

# The Role of Electrolytically Co-Deposited Platinum-Palladium Electrodes On The Electrooxidation Of D. Glucose In Alkaline medium: A Synergistic Effect

İpek BECERİK

*Istanbul Technical University, Faculty of Science and Literature,  
Department of Chemistry, 80626 Maslak, İstanbul-TURKEY*

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The electrooxidation of D. glucose was investigated on platinum-palladium alloy electrodes of different compositions in alkaline aqueous solutions. The surface characteristics of the alloys in contact with electrolytic solution were studied using cyclic voltammetry. In particular, a surface enrichment in platinum due to a preferential dissolution of palladium was shown. Enhanced electrocatalytic activity at about 37 at.% in Pd was obtained when compared to pure metals, thus leading to a synergistic effect. The electrocatalytic activity of different alloys for D. glucose oxidation has been characterized by exchange current densities obtained from extrapolation of Tafel lines to calculated equilibrium potential. An explanation of these effects was suggested on the basis of a decrease of strongly bound residue of D. glucose. The present work supports the proposed mechanism of the appearance of a high catalytic activity of Pt-Pd alloy for D. glucose oxidation.

**Key words:** Electrocatalysis, electrocodeposition, D. glucose, alloy electrodes, synergistic effect

## Introduction

The electrooxidation of D. glucose has become the subject of many investigations in connection with the problem of devising both electrochemical sensors for determining the sugar concentration in blood and implantable glucose fuel cells intended for artificial hearts and heart pacemakers. Nature accomplishes the oxidation of D. glucose in a very elegant manner with the participation of complicated enzyme systems. The resulting energy of the chemical reaction is partly converted into mechanical energy with high efficiency. Although we are not able to compete with nature in this respect, the utilization of inherent body energy reserves is indeed of considerable interest in biomedical engineering. Nonetheless, no catalyst system is available which enables the quantitative oxidation of D. glucose to carbon dioxide rapidly, i.e., with a high current density (1-3).

The electrochemical oxidation of D. glucose on many metal electrodes has been investigated owing to its importance for possible electrical devices to be used in living organisms. Studies have been focused mostly on platinum, palladium, gold, nickel, silver, copper electrodes and their binary alloys, various single

crystals and adatoms, among others. Nevertheless, it is seen from these studies that the oxidation of D. glucose at metals leads to the production of strongly adsorbed intermediates which block the active sites of the electrocatalyst surface and inhibit the subsequent oxidation of D. glucose (3-11). One of the main alternative solutions to this problem is to find ways to avoid the poisoning of existing electrocatalysts.

Investigations on the usefulness of alloy electrodes as electrocatalysts in the oxidations of organic compounds are often stimulated by the desire to find an electrode where specific properties of the components are combined to yield a better catalyst than pure metals. Since the electrocatalytic properties depend on especially the upper part of a surface, it is very important to examine the stability of the alloy electrode surfaces and to check its composition during the course of an electrochemical process (12). The electrocatalytic properties of platinum-palladium alloys are interesting, because they have very similar properties (same group of the periodic table, same fcc crystal structure, similar atomic size), and have a different electrochemical behaviour. For an optimum composition, alloyed metals have been recognized to enhance the electrocatalytic activity of Pt electrodes during the anodic oxidation of different organic compounds such as formic acid (13-16) or methanol (17) particularly in alkaline medium (18). However, up to now, there have been no studies on the activity of Pt-Pd alloy electrodes for D. glucose electrooxidation. In this paper, the role of platinum-palladium alloy electrodes prepared with different surface compositions in the electrooxidation of D. glucose was investigated. A systematic study of these alloys may shed new light on the electrocatalytic mechanism of D. glucose oxidation.

## Experimental

The experiments were carried out in a three-electrode electrochemical cell with a platinum counter electrode and a mercurous sulphate reference electrode (MSE). The working electrode was a microsphere obtained by melting a 0.5-mm diameter wire of a high purity metal (Johnson Matthey, UK) and having an active surface of about  $0.14 \text{ cm}^2$ . A counter electrode jacket was used to separate the counter electrode from the working electrode compartment. The aqueous solutions were prepared with water obtained from a Millipore Milli Q system and Merck suprapure reagents. High purity nitrogen gas was bubbled through the cell to remove dissolved oxygen. All experiments were carried out at  $25^\circ \text{C}$  at a rate of  $50 \text{ mV/s}$ . The voltammograms were recorded using standard electronic equipment (Potentiostat Wenking POS 73, BBC SE 790 X-Y recorder, Nicolet 410 Memory Oscilloscope).

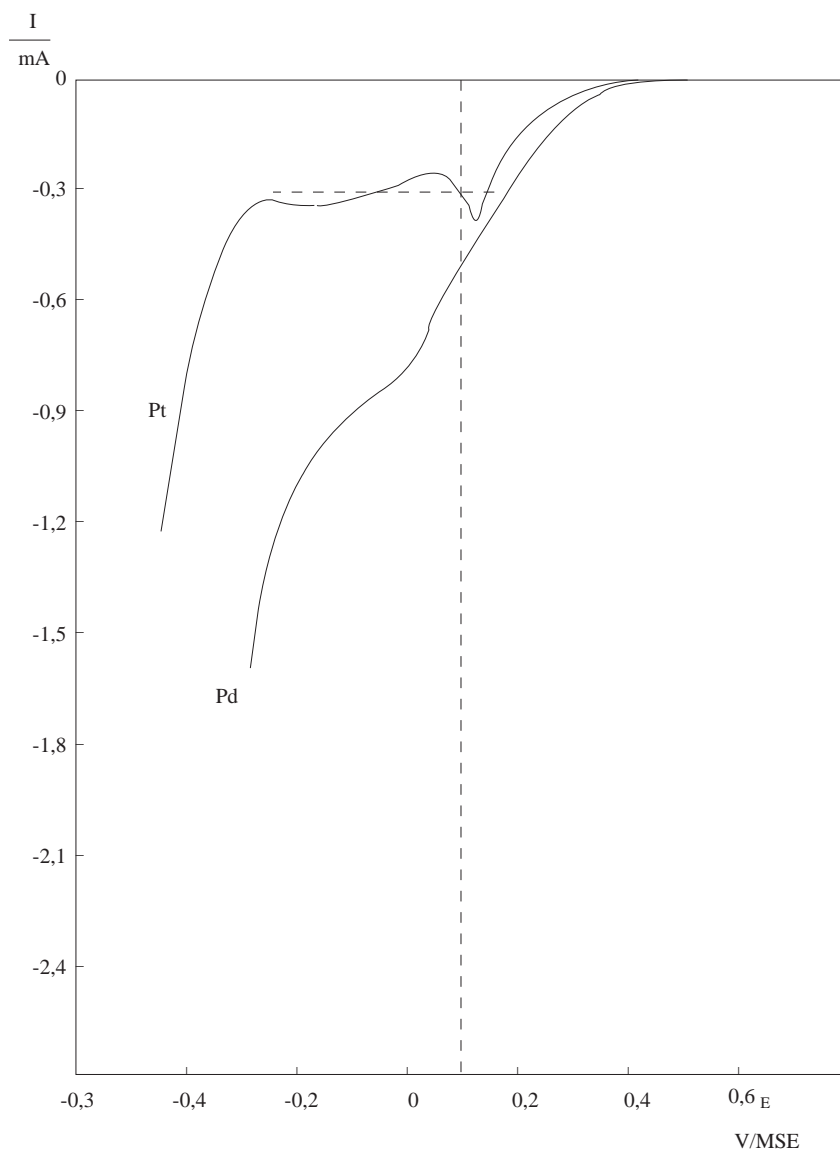
Cyclic voltammetry was used, allowing the superficial composition of the working electrode to be estimated by measuring the potential position of the reduction peak of oxygen layer adsorbed during the anodic sweep, according to the method of Rand and Woods (19-20).

Alloy electrodes were prepared by electrolytic codeposition of Pt and Pd from hydrochloric acid solutions of their soluble salts,  $\text{H}_2\text{PtCl}_6$  and  $\text{PdCl}_2$ , respectively. The deposition potential was determined by means of the I/E curves of the metals. Thus,  $0.10 \text{ V/MSE}$  was selected as the deposition potential of Pt-Pd alloys (Fig.1). In order to decrease the roughness factor, the alloy electrodes were then annealed by warming them to red heat in a hydrogen flame. Then, the electrode wire was mounted in a special electrode holder to prevent any solution leakage.

Surface composition is estimated from the reduction peak potential of the oxygen layer adsorbed. These alloy electrodes have intermediate potentials between those of pure metals.

## Results

Cyclic voltammograms at a sweep rate of 50 mV/s on pure metals and on alloys in supporting electrolyte are given in Fig. 2. The cathodic potential limit of the sweep for palladium and Pd-Pt electrodes has been chosen to be more anodic than the hydrogen adsorption region in order to avoid any hydrogen adsorption which could change the electrode structure. It is very important to stir the electrolyte solution vigorously to avoid local variations of pH. Moreover, stirring may introduce current fluctuations due to mass transfer limitations.

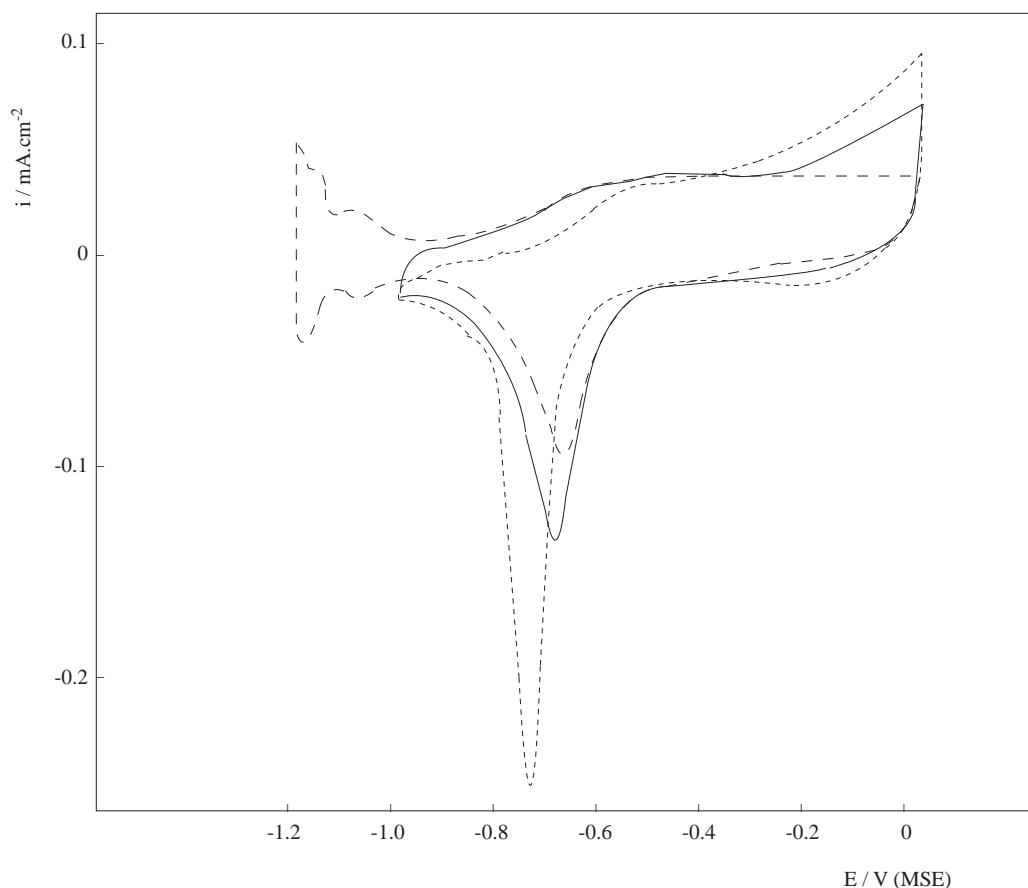


**Figure 1.:** I/E curves of Pt. and Pd.

One can see that the reduction peak potential of the oxygen layer adsorbed on alloy electrodes is intermediate between those of pure metals, thus leading to an estimation of the surface composition. The surface composition on the alloy co-deposits is very often far from the bulk composition (Table 1). The alloy bulk composition was calculated from the lattice parameters determined by X-ray diffraction diagrams

according to the Vegard's linear law. The results obtained show that the initial atomic Pd content is usually higher for the surface than the bulk alloy because Pd content is more easily electrocodeposited than Pt. This could also be due to a preferential chemical or electrochemical dissolution of palladium on the surface in alkaline medium.

The electrocatalytic activity of pure metal electrodes and alloy electrodes for the oxidation of D. glucose was systematically investigated in 0.1M D. glucose-0.1M NaOH. The results are given in Fig.3. In the case of Pt-Pt electrodes, D. glucose oxidation reaches its maximum in alkaline medium ( $1.9 \text{ mA/cm}^2$ ), while Pd-Pd electrodes yield lower current densities ( $0.8 \text{ mA/cm}^2$ ). However, the electrocatalytic activity of alloy electrodes for a certain surface composition is higher than that of pure metals ( $4 \text{ mA/cm}^2$  for 37%Pd). On the other hand, the voltammograms are nearly independent of the sweep rate (in a certain range from 10 to 500 mV/s) during the glucose electrooxidation on Pd-Pt alloy electrodes. Current densities as a function of at. Pd% and sweep rate are presented in Table 2.



**Figure 2.:** Cyclic voltammograms of platinum (—), palladium (.....) and platinum+palladium alloy (— · —) electrodes in alkaline medium, 0.1M NaOH, 25 °C, 50 mV/s.

Analysis of the voltammograms in terms of Tafel plots was carried out (Fig.4) at the most negative part of the  $i(E)$  curves between -0.8 and -1 V vs MSE for the cathodic sweep in alkaline medium. These Tafel plots lead to relatively good straight lines, extrapolation of which to equilibrium potential gives an exchange current density. This exchange current density may be a good test to get an idea about the electroactivity of alloy electrodes despite the diffusion which involves the kinetics of the reaction. However, the D. glucose concentration is kept constant and the transfer coefficients obtained from the slope of Tafel plots are nearly

constant (Table 3). Because of the highly irreversible character of glucose oxidation, it is impossible to measure an equilibrium potential. Therefore, this potential must be calculated from thermodynamic data suggesting that the final oxidation product is  $\text{CO}_3^{2-}$  in alkaline medium.

**Table 1.** Composition of the Pd-Pt Alloys (In Pd atomic%)

Bulk Composition	Surface Composition
1	5
5	10
10	16
20	24
30	37
40	42
50	49
60	53
70	55
80	57
90	61
99	63
99.9	64

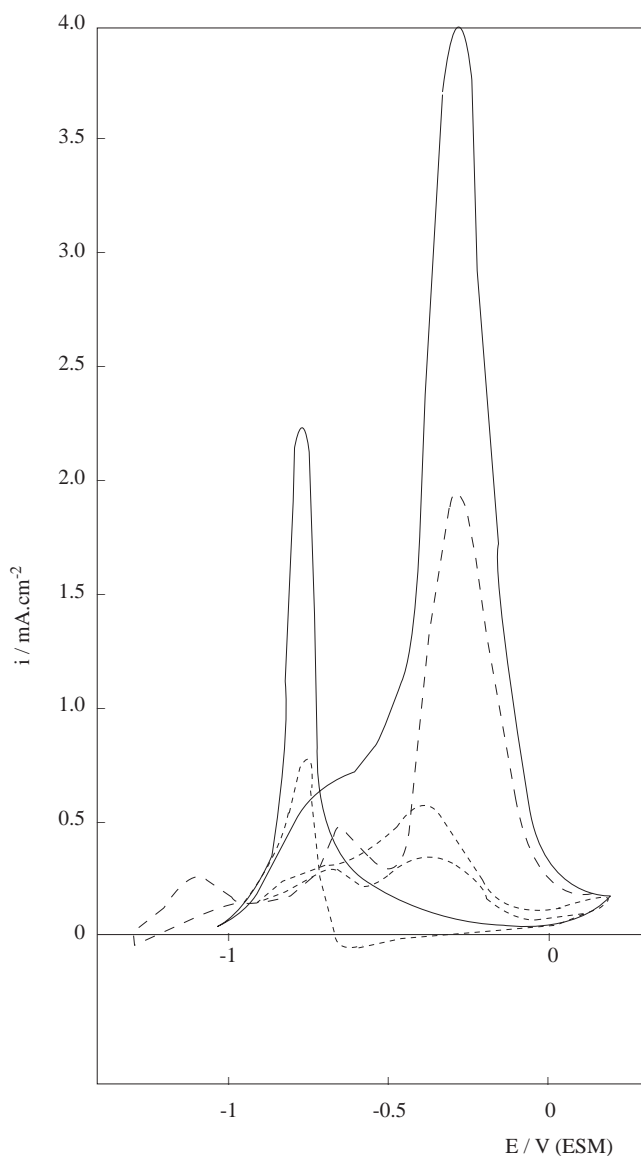
**Table 2.** Current densities as a function of atomic Pd%

At.Pd%	10 mV/s $\dot{i}_p(\text{mA}/\text{cm}^2)$	50 mV/s $\dot{i}_p(\text{mA}/\text{cm}^2)$	100mV/s $\dot{i}_p(\text{mA}/\text{cm}^2)$
10	2.5	2.6	2.7
40	3.8	4.0	4.2
70	3.6	3.7	3.7
90	2.1	2.2	2.2
99	1.5	1.7	1.8

**Table 3.** Transfer coefficients for the electrooxidation of D. glucose on Pt-Pd Alloy in alkaline medium

At. %Pd	5	10	16	24	37	42	49	53	55	57	61	63
$\alpha_n$	0.43	0.43	0.42	0.43	0.46	0.40	0.40	0.39	0.40	0.42	0.41	0.41

The exchange current densities obtained as explained above may be plotted vs. the alloy surface composition. A pronounced maximum occurred for a surface composition of about 37 atomic % in Pd. (Fig.5). This synergistic effect is relatively important since the exchange current densities obtained are greater than those for pure metals. 90% confidence intervals corresponding to each data point are shown in Fig. 5.



**Figure 3.:** Cyclic voltammograms of D. glucose electrooxidation on platinum (—), palladium (.....) and platinum+palladium 37% (— · —), in alkaline medium, 0.1M NaOH, 25 °C, 50 mV/s.

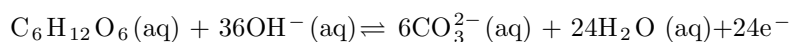
## Discussion

★ It is a very important point that, the real surface composition of the metal binary alloy differs from the bulk composition, as seen in Table 1. This difference is explained as being due to different free energies of components in the surface and bulk phases (21, 22, 23), or to different sizes of atoms constituting an alloy that introduces strain in the crystal lattice (24). As a result, the surface is enriched in the constituent that minimizes the total free energy of the system or minimizes the lattice strain energy.

★ One possible explanation of the increase of the electrocatalytic activity is that the surface of the electrode is not blocked by the intermediates, so that the reaction can progress through subsequent steps.

Also, the dependence of the voltammograms from the sweep rate may be considered quasistationary current-potential curves (Table 2).

★ Transfer coefficients were calculated as approximately 0.40 (Table 3). However, this value was 0.20 in alkaline medium for Pd-Au alloy electrodes (25). Thus, it may be considered that the reaction proceeds via further oxidation steps in the case of Pd-Pt alloy electrodes. It has been found (26) that  $\text{CO}_2$  is the main oxidation product and, in addition to the formation of gluconolactone and gluconic acid, further oxidation of these substances occurs, leading to the generation of  $\text{CO}_2$  as the final product. The overall reaction is assumed to be as follows in alkaline media:



The standard reaction ( $E^\circ$ ) was calculated:

$$E^\circ = -\Delta G^\circ / nF$$

For  $25^\circ\text{C}$ ,  $E^\circ = 0.161\text{ V}$  vs mercurous sulphate reference electrode, assuming that the reaction yields was 0.5 and  $n$  (the number of electrons transferred) was 24.

$$E_{eq} = E^\circ + (RT/nF) \ln [\text{CO}_3^{2-}(\text{aq})]^6 [\text{H}^+]^{24} / [\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})]$$

The value calculated for the equilibrium potential was  $-0.6\text{ V}$  vs MSE in alkaline medium.

★ The exchange current densities obtained as explained above may be plotted vs. the alloy surface composition (Fig.5). In alkaline solution, this curve displays a pronounced maximum for a surface composition of about 37 at. %Pd. This synergistic effect is relatively important, since the exchange current densities are up to 10 times greater than for those platinum, the most active pure metal.

In the present state of our investigations, it is difficult to explain quantitatively the origin of this synergistic effect. Similar effects are also observed in heterogeneous catalysis and in electrocatalysis, either for other electrodes or other reactions. Three main types of explanations may be considered to interpret such effects:

- 1) Modification of the electronic properties and collective surface properties by alloying two metals.
- 2) Modification of the activity through a bifunctional electrocatalysis mechanism. In this explanation, proposed by Motoo and Watanabe (17), each atom plays a definite role in the overall oxidation process. For example, platinum atoms adsorb D. glucose, leading to an adsorbed residue ( $\text{RCO-OH}_{ads}$ ). Then the other metal adsorbs OH radicals at more negative potentials than platinum, which leads to an increase of the oxidation rate by increasing the rate of chemical surface reaction between D. glucose residue and OH radicals through an increase of the OH concentrations.

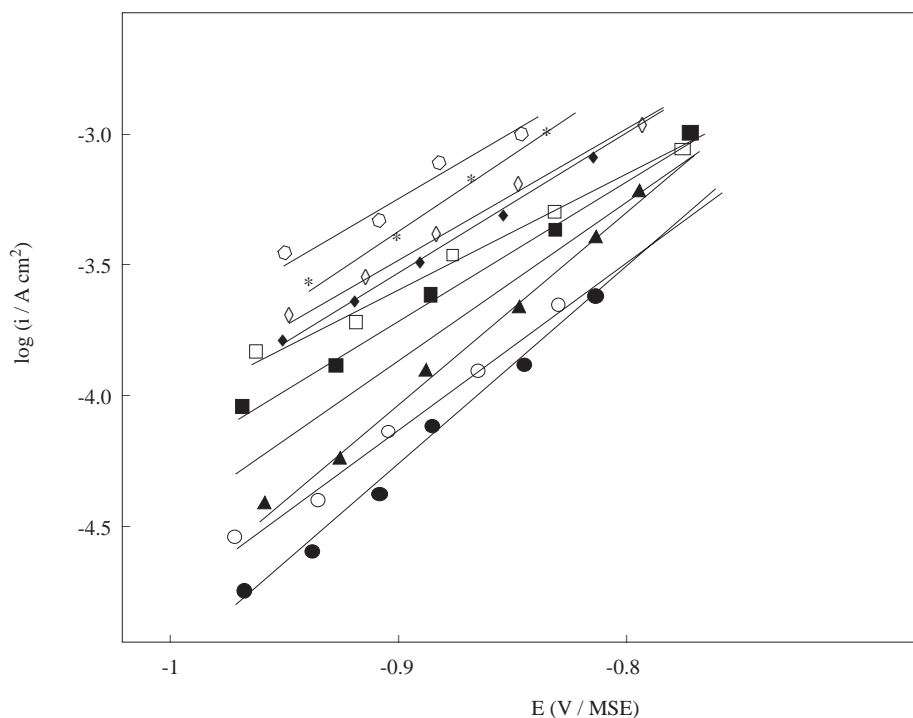
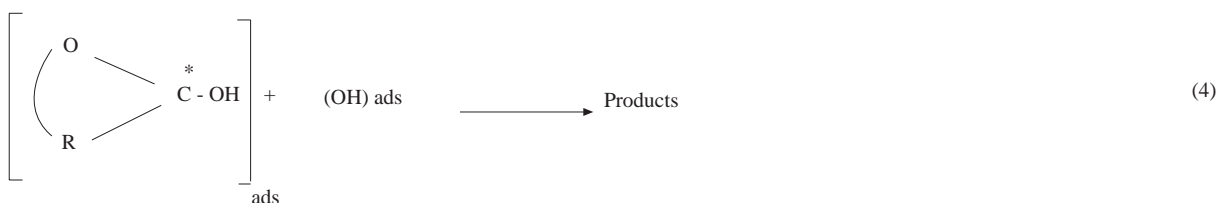
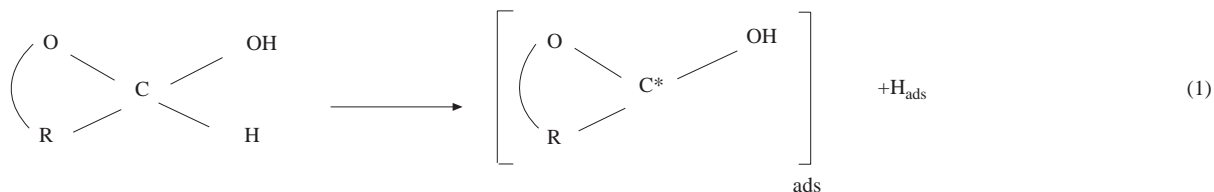
Alloying platinum with palladium results in the dilution of the platinum sites, which prevents the presence of the three adjacent sites necessary for the formation of the strongly bound intermediate. For alloy electrodes of surface composition 37 atomic %Pd, it is statistically difficult to find three adjacent Pt sites.

- 3) Enhancement of the overall reaction rate by decreasing the electrode poisoning. There is no in situ spectroscopic research on the palladium electrode for electrooxidation of D. glucose. Voltammograms have shown that the electrocatalytic activity of a palladium electrode for D. glucose is less than that of a platinum electrode. This type of deactivation may be due to the formation of strongly poisoning intermediates or the accumulation of weakly bound intermediates derived from D. glucose or other reasons, e.g., ageing of the electrode surface structure.

Similar effects are also observed for the oxidation of HCOOH in Pt-Pd alloys (27-28). Pd dissolution is found to be more relevant in processes responsible for the high oxidation charges observed for the alloy with a high Pt content. The oxidative properties of Pd(II) ions in a heterogeneous reaction with electroformed HCOOH intermediates are therefore taken into account to explain the enhancement of the Pt-Pd alloy electrode performance. Increased activity can also be expected for the electrooxidation of D. glucose in the

case of a surface composition rich in Pt, because the surface concentration of adsorbed residues on Pt sites may be lowered by the dissolved Pd(II) species. Thus, a synergistic effect will be needed to obtain additional kinetics and mechanistic information on this reaction.

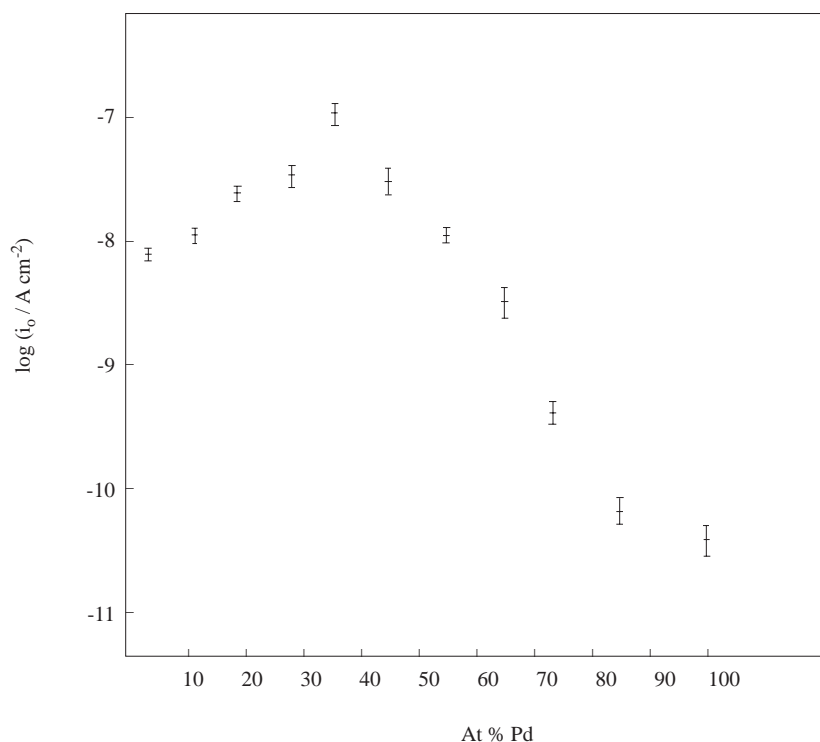
A possible reaction mechanism proposed for D. glucose oxidation on Pd electrode is as follows:



**Figure 4.:** The plots of the quasistationary current density-potential curves for the electrooxidation of D. glucose in alkaline medium on different alloy electrodes.

●●● Pd-Pd; ○○○ 64%Pd; ▲▲▲ 61%Pd; △△△ 57%Pd; ■■■ 53%Pd  
 □□□ 42%Pd; ◆◆◆ 37%Pd; ◇◇◇ 24%Pd; ××× 10%Pd; ◇◇◇ Pt-Pt





**Figure 5.:** Dependence of the exchange current density  $i_0$  for D. glucose electrocatalytic oxidation with the surface composition (at%Pd) of platinum+palladium electrodes (25 °C, 0.1M D. glucose, 0.1M NaOH).

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