

The electro-oxidation of the mixture of formaldehyde and 2-propanol on gold (100) and (111) single crystal planes in alkaline medium*

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The effect of formaldehyde on the oxidation of 2-propanol and *vice versa* on gold single crystal planes (100 and 111) was studied. An activating effect in the reaction of the simultaneous oxidation of 2-propanol and formaldehyde was obtained on a gold (100) plane. In the case of a gold (111) electrode, the activation effect was not obtained. It was concluded that the adsorption of formaldehyde on the electrode surface prevents the adsorption of poisoning species formed during the electro-oxidation of 2-propanol on the Au(100) plane, while this is not the case on the Au(111) plane. The different behaviour is caused by the difference in the symmetry of the surface atoms of these two Au single-crystal planes.

Keywords: electro-oxidation, synergistic effect, 2-propanol, formaldehyde, gold single crystal planes.

INTRODUCTION

The electro-oxidation of small organic molecules such as methanol, 2-propanol, formaldehyde, formic acid *etc.*, has been investigated from the point of view of electrocatalysis, as well as of electrosynthesis.^{1,2} A general problem in the electro-oxidation of these kinds of molecules is the progressive decrease of the current density at a given potential and temperature which occurs with time.³ The formation and build up of adsorbed intermediates or reaction products, which inhibits the main reaction sequence, causes these effects.³ Periodic activation of the electrode, for example by potential pulsing to the value of surface oxide formation, regenerates the electrode activity.³

Activating effects during the electro-oxidation of formic acid have been produced by acetonitrile,³ nitromethane,⁴ as well as by foreign metal adatoms such as Hg, Pb, Cd, Tl, Bi

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and Cu.⁵ The influence of these substances on the electro-oxidation of formic acid was explained by the prevention of the formation of strongly bound intermediates (and/or products) or through some kind of specific interaction between these species and the electrode surface.⁴ An activating effect of formaldehyde in the oxidation of 2-propanol has been observed on a gold polycrystalline electrode in alkaline medium.⁶

The aim of this study was to investigate the effect of formaldehyde during the electro-oxidation of 2-propanol and *vice versa* on gold (100) and (111) single crystal planes. These two planes were chosen since the Au(111) plane is the most active plane in the electro-oxidation of 2-propanol, while the Au(100) plane behaves in a similar manner as polycrystalline gold towards this reaction.⁶ The behaviour of the Au(100) and Au(110) planes in the electro-oxidation of 2-propanol is also similar.⁶ Considering the electro-oxidation of formaldehyde on Au(*hkl*), it was shown that this reaction is not structurally sensitive.⁷

EXPERIMENTAL

The experiments were performed in a standard three-electrode cell at room temperature. The working electrodes were gold (100) and (111) single crystal planes in the form of rotating disc electrodes. They were supplied by Metal Crystals, Cambridge. The gold single crystal electrodes were polished mechanically and electrolytically according to a procedure described elsewhere.⁸ *In situ* identification of the electrode surface was performed using cyclic voltammetry. Stable and reproducible typical voltammograms of Au(*hkl*) planes were an indication of the solution cleanliness and good quality of the electrodes. The counter electrode was a Pt wire and the reference electrode was a saturated calomel electrode (SCE). The electronic circuit consisted of a RDE-4 Pine Instr. Co. bipotentiostat and a Philips PM 8134 X-Y recorder.

The chemicals were p.a. quality and the water was supplied by a Milipore system (18 MΩ cm). The supporting electrolyte was 0.1 M NaOH. Besides the commercially available formaldehyde solution, which contains methanol as a stabilizer, pure formaldehyde obtained by refluxing *para*-formaldehyde was used.⁷ Refluxing process brings the content of polymeric formaldehyde forms to very small value.⁹ The refluxed formaldehyde in the text is denoted as formaldehyde (FA), while methanol containing formaldehyde as formaldehyde stabilized with methanol (FAM). The concentration of formaldehyde solution was determined using UV-spectroscopy.¹⁰

RESULTS AND DISCUSSION

The polarization curves for the oxidation of 2-propanol (IP) and formaldehyde, as well as the oxidation curve of 2-propanol/formaldehyde mixture on a Au (100) plane are shown in Fig. 1. There are two well defined anodic waves in the oxidation of formaldehyde, as well as mixture of formaldehyde and 2-propanol. At the sweep rate of 50 mV s⁻¹, under the same experimental condition, in the reaction of formaldehyde oxidation only one wave was obtained, with typical Levich dependence of limiting current density from the square root of rotation speed.¹¹ Within the potential region of the first wave H₂ evolution was observed.^{11,12} Experiment with hydrogen present in pure electrolyte did not exhibit any apparent electrochemical activity on gold electrode under the same experimental condition.¹¹ As can be seen from Fig. 1, over the whole potential range the total currents of 2-propanol and formaldehyde oxidation exceeded the algebraic sum of the separate currents and to a great extent at potentials more positive than

0.4 V *vs.* SCE. This implies a synergistic effect. Synergistic effect could be the consequence of the catalysis of the electro-oxidation of 2-propanol by formaldehyde or, *vice versa*, of the catalysis of the electro-oxidation of formaldehyde by 2-propanol.

It is known that the formation and build up of strongly bound intermediates or reaction products may produce a self-poisoning effect during the electro-oxidation of some small organic molecules.³ In the literature, CO type species, which could be the intermediates or products of a reaction sequence, are usually claimed to be poisons.¹³

EMIR spectroscopy results have been shown that refluxed formaldehyde (electroactive gem-diol) adsorbs on polycrystalline gold electrode in 0.1 M NaOH and undergoes electro-oxidation without strongly bound intermediates or products, but on polycrystalline platinum, however, the existence of strongly bound CO species have been proved.¹⁵

The surface symmetry of the Au(*hkl*) causes different electrocatalytic behaviour in the electro-oxidation of 2-propanol.⁶ So, the distance between neighbouring atoms of Au(100) plane is suitable for the adsorption of intermediates and/or products of 2-propanol oxidation and this adsorption takes place. The result is the effect of self-poisoning, which has been discussed in an earlier paper.⁶ On the contrary, there is no adsorption of these species on Au(111) plane, which will be commented later. With the mixture of formaldehyde and 2-propanol one can assume that adsorbed formaldehyde may prevent the adsorption of intermediates and products of the electro-oxidation of 2-propanol, which means that formaldehyde prevents the adsorption of poisons in this reaction and synergistic effect can be tentatively explained.

Tafel plots for the oxidation of 2-propanol, formaldehyde and their mixture obtained from the polarization curves shown in Fig. 1, are presented in Fig. 2. The Tafel dependencies for the oxidation of formaldehyde and the mixture of formaldehyde and 2-propanol coincide in the potential range from -0.8 to -0.6 V *vs.* SCE. In this potential range there is no oxidation of 2-propanol, which was also obvious from Fig. 2. The Tafel slope in this potential range is approximately 120 mV dec^{-1} and is related to formaldehyde oxidation. Differential capacitance measurements on a polycrystalline gold electrode under similar experimental conditions (supporting electrolyte 0.5 M NaOH, 2-propanol concentration 0.1 M, sweep rate 100 mV s^{-1}) showed that there was no adsorption of 2-propanol in this potential range.¹⁶ According to literature data, the rate-determining step in the electro-oxidation of formaldehyde is the heterogeneous dehydrogenation of the gem-diol.¹² It could be concluded that in this potential range 2-propanol does not undergo electro-oxidation nor does it affect the mechanism of formaldehyde electro-oxidation.

In the potential range from -0.6 to -0.1 V *vs.* SCE the slope increases, which indicates some kind of limiting current. Similar results have been obtained by other authors.¹²

In the reaction of simultaneous oxidation of 2-propanol and formaldehyde stabilized with methanol on the Au(100) plane, Fig. 3, there is no activating effect. The effect is in fact inhibitive. In this case the solution contains three kinds of electroactive spe-

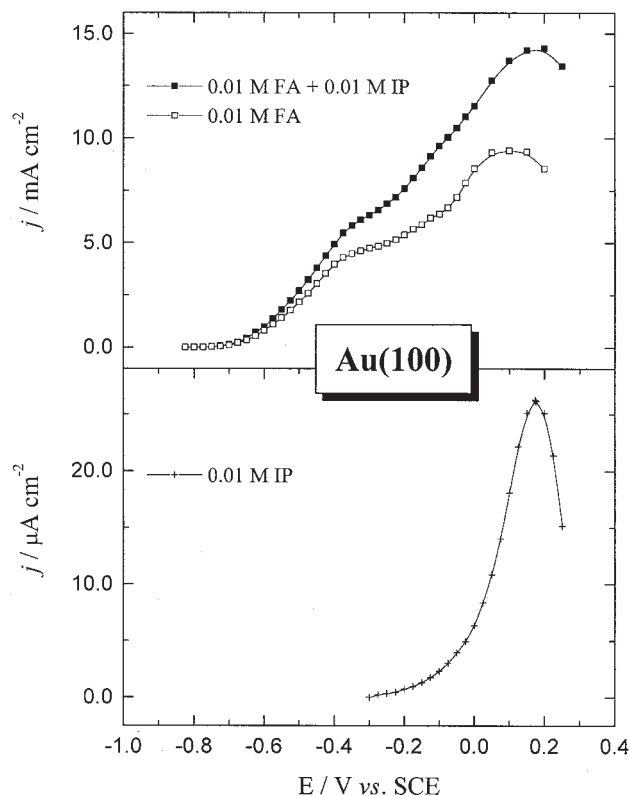


Fig. 1. Polarization curves for the oxidation of 2-propanol (IP), formaldehyde (FA) and an IP-FA mixture on the Au (100) plane in 0.1 M NaOH. Sweep rate 1 mV s^{-1} ; rotation rate 900 rpm.

cies, formaldehyde, 2-propanol and methanol. All of these species could be adsorbed and react on the electrode. The electroactivity of methanol on Au(100) plane in this potential range is negligible and this molecule only undergoes adsorption processes.¹⁷ Since the interaction of formaldehyde with the electrode surface is rather weak,⁷ and the steric effect is more pronounced in the case of 2-propanol as compared to methanol (2-propanol is a secondary while methanol is a primary alcohol), one assumption is that in a competitive adsorption methanol is adsorbed to the highest degree. Consequently, the molecules of methanol minimize the effect of formaldehyde on the reaction of 2-propanol electro-oxidation, but they themselves act as inhibitors.

The polarization curves for the oxidation of formaldehyde, 2-propanol and a mixture of 2-propanol and formaldehyde on a Au(111) plane are shown in Fig. 4. Over the whole potential range the oxidation current for the mixture of formaldehyde and 2-propanol is smaller than the current of formaldehyde itself, which implies an inhibition effect.

The surface of the Au(111) plane is characterized by three-fold symmetry of the surface atoms. Energetically and sterically, the most suitable sites for adsorption are those between the three neighboring atoms. It is known that OH^- adsorption proceeds

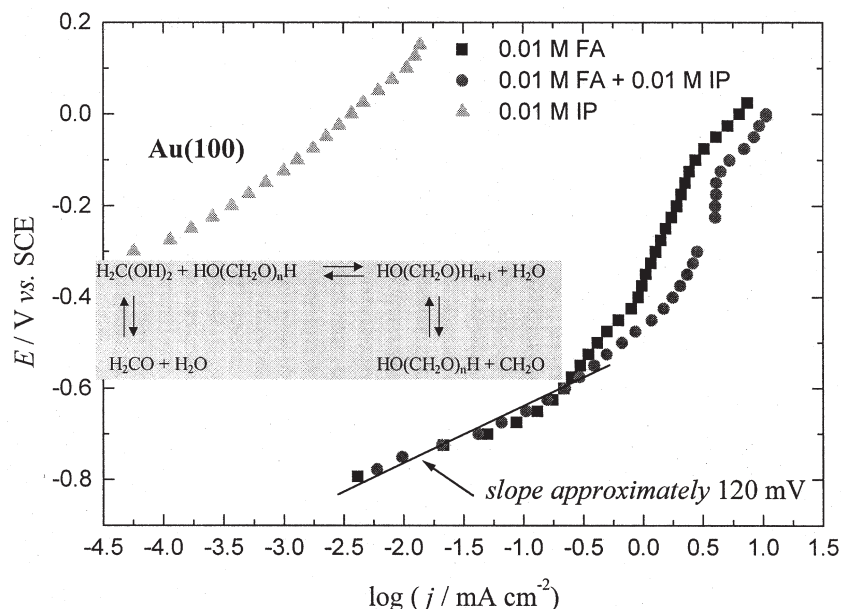


Fig. 2. Tafel plots for the electro-oxidation of 2-propanol (IP), formaldehyde (FA), and a formaldehyde – 2-propanol mixture on the Au (100) plane in 0.1 M NaOH. Inset: Equilibriums of the different formaldehyde forms.⁹

with the lowest coverage on the Au(111) plane, compared to the Au(100) and Au(110) planes.¹⁸ All the possible intermediates and/or products formed during the oxidation of 2-propanol, taking into account CO as the most simple one, are of a much larger radius than OH^- and, consequently, have a low tendency to be adsorbed on the gold(111) plane. As it is already mentioned, formaldehyde does not form strongly bound intermediates during oxidation on gold in alkaline medium.¹⁵ It can be supposed that, if there is no poisoning species from 2-propanol electro-oxidation, then there would be no activating effect of formaldehyde, while 2-propanol oxidation currents itself, are larger than obtained on the Au(100) plane. It is known that the surface of Au(111) has the strongest affinity towards large hydrated anions, such as ClO_4^- and SO_4^{2-} , compared to other planes.¹⁹ This is related to the matching symmetry of the tetrahedral ions with the trigonal symmetry of the Au(111) plane. It can be assumed that in the case of the Au(111) plane, the symmetry of the surface lattice has a stronger effect on the adsorption of formaldehyde polymers as compared to the behaviour of the Au(100) plane. The oxidation currents for formaldehyde oxidation on the Au(100) plane are larger than on the Au(111) plane over the whole potential range which is obvious from Figs. 1 and 4. At the moment this result cannot be explained.

In the reaction of simultaneous oxidation of 2-propanol and formaldehyde stabilized with methanol on the Au(111) plane (not shown) practically neither an activating nor an inhibiting effect was observed. This is to be expected since the 2-propanol does not form strongly bound intermediates on this plane, as well as formaldehyde itself.

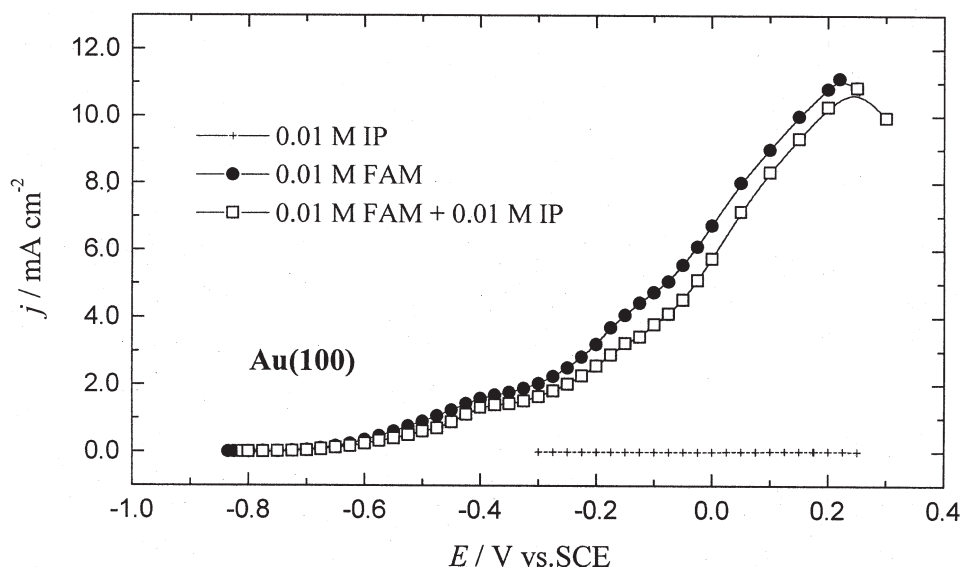


Fig. 3. Polarization curves for the oxidation of 2-propanol (IP), formaldehyde stabilized with methanol (FAM) and an IP-FAM mixture of the Au (100) plane in 0.1 M NaOH. Sweep rate 1 mV s^{-1} ; rotation rate 900 rpm.

This understanding of the synergistic effect in the investigated system is based on the assumption that adsorbed formaldehyde prevents the accumulation of the poison in the electro-oxidation of 2-propanol. However, the reverse situation, *i.e.*, the activating effect of 2-propanol in the reaction of formaldehyde oxidation on the Au(100) plane, could be considered. As can be seen from Fig. 2, at a potential value of -0.35 V vs. SCE , the synergistic effect is approximately half the order of magnitude, but it may be also seen that total oxidation currents of the mixture of 2-propanol and formaldehyde are about four orders of magnitude larger than the currents of 2-propanol. The synergistic effect mostly coincides with the limiting current, while there is no effect in the lower potential region (from -0.8 to -0.6 V vs. SCE). To support the opinion that this reverse situation occurs, it is assumed that 2-propanol decreases the influence of the polymerized forms of formaldehyde. Then, the real surface area would be larger and, consequently, the current would increase.

CONCLUSIONS

In conclusion it can be said that a synergistic effect is obtained in the simultaneous oxidation of formaldehyde and 2-propanol on the Au(100) plane. An inhibition effect is obtained on the Au(111) plane in the same reaction. In the reaction of the simultaneous oxidation of 2-propanol and formaldehyde stabilized with methanol a small inhibition effect is obtained on the Au(100) plane, while there was neither an activation nor inhibition effect on the Au(111) plane. It can be supposed that the influence of form-

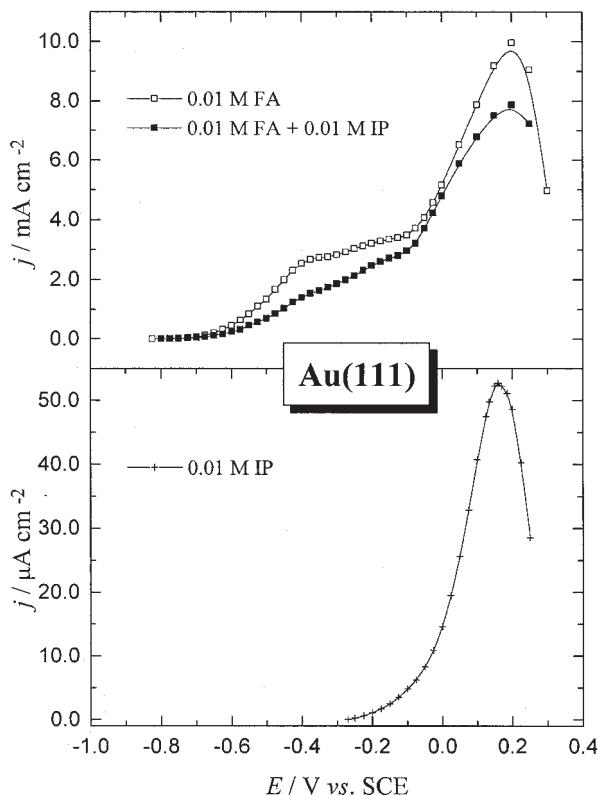


Fig. 4. Polarization curves for the oxidation of 2-propanol (IP), formaldehyde (FA) and IP-FA on the Au (111) plane in 0.1 M NaOH. Sweep rate 1 mV s^{-1} ; rotation rate 900 rpm.

aldehyde in the suppressing of the adsorption of poisoning species in the electro-oxidation of 2-propanol is predominant on the Au(100) plane, which causes the synergistic effect. On the Au(111) plane, since the 2-propanol does not form strongly bound intermediates, as well as formaldehyde, neither an inhibition nor synergistic effect is to be expected. An inhibition effect is obtained in the simultaneous oxidation of formaldehyde and 2-propanol. If the synergistic effect is attributed to the influence of 2-propanol on the electro-oxidation of formaldehyde, the explanation would be in the decreasing of the effects of polymerized forms of formaldehyde, which themselves decrease effective electrode surface.

ИЗВОД

ЕЛЕКТРООКСИДАЦИЈА СМЕШЕ ФОРМАЛДЕХИДА И 2-ПРОПАНОЛА НА
МОНОКРИСТАЛИМА ЗЛАТА ОРИЈЕНТАЦИЈЕ (100) И (111) У АЛКАЛНОЈ СРЕДИНИТАЊА Р. ВИДАКОВИЋ,¹ МИЛКА Л. АВРАМОВ-ИВИЋ² и БРАНИСЛАВ Ж. НИКОЛИЋ¹¹Технолошко-металуришки факултет, Универзитет у Београду, Карнегијева 4, б. бр. 35-03, 11120 Београд и²ИХТМ - Центар за електрохемију, Њевошева 12, б. бр. 815, Београд

Испитиван је утицај формалдехида на оксидацију 2-пропанола и *vice versa* на монокристалима злата оријентација (100) и (111). У реакцији симултане оксидације 2-пропанола и формалдехида на монокристалу злата оријентације (100) добијен је активациони ефекат. Овај ефекат није добијен на електроди од злата оријентације (111). Закључено је да присуство адсорбованог формалдехида онемогућава адсорпцију чврсто везаних интермедијера формираних током електрооксидације 2-пропанола, који се понашају као отрови за електроду, на равни (100). Ово није случај на равни (111). Различито понашање је узроковано разликама у симетрији и енергијама површинских атома на ове две монокристалне равни.

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