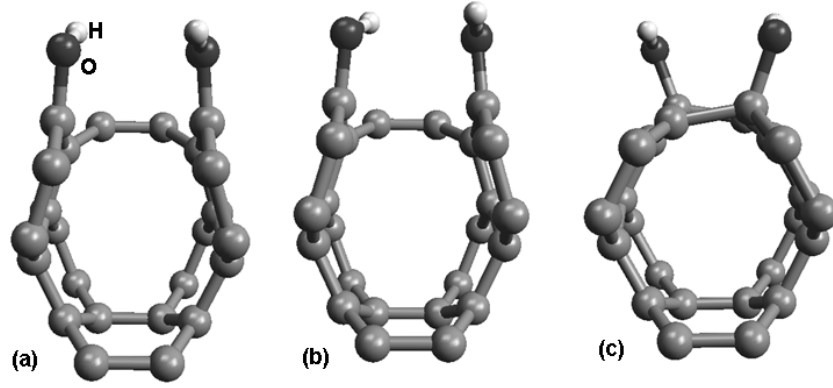


Figure 3. Fully optimized structures of pristine SWNTs (a) B-site, (b) T-site, and (c) H-site.

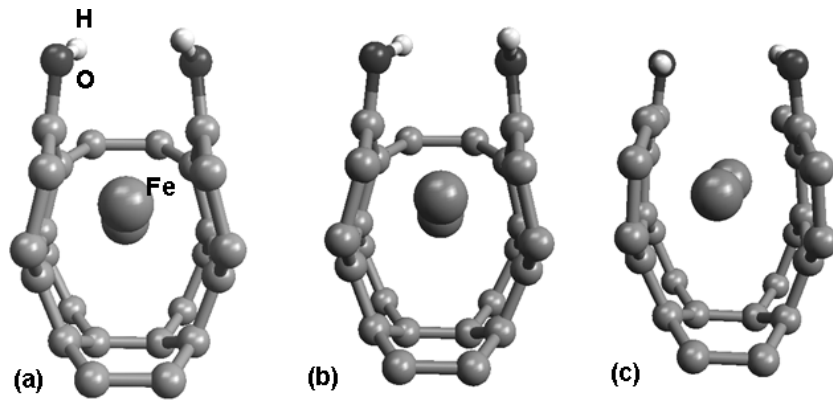


Figure 4. Fully optimized structures of Fe-filled SWNTs (a) B-site, (b) T-site, and (c) H-site.

Table 1. Distance and magnetization data for optimized structures of pristine and Fe-filled SWNTs.

Chemisorption energy (eV)	Distances (Å)					Magnetization (μ_B)			
	O-C	O-H	C-C	O-O	Fe-Fe	O1	O2	Fe1	Fe2
Pristine B-site	-3.86	1.37	0.98	2.90	2.65	—	0	0	—
Pristine T-site	-3.85	1.37	0.98	2.89	2.61	—	0	0	—
Pristine H-site	-2.58	1.43	0.98	1.58	3.63	—	0	0	—
Fe-filled B-site	-4.62	1.37	0.98	3.05	2.72	2.58	0.10	-0.08	0
Fe-filled T-site	-4.60	1.37	0.98	3.04	2.72	2.57	0.03	0.19	0
Fe-filled H-site	-5.84	1.33	1.13	3.18	3.65	2.51	1.26	-1.25	0.06

the Fe atoms in the H-site were magnetized and exhibited anti-ferromagnetic behavior. Using the resulting energies from the optimization, the chemisorption energies (E_{CE}) were calculated using the following equation

$$E_{CE} = E_f - E_{Iso_Systems}, \quad (2)$$

where E_f is the total energy of the optimized structure. The chemisorption energies are summarized in table 1 as well.

The chemisorption energies were found to be larger than the physisorption energy in all cases. However, the Fe-filled cases have larger chemisorption energies than the pristine cases. Therefore, it is more likely for the Fe-filled cases to have a lower dissociation energy barrier as compared to the pristine cases. The existence of this energy barrier will be investigated

in a further study. The Fe-filled H-site case was found to be the most stable. However, since both C-C bonds were broken, there is the possibility that the SWNT may be decomposed, as opposed to the pristine H-site case wherein the SWNT remained intact. This finding supports experimental results that hydrogen peroxide decomposes semiconducting SWNTs selectively [24].

4. Conclusion

In summary, we have investigated the adsorption of hydrogen peroxide to different adsorption sites on pristine and Fe-filled SWNTs. Our results show that the physisorption energies obtained for all cases are small in magnitude (10^{-2} eV) and do

not differ from each other by any significant amount. However, when the systems were all relaxed with the hydrogen peroxide molecule near the SWNT, we found similar optimization results for the T-site and B-site in both pristine and Fe-filled cases. However, different results were found for the H-site. In the pristine case, no C–C bond breaking was observed but for the Fe-filled case, two C–C bonds in the unit cell were broken. The Fe-filled cases have larger chemisorption energies than the pristine cases, and the H-site was found to be the most stable. Therefore, it is more likely for the Fe-filled cases to have a lower dissociation energy barrier as compared to the pristine cases. Lastly, we believe this study has provided the groundwork in investigating the possibility of Fe-filled SWNTs as catalyst material for the proton exchange membrane fuel cell (PEMFC). Studies on larger diameter SWNTs, as well as Fe-filled SWNTs will be discussed in another paper.

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