REVIEWS IN APPLIED ELECTROCHEMISTRY No 46

# Electrocatalytic oxidation of mono- and polyhydric alcohols on gold and platinum

M. BETOWSKA-BRZEZINSKA[*], T. UCZAK

*Uniwersytet im. A. Mickiewicza, Wydzia Chemii, Grunwaldzka 6, PL-60-780 Poznań, Poland*

R. HOLZE

*Technische Universität Chemnitz-Zwickau, Institut für Chemie, D-09107 Chemnitz, Germany*

A survey of representative studies on the oxidation of mono- and polyhydric alcohols on gold and platinum electrodes is given, with a special attention to the reaction mechanisms and the effect of the molecular structure of these compounds on their electrocatalytic reactivity.

Keywords: *platinum electrodes, gold electrodes, reaction mechanisms, organic oxidation, monohydric alcohols, polyhydric alcohols*

## 1. Introduction

The present interest in the catalytic properties of noble metals in electrochemical processes is related to the development of porous graphite or ceramic electrodes containing small amounts of these metals and applied in fuel cells, sensors and electrochemical reactors. Among the noble metals used for electrochemical oxidation of organic compounds, platinum and gold are the most active catalysts. Platinum has highest catalytic activity in acidic solutions [1–37], whereas gold is most active in alkaline environment [23, 30, 38–73]. Palladium shows only low activity, rhodium proves nearly inactive in alkaline solutions [21–23, 26].Thus, only platinum and gold are treated in this review.

The oxidation of organic substances on a platinum electrode is accompanied by a characteristic, though very unfavourable, effect of surface blocking by strongly adsorbed intermediate species [26]. Although, due to the relatively high energy of hydrogen adsorption on platinum, the dehydrogenation of organic compounds may proceed rapidly in the range of low electrode potentials, the inhibition effect is dominant. This effect does not apply to a gold electrode characterized by relatively weak adsorption properties [46, 56, 74–79]. Although these properties account for the poor catalytic activity of gold in acidic solutions, in the case of alkaline solutions, when hydroxyl ions are adsorbed on the gold surface [42, 45, 46, 62, 63, 70, 80–83], the gold electrode proves to be a more effective catalyst for dehydrogenation of organic compounds than platinum. The oxidation rate of organic substances on a gold electrode in alkaline solutions is higher than on the platinum electrode though often, but not always, at higher electrode potentials [23, 41, 42, 44, 46, 50, 54, 56, 66, 84–86].

Alloying of platinum with metals of the sp group leads to an increase in the catalytic activity of electrodes in comparison with the activity of electrodes of pure metals. In particular, a large synergistic effect was obtained in the electrooxidation of monohydric alcohols [46, 85], 1,2-ethanediol [41, 42, 87, 88], 1,3-propanediol [18] and formaldehyde [56, 89] on Pt + Au alloys in alkaline solutions. High catalytic activity was also detected for Pt + Ag alloys [89], while the activity of Pt + Pd, Pd + Au and Pd + Ag alloys is lower [57, 90]. In acidic solutions, numerous binary platinum alloys have also been investigated [91]. Another subject of comprehensive study has been the modification of catalytic properties of platinum and gold, as well as Pt + Au electrodes, by underpotential deposition (u.p.d.) of adatoms of a foreign metal, in particular of Pb, Bi, Tl, Sn, Se, As, Te and Cu [24, 48, 49, 55, 64, 88, 92–113]. In reviews by Adžić *et al.* [114], Parsons *et al.* [26] and Kokkinidis *et al.* [115], various reasons for the increase in catalytic activity of electrode materials by alloying and/or by u.p.d. adatoms were discussed: (i) modification of the electronic properties of the surface resulting in changes of the adsorption properties, (ii) increased surface concentration of adsorbed oxygen containing species involved in the oxidation of organic substances, (iii) suppression of the formation of strongly adsorbed intermediate species due to the 'third body effect'.

Significant progress in the elucidation of the nature of intermediate species and final products in the electrocatalytic processes on the platinum electrode was achieved after a combination of electrochemical methods with *in situ* and online spectroscopic methods (EMIRS, PM–IRRAS, SNIFTIRS, SERS, DEMS), as well as with on line chromatographic techniques [27, 29, 31–33, 36, 37, 62, 66, 116–121], (for reviews up to 1990 see [26, 30]). Analogous studies on gold are scarce [17, 21, 64, 66, 122, 123]. Since all these methods provide identification of relatively stable species, the experimental data, are in

many cases, insufficient for detailed analysis of the reaction mechanism. This limitation has been circumvented in part by using isotopically labelled compounds [124–126]. Measurements of the kinetic isotope effect offer an additional way of obtaining information directly related to the main reaction step [40, 46, 69, 70, 72].

There has been a significant amount of research on the oxidation of aliphatic alcohols. Numerous papers on this subject, up to 1990 were reviewed by Parsons *et al.* [26], Lamy [21] and Beden *et al.* [23, 30], chief attention was focused on the kinetics and mechanism of the oxidation of methanol, ethanol and 1,2-ethanediol on platinum and gold. The purpose of this paper is to present further studies reported in recent years, with a special emphasis on the mechanism of electrooxidation and the reactivity of mono- and polyhydric alcohols containing two and more carbon atoms.
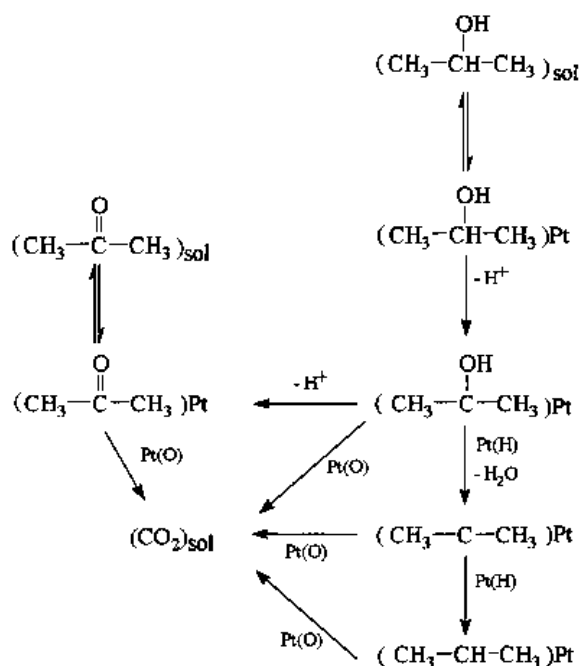
## 2. Monohydric alcohols

The effect of the molecular structure of organic compounds on the kinetics of their electrooxidation has been widely discussed in the literature concerning electrooxidation of monohydric alcohols on platinum electrodes in acidic solutions, and for gold electrodes in alkaline solutions. Sokolova and coworkers [5, 6, 12, 16, 18–20] have found, on the basis of cyclic voltammograms, that the reactivity of monohydric alcohols during oxidation on a platinum electrode decreases with increase of the length of the carbon chain in the substrate molecule. A cause of this relationship is the increasing inhibition of the electrode surface by adsorbed molecules of substrates and intermediates.

According to spectroelectrochemical studies, the oxidation of primary monohydric alcohols on a platinum electrode proceeds along two parallel reaction pathways [26, 27, 30, 32, 33, 101, 116, 118, 119, 121, 124, 126]. A sequence of dehydrogenation steps of the adsorbed substrate molecules, leading to carboxylic acids at pH > 7 and $CO_2$ at pH < 7, is accompanied by formation of strongly adsorbed intermediate species originating from alcohol molecules after cleavage of C—C bonds. Otherwise, adsorbed species maintaining the carbon chain of the substrate molecules are formed from secondary alcohols [36, 37, 117, 127, 128]. Differences in the reaction pathways during electrooxidation of primary and secondary alcohols on Pt in acidic solution are visible in Scheme 1 [32] and Scheme 2 [117] for 1-propanol and 2-propanol, respectively.

As expected from the Pauling's valence bond theory of metals [129], the presence of hydroxide species on the electrode surface is a precondition for the catalytic activity of gold towards the electrooxidation of monohydric alcohols. This reaction on gold in alkaline solutions begins at a potential of about $E_{RHE} \approx 0.6$ V, when the electrode surface is partially covered with adsorbed hydroxyl ions. The relevant mechanism was identified by Betowska-Brzezinska *et al.* [38–40, 44–46, 53, 58] on the basis of the kinetic data determined during electrooxidation of a homologous series of monohydric alcohols, from methanol to heptanol, including isomers and some chloro- and fluoroderivatives and deuterated compounds. It was found that the secondary alcohols are more easily oxidized on a gold electrode than the primary ones of the same number of carbon atoms in a molecule. Moreover, an increase in the length of the aliphatic carbon chain, which is accompanied by an
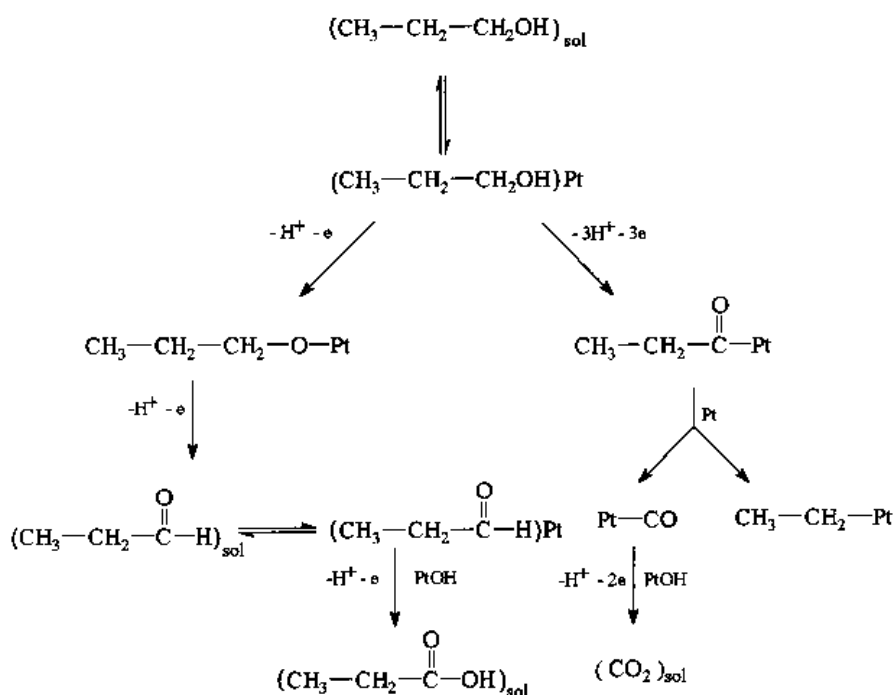


Scheme 1. Reaction scheme of 1-propanol oxidation on a platinum electrode in acidic solution [32].

$$(CH_3-\overset{\underset{\displaystyle |}{OH}}{C}H-CH_3)_{sol}$$

$$(CH_3-\overset{\underset{\displaystyle |}{OH}}{C}H-CH_3)_{Pt}$$

$-H^+$

$$(CH_3-\overset{\underset{\displaystyle |}{OH}}{C}-CH_3)_{Pt}$$

$$(CH_3-\overset{\underset{\displaystyle \|}{O}}{C}-CH_3)_{sol}$$

$$(CH_3-\overset{\underset{\displaystyle \|}{O}}{C}-CH_3)_{Pt} \xleftarrow{\quad -H^+ \quad}$$

$Pt(H)$
$-H_2O$

$Pt(O)$

$$(CH_3-\overset{\underset{\displaystyle |}{\quad}}{C}-CH_3)_{Pt}$$

$(CO_2)_{sol} \xleftarrow{\quad Pt(O) \quad}$

$Pt(H)$

$Pt(O)$

$$(CH_3-CH-CH_3)_{Pt}$$

Scheme 2. Reaction scheme of 2-propanol oxidation on a platinum electrode in acidic solution [117].

increase in the free enthalpy of adsorption of alcohol molecules on gold [53, 58, 78, 79], results in a larger oxidation current by a factor of about 2 and 2.5 per additional C atom in primary and secondary alcohols, respectively. The higher reactivity of 2-butanol in comparison with that of 1-butanol was later confirmed by Takky et al. [50]. All these relationships are converse to those observed for platinum [16, 18–21, 23, 46, 50, 130, 131]. However, analysis of the solutions after electrolysis has shown that the main products of electrooxidation of primary alcohols on gold in alkaline solution are carboxylic acids, and for the secondary alcohols ketones [46], as previously identified for a platinum [30] and nickel electrode [132]. Investigations on the deuterated compounds and the measurement of the kinetic isotope effect has provided insight into the rate determining step (r.d.s.). It was shown, that the rate of alcohol oxidation on a gold electrode is determined by the cleavage of the C—H bond on the α-carbon atom,
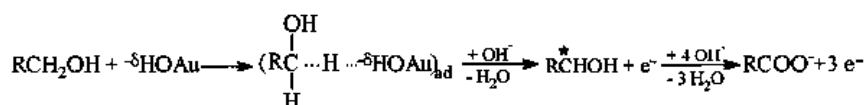
within a symmetric surface transition state formed by the interaction between alcohol molecules and hydroxyl ions in the electric field at the electrode/electrolyte solution interface [40, 46]. Further alcohol electrooxidation steps proceed so fast that they have no influence on the rate of the process. A detailed analysis of the kinetic data reveals, that the rate constants contain contributions of the adsorptive interaction of alcohol molecules with the electrode surface and the charge distribution within the substrate molecule and/or within the intermediate species formed after the cleavage of the α C—H bond [44–46, 53, 58]. An increase in the free enthalpy of adsorption per additional C-atom in an alcohol molecule, together with a decrease in the α C—H bond energy in a secondary alcohol when compared with the corresponding primary one, lead to a lower value of the apparent activation energy [$\Delta(\Delta E^{\#}) = 6$–7 kJ mol$^{-1}$] and a more negative value of the apparent activation entropy [$\Delta(\Delta S^{\#}) = 12$–20 J mol$^{-1}$K$^{-1}$].

A concurrent influence of the kinetics of alcohol electrooxidation on gold by the adsorptive properties of alcohol and by the stability of the intermediate species can be gained, among others, from a comparison of the behaviour of 2-propene-1-ol and 2-propyne-1-ol [71]. The former alcohol is oxidized at a considerably higher rate, although the free enthalpy of its adsorption on a gold electrode is lower than that of the alcohol with the triple bond [133]. Unquestionably, the clue for the difference in the reactivities is a high stability of the intermediates with several resonance structures which are formed after initial abstraction of hydrogen in the electrooxidation of 1,2-propene-1-ol, whereas the intermediate species of 2-propyne-1-ol lack the possibility of internal stabilization.
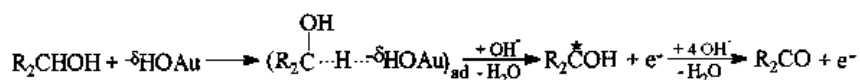
The mechanism of electrooxidation of the primary and secondary aliphatic monohydric alcohols, schematically presented below by the equations in Scheme 3 [45, 46], was confirmed by most authors dealing with the subject of electrocatalysis on gold and Au/Pt in alkaline solutions [49, 50, 59, 62, 64, 67, 134].

Oxidation of 1-propanol on a polycrystalline gold electrode in an alkaline solution was reinvestigated by Ocon et al. [59]. They accepted the earlier proposition

(a) primary alcohol

$$RCH_2OH + {}^{-\delta}HOAu \longrightarrow (R\overset{\underset{\displaystyle |}{OH}}{\underset{\displaystyle |}{\underset{\displaystyle H}{C}}}\cdots H\cdots{}^{-\delta}HOAu)_{ad} \xrightarrow[-H_2O]{+OH^-} R\overset{*}{C}HOH + e^- \xrightarrow[-3H_2O]{+4OH^-} RCOO^- + 3e^-$$

(b) secondary alcohol

$$R_2CHOH + {}^{-\delta}HOAu \longrightarrow (R_2\overset{\underset{\displaystyle |}{OH}}{C}\cdots H\cdots{}^{-\delta}HOAu)_{ad} \xrightarrow[-H_2O]{+OH^-} R_2\overset{*}{C}OH + e^- \xrightarrow[-H_2O]{+4OH^-} R_2CO + e^-$$

Scheme 3. Reaction pathway in the oxidation of primary alcohol (a) and secondary alcohol (b) on a gold electrode in alkaline solution [45, 46].

about alcohol oxidation in this system in a potential range in which the hydroxide species are chemisorbed on the gold surface. The authors claimed that the surface coverage of $\Theta_{OH^-} = 0.5$ was achieved at $E_{RHE} \approx 0.65$ V; $\Theta_{OH^-} = 1$ was obtained at $E_{RHE} \approx 0.9$ V. It was suggested that at $E_{RHE} \approx 0.9$ V a change in the character of the surface layer takes place due to polarization of the O—H bond in the adsorbed ions. The last phenomenon together with the change in the coverage of the electrode by the intermediates of 1-propanol oxidation has been assumed to be the reason for a change in the value of the electron transfer coefficient at $E_{RHE} \approx 0.9$ V. A faster increase in the surface coverage with adsorbed hydroxide species may explain the increase in oxidation rate observed for methanol [61] after voltammetric activation of gold according to the procedure of Arvia et al. [135].

The electrocatalytic activity of gold in acidic solutions is far lower than in alkaline solutions. The behaviour of 1-propanol, 2-propene-1-ol and 2-propyne-1-ol on gold at pH $\simeq 0$ has been compared by Pastor et al. [136]. Their studies confirmed that saturated monohydric alcohols remain inactive in the absence of adsorbed hydroxyl ions at the gold/solution interface. In contrast, unsaturated alcohols undergo oxidation on a gold electrode in an acidic solution. By using differential electrochemical mass spectroscopy (DEMS) the authors identified unsaturated aldehydes and $CO_2$ as the final products of oxidation of 2-propene-1-ol and 2-propyne-1-ol. It was found that only 2-propyne-1-ol forms a relatively stable adsorbate on the gold surface which can be subsequently reduced at $E_{RHE} < 0.2$ V producing propylene, propene, and 2-propene-1-ol. Accordingly, the $CO_2$/aldehyde ratio was much higher in the case of the alcohol with a triple bond when compared with the corresponding ratio for the alcohol with a double bond. The differences in the electrooxidation pathways of 2-propene-1-ol and 2-propyne-1-ol were explained in terms of different interaction of the substrate molecules with the gold surface. This interpretation is supported by the values of the free enthalpy of adsorption of $\Delta G^{\circ}_{ad} = -31.8$ kJ mol$^{-1}$ and $\Delta G^{\circ}_{ad} = -34.0$ kJ mol$^{-1}$ for 2-propene-1-ol and 2-propyne-1-ol respectively, as obtained on a Au(1 0 0) electrode in 0.02 M NaClO$_4$ in the potential range close to the potential of zero charge [133]. Obviously, the adsorption of unsaturated alcohols is sufficiently strong to ensure an appropriate lowering of the activation energy for C—H bond cleavage, as well as for the reaction of an intermediate with water molecules on the electrode surface. This does not occur in the case of 1-propanol because of the much lower value of the free enthalpy of adsorption, $\Delta G^{\circ}_{ad} = -5.0$ kJ mol$^{-1}$ [79].

## 3. Polyhydric alcohols

Several studies were devoted to electrode processes involving diols. For 1,2-ethanediol oxidation, various electrode materials were used as catalysts, such as Au [42, 60, 64, 66, 88, 137, 138], Pt [66, 88, 139–146] as well as alloys of Pt + Pd [138], Pt + Au [41, 88] or Au and Pt modified with u.p.d. adatoms of foreign metals [48, 49, 64, 88, 95, 97, 105, 110, 139]. An effective catalyst, as in the case of oxidation of monohydric alcohols, appeared to be a gold electrode in alkaline solution, though in a range of anodic potentials higher than for a platinum [42].

Hauffe et al. [42] indicated that cleavage of C—H bonds in 1,2-ethanediol is facilitated by OH$^-$ ions adsorbed on the surface of a gold electrode. The rate determining step was formulated as shown in Scheme 4. Kadirgan et al. [49, 64] have also shown that the electrooxidation of 1,2-ethanediol on gold is a first-order process relative to $c_{diol}$ over a wide range of electrode potentials. Only for concentrations of 1,2-ethanediol higher than $c_{diol} \approx 1$ M, was a decrease in the reaction order observed. Analysis of $j/E$ curves (Tafel slopes) showed that $\alpha n = 0.34$, thus confirming the mechanism presented by Hauffe et al. [42]. In this mechanism, dehydrogenation of adsorbed diol molecules, associated with the transfer of the first electron, is the rate determining step. The aforementioned kinetic parameters and the reaction order $z_{OH^-} = 0$ relative to $c_{OH^-}$ in the range from 0.01 to 5 M are in close agreement with those obtained for monohydric alcohols [45, 46]. Lower currents of 1,2-ethanediol oxidation at pH < 12 can be explained by an insufficient degree of coverage of the gold electrode surface with the adsorbed hydroxyl ions. The participation of the latter species in the electrooxidation of 1,2-ethanediol on gold was indicated by the influence of the crystallographic orientation of the metal surface on the reaction rate. It was found by Adžić et al. [48, 60] that on monocrystalline Au(1 1 0) this process starts at a potential more negative than on Au(1 0 0) or Au(1 1 1), which was related to differences in the potential of AuOH formation. However, subsequent stages of the oxidation process taking place on gold [60] were described assuming the same reaction scheme as proposed earlier for the electrooxidation of 1,2-ethanediol on platinum [80].

Studies of the solution after oxidation of 1,2-ethanediol on a gold electrode in 0.1 M NaOH at $E_{RHE} = 1.13$ V using liquid chromatography and IR spectroscopy [49, 64], confirmed the presence of anions of glycolic, formic, and oxalic acids. It was concluded that 1,2-ethanediol may be oxidized stepwise through glyoxal and/or glycolate into glyoxylate and, further, to oxalate, as well as to formate after C—C bond cleavage. In a parallel reaction, glyoxylate may undergo the Cannizaro reaction giving glycolate
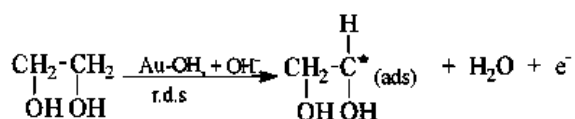


Scheme 4. The initial step in the oxidation of 1,2-ethanediol on a gold electrode in alkaline solution [42].
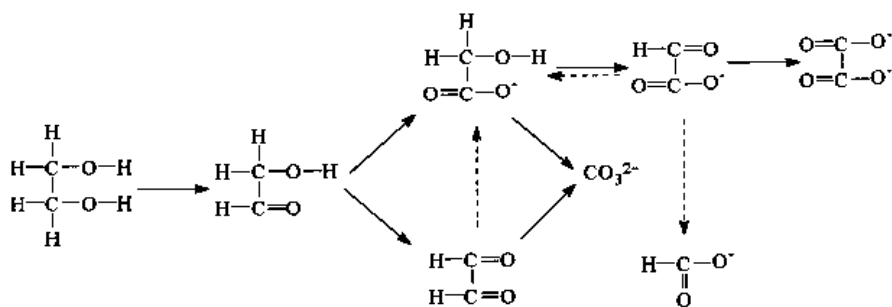
Scheme 5. Reaction scheme of 1,2-ethanediol oxidation on a gold electrode in alkaline solution at $E_{RHE} \geq 1.13V$ [64, 66].
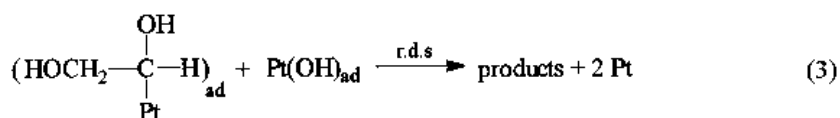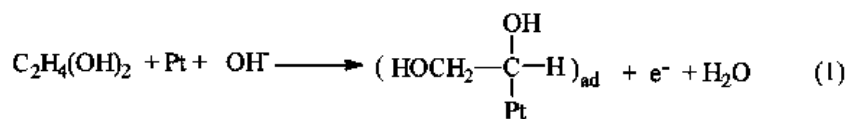
and oxalate. Further information on the electrooxidation pathways was recently provided by Weaver and coworkers [66]. On the basis of *in situ* FTIR spectra, they corroborated successive formation of relatively long-lived solution–phase intermediates: glycolate, glyoxalate and oxalate and, in addition, they observed carbonate. The latter species escaped identification in the liquid chromatographic analysis [64]. On the other hand, the *in situ* FTIR spectra provided no evidence for formate production. A general reaction pathway of 1,2-ethanediol oxidation on a gold electrode in alkaline solutions, including the suggestion of Kadirgan *et al.* [64] and Weaver *et al.* [66] is shown in Scheme 5.

The properties of gold electrodes modified by u.p.d. Pb, Bi, Cd, Ru, Re and Tl adatoms during oxidation of 1,2-ethanediol in alkaline solution were investigated on the basis of cyclic voltammograms [64]. It was shown that only Au + Pb and Au + Bi reveal a higher catalytic activity than a pure gold electrode. The catalytic effects were explained by assuming that the chemisorption of hydroxyl ions on Pb and Bi adatoms occurs at lower electrode potentials when compared with gold. No such effect was detected for the Au + Cd and Au + Re systems, whereas in the Au + Ru and Au + Tl systems strong inhibition of 1,2-ethanediol electrooxidation was observed.

The mechanism of 1,2-ethanediol oxidation on a platinum electrode is different from that reported for gold. This is a result of the stronger adsorptive properties of platinum. Subsequent steps of 1,2-ethanediol oxidation on a platinum electrode in

alkaline solutions, as shown by Hauffe *et al.* [84] and outlined below in Scheme 6, are typical of the electrooxidation of organic substances in this system [140, 147]. The initial step (1) is a dissociative chemisorption of 1,2-ethanediol. Further $Pt(OH)_{ad}$ species are formed in reaction (2). The reaction (3) of the intermediate produced in stage (1) with $Pt(OH)_{ad}$ is the rate-determining step for the whole process. Apart from the oxidation of the adsorbed reactive intermediates to glycolate, oxalate and $CO_3^{2-}$, cleavage of the C—C bond may also take place [49, 66, 142, 146, 148]. Such a conclusion was confirmed after detection of carbon monoxide, sitting on top or in a bridged arrangement on the platinum surface [137], poisoning the electrode and inhibiting the process.

The main reaction product detected upon the electrooxidation of 1,2-ethanediol on Pt in acidic solutions at double layer potentials was $CO_2$ and glycolic acid besides the adsorbed CO species and traces of such intermediate products as: glycolaldehyde, glyoxal, glyoxylic acid and oxalic acid, formaldehyde and formic acid [15, 137, 143, 148–151]. This indicates the simultaneous occurrence of the C—C bond dissociation in the reacting molecules and the subsequent dehydrogenation steps of 1,2-ethanediol [3, 139, 141, 151]. The carboxyl functional groups of the intermediates are oxidized to $CO_2$, whereas a significant part of the alcohol and aldehyde groups, as it was found by Wieland *et al.* [151], is oxidized to adsorbed CO. This explains why a decrease in electrode activity, being a consequence of the progressive blocking of the electrode surface by $CO_{ad}$, poses a serious problem on a platinum elec-

$$C_2H_4(OH)_2 + Pt + OH^- \longrightarrow (HOCH_2{-}\overset{\displaystyle OH}{\underset{\displaystyle Pt}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}{-}H)_{ad} + e^- + H_2O \qquad (1)$$

$$Pt + OH^- \longrightarrow Pt(OH)_{ad} + e^- \qquad (2)$$

$$(HOCH_2{-}\overset{\displaystyle OH}{\underset{\displaystyle Pt}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}{-}H)_{ad} + Pt(OH)_{ad} \xrightarrow{r.d.s} products + 2\,Pt \qquad (3)$$

Scheme 6. Initial steps in the oxidation of 1,2-ethanediol on a platinum electrode in alkaline solution [84].

trode in an acidic rather than an alkaline solution. The modification of a platinum surface by u.p.d. foreign metal adatoms and by electrochemical activating procedures during prolonged electrolysis is a way of limiting the formation of poisonous species, as well as increasing the selectivity of the electrode reaction [139, 150]. Under appropriate conditions a production of the two-carbon compounds can be achieved in long-term electrolysis of 1,2-ethanediol [150].

The influence of Sn and Pb u.p.d. adatoms on the kinetics of 1,2-ethanediol oxidation on a platinum electrode in acidic and alkaline solution was identified by Smirnova et al. [105]. As a result of the surface modification of the Pt electrode by Sn adatoms, the rate of the diol oxidation increases both in acidic (by 2–2.5 orders of magnitude) and alkaline (by 1–1.5 orders of magnitude) solution. The Pb adatoms bring about only a slight increase in the oxidation rate in solution of pH < 7, whereas in an alkaline solution the rate of the process was observed to increase by two orders of magnitude. Jiang et al. [110] detected an enhanced catalytic activity of Pt modified by u.p.d. Bi adatoms. All these catalytic effects were explained in terms of the 'third body effect' and/or of a bifunctional theory of electrocatalysis.

As in the case of gold, the oxidation rate of 1,2-ethanediol on platinum is affected by the crystallographic structure of the electrode surface. This is indicated by different electrode potential values, where this process begins as well as by different values of the oxidation current densities. Marković et al. [140] indicated a correlation between the onset of the oxidation of 1,2-ethanediol and the formation of PtOH on the platinum surface of a particular crystallographic orientation. The structural effects in the oxidation of 1,2-ethanediol were generally weaker in alkaline [140] than in acidic solutions [144, 145], most probably due to the different structure of the intermediates.

It was observed that not only 1,2-ethanediol but also other diols in alkaline solution, were more reactive on a gold electrode than the monohydric alcohols [46, 62, 65, 68–72, 137, 138]. Alonso et al. [62] focused attention on the electrocatalytic oxidation of 1,2-propanediol. Both from the Tafel slopes and the reaction order relative to $c_{diol}$ and $c_{OH^-}$, as well as from the activation energy they concluded, that the

oxidation rate was determined by the rate of the C—H bond cleavage in 1,2-propanediol molecules interacting with the adsorbed hydroxyl ions. This had already been proposed for the oxidation of monohydric alcohols and 1,2-ethanediol on a gold electrode [see above]. The authors suggest, that 1,2-propanediol molecules adsorbed directly on the surface gold atoms are involved in the oxidation process, along with the adsorbed hydroxyl groups lying in their vicinity, whereas the C—H bond in the $CH_2OH$ functional group is preferentially split. The probability of hydrogen abstraction from the CHOH functional group was considered to be lower, as a consequence of formation of a less stable radical. This conclusion is contradictory to the generally accepted rule assuming a higher stability of secondary radicals relative to primary ones [152].

On the basis of NMR spectroscopy which identified the anions of lactic, formic and acetic acid as the final products in the 1,2-propanediol samples after prolonged electrolysis, the general reaction pathway outlined in Scheme 7 for the oxidation of 1,2-propanediol on a gold electrode in alkaline solution was presented [62]. According to this scheme, 1,2-propanediol oxidation may proceed along two different pathways, via methylglyoxal and via the anion of lactic acid as intermediates to the anion of pyruvic acid. Methylglyoxal may be also partially transformed into the anion of lactic acid through a Cannizzaro intramolecular reaction [153]. After cleavage of the C—C bond in the anions of pyruvic and lactic acid, anions of formic, acetic and carbonic acid may be formed.

All the reaction products mentioned in Scheme 7 were also identified during the oxidation of 1,2-propanediol on a Pt electrode, whereas their distribution was strongly dependent on the electrode potential, the structure of the electrode surface and on the pH of the electrolyte [25, 104, 139]. The occurrence of formic acid and acetic acid in solution, as well as hydroxyacetone and lactic acid, was interpreted in terms of a simultaneous cleavage of C—H and C—C bonds in the substrate molecules and in the intermediate species. Evidence for the side reactions leading to poisoning of the electrode surface was provided by in situ FTIR-spectroscopy [29, 31]. Formation of adsorbed CO and ethyliyne species was detected in parallel to a direct oxidation of 1,2-propanediol via
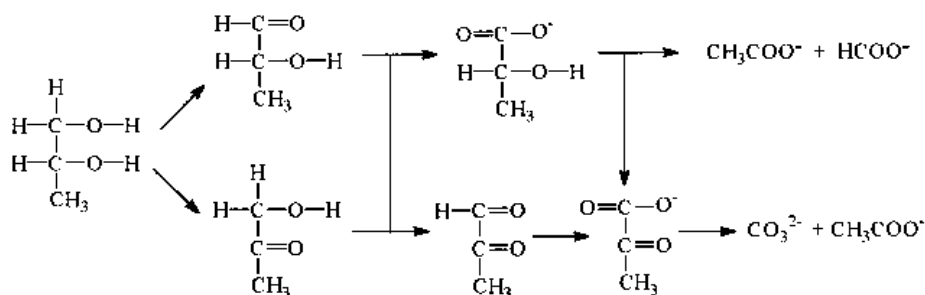


Scheme 7. Reaction scheme of 1,2-propanediol oxidation on a gold electrode in alkaline solution [62].

such reactive intermediates as $(CH_3CHOH\dot{C}HOH)_{ad}$, $(CH_3\dot{C}OHCH_2OH)_{ad}$ and $(CH_3\dot{C}OH\dot{C}HOH)_{ad}$.

Similarly, the direct oxidation of 1,3-propanediol [139] and 2,3-butanediol [14] on a Pt electrode takes place via the corresponding oxy–oxo compounds, whereas the evolution of $CO_2$ is ascribed to the oxidation of strongly chemisorbed species formed in side reactions.

The activity of a platinum electrode during 1,2-propanediol oxidation in acidic solutions [12, 15, 24, 25, 139] is lower than in alkaline solutions [104, 139]. A reason for the observed differences may be a decreased rate of the consecutive dehydrogenation steps in the absence of hydroxyl ions at the electrode/solution interface and an increased poisoning of the electrode surface by adsorbed three-carbon species and $CO_{ad}$ forming as a consequence of the C—C bond cleavage in 1,2-propanediol. A stronger inhibition of the electrode surface by chemisorbed species with a longer carbon chain may be a reason for the lower current density of 1,2-propanediol electrooxidation on Pt in comparison with the corresponding value for 1,2-ethanediol, under the same experimental conditions [25].

U.p.d. Pb, Tl and Bi adatoms considerably enhance the electrocatalytic activity of a platinum electrode for oxidation of 1,2-propanediol from alkaline solutions [104]. An increase in the reaction rate was explained on the basis of a bifunctional theory of electrocatalysis, assuming that two types of compound, Pt–O–M–OH and $(Pt–O)_2$–M–OH, are formed at the electrode/solution interface. In acidic solutions the catalytic action of the foreign adatoms is less pronounced [24]. An enhancement effect was observed with Pt + Re, Pt + Cd and Pt + Pb systems, whereas Tl and Bi adatoms led to a considerable inhibition effect. The positive effect of the adatoms was attributed to a prevention of the reaction between the 1,2-propanediol intermediates and hydrogen atoms on the platinum surface. However, the origin of the catalytic effect of u.p.d. adatoms is certainly much more complicated. As established by Belgsir et al. [139], the presence of u.p.d. foreign metal adatoms on a platinum surface drastically modifies the distribution of reaction products in comparison with that formed on a pure platinum electrode.

A series of reports by Betowska-Brzezinska and co-workers [46, 65, 68–72], gives a comprehensive analysis of the effect of the molecular structure of various diols on their reactivity in the oxidation process on a gold electrode in alkaline solutions. A wide scope of the investigated substrates included acyclic, cyclic, saturated and unsaturated diols with different carbon chain lengths (from two to six C atoms) and with hydroxyl groups in different positions and configurations. The basic kinetic parameters: charge transfer coefficient ($\alpha$), the reaction order relative to substrate ($z_{diol}$) and to hydroxyl ions ($z_{OH^-}$) are found to be either the same or very close for all diols, and almost equal to those for mono-

hydric alcohols. On the basis of the kinetic data, the mechanism of the first steps in the electrooxidation of diols on gold appears to be the same as in the electrooxidation of monohydric alcohols. The heterogenous dehydrogenation of diol molecules, involving electron transfer to the gold electrode and the formation of water molecules, determines the rate of the whole process. Hydrogen abstraction from a diol molecule occurs via a transient adsorbate complex formed as a result of an interaction between the substrate molecules and hydroxide species on the electrode surface. This is evidenced both by the isotope kinetic effect (see below) and the values of electron transfer coefficient $\alpha \leq 0.5$ as well as by the reaction order $z_{diol} \approx 1$ within a wide range of diol concentration in solution and $z_{OH^-} = 1$ and $z_{OH^-} = 0$, respectively, at the concentration of hydroxyl ions $c_{OH^-} \leq 0.01$ M and $c_{OH^-} \geq 0.01$ M. The rate of diol electrooxidation on gold increases proportionally to $c_{diol}$, both when $z_{OH^-} = 1$ and $z_{OH^-} = 0$, that is , at a partial and total coverage of the electrode surface with the adsorbed hydroxyl ions. This testifies to a high rate of desorption of the intermediates. A deviation towards $z_{diol} = 0$ occurs when the surface coverage with diol molecules ($\Theta_{diol}$) reaches a maximum value. The corresponding value of $c_{diol}$ depends on the actual adsorption properties of the substrate molecules [71], thus confirming the conclusion concerning adsorption of diol molecules at the gold/solution interface as a precondition for their dehydrogenation and oxidation. The adsorption of substrate molecules was also demonstrated by a significant decrease in the differential capacity of the electric double layer with increasing diol concentration in solution [65, 68, 70, 71, 76, 133, 154]. A similar effect was indicated when monohydric alcohols were used [58, 78, 79].

The above mechanism of oxidation of mono- and polyhydric alcohols on a gold electrode appears to be analogous to that known in the heterogenous catalysis under the name of the Eley–Rideal mechanism [155]. According to this mechanism, alcohol molecules may be adsorbed on the catalyst surface without being involved in the oxidation reaction, in particular at small coverages of the metal surface with preadsorbed hydroxyl ions at low anodic potentials. They may actually inhibit adsorption of further hydroxyl ions by blocking the electrode surface. This would account for the observed decrease in the rate of alcohol oxidation, with their concentration in solution being high. This effect as well as the analogous decrease in the reaction rate observed at higher concentrations of hydroxyl ions are indicative of the competitive adsorption of alcohol molecules and hydroxyl ions on a gold surface [16, 68, 71].

Some information about the adsorbed complex in the electrooxidation of diols were obtained from the kinetic measurements for chosen vicinal and terminal isomers of diols at different degrees of deuteration of the systems under study [69, 70]. During oxidation of the vicinal diols, both after substitution of hydrogen

atoms by deuterium on carbon atoms bonded with –OH groups in the diol molecule and after deuteration of –OH groups, a primary isotope kinetic effect was observed. This was manifested by a significant decrease in the reaction rate at a simultaneous deuteration of a solvent and the supporting electrolyte. In particular, an anomalously large isotope kinetic effect was observed for 2,3-butanediol. Consequently it was assumed, that the transient complex formed at the gold electrode surface in the process of dehydrogenation of vicinal diols may have a cyclic structure. The possibility of a cyclic transient state and of O—H bond cleavage in the rate-determining step was ruled out in the case of terminal isomers because of the large distance between hydroxyl groups in diol molecules. Only the secondary isotope kinetic effect after deuteration of these groups was found to be in agreement with this conclusion.

The electrocatalytic activity of gold is higher for isomers of acyclic and cyclic diols carrying –OH groups at vicinal position than for terminal isomers [46, 65, 68, 72]. Obviously, the second hydroxyl group in a diol molecule, attached to the neighbouring carbon atom, markedly enhances reactivity in the electrooxidation. The effect of the position of –OH groups in a diol molecule on the kinetics of electrooxidation is well illustrated in Fig. 1 and Fig. 2 by the cyclic voltammograms for butanediol and cyclohexanediol isomers. It can be seen, that the oxidation rate of isomers with functional groups separated by –CH$_2$ groups is much lower as compared with that
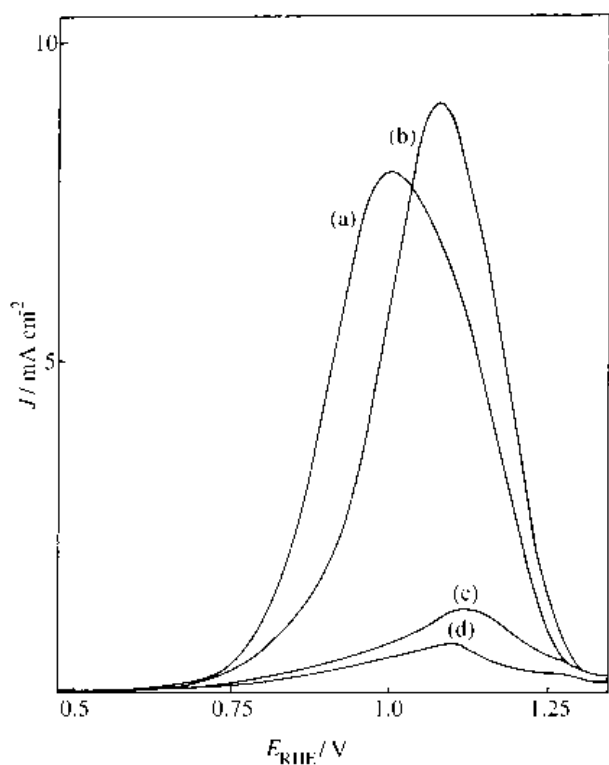
for the appropriate vicinal isomers. When the number of electrons transferred during the formation of the reaction products is considered, the difference in the reactivity of the above mentioned isomers is even more pronounced. The possible reaction pathways for electrooxidation of 1,2-butanediol, 2,3-butanediol and 1,4-butanediol proposed on the basis of the experimental data [65, 68, 70] and the general rules of the chemical reactivity of diols [152] are presented in Scheme 8, 9 and 10, respectively.

As in the case of monohydric alcohols, the rate of electrooxidation of acyclic diols on gold increases with an increasing number of carbon atoms in a substrate molecule, both for vicinal and terminal isomers [68]. This regularity for terminal isomers of diols was recently confirmed by Hilmi et al. [73]. The double bond in a diol molecule increases its reactivity, e.g. the oxidation rate of 2-butene-1,4-diol is several times higher than that of 1,4-butanediol. On the other hand, the oxidation rate of 2-butyne-1,4-diol containing a triple bond in a molecule is significantly smaller [71].

The effect of geometric isomerism on the reactivity of diols was illustrated using cyclohexanediols [72].
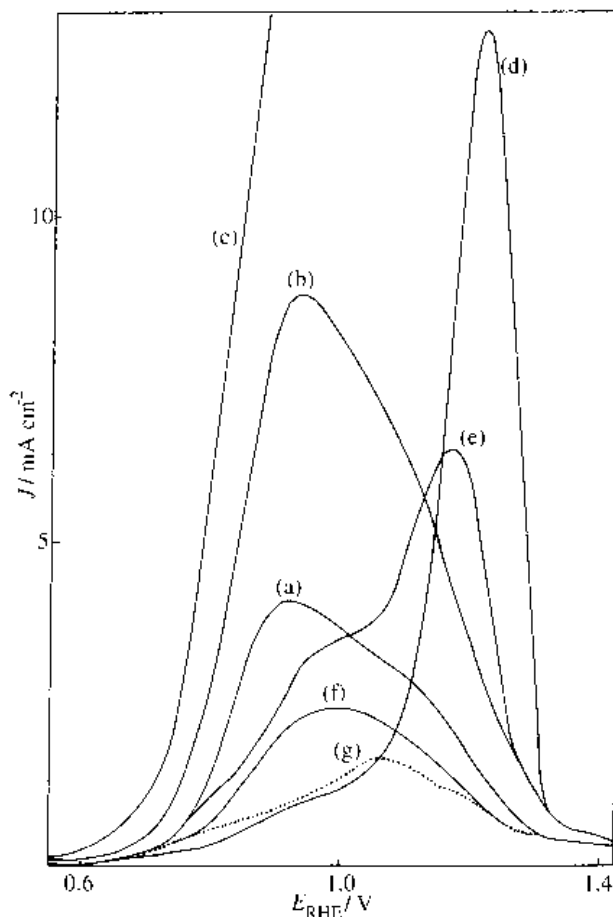


Fig. 1. Cyclic voltammograms of a polycrystalline gold electrode in a solution 0.1 M KOH + (a) 0.01 M 2,3-butanediol; (b) 0.01 M 1,2-butanediol; (c) 0.01 M 1,4-butanediol; (d) 0.01 M 1,3-butanediol. d$E$/d$t$ = 100 mV s$^{-1}$.



Fig. 2. Cyclic voltammograms of a polycrystalline gold electrode in a solution 0.1 M KOH + (a) 0.005 M trans-1,2-cyclohexanediol; (b) 0.01 M trans-1,2-cyclohexanediol; (c) 0.05 M trans-1,2-cyclohexanediol; (d) 0.05 M cis,trans-1,2-cyclohexanediol, (e) 0.01 M cis,trans-1,2-cyclohexanediol; (f) 0.01 M 1,4-cyclohexanediol; (g) 0.01 M 1,3-cyclohexanediol. d$E$/d$t$ = 100 mV s$^{-1}$.
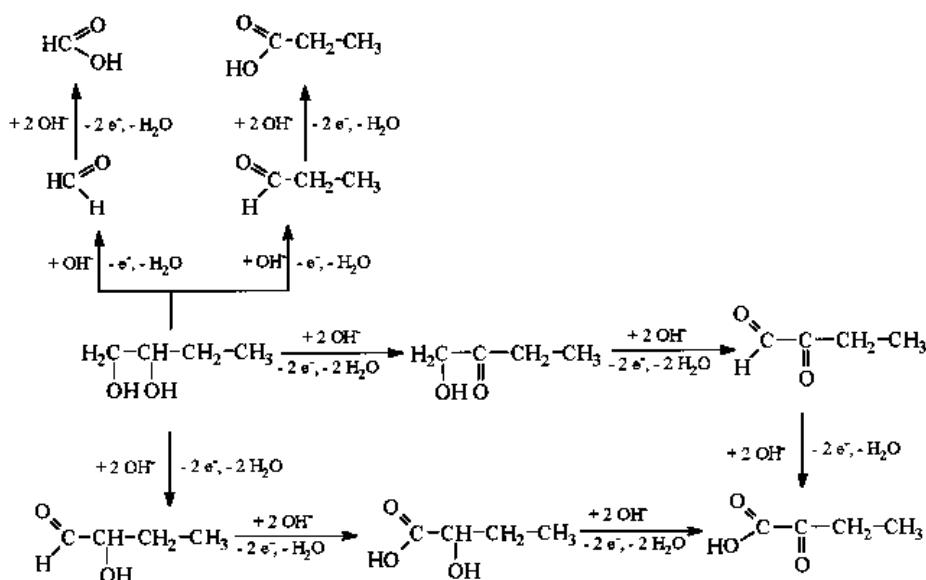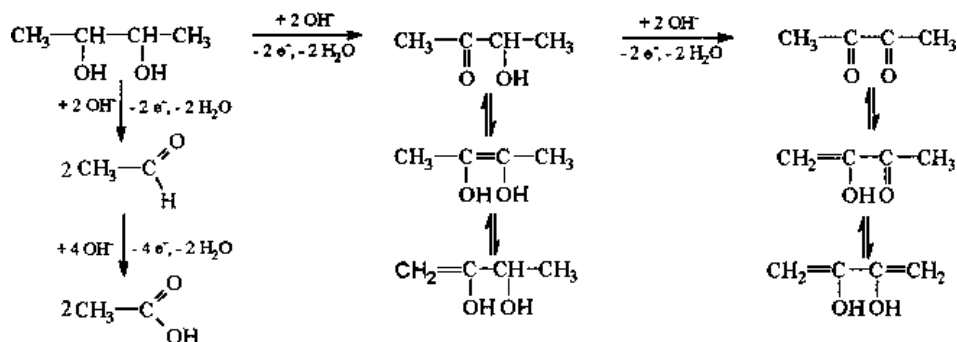
Scheme 8. Possible reaction pathways for the electrooxidation of 1,2-butanediol on a gold electrode in an alkaline solution.

*Trans*-1,2-cyclohexanediol is easily oxidized within the potential range $E_{RHE} = 0.6–1.0$ V, whereas *cis*-1,2-cyclohexanediol is oxidized preferably in the range $E_{RHE} \geq 0.95$ V. A change of concentration of *trans*- and *cis*-1,2-cyclohexanediol, under otherwise unchanged experimental conditions, affects the rate of the process in a different way. In the case of *trans* isomer, with increasing concentration of diol in solution, the current density also increases, whereas at higher concentrations of the *cis*-isomer, the oxidation process is clearly shifted towards more anodic potentials (Fig. 2).

Analysis of the adsorption parameters and the kinetic data on the electrooxidation of aliphatic diols, both acyclic and cyclic, saturated and unsaturated [65, 68–72, 76, 133, 154], suggests that the main reason for the different reactivities of the studied compounds on gold are the differences in the energy of the C—H bond broken in the rate determining step and the stabilities of the intermediates formed thereafter. A less important role is played by the adsorption properties of diols. Differences in the adsorption properties may account for the observed increase in the oxidation rate of acyclic diols with increasing number of carbon atoms in a molecule in the homologous series of vicinal and terminal isomers:

1,2-ethanediol < 1,2-propanediol < 1,2-butanediol
    < 1,2-pentanediol < 1,2-hexanediol
1,2-ethanediol < 1,3-propanediol < 1,4-butanediol
    < 1,5-pentanediol < 1,6-hexanediol

Stronger interactions between a diol molecule and the electrode surface, reflected by the free enthalpy of adsorption increasing for each subsequent member of the homologous series, obviously favour lowering of the energy barrier for dehydrogenation of diol molecules. On the other hand, the oxidation rate of vicinal isomers on a gold electrode is higher than that of terminal isomers, despite a lower value of the free enthalpy of adsorption of vicinal diols and their weaker interaction with the gold surface. Most probably, the adsorption effect is overcompensated by: (i) a lower energy of the C—H bond in a –CHOH group in vicinal isomers, relative to the energy of the C—H bond in a –CH$_2$OH group in terminal isomers; and/or (ii) a higher stability of the secondary radical formed during the oxidation of vicinal diols relative to the stability of primary radical formed during the oxidation of terminal diols. Also, differences in the course of electrooxidation of *cis*- and *trans*-isomers of cyclohexanediol on gold can be assigned to a more effective activation of the reacting C—H bonds in the



Scheme 9. Possible reaction pathways for the electrooxidation of 2,3-butanediol on a gold electrode in an alkaline solution.
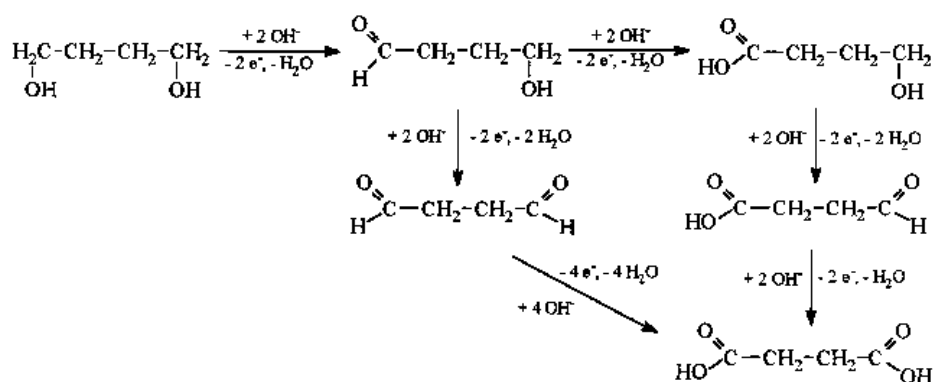
Scheme 10. Possible reaction pathways for the electrooxidation of 1,4-butanediol on a gold electrode in an alkaline solution.

*trans*-isomer by adjacent adsorbed hydroxyl ions, because of the advantagenous distance between the involved functional groups. All the effects, that is, the resonance stabilization and the inductive effect, as well as the lowering of the energy barrier of dehydrogenation of diol molecules induced by strong adsorption, coincide in the case of 2-butene-1,4-diol. This explains a considerable increase in the oxidation rate as compared to that of its saturated analog, 1,4-butanediol. However, as mentioned above, a substitution of the double bond in a diol molecule with the triple bond, significantly reduces the rate of oxidation, although the value of the free enthalpy of adsorption of 2-butyne-1,4-diol is more negative than that of 2-butene-1,4-diol [133]. It seems reasonable that a low reactivity of 2-butyne-1,4-diol is a consequence of the fact that there is no possibility of an internal resonance stabilization of the reaction intermediate, formed after the initial abstraction of hydrogen from a diol molecule [71].

Unlike on a gold electrode, the oxidation rate of terminal isomers of aliphatic diols on a platinum electrode decreases with an increasing number of carbon atoms, both in alkaline and acidic solutions [73]. This relationship is the same as in the case of oxidation of monohydric alcohols on Pt. Undoubtedly, the reason for this is a surface inhibition, equivalent to an increase of the adsorption energy of subsequent members of homologous series of diols and of appropriate monoaldehydes, which appear to be primary oxidation products [65, 68, 76, 156]. The surface inhibition must also be a reason for the lower oxidation rate of 2,3-butanediol relative to 1,2-butanediol reported by Hilmi *et al.* [73]. These authors noticed a very strong influence of stereoisomerism on the oxidation rate of 2,3-butanediol [157, 158]. A comparison of voltammograms recorded both with poly- and monocrystalline platinum electrodes have shown that the *R,R* and *S,S* isomers are less reactive than the *R,S* isomer. Different reactivities of particular stereoisomers of 2,3-butanediol may be caused by different interaction and orientation of their stable conformers at the electrode/solution interface. Due to the formation of intramolecular hydrogen bonds between the vicinal hydroxyl groups in *R,R* and *S,S* isomers of 2,3-butanediol only one of the C—H hy-

drogen atoms at the position 2 or 3 may be directed towards the metal, whereas with *R,S* isomers both of the considered hydrogen atoms may be attached to the electrode surface.

Enea *et al.* [134] compared the voltammograms recorded during the oxidation of polyhydric alcohols containing from two to six C atoms in a molecule (1,2-ethanediol, 1,2,3-propanetriol, *S*-erythrol, D,L-xilithol, D-sorbitol and D-mannitol) on platinum and gold electrodes in alkaline solutions. The authors state, that the rate of oxidation of all these compounds on platinum clearly decreases with increasing number of carbon atoms in their molecules. Considering the results obtained for monohydric alcohols and diols (see above), this appears to be a general rule for the oxidation of organic compounds containing the –OH functional group, on a platinum electrode. For a gold electrode in alkaline solution, as it might also have been inferred from the data on monohydric alcohols and diols, the rate of polyol oxidation increases with increasing number of carbon atoms and –OH groups in a molecule (1,2-ethanediol < 1,2,3-propanetriol < *S*-erythrol). However, data on the adsorption of polyols and the effect of steric position of –OH groups in the substrate molecules on the kinetics of their oxidation on a gold and platinum electrode are incomplete. Recently, the electrooxidation of D-sorbitol was studied on single crystal and polycrystalline platinum in acidic soluion [159–161]. Detailed data on the mechanism of electrocatalytic oxidation are available for 1,2,3-propanetriol. According to Avramov-Ivić *et al.* [67, 162], the initial steps of 1,2,3-propanetriol oxidation on gold and platinum, respectively, are the same as for any other mono- and polyhydric alcohol oxidized on these noble metals. The authors considered the formation of a surface complex between hydroxide species and 1,2,3-propanetriol molecules as the essential condition for the process to occur on gold [67].

A parallelism between the potential of electrosorption of hydroxyl ions and the onset of 1,2,3-propanetriol oxidation was also observed on a platinum electrode in alkaline solution [162]. In this case, however, the dehydrogenation of substrate molecules was accompanied by formation of strongly bonded adsorbate (mainly CO), blocking the plati-

num surface, in a manner similar to that found for monohydric alcohols and diols. The poisoning of the electrode surface by intermediates is very weak on gold and hence the electrooxidation rate of 1,2,3-propanetriol on this metal is three times higher than on platinum. Analogous differences in the catalytic activity of a platinum and gold electrode were indicated upon the oxidation of glucose. The inhibition effect is significant on platinum, mainly due to the production of adsorbed CO and gluconolactone-type species [28, 163–174]. Again, the rate of glucose oxidation on gold, even in acidic solution, is higher than that on platinum and increases with pH [28, 43, 63, 175–177]. According to Larew et al. [63], cleavage of the C—H bond occurs at a particularly high rate when molecules of glucose are linked by hydrogen bridges to more than one AuOH active centre on the surface of a gold electrode. The same is assumed for intermediates formed during electrooxidation of glucose. These processes proceed slowly, when the number of neighbouring active centres on the electrode surface is limited and every glucose molecule interacts with only one active centre. However, even in this case the reactivity of glucose on gold is higher than that of other polyhydric alcohols. This might be a consequence of a preferential adsorption of the aldehyde group of glucose on the Au–OH surface. This conclusion appears to be correct in view of the high reactivity of formaldehyde on a gold electrode [54].

In general, it can be said that an effective catalyst in electrochemical oxidation of organic substances should reveal the following properties: (i) the energy of adsorption of substrate molecules and/or intermediate species formed on the catalyst surface should be sufficiently high to substantially decrease the activation energy for the dehydrogenation step, but sufficiently low for the intermediate and final products to desorb easily, and (ii) the energy released by formation of water molecules as one of the reaction products should be sufficient to compensate for the energy needed for desorption of dehydrogenated organic intermediates from the metal surface.

## Acknowledgements

## References

[1] H. Wroblowa, B. J. Piersma and J. O'M. Bockris, J. Electroanal. Chem. **6** (1963) 401.
[2] S. Gilman, Trans. Faraday Soc. **61** (1965) 61.
[3] A. K. Vijh, Can. J. Chem. **49** (1971) 78.
[4] G. Crépy, C. Lamy and S. Maximovitch, J. Electroanal. Chem. **54** (1974) 161.
[5] S. N. Raicheva, S.V. Kalcheva, M. V. Christov and E. I. Sokolova, ibid. **55** (1974) 213.
[6] I. Sokolova, Electrochim. Acta **20** (1975) 323.
[7] W. Vielstich, 'Fuel Cells', J. Wiley-International, London, (1975).
[8] B. B. Damaskin, O. A. Petrii and V. V. Batrakov, 'Adsorption organischer Verbindungen an Elektroden', Akademie-Verlag, Berlin (1975).
[9] A. Wieckowski and B. Sobkowski, J. Electroanal. Chem. **73** (1976) 317.
[10] K. L. Murugkar and H. Lal, ibid. **72** (1976) 209.
[11] V. S. Bogotzki, Yu. B. Vassiliev and O. A. Khazova, ibid. **81** (1977) 229.
[12] I. Sokolova, Electrochim. Acta **24** (1979) 147.
[13] I. E. Sokolova, S. V. Kalcheva, M. V. Christov and S. N. Raicheva, C. R. Acad. Bulg. Sci. **32** (1979) 189, 317.
[14] G. Horányi, G. Inzelt and K. Torkos, J. Electroanal. Chem. **106** (1980) 305.
[15] G. Horányi and K. Torkos, ibid. **125** (1981) 105.
[16] S. N. Raicheva, M. V. Christov and I. E. Sokolova, Electrochim. Acta **26** (1981) 1669.
[17] B. Beden, A. Bewick, K. Kunimatsu and C. Lamy, J. Electroanal. Chem. **142** (1982) 345.
[18] S. N. Raicheva, Z. Phys. Chem. **264** (1983) 65.
[19] S. N. Raicheva, I. E. Sokolova and M. V. Christov, J. Electroanal. Chem. **175** (1984) 167.
[20] M. V. Christov and I. E. Sokolova, ibid. **175** (1984) 183.
[21] C. Lamy, Electrochim. Acta **29** (1984) 1581.
[22] M. Enyo, J. Electroanal. Chem. **186** (1985) 155.
[23] B. Beden, I. Çetin, A. Kahyaoglu, D. Takky and C. Lamy, J. Catal. **104** (1987) 37 and references therein.
[24] P. Ocon, B. Beden, H. Huser and C. Lamy, Electrochim. Acta **32** (1987) 387.
[25] H. Huser, J. M. Léger and C. Lamy, ibid. **33** (1988) 1359.
[26] R. Parsons and T. VanderNoot, J. Electroanal. Chem. **257** (1988) 9 and references therein.
[27] M. C. Arévalo, C. Gomis-Bas, E. Pastor, S. González and A. J. Arvia, Electrochim Acta **37** (1992) 1083.
[28] B. Kokoh, J. M. Léger, B. Beden and C. Lamy, ibid. **37** (1992) 1333.
[29] S. Shugang, Y. Dongfan and T. Zhaowu, Acta Physico-Chimica Sinica **8** (1992) 59.
[30] B. Beden, J. M. Léger and C. Lamy, in 'Modern Aspects of Electrochemistry', No. 22 (edited by J. O'M Bockris, B. E. Conway and R. E. White), Plenum Press, New York (1992), p. 97 and references therein.
[31] S. Wasmus and W. Vielstich, Electrochim. Acta **38** (1993) 541.
[32] E. Pastor, S. Wasmus, T. Iwasita, M. C. Arévalo, S. González and A. J. Arvia, J. Electroanal. Chem. **350** (1993) 97.
[33] E. Pastor, S. Wasmus, T. Iwasita, M. C. Arévalo, S. González and A. J. Arvia, ibid. **353** (1993) 81.
[34] K. Franaszczuk, E. Herrera, P. Zelenay, A. Wieckowski, J. Wang and R. I. Masel, J. Phys. Chem. **8** (1994) 5074.
[35] H. Hilmi, E. M. Belgsir, J. M. Léger, C. Lamy and R. O. Lezna, Electrochim. Acta **39** (1994) 407.
[36] Shi-Gang Sun, Dong-Fang Yang and Zhao-Wu Tian, J. Electroanal. Chem. **289** (1990) 177.
[37] Shi-Gang Sun and Yan Lin , ibid. **375** (1994) 401.
[38] M. Betowska-Brzezinska, Ext. Abstr. PTCh-Meeting, Toruń, 5–7 Sept. (1974).
[39] Idem, Ext. Abstr. PTCh-Meeting, Pia, 20–22 March (1975).
[40] M. Betowska-Brzezinska and W. Vielstich, Electrochim. Acta **22** (1977) 1313.
[41] W. Hauffe, J. Heitbaum and W. Vielstich, in Proceedings of the Meeting on Electrode Materials and Processes for Energy Conversion and Storage, Vol. 77–6, (edited by J. D. E. McIntyre, S. Srinivasan and F. G. Will), The Electrochemical Society, Princeton, New York (1977), p. 308.
[42] W. Hauffe and J. Heitbaum, Ber. Bunsenges. Phys. Chem. **82** (1978) 487.
[43] S. Ernst, J. Heitbaum and C. H. Hamann, J. Electroanal. Chem. **100** (1979) 173.
[44] M. Betowska-Brzezinska, Electrochim. Acta **24** (1979) 409.
[45] Idem, ibid. **25** (1980) 267.
[46] Idem, Kinetics and mechanism of electrooxidation of alcohols on gold, platinum and gold/platinum alloys in alkaline solution, UAM-Monogr., Chemistry, Vol. 38, Ed. UAM, Poznań (1980).
[47] R. R. Adžić and M. L. Avramov-Ivić, J. Electroanal. Chem. **134** (1982) 177.
[48] R. R. Adžić and S. Lerato, Bull. Soc. Chim., Beogard **47** (1982) 83.

[49] F. Kadirgan, B. Beden and C. Lamy, *J. Electroanal. Chem.* **143** (1983) 135.
[50] D. Takky, B. Beden, J. M. Léger and C. Lamy, *ibid.* **145** (1983) 461.
[51] R. R. Adžić and M. L. Avramov-Ivić, *Electrochim. Acta* **29** (1984) 1353.
[52] A. Kahyaoglu, B. Beden and C. Lamy, *ibid.* **29** (1984) 1488.
[53] R. Holze and M. Betowska-Brzezinska, *ibid.* **30** (1985) 937.
[54] M. Betowska-Brzezinska, *ibid.* **30** (1985) 1193.
[55] M. Betowska-Brzezinska, J. Heitbaum and W. Vielstich, *ibid.* **30** (1985) 1465.
[56] M. Betowska-Brzezinska and J. Heitbaum, *J. Electroanal. Chem.* **183** (1985) 167.
[57] M. Enyo, *J. Appl. Electrochem.* **15** (1985) 907.
[58] R. Holze and M. Betowska-Brzezinska, *DECHEMA-Monogr.* **102** (1986) 383.
[59] P. Ocon, C. Alonso, R. Celdran and J. Gonzáles-Velasco, *J. Electroanal. Chem.* **206** (1986) 179.
[60] R. R. Adžić and M. Avramov-Ivić, *J. Catal.* **101** (1986) 532.
[61] E. Gonzalez Herman, C. Alonso and J. González-Velasco, *J. Electroanal. Chem.* **223** (1987) 277.
[62] C. Alonso and J. Gonzáles-Velasco, *ibid.* **248** (1988) 193.
[63] L. A. Larew and D. C. Johnson, *ibid.* **262** (1989) 167.
[64] F. Kadirgan, E. Bouhier-Charbonnier, C. Lamy, J. M. Léger and B. Beden, *ibid.* **286** (1990) 41.
[65] R. Holze, T. uczak and M. Betowska-Brzezinska, *Electrochim. Acta* **35** (1990) 1345.
[66] S.-C. Chang, Y. Ho and M. J. Weaver, *J. Am. Chem. Soc.* **113** (1991) 9506.
[67] M. Avramov-Ivić, J. M. Léger, C. Lamy, V. D. Jović and S. D. Petrović, *J. Electroanal. Chem.* **308** (1991) 309.
[68] T. uczak, M. Betowska-Brzezinska and R. Holze, *J. Appl. Electrochem.* **3** (1993) 1039.
[69] R. Holze, M. Betowska-Brzezinska and T. uczak, Proceedings of the 44th Meeting of the International Society of Electrochemistry, Berlin (1993).
[70] R. Holze, T. uczak and M. Betowska-Brzezinska, *Electrochim. Acta* **39** (1994) 485.
[71] R. Holze, T. uczak and M. Betowska-Brzezinska, *ibid.* **39** (1994) 991.
[72] T. uczak, R. Holze and M. Betowska-Brzezinska, *Electroanalysis* **6** (1994) 773.
[73] A. Hilmi, E. M. Belgsir, J. M. Léger and C. Lamy, *J. Electroanal. Chem.* **380** (1995) 177.
[74] J. Lipkowski and L. Stolberg, in 'Adsorption of Molecules at Metal Electrodes' (edited by J. Lipkowski and P.N. Ross), VCH, New York (1992).
[75] A. Wieckowski, *J. Electrochem. Soc.* **122** (1975) 252.
[76] T. uczak, M. Betowska-Brzezinska and R. Holze, *Electrochim. Acta* **38** (1993) 717.
[77] S. Trasatti, *J. Electroanal. Chem.* **54** (1974) 19.
[78] M. Betowska-Brzezinska, E. Dutkiewicz and P. Skouda, *ibid.* **181** (1984) 235.
[79] R. Holze and M. Betowska-Brzezinska, *ibid.* **201** (1986) 387.
[80] J. Desilvestro and M. J. Weaver, *ibid.* **209** (1986) 377.
[81] L. D. Burke and B. H. Lee, *ibid.* **330** (1992) 637.
[82] L. D. Burke, *Electrochim. Acta* **39** (1994) 1841.
[83] L. D. Burke, D. T. Buckley and J. A. Morrissey, *Analyst* **119** (1994) 841.
[84] W. Hauffe and J. Heitbaum, *Electrochim. Acta* **23** (1978) 299.
[85] M. Betowska-Brzezinska, *ibid.* **24** (1979) 247.
[86] H. Baltruschat, N. A. Anastasijevic, M. Betowska-Brzezinska and G. Hambitzer, *Ber. Bunsenges. Phys. Chem.* **94** (1990) 996.
[87] R. Holze and W. Vielstich, *Electrochim. Acta* **29** (1984) 607.
[88] B. Beden, F. Kadirgan, A. Kahyaoglu and C. Lamy, *J. Electroanal. Chem.* **135** (1982) 329.
[89] J. Stelmach, R. Holze and M. Betowska-Brzezinska, *ibid.* **377** (1994) 241.
[90] K. Nishimura, K. Machida and M. Enyo, *ibid.* **251** (1988) 117.
[91] T. Iwasita, F. C. Nart and W. Vielstich, *Ber. Bunsenges. Phys. Chem.* **94** (1990) 1030.
[92] R. R. Adžić, D.N. Simić, D. M. Drazić and A. R. Despić, *J. Electroanal. Chem.* **65** (1975) 587.
[93] N. Furuya and S. Motoo, *ibid.* **98** (1979) 195.
[94] D. Pletcher and V. Solis, *ibid.* **131** (1982) 309.
[95] G. Kokkinidis and D. Jannakoudakis, *ibid.* **133** (1982) 307.
[96] *Idem, ibid.* **153** (1983) 185.
[97] F. Kadirgan, B. Beden and C. Lamy, *ibid.* **136** (1982) 119.
[98] S. Motoo and M. Shibata, *ibid.* **139** (1982) 119.
[99] E. P. M. Leiva and M. C. Giordano, *J. Electrochem. Soc.* **130** (1983) 1305.
[100] M. Shabrang, H. Mizote and S. Bruckenstein, *ibid.* **131** (1984) 306.
[101] T. Hartung, J. Willsau and J. Heitbaum, *J. Electroanal. Chem.* **205** (1986) 135.
[102] I. T. E. Fonseca, A. C. Morin and D. Pletcher, *ibid.* **218** (1987) 327.
[103] G. Kokkinidis and G. Papanastasiou, *ibid.* **221** (1987) 175.
[104] P. Ocon, B. Beden and C. Lamy, *Electrochim. Acta* **32** (1987) 1095.
[105] N. W. Smirnowa, O. A. Petrii and A. Grzejdziak, *J. Electroanal. Chem.* **251** (1988) 73.
[106] J. Clavilier, A. Fernandez-Vega, J. M. Feliu and A. Aldaz, *ibid.* **258** (1989) 89.
[107] A. Fernandez-Vega, J. M. Feliu, A. Aldaz and J. Clavilier, *ibid.* **305** (1991) 229.
[108] P. N. Ross, *Electrochim. Acta* **36** (1991) 2053.
[109] A. A. El-Shafei, H. M. Shabanah and M. N. H. Moussa, *J. Electroanal. Chim.* **362** (1993) 159.
[110] X.-D. Jiang, S.-C. Chang and M. J. Weaver, *J. Chem. Soc. Faraday Trans.* **89** (1993) 223.
[111] M. Betowska-Brzezinska and J. Stelmach, *Z. Phys. Chem.* **185** (1994) 91.
[112] M. J. Llorca, E. Herrero, J. M. Feliu and A. Aldaz, *J. Electroanal. Chem.* **373** (1994) 217.
[113] E. Herrero, M. J. Llorca, J. M. Feliu and A. Aldaz, *ibid.* **383** (1995) 145.
[114] R. R. Adžić, in 'Advances in Electrochemistry and Electrochemical Engineering', Vol. 13, (edited by M. Gerischer and C. W. Tobias) J. Wiley & Sons, New York, (1984), p 159.
[115] G. Kokkinidis, *J. Electroanal. Chem.* **201** (1986) 217.
[116] E. Pastor, S. Wasmus, T. Iwasita, M. C. Arévalo, S. González and A. J. Arvia, *ibid.* **371** (1994), 167.
[117] E. Pastor, S. González and A. J. Arvia, *ibid.* **395** (1995) 233.
[118] J. A. Caram and C. Gutiérrez, *ibid.* **323** (1992) 213.
[119] J. M. Pérez, E. Muňoz, E. Morallón, F. Cases, J. L. Vázquez and A. Aldaz, *ibid.* **368** (1994) 285.
[120] P. A. Christensen, A. Hamnett, J. Munk and G. L. Troughton, *ibid.* **370** (1994) 251.
[121] E. Morallón, A. Rodes, J. L. Vázquez and J. M. Pérez, *ibid.* **391** (1995) 149.
[122] M. A. Tadayoni and M. J. Weaver, *Langmuir* **2** (1986) 179.
[123] B. Westerhoff and R. Holze, *Ber. Bunsenges. Phys. Chem.* **97** (1993) 418.
[124] B. Bänsch, T. Hartung, H. Baltruschat and J. Heitbaum, *J. Electroanal. Chem.* **259** (1989) 207.
[125] N. A. Anastasijević, H. Baltruschat and J. Heitbaum, *Electrochim. Acta* **38** (1993) 1067.
[126] T. Iwasita, F. C. Nart and W. Vielstich, *ibid.* 37 (1992) 2361.
[127] P. T. A. Sumodjo, E. J. da Silva and T. Rabockai, *J. Electroanal. Chem.* **271** (1989) 305.,
[128] S.-G. Sun and Y. Lin, *Electrochim. Acta* **41** (1996) 693.
[129] L. Pauling, 'Nature of the Chemical Bond', Cornell University Press, Ithaca, New York (1948).
[130] D. Takky, B. Beden, J. M. Léger and C. Lamy, *J. Electroanal. Chem.* **193** (1985) 159.
[131] *Idem, ibid.* **256** (1988) 127.
[132] J. Kaulen and H. J. Schäfer, *Electrochim. Acta* **38** (1982) 3299.
[133] T. uczak, M. Betowska-Brzezinska and R. Holze, *Electroanalysis* **7** (1995) 251
[134] O. Enea and J. P. Ango, *Electrochim. Acta* **34** (1989) 391.
[135] A. C. Chialvo, W. E. Triaca and A. J. Arvia, *J. Electroanal. Chem.* **171** (1984) 303.
[136] E. Pastor, V. M. Schmidt, T. Iwasita, M. C. Arévalo, S. González and A. J. Arvia, *Electrochim. Acta* **38** (1993) 1337.
[137] F. Hahn, B. Beden, F. Kadirgan and C. Lamy, *J. Electroanal. Chem.* **216** (1987) 169.
[138] H. Cnobloch, D. Gröppel, H. Kohlmüller, D. Kühl and G. Siemsen, *J. Power Sources* **24** (1979) 389.
[139] E. M. Belgsir, E. Bouhier, H. Essis-Yei, K. B. Kokoh, B. Beden, H. Huser, J. M. Léger and C. Lamy, *Electrochim. Acta* **36** (1991) 1157.
[140] N. M. Marković, M. L. Avramov-Ivić, N. S. Marinković and R. R. Adžić, *J. Electroanal. Chem.* **312** (1991) 125.
[141] G. Horányi and G. Inzelt, *Acta Chim. Acad. Sci. Hung.* **100** (1979) 229.
[142] E. Santos and G. Giordano, *Electrochim. Acta* **30** (1985) 871.

[143] L.-W. H. Leung and M. J. Weaver, *J. Phys. Chem.* **92** (1988) 4019.
[144] J. M. Orts, A. Fernandez-Vega, J. M. Feliu and A. Aldaz, *J. Electroanal. Chem.* **290** (1990) 119.
[145] S.-G. Sun, A.-C. Chen, T.-S. Huang, J.-B. Li and Z.-W. Tian, *ibid.* **340** (1992) 213.
[146] H. Spengler and G. Grünberg, *DECHEMA-Monogr.* **38** (1960) 579.
[147] V. S. Bagotzky and Yu. B. Vassiliev, *Electrochim. Acta* **9** (1964) 869.
[148] G. Horányi, V. E. Kazarinov, Yu. B. Vassiliev and V. N. Andreev, *J. Electroanal. Chem.* **147** (1983) 263.
[149] P. A. Christensen and A. Hamnett, *ibid.* **260** (1989) 347.
[150] G. Pierre, A. Ziade and M. El Kordi, *Electrochim. Acta* **32** (1987) 601.
[151] B. Wieland, J. P. Lancaster, C. S. Hoaglund, P. Holota and W. J. Tornquist, *Langmuir* **12** (1996) 2594
[152] R. T. Morrison and R. N. Boyd, 'Organic Chemistry', PWN, Warszawa (1985).
[153] S. Letellier, J. C. Dufreuse and M. B. Fleury, *Electrochim. Acta* **25** (1980) 1043.
[154] R. Holze and G. Fischer, *DECHEMA-Monogr.* **117** (1989) 331.
[155] G. C. Bond, 'Catalysis by Metals', Academic Press, London, New York (1962).
[156] A. Hilmi, E. M. Belgsir, J. M. Léger and C. Lamy, *J. Electroanal. Chem.* **410** (1996) 101.
[157] A. Hilmi, M. Dupont, E. M. Belgsir, J. M. Léger and C. Lamy, *J. Electroanal. Chem.* **376** (1994) 161.
[158] A. Hilmi, E. M. Belgsir, J. M. Léger and C. Lamy, *ibid.* **382** (1995) 53.
[159] J. M. Léger, I. Fonesca, F. Bento and I. Lopes, *ibid.* **285** (1990) 125.
[160] J. M. Léger, F. Hahn, B. Beden, C. Lamy, I. Fonesca, M. F. Bento and M. I. S. Lopes, *ibid.* **356** (1993) 255.
[161] I. Fonesca, M. I. S. Lopes, J. L. Santos and L. Proença, *Electrochim. Acta* **40** (1995) 2701.
[162] M. Avramov-Ivić, J. M. Léger, B. Beden, F. Hahn and C. Lamy, *J. Electroanal. Chem.* **351** (1993) 285.
[163] E. M. Skou, *Electrochim. Acta* **22** (1977) 313
[164] S. Ernst, J. Heitbaum and C. H. Hamann, *Ber. Bunsenges. Phys. Chem.* **84** (1980) 50
[165] Yu. B. Vasiliev, O. A. Khazova and N. N. Nikolaeva, *J. Electroanal. Chem.* **196** (1985) 105,127.
[166] K. D. Popović, N. M. Marković, A. V. Tripković and R. R. Adžić, *ibid.* **165** (1986) 532.
[167] N. Xonoglou, I. Moumtzis and G. Kokkinidis, *ibid.* **237** (1987) 93.
[168] G. Kokkinidis, J. M. Léger and C. Lamy, *ibid.* **242** (1988) 221.
[169] L. H. Essis Yei, B. Beden and C. Lamy, *ibid.* **246** (1988) 349.
[170] I. T. Bae, X. Xing, C. C. Liu and E. Yeager , *ibid.* **284** (1990) 335.
[171] I. T. Bae, X. Xing, C. C. Liu and E. Yeager, *ibid.* **309** (1991) 131.
[172] K. D. Popović, A. V. Tripković and R. R. Adzić, *ibid.* **339** (1992) 227.
[173] C. P. Wilde and M. Zhang, *ibid.* **340** (1992) 241.
[174] B. Beden, F. Largeand, K. B. Kokoh and C. Lamy, *Electrochim. Acta* **41** (1996) 701.
[175] R. R. Adzić, M. W. Hsiao and E. B. Yeager, *J. Electroanal. Chem.* **260** (1989) 475.
[176] A. M. Castro Luna, M. F. L. de Mele and A. J. Arvia, *ibid.* **323** (1992) 149.
[177] L. D. Burke and G. T. Ryan, *Electrochim. Acta* **37** (1992) 1363.