The effect of single and double vacancy on hydrogenated graphene for hydrogen storage application

M S Yahya¹, G K Sunnardianto¹,², M Handayani³

¹Faculty of Engineering and Technology, Sampoerna University, Jl. Raya Pasar Minggu, Kav 16, Jakarta, Indonesia
²Research Center for Chemistry, Indonesian Institute of Science (LIPI), Kawasan Puspiptek Serpong, Tangerang Selatan, 15314, Indonesia
³Research Center for Metallurgy and Material, Indonesian Institute of Science (LIPI), Puspiptek Serpong, Tangerang Selatan, 15314, Indonesia

Email: sulthon_yahya@yahoo.com

Abstract. We investigated the effect of single and double vacancy on the charge transfer rate of dissociation of hydrogen molecule adsorb on graphene based upon density functional theory calculation for hydrogen storage application. Here, we would like to compare the effect of the single and double vacancy on the charge transfer rates of hydrogen molecule dissociation adsorbed on graphene. Before investigated the charge transfer rates, we optimized the structure of graphene, graphene with single and double vacancy and observed the interaction with hydrogen molecule. Preliminary result revealed that once hydrogen molecule is dissociated to be hydrogen atoms and adsorbed to the dangling bond, the charge transfer rates is decrease compared with the charge transfer from hydrogen to pristine graphene indicated that hydrogen atom absorbed on dangling bond changing the orientation of hydrogen adsorbed. As for the C-H bond length is decrease around to be 1.11 Å compare to the pristine one 1.12 Å. We need to explore more on the reaction pathways to get the global picture on the effect of single and double vacancy on the dissociation of hydrogen molecule on graphene surface.

1. Introduction

Nowadays, hydrogen-based technology is one of the best alternative energy to decrease the using of fossil energy. Graphene is molecules composed of pure carbon atoms. These atoms are related to each other, forming a two-dimensional hexagonal pattern resembling a honeycomb. In short, it can be said that graphene is a structural unit of graphite. The functionality of hydrogenated graphene was predicted by Roman et al. [1] and Sofo et al. [2] by using density functional theory calculation. Hydrogen molecules is interacting weakly with graphene. In molecular hydrogen adsorption, it is physisorption that occurs primarily, and the dissociation rate of hydrogen molecules on pristine graphene is very low. This is because the energy barriers against dissociating a H₂ molecule on pristine graphene are high [3]. One of facile way to increase the interaction between of hydrogen molecule on graphene surfaces. It has been observed the reaction of hydrogen molecule dissociation on hydrogenated graphene with single vacancy [⁴,⁵]. However,
to best of our knowledge, the effect of single and double vacancy on the charge transfer rate still not observed yet in detail.

Gagus et al. reported the rule that determined the CTR from hydrogen to pristine graphene over a wide range of coverage [6]. Thus, in this study, we would like to investigate the effect of single and double vacancy from hydrogen to graphene since the interaction between hydrogen and graphene is mediated by CTR.

2. Method
We used density functional theory to performed the structural and electronic structure [7] by using density functional theory calculation framework and Quantum Espresso (QE) code [8]. We used the ultra-soft pseudopotential and the projector-augmented-wave method [9] and adopt the Perdew-Zunger parameterization [10] for local density approximation. The parameter for hydrogenated graphene with a vacancy in super cell were the energy cut off 400 Ry for the expansion of the augmented charge and 40 Ry for the plane wave expansion of the wave function. The total absolute value of the inter-atomic force vector is less than $10^{-4}$ Ry/a.u. for the convergence criterion.

The distance between graphene planes was separated by 10 Å in order to avoid the interaction between layers. Distribution of k-points on a mesh of 12x12x1 was chosen via Monkhost-Pack scheme [11] and the structure of the model for the simulation are graphene that used 48 carbon atoms in rectangular super cells for pristine graphene, 47 carbon atoms for graphene single vacancy and 46 carbon atoms for graphene with double vacancy. The charge transfer from hydrogen to graphene is calculated by using lowdin charge analysis [12].

3. Result and Discussion
3.1 Charge transfer rate (CTR)
Hydrogenation should happen both at each vacancy and on the flat graphene surface. For the comparison, we will discuss hydrogenated graphene at first and then hydrogenated graphene vacancy either with single or double vacancy.

We observed the effect of double vacancy on graphene to the charge transfer rates from hydrogen to graphene by comparing the CTR from hydrogen to pristine graphene and graphene with single vacancy.

Table 1. Value of Ave-CTR on Graphene, Graphene with Single and Double Vacancy

| Materials             | Nc       | Ave-CTR [e] |
|-----------------------|----------|-------------|
| Graphene              | 48C+3H   | 0.2035      |
| Graphene single vacancy | 47C+3H  | 0.1864      |
| Graphene double vacancy | 46C+3H  | 0.1869      |

The results indicated that single vacancy decreasing the CTR from hydrogen to the graphene. As for the di-vacancy in graphene, a similar trend to single vacancy is found for the charge transfer rate. Thus, there is no meaningful changes are seen in the graphene di-vacancy. We could analyze the result of decreasing the CTR from the optimized structure of hydrogenated graphene with single vacancy and hydrogenated graphene with double vacancy.
3.2 Deformed structure
Once the structure of hydrogenated graphene with and without vacancy are optimized, we could predict why the vacancy either single or double decreasing the CTR. The optimized structures can be seen in Figure 1.

Figure 1. Structures of hydrogenated pristine graphene (a), hydrogenated graphene with single vacancy (b), and hydrogenated graphene with double vacancy (c). The yellow and blue atoms denote carbon and hydrogen, respectively.

We analyzed from the optimized structure, the selection of structured based on the most stable of hydrogenated graphene with single vacancy, where each carbon atom is mono-hydrogenated at the edge of vacancy ($V_{111}$), there are 3 hydrogen atoms adsorbed at vacancy site, thus we consider trimer hydrogen adsorption of pristine graphene and graphene with single and double vacancies.

We found the orientation of hydrogen atom adsorb on graphene surface determine the amount of the charge transferred. If the hydrogen orientation in the “up” position (figure 1 (a)), the charge transfer rate is bigger than if the hydrogen atom adsorbed to the vacancy in “side” orientation.

3.3 The formation of C-H bonding

| Materials                | $dC-H$ (Å) | Buckling (Å) |
|--------------------------|------------|--------------|
| Graphene                 | 1.1189     | 0.63         |
| Graphene single vacancy  | 1.0806     | 0.23         |
| Graphene double vacancy  | 1.1073     | 0.17         |

The optimized distance $dC-H$ of graphene with single vacancy is 1.0806 Å, which is shorter than the $dC-H$ of pristine graphene (1.1189 Å). As for the puckered of hydrogenated carbon atom of graphene with single vacancy is 0.23 Å, which is lower than the puckered of hydrogenated carbon atom of pristine graphene (0.63 Å) indicate that the reduced of charge transfer rates in the graphene with single vacancy.

4. Conclusion
We have investigated the effect of single and double vacancy on the charge transfer rate from hydrogen to graphene by using Density Functional Theory. We found that the charge transfer rates and C-H bond length are decrease compared with the pristine one, but we need to explore more about the reaction pathways of double vacancy and charge to system for hydrogen storage application.
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