First-Principles Calculations of M\textsubscript{10}/Graphene (M = Au, Pt) Systems

—Atomic Structures and Hydrogen Adsorption—

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The usage of Au nano-particles as a catalytic electrode may be effective for the CO-poisoning problem in the anode of a proton-exchange membrane fuel cell (PEMFC), because Au nano-particles supported on metal oxides have novel catalytic activity of low-temperature CO oxidation or water gas-shift reaction. As the first step to examine this possibility, we have performed first-principles calculations of a Au\textsubscript{10} cluster on graphene as well as a Pt\textsubscript{10} cluster on graphene, based on the density functional theory (DFT). There are no strong interactions between the cluster and graphene such as substantial charge transfer or orbital hybridization, although the interaction for Pt is stronger than that for Au. We have further examined the H-atom adsorption on the clusters on graphene, and found that the adsorption energy is much larger for the Pt cluster than for the Au cluster. However, we have observed that the energy gain in the dissociation and adsorption from a H\textsubscript{2} molecule is indeed obtained for the Au small cluster in spite of no energy gain for the Au(111) surface. [doi:10.2320/matertrans.MB200812]

\textbf{Keywords:} platinum, gold, carbon, fuel cell, first-principles calculation, pseudopotential, catalysis, hydrogen

1. Introduction

In a proton-exchange membrane fuel cell (PEMFC), the dissociation and oxidation of hydrogen molecules into protons at an anode and the formation of water molecules through reduction of oxygen molecules at a cathode are essential reactions, and Pt nano-particles supported on carbon materials are used as electrode catalysts. This is because nano-particles of Pt are considered to be the best for both hydrogen oxidation and oxygen reduction at low temperature.\textsuperscript{3,4} However, in the anode, there is a CO-poisoning problem. Namely, the catalytic activity of the anode is rapidly decreased if the fuel H\textsubscript{2} gas contains small amount of CO as impurities.\textsuperscript{5,6} In order to prevent this phenomenon, PtRu alloys are used at the anode,\textsuperscript{3} where it is known that CO molecules are preferentially captured or oxidized by Ru. On the other hand, it is known that nano-particles of Au supported on some metal oxides have superior catalytic activity for low-temperature CO oxidation\textsuperscript{5} or for water gas-shift reaction, namely CO oxidation with H\textsubscript{2}O, at low temperature.\textsuperscript{5,7} There is a possibility that electrode catalysts containing Au nano-particles with (or instead of) usual Pt particles supported on carbon materials could be effective for the CO-poisoning problem. To examine this possibility, it is important to examine the stability, atomic and electronic structures and catalytic activity of Au particles on carbon materials as compared with the Pt particles on carbon materials.

For the catalytic performance at the anode, the interaction with hydrogen molecules or atoms is crucial. Recently, the adsorption of hydrogen atoms on the Pt/C catalysts of the PEMFC has been investigated by inelastic neutron scattering spectroscopy.\textsuperscript{8} It was reported that the dissociation of a hydrogen molecule on the catalysts occurs well below room temperature in the range 60 to 120 K and that the sites occupied by hydrogen atoms are not only C\textsubscript{3v} sites but also on-top sites. However, there are few theoretical studies to deal with the H adsorption on Pt clusters supported on carbon materials.

There are also few studies to make comparison between the H adsorption on the Pt/C system and that on the Au/C system. Recently, Okamoto has made a comparison between the H adsorption energies on the top and hcp sites of the metal (Pt and Au) clusters on graphene using the \textit{ab initio} pseudopotential method.\textsuperscript{7} He reported that the adsorption energy on the top site is larger than that on the hcp site for the Au cluster and that the adsorption energy on the top site is smaller than that on the hcp site for the Pt cluster.

In this paper, we first examine the stability and the atomic and electronic structures of Pt and Au clusters on graphene. We deal with Au\textsubscript{10} and Pt\textsubscript{10} clusters with a common hemispherical shape on graphene, and make clear comparison between Pt and Au. Second we examine the H-atom adsorption on the M\textsubscript{10}/graphene (M = Au or Pt) systems as the first step to understand the reaction mechanism of the dissociation of a H\textsubscript{2} molecule on the electrode catalyst. We make comparison on the reactivity between the Pt and Au clusters.

2. Methods

We examined atomic and electronic structures of Au\textsubscript{10} and Pt\textsubscript{10} clusters supported on graphene, using the first-principles calculations based on the density functional theory (DFT). All the calculations are carried out using the program package STATE (Simulation Tool for Atom TEchnology). We constructed pseudopotentials by Vanderbilt’s ultra-soft scheme\textsuperscript{8} and by the norm-conserving scheme.\textsuperscript{9} We adopted the local density approximation (LDA) in the DFT with Perdew-Wang formula (PW91) as the exchange-correlation energy functional.\textsuperscript{10} The cutoff energy of the plane-wave basis is 25 Ry and that of the augmentation charge is 225 Ry.
The calculated lattice constant for graphene is 2.46 Å. This value is in very good agreement with the experimental value of 2.46 Å. We have treated the 8 × 8 units including 128 carbon. For the direction normal to the surface, neighboring graphene sheets are separated by a vacuum region of about 25 Å. Sampling k-point is the only Γ point in the Brillouin zone.

3. Results and Discussions

3.1 Stable structures

We have dealt with Au$_{10}$ and Pt$_{10}$ clusters on a graphene sheet. Each cluster consists of a hexagonal layer of seven atoms and a triangle layer of three atoms. The stable configurations are shown in Fig. 1. The interaction energy between graphene and metal-cluster, namely the energy gain to make the interface from separated systems, is 1.12 eV/cluster for Au and 1.33 eV/cluster for Pt. The interaction energy for the Au$_{10}$ cluster is smaller than that for the Pt$_{10}$ cluster. These values are larger than the interaction energies between graphene and the mono layer of metal (0.06 eV/adatom for Au and 0.09 eV/adatom for Pt).

The nearest Au-C distance is 3.17 Å and the nearest Pt-C distance is 3.02 Å. The central atom, No. 1 in Fig. 1, is clearly displaced toward to the graphene for each system. The displacement from the other atoms of the interface plane is 0.21 Å for Au and 0.26 Å for Pt. The metal-metal bond lengths are listed in Table 1. The distance between the nearest neighbor atoms is 2.88 Å and 2.77 Å for the fcc bulk Au and Pt, respectively. For both clusters, the distances between the in-plane atoms (bonds between No. 2 and No. 3 atoms in Fig. 1, for example) are shorter than the fcc bulk ones. This is consistent with the general tendency that small metal clusters with reduced numbers of neighbors have reduced bond lengths. This may be also affected by the coherency with the configuration of graphene, because of a tendency that the in-plane atomic distances are smaller than those between the planes (bonds between No. 1 and No. 8 atoms in Fig. 1, for example). In Table 1, the reason why the bond length between No. 1 and No. 2 atoms is a little shorter than between No. 2 and No. 3 atoms in spite of the sink of No. 1 atom for the Au cluster is that the bond lengths along the x axis in Fig. 1, the bond between No. 3 and No. 4 atoms for example, are a little compressed with breaking the six-fold symmetry.

In Fig. 2, we show the valence electron density distributions of the cluster/graphene systems. The charge transfer between the graphene and the metal cluster is negligible for each system, although the transfer value itself is larger for the Pt/graphene system. This is the reason why the interaction with graphene of the Au$_{10}$ cluster is weaker than that of the Pt$_{10}$ cluster. Of course, there seem to exist no substantial orbital hybridizations between the metal cluster and the graphene in each system.

It can be said that the interaction between the M$_{10}$ cluster and graphene without any defects is not so strong. However, it can be said that the adhesive interaction is greater for the Pt cluster than for the Au cluster from the present results of the adhesive energies, configurations and charge transfers. Of course, even for the Au clusters, there should occur strong interfacial interactions for defective graphene or edges of graphene sheets, as recently examined for the vacancy on graphene. This problem will be examined in detail in the near future.

3.2 Hydrogen adsorption

About the adsorption of H atoms, we dealt with three adsorption sites on the M$_{10}$ cluster, namely the three-fold hollow (3H) site, the top (T) site above the metal atom in the top layer, and the bridge (B) site between the two metal atoms in the top layer. The adsorption energy, $E_{ad}$ is defined by

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![Fig. 1 Stable configurations of Au$_{10}$/graphene (a) and Pt$_{10}$/graphene (b). Black, gray, and white circles represent C, Au, and Pt atoms, respectively.](image1.png)

![Table 1 Bond lengths between metal atoms. Unit is Å.](table1.png)

<table>
<thead>
<tr>
<th></th>
<th>1-2</th>
<th>2-3</th>
<th>1-8</th>
<th>2-8</th>
<th>8-9</th>
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<tr>
<td>Au</td>
<td>2.72</td>
<td>2.73</td>
<td>2.85</td>
<td>2.70</td>
<td>2.70</td>
</tr>
<tr>
<td>Pt</td>
<td>2.59</td>
<td>2.55</td>
<td>2.76</td>
<td>2.55</td>
<td>2.55</td>
</tr>
</tbody>
</table>
Pt adsorption on the B site is more favorable in the present surface as corresponding to the present 3H site. The most stable adsorption site for the bulk Pt(111) adsorption energy represents the energy change from a H$_2$ molecule to the H-atom adsorption through the dissociation of the molecule. Values from a H atom can be obtained by adding the dissociation energy of about 2.45 eV.

Table 2 Adsorption energies of H atom on the M$_{10}$/graphene. Unit is eV/atom.

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>3H</td>
<td>0.28</td>
<td>1.18</td>
</tr>
<tr>
<td>T</td>
<td>−0.02</td>
<td>1.22</td>
</tr>
<tr>
<td>B</td>
<td>0.32</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Table 3 Bond lengths M-H. Unit is Å.

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>3H</td>
<td>1.88</td>
<td>1.91</td>
</tr>
<tr>
<td>T</td>
<td>1.57</td>
<td>1.57</td>
</tr>
<tr>
<td>B</td>
<td>1.76</td>
<td>1.78</td>
</tr>
</tbody>
</table>

$E_{ad} = 1/2E_{H_2} + E_{M/C} - E_{H/M/C}, \quad \text{(1)}$

where $E_{H_2}, E_{M/C},$ and $E_{H/M/C}$ represent the total energies of the H$_2$ molecule, M$_{10}$/graphene system, and the H adsorption on the M$_{10}$/graphene system, respectively. Note that this adsorption energy represents the energy change from a H$_2$ molecule to the H-atom adsorption through the dissociation of the molecule. Values from a H atom can be obtained by adding the dissociation energy of about 2.45 eV.

Results of $E_{ad}$ and a metal-H bond length for each adsorption site are listed in Tables 2 and 3. For the Au$_{10}$/graphene system, a H atom is favorably adsorbed on the B site among three sites and the Au-H bond length is 1.76 Å. The adsorption energy of the 3H site is close to that on the B site. For the (111) surface of bulk Au, the adsorption of H atoms from H$_2$ molecules is not possible. Namely, the adsorption energy defined by eq. (1) is negative. It is quite interesting that the adsorption from a H$_2$ molecule is favorable for the small Au cluster, although the adsorption on the T site is not favorable.

For the Pt$_{10}$/graphene system, the H atom is favorably adsorbed on the B site among the three sites as well as the Au$_{10}$/graphene system, and the Pt-H bond length is 1.78 Å. Although the most stable adsorption site for the bulk Pt(111) surface is that corresponding to the present 3H site, the adsorption on the B site is more favorable in the present Pt$_{10}$ cluster on graphene.

Table 2 shows that the metal-H bond length is longer for the site with a larger number of contact metal atoms for each system. Thus the length of the T site is the shortest and that of the 3H site is the longest in each system. There is a tendency that the Pt-H bond length is a little longer than the Au-H bond length in each site, which seems to be contradictory to the larger adsorption energy for the Pt$_{10}$/graphene system. This should be caused by different bonding characters of the Pt-H and Au-H bonds. There should exist covalent nature with H s-orbital and Pt d-orbital hybridizations for the Pt-H bonds, in contrast to bonding of s electrons of H and Au atoms for the Au-H bonds.

4. Discussions and Conclusion

In order to investigate the probability of the usage of Au nano-particles as the electrode catalyst in a PEMFC, we have examined the stability of a Au$_{10}$ cluster on graphene compared with a Pt$_{10}$ cluster. The charge transfer between the Au$_{10}$ cluster and graphene is smaller than that between the Pt$_{10}$ cluster and graphene. And the interaction energy between the Au$_{10}$ cluster and graphene (1.12 eV) is smaller than that for the Pt$_{10}$ cluster (1.33 eV). Therefore, the Au$_{10}$ cluster is unstable on graphene in comparison with the Pt$_{10}$ cluster. Au nano-particles do not seem to have strong interactions with carbon materials, although the presence of defects or edges of graphene sheets should stabilize Au nano-particles on carbon materials, similarly to the case of Pt nano-particles.

We have further investigated the adsorption of H atoms on the M$_{10}$/graphene systems as a first step to understand the reaction mechanism of the dissociation of a H$_2$ molecule into H atoms and to make comparison on the reactivity between Au and Pt. For both the Au$_{10}$/graphene and Pt$_{10}$/graphene systems, a H atom is favorably adsorbed on the bridge site of the two atoms on the top layer, although the most favorable site is the 3H site for the bulk Pt(111) surface and there is no favorable site for the bulk Au(111) surface. It is interesting that the dissociation of a H$_2$ molecule into the adsorbed H atom is possible for a small Au cluster, differently from the bulk Au surfaces, which is consistent with the experimentally-observed catalytic activity of Au nano-particles. Of course, the adsorption energy for the Au cluster (0.32 eV) is much smaller than the Pt cluster (1.31 eV), which is also consistent with the high catalytic activity of Pt. The differ-
ence in the Pt-H and Au-H bond lengths seems to be concerned with the different bonding characters of the two kinds of bonds.

Okamoto has investigated the adsorption energies of a H atom on Pt_{55} and Au_{55} clusters, on Pt(111) and Au(111) surfaces, and on Pt_{13} and Au_{13} clusters on a graphene sheet. He reported that a H atom cannot be adsorbed on the Au(111) surface and the T site of the Au_{55} cluster, but can be adsorbed on the 3H site of the Au_{55} cluster. These results are consistent with our results about the 3H and T sites of the Au_{10} cluster on graphene. He also reported that a H atom can be adsorbed on both the 3H and T sites of the Au_{13} cluster on graphene, which is different from our results on the T site of the Au_{10} cluster on graphene. This may be caused by the difference of the shape and size of the clusters. For Pt, he reported that a H atom is favorably adsorbed on the T site of the Pt_{55} cluster and on the 3H site of the Pt_{13} cluster on graphene, which are different from our results on the Pt_{10} cluster on graphene, where a H atom is favorably adsorbed on the B site. It seems that the favorable adsorption site greatly depends on the shape and size of the cluster, and the detailed effects of the presence of graphene is not so clear at present.

For the Pt/C fuel cell catalyst, Perker et al. investigated the adsorption of H atoms by inelastic neutron scattering spectroscopy, and reported that the sites occupied by a H atom are not only the 3H site but also the T site. In our results, the adsorption energy on the T site is larger than that on the 3H site, although the most stable adsorption site is the B site among the three sites. This point is not consistent with the above experimental results. Of course, it is not proper to make direct comparison between the present results and the experiments of real Pt/C catalysts. First, the size of Pt particles in the real catalytic electrode ranges from 2 to 8 nm, while the size of our Pt_{10} cluster is about 0.5 nm. Second, the experiments deal with the behavior of H atoms at the finite temperature, while the present DFT calculation deals with the behavior at zero temperature. Third, we only dealt with only one H atom per cluster, which may be too few in comparison with the experiment.

The present calculations are very fundamental ones in order to understand the interaction between the electrode catalysts and the hydrogen, as the first step to examine the possibility that Au nano-particles supported on carbon materials can use as catalytic electrodes of PEMFC. We found that there are some adsorption sites for H atoms on a Au cluster as well as a Pt cluster. However, the interaction between a Au cluster and graphene is weaker than that between a Pt cluster and graphene, and the adsorption energies of H atoms on a Au/graphene system are smaller than those on a Pt/graphene system. Therefore, it seems to be difficult to use Au nano-particles as the electrode catalyst. Recently, it was reported that the PtAuFe/C catalysts were prepared via a microwave-irradiated polyol process and showed a superior CO-tolerant activity for hydrogen oxidation reaction as anode catalyst for PEMFC because of the Au and Fe additives. It was also reported that the AuPt nanoparticles with 2 to 3 nm in size generate approximately 4.8 times higher oxygen reduction current per unit area than that of commercial platinum catalyst. Thus in future, we should theoretically investigate the catalytic activities of Pt-Au alloys or Pt-Au mixing particles on carbon as cathode or the anode electrodes of PEMFC.

Acknowledgments

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