Density functional investigation of oxygen reduction reaction on Pt$_3$Pd alloy electrocatalyst

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Abstract

We have investigated the surface structure and electronic properties of Pt segregated Pt$_3$Pd (111) surface within the framework of density-functional theory. Surface adsorption of the oxygen reduction reaction (ORR) mediators including H, O, OH, O$_2$, OOH, H$_2$O$_2$ and H$_2$O and the related reaction pathways have then been thoroughly examined via determining the corresponding activation energies and reaction heats using climbing-image nudged elastic band (CI-NEB) calculations. It is found that the ORR preferably proceeds via OOH dissociation mechanism on the Pt$_3$Pd (111) surface. Surface corrosion resistivity has also been investigated via evaluating the electrochemical potential shift of the surface Pt atoms. Results verify an enhanced stability against pure Pt (111) in the presence of an oxygen atom and nearly the same stability compared to clean pure Pt (111) surface.

Introduction

Proton exchange membrane fuel cells (PEMFCs) can generate electricity through direct electrochemical conversion of hydrogen and oxygen from water. Switching from conventional fossil fuel-based vehicles to modern hydrogen fuel cell-enhanced vehicles could benefit our society from many aspects such as improved air quality, healthy climate, and accordingly better public health [1]. Polymer electrolyte fuel cells are great sources for power generation with widespread portable applications [1–3]. One of the most important part of membrane electrode assemblies is the Pt-containing electrocatalysts. The main challenge along the way of large-scale applications of PEMFCs is related to the preciousness of Pt [4–7]. Therefore, a reasonable alternative for cost reduction purposes is reducing the Pt content using alloying, and then simultaneously increasing the electrochemical reactivity via maintaining or enhancing the corrosion resistivity [8–11]. There is still an enormous interest in designing PEMFCs with Pt-TM alloys as oxygen reduction reaction (ORR) electrocatalysts [12–15], passionately drawn by noble examples of binary and ternary Pt alloys in the literature with excellent ORR activities [16, 17]. Recently, Pd-supported Pt monolayers have garnered a considerable attention due to their superior catalysis performance, which accordingly makes them to be economical [18–22]. However, further enhancement of them can be achieved by weakening the adsorption ability for the Pt$_3$Pd (111) [18, 23]. The interaction between Pd and Pt results in the downshift of the d band, leading to the weakening adsorption energy of ORR intermediates on the Pd$_x$Pt (111) [24]. Several efforts have so far been devoted to searching alternative materials with superior oxygen evolution reaction (OER) catalysis performance and cost-effectiveness. For example, Pt-based metal nanospheres have been designed and successfully synthesized by a cost-effective aqueous solution method, exhibiting a superior hydrogen evolution reaction (HER) electrocatalytic activity with an excellent catalytic durability for both ORR and HER [25, 26]. FePtPd alloy nanowires (NWs) with tunable compositions and controlled length (<100 nm) have also been synthesized with a composition-dependent catalytic activity and stability for methanol oxidation reaction [27]. As well as low Pt-based quaternary, PtPdRuTe nanotubes exhibit enhanced activity and stability towards efficient methanol oxidation reactions [28]. Recently, it has been shown that an excellent catalytic stability for ternary TePtCo nanotubes, much higher than that of the Pt catalyst [29].
As an illustration, Pt$_3$Ni (111) has been found to possess a 10-fold increase in ORR activity than the pure Pt. The PtXY (X = Ti, Y = Cu, Ni, V) ternary alloys have shown a similar enhancement in chemical ORR compared to the pure Pt. This enhancement has been theoretically and experimentally proved to be due to 0–0.4 eV weaker surface binding energy of the ORR mediators compared to pure Pt [30–32]. Another important aspect of these Pt-containing alloys is their durability in severe acidic environments at high electrode potentials. A thermodynamic formulation proposed by Greeley and Norskov introduced the quantity electrode chemical shift (DU) as a measure of the tendency of the alloy to metal dissolution compared to the pure system [33].

Previous studies suggested that the pure Pt overlayer is the most thermodynamically stable configuration in alloyed systems [34–36]. In the present work, we therefore study the adsorption of seven ORR mediators (namely, H, O, OH, O$_2$, OOH, H$_2$O, H$_2$O$_2$) via calculating the related activation energies and pathways using density-functional theory. We also investigate the corrosion resistance in harsh environments.

Computational details

Density-functional theory [37] has been applied to investigate the surface structure and electronic properties of Pt segregated Pt$_3$Pd (111) surface via adopting a self-consistent, plane-wave, pseudopotential approach [38] at the PBE-GGA [39, 40] level of theory as implemented in the QUANTUM ESPRESSO [41, 42] computational software. Scalar–relativistic ultrasoft pseudopotentials [43, 44] have been used to model the behavior of the core (non–valence) electrons for each atomic type. The kinetic energy cutoff of about 400 eV for the wave functions, and 1600 eV for the charge densities and the potentials have been found enough to reach energy convergence. The Brillouin zone has been sampled by a regular 6 × 6 × 1 Monkhorst–Pack grid using Fermi–Dirac smearing method. The atomic positions have been relaxed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) optimization method [45–47] in a way that the magnitude of each component of the total force on each atom becomes less than 10$^{-4}$ eV Å$^{-1}$, the atoms at the bottom of the two surface layers have been kept fixed during relaxation. Pt$_3$Pd alloy has L1$_2$ crystal structure in that three Pt atoms lie at the face-centered positions and one Pd atom at the corner of a face-centered cubic (fcc) unit cell. A 2 × 2 super cell of the (111) surface has been used for this alloy figure 1(a) with a vacuum space of about 15 Å perpendicular to the surface of the crystal in order to decouple the weakest periodic interactions between the replicas.

Results and discussion

The pure Pt slab has 4 inequivalent adsorption sites [48–52]. This number approaches to 9 if we take into account the Pd atoms in second layer of alloyed Pt$_3$Pd (111) surface figure 1(b). We first determine the most favorable surface adsorption sites for each ORR mediator (H, O, OH, O$_2$, OOH, H$_2$O, and H$_2$O$_2$) via optimizing the crystal structure, and then calculate the binding energy for a specific adsorbate on each of the adsorption sites. Adsorption energy is defined as the difference between the energy of the adsorbate–surface system and that of the isolated adsorbate–free surface and the gas molecule. Comparing the calculated binding energies reveals the most favorable site as tabulated in table 1. According to the previous studies, we have investigated the adsorption of H on the F and T sites, O on the F sites, O$_2$ and H$_2$O$_2$ on the B sites, OOH and H$_2$O on the T sites, and OH on both the T and B sites of the Pt-segregated Pt$_3$Pd(111) surfaces [53–56].
The optimized geometries of adsorbed ORR mediators on the Pt3Pd (111) substrate are also shown in figure 2. It is found that the H atoms mostly tend to be adsorbed on the top T2 site while the O atom prefers to bind to the fcc F1 site. According to table 1, the O atom is adsorbed on the surface more strongly than the other ORR mediators. It has been found that atomic species such as O could bind to the Pd surface more strongly than the Pt surface. Consistently, we also have found that O binds to the surface at the F1 site with one nearest neighboring Pd atom more strongly than the F2 site with only nearest neighboring Pt atoms. Formation of a bimetallic surface results in changes in the surface d band widths due to the combination of strain and ligand effects. Both of these effects are manifested in the interatomic matrix element describing bonding interactions between an atom and its nearest neighbors [57]. The hydrogen monoxide (OH) molecule could bind to the T and B sites. The oxygen molecule (O2) can also bind to the B sites so that its most favorable adsorption site is the bridge B2 site. The lowest binding energies have been found for OOH, H2O and H2O2 binding to the T2, T1 and bridge B2 sites, respectively.

Comparing the adsorption energies of the ORR mediators on the Pt3Pd (111) surface reveals that OH, O, H, and H2O2 have lower binding energies compared to O2, OOH, and H2O, and then make stronger bonds to the surface. As a result, the O2, OOH, and H2O molecules can leave the surface more easily due to weaker surface bonds. Likewise, comparing the adsorption energies of O2 and OOH on the Pt3Pd (111) and pure Pt (111) surfaces indicates that these molecules make weaker bonds to the alloy surface compared to the pure Pt, being detached more easily [58].

All the mediators are adsorbed on the slab more weakly than on the pure Pt (111) surface largely due to the action of the d-band center, so that the presence of a transition metal element could lower the d-band center

| Adsorption site | F1 | F2 | F3 | F4 | F5 |
|-----------------|----|----|----|----|----|
| H               | 2.75 | 2.73 | 2.72 | 2.81 | 2.70 |
| O               | 4.27 | 4.09 | 4.03 | 4.07 | 4.07 |
| OH              | 2.21 | 2.25 | 2.29 | 2.35 | 2.36 |
| O2              | 0.26 | 0.28 | 0.30 | 0.32 | 0.37 |
| OOH             | 1.04 | 1.03 | 1.03 | 0.91 | 1.05 |
| H2O             | 0.23 | 0.21 | 0.25 | 0.24 | 0.21 |
| H2O2            | 1.85 | 1.86 | 1.86 | 1.83 | 1.91 |

Figure 2. Ground-state geometries of the Pt3Pd (111) surface with various ORR mediators adsorbed on it. (a) The H atoms adsorbed on the top T2 site, (b) the O atom adsorbed on the fcc F1 site, (c) OH adsorbed on the bridge B1 site, (d) O2 adsorbed on the bridge B2 site, (e) OOH adsorbed on the top T2 site, (f) H2O adsorbed on the top T1 site, and (g) H2O2 adsorbed on the bridge B2 site. The red and blue balls represent oxygen and hydrogen atoms, respectively.
when comparing to the pure Pt (111) surface. As a result, electronic structure of the slab can play an important role in the ORR mechanisms in addition to its specific geometry [59].

There are three possible scenarios for the ORR mechanisms after chemisorption of the oxygen molecules on the Pt3Pd (111) surface as schematically illustrated in figure 3. If the O2 adsorbate immediately split into two chemisorbed oxygen atoms on the surface, then it undergoes O2 dissociation; else a hydrogenation reaction of O2 will result in either OOH dissociation reaction to form O− and OH− or H2O2 dissociation reaction to form H2O2−.

There are 7 intermediate reactions on the Pt3Pd (111) surface, which we treat them using CI-NEB. For simulating each elementary reaction, the energy difference between the initial and final states is then determined based on the formerly calculated optimized geometries. Another important quantity is the transition energy (Ea) which could be obtained by setting path threshold to 0.01 eVÅ−1 within the CI-NEB scheme.

Figure 4(a) shows the initial and final states of the O2 dissociation mechanism. The first image corresponds to the O2 ORR mediator adsorbed on the B site, and the final image corresponds to two oxygen atoms both adsorbed on two adjacent F1 sites. These images have been fully optimized in order to have the minimum energy configuration. Similarly, Figures 4(b) and (c) show the OOH and H2O2 dissociation reactions as well as the O2, OH, O, and OOH hydrogenation reactions, respectively. Results of the CI-NEB calculations are displayed in table 2 for the initial, intermediate, and final states of the ORR mediators.

**Dissociation reactions**

In Figure 4(a), the initial state is the adsorption of O2 at a B2 site and the final state is the co-adsorption of two O atoms at the two adjacent F1 sites. One oxygen atom stays at the bridge while the other moves toward the F1 site. Figure 4(b) shows a situation in which the initial state is the adsorption of OOH at a T1 site and the final state is the co-adsorption of OH at a T1 site and O at a F1 site. The OOH molecule moves toward the F1 and T1 sites and then an O−O bond scission occurs, accompanying the rotation of the OH molecule toward the O atom along a straight line.

In Figure 4(c), the initial state is the adsorption of H2O2 at a B2 site and the final state is the adsorption of the OH molecules at the two nearby top sites. The OH molecules rotate in order to be aligned with the x-axis of the crystal.

**Hydrogenation reactions**

In Figure 4(d), the initial state is composed of both the co-adsorption of O2 at a bridge (B1) site and that of the H on a nearby top (T2) site, while the final state is the adsorption of OOH at a top (T1) site. The O2 molecule rotates
toward the hydrogen atom, and then in the final state, the H atom moves closer to the oxygen molecule. For the hydrogenation of the OH molecule Figure 4(e), the initial state corresponds with the co-adsorption of both the OH molecule at a top (T1) site and the H atom at a nearby top (T2) site, while the final state is the adsorption of the H$_2$O molecule at a top (T1) site. The H atom moves closer to the OH molecule and the OH rotates toward the...
H atom simultaneously. Figure 4(f) shows the hydrogenation of the oxygen atom. Its initial state is the co-adsorption of O and H at a fcc (F1) and a nearby top site, respectively; the final state is the adsorption of the OH atom at a bridge (B1) site. During the transition state, O and H get closer to form the OH molecule.

For the OOH hydrogenation process Figure 4(g), the initial state is the co-adsorption of OOH and H at two top T1 and T2 sites, respectively; the final state is the adsorption of H2O2 at a bridge (B1) site. The OOH molecule stays almost stationary while H moves closer to that to form the OH bond. Therefore, in the final state and after complete relaxation, the OH molecules rotate around the OH–OH bond to be adsorbed on the surface, while having the minimum forces.

**ORR Mechanisms on Pt3Pd (111) Surface**

Table 2 indicates the results of our CI-NEB calculations for activation energies (\(E_a\)) and heats of reaction (\(\Delta E\)).

As figure 3 suggests, the first reaction to be considered is either \(O_2\) hydrogenation or \(O_2\) dissociation. In this case, the \(O_2\) adsorbate hydrogenation reaction is energetically more favorable than the dissociation one. Moreover, the activation energy for OOH dissociation reaction is lower than that of the OOH hydrogenation reaction, indicating that the preferred mechanism of ORR on the Pt3Pd (111) surface is via oxygen hydrogenation. The estimated rate determining step (RDS) for the OOH dissociation mechanism is also the OH hydrogenation reaction with the activation energy of about 0.8 eV.

From the literature [58], we know that the RDS of the pure Pt (111) for OOH dissociation ORR mechanism is \(O_2\) hydrogenation reaction and has been predicted to have an activation energy of about 0.79 eV. There is a slight difference between our calculated RDS for Pt3Pd (111) and pure Pt (111). However, the overall activation energy of our favorable mechanism is higher than that of the pure Pt (111).

To analyze Pt dissolution in the PEMFC cell, we adopt the approach mentioned in the reference [56], and we use chemical potential shift to describe the resistivity of Pt dissolution against degradation. The chemical shift observed in alloying is a measure of how slow the formation of oxide surface could happen. For \(Pt \rightarrow Pt^{2+} + 2e^-\) reaction, the chemical potential shift is \(\Delta U = -\left(\mu_{\text{alloy}} - \mu_{\text{pure Pt}}\right)/2e\), where \(\mu_{\text{alloy}}\) and \(\mu_{\text{pure Pt}}\) are the chemical potentials of alloy and pure Pt surface, respectively.

The chemical potentials have also been calculated using

\[
\mu N = \frac{(E_{\text{slab}} - E'_{\text{slab}})}{N}
\]

where \(N\) is the total number of atoms removed, \(E_{\text{slab}}\) is the energy of the original slab, and \(E'_{\text{slab}}\) is the energy of the slab with \(N\) atoms removed and contains surface cavities.

In this case, the chemical potential depends on the crystallographic structure, surface and sub-surfaces in the compound. From figure 5, we found that removing the indicated Pt atoms would cost the lowest energy, thus they dissolve easier than other atoms on the surface. Figure 5(a) shows a situation in which we used this lower bound to determine the chemical potential shift. We estimated \(\Delta U = -0.04689\) V for Pt3Pd (111) showing that the surface Pt atoms on Pt3Pd (111) alloy could separate slightly easier than the pure Pt (111).

Another question to be addressed is the stability of Pt surface atoms in the chemical environment. Generally, separating these atoms is easier in the presence of oxygen atoms bound to the surface. For oxygenated Pt3Pd (111), the electrode potential shift with respect to the clean surface is \(-0.567\) V, while the corresponding value for the pure Pt (111) is \(\Delta U = -0.64\) V. To compare the thermodynamic stabilities of the oxygenated Pt3Pd (111) and the pure Pt (111) surfaces, the related electrode potential shift value has then been calculated, which is \(\Delta U = 0.02690385\) V. Therefore, the Pt dissolution from Pt3Pd (111) could occur at higher electrode potentials compared to the pure Pt (111) surface in the presence of oxygen atoms, resulting in a higher stability as well.

| Reactions                          | Pt (111) (This work) | Pt (111) (from [31]) | Pt3Pd (111) (This work) |
|-----------------------------------|----------------------|----------------------|-------------------------|
| \( \Delta E \)                    | \( E_a \)            | \( \Delta E \)       | \( E_a \)               |
| \( O_2 \rightarrow O^+ + O^- \)  | -1.098703            | 0.724513             | -1.02                   | 0.63                    | -1.432709               | 1.007787               |
| \( OOH \rightarrow O^+ + OH^- \) | -1.609362            | 0.096205             | -1.51                   | 0.05                    | -2.091263               | 0.345550               |
| \( H_2O_2 \rightarrow OH^- + OH^- \) | -1.849876         | 0.348914             | -1.75                   | 0.26                    | -1.639348               | 0.468708               |
| \( O_2 + (H^+ + e^-) \rightarrow OOH \) | -0.229989          | 0.339075             | -0.14                   | 0.25                    | -0.599247               | 0.727319               |
| \( O + (H^+ + e^-) \rightarrow OH^- \) | -0.812252         | 0.176951             | -0.70                   | 0.09                    | -0.561475               | 0.802151               |
| \( O + (H^+ + e^-) \rightarrow OOH \) | -0.219183         | 0.874961             | -0.14                   | 0.79                    | -0.199850               | 0.588821               |
| \( OOH + (H^+ + e^-) \rightarrow H_2O_2 \) | -0.339479         | 0.259361             | -0.28                   | 0.19                    | -0.182503               | 0.794048               |

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Conclusions

Density-functional theory has been applied to systematically evaluate the performance of the Pt-segregated Pt$_3$Pd (111) surface as a cathode electrode electrocatalyst for promoting the ORR mechanisms in PEMFCs. We calculated the activation energies for all possible elementary reaction steps of the ORR on the Pt$_3$Pd (111) surface and further predicted that this mechanism proceeds following the oxygen hydrogenation process. We also identified the rate determining step (RDS) of the ORR on the Pt$_3$Pd (111) surface which was the OH hydrogenation reaction with an activation energy of 0.80 eV. On the other hand, the RDS of the pure Pt (111) for OOH dissociation ORR mechanism was found to be O hydrogenation reaction and predicted to have an activation energy of about 0.79 eV. There has been a slight difference between our RDS results for Pt$_3$Pd and that of the pure Pt (111). However, the overall activation energy of our favorable mechanism has been higher than the pure Pt (111). We compared the stability of the Pt$_3$Pd bimetallic catalyst with the pure Pt one via evaluating the tendency of surface Pt atoms. Results verify that the Pt dissolution would take place at higher electrode potentials on the oxygenated Pt$_3$Pd (111) surfaces when comparing to the corresponding pure Pt (111) surface.

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