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# Electrocatalytic oxidation of methanol at Pd and Pt ad-layer modified Au(111) electrodes in alkaline solution

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The electrochemical oxidation of methanol was investigated by using various ad-layer modified Au(111) electrodes in alkaline media in comparison to Au(111), polycrystalline Pd, and polycrystalline Pt electrodes. Catalytic activity of gold toward methanol oxidation has tended to increase in more alkaline media, as reflected in the oxidation peak in the concentration range of NaOH (0.1-3.0 M) studied here. The oxidation peak potential of methanol shifted to more negative potentials, indicating a pH-dependent surface reaction. Among the electrodes studied, single-crystal gold electrode surfaces modified with Pd and Pt ad-layers displayed the highest catalytic activity for methanol oxidation. Additional shifts of about 350 mV in the oxidation peak potential of methanol was observed for both ad-layer modified electrodes to more negative potentials compared to that of bare electrodes. The Pd and Pt ad-layer modified Au(111) electrode surfaces did not only supply a superior electrical contact, but also accelerated electron transfer, as shown by the increase in peak current and the positive shift in peak potential. This effect was supported by the doublelayer capacitance measurements of bare Au(111) and Pd ad-layer modified singlecrystal electrodes where the potential of zero charge changed from 15 to 5 mV.

**Key Words:** Methanol, fuel cell, Pd ad-layer, Pt ad-layer, underpotential deposition

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# Introduction

Direct methanol fuel cells (DMFCs) are one of the most attractive sources of electrical power due to their ease of handling and high energy densities.[1–3] Methanol has a great potential for low-temperature fuel cells, and platinum is commonly employed as the anode material for its electrocatalytic oxidation.[4–6] However, these electrodes are very expensive and easily poisoned by reaction intermediates, resulting in serious deactivation.[7] To avoid this poisoning, researchers have extensively used bimetallic catalysts such as Pt-Ru, Pt-Pd, and Pt-Au.[5,8–10] The Pt-Au combination has proved to be beneficial and performed better than bare platinum electrodes in oxygen reduction at a fuel cell cathode.[11]

Besides platinum, gold electrodes are also used as a catalyst toward methanol oxidation in alkaline solutions, which can avoid the generation of the poisoning intermediates.[9] Electrooxidation of methanol on polycrystalline and single-crystal gold electrodes was investigated in acidic, neutral, and alkaline solutions.[9,10] Overall results revealed that the reaction is catalyzed by chemisorbed $OH^-$ anions and, therefore, the catalytic activity strongly depends on the medium's pH. In fact, Borkowska et al.[3,10] reported that the highest oxidation current was observed in 0.01 and 0.1 M KOH solutions.

Major developments in this area have been prompted by the introduction of foreign metal atoms onto electrode surfaces to enhance the catalytic activity toward organic compounds.[11–15] The conventional electrodeposition processes in general lead to bulk deposition rather than ad-layer modification. Therefore, accepted modification methods involve spontaneous deposition[16] and other complex methods, such as electron beam lithography and scanning tunnel microscopy (STM).[16,17] In addition, underpotential deposition (UPD) has received much attention as a versatile tool for the preparation of ad-layer modified surfaces.[14,15] Studies have revealed that metal electrode surfaces modified with deposited metal ad-layers by UPD are different in physical and chemical properties from both substrate metal and isolated bulk deposited metal.[15] Generally, Pt, Pd, Rh, Ir, Ru, Au, and Ag electrodes have been employed as the substrate, and the catalytic activity has been tested upon modification of the electrode surface with Cu, Ag, Cd, Pb, and Sn ad-layers.[5,8,12,15,18] These modified electrodes have been applied to the electrochemical reactions of a variety of compounds, such as glucose,[15,18,19] methanol,[20] ethanol, formic acid, and carbon monoxide.[21]

Among these electrodes, gold-based electrocatalysts are the most promising, in addition to their viability compared to platinum group metals. The surface changes by UPD of an ad-layer on a Au(111) electrode have been characterized by a number of techniques such as IR, AFM, SEM, in situ STM,[16,22,23] and surface X-ray diffraction (SXD).[22–24]

The catalytic activity of ad-layer modified single-crystal gold electrodes toward small organic molecules has been investigated.[24] Methanol, for instance, requires hydroxide ions chemisorbed at the gold electrode surface for oxidation.[20] On the other hand, few data are available on methanol oxidation in high concentrations of KOH or NaOH on single-crystal gold electrodes.[3,10] The main objective of the present study was to investigate the electrocatalytic oxidation of methanol at different ad-layer modified single-crystal gold electrodes prepared by UPD in alkaline media. The results were compared with the performances of bare Au(111) and polycrystalline gold electrodes.

## Experimental

The methanol used was of analytical grade (Merck). Solutions were prepared from ultrapure grade NaOH and concentrated $H_2SO_4$. All solutions were prepared using ultrapure water (Millipore).

Cyclic voltammetry was carried out using a BAS 100W. The counter electrode was a platinum wire and the reference electrode was Ag/AgCl (sat. KCl). The 3-electrode system was completed by using either a single-crystal or a gold polycrystalline electrode. The gold polycrystalline electrode (diameter: 1.5 mm) was polished using an $Al_2O_3$ slurry on a piece of cloth. After rinsing with ultrapure water, the electrode was immersed in solution.

Single-crystal electrodes were prepared from Au wire (99.99% in purity; Tanaka Kikinzoku Kogyo Co., Ltd.) using the flame-annealing-quenching method as described elsewhere in detail.[15] The electrodes were cleaned thoroughly with ultrapure water, flame-annealed, quenched, and water-protected with a drop of water before being transferred to the cell.

The performance of the Au(111) single-crystal electrode was tested by recording cyclic voltammograms (CVs) in a 0.1 M $H_2SO_4$ solution to see the characteristic peaks. Prior to the measurement, solutions were deoxygenated by purging with $N_2$ gas, and then scanning was initiated from –800 mV at a rate of 50 mV $s^{-1}$.

For Pd-UPD experiments, 9.4 mM $Pd^{2+}$ solutions were prepared from Pd powder (99.9%, $<75$ $\mu$m) in 0.1 M $H_2SO_4$ acid medium. For preparation of Pd-UPD electrodes, an Au(111) single-crystal electrode was immersed in a 0.2 mM $PdSO_4$ + 0.1 M $H_2SO_4$ solution and the potential scan was initiated immediately from 200 mV (vs. Pt-plate) at a scan rate of 5 mV $s^{-1}$ until the deposition of the Pd ad-layer gave a coverage of 1/5, 2/5, or 1 monolayer (ML) or bulk layer at –50, –110, –350, and –1100 mV (vs. Pt-plate), respectively.

Pt ad-layer modified Au(111) electrodes were prepared either electrochemically or by replacement with Cu on bare Au(111). In the usual replacement technique, Pt ad-layer modified electrodes were obtained by transferring the electrodes with a Cu ad-layer coverage of 1/1 ML, prepared by the same method described in a previous study[12] into a 1 mM $K_2PtCl_6$ + 0.1 M $H_2SO_4$ solution and keeping it for 10 min to allow all of the Cu ad-layer to exchange with the Pt ad-layer[18] The coverage obtained was estimated stoichiometrically to be either approximately 0.17 or 0.5 ML of Pt ad-layer for the replacement of either 1/3 ML or 1 ML of Cu ad-layer, respectively.[19]

In the second technique, a Pt ad-layer modified Au(111) electrode was prepared by reduction of $K_2PtCl_6$ on a Au(111) electrode surface at –40 mV before bulk deposition potential for deposition times of 15, 30, 60 and 90 s. In both methods, the extent of Pt coverage was maintained by controlling the time elapsed for the chemical or electrochemical process and then CVs were monitored in deaerated $H_2SO_4$ media. All modified electrodes were rinsed thoroughly with ultrapure water (Milli-Q 18.2 M$\Omega$ $cm^{-1}$, Millipore) prior to transfer to another electrochemical cell filled with a methanolcontaining solution, and voltammograms were measured at a scan rate of 50 mV $s^{-1}$ using Ag/AgCl, KCl (sat) and the Pt-plate as the reference and counter electrodes, respectively.

All ad-layer modified electrodes were rinsed thoroughly with ultrapure water prior to transfer to another electrochemical cell filled with a methanol- or NaOH-containing solution, and CVs were measured at a scan rate of 50 mV $s^{-1}$ using Ag/AgCl, KCl (sat.), and the Pt-plate as the reference and counter electrodes, respectively. The Pd ad-layer at the electrode surfaces was cleared out by applying a potential of +900 mV (vs. Pt-plate)

for 10 min. For the double-layer capacitance measurements of the electrodes, an AUTOLAB ECO CHEMIE analyzer system was used.

# Results and discussion

## Electrooxidation of methanol on bare gold electrodes in alkaline media

The electrooxidation of methanol on gold materials, namely a polycrystalline Au disk and single-crystal Au(111) electrode, was investigated in highly alkaline media. Initial studies were conducted to see the performance of the electrodes in 1.0 M NaOH electrolyte solution, and CVs were recorded in the absence and presence of methanol for comparison with the literature data.[3]

The CVs obtained in deaerated 1.5 M methanol solution in 1.0 M NaOH medium for polycrystalline gold and Au(111) electrodes are given in Figure 1. In accordance with the mechanism described earlier,[3] the polycrystalline gold electrode had an oxidation peak at 240 mV and a reduction peak around 80 mV in the reverse scan, indicating a quasireversible electrode process. In case of the single-crystal electrode, the anodic peak appeared at 120 mV and doubled in size for the same concentration. This negative shift in peak potential and increase in the peak current density indicates the pronounced effect of the crystal structure and its catalytic effect on charge transfer. A reverse peak formation was observed on the cathodic scan, which is associated with the removal of carbonaceous species not completely oxidized in the forward scan and then the oxidation of freshly chemisorbed methanol species.[25]

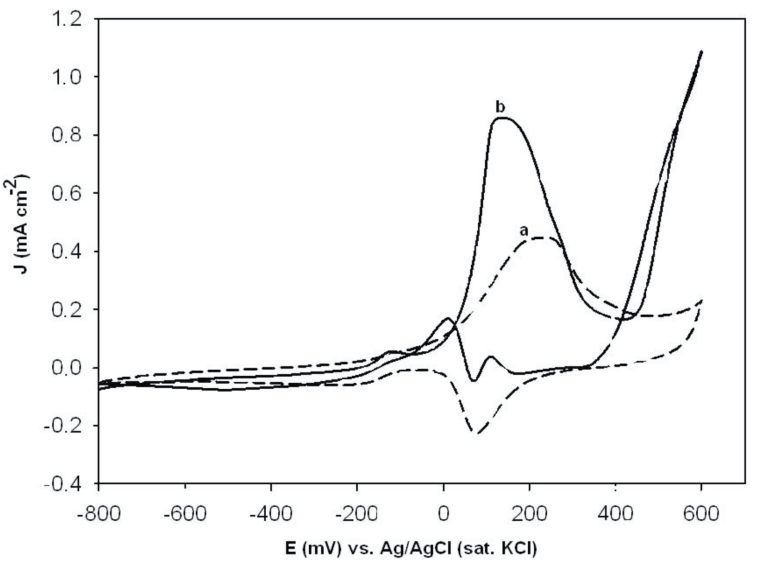



**Figure 1.** Cyclic voltammograms recorded for 1.5 M methanol at a) Au polycrystalline and b) Au(111) electrodes in 1.0 M NaOH medium.

Further studies dealt with the electrooxidation of 1.0 M methanol at a Au(111) electrode in extremely alkaline conditions by introducing NaOH into the cell from 0.1 to 3.0 M. CVs recorded in 0.1 M NaOH medium

displayed an oxidation peak at +230 mV, which shifted to more negative potentials as the cell content was made more alkaline. As can be seen in Figure 2, the peak potential eventually shifted to 80 mV in 3.0 M NaOH solution. The peak current also displayed an increase in proportion to the NaOH concentration. This change in the peak characteristics can be attributed to the improved catalytic activity by increasing the coverage of $OH^-$ anions on the electrode depending on the chemical structure of the gold surfaces.

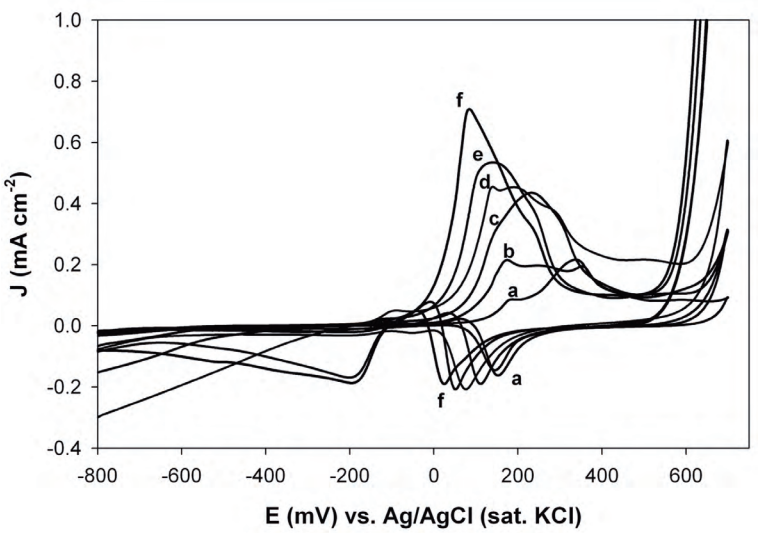



**Figure 2.** Cyclic voltammograms of 1.0 M methanol at Au(111) electrode in a) 0.1, b) 0.25, c) 0.5, d) 1.0, e) 2.0, and f) 3.0 M NaOH.

## Pd ad-layer modified Au(111) electrode

Pd ad-layer modified electrodes were prepared by UPD to compare their performance in highly alkaline media with those of the bare electrodes. For this purpose, the Au(111) single-crystal electrode was immersed in 0.2 mM $PdSO_4$ + 0.1 M $H_2SO_4$ solution and the potential was scanned from 200 mV to –1200 mV at a rate of 5 mV $s^{-1}$. In accordance with the literature,[25–29] peaks were observed at –50, –110, –350, and –1100 mV vs. Pt-plate, with surface coverage of 1/5, 2/5, and 1/1 ML and bulk layer, respectively.

The catalytic effect of the Pd ad-layer modified single-crystal electrode on methanol oxidation was studied with different Pd ad-layer coverage. Shown in Figure 3 is a representative set of CVs obtained in deaerated 1.0 M methanol prepared in 1.0 M NaOH solution for Pd ad-layer modified electrodes with different coverage ratios (1/5, 2/5, 1/1 ML). The CVs of supporting electrolytes are given in the inset of Figure 3. For comparison, the CV of the Pd disk electrode and the bare Au(111) electrode are also included.

The oxidation peak for methanol was observed at about 120 mV (vs. Ag/AgCl) on the bare Au(111) electrode in 1.0 M NaOH solution. As the coverage ratio increased, the peak related to the palladium reduction shifted to more negative potentials and increased in height, as well. Overall data showed that the best catalytic activity was observed with the 1 ML Pd ad-layer modified Au(111) electrode in comparison to the bare Au(111), with a 320-mV shift from +130 mV to –190 mV (vs. Ag/AgCl (sat. KCl)). On the other hand, the peak current density of methanol at this electrode was found to be smaller than that of the Pd polycrystalline electrode.

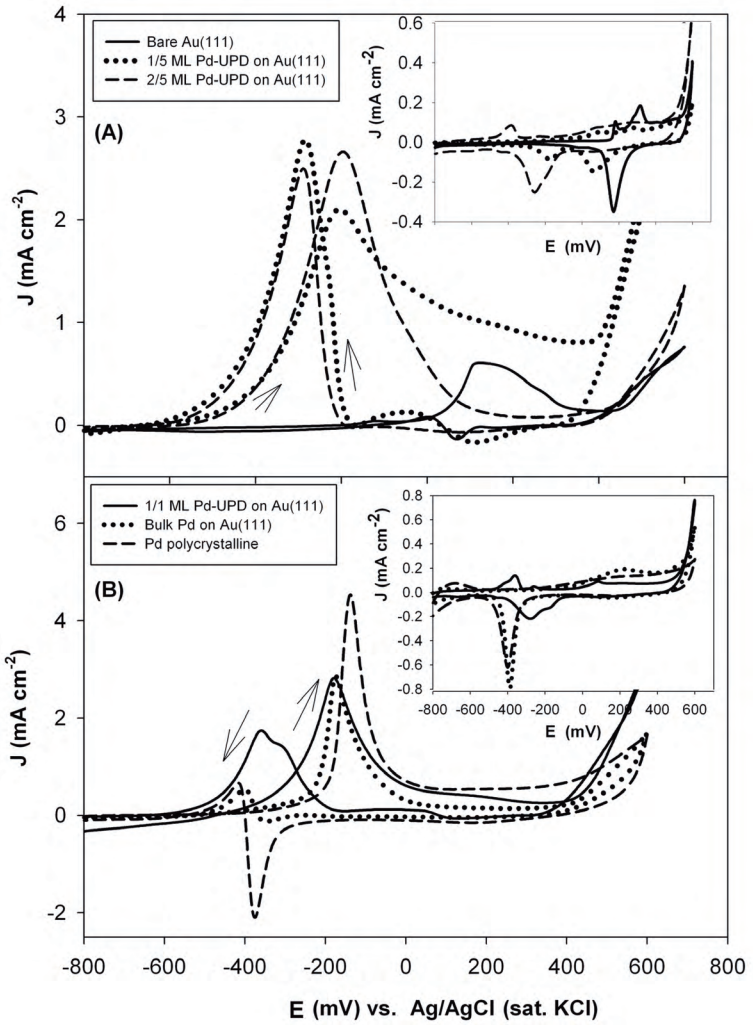



**Figure 3.** Cyclic voltammograms for 1.0 M methanol oxidation in 1.0 M NaOH: A) bare Au(111) and 1/5 and 2/5 ML Pd-UPD on Au(111); B) 1 ML Pd-UPD on Au(111), bulk and Pd polycrystalline electrodes. CVs of supporting electrolytes are given in the inset.

Tafel plots obtained from CVs of 1.0 M methanol oxidation at Pd ad-layer modified Au(111) and Pd polycrystalline electrodes in 1.0 M NaOH solution are given in Figure 4. It can be clearly seen that the best activity toward methanol oxidation was observed with 2/5 ML Pd ad-layer modified on a Au(111) electrode. For the low current density region in a range of 0.14-0.10 V $dec^{-1}$ for Au crystal electrodes and 0.10 V $dec^{-1}$ for polycrystalline Pd electrodes, 2 different Tafel slopes were obtained. The high current density region corresponds to a slope of 0.21 V $dec^{-1}$ for all Pd ad-layer modified Au(111) electrodes and Pd polycrystalline electrodes.

The Tafel slopes in each potential region can be concluded as being in agreement with published data.[3,10] In the low current density region, the adsorption of methoxy species could be independent of the potential and the amount of the Pd ad-layer on the electrodes. It can be claimed that surface reaction follows a Temkin-type isotherm, in agreement with a study carried out with ethanol at a Pd electrode.[30] In the high current density

region, the Tafel slopes increase from 0.10 V $dec^{-1}$ to 0.2 V $dec^{-1}$.

Figure 5 shows the double-layer capacitance measurements of the bare and Pd ad-layer modified Au(111) electrodes in 1.0 M NaOH medium. All capacitance measurements were done by scanning the potential from –800 to 600 mV, and the potential of zero charge (pzc) of the bare Au(111) electrode was observed at 150 mV vs. Ag/AgCl. The pzc values of the polycrystalline Pd and Au electrodes were found to be –180 mV and 280 mV, respectively. Upon covering the surface of the single-crystal electrode by the UPD technique with 1 ML of Pd ad-layer, the pzc shifted to 50 mV vs. Ag/AgCl. The electrocatalytic activity of the Pd ad-layer-modified Au(111) electrode upon methanol oxidation reaction can be attributed to the change in the electrode surface charge after Pd deposition.

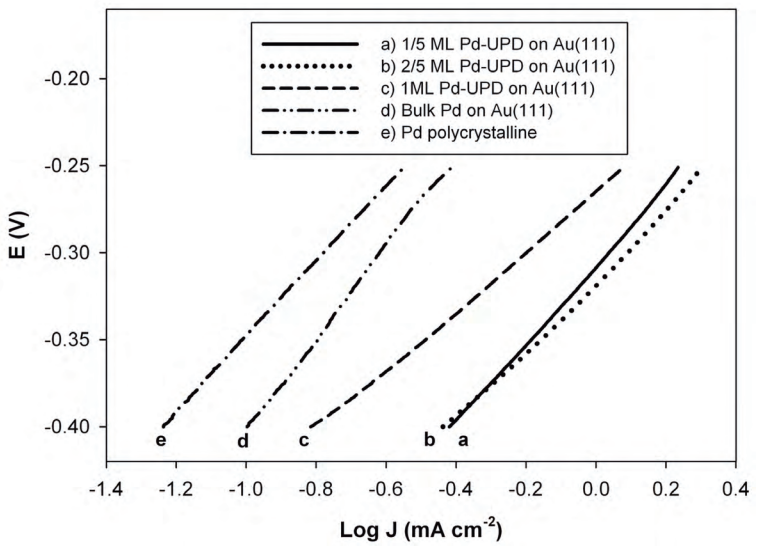



**Figure 4.** Tafel slopes for methanol oxidation in 1.0 M NaOH on Pd ad-layer modified Au(111) electrodes and Au(111) electrodes.

## Pt ad-layer modified Au(111) electrode

Platinum films were deposited on the Au(111) surface by means of the replacement technique.[12] In this technique, an atomic layer of copper is deposited on the electrode by UPD and a Cu-coated electrode is immersed in a platinum solution for a chemical replacement reaction. The performance of the electrode depends on both the coverage ratio of the platinum, which is controlled by the time elapsed in platinum solution, and the coverage ratio of the copper on the surface, where the replacement reaction is undertaken. In this study, UPD-deposited 1/3 and 1/1 ML Cu ad-atom Au(111) electrodes were immersed in platinum solution for 30-120 s. Best results were obtained with 60 s of immersion, and from the calculations made with peak areas, the platinum coverage ratios of 1/3 and 1/1 ML copper modified electrodes were found to correspond to 0.17 and 0.5 ML, respectively.

Figure 6 shows the CVs of 1.0 M methanol obtained with these modified electrodes in comparison to the bare Au(111) and platinum disk electrodes. For both modified electrodes, the oxidation peak of methanol shifted to negative potentials, from 120 mV to –180 mV (vs. Ag/AgCl). The peak current density of methanol

was twice as large as that of the platinum disk at the 0.5 ML Pt ad-layer modified single-crystal electrode. Therefore, the replacement technique can be concluded to improve the catalytic activity for methanol oxidation in terms of peak potentials and peak current densities, as well.

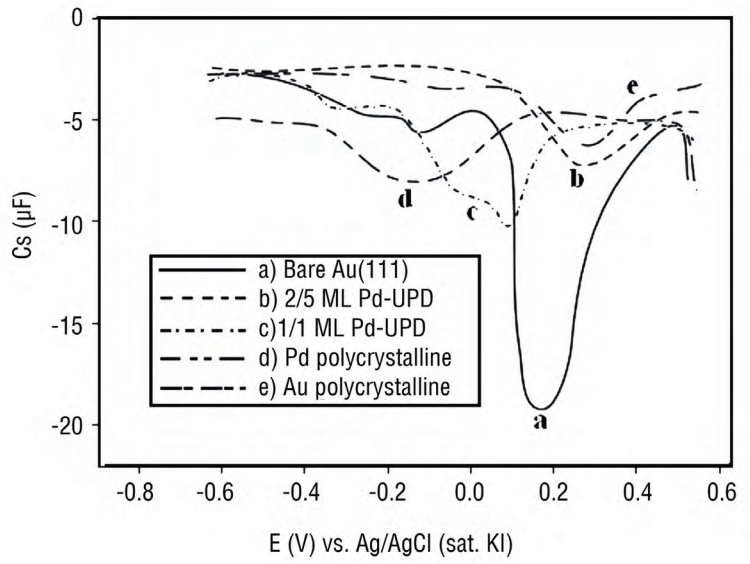



**Figure 5.** Impedance behavior of a) bare Au(111), b) 2/5 ML, c) 1/1 ML Pd UPD, d) Pd polycrystalline, and e) Au polycrystalline electrodes in 1.0 M NaOH (frequency: 10 Hz).

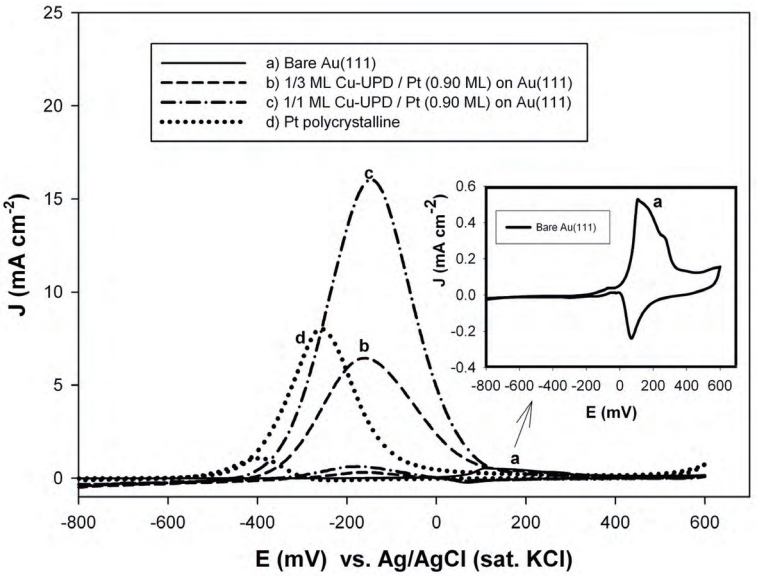



**Figure 6.** Cyclic voltammograms of 1.0 M methanol in 1.0 M NaOH at a) bare Au(111) electrode, b) Pt (0.17 ML) deposits by replacement of 1/3 ML Cu-UPD, c) Pt (0.50 ML) deposits by replacement of 1 ML Cu-UPD bare Au(111), and d) Pt polycrystalline electrodes.

Platinum ad-layers can also be deposited electrochemically by simply applying a sufficiently negative and constant potential for certain time intervals. Figure 7 shows the CVs of the modified electrodes in comparison to the bare Pt and Au(111) electrodes. The coverage ratios of the Au(111) surface by Pt ad-layer electrochemically deposited at –450 mV for 30, 60, and 90 s were calculated from the charge values to be 0.48, 0.64, and 0.90 ML, respectively. The voltammetric behavior of this modified electrode with less than monolayer coverage differed from that of both the Pt polycrystalline and Au(111) electrodes, and, therefore, they can be considered for use in catalytic reactions. The methanol oxidation peak potential in alkaline media was observed at 120 mV for the bare Au(111) electrode. The Pt ad-atom Au(111) electrodes deposited for various times had a peak around –200 mV with different peak heights. In terms of peak shape and location, the performance of the Pt ad-layer modified Au(111) electrode toward methanol oxidation was found to be very effective compared to the bare electrodes. The most promising response was obtained with the 30-s electrochemically deposited Pt ad-layer modified Au(111) electrode, which corresponds to 0.48 ML platinum ad-metal. Significant current enhancement, appearing as a peak rise about 40.0 times greater than that of bare Au(111) and 2.5 times that of the Pt polycrystalline electrode, was observed, while the peak potential shifted about 350 mV in negative directions compared to the bare Au(111) electrode. Improved peak characteristics imply that faster electron transfer can be achieved through a bimetallic surface prepared in controlled composition by simply adjusting the deposition time on Au(111). The modification of the Au(111) electrode surface with a Pt ad-layer provides superior electrical contact and also accelerates the electron transfer, which was demonstrated by the increase in peak current and the positive shift in the peak potential.

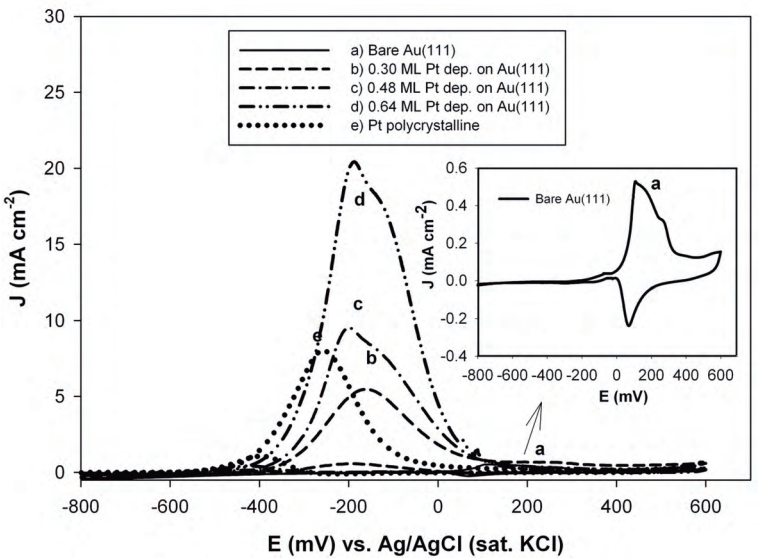



**Figure 7.** Cyclic voltammograms of 1.0 M methanol in 1.0 M NaOH at a) bare Au(111), b) 0.30 ML Pt ad-layer modified on Au(111) electrodes, c) 0.48 ML Pt ad-layer modified on Au(111) electrodes, d) 0.64 ML Pt ad-layer modified on Au(111) electrodes, and e) comparison of Pt polycrystalline.

Selected voltammograms obtained with Pt ad-metal Au(111) electrodes modified by means of both techniques for methanol oxidation are displayed in Figure 8 for comparison. These results clearly demonstrate that the methanol oxidation proceeds at more negative potentials on Pt ad-layer modified Au(111) electrodes

in comparison to the bare electrodes. Other UPD-modified electrodes with Cu, Cd, Mo, and Zn ad-layers investigated in this study had oxidation peaks similar to that of the Au(111) electrode, with peak current densities lower than that of the bare electrode.

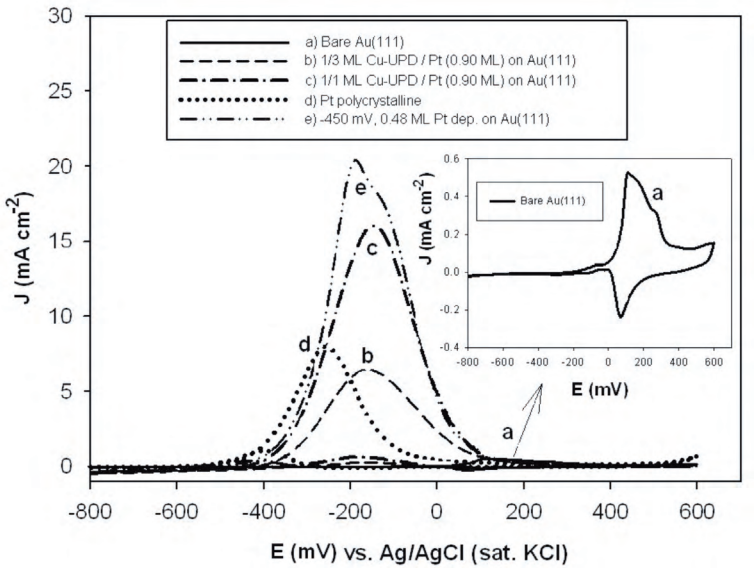



**Figure 8.** Cyclic voltammograms of 1.0 M methanol in 1.0 M NaOH at a) bare Au(111), b) 0.17 ML Pt ad-layer modified Au(111) electrodes prepared by replacement with 1/3 ML Cu-UPD, c) 0.50 ML Pt ad-layer modified Au(111) electrodes prepared by replacement with 1/1 ML Cu-UPD, d) comparison of Pt polycrystalline, and e) 0.48 ML Pt dep. on Au(111).

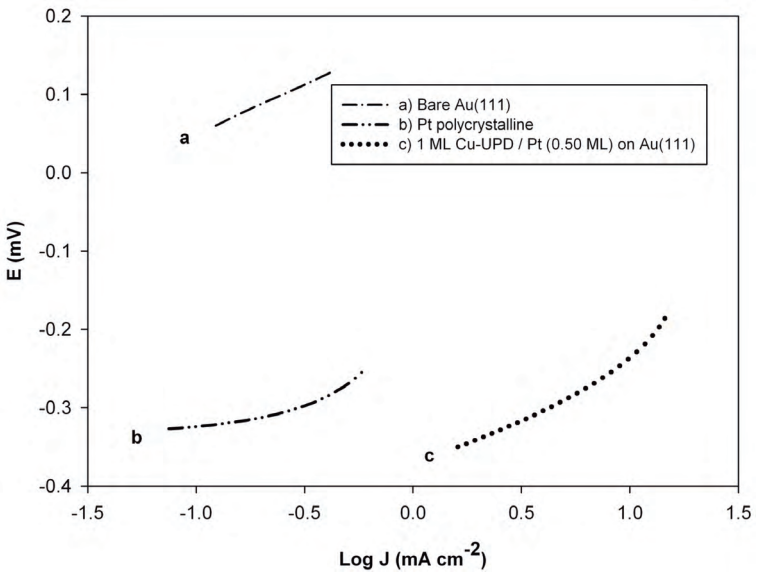



**Figure 9.** Tafel slopes for methanol oxidation in 0.1 M NaOH at a) bare Au(111), b) comparison of Pt polycrystalline, and c) 0.50 ML Pt ad-layer modified prepared by replacement with 1/1 ML Cu on Au(111) electrodes.

Tafel plots for methanol oxidation were obtained from the mixed kinetic diffusion control region by using mass-transport currents with a scan rate of 5 mV $s^{-1}$ at all ad-layer modified Au(111) and bare electrodes (Figure 9). Tafel slopes of approximately 129, 183, and 203 mV were measured on Au(111), Pt polycrystalline, and 0.48 ML Pt ad-layer Au(111) electrodes for methanol oxidation, respectively. It is obvious that the 0.48 ML Pt ad-layer Au(111) electrode was more active than the bare Au(111) and Pt polycrystalline electrodes for methanol electrooxidation.

## Conclusions

Oxidation of methanol occurs with an effect catalyzed by chemisorbed $OH^-$ anions on gold polycrystalline and single-crystal gold electrodes. The highest oxidation currents are observed in high alkaline solutions. The oxidation peak potential also shifts depending on the crystallographic structure of single-crystal electrodes. The greatest effect in the shift and the peak current oxidation of methanol was observed at the Au(111) single-crystal electrode in 1.0 M NaOH.

Pd ad-layer modified single-crystal electrodes act as good catalysts for methanol oxidation, and activity increased after the Au surface was modified with Pd and Pt ad-layers. The catalytic effect on the oxidation peak potential and peak current were found to be dependent upon the surface coverage.

Finally, Pd and Pt ad-layer modified Au(111) electrode surfaces showed the best electrocatalytic activity toward methanol oxidation by the increase in peak current and positive shift in the peak potential in alkaline solution.

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