

# Electrocatalytic reactivity of Pt ad-layer modified Au(111) single crystal electrodes on reduction of oxygen

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Electrocatalytic reduction of oxygen at electrochemically deposited Pt ad-layer modified Au(111) electrodes was studied in an O<sub>2</sub>-saturated NaOH (0.1 M) solution. The results were compared with those obtained by using a polycrystalline Pt electrode and another Pt-deposited electrode prepared by replacement with Cu on bare Au(111). Linear sweep voltammetry displayed a positive shift of the oxygen reduction potential by about 0.14 V compared to the bare Au(111) electrode. This shift was about 0.06 V compared to a Pt disk electrode. Tafel slopes gradually changed between 0.06 and 0.1 V/dec, from 0.075 to -0.10 V/dec, from lower to higher current density region. The Pt ad-layer clearly served as a catalyst for oxygen reduction via 4-electron transfer. In terms of the desired shift in reduction potential and increased current density, the best electrocatalytic activity was obtained with a 30-s electrodeposited Pt ad-layer modified Au(111) electrode.

**Key Words:** Oxygen reduction, Pt ad-layer, Au(111) single crystal electrode, fuel cell

## Introduction

The electrochemical reduction of oxygen is especially important in fuel cell technology because the overpotential for oxygen reduction on noble metals, such as gold and platinum, is relatively large compared to that for hydrogen oxidation.<sup>1</sup> Electrocatalytic oxygen reduction in fuel cell cathodes has been the focus of attention due to its slow kinetics, and, therefore, the reduction mechanism has been studied at various electrode materials.<sup>2–10</sup> It has been established that the reaction can proceed as a 2- or 4-electron process, depending on the cathode material and cell composition.<sup>5–9</sup> The former pathway involves peroxide formation as the intermediate, which

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can undergo a further 2-electron reduction or decomposition. On platinum electrodes, the oxygen reduction follows the latter mechanism, where direct 4-electron reduction occurs in both acidic and alkaline media.<sup>11</sup> The necessity for better and less expensive electrocatalysts with decreased platinum content has led to an intensive search for alternative electrodes.

Single crystal gold electrodes serve as the most active catalysts for electrochemical oxygen reduction. On the Au(100) plane, 4-electron reduction is observed at low overpotentials, possibly through an adsorbed  $\text{HOO}^-$  intermediate in alkaline media.<sup>5,12</sup> On the other hand, the reduction of oxygen on Au(111) electrodes proceeds as a 2-electron process to hydrogen peroxide.

Over the last decade, much attention was paid to the use of nanoparticles of noble metals such as Pt, Au, and Pd, as their electrocatalytic activities differ from those of bulk metals. Improved catalytic activity was observed with single crystal electrodes modified with different metal layers.<sup>12–16</sup> A previous study was carried out with Au(111) electrodes modified with Cu, Bi, and Ag ad-atoms by the underpotential deposition technique.<sup>17,18</sup> The results of this study, together with those of Pd, Cd, and Zn ad-atom modified Au(111) electrodes, have revealed the enhanced catalytic activity of the modified electrode surfaces toward the oxygen reduction in alkaline solution, as higher peak currents were obtained compared to a bare Au(111) electrode.<sup>19</sup> This enhancement was also evident in the corresponding cyclic voltammograms, where the positive shift in the peak potential of oxygen was observed.

The excellent catalytic activity of platinum was utilized in a similar manner for obtaining less expensive ad-atom modified electrodes, and it was revealed that electrocatalytic activity depends on the particle size of the Pt and the shape of the electrode surface. Therefore, Pt deposition on the Au(111) electrode surface has been studied by several groups. Uosaki et al. have reported that Pt deposition took place as a layer-by-layer formation on a Au(111) electrode.<sup>20</sup> According to Kolb et al.<sup>21</sup> and Friedrich et al.<sup>22</sup>, Pt deposition on the Au(111) electrode starts at defects on the surface. Overall studies have revealed that submonolayer deposition of Pt could be carried out by the electrochemical reduction of a  $\text{PtCl}_6^{2-}$  solution in an acidic medium. The performances of these electrodes are required to be compared on the same basis for developing a reliable alternative.

The present work describes the comparative results of electrocatalytic oxygen reduction on Pt ad-layer modified Au(111) electrodes prepared by 2 different techniques and those of bare Au(111) and Pt electrodes deduced from the corresponding voltammetric curves, recorded in an  $\text{O}_2$ -saturated NaOH (0.1 M) solution. The Pt ad-layer was deposited either electrochemically or by replacement with Cu on the bare Au(111) and polycrystalline Pt electrodes to expose a better substitute for the oxygen reduction process.

## Experimental

Au(111) single crystal electrodes were prepared with Au wire (99.99% in purity, Tanaka Kikinzoku Kogyo Co., Ltd.) using the flame annealing-quenching method as described elsewhere in detail and references therein.<sup>17,23</sup> The quality of the single crystal plane was judged by measuring the cyclic voltammogram in a  $\text{H}_2\text{SO}_4$  solution (0.1 M). NaOH,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$  (ultrapure grade, Merck) were used to prepare the electrolytes.  $\text{K}_2\text{PtCl}_6$  was purchased from Sigma and served to prepare solutions for the underpotential deposition (UPD) experiments.  $\text{H}_2\text{O}_2$  (30%-35%, Merck) was also used. All solutions were prepared using ultrapure water (Milli-Q 18.2

M $\Omega$ /cm, Millipore System Inc.).

Voltammetric measurements were made with an IviumStat potentiostat and a BAS 100B/W voltammetric analyzer (Bioanalytical Systems, Inc.). Pt ad-atom modified Au(111) electrodes were prepared either electrochemically or by replacement with Cu on bare Au(111). In the usual replacement technique, Pt ad-atom modified electrodes were obtained by transferring the electrodes with a Cu ad-atom coverage of a 1/1 monolayer (ML), prepared by the same method described in a previous study,<sup>23</sup> into a 1 mM K<sub>2</sub>PtCl<sub>6</sub> + 0.1 M H<sub>2</sub>SO<sub>4</sub> solution, kept for 10 min to allow all of the Cu ad-atoms to exchange with the Pt ad-atoms.<sup>24</sup> The coverage obtained was estimated stoichiometrically to be either approximately 0.15 ML or 0.5 ML of Pt ad-atoms for the replacement of either 1/3 ML or 1 ML of Cu ad-atoms, respectively.

In the second technique, a Pt ad-atom modified Au(111) electrode was prepared by reduction of K<sub>2</sub>PtCl<sub>6</sub> on a Au(111) electrode surface at -0.40 V before bulk deposition potential for several deposition times, such as 15, 30, 60, and 90 s. In both methods, the extent of the Pt coverage was maintained by controlling the time elapsed for the chemical or electrochemical process, and then cyclic voltammograms were monitored in a deaerated H<sub>2</sub>SO<sub>4</sub> medium. All modified electrodes were rinsed thoroughly with ultrapure water (Milli-Q 18.2 M $\Omega$ /cm) prior to being transferred to another electrochemical cell filled with a solution containing oxygen or hydrogen peroxide. Voltammograms were measured at a scan rate of 0.050 V/s using Ag/AgCl:KCl (sat.) and the Pt-plate as the reference and counter electrodes, respectively. The experiments in an oxygen-free solution were done under a N<sub>2</sub> gas atmosphere of high purity. The surface area was simply estimated from the diameter of the electrode surface, and this value was used in current density calculations.

## Results and discussion

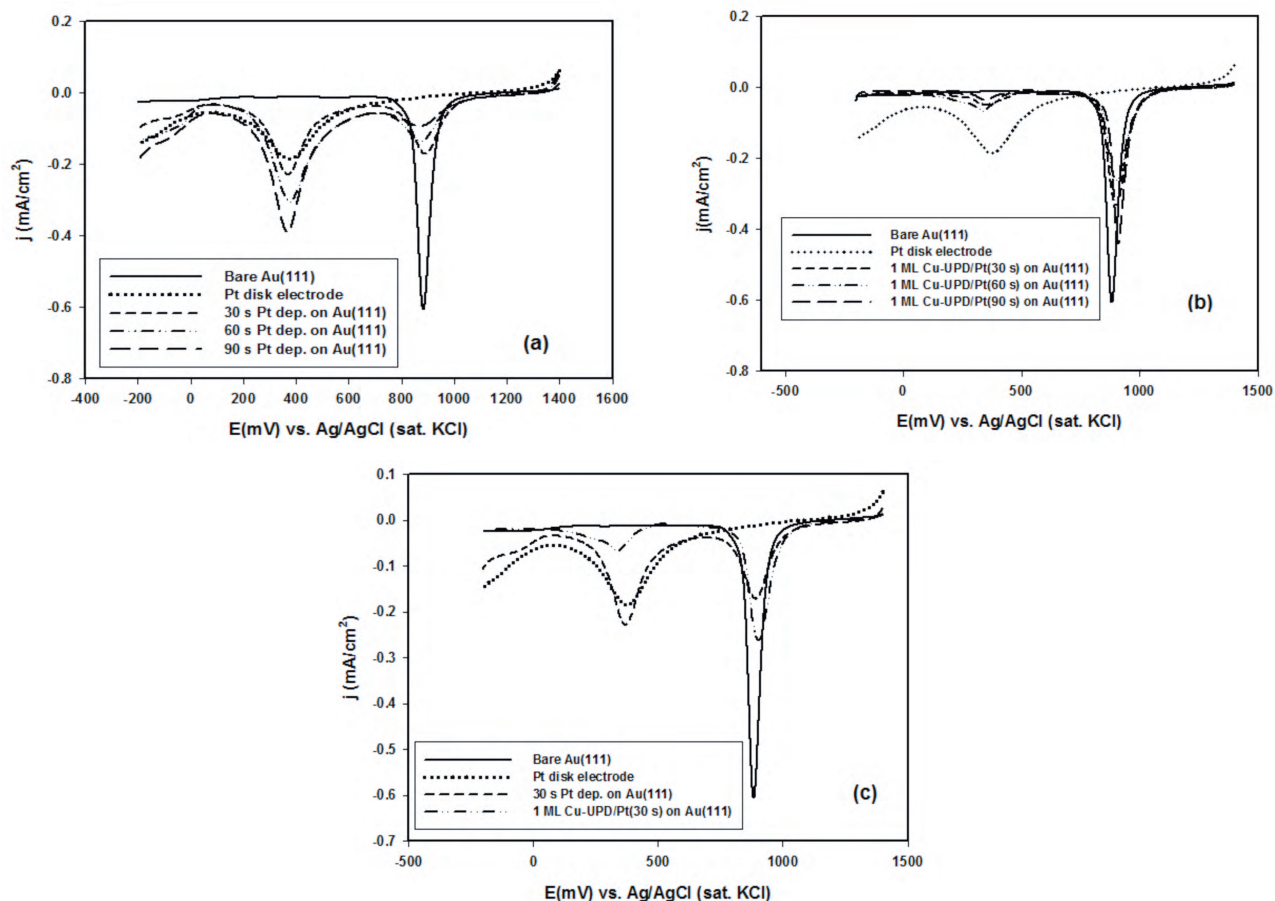
Prior to electrode modification and oxygen reduction measurements, the single crystal Au(111) electrode was electrochemically characterized by running cyclic voltammograms in a potential range of -0.80 to 0.35 V in a H<sub>2</sub>SO<sub>4</sub> medium.

The cyclic voltammograms obtained were found to be in agreement with those given in the literature.<sup>25</sup> The cycling was repeated in the presence of PtCl<sub>6</sub><sup>2-</sup> and the resulting voltammograms were in good agreement with those in the reported works for Pt ad-layers.<sup>21</sup>

The voltammetric behavior of the modified electrodes, in comparison to those of the bare Pt and Au(111) electrodes, can be seen in Figures 1a-1c. The reduction peak of platinum was located at 0.35 V on the Pt disk electrode, whereas surface oxide was reduced at 0.88 V on the bare Au(111) electrode. Pt ad-atom modified electrodes were prepared either by using electrochemical deposition (Figure 1a) or a displacement reaction (Figure 1b) between the platinum ions and the Cu ad-atoms formerly deposited by the UPD technique. In both methods, the linear voltammetric behavior of the Pt ad-layer modified Au(111) electrodes displayed some similarities with those of the bulk Au(111) electrode and the Pt polycrystalline electrode. As can be seen from Figure 1c, the voltammograms exhibited reduction peaks of gold and platinum oxides, indicating that the Au(111) surface was not fully covered by platinum ad-atoms, even after 90 s of deposition. The voltammetric behavior of this modified electrode with less than monolayer coverage differed from both the Pt disk and the Au(111) electrode, and, therefore, they can be considered for use in catalytic reactions.

Representative current-potential curves for the Pt ad-layer modified Au(111) electrode formed by elec-

trodeposition and replacement method at various reaction times are given in Figures 1b and 1c, respectively. The voltammetric signal of the 30-s deposited Pt ad-atom and the Pt replacement with 1/1 ML Cu ad-atom modified Au(111) electrodes showed good agreement with those in the reported works.<sup>11,21</sup>

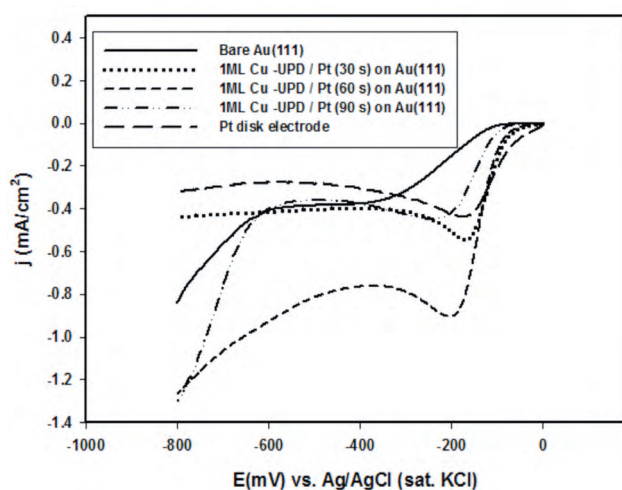


**Figure 1.** Linear voltammetric behavior of a) Pt ad-atom modified Au(111) electrodes prepared by electrodeposition technique; b) Pt ad-atom modified Au(111) electrodes prepared by replacement with 1/1 ML Cu; c) comparison of Au(111), Pt disk, Pt ad-atom modified with 30 s of electrodeposition of Pt at -0.4 V, and Pt ad-atom modified with replacement with 1/1 ML Cu at 90 s of reaction time in a deaerated H<sub>2</sub>SO<sub>4</sub> solution.

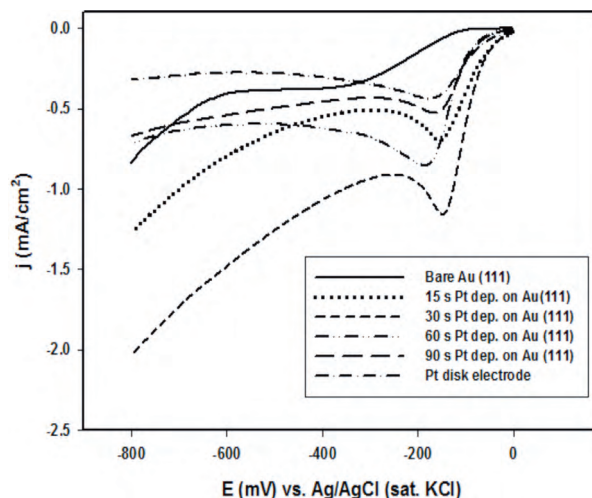
Linear voltammograms recorded for the oxygen reduction in alkaline media on Au(111), polycrystalline Pt disk, and Pt ad-atom modified Au(111) electrodes prepared with different reaction times of replacement of 1/1 ML Cu ad-atoms are given in Figure 2. A broad reduction wave at around -0.35 V was observed for oxygen at the single crystal Au(111) electrode, in good agreement with the literature.<sup>20,26</sup> On the other hand, a single well-defined reduction peak was observed at approximately -0.19 and -0.20 V for the oxygen reduction in a NaOH (0.1 M) solution at the Pt replacement with the 1/1 ML Cu ad-atom on Au(111) and Pt disk electrodes, respectively. If we compare the polarization curves with those obtained under the same experimental conditions only with modified Au(111) electrodes via replacement reaction, it can be clearly said that surface modifications

maintained the desired change in peak characteristics in terms of peak potentials and current densities. The Pt ad-layer modified Au(111) electrodes prepared with different coverage depending on the reaction time, in the range of 30 to 120 s, showed similar electrocatalytic activity toward oxygen reduction in terms of peak location. A marked shift in the oxygen reduction peak, almost 0.15 V toward the positive potentials, indicated the improved kinetics of the electron transfer reaction in the presence of Pt ad-atoms. The best enhancement in peak current density was observed with a 60-s replacement reaction, which corresponds to the 0.5 ML Pt ad-layer on the Au(111) electrode surface.

For comparison, oxygen reduction was studied using Pt ad-atom modified Au(111) electrodes, which were electrochemically deposited at  $-0.40$  V for different deposition times in acidic solution. Figure 3 shows the overlaid voltammograms of oxygen on bare Au(111), polycrystalline Pt disk, and Pt ad-atom modified Au(111) electrodes for evaluation in the same potential range. The oxygen reduction peak appeared as a broad peak at the bare Au(111) electrode, as the electron transfer process was slow-moving in alkaline media. On the other hand, a distinct peak was observed at  $-0.20$  V for the polycrystalline Pt electrode, indicating a fast electron transfer. In terms of peak shape and location, the performance of the Pt ad-layer modified Au(111) electrode toward oxygen reduction was found to be very effective compared to the bare electrodes. The most promising response was obtained with a 30-s electrochemically deposited Pt ad-layer modified Au(111) electrode. Significant current enhancement, as a peak rise about 3.4 times that of the bare Au(111) and 2.8 times that of the Pt disk electrode, was observed, while the peak potential shifted about 0.2 V and 0.06 V in positive directions, respectively. Improved peak characteristics implied that faster electron transfer can be achieved through a bimetallic surface prepared in controlled composition by simply adjusting the deposition time on Au(111).



**Figure 2.** Linear sweep voltammograms of oxygen reduction on bare Au(111), Pt disk, and Pt ad-atom modified Au(111) electrodes prepared with different reaction times of replacement of 1/1 ML Cu ad-atoms.

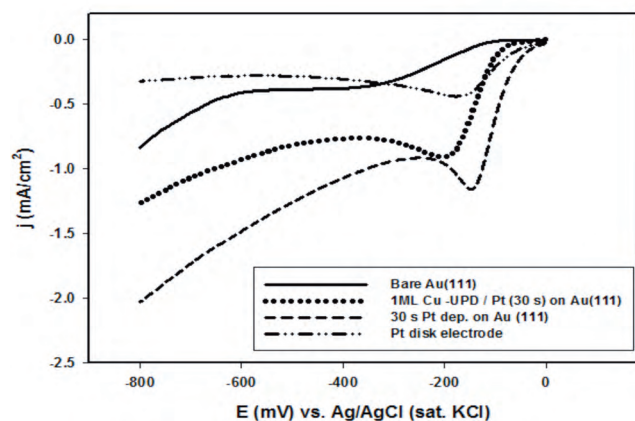


**Figure 3.** Linear sweep voltammograms of oxygen on bare Au(111), polycrystalline Pt disk, and Pt ad-atom modified Au(111) electrodes.

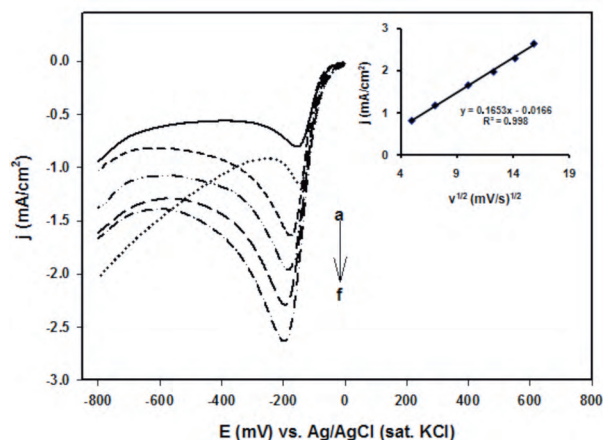
Overall results revealed that both methods used for modifications of Au(111) electrodes with a Pt

ad-layer maintained a satisfactory enhancement in peak characteristics related to oxygen reduction. Figure 4 clearly demonstrates the distinction in the performances of the modified and bare electrodes for oxygen reduction in alkaline media. Here, 30 s was taken as the reaction or deposition time to see the difference between the techniques. A major contribution to the electrocatalytic activity of the electrode was maintained by electrochemical deposition of platinum ad-layers, resulting in an increase in peak current densities 3 times that of the bare Au(111) and polycrystalline platinum electrodes. Chemical replacement of copper with platinum probably proceeded slower than expected, and, therefore, submonolayer coverage of Pt as a mixture with the remaining copper ad-atoms on the single crystal gold surface served as a less effective surface for catalysis. This finding was in agreement with a former study in which Cu(I) species were detected on the gold surface after the replacement reaction.<sup>21</sup>

Plots of the oxygen reduction peak current and peak potential vs. (scan rate)  $1/2$  for the Pt ad-layer modified Au(111) electrode are given in Figure 5. The peak current showed a linear increase with the square root of the scan rate, indicating a diffusion-controlled reduction process.



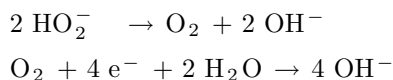
**Figure 4.** Comparative linear voltammograms of the bare Au(111), Pt disk, and Pt ad-atom modified Au(111) electrodes.



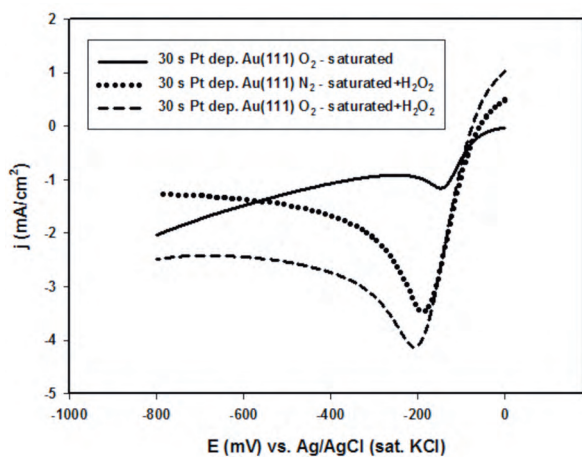
**Figure 5.** Cyclic voltammograms of different scan rates of oxygen reduction on 30-s Pt dep. on Au(111): a) 0.025, b) 0.050, c) 0.10, d) 0.15, e) 0.20, and f) 0.25 V/s; inset: square root of the scan rate vs. current density.

The electrochemical behavior of hydrogen peroxide was studied in the presence or in the absence of oxygen in alkaline solution, to ensure that the peaks were related to the electrode reaction. Hydrogen peroxide was added to the electrolyte in the presence or in the absence of oxygen, and in both cases, a reduction peak was observed at the same potential as that of the oxygen reduction at the Pt ad-layer modified Au(111) electrode, as given in Figure 6. For the solutions saturated with oxygen, current densities were found to be 4.8 and 1.2 mA/cm<sup>2</sup> in the presence and absence of hydrogen peroxide, respectively. After bubbling the solution with nitrogen, the current density resulting from hydrogen peroxide was observed to be 3.7 mA/cm<sup>2</sup>. The difference in the current density values of hydrogen peroxide agrees well with the density figure obtained in the absence of hydrogen peroxide. As mentioned in our previous studies,<sup>19,23</sup> catalytic decomposition of dissolved oxygen is expected to be very fast, and a 4-electron reaction takes place on the electrode surface. The anodic peak at -0.07 V in the presence of peroxide indicates that an electrochemical decomposition takes place on the electrode

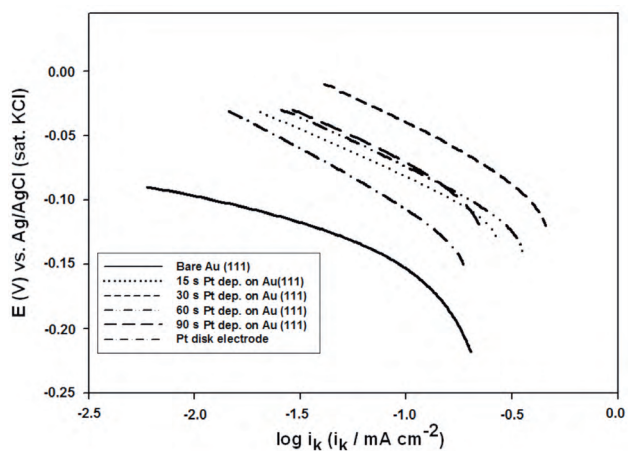
surface with a pathway as given below.



Tafel behavior was also studied in the mixed kinetic-diffusion control region by using mass-transport currents with a scan rate of 0.003 V/s at the Pt ad-layer modified Au(111) electrode (Figure 7). Tafel slopes gradually changed between the potential range of 0.06 to -0.10 V, from 0.075 V/dec at lower current densities to -0.10 V/dec in the higher current density region. These slopes were found to be similar to those of Pt films on polycrystalline Au and Pt electrodes,<sup>8</sup> and Pd/C and Pt/C.<sup>27</sup> In the low current densities, all Pt ad-layer modified electrodes led to Tafel slopes around 0.07-0.08 V/dec, whereas the Pt disk gave a slope of -0.10 V/dec. This value in the presence of an ad-layer was found to be independent of the Pt amount until bulk deposition. The data indicate a stage of low first electron transfer step, being the rate-determining step for oxygen reduction at Pt ad-layer modified Au(111) electrodes in the low current densities. In high current density regions, polycrystalline Pt, Au(111), and Pt ad-layer modified Au(111) electrodes gave Tafel slopes of about -0.10 V/dec.



**Figure 6.** Influence of  $\text{H}_2\text{O}_2$  on oxygen reduction on 30-s Pt dep. Au(111).



**Figure 7.** Tafel slopes for oxygen reduction in 0.1 M NaOH at 25 °C on Pt ad-layer modified Au(111) electrodes and bare Pt and Au(111) electrodes. The scan rate was 0.003 V/s.

Two Tafel slope regions can be attributed to the change from Temkin to Langmuir conditions for changing the coverage of the surface by adsorbed oxygen species or to the change in the surface coverage of OH, which affects the oxygen adsorption on the electrode surface.<sup>28</sup>

## Conclusion

A purely bimetallic electrode surface was prepared by electrochemically depositing Pt on a single crystal Au(111) electrode, and voltammetric characterization depicted that a submonolayer Pt ad-layer modified Au(111) can

be prepared by this technique. Electrocatalytic reduction of oxygen was studied at the electrochemically deposited Pt ad-layer modified Au(111) and compared with Pt deposited by replacement with Cu on Au(111), bare Au(111), and polycrystalline Pt electrodes in an O<sub>2</sub>-saturated NaOH (0.1 M) solution. Linear sweep voltammetry displayed a 0.14 V positive shift compared with the bare Au(111) electrode and a 0.06 V positive shift compared with the Pt disk electrode for the oxygen reduction potential. A significant increase in the current density was observed at almost all Pt ad-layer modified Au(111) electrodes, showing that a fast electron transfer occurs on the modified electrode surfaces compared to both bare Au(111) and polycrystalline Pt electrodes. The most electrocatalytic activity toward oxygen reduction was obtained with 30 s of electrodeposition of Pt as less than 1.0 ML on the Au(111) electrode. Surface modification with both electrochemical preparation and replacement with Cu ad-atoms proved to be effective on the electrocatalytic behavior of the Au(111) electrode and promising for its utility in metal-air batteries, fuel cells, oxygen sensors, and metal corrosion applications.

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