

# Electrocatalytic oxidation of ethanol on various metal ad-layer modified Au(111) electrodes in alkaline solution

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Ethanol oxidation was studied on single-crystal Au(111) electrodes that were modified by platinum, palladium, and cadmium metal ad-layers. The metal ad-layer modification was carried out by the underpotential deposition process, in which controlled amounts of Pt, Pd, and Cd were electrodeposited onto the substrate as submonolayer or monolayer coverage. The activity of the metal ad-layer modified Au(111) electrodes toward ethanol oxidation was studied in alkaline media, and recorded voltammograms were compared to those of bare single crystal Au(111) and polycrystalline gold and platinum disk electrodes. 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:** Ethanol oxidation, Pt ad-layer, Pd ad-layer, Cd ad-layer, Au(111) single crystal electrode, fuel cell, catalyst

## Introduction

Recently, a great deal attention has been paid to the electrochemical oxidation of small organic molecules for direct alcohol fuel cells.<sup>1,2</sup> Compared to other small organic molecules and especially to methanol, ethanol has been used more extensively as an alternative fuel in direct alcohol fuel cells since it is less toxic and has low volatility together with a higher energy density (8.01 kWh/kg versus 6.09 kWh/kg). It can easily be formed in huge quantities by the fermentation of sugar containing raw materials and biomass.<sup>3-6</sup>

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On the other hand, the electrochemical reactivity of ethanol is slightly lower than that of methanol. It is necessary to achieve its complete oxidation to  $\text{CO}_2$  with 12 electrons per molecule for maximum energy recovery from ethanol. Nevertheless, breaking the C-C bond is difficult to promote by electrochemical means. Partial oxidation of ethanol can lead to the formation of acetaldehyde, acetic acid, or carbon monoxide, which can be easily adsorbed on the electrode surface and decrease its catalytic activity towards ethanol oxidation.<sup>7–13</sup> Therefore, many new kinds of catalysts have been developed toward ethanol oxidation at low potentials, such as Pd, Pt, and Au, and their metallic nanoparticles<sup>14–17</sup> and alloys<sup>18–20</sup> prepared with other transition metals, which have higher electrocatalytic activity toward the oxidation of ethanol.

Platinum alloy catalysts such as Pt-Ru-Mo/C<sup>21</sup>, Pt-Mo<sup>22</sup>, Pt-Ru/C<sup>23</sup>, PtSn/C<sup>24</sup>, and Pt-ZrO<sub>2</sub>/C<sup>25</sup> have been used for the electrooxidation of ethanol. On the other hand, the oxidation of ethanol on a bulk Pt electrode is followed by the formation of  $\text{CH}_x\text{O}$ -like intermediates that are strongly adsorbed on the catalyst surface. These formations considerably reduce the electroactivity of ethanol. Electrochemical experiments have shown that carbon dioxide, acetaldehyde, and acetic acid are produced in the oxidation of ethanol on polycrystalline platinum electrodes.<sup>26–28</sup> To overcome these problems, preparation of new Pt-containing modified electrodes has been proposed.<sup>22,23</sup>

Alternatively, gold is considered a poor electrocatalyst toward ethanol oxidation, especially in acidic solutions, but its electrocatalytic activity toward electrooxidation of many organic compounds was found to be larger in an alkaline medium.<sup>29</sup> Since underpotential deposition of ad-metals on the gold electrode surface offers a unique property as an electrocatalyst, the ad-metal modified gold electrodes as monolayers or submonolayers offer different catalytic activity resulting from both the substrate and the deposited metal. These ad-atom modified electrodes have been applied to electrochemical reactions of a variety of compounds, such as glucose,<sup>30</sup> methanol,<sup>31–33</sup> formic acid,<sup>34</sup> carbon monoxide,<sup>35–37</sup> oxygen,<sup>38,39</sup> and ethanol.<sup>40</sup>

In the present work, gold single-crystal electrodes modified with a variety of metal ad-layers, including Pt<sup>41</sup>, Pd,<sup>42,43</sup> Cd,<sup>44</sup> Cu,<sup>30–45</sup> and Ag<sup>46</sup> were prepared by using reported UPD systems for gold electrodes. The electrocatalytic activities of each electrode on ethanol oxidation were also compared in alkaline media.

## 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>47</sup> The quality of the single-crystal plane was verified by measuring the cyclic voltammogram in a 0.1 M  $\text{H}_2\text{SO}_4$  solution.<sup>48</sup> The electrolytes were prepared from ultrapure grade NaOH,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$  (Merck) reagents.  $\text{PdSO}_4$  (99.5%),  $\text{CdSO}_4 \cdot 5\text{H}_2\text{O}$  (99.5%), and  $\text{K}_2\text{PtCl}_6$  (99.9%) were purchased from Sigma and used 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 supplied from a Milli-Q purification system (18.2 M $\Omega$ /cm, Millipore).

Voltammograms were recorded by using either an IviumStat potentiostat or a BAS 100B/W voltammetric analyzer (Bioanalytical Systems, Inc.). Pd ad-layer modified Au(111) electrodes were obtained in a 0.2 mM  $\text{PdSO}_4$  + 0.1 M  $\text{H}_2\text{SO}_4$  solution by following the procedure recorded in the literature.<sup>42,43</sup>

Cd ad-layers were deposited onto the Au(111) surface in a 1.0 mM  $\text{CdSO}_4$  + 0.1 M  $\text{H}_2\text{SO}_4$  solution; the

potential scanning was immediately started after immersion of the electrode from 0.0 mV (vs. Pt plate) with a scan rate of 5 mV/s. Scanning was terminated with the deposition of 1/5 ML and 1/1 ML of Cd ad-layer and bulk Cd at approximately -690 mV, -1380 mV, and -1500 mV vs. Pt plate, respectively.<sup>44</sup>

The Pt ad-atom modified Au(111) electrode was prepared by the reduction of  $K_2PtCl_6$  on the Au(111) electrode surface at -400 mV before bulk deposition potential for several deposition times, such as 15, 30, 60, and 90 s. The extent of Pt coverage was maintained by controlling the time elapsed for chemical or electrochemical processes, and then cyclic voltammograms were monitored in deaerated  $H_2SO_4$  media.<sup>48</sup>

All ad-layer 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 an ethanol-containing solution. Voltammograms were measured at a scan rate of 50 mV/s using Ag/AgCl (saturated KCl) and the Pt plate as reference and counter electrodes, respectively. The experiments in an ethanol-free solution were carried out under a high purity  $N_2$  gas atmosphere.

## Results and discussion

### Underpotential deposition of Pd and Cd and electrodeposition of Pt on a single-crystal Au(111) electrode

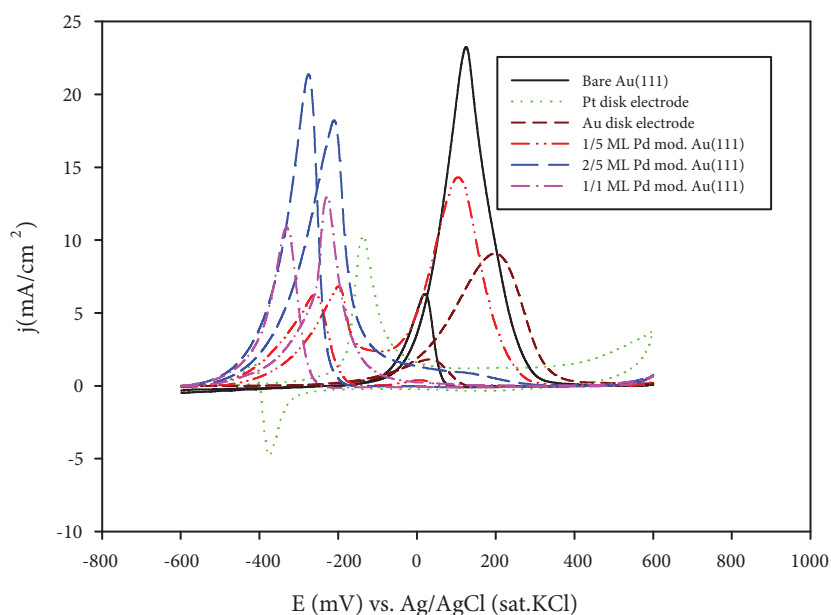
Initial studies were conducted to control the performance of prepared Au(111) electrodes in terms of their electrochemical signal. In the first step, single-crystal electrodes were electrochemically characterized by cycling the potential in the range of -800 to 350 mV in 0.1 M  $H_2SO_4$ . The cycling was then repeated in the presence of reagents like  $CdSO_4$ ,  $PdSO_4$ , and solutions for observing the effect of modification on catalytic activity. Obtained voltammograms were in good agreement with those in the reported works that contained Cd and Pd ad-layers.<sup>42-44</sup> To test the Pt ad-layer modified Au(111), the cycling was repeated in the presence of  $PtCl_6^{2-}$ ; the resulting voltammograms were in good agreement with those in the reported works for Pt ad-layers.<sup>41</sup>

### Ethanol oxidation at modified Au(111) electrodes

The Au(111) electrode surface was modified as a submonolayer by different types of ad-layers to improve the electrocatalytic activity of the bare Au(111) single-crystal electrode for ethanol oxidation of the electrocatalytic activity of the Au(111) electrode.

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

The oxidation peaks of ethanol at bare Au(111), Au disk, polycrystalline Pd disk, and Pd ad-layer modified Au(111) single-crystal electrodes were recorded in 1.0 M NaOH solution, including 1.0 M ethanol (Figure 1).

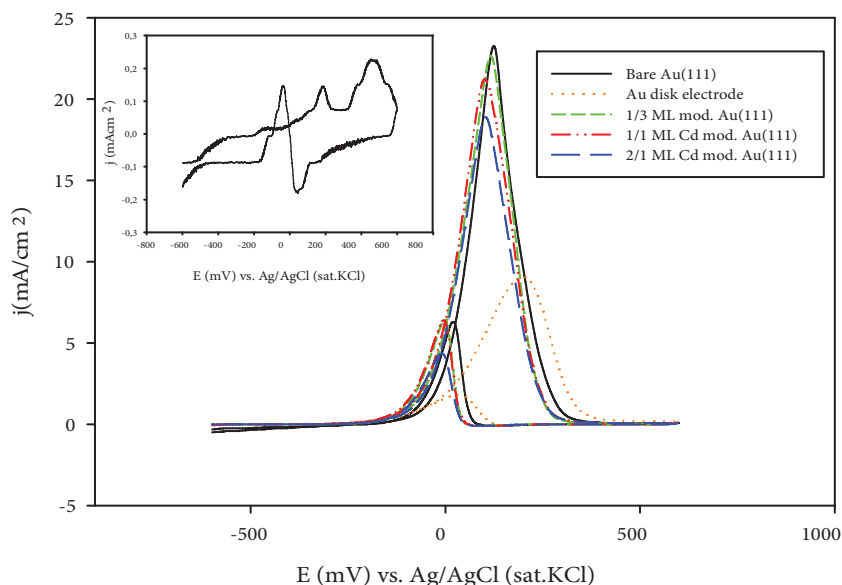


**Figure 1.** Cyclic voltammograms of bare and Pd ad-layer modified Au(111) electrodes prepared in different ratios 1/5, 2/5, 1/1 ML, Pd disc and Au disc electrode in a 1.0 M ethanol at 1.0 M NaOH solution at a scan rate of 50 mV/s.

The ethanol oxidation peak potential in alkaline media was observed at 130 mV for the bare Au(111) electrode. On the other hand, with Pd ad-atom modified electrodes, with a different coverage ratio, the most negative potential was observed at about -200 mV for the 2/5 ML and 1/1 ML Pd ad-atom modified Au(111) electrode. It was observed that the anodic current for ethanol oxidation did not increase with Pd modification. The electrooxidation on Pd ad-layer Au(111) and other electrodes was characterized by 2 well-defined current peaks on the forward and reverse scans. In the forward scan, the oxidation peak corresponded to the oxidation of freshly chemisorbed species coming from ethanol adsorption. The reverse scan peak was primarily associated with the removal of carbonaceous species that were not completely oxidized in the forward scan rather than the oxidation of freshly chemisorbed species.<sup>49,50</sup> The magnitude of the forward peak current indicated the electrocatalytic activity of the modified electrodes.

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

To investigate the electrocatalytic activity of the Cd ad-layer, the Au(111) surface was modified with 1/5 ML, 1/1 ML, and 2/1 ML Cd by the underpotential deposition technique. However, the Cd ad-layer modified Au(111) electrodes did not show electrocatalytic activity for ethanol oxidation, because ethanol oxidation on the Cd ad-layer modified electrodes was observed at almost the same potential and had approximately the same peak current compared with the bare Au(111) electrode. As can be seen from the inset of Figure 2, ethanol oxidation did not occur upon bulk deposition of Cd on the Au(111) electrode. This indicates that Cd cannot catalyze the ethanol oxidation reaction.



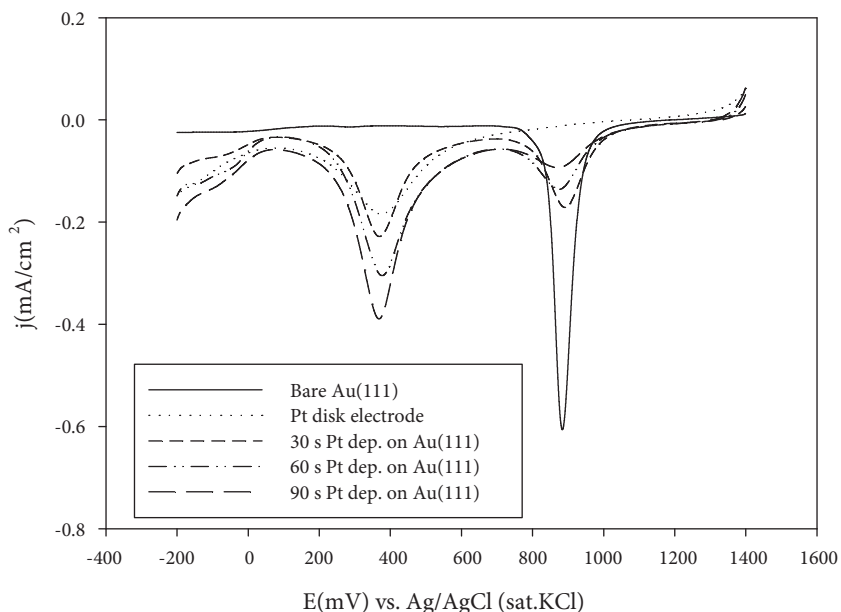
**Figure 2.** Cyclic voltammograms of bare and Cd ad-layer modified Au(111) electrodes prepared in different ratios 1/5, 1/1 and 2/1 ML, Cd bulk and Au disc electrode in a 1.0 M ethanol at 1.0 M NaOH solution at a scan rate of 50 mV/s.

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

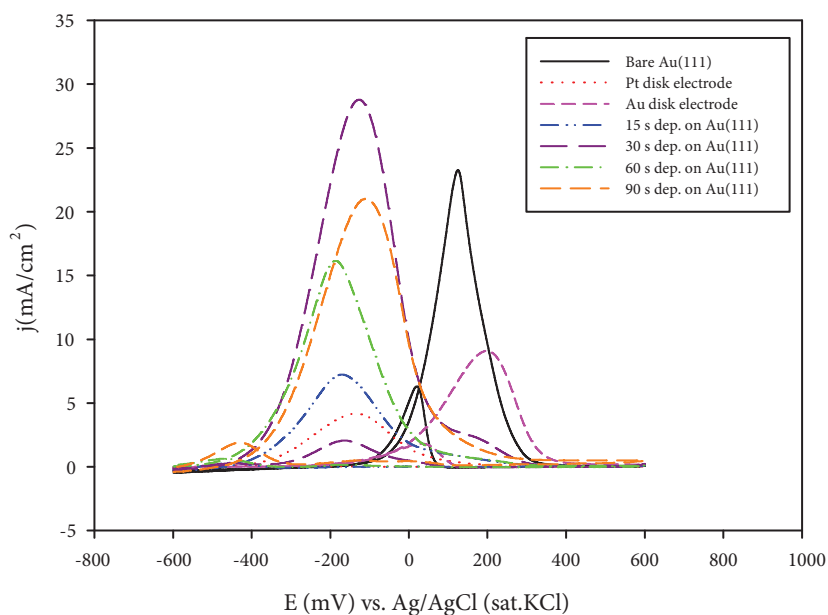
The voltammetric behavior of the modified electrodes, Au(111) and Au disk electrodes, in comparison to the bare Pt, can be seen in Figure 3. The reduction peak of platinum was located at 350 mV on the Pt disk electrode, whereas surface oxide was reduced at 880 mV on the bare Au(111) electrode. Pt ad-atom modified electrodes with various deposition times were prepared by using electrochemical deposition. The linear voltammetric behavior of Pt ad-layer modified Au(111) electrodes displayed some similarities with those of bulk Au(111) and Pt polycrystalline electrodes. As can be seen from Figure 3, 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 coverage ratios of the gold surface by Pt ad-atoms electrochemically deposited at -400 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 submonolayer coverage differed from both Pt disk and Au(111) electrodes and, therefore, they can be considered for use in catalytic reactions.

The ethanol oxidation was studied by using Pt ad-atom modified Au(111) electrodes, which were electrochemically deposited at -400 mV for different deposition times in an acidic solution. Figure 4 shows the overlaid cyclic voltammograms of ethanol on bare Au(111), polycrystalline Au disk, polycrystalline Pt disk, and Pt ad-atom modified Au(111) electrodes for evaluation in the same potential range. The ethanol oxidation peak potential occurred at about 130 mV in alkaline media. On the other hand, the oxidation peak was observed at -110 mV 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 ethanol 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. Significant current enhancement as a peak rise of about 1.5 times that of bare Au(111) and 7.3 times that of Pt disk electrodes was observed, while the

peak potential shifted about 270 mV and 20 mV in negative directions, respectively. Improved peak characteristics imply that faster electron transfer can be achieved through a bimetallic surface prepared in controlled composition, simply by adjusting the deposition time on Au(111). The Pt ad-layer modified Au(111) electrode surface not only supplied a superior electrical contact, but also accelerated electron transfer, as proven by the increase in peak current and the positive shift in the peak potential.

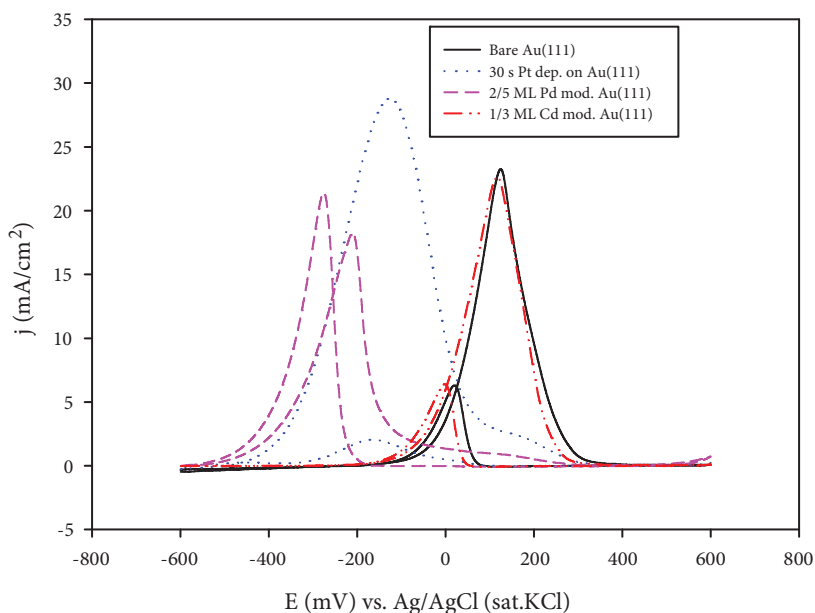


**Figure 3.** Linear sweep voltammetric behavior of Pt disk, Au(111) and Pt ad-atoms modified Au(111) electrodes in deaerated  $H_2SO_4$  solution.



**Figure 4.** Cyclic voltammograms of 1.0 M ethanol oxidation in 1.0 M NaOH on bare Au(111), Pt disk and Pt ad-atom modified Au(111) electrode prepared with different deposition time.

Figure 5 shows the comparison of Pd, Cd, and Pt ad-layer modified electrodes for ethanol oxidation in 1.0 M NaOH. Among them, Pt was the best catalyst material. Therefore, the kinetics of ethanol electrooxidation was studied at a 30-s Pt ad-layer modified Au(111) electrode. The effects of NaOH concentration, ethanol concentration, and scan rate on ethanol oxidation were investigated by cyclic voltammetry.



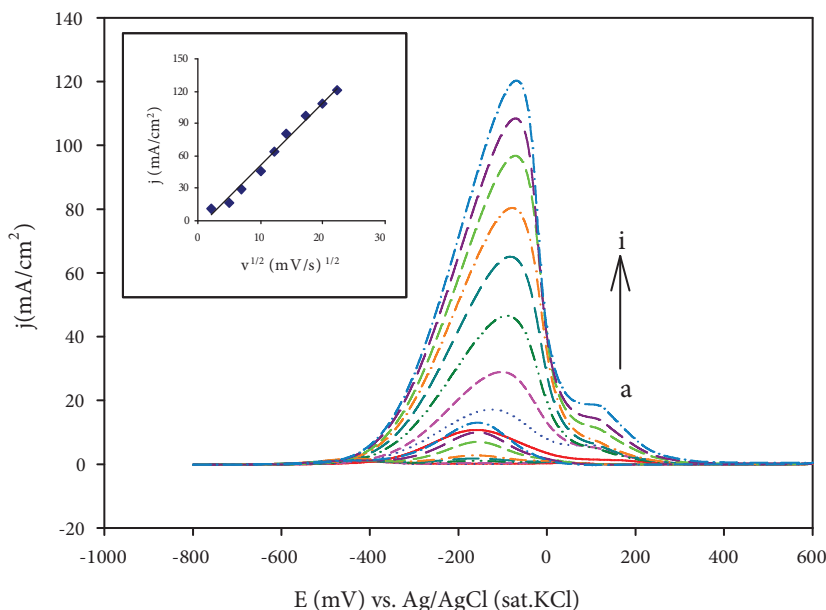
**Figure 5.** Comparative cyclic voltammograms of ethanol oxidation on the bare Au(111), Pt, Pd and Cd ad-atoms modified Au(111) electrodes.

It is known that different pH values affect the electrooxidation of ethanol on Pt ad-layer Au(111) electrodes. For this reason, the influence of NaOH concentration on the oxidation of 1.0 M ethanol was studied with a Pt ad-layer Au(111) electrode. It was observed that increasing the NaOH concentration from 0.1 to 3.0 M resulted in improved ethanol oxidation reaction. This might be explained as follows: the kinetics of the ethanol oxidation reaction might be developed because of the greater availability of  $\text{OH}^-$  ions in the solution and/or a higher  $\text{OH}^-$  coverage of the electrode surface.<sup>50,51</sup> On the other hand, the peak potential shifted negatively with increasing NaOH concentrations and the peak current decreased after a NaOH concentration of 1.0 M, owing to the  $\text{OH}^-$  species covering the Au(111) electrode surface. The value for the shifted potential is determined by the following equation:  $\Delta E = -0.0607 \text{ pH}$ . The best result was found when the NaOH concentration was 1.0 M at an ethanol concentration of 1.0 M.

The effect of ethanol concentration was studied at a fixed NaOH concentration of 1.0 M. The oxidation current increased with the ethanol concentration, showing that the ethanol oxidation reaction was controlled by the ethanol concentration at the electrode surface. The best performance was observed with an ethanol concentration of 3.0 M. The oxidation current of ethanol decreased at a higher ethanol concentration of about 4 M. This might be explained due to the exhaustion of adsorbed  $\text{OH}^-$  by adsorbed  $\text{CH}_3\text{CH}_2\text{OH}$  at the Pt ad-layer modified Au(111) electrode surface. According to these observations, it can be concluded that at lower ethanol concentrations, the peak currents were controlled by the diffusion transport of ethanol due to the excess

availability of  $\text{OH}^-$  ions. At higher ethanol concentrations, peak currents were controlled by the diffusion transport of  $\text{OH}^-$  ions because of the excess availability of ethanol and insufficient  $\text{OH}^-$  ions.<sup>50,52</sup>

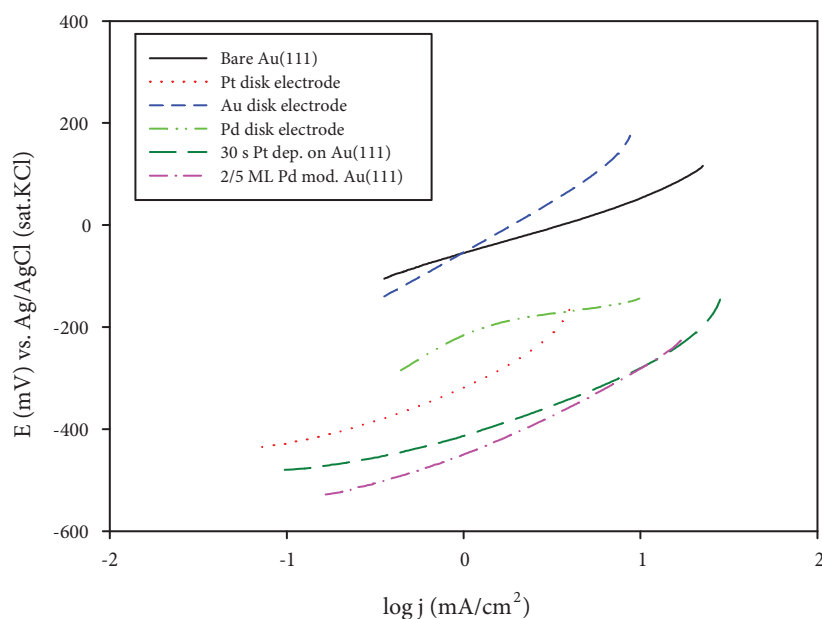
Plots of ethanol oxidation peak current vs.  $(\text{scan rate})^{1/2}$  for the Pt ad-layer modified Au(111) electrode are given in Figure 6. The peak current showed a linear increase with the square root of the scan rate, indicating diffusion and surface-controlled electrocatalytic reduction.



**Figure 6.** Cyclic voltammograms of different scan rate (a:5 mV/s, b:25 mV/s, c:50 mV/s, d:100 mV/s, e:150 mV/s, f:200 mV/s, g:300 mV/s, h:400 mV/s and i:500 mV/s ) of ethanol oxidation on 30 s Pt dep. on Au(111) inset: square root of the scan rate vs. current density.

Tafel plots for ethanol oxidation were obtained from the mixed kinetic-diffusion control region by using mass-transport currents with a scan rate of 5 mV/s at all ad-layer modified Au(111) and bare electrodes (Figure 7). It was obvious that the 2/5 ML Pd ad-layer Au(111) and the 30-s electrochemically deposited Pt ad-layer Au(111) electrodes were more active than the bare Au(111), polycrystalline Au, Pd, or Pt electrodes for ethanol electrooxidation. Tafel slopes of approximately 121 and 115 mV were measured on 2/5 ML Pd ad-layer Au(111) and 30-s electrochemically deposited Pt ad-layer Au(111) electrodes for ethanol oxidation. The Tafel slopes that were obtained at the 2 catalysts were very similar, indicating that the same rate-determining step occurred at the 2 catalysts. All of the above results from cyclic voltammetry and Tafel plots show that the 2/5 ML Pd ad-layer Au(111) and 30-s electrochemically deposited Pt ad-layer Au(111) electrodes exhibited higher catalytic activity for ethanol oxidation than any of the bare electrodes.





**Figure 7.** Tafel slopes for ethanol oxidation in 0.1 M NaOH at 25 °C on metal ad-layer modified Au(111), bare Au(111) and polycrystalline Au, Pd and Pt electrodes. The scan rate was 5 mV/s.

## Conclusions

Purely bimetallic electrode surfaces were prepared by the UPD technique (Cd and Pd) along with electrochemically deposited Pt on a single-crystal Au(111) electrode. The voltammetric characterization depicted that a submonolayer Pt ad-layer modified Au(111) electrode can be prepared by the electrochemical deposition technique. Electrocatalytic oxidation of ethanol was studied at electrochemically deposited Cd, Pd, and Pt ad-layer modified Au(111) electrodes and compared with bare Au(111) and polycrystalline Pt, Pd, and Au electrodes in alkaline solution. Cyclic voltammograms displayed a 330-mV negative shift with the Pd ad-layer and a 315-mV negative shift with the Pt ad-layer compared with the bare Au(111) electrode for ethanol oxidation potential. A significant increase in the current density was observed at almost all Pd and Pt ad-layer modified Au(111) electrodes, showing that a fast electron transfer occurred on the modified electrode surfaces compared with both bare Au(111) and polycrystalline Pt electrodes. The most electrocatalytic activity toward ethanol oxidation was obtained with the 30-s electrodeposition of Pt as less than 1 ML on a Au(111) electrode.

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## References

1. Kuk, S. T.; Wieckowski, A. *J. Power Sources* **2005**, *141*, 1-7.
2. Arico, A. S.; Baglio, V.; Di Blasi, A.; Modica, E.; Monforte, G.; Antonucci, V. *J. Electroanal. Chem.* **2005**, *576*, 161-169.
3. Lamy, C.; Belgsir, E. M.; Léger, J. M. *J. Appl. Electrochem.* **2001**, *31*, 799-809.
4. Maillard, F.; Gloaguen, F.; Hahn, F.; Léger, J. M. *Fuel Cells* **2002**, *2*, 143-152.
5. Rousseau, S.; Coutanceau, C.; Lamy, C.; Léger, J. M. *J. Power Sources* **2006**, *158*, 18-24.
6. Wang, J.; Wasmus, S.; Savinell, R. F. *J. Electrochem. Soc.* **1995**, *142*, 4218-4224.
7. Wang, H.; Jusys, Z.; Behm, R. J. *J. Phys. Chem. B* **2004**, *108*, 19413-19424.
8. Tarnowski, D. J.; Korzeniewski, C. *J. Phys. Chem. B* **1997**, *101*, 253-258.
9. Lamy, C.; Belgsir, E. M.; Léger, J. M. *J. Appl. Electrochem.* **2001**, *31*, 799-809.
10. Vigier, F.; Coutanceau, C.; Perrard, A.; Belgsir, E. M.; Lamy, C. *J. Appl. Electrochem.* **2004**, *34*, 439-446.
11. Mann, J.; Yao, N.; Bocarsly, A. B. *Langmuir* **2006**, *22*, 10432-10436.
12. Simoes, F. C.; Dos Anjos, D. M.; Vigier, F.; Leger, J. M.; Hahn, F.; Coutanceau, C.; Gonzalez, E. R.; Tremiliosi-Filho, G.; Andrade, A. R.; Olivi, P.; Kokoh, K. B. *J. Power Sources* **2007**, *167*, 1-10.
13. Wang, H.; Liu, Z. P. *J. Phys. Chem. C* **2007**, *111*, 12157-12160.
14. Bambagioni, V.; Bianchini, C.; Marchionni, A.; Filippi, J.; Vizza, F.; Teddy, J.; Serp, P.; Zhiani, M. *J. Power Sources* **2009**, *190*, 241-251.
15. Zheng, H. T.; Li, Y.; Chen, S.; Shen, P. K. *J. Power Sources* **2006**, *163*, 371-375.
16. He, Q.; Chen, W.; Mukerjee, S.; Chen, S.; Laufek, F. *J. Power Sources* **2009**, *187*, 298-304.
17. Alvisi, M.; Galtieri, G.; Giorgi, L.; Giorgi, R.; Serra, E.; Signore, M. A. *Surf. Coat. Tech.* **2005**, *200*, 1325-1329.
18. Godoi, D. R. M.; Perez, J.; Villullas, H. M. *J. Power Sources* **2010**, *195*, 3394-3401.
19. Colmenares, L.; Wang, H.; Jusys, Z.; Jiang, L.; Yan, S.; Sun, G. Q.; Behm, R. J. *Electrochim. Acta* **2006**, *52*, 221-233.
20. Chu, D.; Wang, J.; Wang, S.; Zha, L.; He, J.; Hou, Y.; Yan, Y.; Lin, H.; Tian, Z. *Catal. Commun.* **2009**, *10*, 955-958.
21. Neto, A. O.; Franco, E. G.; Arico, E.; Linardi, M.; Gonzalez, E. R. *J. Eur. Ceram. Soc.* **2003**, *23*, 2987-2992.
22. Dos'Anjos, D. M.; Kokoh, K. B.; Leger, J. M.; Dee'Andrade, A. R.; Olivi, P.; Tremiliosi-Filho, G. *J. Appl. Electrochem.* **2006**, *36*, 1391-1397.
23. Wang, M. Y.; Chen, J. H.; Fan, Z.; Tang, H.; Deng, G. H.; He, D. L.; Kuang, Y. F. *Carbon* **2004**, *42*, 3257-3260.
24. Garcia-Rodriguez, S.; Somodi, F.; Borbath, I.; Margitfalvi, J. L.; Pena, M.; Fierro, J. G.; Rojas, S. *Appl. Catal. B Environ.* **2009**, *91*, 83-91.
25. Bai, Y.; Wu, J.; Xi, J.; Wang, J.; Zhu, W.; Chen, L.; Qiu, X. *Electrochem. Commun.* **2005**, *7*, 1087-1090.
26. Souza, J. P. I.; Rabelo, F. J. B.; De Moraes, I. R.; Nart, F. C. *J. Electroanal. Chem.* **1997**, *420*, 17-20.
27. Ianniello, R.; Schmidt, V. M.; Rodrigues, J. L.; Pastor, E. *J. Electroanal. Chem.* **1999**, *471*, 167-179.
28. Fujiwara, N.; Friedrich, K. A.; Stimming, U. *J. Electroanal. Chem.* **1999**, *472*, 120-125.

29. Tremiliosi-Filho, G.; Gonzalez, E. R.; Motheo, A. J.; Belgsir, E. M.; Leger, J. M.; Lamy, C. *J. Electroanal. Chem.* **1998**, *444*, 31-39.
30. Aoun, S. B.; Dursun, Z.; Koga, T.; Bang, G. S.; Sotomura, T.; Taniguchi, I. *J. Electroanal. Chem.* **2004**, *567*, 175-183.
31. Vigier, F.; Gloaguen, F.; Leger, J. M.; Lamy, C. *Electrochim. Acta* **2001**, *46*, 4331-4337.
32. Crown, A.; Moraes, I. R.; Wieckowski, A. *J. Electroanal. Chem.* **2001**, *500*, 333-343.
33. Beden, B.; Kadirgan, F.; Lamy, C.; Leger, J. M. *J. Electroanal. Chem.* **1982**, *142*, 171-190.
34. Baladauf, M.; Kolb, D. M. *J. Phys. Chem.* **1996**, *100*, 11375-11381.
35. Friedrich, K. A.; Geyzers, K. P.; Linke, U.; Stimming, U.; Stumper, J. *J. Electroanal. Chem.* **1996**, *402*, 123-128.
36. De Mongeot, F. B.; Scherer, M.; Gleich, B.; Kopatzki, E.; Behm, R. J. *Surf. Sci.* **1998**, *411*, 249-262.
37. Davies, J. C.; Hayden, B. E.; Pegg, D. J.; Rendall, M. E. *Surf. Sci.* **2002**, *496*, 110-120.
38. Dursun, Z.; Ulubay, Ş.; Gelmez, B.; Ertas, F. N. *Catal. Lett.* **2009**, *132*, 127-132.
39. Ben Aoun, S.; Dursun, Z.; Sotomura, T.; Taniguchi, I. *Electrochem. Commun.* **2004**, *6*, 747-752.
40. Lai, S. C. S.; Kleijn, S. E. F.; Öztürk, F. T. Z.; Vellings, V. C. R.; Koning, J.; Rodriguez, P.; Koper, M. T. M. *Catal. Today* **2010**, *154*, 92-104.
41. Waibel, H. F.; Kleinert, M.; Kibler, L. A.; Kolb, D. M. *Electrochim. Acta* **2002**, *47*, 1461-1467.
42. El-Aziz, A. M.; Kibler, L. A.; Kolb, D. M. *Electrochem. Commun.* **2002**, *4*, 535-539.
43. Naohara, H.; Ye, S.; Uosaki, K. *J. Electroanal. Chem.* **2001**, *500*, 435-445.
44. Niece, B. K.; Gewirth, A. A. *Langmuir* **1997**, *13*, 6302-6309.
45. Uchida, H.; Hiei, M.; Watanabe, M. *J. Electroanal. Chem.* **1998**, *452*, 97-106.
46. Kondo, T.; Morita, J.; Okamura, M.; Saito, T.; Uosaki, K. *J. Electroanal. Chem.* **2002**, *532*, 201-205.
47. Ben Aoun, S.; Bang, G. S.; Koga, T.; Nonaka, Y.; Sotomura, T.; Taniguchi, I. *Electrochem. Commun.* **2003**, *5*, 317-320.
48. Hamelin, A. *J. Electroanal. Chem.* **1996**, *407*, 1-11.
49. Huang, J. C.; Liu, Z. L.; He, C. B.; Gan, L. M. *J. Phys. Chem. B* **2005**, *109*, 16644-16649.
50. Yu, E. H.; Scott, K.; Reeve, R.W.; Yang, L. X.; Allen, R. G. *Electrochim. Acta* **2004**, *49*, 2443-2452.
51. Liu, J.; Ye, J.; Xu, C.; Jiang, S. P.; Tong, Y. *Electrochem. Commun.* **2007**, *9*, 2334-2339.
52. De Lima, R. B.; Varela, H. *Gold Bull.* **2008**, *41*, 15-22.