First Principle Calculation : Investigation on interaction of Pt/Graphene as Catalyst

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Abstract. The increasing in energy needs and the lack of non-renewable energy sources becomes a challenge for the human being to be able to use renewable energy sources. One of the devices to process renewable energy is Polymer Electrolyte Membrane Fuel Cell (PEMFC) . PEMFC use hydrogen and Oxygen as an energy sources . The most important reaction in fuel cell is Oxidation and reduction process. Therefore, a catalyst is needed to help the OR process. Study of catalyst shows that the most effective fuel cell for now is Platinum. Many fuel cell have use platinum as the catalyst. However, Platinum is a rare and expensive element. Therefore, to reduce the cost of fuel cell fabrication, we need to increase the activity of platinum. In this research, we use graphene as a support material. Then, we will study about the interaction of platinum on graphene and analyze its morphological change and electronic properties.The research conduct using Density Functional Theory (DFT). The calculation result shows that Pt/graphene can break H_2 into H^+ and the binding between Pt cluster is stronger than binding with the substrate.

1. Introduction

Human population is increasing everyday. Therefore, energy demands is also increasing. There are two types of energy : non-renewable and renewable. Non-renewable energy is an energy which comes from the sources that can't be replenished in a short period of time, such as fossil fuel. Meanwhile, renewable energy is an energy which comes from a renewable sources that can be replenished in a short time such as solar and wind. Until now, many country such as Indonesia and other develop country still depend on non-renewable energy. If this condition is continue, petroluem is predicted to run out in the next 14 years . Because of that, we need to consider to use renewable energy. However, renewable energy has some disadvantages, the cost of technology is still expensive.

One of the technology that we use for renewable energy processing is fuel cell. Fuel cell produces electricity through chemical reaction. Some of the advantages of fuel cell are eco-friendly and has higher efficiency than diesel or gas engines. One of the most efficient type of fuel cell is Polymer Electrolyte Membrane Fuel Cell (PEMFC). This fuel cell use Platinum as a catalyst. The main fuel of this fuel cell is just Hydrogen and Oxygen. Therefore, it is an eco-friendly technology. The most important part of the fuel cell is catalyst, it determines how fast the reaction works. But, as we know, platinum as the catalyst is an expensive material . That is why the cost of the fuel cell is still high. Because of that, to lower the cost, some researcher try to add support material into the catalyst to get

higher activity of catalyst without using much platinum. Nowadays, researcher try to use graphene as a support material because it has high surface area ($\sim$2630 m^2/g) which is higher than graphite ($\sim$10m^2/g) and CNT (1300 m^2/g). The experimental work also shows that using graphene as a support material will give *Electrochemical Active Surface Area* (ECSA) about 53 m^2/g which is higher than using carbon black (26 m^2/g). [1]

Better understanding of the interaction between platinum and graphene is needed to achieve the highest activity of platinum and to be able to do the optimation of platinum use. In this research, we will do the investigation on Pt/graphene interaction.

2.   Computational Details

All of the calculation in this work is performed using Vienna *ab initio* simulation package VASP that based on DFT. We use the generalized-gradient approximation (GGA) as an exchange correlation. The K-points that we use is 5x5x1 Monkhorst-Pack grid with energy cut-off 400.00 eV. We also use 5x5 graphene on this work.

3.   Results and Discussion

In this work, we will calculate energy adsorption. For a single platinum on graphene (Pt/graphene) system, we will calculate the energy using this equation [2]

$$E_{ad} = \left(E^{Pt} + E^{graph}\right) - E^{Pt/graph} \qquad (1)$$

$E^{Pt/graph}$ is the total energy of the Pt-graphene layer, E^{graph} is the total energy of clean graphene layer, and E^{Pt} is the total energy of an isolated Pt-atom. For the other Pt cluster, we will calculate 2 types of adsorption energy taken from Pitor Bloński,et all work. [3] First, we will calculate interaction energy of Pt-cluster of a certain size and shape with graphene sheet, defined by

$$E_{ad}^{int} = \frac{1}{n}\left(E^{Pt_n/graph} - E^{graph} - E^{Pt_n}\right) \qquad (2)$$

$E^{Pt_n/graph}$ is the total energy of the Pt$_n$-graphene system, E^{Pt_n} is the total ground-state energy of the Pt$_n$ cluster in the gas phase. Next, we wil calculate cohesive energy of the adsorption, defined by

$$E_{ad}^{coh} = \frac{1}{n}\left(E^{Pt_n/graph} - E^{graph} - nE^{Pt}\right) \qquad (3)$$

The Equation (3) measures the binding between Pt in the cluster.

3.1 Adsorption of H$_2$

A catalyst in fuel cell have a function to break H$_2$ into ion H$^+$. In this section, we will prove that Pt/graphene can be use as a catalyst.
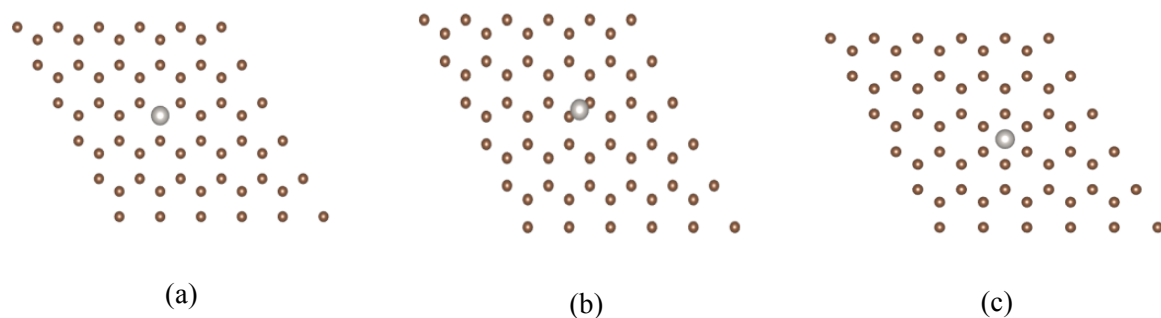
Figure 1. H_2 on Pt/graphene (a) initial position (b) after relaxation

Figure 1 (a) shows the initial position of Pt/graphene. Figure 1 (b) shows the final position after the relaxation. From the Figure 1 above , we can see that H_2 is break into H^+ after interact with Pt/graphene.
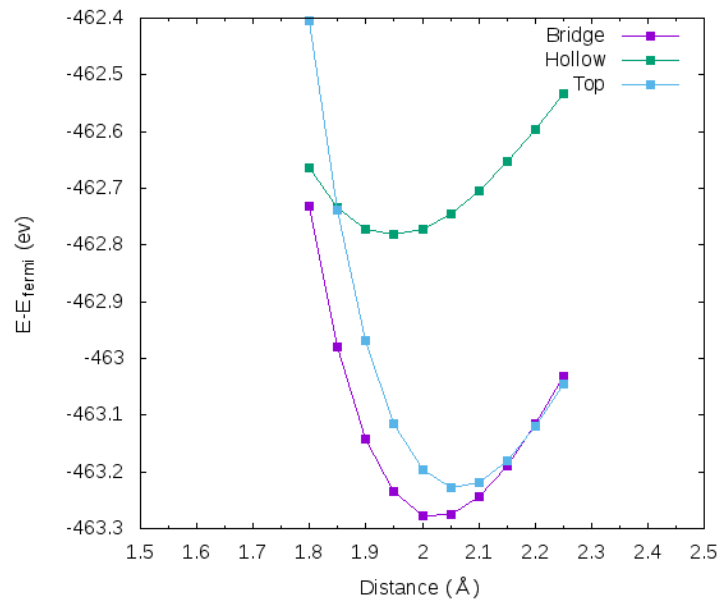
3.2 Pt/graphene

Before we calculate the energy adsorption, first of all, we have to find the most stable position of Pt on graphene. In this work, we placed the graphene in 3 site : Top, Bridge, and Hollow. Top is the position on top of C atom, Bridge is the place between C-C bonds, and Hollow is the place between 6 atom carbon (see figure below)
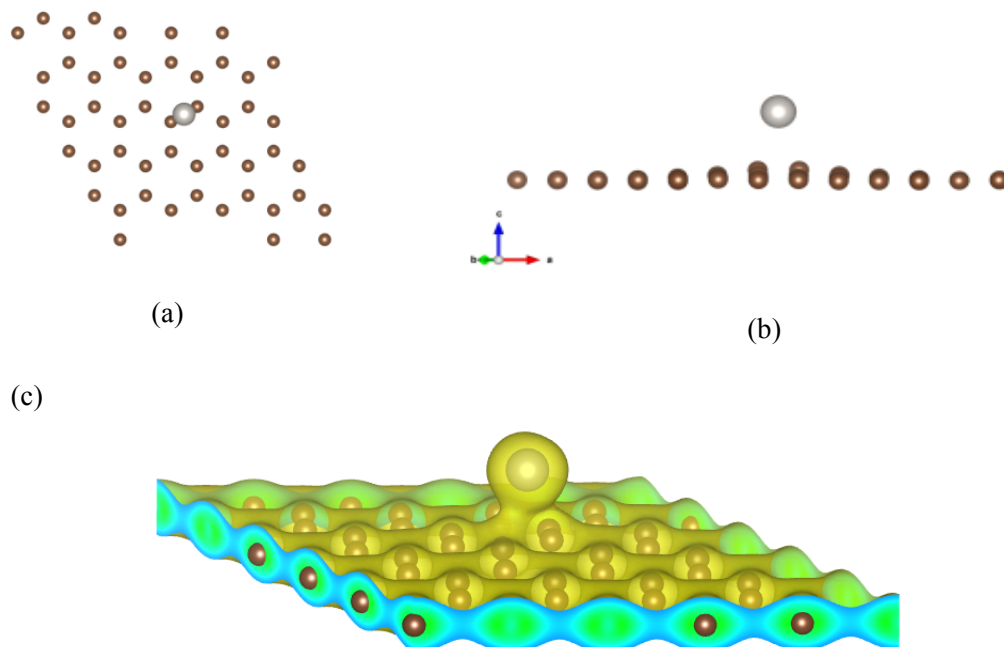

Figure 2. Adsorption site of Pt (a) Top (b) Bridge (c) Hollow

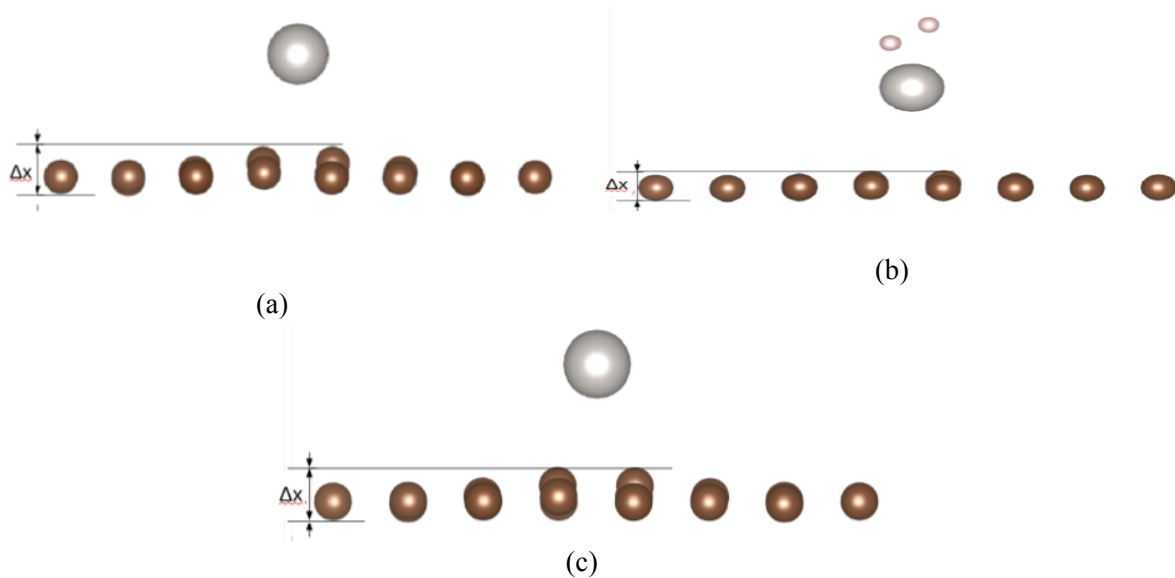Static calculation was performed to get the most stable position

Figure 3. Total energy on every adsorption site

Figure 3, shows that the most stable position is Bridge with distance 2Å from the graphene layer. After that, relaxation was performed on the structure to get the most stable structure (Figure 4) . We can see from the figure 4 that the structure of graphene is change and there is some transfer charge between platinum and graphene.
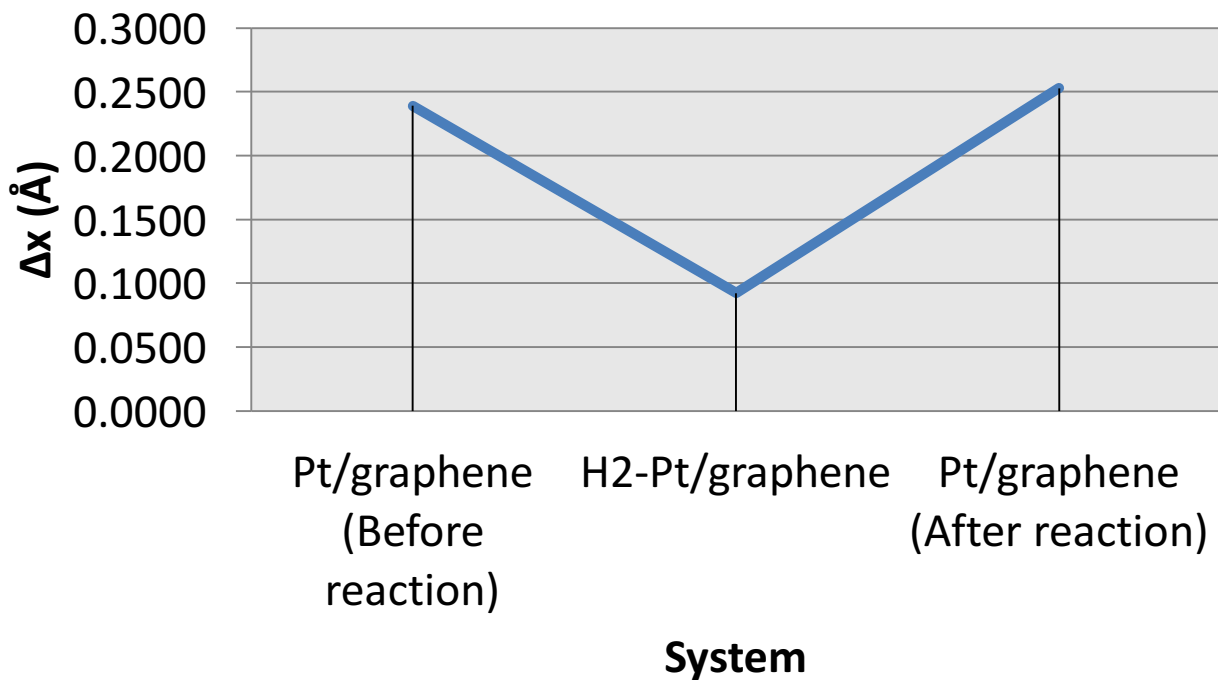

(a)

(b)

(c)

Figure 4. Structure of Pt/graphene after relaxation (a) Top view (b) Side view (c) Transfer charge

Next, we will investigate the reversibility of Pt/graphene. Figure 5 shows Pt/graphene structures before react with H_2, when react with H_2, and after reacted with H_2. The figure shows that there are some changes in the height of graphene structure (Δx) when react with H_2.

Figure 5 Structure of Pt/graphene (a) without H_2 ,(b) react with H_2, (c) after H_2 removed
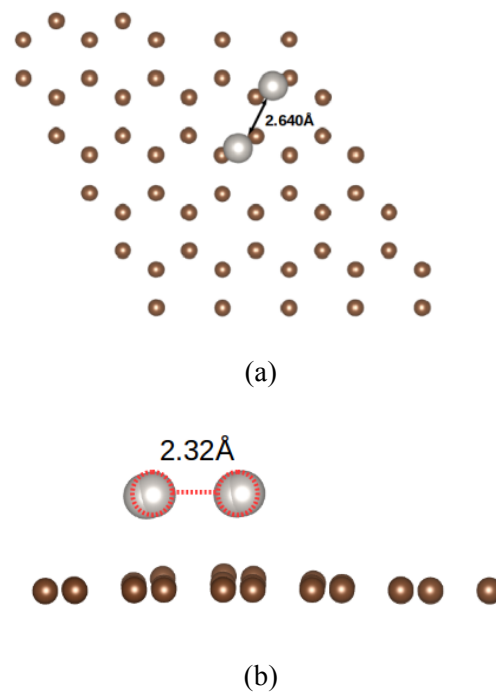
If we calculate Δx on each condition we will get the graph on figure 6. On the graph below, we can see that Pt/graphene structure is 95% reversible. Therefore, it can be use for many times.

Figure 6. Graph that shows the reversibility of Pt/graphene

3.3 *Pt₂/graphene*

Now, we will investigate the structure of Pt_2 cluster on graphene. In this work, we use parallel position of Pt_2 cluster.
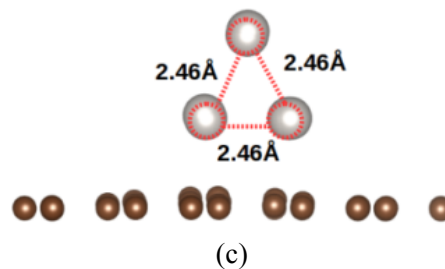

(a)

(b)

Figure 7. Structure of Pt_2/graphene after relaxation (a) Top view (b) Side view

The red circles in Figure 7(b) shows the distance between Pt before relaxation. If we compare the result with Figure 7(a) which shows the Pt distance after relaxation, we can see that the distance between Pt is become longer.

3.4 *Pt₃/graphene*

For Pt_3 cluster, we will use Pt_3 cluster with flat triangular configuration where every Pt is in the bridge site.

(a)

(b)

(c)

Figure 8. Structure of Pt_3/graphene after relaxation (a) Top view (b) Side view(c) Side view with Pt position before relaxation

Figure 8 shows that the distance between the platinum is larger after the relaxation, it means that they encounter repulsive force with each other

3.5 Energy adsorption

Using equation (1), we get that the adsorption energy of Pt/graphene system 1.97 eV and this is compareable with previous work [2] .

For the Pt_2/graphene and Pt_3/graphene, we calculate the adsorption energy using equation (2) and (3)

Table 1. Adsorption energy of Pt-cluster on graphene

System	E^{int} (eV)	E^{coh} (eV)
Pt_2/graphene	-0.595	-2.483
Pt_3/graphene	-0.38	-3.188

From Table 1, we can see that when we add more platinum, the energy adsorption between cluster and substrate is getting lower while the binding between cluster is getting stronger.

4. Conclusion

Structural and electronic properties of Pt cluster on graphene has been investigated using DFT method. The Calculation of adsorption energy shows that the binding between the cluster is much stronger than the binding with the substrate. From the calculation above, we can see that Pt/graphene can break H_2 into H^+, it means that it can be use as catalyst. The calculation also shows that Pt/graphene structure is 95% reversible. Therefore, we can use it many times .

References

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[2] O. M. K., M. Yoshitada, T. S dan K. M, "Structures of Pt clusters on graphene by first-principles calculations," *Surface Science,* vol. 604, pp. 144-154, 2010.

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