Combinatorial Screening of Highly Active Pd Binary Catalysts for Electrochemical Oxygen Reduction

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ABSTRACT: Electro-catalysts omitting platinum are of interest to reduce the cost of fuel cells. The development of non-Pt alloys for this purpose would require a large number of experiments. Palladium-based bimetallic electro-catalysts using eight different metals were computationally evaluated for the oxygen reduction reaction (ORR) and were made and tested in acidic media using combinatorial methods . A Pd−Co alloy showed the closest oxygen adsorption energy to platinum in simple theoretical model calculations, suggesting the highest ORR activity. This prediction was confirmed experimentally, suggesting that the single parameter of oxygen adsorption energy can be a useful guide to developing non-Pt oxygen reduction catalysts in the future.

KEYWORDS: *thermodynamic guideline, combinatorial research, oxygen reduction reaction, fuel cells, non-Pt catalysts*
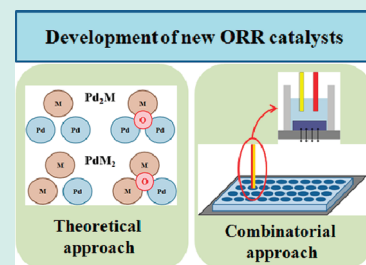
1. INTRODUCTION

The need for cheap, abundant, and highly active electro-catalytic oxygen reduction materials to substitute for Pt in polymer electrolyte membrane fuel cells (PEMFCs) has been a challenging area of research, where many of the improved catalysts reported in the literature are mainly platinum-based materials that are still costly. Some binary Pt−M (M = metal) catalysts have been shown to have greater oxygen reduction reaction (ORR) activity in acid media than pure Pt.[1−3] Two mechanisms have been proposed to explain the enhanced catalytic activities of bimetallic surfaces.[4,5] One is a direct bifunctional mechanism where the two metals play separate but synergetic roles in the overall catalysis cycle. For example, one metal may be used for easy adsorption of O_2 and the other metal is used for its chemical transformation into water. The other is an indirect mechanism, in which the second metal in an alloy alters the electronic structure of the primary metal to improve catalytic activity. However, detailed experimental mechanisms of oxygen reduction and the nature of improved metal alloy catalysts remain unclear. Although advanced nanostructured platinum catalysts have been developed,[6,78,9] platinum-based catalysts are not economical for routine commercial applications in fuel cells and, therefore, less expensive alternative materials are essential. Here, we provide an evaluation of alloys of palladium, which is approximately one-third the cost and approximately one-third as effective in ORR compared to Pt, when the pure metals are used alone.[10]

Recent reports have shown the improved ORR activity for various Pd-based catalysts, such as Pd−Co, Pd−Ni, Pd−Fe, and Pd−Mo compositions.[11−15] Metal@Pd core−shell structures were also suggested as a way to improve catalytic activity because of increased electrochemically active surface area and changes in the electronic configuration of palladium.[16,17] To understand these palladium-based catalysts, factors which affect

the oxygen reduction activity have been studied experimentally. For example, Zhang et al. changed the lattice parameter of Pd and the degree of alloying of Co with Pd using the heat treatment method and demonstrated improved the ORR activity,[11] whereas Adzic et al. changed the atomic percentage of Fe to Pd lattice parameters.[14] Some selected Pd-alloys have been reported to have an improved ORR activity as briefly summarized above, but the mechanistic reasons for this improvement are not clearly known. It has been suggested that different lattice parameters modify the electronic structure of palladium by changing the orbital overlap, which in turn downshifts the d-band center.[18]

Combinatorial methods were was introduced to the area of electrochemistry more than a decade ago,[19] and various methods have been developed since then for rapid and efficient studies of new fuel cell catalysts. Most library syntheses have been accomplished by sputtering, electro-deposition, or physical vapor deposition methods.[21−23] For catalytic evaluation of such libraries, high-throughput tools, such as optical screening, scanning electrochemical microscopy, multielectrode half cells, and multielectrode fuel cells have been introduced.[24−28] In a previous study, we developed a reductive library synthesis method for the preparation of anode electrode materials for the direct methanol fuel cell (DMFC).[20] The library was analyzed by a multielectrode half-cell method and exhibited good reliability.[20] We report here the use of the same method to find a Pd-based catalyst that has a higher ORR activity than Pt-based ones in fuel cell applications.

From the theoretical point of view, Norskov and co-workers suggested that the trends in the oxygen reduction activities of

many different metals are related to their oxygen adsorption energies.[29] Bard and co-workers suggested a simple thermodynamic model to interpret enhanced activities upon alloying.[30] By incorporating transition metals, such as Co and Ni, to Pd they predicted an improved dissociative adsorption of O_2 (eq 1) onto the latter metals and easy electro-reduction of adsorbed oxygen (eq 2) with migration from incorporated metal to Pd. However, the latter suggestion was concerned with the thermodynamics of bulk metal oxides, which are different from metallic alloy surfaces. Balbuena independently advanced the thermodynamic guideline for the design of ORR catalysts.[31] Bimetallic combinations with one kind of metal which favors the formation of $M-OOH_{ads}$ bonds and another kind which favors the reduction of $M-O_{ads}$ species was suggested to enhance the ORR activity of existing pure catalysts with a single component.

$$2M + O_2 \leftrightarrow 2MO \tag{1}$$

$$2MO + 4H^+ + 4e^- \leftrightarrow 2M + 2H_2O \tag{2}$$
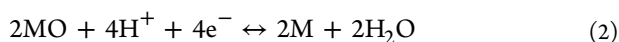
Combined theoretical and experimental studies of Pt and Pd metal alloys have been reported by Norskov et al.[32] and Su et al,[33] respectively. However, their slab-model computation method is too time-consuming to calculate many different systems. We focused on calculated atomic oxygen adsorption energies as an indicator of ORR activity of Pd-alloys that have not been studied previously. For this purpose, we tested the simple trimer cluster model to approximate metal alloy surfaces and calculate oxygen adsorption energies in a simple and reliable manner.

2. EXPERIMENTAL PROCEDURES

2.1. Theoretical Method. Binary combinations of Pd and eight atoms (Ru, Au, Ir, Mo, Fe, Co, Ni, and V) are considered in this study. The pure Pt cluster is also considered for comparison. Although the slab model is more realistic than simpler cluster models that sometimes suffer from edge effects, cluster models have advantages of simplicity and, hence, the possibility of using more accurate quantum chemical methods when needed. As the simplest model system for the alloy surfaces, here we use a trimer model. The trimer model has been used to study the formation of larger clusters and to understand the behavior of metals, such as electronic states, spin−orbit coupling, and intricate d-orbital bonding.[34−36] Of course, more sophisticated models would be needed for quantitative absolute energetics, but the primary purpose of using trimers in this study is to obtain the correct relative trends qualitatively. As we will show in the Results section, this simple trimer model reproduces the experimental trend quite well.

We consider two kinds of binary systems, Pd_2-M and $Pd-M_2$, as a model for palladium-rich alloys and palladium-deficient alloys as shown in Figure 1. Quantum chemical density functional (B3LYP) calculations are performed with the Lanl2DZ effective core potential (ECP) basis for metal elements and aug-cc-pVDZ for oxygen. The main thermodynamic quantity we calculate is the adsorption energies (AE) of oxygen onto the Pd−Pd−M or Pd−M−M trimers as calculated by eq 3.[37]

$$AE = 2E(cluster - O_{ads}) - E(cluster) - E(O_2) \tag{3}$$

The rate determining step of ORR on the metal surface is not clear. In a previous study, however, the first electron transfer to
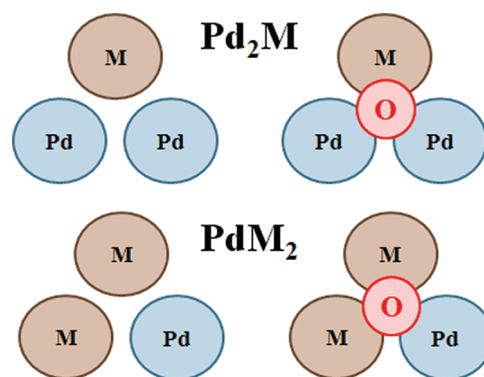

Figure 1. Description of the trimer model.

adsorbed oxygen was mainly related to the overpotential of ORR.[29] Additionally, adsorption of oxygen and the desorption of intermediate oxygen species on the surface have been considered as one of the most important factors for oxygen reduction activity. Hence, oxygen adsorption energies are calculated for theoretical consideration in this study. The Q-CHEM electronic structure package is used for all computations.

2.2. Combinatorial Approach. The Pd−M binary library is synthesized by the method described in a previous study.[20] The compositions of the library are shown in Figure 2. All
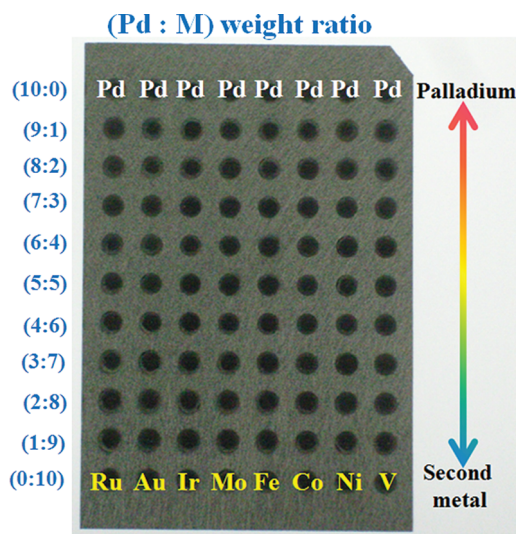

Figure 2. Pd−M compositions of the prepared library.

carbon spots are prepared by spraying carbon ink on a polytetrafluoethylene (PTFE) treated carbon paper. Then, the metal precursor solutions are deposited on the carbon spots. After being dried at room temperature, the library is reduced by $NaBH_4$ solution. The reduced library is washed with deionized (DI) water. The total loading of the metals is adjusted to 31 wt. %. All metal ratios in combinatorial results are shown in weight basis.

The library compositions are characterized by a multi-electrode half-cell method.[20,38] The prepared library is used as a working electrode. A platinum wire and an Ag/AgCl electrode (BAS Co., Ltd., MF2052 RE-5B) are used as the counter and reference electrodes, respectively. To separate electrolyte and measure ORR activity of each composition, PTFE mask which

Table 1. Theoretical Results for Oxygen Adsorption Energy of Pd_2-M and $Pd-M_2$ Trimer Systemi=GH>MGTCRCOa:5DIjST6^fDVnbiioVlaSLSk26JE]:D`aQkR1m8MOkgga^kkPTfRfo2;j\JI^N??6I8>4`L^MP=Jm\?>4l8EmQ38G27N]J@>_O0T`VA8m:bGK78^c^>;MFl`n=gVa[nVU2IT9_O^84ZgN_63DkjY1o`h]E9dYgSMAnZlM1_X157UNMS?JRaLT;U;YSZ4;kNM?A0I212?ZLE>i@Sb`mSh?W?NlSA:bETSBDkD0ie=:QME>@Udj]Um[i\::a^MlgL:eeW5:OWmL5PVc]FfQJV==INfQeTc[◆◆0

	adsorption energy (eV)							
	Au	Ir	Co	Fe	Ru	Mo	Ni	V
Pd_2-M	−0.15	−1.06	−1.49	−2.03	−2.74	−3.37	−4.40	−6.18
$Pd-M_2$	1.57	−1.86	−2.26	−2.50	−2.85	−3.86	−4.65	−8.52

Pt_3 −1.44 (reference $Pt_{(111)}$: −1.64,[33] −2.03[36]) Pd_3 −1.72 (reference $Pd_{(111)}$: −1.76,[33] −2.18[36])

has 88 holes with 5 mm diameter and 10 mm depth is used. The counter and reference electrodes are put in each hole and the ORR activity measurement is performed. After measuring one composition, both electrodes are moved to the next composition. The ORR activities are measured three times by potential sweep from 1.0 to 0.6 V (vs reversible hydrogen electrode (RHE)) at a scan rate of 5 mV s^{-1}. The current densities of the library compositions are compared at 0.7 V in terms of ORR activity. Oxygen-saturated 1 M perchloric acid is used as an electrolyte. All potentials in this paper are converted to the RHE scale.

Surface composition and adsorption energy of Pd for Pd−M spots (Pd/M = 8:2 wt %) are analyzed by X-ray Diffraction spectroscopy (XRD) and X-ray photoelectron spectroscopy (XPS).

3. RESULTS AND DISCUSSION

3.1. Caculated Oxygen Adsorption Energy of Pd Binary Catalysts by a Trimer Model. All theoretical results are listed in Table 1. We first consider the oxygen adsorption energies of pure metals using the trimer cluster models, Au_3, Pt_3, Pd_3, Cu_3, Ni_3, and V_3. In Figure 3, the experimental
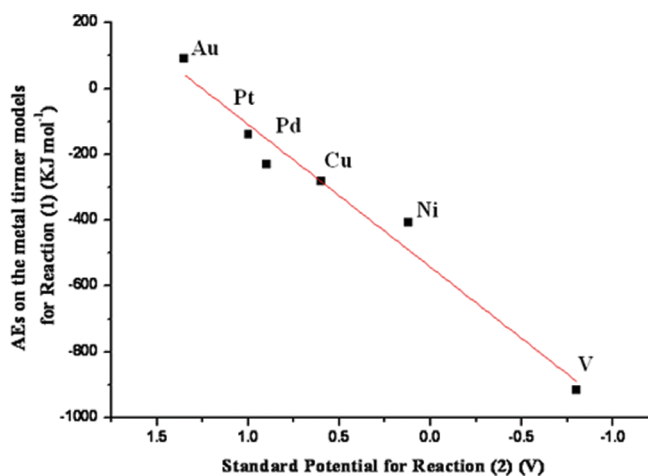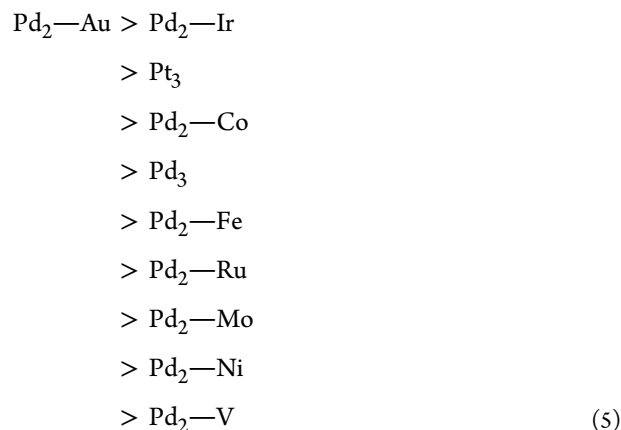

Figure 3. Graph of the AEs for eq 1 versus the standard potential for eq 2.

standard potentials for the reaction in eq 2 are plotted as a function of the calculated AE.[39,40] The plot shows a linear relationship between the standard potential for eq 2 and the calculated AE of eq 1, which is consistent with that in ref 30. This means that the calculated AEs from the trimer model show the same trend as the experimental Gibbs free energy of reaction for eq 1, and the trimer model yields reasonable results. The AEs are, however, different from the results of Norskov et al. (Au, 2.75 eV; Pt, 1.57 eV; Pd, 1.53 eV; Cu, 1.2 eV; Ni, 0.34 eV), since in refs 29 and 31, they used a different definition of the oxygen adsorption reaction, namely

$$H_2O + * \rightarrow O* + H_2 \qquad (4)$$

where * represents an adsorption site on the surface. Since the main source of atomic oxygens in the cathode in an experimental setup is gaseous O_2, we instead used eq 1 as a definition of the oxygen adsorption energy, as in refs 30 and 32. It is encouraging that the oxygen AEs for Pt_3 and Pd_3 calculated here show relative energies similar to previous slab calculations,[33,41] which suggests that a simple trimer cluster might serve as a reasonable qualitative model for metal alloy surfaces as well. Thus, calculated AEs of Pd−M alloys are tabulated in Table 1. We considered two kinds of binary systems, Pd_2-M and $Pd-M_2$, as a model for palladium-rich and palladium-poor alloys, respectively. In the case of the Pd_2-M trimer system, the magnitude of the AE has the following order:

$$Pd_2-Au > Pd_2-Ir$$
$$> Pt_3$$
$$> Pd_2-Co$$
$$> Pd_3$$
$$> Pd_2-Fe$$
$$> Pd_2-Ru$$
$$> Pd_2-Mo$$
$$> Pd_2-Ni$$
$$> Pd_2-V \qquad (5)$$

The Pd_2-Co binary system (AE = −1.49 eV) shows the binding energy that is closest to the platinum trimer (AE = −1.44 eV) among the ones considered in this study. On the right side of Pt in eq 5, the binary system thermodynamically favors the M−O bonding while those in the left side of Pt have the opposite performance, which means that they favor the desorption of the oxygen on the surface. Apparently, the high ORR activity is related to a suitable oxygen adsorption energy. We show a volcano relation between the oxygen adsorption energy and the oxygen reduction activity as suggested by Norskov et al.[29] Theoretically, therefore, the Pd−Co binary composition appears to be the most promising catalyst tested in the present study. The Bard group also recently reported a thermodynamic guideline for the design of electrocatalysts for the ORR with Gibbs free energy for eq 1 and the standard reduction potential for eq 2.[39] In the case of $Pd-M_2$ trimer system, the oxygen AE of binary compositions has a larger deviation than that of Pt. The decreasing order of the AE in $Pd-M_2$ is

Table 2. Combinatorial Results of ORR Activity (Normalized Pd Mass Activity) for Pd−M Library

Au	Ir	Co	Fe	Ru	Mo	Ni	V	(Pd : M)
- 2.55 (Pd spot)								(10 : 0)
-3.29 (- 0.36)	-2.85 (- 0.31)	-3.32 (- 0.36)	-3.16 (- 0.35)	-3.15 (- 0.35)	-2.58 (- 0.29)	-2.67 (- 0.30)	-2.52 (- 0.28)	(9 : 1)
-1.42 (- 0.18)	-2.06 (- 0.26)	-2.86 (- 0.36)	-2.81 (- 0.35)	-2.56 (- 0.32)	-1.61 (- 0.20)	-1.51 (- 0.19)	-1.21 (- 0.15)	(8 : 2)
-1.29 (- 0.18)	-1.57 (-0.22)	-2.67 (-0.38)	-2.64 (-0.38)	-1.61 (-0.23)	-1.51 (-0.22)	-1.34 (-0.19)	-1.57 (-0.22)	(7 : 3)
-1.46 (- 0.21)	-1.78 (-0.29)	-1.68 -(-0.28)	-1.34 (-0.22)	-1.25 (-0.21)	-1.21 (-0.20)	-1.42 (-0.24)	-1.13 (-0.19)	(6 : 4)
-0.80 (- 0.24)	-1.26 (-0.25)	-0.71 (-0.14)	-0.78 (-0.16)	-1.19 (-0.24)	-0.53 (-0.11)	-0.52 (-0.10)	-0.58 (-0.12)	(5 : 5)
-0.62 (-0.16)	-0.87 (-0.22)	-0.51 (-0.13)	-0.45 (-0.11)	-0.79 (-0.20)	-0.42 (-0.11)	-0.52 (-0.13)	-0.47 (-0.12)	(4 : 6)
-0.62 (- 0.21)	-0.54 (-0.18)	-0.67 (-0.22)	-0.33 (-0.11)	-0.94 (-0.31)	-0.63 (-0.21)	-0.33 (-0.11)	-0.42 (-0.14)	(3 : 7)
-0.45 (- 0.23)	-0.53 (-0.25)	-0.52 (-0.25)	-0.27 (-0.14)	-1.12 (-0.56)	-0.30 (-0.15)	-0.21 (-0.11)	-0.35 (-0.18)	(2 : 8)
-0.31 (-0.31)	-0.33 (-0.33)	-0.31 (-0.31)	-0.24 (-0.24)	-1.02 (-1.02)	-0.22 (-0.22)	-0.20 (-0.20)	-0.19 (-0.19)	(1 : 9)
-0.28	-0.14	-0.19	-0.19	-0.67	-0.17	-0.19	-0.16	(0 : 10)
Au	**Ir**	**Co**	**Fe**	**Ru**	**Mo**	**Ni**	**V**	(Pd : M)

$$Pd\text{—}Au_2 > Pd\text{—}Ir_2$$
$$> Pt_3$$
$$> Pd_3$$
$$> Pd\text{—}Co_2$$
$$> Pd\text{—}Fe_2$$
$$> Pd\text{—}Ru_2$$
$$> Pd\text{—}Mo_2$$
$$> Pd\text{—}Ni_2$$
$$> Pd\text{—}V_2 \tag{6}$$

Considering only the oxygen adsorption energy and its thermodynamic relation to the ORR activity as compared to pure Pt, the Pd-rich (Pd_2−M) systems have oxygen AEs closer to that of Pt than Pd-poor (Pd−M_2) systems, and hence higher activity is predicted for the Pd-rich systems. This point will be discussed in the following section with normalized Pd mass activity.

3.2. Characterization of a Combinatorial Pd Binary Library.

A combinatorial study is conducted to verify the theoretical results. For reliability of the combinatorial results, eight Pd spots are prepared and tested. The average value of all the Pd (-2.55 mA cm^{-2}) spots is adopted for comparison. ORR activities of the library are expressed with a color gradient. White indicates high activity and black refers to low activity. The combinatorial ORR results and normalized Pd mass activity of all the spots are listed in Table 2. Pd−Co (9:1) composition (-3.32 mA cm^{-2}) is the most active ORR catalyst and exhibits higher activity by 30% than Pd. Pd−Co binary catalysts have been suggested as proper compositions as ORR catalysts.[12,42] Lee et al. suggested a 6:4 atomic ratio as a suitable composition of a Pd−Co system.[43] Comparing Pd−Co

combinatorial systems, Pd−Co (8:2) composition (2:1 atomic ratio) shows the highest normalized Pd mass activity (-0.33 mA cm^{-2}). In a Pd poor region, all catalysts show low ORR activity. This means that Pd played a direct and important role in the ORR. These results are in good agreement with the theoretical study. However, the Pd−Ru binary system shows higher activity than other binary compositions in the Pd poor region because of the oxygen reduction activity of the Ru element. Ru has been widely studied as ORR catalysts to replace Pt because of their good ORR activity.[44−46] In a previous study, the Pd_6Co_4 catalyst showed increased activity by 50% over Pd_6Ni_4 catalysts.[43] Comparing Pd−M (8:2) compositions in the combinatorial library, the ORR activity of Pd−Co (8:2) (-2.86 mA cm^{-2}) is higher by 89% than that of the Pd−Ni (8:2) composition (-1.51 mA cm^{-2}). These combinatorial results are well explained by previous studies.

XRD results are shown in Figure 4a. The average particle sizes of Pd_8Au_2, Pd_8Ir_2, Pd_8Co_2, Pd_8Fe_2, Pd_8Ru_2, Pd_8Mo_2, Pd_8Ni_2, and Pd_8V_2, caculated by the Debye−Scherrer equation, are 17.2, 14.1, 12.5, 13.2, 15.4, 14.7, 15.2, and 16.8 nm, respectively. No significant difference is detected. Figure 4b shows the XPS results of the Pd 3d core level for the Pd−M (8:2) compositions. The Pd 3d core level peaks for all of the Pd-M binary compositions shift to a higher binding energy compared with the pure metallic Pd 3d peak (335.2 eV).[43] Pd 3d chemical shifts in Pd alloys might be effected by bimetallic interaction because the 3d core level of PdO is shown in 337.1 eV, which is far from the Pd 3d peak.[43,47] In the case of the surface composition, all binary compositions show Pd rich surface properties. Pd−Co, PdFe, PdNi and PdV show almost a Pd/M = 2:1 atomic ratio, which is the targeted atomic ratio of our theoretical study. However, the Pd−Au and Pd−Ir combination shows higher Pd amounts in the surface than the other binary compositions. Because library compositions were prepared in weight basis, there are smaller atomic amounts of heavy metals, such as Au and Ir, than other metals in the same composition. Furthermore, the Au and Ir ion
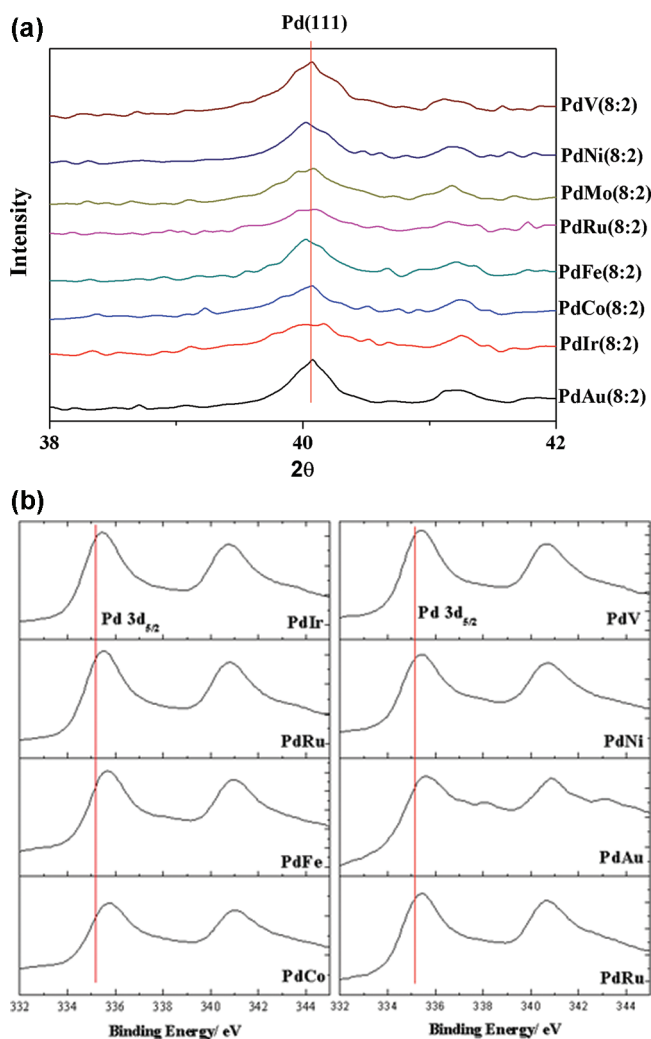
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dx.doi.org/10.1021/co200056d | ACS Comb. Sci. 2012, 14, 10−16

(a)

(b)

Figure 4. (a) XRD spectroscopy for Pd−M (8:2 weight ratio) compositions. (b) XPS spectra (Pd 3d region) for Pd−M (8:2 weight ratio) compositions.
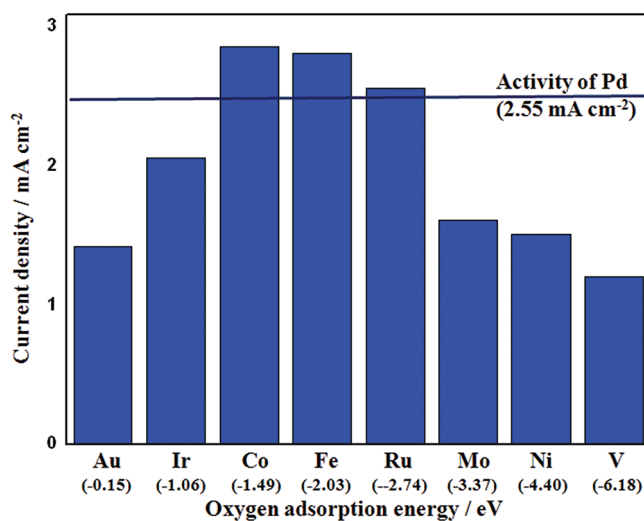

Figure 5. Volcano plot between oxygen adsorption energy and ORR activity (activity Pd−M (8:2) composition).

alloy was simplified by the trimer model and experimental characterization of the prepared library was rapidly carried out by the combinatorial method. The optimized Pd alloy catalyst was successfully developed by this economical method.

4. CONCLUSIONS

We used a simple trimer cluster model to calculate the AE of atomic oxygen on various binary compositions of Pd. The Pd−Co alloy was shown to be, both theoretically and experimentally, the best potential candidate for ORR catalysts among the eight metals considered. Experimentally the most active composition of the Pd−Co alloy is found to be 9:1 wt %, which shows an ORR activity that is higher than Pd by 30%. Furthermore, a volcano relationship between the AE and ORR activity was observed as in literature.

The combination of theoretical and experimental approaches using a trimer model and combonatorial method make the development of new metal alloy catalysts for oxygen reduction simple and time saving. This approach suggests that finding metal alloys that show adsorption energies closest to Pt may be the key to designing new non-Pt catalysts.

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■ ACKNOWLEDGMENTS

exhibit higher reduction potential than the Pd ion and both ions are easily reduced to metal, which is not the case with the Pd ion.[48] The characterized XRD and XPS results are summarized in Table 3.

To confirm the relation between the AE and the ORR activity, all activities of Pd-M (8:2) compositions are plotted in Figure 5. A horizontal blue line means the ORR activity of a Pd spot. This system exhibits a volcano plot and the Pd−Co (8:2) which is theoretically the closest AE to Pt shows the highest ORR actvity. The alloy compositions that have large differences in AE as compared to Pt show lower activity than other alloy compositions. These results are in good agreement with previous results that theoretically showed the relation between the ORR activity and oxygen adsorption energy in single metal (111) surface.[29] The theoretical prescreening of the Pd metal

Table 3. Summary of XRD and XPS Analysis of the Pd−M (8:2 Weight Ratio) Compositions i=GH>MGTCRCOa:5DIjST6^fDVnbiioVlaSLSk26JE]:D`aQkR1m8MOkgga^kkPTfRfo2;j\JI^N?? 6I8>4`L^MP=Jm\?>4l8EmQ38G27N]J@>_O0T`VA8m:bGK78^c^>;MFl`n=gVa[nVU2IT9_O^84ZgN_63DkjY1o`h] E9dYgSMAnZlM1_X157UNMS?JRaLT;U;YSZ4;kNM:A0I212?ZLE>i@Sb`mSh?W?NlSA:bETSBDkD0ie=:QME>@Udj]Um[i \::a^MlgL:eeW5:OWmL5PVc]FfQJV==INfQeTc[��0XRD and XPS analysis for Pd/M (8:2 wt %)

PdAuPdIrPdCoPdFePdRuPdMoPdNiPdVparticle size of Pd (nm)17.214.112.513.215.414.715.216.8surface composition

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper published November 9, 2011 with errors throughout the text. The correct version published November 10, 2011.