Electrocatalysis

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First-Principles Considerations in the Design of Pd-Alloy Catalysts for Oxygen Reduction**

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We report first-principles considerations of the enhanced catalytic activity of Pd-alloy catalysts in the oxygen reduction reaction (ORR) and the "volcano" relationship between the activity and the degree of alloying, and elucidate contrary influences from the lattice-strain and surface-ligand effects. In the past two years, much effort has been devoted to employing Pd alloys as catalysts for ORR.[1–3] Alloying with, for example, Co, Fe, and Ni was found to increase strongly the catalytic activity of Pd, and this represented significant progress in research on non-Pt catalysts for proton-exchange membrane fuel cells (PEMFC). Although promising performances have been preliminarily demonstrated, systematic work is required, especially for comprehending the enhancing effect of alloying.

A simple thermodynamic model based on the data of bulk metal oxides was proposed by Fernández et al.[2a] to interpret the enhanced activity upon alloying. They suggested that the incorporation of more active metals, such as Co, would facilitate the dissociative adsorption of O_2 [Reaction (1)], and the thus-produced O_{ads} could migrate from the Co site to the Pd site, where electroreduction [Reaction (2)] could occur with less polarization.

$$1/2\,O_2 + M \rightarrow M{-}O_{ads} \tag{1}$$

$$M{-}O_{ads} + 2\,H^+ + 2\,e^- \rightarrow M + H_2O \tag{2}$$

As the authors stated, this model was very approximate because it relied solely on the thermodynamics of a bulk oxide, which are clearly different from those of either an alloy or a surface phase. Furthermore, a bimetallic surface such as that proposed was proved to be unstable;[4] the alloying component tends to leach out under electrochemical conditions, and this results in a surface rich in noble metal. The fact that the enhanced catalytic activity can still be attained even on these surfaces depleted of alloying components obviously cannot be interpreted by the above bifunctional-surface model. Since alloying always modulates the electronic nature of a catalyst, consideration of the surface electronic properties from a quantum-chemical standpoint would be more helpful for a mechanistic understanding.

In this work, we attempted to gain insight into Pd-alloy-catalyzed ORR by combining experimental studies and DFT calculations. Considering the pivotal role of O_{ads} in the above reactions, we calculated the adsorption energy (AE, Table 1) of O_{ads} on various metal surfaces and sought a correlation with the catalytic activity.[5] Here AE is defined as the change in the potential energy E of the system (substrate + adsorbate) on adsorption [Eq. (3)].[6]

Table 1: Calculated adsorption energies (AE) of O_{ads} on various metal surfaces at the preferred fcc hollow site.[5]

Surface:	Co(001)	Pd(111)	$Pd_{11}Co(111)$[a]	Pt(111)
AE [eV]:	−2.95	−0.88	−0.83	−0.82

[a] The $Pd_{11}Co$ model surface was constructed with a strained lattice constant of 3.862 Å[7] and the Co atom was positioned in the third layer (see the Supporting Information).

$$AE = E(M{-}O_{ads}) - E(M) - 1/2\,E(O_2) \tag{3}$$

Since this definition takes the dissociation energy of O_2 into account, a negative AE implies that Reaction (1) is thermodynamically spontaneous.

A $Pd_{11}Co(111)$ model surface was constructed to mimic a Pd–Co alloy with an alloying degree of 8.3 atom% Co, close to that of the best catalyst found in our experiments (see below). The lattice constant was shrunk accordingly,[7] and the Co atom was deliberately placed in the third layer of the Pd slab (see the Supporting Information) to mimic a Pd-rich surface, which was revealed by X-ray photoelectron spectroscopy (XPS) in our experiments (see the Supporting Information). As shown in Table 1, the AE of $Pd_{11}Co{-}O_{ads}$ is surprisingly not in-between those of $Co{-}O_{ads}$ and $Pd{-}O_{ads}$; it is smaller than that on Pd and slightly greater than that on Pt. The sequence of AEs on Pd, $Pd_{11}Co$, and Pt proved to correlate well to the sequence of catalytic activities of the corresponding catalysts (see the Supporting Information), that is, the smaller the AE, the higher the activity. Since Reaction (1) is spontaneous on all the considered surfaces, it is understandable that smaller AE supports the reductive desorption step [Reaction (2)]. From the above-mentioned correlation, it may be further inferred that Reaction (2) should be the rate-determining step.

To further investigate the alloying effect, a series of Pd–Co/C catalysts with different degrees of alloying were prepared.[5] The degree of alloying was estimated according to the line shift in the X-ray diffraction (XRD) pattern (see

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the Supporting Information) of Pd–Co alloys.[7] The catalytic activity of Pd–Co alloys was evaluated with a rotating disk electrode (RDE) in O_2-saturated 0.5 M H_2SO_4 solution.[5] The kinetic current of ORR obtained from RDE data was normalized by the electrochemical surface area of Pd–Co alloy to give a surface specific activity (SA),[5] which was used for the strict comparison of intrinsic activities among catalysts. The "volcano" trend in the relationship between SA and the degree of alloying (Figure 1) indicates that two contrary factors may underlie the alloying effect.

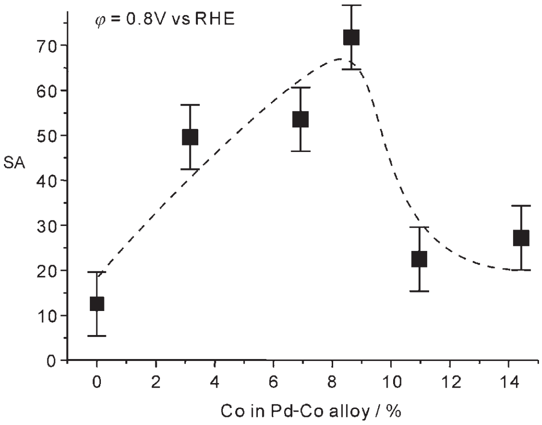

Figure 1. Relationship between surface specific activity (SA) of Pd–Co alloys and degree of alloying. The kinetic current obtained from RDE experiments (25 °C, 5 mV s^{-1}, O_2-saturated 0.5 M H_2SO_4, 1600 rpm) was normalized by the electrochemical surface area of Pd–Co alloys to give SA (see the Supporting Information).

We found that the calculated AE of O_{ads} is very sensitive to the position of the Co atom in the Pd slab (Table 2). If the Co atom is located in the first layer of the Pd(111) slab, the preferred adsorption site of O_{ads} is the Co-involving fcc hollow site (see the Supporting Information), and AE in this case increases remarkably to −1.63 eV, almost twice that of Co atoms located in the third layer. Such a surface-ligand effect, however, is a short-range interaction; it becomes negligible if the Co atom sinks into the second layer of the Pd slab (Table 2).

Table 2: Adsorption energies (AE) of O_{ads} on modified Pd(111) slabs.

Surface:	$Pd_{11}Co$ (Co in 1st layer)	$Pd_{11}Co$ (Co in 2nd layer)	Pd (lattice-shrunk)[a]	$Pd_{11}Fe$ (Fe in 3rd layer)[b]
AE [eV]:	−1.63	−0.83	−0.83	−0.82

[a] A virtual Pd slab was constructed with the lattice constant deliberately shrunk to the same degree as in the $Pd_{11}Co$ slab. [b] The $Pd_{11}Fe$ model surface was constructed with a strained lattice constant of 3.859 Å.[7]

The intrinsic reason for the decrease in AE of O_{ads} on Pd alloys with a Pd-rich surface is the lattice contraction induced by the incorporation of smaller atoms, such as Co, into the Pd lattice. This lattice-strain effect causes a downshift in the metal d-band center and weakens the interaction between the substrate and the adsorbate.[8] To evaluate this argument, we constructed a virtual Pd(111) slab with the lattice constant deliberately shrunk to the same magnitude as that of the $Pd_{11}Co(111)$ slab; the AE of O_{ads} on this virtual surface was −0.83 eV, the same as that on the $Pd_{11}Co$ slab with Co atoms located at the second or third layer. Therefore, in a Pd alloy with a Pd-rich surface, the alloying effect is predominantly a lattice-strain effect.

The lattice-strain effect and the surface-ligand effect have opposed influences on the M−O_{ads} bonding, which would lead to the observed volcano relationship between activity and degree of alloying (Figure 1). At low degrees of alloying, the surface concentration of Co is negligible (especially under electrochemical conditions, where surface Co tends to be leached out) and the lattice-strain effect is predominant and results in weakened M−O_{ads} bonding and increased activity for ORR. At high degrees of alloying, the surface concentration of Co could increase to such an extent that the surface-ligand effect becomes overwhelming and leads to a decrease of catalytic activity.

Now that the change in AE due to the lattice-strain effect is thought to be the main reason for the enhanced activity, it would be significant to calculate AE as a function of lattice strain, described by the ratio of lattice constants a/a_0. The resulting relationship (Figure 2) proved to be linear and might serve as a guideline for the design of Pd-alloy catalysts for ORR. According to Figure 2, any alloying elements that reduce a/a_0 will benefit the activity. For example, because an Fe atom is smaller than a Co atom, alloying with Fe should give a better performance than with Co. The calculated AE of O_{ads} on $Pd_{11}Fe$ (Table 2) is the same as that on Pt (Figure 2), so the activity of the Pd–Fe alloy is predicted to be comparable to that of Pt. This prediction is supported by recent work of Shao et al.[3a] The degree of alloying of their best Pd–Fe alloy catalyst was 8.4 atom % Fe (estimated from the XRD data in reference [3a]),[7] very close to that of the $Pd_{11}Fe$ slab considered here, and the catalytic activity was equal to, or even slightly better than, that of Pt catalyst (see the Supporting Information).

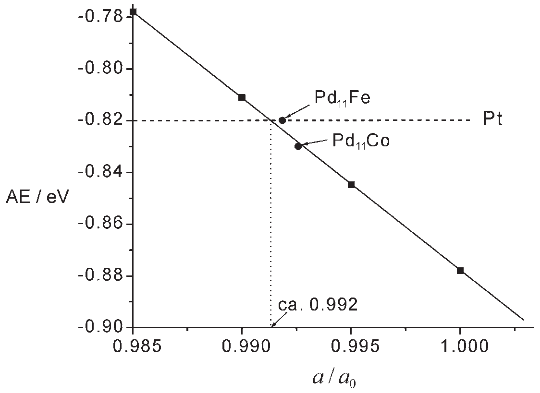

Figure 2. Relationship between the AE of O_{ads} and the strain ratio in the lattice constant of Pd, which may serve as a guideline for the design of Pd-alloy catalysts for ORR.

In conclusion, the key to improving Pd-based catalysts for ORR is alloying Pd with elements of smaller atomic size to form a "Pd-shell/alloy-core" structure so as to take advantage of the lattice-strain effect and to prevent the disadvantageous surface-ligand effect. According to Figure 2, it is possible to find Pd-based alloys that are more active than Pt for ORR by reducing the AE through lattice contraction. However, there must be a lower limit for reducing AE of O_{ads} to ensure successful competition of oxygen with solvent and/or electrolyte for adsorption sites. Further experimental verification of this proposed guideline is underway.

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[7] The degree of alloying, denoted as the atomic percentage x of Co in the alloy, was estimated from the XRD lattice constants of Pd and the alloy, a_{Pd} and a_{alloy}, by an empirical equation:

$$x\left(1-\frac{r_{Co}}{r_{Pd}}\right)=1-\frac{a_{alloy}}{a_{Pd}}$$

where r is the metallic radius of an alloy component. The results of this equation agreed with DFT calculations to a degree acceptable for the problem dealt with in this work.

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