Simulation of growth process of Pt-particles
- First-principles calculations

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Abstract. First-principles calculations have been applied to investigate the interactions between Ptₙ (n = 1 ~ 4) clusters and a graphene sheet as models of Pt/C fuel-cell catalytic electrodes. A Pt atom is stably adsorbed on the bridge site between two carbon atoms with the adsorption energy of about 2eV. For the case of Pt₂, both of the Pt atoms are adsorbed on the bridge site. For the case of Pt₃, the triangular cluster is more stable than the linear cluster. For the case of Pt₄, the tetrahedral cluster is more stable than the planar cluster. The adsorption energies on the surface without defects are 0.55 eV/adatom for Pt₂ and 0.05 eV/adatom for Pt₃. The interaction energy between the Pt cluster and the graphite surface per Pt atom becomes weaker as the number of Pt atoms increases. The adsorption energy for a Pt atom on the vacant site is 8.00 eV/adatom, which is stronger than the formation energy of a Pt-Pt bond (about 2 eV/bond) for small clusters.

1. Introduction

In a proton-exchange membrane fuel cell (PEMFC), Pt nano-particles supported on carbon materials are use as the electrode catalysts of an anode, because Pt are considered to be the best catalyst for both hydrogen-dissociation and hydrogen-oxidation at low temperature [1]. In order to attain excellent catalytic activity, it is necessary to understand and control the microstructures of Pt/C electrodes. For this purpose, we have investigated the interactions between Pt and carbon materials, using the first-principles calculations based on the density functional theory. Carbon black is used as the supports of carbon materials. It is reported that carbon black consists of many graphitic sheets at an atomic scale [2]. Thus we have treated the systems of Pt clusters on a graphene sheet as the model of the Pt/C catalysts. In this paper, we concentrate on the initial stage of the Pt cluster growth through the models of Ptₙ/graphene systems (n = 1 ~ 4). We have also examined stable Pt cluster configurations on carbon at the initial stage of growth process.
Table 1. Adsorption energies, $E_{ad}$ of one Pt atom adsorbed on graphene and distance, $d_{Pt-C}$. Unit is eV and A, respectively.

|           | $E_{ad}$ (Present) | VASP [9] | $d_{Pt-C}$ (Present) | VASP [9] |
|-----------|-------------------|----------|----------------------|----------|
| 6H        | −1.45             | −1.41    | 2.38                 | 2.43     |
| T         | −1.97             | −1.89    | 2.01                 | 2.04     |
| B         | −2.17             | −2.03    | 2.08                 | 2.12     |
| Defected  | −8.01             | −7.68    | 1.92                 | 1.94     |
| Zigzag    | −7.32             | −7.12    | 1.96                 | 2.00     |
| Armchair  | −5.50             | −6.08    | 1.99                 | 2.03     |

2. Method of calculations

All the calculations were carried out using the program package STATE (Simulation Tool for Atom TEchnology), which has been successfully applied to Pt(111)/graphene [3] and Pt$_{13}$/graphene [4]. We adopted the generalized gradient approximation in the DFT with the Perdew, Burke, and Ernzerhof formula [5] as the exchange-correlation energy functional. All pseudopotentials are generated from scalar relativistic [6] all-electron atomic calculations to include relativistic effects which are important for heavy elements like Pt. We constructed pseudopotentials by Vanderbilt’s ultra-soft scheme [7] and by the norm-conserving scheme [8]. Two projectors are used for ultra-soft pseudopotentials. The cutoff energy for the wave function is 25 Ry and that for the augmentation charge is 225 Ry.

A repeated slab model is used to simulate the graphene sheet. Each sheet was separated by a vacuum region of about 25 Å. Pt$_n$ clusters are introduced on one side of each sheet. For structural optimization, clusters and the substrate sheet are allowed to relax. In the present work, we treat the $4 \times 2\sqrt{3}$ cell of the graphene sheet. The surface Brillouin zone is sampled by the $3 \times 3$ uniform mesh of k-points.

We have examined two types of the energies; one is the adsorption energy including the cohesive energy of Pt clusters, $E_{ad} = E_{Pt_n/C} - (n \times E_{Pt} + E_C)$ and the remainder is the interaction energy between Pt$_n$ cluster and graphene, $E_{int} = E_{Pt_n/C} - (E_{Pt_{n}} + E_C)$. Where $E_{Pt}$, $E_{Pt_n}$, $E_C$, $E_{Pt_n/C}$ are the total energies of a Pt atom, a Pt$_n$ cluster, graphene, and a system of Pt$_n$-cluster adsorbed on graphene, respectively.

3. Results and Discussion

First, we examined the interaction energy between one Pt atom and graphene sheet. We considered three adsorption sites for the non-defected graphene sheet, the center of a hexagon which consists of six C atoms (6H), the top above a C atom (T), and the bridge between two nearest carbon atoms (B). We have also treated Pt adsorption on the vacancy site and the zigzag and armchair edges of a graphene sheet. Table 1 lists the adsorption energies between one Pt atom and graphene, $E_{ad}$ and the distance between Pt and C atoms, $d_{Pt-C}$. For the non-defected graphene sheet, one Pt atom is stably adsorbed on the B site. However, the adsorption energies on the vacancy site and the edges are much larger than that on the B site. Fig. 1 shows the stable configurations for each adsorption site. These results are in good agreement with the results in Ref. [9].

Next, we examined $E_{ad}$ and $E_{int}$ for Pt$_n$ ($n = 1 \sim 4$) clusters adsorbed on the non-defected graphene sheet. Table 2 lists $E_{ad}$’s and $E_{int}$’s. We treated the linear and triangular shapes for Pt$_3$ clusters and the planer and tetrahedral shapes for Pt$_4$ clusters. Fig. 2 shows the relaxed
defected
zigzag armchair

Figure 1. Stable configuration for each adsorption site. Black and white circles indicate C and Pt atoms, respectively.

Table 2. \( E_{\text{ad}} \)'s and \( E_{\text{int}} \)'s for \( \text{Pt}_n \) adsorbed on the non-defected graphene sheet. Unit is eV.

|        | \( E_{\text{ad}} \) | \( E_{\text{int}} \) |
|--------|------------------|------------------|
| Pt_1   | \(-2.17\)        | \(-2.17\)        |
| Pt_2   | \(-5.41\)        | \(-1.25\)        |
| Pt_3 Line | \(-8.53\)      | \(-0.74\)        |
| Pt_3 Triangle | \(-8.73\)   | \(-0.29\)        |
| Pt_4 Plane | \(-12.74\)   | \(0.01\)          |
| Pt_4 Tetrahedron | \(-14.71\)   | \(-1.89\)        |

configurations for \( \text{Pt}_n \)-cluster/graphene systems. For \( \text{Pt}_2 \) cluster, the distance between Pt atoms is \(2.56\) Å, which is shorter than that for the fcc bulk of Pt, \(2.77\) Å. The distances between Pt and C atoms are \(2.09\) Å and \(2.18\) Å. Both of the Pt atoms are adsorbed near the B site. For the linear \( \text{Pt}_3 \), the distance between the neighboring Pt pairs are all \(2.45\) Å. The distance between the edge-Pt and C atoms is \(2.20\) Å and that between the center-Pt and C atoms is \(3.05\) Å. For the triangular \( \text{Pt}_3 \), the distances among the Pt atoms are all about \(2.6\) Å. The distances between Pt and C atoms are \(2.1\) and \(2.3\) Å. The adsorption energy, \( E_{\text{ad}} \), for the triangular cluster is larger than that for the linear cluster. However, \( E_{\text{int}} \) for the triangular cluster is smaller than that for the linear cluster. The coordination number of the edge atoms for the linear cluster is one and is less than all the other atoms in both the linear and triangular clusters. Therefore, the edge atoms for the linear cluster strongly interact with graphene. For the planar \( \text{Pt}_4 \), the first-neighbor Pt-Pt distances are all about \(2.6\) Å. The length of the nearest Pt-C bond is \(2.18\) Å.
Å. The interfacial interaction between the planar cluster and graphene is very weak. For the tetrahedral Pt$_4$ cluster, the first-neighbor Pt-Pt distances are all about 2.6 Å and the length of Pt-C bond is about 2.2 Å. The tetrahedral cluster on graphene is more stable than the planar cluster on graphene. The interaction with graphene of the tetrahedral cluster is stronger than that of the planar cluster and Pt$_3$ clusters.

We have previously found that the interaction between graphene and Pt decreases in order of a single atom, a cluster, and a (111) monolayer by the first-principles calculations [10]. Yamakawa et al. investigated the deposition process of Pt particles on carbon black by using the phase-field method [11]. They reflected the present and previous results and treated the interaction between Pt and graphene as a function of the coordination number of adsorbed Pt. They explained that the Pt density profile concentrated on the carbon black led to the formation of threedimensional islands in accordance with the Volmer-Weber mode of growth and the size distributions of the Pt particles were sensitive to the heterogeneity of the substrate surface and to the competitive nucleation and growth processes. These results are in good agreement with the experimental results which were observed the real electrode catalysts by high-resolution transmission electron microscopy [12, 13]. It is difficult to simulate growth of the Pt nano-particle in real electrode catalysts by only using the first-principles calculation. However, it becomes possible to simulate growth of the real electrode catalysts by using the mesoscopic method such as the phase-field method cooperating with the first-principles calculations.

4. Conclusion
We have investigate the interaction of Pt$_n$ ($n = 1 \sim 4$) clusters with graphene by first-principles calculations based on DFT. For the non-defected graphene sheet, the interfacial interaction between Pt$_n$ and graphene becomes weaker as increasing of the number of Pt atoms in clusters; 2.17 eV/atom for Pt$_1$, 0.63 eV/atom for Pt$_2$, 0.15 eV/atom for triangular Pt$_3$. However, the tetrahedral Pt$_4$ cluster strongly interacts with the non-defected graphene sheet in comparison with the triangular Pt$_3$ cluster. We supposed that the orbital hybridization between the cluster and graphene for a tetrahedral cluster occurs more easily than that for a planar and a triangular clusters because the tetrahedral Pt-cluster makes three-dimensional structure. In order to clarify this reason, however, we need to analyze the electronic state in detail.

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