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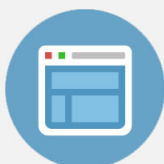
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## Communication: Enhanced oxygen reduction reaction and its underlying mechanism in Pd-Ir-Co trimetallic alloys

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Based on a combined density functional theory and experimental study, we present that the electrochemical activity of Pd<sub>3</sub>Co alloy catalysts toward oxygen reduction reaction (ORR) can be enhanced by adding a small amount of Ir. While Ir tends to favorably exist in the subsurface layers, the underlying Ir atoms are found to cause a substantial modification in the surface electronic structure. As a consequence, we find that the activation barriers of O/OH hydrogenation reactions are noticeably lowered, which would be mainly responsible for the enhanced ORR activity. Furthermore, our study suggests that the presence of Ir in the near-surface region can suppress Co out-diffusion from the Pd<sub>3</sub>Co substrate, thereby improving the durability of Pd-Ir-Co catalysts. We also discuss the relative roles played by Ir and Co in enhancing the ORR activity relative to monometallic Pd catalysts. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4837176>]

Polymer electrolyte membrane (PEM) fuel cells also known as proton exchange membrane fuel cells have received much attention in recent years as a promising alternative for power generation, especially for automotive applications. They use hydrogen and oxygen to generate electricity through an electrochemical process which involves the oxygen reduction reaction (ORR:  $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ) at the cathode; protons and electrons are supplied from the anode where hydrogen is oxidized to protons.<sup>1</sup> Currently, platinum (Pt) and Pt-based catalysts are most widely used to speed up the sluggish ORR that limits the efficiency of low temperature PEM fuel cells. However, Pt is expensive and scarce, drawing much interest in developing non-Pt catalysts.<sup>2</sup>

Palladium (Pd) is considered as a viable replacement for Pt because it is more abundant and less expensive, and also has a higher CO tolerance, in addition to showing similar catalytic behavior and long term durability in acidic media.<sup>3</sup> While the catalytic activity of Pd towards ORR is lower than that of Pt,<sup>4-6</sup> recent investigations have demonstrated that alloying Pd with some transition metals (such as Co, Fe, Ni) can lead to a significant improvement in the catalytic activity.<sup>7,8</sup> However, Co-like metals can be dissolved out into the electrolyte under PEM fuel cell operating conditions, thereby causing catalyst degradation.<sup>9</sup> It is, therefore, imperative to find an alternative way to improve the stability of Pd-based alloy catalysts under acid conditions, while maintaining their high activity for the ORR. This issue can be addressed by adding third elements with high acid stability.

In this work, we examined a ternary alloy constituting Pd, Co, and Ir. Iridium (Ir) has a high reduction potential of 1.16 V above a typical operating fuel cell voltage (~0.7 V); hence, we anticipated that the addition of Ir might result in an improvement in the acid stability of Pd-Co alloy catalysts. It has been experimentally known that the Pd-Co alloy is completely miscible over the whole composition range, while Pd and Ir are partially miscible in a limited range of Ir composition (<15 wt. %). Therefore, in this work, we considered Pd<sub>3</sub>Co as the substrate for the ternary alloy and alloyed it with a small amount of Ir; this would be also a reasonable choice given the high cost of Ir.

The calculations reported herein were performed on the basis of spin polarized density functional theory (DFT) within the generalized gradient approximation (GGA-PW91),<sup>10</sup> as implemented in the Vienna *Ab initio* Simulation Package (VASP).<sup>11</sup> The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between ion cores and valence electrons. An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigenfunctions. For the Brillouin zone integration, we used a (5 × 5 × 1) Monkhorst-Pack mesh of *k* points to determine the optimal geometries and total energies of systems examined, and increased the *k*-point mesh size up to (10 × 10 × 1) to reevaluate corresponding electronic structures. Reaction pathways and barriers were determined using the climbing-image nudged elastic band method<sup>12</sup> with eight intermediate images for each elementary step. A surface is modeled using a slab supercell that consists of a rectangular 2 × 2 surface unit cell with five atomic layers each of which contains 4 atoms, unless stated otherwise. The slab is separated from its periodic images in the vertical direction by a vacuum space corresponding to seven atomic layers. While

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the lower two layers are fixed at corresponding bulk positions, the upper three layers are fully relaxed using the conjugate gradient method until residual forces on all the constituent atoms become smaller than  $5 \times 10^{-2}$  eV/Å. The lattice constant for bulk Pd is predicted to be 3.95 Å, which is virtually identical to previous DFT-GGA calculations and also in good agreement with the experimental value of 3.89 Å.

We first looked at an energetically preferred location for Ir in the near-surface region of Pd<sub>3</sub>Co(111) by calculating the total energy variation as a function of Ir layer location. At least the top two layers are found to be energetically unfavorable for Ir; hence, two Ir layers are placed in the second and third subsurface layers. To see more clearly the effect of Ir in the subsurface layers on the Pd surface reactivity, we consider the Pd/Pd/Ir/Ir/Pd<sub>3</sub>Co(111) system (hereafter Pd-Ir-Co system) by assuming that Co atoms were leached out from the two overlayers; the real structure in the near surface region could be more complex, but we think the simple model is physically reasonable and can be sufficient to provide important insight into the effects of Ir and Co on the catalytic activity of the Pd-Ir-Co ternary alloy, as discussed later.

Next, we examined how the presence of Ir layers affects Co out-diffusion to the surface from the Pd<sub>3</sub>Co substrate. Figure 1 shows the total energy variation as a function of Co atom location for the Pd-Ir-Co system, with comparison to the Pd/Pd/Pd/Pd/Pd<sub>3</sub>Co(111) (hereafter Pd-Co) system. Here, we used seven-layer slabs, in each of which the bottom three layers are Pd<sub>3</sub>Co. For each system, the reference energy is set to zero. The Co atom in the 5th layer is swapped with an atom in one of the layers above it and the energy is calculated. For example, on swapping Co in the 5th layer with Ir in the 4th layer, the energy increase in the Pd-Ir-Co system is predicted to be 0.05 eV. This value is higher than the corresponding energy increase in the Pd-Co system (where Co is swapped with Pd in the 4th layer). Similarly, the energy of Pd-Ir-Co with Co on the surface ( $\Delta E = 0.54$  eV) is significantly higher compared to the Pd-Co case ( $\Delta E = 0.2$  eV). The results suggest that the out-diffusion of Co can be significantly suppressed by the existence of Ir in the subsurface layers, thereby improving the durability of Pd-Ir-Co alloys.

Figure 2 shows the electron density of states (DOS) projected onto the surface atoms of Pd-Ir-Co and pure Pd(111);

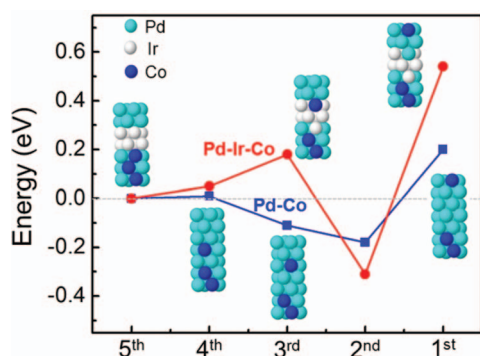


FIG. 1. Predicted energy variation as a function of Co atom location for Pd/Pd/Ir/Ir/Pd<sub>3</sub>Co(111) (indicated as Pd-Ir-Co) and Pd/Pd/Pd/Pd/Pd<sub>3</sub>Co(111) (Pd-Co) systems. 1st indicates the presence of a Co atom in the surface layer, and the Co atom is subsequently swapped with a Pd or Ir atom underneath (2nd–5th).

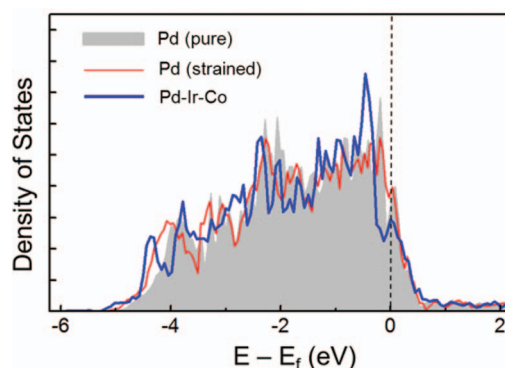


FIG. 2. Electron density of states projected onto surface Pd atoms in three different systems indicated.

the Fermi level is set at zero eV. The comparison demonstrates how the surface electronic structure is modified by the presence of the underlying Ir layers and the compressive strain caused by the Pd<sub>3</sub>Co(111) substrate. Note that the calculated lattice parameter of Pd<sub>3</sub>Co ( $\approx 3.88$  Å) is smaller than that of Pd ( $\approx 3.95$  Å), imposing compression on the Pd surface layer. The compressive strain may lead to an increase in the *d*-orbital overlap, which in turn broadens the *d*-valence band while lowering its average energy. Our previous DFT study<sup>13</sup> shows that the chemical effect of Co tends to be restricted to the first subsurface in the Pd/Pd<sub>3</sub>Co system; this may suggest that, in the Pd-Ir-Co case, the Pd<sub>3</sub>Co substrate merely acts like a strain inducer while the presence of Co has no significant effect on the surface electronic structure. In order to decouple the strain effect induced by the Pd<sub>3</sub>Co substrate from the Ir contribution, we also plot the DOS of the surface atoms of 1.77% compressively strained Pd(111) (corresponding to Pd<sub>3</sub>Co with respect to pure Pd). Under compression, as expected, the DOS on surface Pd atoms becomes somewhat wider, but no significant change near the Fermi level. For the Pd-Ir-Co system, there is a noticeable reduction in the DOS peak intensity near the Fermi level and the extent of downshift in energy is more than the strained Pd(111) case; the calculated *d*-band centers for pure Pd, strained Pd, and Pd-Ir-Co are  $-1.41$  eV,  $-1.45$  eV, and  $-1.58$  eV, respectively. The results suggest that Ir atoms in the subsurface layers, besides the strain effect, would play an important role in modifying the surface electronic structure of the Pd-Ir-Co alloy.

We further examined how the surface binding strengths of isolated O, OH, and H are affected by the alloying-induced modification of the surface electronic structure; our calculation results are summarized in Table I. The binding energy

TABLE I. Calculated adsorption energies (in eV) of O, OH, and H atoms in monometallic Pd(111) (pure and strained) and Pd-Ir-Co systems.

	O	OH	H
Pd-Ir-Co	4.49	2.40	2.72
Pd (strained)	4.64	2.50	2.76
Pd (pure)	4.74	2.55	2.79

TABLE II. Calculated total energy changes ( $\Delta E$ ) and activation barriers ( $E_a$  in parenthesis) for O/OH hydrogenation and O<sub>2</sub> scission reactions in monometallic Pd(111) (pure and strained) and Pd-Ir-Co systems. All energy values are given in eV.

	(A) O <sub>2</sub> → O + O	(B) O + H → OH	(C) OH + H → H <sub>2</sub> O(g)
Pd-Ir-Co	-1.37 (0.88)	-0.27 (0.94)	-0.39 (0.64)
Pd (strained)	-1.45 (0.89)	-0.18 (0.97)	-0.25 (0.66)
Pd (pure)	-1.58 (0.82)	-0.10 (1.02)	-0.17 (0.74)

( $E_b$ ) is given by:  $E_b = E_X + E_M - E_{X/M}$ , where  $E_X$ ,  $E_M$ , and  $E_{X/M}$  represent the total energies of the gas phase X (X = O, OH, H), the slab, and the X/slab system, respectively. The binding energies of O/OH/H in the Pd-Ir-Co system are predicted to be lower by 0.25/0.15/0.07 eV than those on Pd(111). As demonstrated earlier, the surface electronic structure of Pd-Ir-Co can be modified by a combination of the compressive strain caused by the Pd<sub>3</sub>Co substrate and the Ir atoms in the subsurface layers. Given that, the noticeable binding energy difference between Pd-Ir-Co and strained Pd(111) may imply that the presence of subsurface Ir would have a large impact on the surface reactivity.

Next, as summarized in Table II, we calculated the total energy changes ( $\Delta E$ ) and activation barriers ( $E_a$ ) for (A) O–O bond scission [O<sub>2</sub> → O + O], (B) O hydrogenation [O + H → OH], and (C) OH hydrogenation [OH + H → H<sub>2</sub>O(g)] on the Pd-Ir-Co surface, and compared the results with those on the unstrained/strained Pd(111) surfaces. Although the ORR is a complex process and its detailed mechanisms still remain under debate, the comparisons of the reaction energetics would give important insight into the activity of different catalyst surfaces toward the ORR. Perhaps, O<sub>2</sub> hydrogenation [O<sub>2</sub> + H → O – OH] and subsequent O–O bond cleavage [O – OH → O + OH] would also occur, but their relative contributions to the H<sub>2</sub>O formation kinetics are likely less important than the aforementioned elementary reactions, particularly on the Pd surfaces considered.

For the O–O scission reaction, the activation barrier of 0.88 eV on the Pd-Ir-Co surface is somewhat higher than 0.82 eV on the pure Pd surface, but about the same as (or even slightly lower than) 0.89 eV on the strained Pd surface. This suggests that the kinetics of O–O scission can be affected mainly by the compressive surface strain which causes an increase in the activation barrier.

For the O/OH hydrogenation reactions, our calculations predict a substantial reduction in the activation barriers on Pd-Ir-Co ( $E_a = 0.94/0.64$  eV), compared to pure Pd ( $E_a = 1.02/0.74$  eV). Given the relatively higher barriers on strained Pd ( $E_a = 0.97/0.66$  eV), we can also expect that the subsurface Ir layers, along with the compressive surface strain, play an important role in promoting the hydrogenation of O and OH in the Pd-Ir-Co system. The notable enhancement in O/OH hydrogenation is expectably related to the change of relative binding strengths of reaction intermediates (O/OH/H) when alloying Pd with Ir and Co. As displayed in Table I, the OH binding strength on Pd-Ir-Co is reduced by 0.15 eV compared to that on pure Pd, which is less than

0.29 eV for the reduction of O binding energy [4.74 eV (pure Pd) → 4.49 eV (Pd-Ir-Co)]; a reduction is also observed in the H binding energy, i.e.,  $E_b(\text{H}) = 2.79$  eV (pure Pd) and 2.72 eV (Pd-Ir-Co). As a result, for the O + H → OH reaction, there is an increase of potential energy in the reactant side (O + H) compared to the product side (OH), leading to the enhanced exothermicity in O hydrogenation. Similarly, for the OH + H → H<sub>2</sub>O(g) reaction, the reduced binding strengths of OH and H on Pd-Ir-Co contribute to the increase of potential energy in the reactant side and consequently results in the enhanced exothermicity in OH hydrogenation.

From the above results, we see that adding Ir to Pd<sub>3</sub>Co may contribute to lowering substantially the activation barriers of O/OH hydrogenation reactions, at the cost of a relatively smaller increase in the O–O scission barrier. Considering that the hydrogenation reactions can be rate controlling in the cathode, we think it is reasonable to expect that Ir-modified Pd<sub>3</sub>Co alloy catalysts would lead to an enhancement in the ORR activity. Furthermore, the presence of Ir in the near-surface region is predicted to suppress Co out-diffusion from the Pd<sub>3</sub>Co substrate, which will in turn improve the catalyst durability, as shown earlier (see Fig. 1).

Motivated by the theoretical prediction, we experimentally examined the ORR activities of carbon-supported Pd, Pd<sub>3</sub>Co, and Pd<sub>3</sub>Ir<sub>0.6</sub>Co nanoparticles under actual fuel cell operation conditions. Admittedly, it might be practically impossible to synthesize alloy nanoparticles that provide the exact same surface structures as the strained Pd(111) and Pd-Ir-Co systems examined theoretically. However, this experiment can offer important insight into the effect of the ternary Pd-Ir-Co alloying. Details regarding the synthesis and electrochemical characterization of nanoparticles can be found in the supplementary material<sup>14</sup> and our recent paper.<sup>15</sup>

Figure 3 shows a comparison of ORR catalytic performance between the Pd-based nanoparticles. The measured operating voltage is found to be highest for Pd<sub>3</sub>Ir<sub>0.6</sub>Co, followed by those for Pd<sub>3</sub>Co and Pd. In addition, as presented in the inset, the higher open circuit voltage for Pd<sub>3</sub>Ir<sub>0.6</sub>Co indicates a reduction in the ORR overpotential as compared to the Pd<sub>3</sub>Co and Pd cases. The experimental results clearly support the theoretical prediction that the ORR activity can be enhanced by

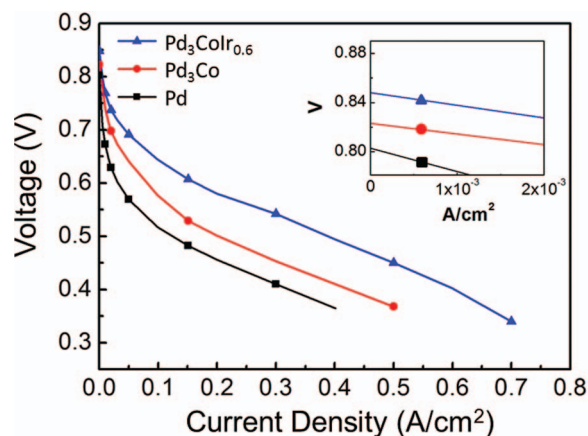


FIG. 3. PEM fuel cell performance of monometallic Pd, bimetallic Pd-Co, and trimetallic Pd-Ir-Co nanocatalysts for the ORR in the cathode. The inset shows a zoom-in view near the open circuit voltage.



adding Ir and Co to Pd; the ternary Pd-Ir-Co catalyst exhibits an even higher enhancement in ORR activity than the binary Pd<sub>3</sub>Co catalyst.

We also calculated Tafel slopes for the Pd, Pd<sub>3</sub>Co, and Pd<sub>3</sub>Ir<sub>0.6</sub>Co catalysts based on the Tafel plots (see the supplementary material<sup>14</sup>). For the current densities ranging from 0.01 to 0.1 A/cm<sup>2</sup>, the Tafel slope for Pd<sub>3</sub>Ir<sub>0.6</sub>Co is estimated to be 114 mV/dec, which is smaller than 142 mV/dec (for Pd<sub>3</sub>Co) and 146 mV/dec (for Pd); this also implies the enhanced ORR activity by the ternary alloying. In particular, the sizable slope difference between Pd<sub>3</sub>Ir<sub>0.6</sub>Co and Pd<sub>3</sub>Co highlights the important role played by Ir in the enhancement of ORR activity.

In summary, this communication reports ORR activity enhancement of Pd-Ir-Co alloy catalysts relative to monometallic Pd and Pd-Co alloy catalysts, and possible mechanisms for the ORR promotion based on a combined DFT and experimental study. We considered Pd<sub>3</sub>Co as the substrate and alloyed it with a small amount of Ir, mainly because of the high cost of Ir. According to our DFT calculations, Ir energetically prefers to remain in the second sub-surface layer and below; hence, the Pd-Ir-Co alloy was mimicked using the Pd/Pd/Ir/Ir/Pd<sub>3</sub>Co(111) slab model (the rationale behind is explained in the text). The near-surface Ir layers are found to substantially suppress Co out-diffusion from the Pd<sub>3</sub>Co substrate, which may contribute to improving the durability of Pd-Ir-Co catalysts. In addition, our calculations show that the Pd-Ir-Co ternary alloying leads to a noticeable reduction in the DOS peak intensity near the Fermi level and a downshift in the *d*-valence band center, compared to the monometallic Pd(111) surface. Due to the modification of surface electronic structure, the binding energies of O and OH on the Pd-Ir-Co alloy are predicted to be lower by 0.25 eV and 0.15 eV, respectively, than those on pure Pd(111). Moreover, we find that adding Ir to Pd<sub>3</sub>Co causes a substantial reduction in the activation barriers of O/OH hydrogenation reactions, while the O–O scission barrier only slightly increases. This

can explain the enhanced ORR activity of Ir-modified Pd<sub>3</sub>Co alloy catalysts, considering that the hydrogenation reactions are the most likely rate controlling steps in the cathode. Our study highlights that the alloying effect is attributed to the synergetic interplay between the surface electronic structure modification due to underlying Ir atoms and the compressive strain caused by Pd<sub>3</sub>Co substrate. This finding may suggest the possibility of maximizing the ORR activity of Pd-based catalysts by alloying with multiple elements.

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<sup>14</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4837176> for the synthesis and electrochemical characterization of catalysts.

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