Platinum monolayer electrocatalysts for oxygen reduction: effect of substrates, and long-term stability

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Abstract: We describe a novel concept for a Pt monolayer electrocatalyst and present the results of our electrochemical, X-ray absorption spectroscopy, and scanning tunneling microscopy studies. The electrocatalysts were prepared by a new method for depositing Pt monolayers involving the galvanic displacement by Pt of an underpotentially deposited Cu monolayer on substrates of Au (111), Ir(111), Pd(111), Rh(111) and Ru(0001) single crystals, and Pd nanoparticles. The kinetics of O₂ reduction showed significant enhancement with Pt monolayers on Pd(111) and Pd nanoparticle surfaces in comparison with the reaction on Pt(111) and Pt nanoparticles, respectively. This increase in catalytic activity is attributed partly to the decreased formation of PtOH, as shown by in situ X-ray absorption spectroscopy. The results illustrate that placing a Pt monolayer on a suitable substrate of metal nanoparticles is an attractive way of designing better O₂ reduction electrocatalysts with very low Pt contents.

Keywords: electrocatalysis, oxygen reduction, platinum, monolayers, stability.

INTRODUCTION

As interest in a hydrogen-based economy grows, research is expanding on its major elements, viz., hydrogen production, and storage and energy conversion in fuel cells.¹ Electrocatalytic oxygen reduction, the reaction at fuel-cell cathodes, has been the focus of considerable attention because of its slow kinetics and the need for better electrocatalysts with decreased Pt content.²⁻⁴ A particularly troubling feature of this reaction is the large loss in potential of 0.3–0.4 V during the initial part of the polarization curves that is the source of a major decline in the fuel cell’s efficiency. Part of this polarization was attributed to the inhibition of O₂ reduction caused by OH adsorption on Pt in the potential region of 0.75 – 1 V.³⁻⁵

To alleviate these impediments, we developed a new approach to designing the low-Pt electrocatalysts for the cathode⁶⁻¹⁰ and for the anode.¹¹⁻¹² This approach involves depositing a Pt sub-monolayer or monolayer on suitable substrates...
of carbon-supported metal nanoparticles. We developed two methods of deposition. In the first, the Pt submonolayer is deposited in an electroless (spontaneously) fashion on suitable substrate, while, in the other, Pt is laid down by the redox replacement of a Cu monolayer. Both methods form Pt deposits in which all Pt atoms can be involved in the catalytic reaction. Consequently, Pt loading can be greatly reduced compared with other catalysts.

The catalytic properties of bimetallic surfaces consisting of metal monolayers on single-crystal metal surfaces have been extensively studied in ultra-high vacuum systems and, to a lesser extent, in electrochemical ones. In many cases, the formation of a surface metal–metal bond significantly changed the electronic properties of the metal overlayer, and pronounced differences were observed in the reactivity of some transition metal monolayers on various substrates. Norskov and coworkers recently proposed a description of the activity of metal monolayers, according to which the characteristics of the surface metal d-bands, particularly the weighted center of the d-band ($\epsilon_d$) play a decisive role in determining surface reactivity. Density functional theory (DFT) calculations showed that the binding energies and reactivity of small adsorption correlate well with the position of $\epsilon_d$ on strained surfaces and metal overlayers, in accord with data from numerous experimental studies. The framework of that description is implemented in the present study to elucidate trends governing the behavior of Pt monolayers deposited on the surfaces of other transition metals.

In the present communication we describe the kinetics of the O$_2$ reduction reaction (ORR) of a Pt monolayer on several single-crystal electrodes and on carbon-supported Pd nanoparticle electrocatalysts. A rotating disk or disk–ring electrode (RRDE) technique was used for the majority of the electrochemical measurements. The long-term test was carried out in a 50 cm$^2$ fuel cell. The data obtained using in situ X-ray absorption spectroscopy (XAS) measurement, i.e., X-ray absorption near edge structure (XANES), rationalize the origins of the high catalytic activity for O$_2$ reduction. We emphasize that this XAS study provided unique spectra obtained only from the monolayer of Pt atoms on the surface of the metal nanoparticles, which take part in electrocatalytic reaction. These data facilitate a direct comparison between electronic/structural properties and catalytic activity. Previous data on Pt and Pt alloys were predominantly determined by the Pt atoms in the bulk material.

**EXPERIMENTAL**

The ORR electrocatalysts were prepared by our new method for depositing Pt monolayers involving the galvanic displacement by Pt of an underpotentially deposited ( upd) Cu monolayer on the surfaces of single crystal of Au(111), Rh(111), Pd(111), Ru(0001), and Ir(111), and on Pd nanoparticles deposited on glassy carbon disk. The Rh(111), Pd(111), Ru(0001) and Ir(111) crystals were mechanically polished with diamond pastes and alumina down to 0.05 μm and annealed by inductive heating in an Ar atmosphere. The surface preparation for Au (111) followed a standard procedure involving electropolishing and flame annealing. Immediately after depositing a Cu upd monolayer from deoxygenated 0.05 M CuSO$_4$ in a 0.05 M H$_2$SO$_4$ solution, the electrode covered with this Cu adlayer was rinsed to remove Cu$^{2+}$ from the solution film, and placed into a
deoxygenated 1.0 mM K₂PtCl₄ in 50 mM H₂SO₄ solution. After a 1–2 min immersion to allow the complete replacement of Cu by Pt, the electrode was rinsed again. All these operations were carried out in a multi-compartment cell in a N₂ atmosphere that prevents the oxidation of Cu adatoms in contact with O₂. Pd nanoparticles were first deposited on glassy carbon RRDE with a Pt ring, and then a Pt monolayer was deposited using the same procedure described above for single crystals. Finally, the electrode was covered with a small amount of a Nafion solution and dried in air before the RRDE measurements. Solutions were prepared from Optima* sulfuric acid obtained from Fisher and MilliQ UV-plus water (Millipore). An Ag/AgCl/KCl(3M) leak-free electrode was used as a reference. All potentials are quoted with respect to a reversible hydrogen electrode (RHE).

In situ scanning tunneling microscopy (STM) study was performed using a Molecular Imaging Pico STM with a 300S scanner and a 300S Pico Bipotentiostat. The tunneling tips were made of a polycrystalline Pt–20 % Ir wire and coated with Apiezon wax. The cell was made of Teflon, and Pt wires served as the reference and counter electrodes.

The electrochemical cell for XAS was designed for data acquisition in both transmission and fluorescence modes. A Pt/Pd/C catalyst electrode, a proton exchange membrane (Nafion 117, DuPont Chemical Co., DE), and a carbon counter electrode (Grafoil, Union Carbide Corp.) were sandwiched together and held in PTFE gaskets. An electrolyte 1 M HClO₄ was added to the cell to increase the wetting of the sample. It did not affect the measurements because of its low X-ray absorption and anion adsorption characteristics. The total amount of Pt in the Pt/Pd/C electrode was ca. 0.7 mg/cm², small enough to avoid self-adsorption in fluorescence-type measurements. XAS measurements were carried out at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) using Beam Line X11A and X-9B. The measurements were carried out in the fluorescence mode at the Pt L₃ and L₂ edges at different potentials at room temperature.

RESULTS AND DISCUSSION

As an example of the results obtained for a Pt monolayer deposition on single crystal electrodes we show the data for an Rh(111) surface. Figure 1a shows the typical voltammetry curve with two peaks for the upd of Cu on a Rh(111) surface. The charge associated with these peaks is 540 μC/cm², which is close to 524 μC/cm², needed for depositing a pseudomorphic monolayer of Cu on an ideal Rh(111) surface. The most negative peak is very close to the bulk deposition of Cu, which imposes careful control of the Cu upd deposition to avoid deposition of more than a monolayer of Cu. This is critical since the amount of deposited Pt corresponds to the upd Cu coverage. The dashed line shows the curve for a Rh(111) surface in the absence of Cu ions in solution. Figure 1b depicts the voltammetry curves for the Pt monolayer on a Rh(111) surface (solid line) and that for a Rh(111) surface without Pt (dashed line). As expected, the deposition of the Pt monolayer partially block oxide formation on Rh(111) since Pt is oxidized at more positive potentials.

Figure 2 is the STM image of the Pt monolayer deposited using a galvanic displacement of a Cu monolayer on a Rh(111) surface obtained at 0.8 V in 0.1 M HClO₄ solution. The deposit consists of two-dimensional interconnected Pt islands. With the small difference between the Pt and Rh lattice constants, these islands are expected to be epitaxial with the Rh(111) substrate. There are a certain number of holes between the islands, and also a few sites with Pt atoms in the second layer. Similar deposits were obtained with the other substrates used for this study.
Figure 3 shows the rotating disk–ring measurements for O₂ reduction on Pt monolayers on the five different single crystal surfaces and, for comparison, on a Pt (111) surface taken from the Reference 26. The most active surface is PtML/Pd(111), and the least active is PtML/Ru(0001). The oxidation at the ring electrode of H₂O₂ generated by ORR at the disk was measured by keeping its potential at 1.1V where the reaction is under diffusion control. Less active electrodes generated a larger amount of H₂O₂. However, O₂ reduction involves a four-electron reduction on all Pt surfaces, including the least active Pt/Ru(0001)²7 where 6.8 % H₂O₂ is generated at the peak current. Therefore, the overall reaction can be written as

\[
O_2 + 4H^+ + 4e^- = 2H_2O
\]
Analysis involving the Koutecky–Levich plots and Tafel slopes indicates that the reaction is a first order one for the concentration of dissolved O₂ and that the
first charge-transfer is rate determining. Therefore, it is highly likely that the reaction mechanism is same for Pt monolayers on all five substrates investigated. Accordingly, comparison of the O₂ reaction rates on these surfaces is a reliable and valid procedure.

Plotting the kinetic currents obtained from Koutecky–Levich plots (not shown) for O₂ reduction on the Pt monolayers on various substrates at 0.8 V as a function of the calculated d-band centers for Pt monolayers, ε_d (Fig. 4), produces a volcano-like curve, with Pt\(_{\text{ML}}/\text{Pd}(111)\) possessing the maximum activity.\(^{28}\) This increase in O₂ reduction kinetics on Pt\(_{\text{ML}}/\text{Pd}(111)\) compared with that on Pt(111) is surprising since Pt(111) and Pt(110) are the most active electrocatalysts for ORR known so far in HClO₄ solutions. As Xu \textit{et al.} demonstrated,\(^{21}\) 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 O₂ dissociation reactions. On the other hand, a surface with a lower-lying ε_d tends to bind adsorbates more weakly and facilitates the formation of bonds between them. Too strong an adsorption of intermediates for Pt/Au(111), the surface with the highest ε_d (the most stretched Pt lattice), causes a decrease in activity. The observed increase in the catalytic activity of the Pt monolayer surfaces on Pd substrates compared with those on Pt may also partly reflect the decreased formation of PtOH on Pd-supported Pt monolayers (\textit{vide infra}).

![Fig. 4. Kinetic currents at 0.8 V for O₂ reduction on the Pt monolayers supported on the indicated single crystal surfaces in a 0.1 M HClO₄ solution and calculated binding energies (B.E.s) of atomic oxygen as functions of calculated d-band center (ε_d) of the respective clean Pt monolayers. The data for (ε_d) obtained from Ref. 28.](image.png)
**Activity of oxygen reduction at a Pt monolayer on C-supported Pd nanoparticles**

Figure 5 shows polarization curves of O₂ reduction on Pd and Pt nanoparticles (10 nmol each) and on a Pt monolayer on Pd nanoparticles (10 nmol and 20 nmol Pd) at a rotation rate of 1600 rpm. In these measurements, the ring-electrode currents were negligible. TEM measurement showed an average diameter of 9 nm for the Pd nanoparticles used for the Pt/Pd/C electrocatalyst. Comparing the activity of the Pt/C electrocatalyst with an average particle size of 3.1 nm with that of the 9 nm Pt/Pd/C electrocatalyst does not adequately reflect the difference in their activities because of their different surface areas. However, this does not affect our main conclusion, as follows. The activity of the Pt monolayer on Pd nanoparticles (10 nmol) is much higher than that of Pd nanoparticles (10 nmol) as indicated by a shift of the half-wave potential by 120 mV to positive values. More importantly, the activity of this surface is somewhat higher (25 mV in half-wave potential) than that of Pt nanoparticles (10 nmol). For the Pd loading of 10 nmol or 6.4 μg Pd/cm², the amount of Pt in the monolayer on this surface is 1.5 nmol/cm² or 1.7 μg Pt/cm², based on Benfield’s calculation using an icosahedral particle model. The half-wave potential for this electrode is 0.838 V. Importantly, we note that the activity of this surface is higher than that of 10 nmol (12 μg Pt/cm²) of Pt nanoparticles, despite the fact that average diameters of the Pd nanoparticles and the Pt nanoparticles are 9 nm and...
3 nm, respectively, and the former have a smaller real surface area. The electrode consisting of a Pt monolayer on 20 nmol Pd had the highest activity, mainly due to the increased Pt surface area. The higher activity of the Pt monolayer electrocatalysts compared with those of Pt and Pd indicate a synergetic effect of Pt and Pd, which is particularly interesting since the activity of the Pt/Pd surface surpasses that of Pt nanoparticles with a seven times larger loading.

In addition to the polarization curves, a useful way of comparing the activities of electrocatalysts is by their mass-specific activities. Figure 6 shows the Pt mass-specific activity of the three electrodes containing Pt expressed as the current at 0.85 and 0.80 V divided by the Pt mass. The Pt mass-specific activity of the Pt/Pd/C electrode is 5–8 times higher than that of the Pt/C electrocatalyst. The noble metal (Pt + Pd) mass-specific activity, defined as the current at given potential divided by total noble metal mass (Pt + Pd) is twice as high as that of Pt/C. This finding underlines the importance of the monolayer-level electrocatalysts that can greatly lower the amount of Pt in the fuel cell’s electrode.

**Decreased oxidation of Pt on Pd**

As described in the introduction, one of the problems for O2 electrocatalysis is the large potential loss in the initial part of the polarization curve, which is a source of major inefficiency. The initial potential loss was partly attributed to inhibitory effect of OH adsorption on Pt at very positive potentials. The role of adsorbed OH (PtOH) is controversial. It was considered to be the reaction intermediate, but several workers proposed that PtOH is not derived from the reduction of O2 but rather from the reaction of H2O with Pt, thereby inhibiting the ORR. Recently, we demonstrated that PtOH had a negative electronic effect on O2 reduction kinetics, in addition to site blocking. To quantitatively evaluate these effects of the
Fig. 7. XANES spectra obtained with the Pt/Pd_{10}/C (a) and Pt/C (b) electrocatalysts at four different potentials in 1 M HClO_{4}. (c) A comparison of the change of the absorption peak as a function of potential for Pt/Pd_{10}/C and Pt/C expressed as a ratio of peak value at given potential and the peak value at 0.47 V.
PtOH species, the following equation was used,

\[ j_k (E) = j_0^* \left( 1 - \frac{\gamma_{OH}\theta_{OH}(E)}{e^{\theta^*}} \right)^m \exp \left( \frac{2.303 (E - E^*) - \varepsilon_{OH}\theta_{OH}(E)}{b^*} \right) \]  

(2)

where \( j_0^* \) and \( b^* \) are, respectively, the intrinsic exchange current and Tafel slope for an adsorbate-free Pt surface. The \( (1 - \gamma^* \theta)^m \)-term accounts for the geometric site-blocking effect, while the electronic effect is described by a coverage-dependent potential shift through the exponential term, \( \varepsilon \theta^* \), and \( m \) is the number of Pt sites involved in the rate-determining step. Equation (2) shows that a decrease in the coverage of PtOH can enhance the kinetics of \( \text{O}_2 \) reduction.

As discussed above, the observed increase in the catalytic activity of the Pt monolayer surfaces on Pd nanoparticles compared with the Pt nanoparticle electrodes appears to be caused partly by decreased formation of PtOH. This is in accord with the results of the DFT calculations which show a slightly smaller reactivity. Clear evidence of delayed oxidation of a Pt monolayer on Pd nanoparticles compared with the oxidation of Pt nanoparticles was obtained from \textit{in-situ} XANES measurements as a function of potential. Figure 7a shows the Pt L\textsubscript{3} edge spectra obtained with the Pt/Pd\textsubscript{10}/C electrocatalysts at different potentials. Only at the highest potentials there is an increase in the intensity of white line (edge peak) as a consequence of the formation of PtOH depleting Pt’s-band. The increase in the intensity of the white line for the Pt/C electrocatalyst commences at considerably less positive potentials (Figure 7b). This demonstrates that the oxidation of a Pt monolayer on Pd substrate requires higher potentials than do Pt nanoparticles on a carbon substrate. Figure 7c compares the change of the absorption peak as a function of potential for Pt/Pd\textsubscript{10}/C and Pt/C expressed as a ratio of peak value of given potential and the peak value at 0.47 V. As seen, there is a negligible change in the electronic properties of a Pt monolayer on Pd in comparison with Pt/C. No effect of the potential change is observed below 1 V. This suggests that PdOH plays a role in suppressing a PtOH formation. Pd is more easily oxidized than Pt and the coverage of PdOH already is high before PtOH formation commences. Repulsion between PtOH and PdOH delays the oxidation on Pt. This view is confirmed by the behavior of mixed monolayer on Pd(111). We note that voltammetry also recorded the decreased formation of PtOH on the Pt/Pd/C electrocatalysts with increasing potentials.

Long-term stability of a Pt monolayer on Pd nanoparticles

The long-term stability tests were carried out using the fuel cell with electrodes of 5.0 cm\textsuperscript{2} in area. The cathode was Pt/Pd/C catalyst containing 77 \( \mu \)g/cm\textsuperscript{2} of Pt (0.21 g/kW of Pt) and 385 \( \mu \)g/cm\textsuperscript{2} of Pd. Figure 8 illustrates the trace of the cell voltage at a constant current of 0.6 A/cm\textsuperscript{2} against time at 80 \( ^\circ \)C. Up to 1000 h, the cell voltage dropped about 120 mV, and then showed a much lower rate of decrease with time. The total loss in voltage was approximately 130 mV at 2300 h, the end of the test. Cyclic voltammetric measurements occasionally were made during the test to investigate changes in active
surface area of Pt in the cathode from charges determined by hydrogen adsorption/desorption peaks. This indicated losses of the active Pt surface area, by approximately 26\% at 1200 h and 29\% at 2000 h compared with the initial surface area before testing. These losses in Pt could reflect the dissolution of Pt at the operating potential, or the embedding of Pt atoms into the Pd substrate. The latter is predicted by the anti-segregation of Pt from Pd according to DFT calculations.\textsuperscript{19} We note that a part of the observed drop in voltage also may be due to losses at the anode (a commercial Pt/C electrocatalyst) since the measurements did not separate the losses at the anode and cathode in these fuel cells. The results are promising but further investigation is necessary to improve the long-time durability of the electrocatalyst.\textsuperscript{36}

CONCLUSIONS

The kinetics of O\textsubscript{2} reduction was studied on Pt monolayers deposited on the surface of Au(111), Ir(111), Pd(111), Rh(111) and Ru(0001) single crystals, and Pd nanoparticles. There was a small enhancement of the activity of this Pt monolayer on Pd substrates compared with that of Pt electrocatalysts. The ORR electrocatalytic activity of Pt monolayers supported on the single crystal surfaces showed a volcano-type dependence on the d-band center of the Pt monolayer structures.\textsuperscript{28} The heightened activity is partly attributed to a decreased OH adsorption shown by in situ XANES experiments.

Our findings demonstrate that the approach of placing sub-monolayer-monolayer Pt on a suitable nanoparticle substrate is an attractive way of designing ultra-low Pt loading electrocatalysts with improved ORR performance.

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ELEKTROKATALIZATORI ZA REDUKCIJU KISEONIKA SA PLATINSKIM MONOSLOJEM. UTICAJ SUBSTRATA I POSTOJANOST U VREMENU

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Описан је нов концепт добијања електрокатализатора који чине само монослој Pt на носику, илустрован резултатима добијеним електрохемијским техникама, апсорпцијом спектроскопијом X-зрака и скенирајућом тунелском микроскопијом. Електрокатализатори су синтетизовани новим методом депозиције Pt монослоја који се састоји од галванске замене Pt монослојем Cu депонованог на подпотенцијалима на Au(111), Ir(111), Pd(111) и Ru(0001) монокристалима и Pd наночестицама. Показано је значајно увећање кинетике редукције кисеоника на Pt монослоју на Pd(111) i Pd наночестицама у поређењу са Pt(111) и Pt наночестицама. Повећање катализичке активности је делимично пруžаковано умањеним стварањем PtOH, што је показано апсорпцијом спектроскопијом X-зрака. Резултати показују да је депозиција Pt монослоја на одговарајуће металне наночестице примаљив начин синтезе бољих катализатора за редукцију кисеоника са минималном количином Pt.

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