I. INTRODUCTION

Energy storage and generation devices are becoming increasingly important in order to enhance the sustainability of our society. There has been active research on fuel cell technology on this regard for the last decades. So far, the practical use of fuel cell technology has been limited by the inefficient catalysts used in the electrodes. In spite of using one of the highly pronounced catalysts, platinum, the oxygen reduction reaction in the electrodes still requires substantial overpotential. In recent years, platinum-based bimetallic catalysts have been found to exhibit the high activity for the oxygen reduction reaction (ORR). Pt-Ni and Pt-Co bimetallic catalysts show the enhancement in the efficiency, mainly benefited from the strain effect originating from core-shell type nano-structure, where the core part consists of the bimetallic alloy. The atomic radiiuses of alloying metals are generally smaller than that of Pt, resulting in the compressive strain to the outermost Pt layer. Other 3d transition metallic elements are also employed in Pt-based bimetallic alloys, e.g., Pt-Cu or Pt-Fe. The relation between compressive strain and increased activity is interpreted in terms of geometric strain effect and electronic structure modification, enhancing the overall kinetic rate by optimizing the oxygen binding strength. In ORR, it is known that an optimal degree of weakening Pt-O binding strength to achieve the higher ORR activity is ranging from 0.2 to 0.4 eV. The metallic element alloyed with Pt is frequently chosen among late 3d transition metals in order to maximize the geometric strain effect benefited from their smaller atomic radius. However, Pt-M bimetallic alloy catalyst is prone to segregation loss and dissolution in such highly acidic environment usually found in ORR. One of the approaches to alleviate this problem is that noble metals have been used to form the alloy with Pt. Pt-Au alloying was found to cast the energetic barrier to the segregation loss of metal atoms from the bulk (inside) region, which can enhance the durability of Pt-M based catalytic system in oxygen reduction condition at fuel cell devices. This study highlights that a gold subsurface hetero layer can provide an additional mean to tune the surface activity toward oxygen species and in turn the oxygen reduction reaction, where the utilization of geometric strain already reaches its practical limit. © 2015 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4905919]
this, we modeled a widely adopted Pt$_3$M model to calculate the effect of a gold subsurface layer, estimated its role as a geometric barrier against the segregation loss of the metallic component, and captured the interesting variation from the calculated electronic structures. The use of a gold subsurface layer is predicted to weaken the binding energy between oxygen and Pt surface by about 0.2–0.4 eV, which coincides with the optimal range of weakening oxygen binding energy for efficient ORR. A slight decrease in the oxygen binding energy on Pt$_3$M compared to on Pt(111) is important to improve the ORR activity because the number of available active sites can be increased. In the reference article, the observed effect was related to the geometric strain caused by the bulk (inside) part of Pt-Ni bimetallic alloy. Such geometric effect has been widely adopted to manipulate the oxygen binding interaction and has been well explained by the d-band shift model. In the present work, we extend the conventional approaches from geometric to chemical problem, considering the ligand-like effect by the hetero-nano structure.

The use of compressive geometric strain has already approached close to its physical limits inferred by the given atomic radius of transition metal elements. Also, the effect of such extreme degree of strain is not readily estimated. In order to explore the different approaches to optimize surface-adsorbate interactions, we examined the role of gold subsurface layer in the conventional Pt/Pt$_3$M catalyst and found that this may provide an effective means to achieve the further enhancement in the ORR activity for the better polymer electrolyte membrane (PEM) fuel cell devices.

Modern nanotechnology has advanced to an extent of controlling the nanostructure within monolayer level. In this study, we conducted the first-principles calculations to understand the effect of the heterogeneous subsurface layer to the catalytic activity of the surface layer. As the first step to validate this strategy, the subsurface layer consisting of the noble metal (Au in this study) is constructed beneath the Pt skin layer in the computational model of Pt$_3$M(111) (where M = 3d transition metals). For this purpose, density-functional theory (DFT) calculations have been successfully used. The results clearly suggest that the use of subsurface nano structuring may lead to the greater improvement in the use of Pt-based bimetallic catalyst for ORR. The Au subsurface layer induces the geometric barrier to segregation loss, and it affects both the oxygen binding energy and the electronic structure of the Pt catalytic surface.

### II. COMPUTATIONAL METHODOLOGY

DFT calculations were conducted within generalized gradient approximation (GGA) for exchange-correlation (xc) functional devised by Perdew, Burke, and Ernzerhof (PBE), as implemented in the Vienna *ab initio* simulation package (VASP). The kinetic energy cutoff for the planewave basis set is set to 500 eV, and the electron-ion interactions are represented by the projector augmented wave (PAW) potentials. $k$-Points sets used for each model were carefully tested and convergence was found where total energy was converged within 10 meV per atom. Monkhorst-Pack grid of $8 \times 8 \times 8$ was used for bulk Pt$_3$M structures and $8 \times 8 \times 1$ was used for slab models including O adsorption model. Initial magnetic polarization of 3.0 was given to each atom to allow the magnetic moment of the system to be well optimized, which was found to be critical to find the ground state total energies of Pt-alloys with magnetic 3d elements. For density-of-state calculations, $15 \times 15 \times 1$ Monkhorst-Pack grid was used. Bader charge calculation is used to support the analysis in this study. In terms of atomic models, Pt/Pt$_3$M(111) structures are used to represent Pt-based bimetallic catalyst. The calculated lattice parameters from those Pt$_3$M bulk structures are used to construct Pt$_3$M(111) surface, resulting in the respective degree of strain to the outermost Pt-skin layers. Lateral strain is applied with respect to the choice of M element in the core part. The core part consists of four layers of Pt$_3$M surface oriented to (111) direction of its bulk unit cell, with bottommost two layers fixed in the bulk equilibrium lattice parameter, other atoms in the supercell are allowed to relax by conjugate-gradient minimization algorithm. Two Pt skin layers are built upon the Pt$_3$M(111) substrates and these are called Pt/Pt$_3$M models. An oxygen atom is placed at the FCC (Face centered cubic) hollow site of the surface, in order to calculate oxygen binding energy and changes in the electronic structure later. For the case of Pt/Au/Pt$_3$M models, a gold monolayer substituted a subsurface of Pt/Pt$_3$M to acquire the qualitative analysis of the effect of a gold subsurface layer on the catalytic system. Details regarding the stability of Au and Pt monolayer can be found in the supplementary material. The two models have similar thickness and identical lateral strain as described in Figure 1. Finally, a set of pure Pt(111) surface models are constructed, with lateral strains identical to the first and the second models with respect to the choice of metallic element. This attempts to understand the effect of pure strain imposed by M elements. By comparing energetic properties such as oxygen binding and segregation energy, along with electronic properties such as d-band center and density-of-states, we find a distinct role of a gold subsurface layer in modifying the oxygen binding interaction and the electronic structure of Pt-based core-shell catalyst.

The oxygen binding energy can be predicted by DFT calculations which proved to be useful in understanding the physicochemical interactions related to catalytic activity. The oxygen binding energy can be calculated by

$$E_b = E_{O/\text{sub}}^{\text{tot}} - E_{\text{sub}}^{\text{tot}} - \frac{1}{2} E_{O_2}$$

(1)

where $E_b$ is the oxygen binding energy, $E_{O/\text{sub}}^{\text{tot}}$ the calculated total energy of the adsorbed oxygen and the catalytic substrate, $E_{\text{sub}}^{\text{tot}}$ energy of catalytic substrate, and $\frac{1}{2} E_{O_2}$ energy of gas phase oxygen molecule divided by half.

We brought all the 3d transition metallic atoms into account, covering from Ni to Sc. We used asymmetric slab models, and the dimensions of supercell models are determined from the bulk lattice parameters of FCC Pt$_3$M phase where one of the four basis atoms is a 3d metal and others are Pt atoms. This resulted in the wide range of geometric strain [compressive $-2.41\%$ (Pt$_3$Ni) to extensive $+0.86\%$ (Pt$_3$Sc)] compared to the pure Pt case. The bulk structures of Pt$_3$M were fully relaxed until the total energy change due to geometric
variation converged below $10^{-4}$ eV per unit cell. Here, we focus on the (111) facet which is known to give the highest catalytic activity for ORR in the strained bimetallic systems, unlike pure Pt surface where the (110) facet is found to be more effective for ORR.

In our previous work, we found alloying with noble metal improved the durability of Pt-based catalyst during the ORR, due to improved resistance to segregation loss of the transition metal from the core. We define the segregation energy ($\Delta E_{\text{seg}}$) as follows:

$$\Delta E_i = E_{\text{tot}}^i - E_0^i,$$

where $E_{\text{tot}}^i$ is the total energy of the atomic model where the segregation of core metallic element toward surface is occurred and $E_0^i$ is the reference state where no segregation is proceeded. Schematic illustration is given in a later section with a representative case of Pt$_3$Ti. The magnitude of the strain, the choice of 3$d$ transition metal elements, and the effect of a gold subsurface layer are the major concerns in the current study.

III. RESULTS AND DISCUSSION

Figure 1 represents the atomic structures of the models used in the current study. The optimized lattice parameters of Pt$_3$M are given in Table I. The ground state lattice parameter of pure Pt is calculated to be 3.97 Å in parallel with other theoretical and experimental work. The use of 3$d$ transition metallic element to substitute one of the basis atoms in Pt FCC lattice resulted in the wide range of lattice parameter: compressive $-2.41\%$ (Pt$_3$Ni) to expansive $+0.86\%$ (Pt$_3$Sc). In an experimental study about Pt-Co bimetallic alloy, X-ray diffraction determined that the Pt-Pt distance was decreased by about 1.9% by the formation of Pt-Co bimetallic alloy due to compressive strain, as in agreement within 0.02 Å with our calculation (2.3% compressive strain for Pt$_3$Co). First, we examined the property of a gold layer as the geometric barrier against the segregation loss of transition metallic component from the bulk (inside) region. A schematic description of the segregation process is shown in Figure 2. The calculated energy differences ($\Delta E_i$) are listed in Table II. At the second segregation step where the transition metallic atom of the bulk (inside) part segregated out to the surface by forming metal-oxygen bonding with the adsorbed oxygen, some of the transition metals showed negative energy change (which indicates that the reaction can be spontaneous). However, all of the systems in the first segregation step showed the positive energetic change (which means endothermic reaction, non-spontaneous) with various magnitude, ranging from 0.15–1.31 eV. Taking into account the Boltzmann temperature scale ($kT$), the magnitude of the non-spontaneity is considerably higher than the thermal energy in reaction temperature at PEM fuel cells. The result also shows that the 3$d$ element with larger atomic radius tends to experience higher energetic penalty during the segregation, e.g., drastic comparison can be found between Ni (0.25 eV) and Sc (1.09 eV) from Table II. The results support the idea that the Au layer may induce the geometric barrier to the segregation loss of M element. For the segregation behavior of Au atoms, there is a theoretical prediction where embedded atomic method (EAM) force field

| TABLE I. Calculated lattice parameters for Pt$_3$M bimetallic alloys. |
|-------------------------|-------------------------------|
| $\text{Pt}_3\text{M}$   | Lattice parameter (Å)        | Percent difference to Pt bulk (%) |
| Pt$_3$Ni                | 3.874                        | -2.41                            |
| Pt$_3$Co                | 3.880                        | -2.26                            |
| Pt$_3$Cu                | 3.894                        | -1.89                            |
| Pt$_3$Fe                | 3.907                        | -1.58                            |
| Pt$_3$Cr                | 3.909                        | -1.51                            |
| Pt$_3$V                 | 3.917                        | -1.31                            |
| Pt$_3$M$_n$             | 3.924                        | -1.14                            |
| Pt$_3$Ti                | 3.946                        | -0.59                            |
| Pt$_3$Sc                | 4.003                        | 0.86                             |
| Pt bulk                 | 3.969                        | ...                              |

FIG. 1. Schematic descriptions of atomic models used in the study: (a) bulk Pt$_3$M, (b) strained Pt(111) surface with adsorbed oxygen, (c) Pt-skin/Pt$_3$M core-shell composite, and (d) Pt-skin/Au-layer/Pt$_3$M composite models are used.

FIG. 2. A schematic description of segregation energy calculations. The calculations examine the energetic difference related to direct substitutive diffusion of the transition metal atoms from the core out to the surface. The positive sign of the vertical axis denotes that the reaction step is unspontaneous.
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TABLE II. The segregation energy as discussed in the text. The positive values indicate that the process is not spontaneous. The transition metals are listed in the order of strains in the Pt$_3$M. The segregation energy increases when transition metallic elements induce less geometric strain the Pt$_3$M compared to pure Pt.

<table>
<thead>
<tr>
<th>Transition metals</th>
<th>$\Delta E_1$ (eV)</th>
<th>$\Delta E_2$ (eV)</th>
<th>$\Delta E_3$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.25</td>
<td>0.37</td>
<td>0.34</td>
</tr>
<tr>
<td>Co</td>
<td>0.55</td>
<td>0.05</td>
<td>0.45</td>
</tr>
<tr>
<td>Cu</td>
<td>0.15</td>
<td>0.40</td>
<td>0.52</td>
</tr>
<tr>
<td>Fe</td>
<td>0.72</td>
<td>0.05</td>
<td>0.31</td>
</tr>
<tr>
<td>Cr</td>
<td>0.78</td>
<td>-0.31</td>
<td>0.42</td>
</tr>
<tr>
<td>V</td>
<td>0.95</td>
<td>-0.91</td>
<td>0.21</td>
</tr>
<tr>
<td>Mn</td>
<td>0.74</td>
<td>0.08</td>
<td>0.45</td>
</tr>
<tr>
<td>Ti</td>
<td>1.31</td>
<td>-0.44</td>
<td>0.32</td>
</tr>
<tr>
<td>Sc</td>
<td>1.09</td>
<td>-0.28</td>
<td>0.35</td>
</tr>
</tbody>
</table>

molecular dynamics (MD) was employed to simulate the segregation behavior in a Pt-Au bimetallic cluster. In the MD calculation, the gold layer tends to be segregated out to the surface in elevated temperature in vacuum condition. However, it is not clear whether the identical viewpoint can be applicable to the oxygen rich environment. As the first step to address this issue, we calculated the segregation energy of subsurface Au atoms under adsorbed oxygen (referred to $\Delta E_3$) in the Pt/Au/Pt$_3$M(111) slab. As shown in Table II, all model surfaces exhibit the non-spontaneity (endothermic $\Delta E_3$) for the Au segregation under the oxygen-adsorbed condition, suggesting that the subsurface Au layer can be stabilized at the oxygen rich condition. Until it becomes clear, there should be additional investigations along this direction employing diverse tools at different scale of the models, e.g., surface alloy modeling, potential energy surface analysis, solvation effect (implicit/explicit) or ab-initio molecular dynamics, and so on.

Also, given that the role of interfacial vacancy is not taken into account in the calculations, this argument is applicable to practices when the concentration of interfacial defect is maintained low by conventional experimental means such as annealing.

In order to understand the effect of a gold subsurface layer on the catalytic activity in ORR, we calculated oxygen binding energy as a primary descriptor of the activity. We can assume that the catalytic activity may be enhanced if the oxygen binding energy falls within the optimal binding energy domain (0.2–0.4 eV lower than that of pure Pt(111)). Benefitting from the use of computational modeling, we separately consider the following major factors that affect the oxygen binding energy: the geometric strain, the presence of Pt$_3$M substrate instead of pure Pt, and the ligand effect originating from the gold subsurface layer. For this purpose, we repeated the same analysis on three different models: Pt$_{str}$(111), Pt/Pt/Pt$_3$M(111), and Pt/Au/Pt$_3$M(111) (see Figure 1).

The results are shown in Figure 3. For the Pt$_{str}$(111) case (here, the ligand contribution of the gold subsurface layer and the transition metal (M) third layer to the activity of Pt skin surface toward oxygen species are decoupled from the strain contribution of Pt$_3$M substrate), the oxygen binding energy monotonically decreased with respect to increasing the degree of the compressive lateral strain. The name of the transition metal elements in the horizontal axis represents the respective strain found in Pt$_3$M. The optimal range of oxygen binding energy (marked as (A) in the figure) is achieved when the relatively smaller 3$d$ transition metals such as Ni and Co are employed, which are the latest 3$d$ transition metals available in the periodic table. Interestingly, Sc shows different behavior compared to other 3$d$ transition metals. Sc is the only element that induces the expansive strain to the Pt surface. It is clear from the result that the compressive geometric strain contributes to lowering the oxygen binding energy; however, this effect can be only harnessed when we employ bimetallic alloy (Pt$_3$M in the study) in the bulk (inside) part, yielding drastic compressive strain.

As we calculate the same property with the models with Pt skin layers on Pt$_3$M substrate [Pt/Pt/Pt$_3$M(111)], the oxygen binding energy becomes slightly more exothermic. These results surprisingly match well with the volcano plot reported in Ref. 23, which puts Co on the top, Ni the next, followed by Fe, V, and Ti. The results from both Pt$_{str}$(111) and Pt/Pt/Pt$_3$M(111) agreed well in parallel with our $d$-band calculation (see supplementary material), where the lower shift in $d$-band center is associated with less exothermic oxygen binding energy. This also shows that the transition metal buried inside Pt atom has nominal effect to the surface-adsorbate interaction.

When it comes to Pt/Au/Pt$_3$M(111) models where a gold subsurface layer is employed, the drastic changes in the oxygen binding energy are observed. There exist the combined effects of the geometric strain, M transition metals, and gold subsurface. About 0.25–0.4 eV range of decrease in the oxygen binding energy is predicted except for Sc, pushing most of the mid 3$d$ transition metals (such as Fe, Cr, V, Mn, and Ti) into the optimal binding energy range. This prediction may be worthy of a thorough investigation since it may allow modifying the oxygen binding interaction with the Pt surface without the extreme degree of compressive strain, which may introduce the novel nano-structuring principle to design of core-shell catalyst.
For more detailed investigation, we calculated various physical properties of Pt/Au/Pt₃M structure including electronic charge transfer (based on Bader charge analysis) and electronic structure calculations. The results suggest that such drastic changes in the oxygen binding energy originate from the substantial modification in the electronic structure of the surface Pt atoms caused by a gold subsurface layer.

First, we analyzed the change in the electronic structure of a gold subsurface layer and a Pt skin layer by comparing the local density of states (LDOS) projected onto the d states of Pt skin surface and Au subsurface atoms with reference to the strained Pt surfaces (see Figure 4). Regardless of the choice of M elements in the bulk (inside) region, the comparison betwen Pt/Au/Pt₃M and Pt₃M(111) demonstrates an important feature about the role of a gold subsurface layer. The gold subsurface atoms mostly occupied the low energy state region. On the other hand, the surface Pt atoms established the skewed Fermi level robustly. The d-bands of the Pt-Au system become rather dispersed throughout the energy axis, resulting in additional complexity to a straightforward analysis by measuring d-band center (see the supplementary material for the calculated d-band center). Still, we find another clue to interpret the origin of changes in the oxygen binding interactions. The occupation levels crossing the Fermi level display the clear comparison between Pt/Au/Pt₃M(111) and Pt₃M(111). In particular, the LDOS near the Fermi level (–0.5 eV < E – Eₐ < 0.5 eV) for the surface Pt atoms in Pt/Au/Pt₃M(111) is drastically decreased when a gold layer is employed in the subsurface, suggesting that the surface Pt atoms affected by the gold subsurface atoms can be less reactive in oxygen adsorption than the Pt₃M(111) case. Note that the higher LDOS near the Fermi level is associated with high reactivity in adsorption process than the lower LDOS case.

The striking modification of d states in Pt skin surface in Pt/Au/Pt₃M(111) may be related to the surface charge polarization by the electron transfer from Au to Pt. Table III shows the electronic charge variation with respect to the neutral valence state population of the pseudo potentials used in the study (which is calculated by the Bader charge analysis). For the Pt/Au/Pt₃M(111) case, we find the increase of electronic charge in surface Pt atoms compared to the corresponding Pt₃M(111) case, implying the fill-up of unoccupied d states and the reduction of LDOS near the Fermi level. This observation is in correspondence with other studies where noble metal is used to substitute Pt in bimetallic ORR catalyst. In a theoretical study with Pt/Pt-Ir-Co catalyst, electronic charge was found to transfer from Ir to Pt-skin, resulting in slightly decreased oxygen binding energy. Interestingly, the compressive strain imposed by Pt₃M substrate also affects the degree of this charge transfer. For example, Sc showed almost no change in the electronic charge of Au, showing relatively smaller

![Image](https://example.com/figure4.png)

**FIG. 4.** The calculated electronic density-of-states of Pt/Au/Pt₃M and Pt₃M(111).

<table>
<thead>
<tr>
<th>Transition metals</th>
<th>Pt/Au/Pt₃M</th>
<th>Pt/Au/Pt₃M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb̅sub</td>
<td>Pb̅surf</td>
</tr>
<tr>
<td>Ni</td>
<td>0.00</td>
<td>0.17</td>
</tr>
<tr>
<td>Co</td>
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<td>0.20</td>
</tr>
<tr>
<td>Cu</td>
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<td>0.18</td>
</tr>
<tr>
<td>Fe</td>
<td>0.07</td>
<td>0.21</td>
</tr>
<tr>
<td>Cr</td>
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<td>0.22</td>
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<tr>
<td>V</td>
<td>0.27</td>
<td>0.24</td>
</tr>
<tr>
<td>Mn</td>
<td>0.16</td>
<td>0.21</td>
</tr>
<tr>
<td>Ti</td>
<td>0.33</td>
<td>0.24</td>
</tr>
<tr>
<td>Sc</td>
<td>0.30</td>
<td>0.23</td>
</tr>
</tbody>
</table>

**TABLE III.** Change in the Bader charge of the Pt-skin in comparison to cases without gold subsurface. The transition metals in the left column are listed in the order of strain. The result shows that with gold subsurface layer, the surface Pt layer accumulates more electronic charge. The relative increase of the accumulated surface electronic charge values is noted in the parenthesis in percentage (unit: electronic charge per layer).
FIG. 5. The projected local density of states are shown in comparisons. An oxygen atom is adsorbed on FCC hollow site of Pt surf in all the models. The Pt atom closest to the oxygen (PtOsurf) is shown separately (solid blue line) from other Pt atoms (PtOsurf, dashed blue line) of the Pt skin.

change in the binding energy. The magnitude of transferred charge does not strictly scale with the change in the oxygen binding energy. Still, we find this charge transfer supports the above results from our electronic structure calculations: the significant reduction of LDOS projected on the d states of Pt skin surface near the Fermi level by a gold subsurface layer.

We further present the nature of the interaction between the adsorbed oxygen atom and the Pt surface layer in Pt/Au/Pt3M(111) system. In Figure 5, the projected LDOS of O-Pt/Au/Pt3Ti structure is shown (here, we only display the Ti metal case as the representative system since other M element cases show the similar behavior of LDOS to the Ti metal case). An oxygen atom is bound to the FCC hollow site at a coverage equivalent to 0.25 monolayer (ML) for pure Pt(111). First, we see the peak of the occupied oxygen 2p states at the low energy state region (−7.5 eV < E − Ef < −6.5 eV) (which is related to the bonding states of O-Pt), while the peak of unoccupied oxygen 2p states at the high energy state region (0 eV < E − Ef < 0.5 eV) (which is linked to the anti-bonding states of O-Pt). Due to inherent limits in the Kohn-Sham solution, the accurate energy levels of the unoccupied states are not guaranteed; however, we do find that the adsorbed oxygen strongly interacts with the Pt 5d states. Second, we find that the high peak of d states of surface Pt atoms near the Fermi level (−1.0 eV < E − Ef < −0.5 eV) [the dotted blue line (PtOsurf)] in the bare Pt/Au/Pt3M(111) system is significantly reduced by the oxygen adsorption onto the Pt surface. Notice the diminishment of peak near the Fermi level for the surface Pt atom connected to the oxygen atom [the solid blue line (PtOsurf)]. This observation indirectly supports the argument, how the electronic occupancy near the Fermi level associates with the oxygen binding behavior. The gold subsurface affects the Pt surface atoms resulting in the distinct variations in the unoccupied state near the Fermi level, and the adsorbed oxygen atom strongly interacts with the high-energy valence states of Pt 5d.

IV. CONCLUSION

In this study, we investigated the effect of a gold subsurface layer as an anti-segregation barrier, at the same time as an electronic structure modifier to Pt3M bimetallic catalyst. We found that the gold subsurface layer increased the electronic charge accumulation at the Pt skin surface layer in Pt/Au/Pt3M(111) system and in turn reduced the LDOS projected onto the d states of Pt skin surface near the Fermi level. As a result, the oxygen binding strength of the Pt skin surface is substantially decreased compared to the Pt/Pt/Pt3M case. Our calculation also shows that the high peak of d states of surface Pt atoms near the Fermi level (−1.0 eV < E − Ef < −0.5 eV) in Pt/Au/Pt3M(111) system is closely associated with oxygen adsorption process, suggesting that the occupancy of LDOS near the Fermi level plays an important role in determining the surface activity toward oxygen species. In addition, the presence of gold subsurface layer was predicted to induce the energetic barrier to the segregation loss of bulk 3d alloying components, which can enhance the durability of Pt3M based catalytic system at oxygen reduction condition in fuel cell devices. The study highlights that the nanostructure control of near surface region by introducing a hetero gold subsurface atoms may provide a promising strategy to additionally modify the activity of Pt skin surface toward oxygen species (where the utilization of geometric strain already reaches its practical limit) and enhance the stability of Pt surface in ORR condition alleviating the delicate control of a novel catalyst design.

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38See supplementary material at http://dx.doi.org/10.1063/1.4005919 for the stability of Au and Pt monolayers and calculated d-band centers.