Electrocatalysis

Controlling the Catalytic Activity of Platinum-Monolayer Electrocatalysts for Oxygen Reduction with Different Substrates**

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As the interest for "hydrogen-based economy" grows, the research on its major elements, that is, hydrogen production and storage[1–3] and energy conversion in fuel cells is expanding.[4,5] Electrocatalytic oxygen reduction, the reaction at fuel-cell cathodes, has been the focus of attention because of its slow kinetics and because of the need for better electrocatalysts with decreased platinum content.[6–8] Herein we report the results of a study on the electrocatalytic activity for the oxygen reduction reaction (ORR) of platinum monolayers supported on Au(111), Rh(111), Pd(111), Ru(0001), and Ir(111) surfaces in a 0.1 M $HClO_4$ solution. The experimentally measured electrocatalytic activity of platinum monolayers for the ORR shows a volcano-type dependence on the center of their d-bands as determined by density functional theory (DFT) calculations. The platinum monolayer supported on Pd(111) (denoted by Pt_{ML}/Pd(111)) is at the top of the volcano curve and shows improved ORR activity over pure Pt(111). We demonstrate that this behavior is determined by two opposite trends: while a higher lying d-band center tends to facilitate O–O bond breaking, a lower lying one tends to facilitate bond formation (e.g.: hydrogen addition). Our results suggest that improvement in the overall fuel-cell efficiency can be combined with substantial cost savings that result from using less platinum at the cathode.

The catalytic properties of bimetallic surfaces consisting of metal monolayers on single-crystal metal surfaces have been extensively studied in ultrahigh vacuum[9] and, to a lesser extent, in electrochemical systems.[10–13] In many cases, the formation of a surface metal–metal bond produced significant changes in the electronic properties of the metal overlayer, and pronounced differences were observed in the reactivity of some transition-metal monolayers on various substrates.[9] A description of the activity of metal monolayers has been proposed by Nørskov and co-workers.[14,15] According to these authors, the characteristics of the surface metal d-bands, particularly the weighted center of the d-band (ε_d), play a decisive role in determining surface reactivity. DFT calculations have shown that the binding energies and reactivity of small adsorbates correlate well with the position of ε_d on strained surfaces and metal overlayers,[3,16] in accord with data from numerous experimental studies.[17–20] The framework of that description is implemented herein to elucidate trends governing the behavior of platinum monolayers on other transition-metal surfaces.

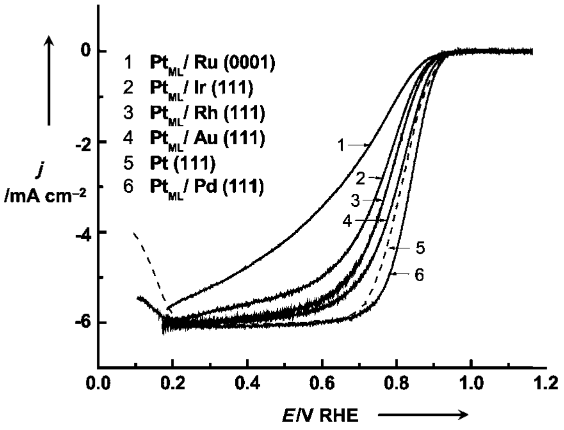

Figure 1. Polarization curves for O_2 reduction on platinum monolayers (Pt_{ML}) on Ru(0001), Ir(111), Rh(111), Au(111), and Pd(111) in a 0.1 M $HClO_4$ solution on a disk electrode. The curve for Pt(111) is taken from ref. [21] and included for comparison. The rotation rate is 1600 rpm, and the sweep rate is 20 $mV\,s^{-1}$ (50 $mV\,s^{-1}$ for Pt(111)); j = current density, RHE = reverible hydrogen electrode.

Figure 1 shows the rotating disk measurements for O_2 reduction on platinum monolayers on the five different single-crystal surfaces and, for comparison, on a Pt(111) surface.[21] The most active of all surfaces is Pt_{ML}/Pd(111), and the least active is Pt_{ML}/Ru(0001). When the kinetic currents obtained from Koutecky–Levich plots (not shown) for O_2 reduction on the platinum monolayers on various substrates at 0.8 V are plotted as a function of the calculated ε_d (Figure 2), a volcano-like curve is generated, with Pt_{ML}/Pd(111) showing the maximum activity. The use of kinetic current instead of the exchange current density in this plot is preferred because there is no reliable method for determining the exchange current density for the ORR. Other authors have used the same approach.[22] The increase in the O_2 reduction kinetics on Pt_{ML}/Pd(111) compared with that on Pt(111) is surprising since Pt(111) and Pt(110) are the most active electrocatalysts for ORR in $HClO_4$ solutions known to date. In addition, to our knowledge, the finding of this volcano-type dependence of monolayer catalytic activity on the substrate is novel both in the field of electrocatalysis and in catalysis in general. For a number of catalytic reactions, it has been shown that the activity of catalysts exhibits volcano-type dependence on some variable and that the best of the

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[**] Work at BNL was supported by the Divisions of Chemical and Material Sciences, U.S. Department of Energy (Contract No. DE-AC02-98CH10886). Work at UW-Madison was supported by NSF-CTS and DOE-BES and used CPU time at NPACI, DOE-NERSC, and PNNL supercomputing centers. Y.X. and M.M. thank Denise Ford, Amit Gokhale, and Shampa Kandoi for their valuable help.

DOI: 10.1002/ange.200462335

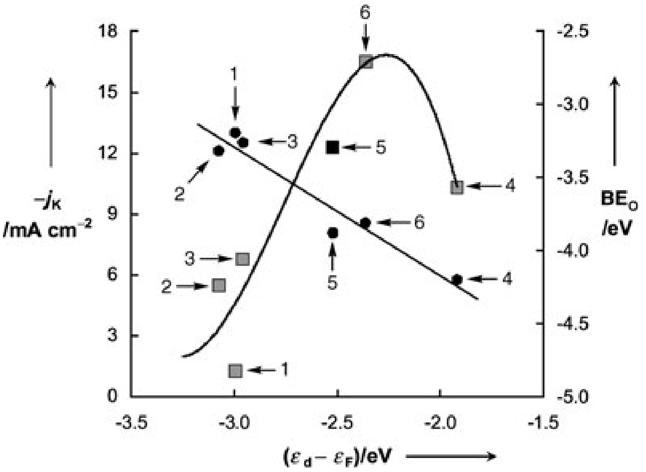

Figure 2. Kinetic currents (j_K; square symbols) at 0.8 V for O_2 reduction on the platinum monolayers supported on different single-crystal surfaces in a 0.1 M $HClO_4$ solution and calculated binding energies of atomic oxygen (BE_O; filled circles) as functions of calculated d-band center ($\varepsilon_d - \varepsilon_F$; relative to the Fermi level) of the respective clean platinum monolayers. The current data for Pt(111) is taken from ref. [21] and included for comparison. Labels: 1. Pt_{ML}/Ru(0001), 2. Pt_{ML}/Ir(111), 3. Pt_{ML}/Rh(111), 4. Pt_{ML}/Au(111), 5. Pt(111), 6. Pt_{ML}/Pd(111).

catalysts strikes a balance between two competing influences.[23–25] To ascertain the competing influences in the present case, it is necessary to have an understanding of the ORR mechanism, which, however, is still the subject of extensive discussions.[7,26–28] Evidence suggests that the first charge-transfer step, or O_2 adsorption with simultaneous charge and proton transfer, appears to be the rate-determining step on pure platinum.[7] The exchange of a second electron with the addition of another proton forms two OH species or hydrogen peroxide (H_2O_2). H_2O_2 can escape into the solution phase, which terminates the reaction in a two-electron process. An additional exchange of two electrons and two protons in reactions with OH or H_2O_2 completes the four-electron reduction of O_2 to H_2O.

Despite the lack of consensus in regard to this mechanism, the four-electron O_2 reduction reaction must involve both the breaking of the O–O bond (whether in O_2, O_2H, or H_2O_2) and the formation of an O–H bond. As has been demonstrated,[16] a more reactive surface, such as one characterized by a higher-lying ε_d, tends to bind adsorbates more strongly, thereby enhancing the kinetics of dissociation reactions producing these adsorbates. On the other hand, a surface with a lower-lying ε_d tends to bind adsorbates more weakly and facilitates the formation of bonds amongst them. Thus, it may be expected that the most active platinum monolayer should have an ε_d with an intermediate value.

DFT studies have shown that compressive strain tends to down-shift ε_d in energy, whereas tensile strain has the opposite effect.[29] The platinum monolayers on Ru(0001), Rh(111), and Ir(111) are compressed compared with Pt(111), whereas Pt_{ML}/Au(111) is stretched by more than 4%. Indeed their ε_d are calculated to be accordingly either lower or higher in energy than that of Pt(111) (see Figure 2). The positions of the ε_d of the platinum monolayers do not correlate strictly with the amount of strain present because the position of the ε_d for the platinum monolayers depends both on the strain (geometric effects) and on the electronic interaction between the platinum monolayer and its substrate (ligand effect).[30]

When the binding energy of atomic oxygen on the six surfaces considered herein is plotted against the corresponding ε_d in Figure 2, a nearly linear correlation results. Pt_{ML}/Au(111) lies at the high ε_d end of the plot and binds oxygen much more strongly than Pt(111), whereas Pt_{ML}/Ru(0001), Pt_{ML}/Rh(111), and Pt_{ML}/Ir(111) lie at the other end and bind oxygen considerably less strongly than Pt(111). If Pt(111) is taken to be close to the optimum balance described above, then the position of the ε_d would suggest that Pt_{ML}/Ru(0001), Pt_{ML}/Ir(111), and Pt_{ML}/Rh(111) are less active for O_2 reduction than platinum because breaking the O–O bond is more difficult on these surfaces than on Pt(111). This situation would facilitate H_2O_2 formation at the expense of the complete reduction of oxygen to water. On the other hand, Pt_{ML}/Au(111) may suffer from hindered oxygen atom or OH hydrogenation kinetics owing to the stronger binding of oxygen atoms or oxygen-containing fragments and is therefore less active than Pt(111) as well. Slow O or OH hydrogenation rates may also cause surface O or OH coverage to build up and block O_2 adsorption, dissociation, or hydrogenation sites. Pt_{ML}/Pd(111) is most similar to pure Pt(111) and should possess greater activity than the other platinum monolayers. Indeed, the ORR kinetics on Pt_{ML}/Pd(111) is measured to be higher than even that on Pt(111). In addition, the production of H_2O_2 is higher on Pt_{ML}/Ru(0001) and Pt_{ML}/Ir(111) than on the rest of the platinum monolayers (Figure 3). Both of these experimental findings are in line with our predictions, which are based on the premise that the optimal ORR catalyst should strike a balance between O–O bond breaking and O–H bond-making activity.

To interpret the experimental data for the ORR activity of the platinum monolayers, additional DFT calculations have been performed to study the thermochemistry and kinetics of two representative elementary reaction steps [Eq. (1)] and [Eq. (2)] on Pt_{ML}/Au(111) (stretched platinum monolayer),

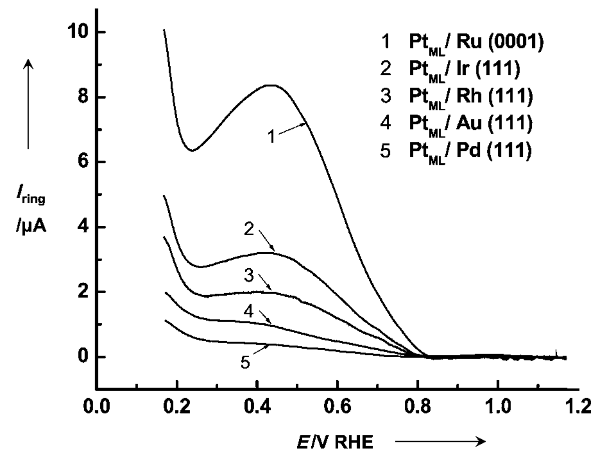

Figure 3. The currents for H_2O_2 oxidation on a ring electrode (I_{ring}) as a function of the disk potential corresponding to the polarization curves for O_2 reduction shown in Figure 1. The ring potential is 1.1 V, and the collection efficiency is 0.20.

Pt(111) (normal platinum surface), and Pt_{ML}/Pd(111) and Pt_{ML}/Ir(111) (compressed platinum monolayers).

$$O_2 \rightarrow O + O \quad (1)$$

$$O + H \rightarrow OH \quad (2)$$

These two reactions are chosen because O_2 dissociation can be viewed as a representative O−O bond-breaking step, whereas the hydrogenation of O can be viewed as a representative O−H bond-forming step, both of which are relevant types of elementary step in the ORR regardless of the detailed mechanism. We note here that Equation (2) does not necessarily imply that H is adsorbed on the surface before adding to O, under ORR conditions. We use this step only to trace the energy needed for activating adsorbed O to accomplish a hydrogen addition to O, since the largest component of the OH formation energy barrier is the activation of O.

The experimentally measured kinetic currents shown in Figure 2, along with the calculated activation energies (E_a) of the elementary steps [Eq. (1) and (2)], are re-plotted against the binding energy of O on each of the platinum monolayers (Figure 4). The binding energy of O is used as a descriptor of surface reactivity both for simplicity and for the fact that atomic oxygen probably interacts more strongly with the surface than any other intermediate in the ORR mechanism and is, therefore, most sensitive to changes in surface properties. The E_a for O_2 dissociation is smallest on Pt_{ML}/Au(111) and largest on Pt_{ML}/Ir(111). The trend is just the opposite for the hydrogenation of O, which has the highest barrier on Pt_{ML}/Au(111) and the lowest on Pt_{ML}/Ir(111). Pt(111) lies close to the crossing of the two E_a trend lines, suggesting that it is close to where the optimum compromise lies. Although the crossing point may depend on factors including coverage, field, and solvent, it appears to be a good indicator of the ORR activity of these surfaces. The only platinum monolayer in this study that falls in the vicinity of the crossing is Pt_{ML}/Pd(111), which also turns out to be the only one whose experimentally measured activity is comparable to that of pure Pt(111).

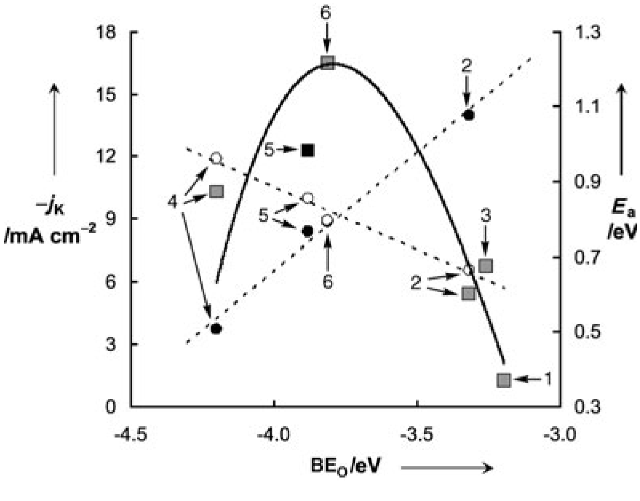

Figure 4. Kinetic currents (j_K; square symbols) at 0.8 V for O_2 reduction on the platinum monolayers in a 0.1 M $HClO_4$ solution and the activation energies for O_2 dissociation (filled circles) and for OH formation (open circles) on Pt_{ML}/Au(111), Pt(111), Pt_{ML}/Pd(111), and Pt_{ML}/Ir(111), as functions of the calculated binding energy of atomic oxygen (BE_O). The current data for Pt(111) is obtained from ref. [21]. Labels: 1. Pt_{ML}/Ru(0001), 2. Pt_{ML}/Ir(111), 3. Pt_{ML}/Rh(111), 4. Pt_{ML}/Au(111), 5. Pt(111), 6. Pt_{ML}/Pd(111).

Experimentally, we found that the superior ORR catalytic activity of Pt_{ML}/Pd(111) is associated with a reduced OH coverage,[31] which may be explained, in view of our DFT findings, as the result of enhanced OH hydrogenation rates, which should follow a trend similar to that of O hydrogenation rates. Furthermore, voltammetry and X-ray absorption near-edge structure spectroscopy (XANES)[31] have identified a shift of OH adsorption on Pt_{ML}/Pd(111) to potentials more positive than those on Pt(111), which can be attributed to an enhanced repulsive interaction of OH groups on the Pt_{ML}/Pd(111) compared to on pure Pt(111). Pd-OH, on the other hand, forms at less positive potentials than Pt-OH. This result is also in agreement with our DFT findings that the binding energy of OH is weaker on Pt_{ML}/Pd(111) than on Pt(111), which, in turn, binds OH weaker than Pd(111).

In conclusion, the ORR electrocatalytic activity of platinum monolayers supported on Au(111), Ir(111), Pd(111), Rh(111), and Ru(0001) surfaces show a volcano-type dependence on the d-band center of the platinum monolayer structures. Our results elucidate, for the first time, that for a good ORR electrocatalyst the kinetics of both the O−O bond breaking and the hydrogenation of reactive intermediates have to be facile at the cathode. More importantly and from a practical perspective, we show that it is possible to devise an ORR electrocatalyst that contains only a fractional amount of platinum but can surpass the activity of pure platinum (e.g.: Pt monolayer on Pd(111)). Therefore, platinum monolayers supported on appropriate metal substrates represent a viable way to reduce platinum loadings and the associated cost of fuel-cell electrodes. Our results also point to the fundamentally important possibility of fine-tuning the electrocatalytic activity of transition metals.

Experimental Section

The working electrodes were (111)-oriented Au, Pd, Ir, Rh, and Ru(0001) single crystals of 6 mm (used in rotating electrode) and 8 mm (used for the STM measurements) in diameter (obtained from Metal Crystals and Oxides). The surface preparation followed a standard procedure.[31] The electrochemical measurements were taken at room temperature using an interchangeable rotating disk-ring electrode (Pine Instruments). A platinum monolayer was deposited using the galvanic displacement of a Cu adlayer deposited at underpotentials by platinum from a K_2PtCl_4 solution.[32] The deposits were characterized using STM and the charge associated with hydrogen adsorption on platinum. A lack of significant change of the platinum deposit by ORR was verified by comparing the charges for H adsorption measured before and after the kinetic measurements, and by the stability of the catalytic activity.

Theoretical Methods: The spin-polarized DFT calculations were performed in the generalized gradient approximation (GGA-PW91) using ultrasoft pseudopotentials[33] as implemented in the DACAPO code.[15,34] The parameters of our calculations were identical to those used in previous studies.[16] Convergence of the results with respect to calculation parameters has been verified in all cases. The platinum monolayer surfaces were modeled by a single layer of platinum placed on top of Au(111), Pd(111), Ir(111), Rh(111), and Ru(0001), at the substrate's lattice constants. Each surface was constructed from a (2 × 2) surface unit cell and modeled by a slab consisting of four layers of metal atoms. The top two layers, that is, the platinum monolayer and the first layer of the substrate metal, were relaxed. The binding energies ($E_b = E_{total} - E_{substrate} - E_{gas\text{-}phase\ adsorbate}$) and geometries of adsorbed O, O_2, and OH, as well as O_2 dissociation and O hydrogenation, were studied on the relaxed surfaces. Minimum-energy reaction paths were calculated using the climbing-image nudged elastic band method.[35] The equilibrium PW91 lattice constants for bulk metals were calculated to be 4.18 (Au), 4.00 (Pt), 3.99 (Pd), 3.86 (Ir), 3.85 (Rh), and 2.74 Å (Ru), in good agreement with the experimental values[36] (4.08 (Au) 3.92 (Pt), 3.89 (Pd), 3.84 (Ir), 3.80(Rh), and 2.70 Å (Ru)).

Received: October 17, 2004

Keywords: density functional calculations · electrochemistry · heterogeneous catalysis · oxygen reduction · surface chemistry

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