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Electrocatalytic Properties of Au(h k l) Electrodes Towards Oxidation of Ethanol in Alkaline Media

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In alkaline media, the mechanism of the oxidation of ethanol on gold single crystal electrodes was investigated over a range of OH^- and ethanol concentrations using cyclic voltammetry. The influence of crystallographic orientation and the role of OH^- on the oxidation of ethanol were suggested. The electrocatalytic activity for ethanol oxidation was increased with increasing OH^- concentration in the solution and/or higher OH^- coverage on the electrode surface. The kinetic parameters such as Tafel slope and reaction orders in respect to OH^- and ethanol were determined. Two Tafel slopes were observed during ethanol oxidation on gold in alkaline media. At low potentials, the Tafel slope was found to be close to 120 mV dec^{-1}, whereas the high Tafel slope over 300 mV dec^{-1} at high potentials, indicating the increasing the surface oxide coverage on the gold electrodes. The reaction orders with respect to OH^- was found to be potential-dependent and involved in the rate determining step.

Keywords: Ethanol electrooxidation; Gold single crystal electrode; Alkaline media; Electrocatalysis

1. INTRODUCTION

The electrocatalytic activity of gold towards oxidation of several organic compounds such as monohydric alcohols [1-7], polyhydric alcohols [8-10], unsaturated aliphatic alcohol [11] and mesoxoalate [12] has been studied in alkaline media. In previous studies from Beltowska-Brzezinska et al. [13-16] it has been shown, first, that the cleavage of the α-C-H bond in the monohydric alcohols, which is facilitated by the adsorbed OH^- ions on the gold surface in alkaline media, is the rate determining step in the oxidation process. Therefore, the OH^- anion adsorption on the gold in alkaline media plays a governing role in the reaction mechanism. Based upon adsorption data for OH^- [5], Ocon et al. suggested the oxidation of n-propanol on gold in alkaline media starts at the potentials where sufficient OH coverage present on the surface. Moreover, they supposed the reaction takes place on the Au-OH coverage via hydrogen bond between O-H group of the alcohol and Au-OH.

Especially in alkaline media, gold is very favourable without being poisoned by the strong adsorbed intermediate species on its surface. Therefore, the effect of the crystallographic orientation of gold is also of particular interest for the adsorption and oxidation of organic molecules. However, only a few studies of the oxidation of ethanol on gold electrodes in alkaline media have been reported [17-21]. Lai et al. [19] suggested that the activity of polycrystalline gold electrode for ethanol oxidation depends strongly on the pH of the electrolyte, showing an increase with pH higher than 10. Recently, Kwon et al. [20] reported that the solution OH^- promotes the initial deprotonation of the alcohol in alkaline media. In our recent study [21], we found that the reaction product of ethanol oxidation on gold can be considered as independent from the electrode's orientation and is essentially defined by the changing local pH on the surface. Thus, the role of solution OH^- on the ethanol oxidation can be especially important at high potentials. To date, however, there has been no systematic study available on the reaction mechanism of ethanol oxidation using different crystallographic orientation of gold electrodes based on the function of pH and ethanol concentration in the solution.

In this work, the oxidation of ethanol was investigated in alkaline medium on Au(h k l) single crystal electrodes. The influence of surface orientation on the adsorption and oxidation of ethanol was studied and its role in the reaction mechanism was discussed. In order to have more information about the mechanism of ethanol oxidation on gold in alkaline media, the effects of ethanol concentration as well as OH^- ion concentration were examined. Based on the obtained experimental data, the kinetic parameters were defined and the mechanism of the ethanol oxidation reaction was proposed.

2. EXPERIMENTAL

The electrochemical experiments were carried out at room temperature using a conventional standard three-electrode electrochemical cell. The electrode potential was controlled at 0 V using an EG&G PARC 175 signal generator in combination with an eDAQ EA161 potentiostat and currents were recorded using an eDAQ e-corder ED401 recording system. Cyclic voltammetry was employed as the experimental method and curves were recorded in the range of sweep rates from 5 to 50 mV s^{-1}. Au(1 1 1), (1 0 0), (1 1 0) and (2 1 0) working electrodes with respective surface areas 3.91; 4.00; 3.85; 4.22 mm^2 were prepared by flame annealing method according to the procedure described previously for Pt beads [22, 23]. They were flame-annealed and quenched with a droplet of ultrapure water before transferring electrochemical cell. Reversible hydrogen electrode (RHE) and gold wire were used as a reference and counter electrodes, respectively. For the kinetic analysis, the reversible hydrogen potential value corrected with respect to the pH of the solution ($E_{RHE} = E_{SHE} + 0.059$ pH). Solutions were prepared with ultrapure water Purelab Ultra® (Elga Vivendi) and from NaOH pellets (Suprapur, Merck), $NaClO_4.H_2O$ (Aldrich, 99% pure) and ethanol. Solution was purged with argon (Air Liquide, N50) and during the experiment, a continuous flow of Argon atmosphere was maintained above the solution. Before addition of ethanol, cyclic voltammetry of the working electrode was done in alkaline solution to check the cleanliness of the solution and the good quality of the electrode surface.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammograms

The electrocatalytic activity of Au(h k l) electrodes for the ethanol oxidation was investigated in 1 M NaOH + 1 M EtOH and the result is given in Fig. 1. On Au(1 1 1) electrode, the oxidation of ethanol in alkaline media starts in a potential range corresponding to the electrode surface coverage by OH^- ions and is reached its maximum value of 24 mA cm^{-2} at ~1.1 V. During the cathodic sweep, electrode sites was significantly inhibited due to the present of surface oxidation until the reduction takes place, so that the oxidation of ethanol starts again, giving a peak current at ~1 V. There is a hysteresis between the anodic and cathodic sweep in the potential range of ethanol oxidation (Fig.1), therefore, it can be deduced that the presence of adsorbed species on the Au(h k l) surface effects on the ethanol oxidation reaction.

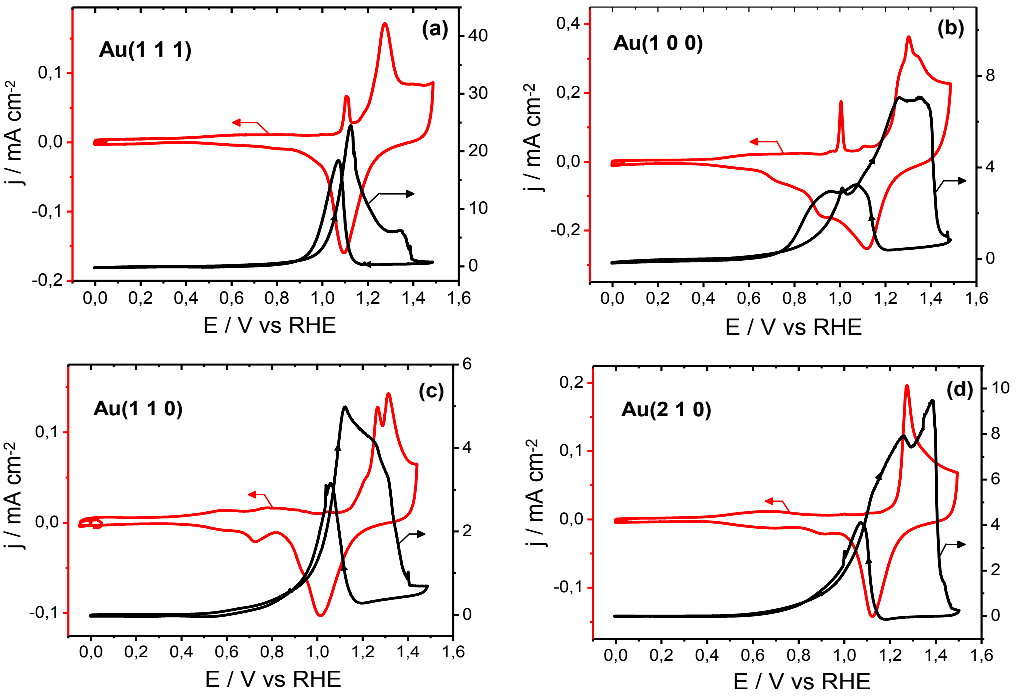

Figure 1. Cyclic voltammograms for the oxidation of 1M EtOH on (a) Au(1 1 1), (b) Au(1 0 0), (c) Au(1 1 0), (d) Au(2 1 0) surfaces in 1 M NaOH solutions. Dashed lines are the voltammetric curves in the absence of NaOH. Sweep rate: 50 mV s^{-1}.

3.2. Effect of the concentration of ethanol

The kinetics of the ethanol oxidation process at a Au(h k l) electrode for different ethanol concentrations (from 0.1 M to 1 M) in 1 M NaOH solution was investigated under the quasi-stationary conditions (υ = 5 mV s^{-1}) and the corresponding Tafel plots are shown in Figs. 2a, 2b, 2c and 2d. The double layer current is subtracted from the total current of the voltammogram, leaving only the contribution of adsorption and oxidation of ethanol.

Two Tafel slopes are observed. At low potential (E<-0.13 V vs. SHE), it is found to be 104-139 mV decade^{-1}, while at high potential (E>-0.13 V vs. SHE), the measured value is around 214-438 mV decade^{-1}. The transfer coefficient, αn, value is calculated from the (Eq. 1), which is found to be close to 0.5 at the low potential values (Table 1).

$$\frac{\partial log i}{\partial \log E} = \alpha \frac{nF}{2.303RT} \tag{1}$$

The reaction order for ethanol was determined from the slope of log j/log C_{EtOH} plot at fixed low potentials, as shown in Figs. 2e, 2f, 2g and 2h. The resulting order with respect to ethanol concentration is close to 1 for Au(1 1 1) and Au(2 1 0), whereas the reaction order is around 0.9 for Au(1 0 0) and Au(1 1 0) electrodes.

Table 1. Tafel slopes and corresponding transfer coefficients for the oxidation of ethanol on Au(h k l) electrodes at low potential (E<-0.13 V) and high potential (E>-0.13 V) in 1 M NaOH, υ = 5 mV s^{-1}.

	Au(1 1 1)				Au(2 1 0)				Au(1 0 0)				Au(1 1 0)			
[EtOH]/M	b_1	αn_1	b_2	αn_2	b_1	αn_1	b_2	αn_2	b_1	αn_1	b_2	αn_2	b_1	αn_1	b_2	αn_2
0.1	124	0.48	245	0.24	116	0.51	324	0.18	115	0.51	256	0.23	115	0.51	438	0.14
0.3	104	0.57	214	0.28	118	0.50	395	0.15	114	0.52	235	0.25	124	0.48	433	0.14
0.5	123	0.48	264	0.22	139	0.43	346	0.17	119	0.50	285	0.21	128	0.46	316	0.19
0.75	120	0.49	267	0.22	128	0.46	336	0.18	123	0.48	310	0.19	127	0.47	366	0.16
1	130	0.46	282	0.21	117	0.51	355	0.17	119	0.50	301	0.20	123	0.48	368	0.16

"b_1" corresponds to the tafel slope for the potential lower than -0.13 V vs. SHE, while the "b_2" refers to tafel slope for the potential higher than -0.13 V vs. SHE (See Figs. 2a, 2b, 2c and 2d). The values of αn_1 and αn_2 are estimated from the Eq. 1.

Fig. 3 shows the variation of peak current density with ethanol concentration. The reaction order deduced for ethanol is found to be 1 for Au(1 1 0) and Au(2 1 0), and 0.7 and 0.6 for Au(1 1 1) and Au(1 0 0), respectively. The change in the reaction orders (from 1 to 0.7 and 0.9 to 0.6) as well as the change in the Tafel slopes explains that the different reaction mechanism could occur in the different two potential regions (i.e, E<-0.13 and E>-0.13). In the high Tafel slope region, the adsorbed oxygenated species would be expected to be high, and thus, the dependence on the bulk concentration of ethanol becomes weaker.

The peak current density for the ethanol oxidation on Au(1 1 1) and Au(1 0 0) electrodes (Fig. 3) shows a gradual decrease that tends to plateau with increasing concentrations of ethanol (>0.75 M), which indicate that the change in the behaviour of the reaction from diffusion controlled to adsorption controlled due to the inhibiting effect of the adsorbed species on the surface and insufficient availability of OH^- in the solution. Therefore, it seems that the ethanol is adsorbed on the Au-OH_{ads} via the formation of hydrogen bridges between surface hydroxyl (OH_{ads}) species and the OH group of the alcohol, in a similar way to the previously suggested the mechanism on gold in alkaline media for the oxidation of n-propanol [5], methanol [1] and 1,3-propanediol [10].

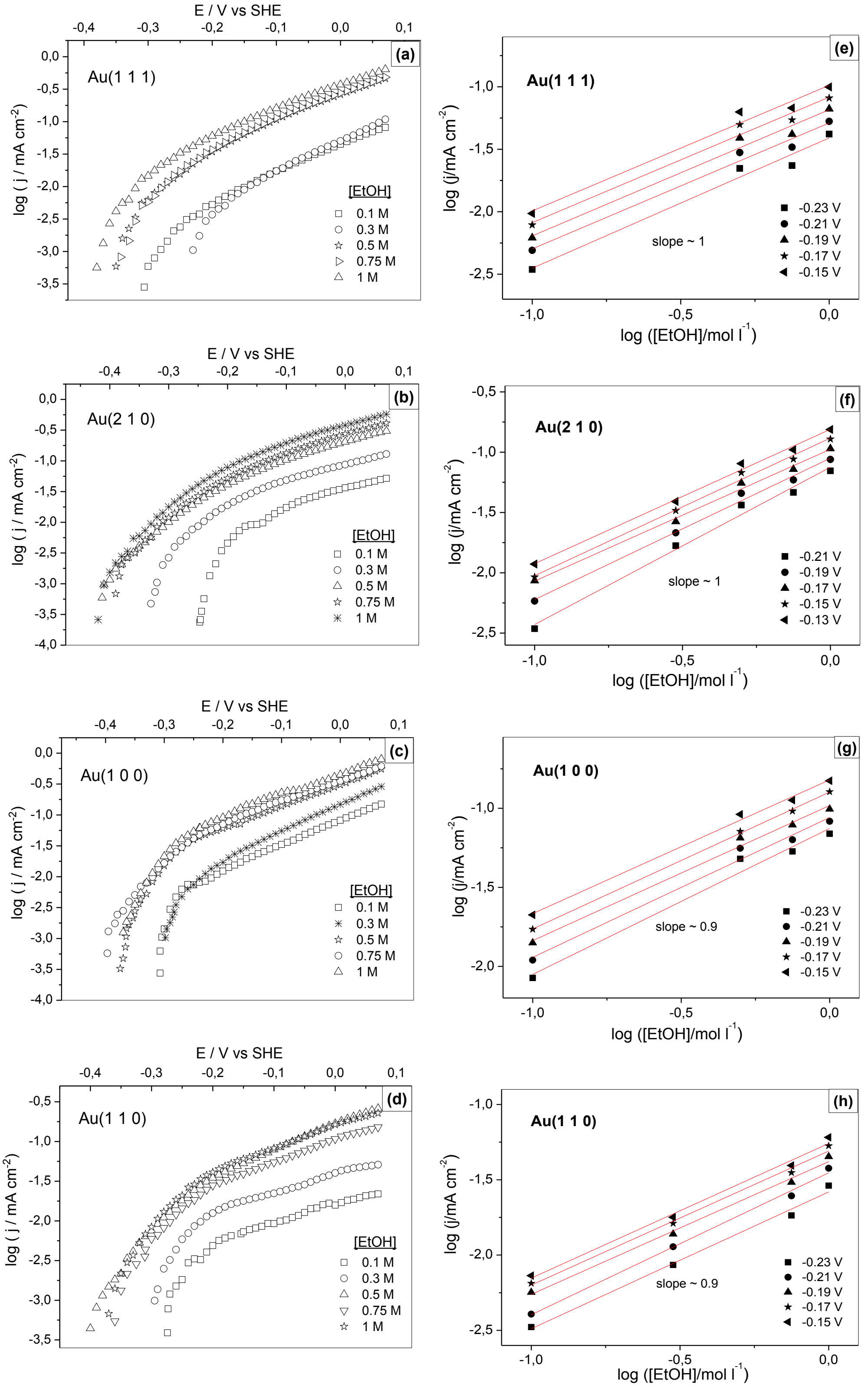

Figure 2. Tafel slopes of Au(1 1 1) (a), Au(2 1 0) (b), Au(1 0 0) (c), and Au(1 1 0) (d) electrodes for different ethanol$^-$ concentration. C_{NaOH} = 1 M, and reaction order plots (log j vs. log [OH$^-$]) of Au(1 1 1) (e), Au(2 1 0) (f), Au(1 0 0) (g) and Au(1 1 0) (h) electrodes at a given value of potential. Sweep rate: 5 mV s^{-1}.

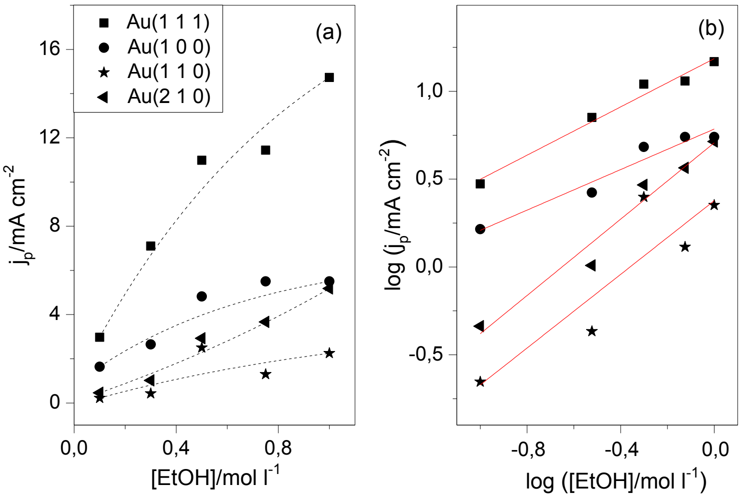

Figure 3. Plot of peak currents vs. ethanol concentration in 1 M NaOH solution (a), and corresponding fitted lines on the log-log scale (b). Sweep rate: 5 mV s^{-1}.

3.3. Effect of the concentration of OH^- ions

The effect of OH^- anions concentration (0.001 M - 1 M) was investigated at an ethanol concentration of 1 M and 0.1 M. In order to keep the ionic force constant, $NaClO_4$ was added. Figs. 4a, 4b and 4c give the Tafel slopes obtained for ethanol oxidation at different OH^- concentrations. The measured Tafel slopes and the corresponding transfer coefficient values as a function of the OH^- ions concentration are presented in the Table 2.

Table 2. Tafel slopes and corresponding transfer coefficient at low potential (E<-0.13 V) and high potential (E>-0.13 V) in 1 M EtOH for Au(1 1 1), Au(2 1 0) and in 0.1 M EtOH for Au(1 0 0), υ = 5 mV s^{-1}.

	Au(1 1 1)				Au(2 1 0)				Au(1 0 0)			
[OH] / M	b_1	αn_1	b_2	αn_2	b_1	αn_1	b_2	αn_2	b_1	αn_1	b_2	αn_2
0.001	297	0.20	308	0.19	316	0.19	251	0.23	565	0.10	444	0.13
0.005	-	-	-	-	-	-	-	-	-	-	500	0.12
0.01	158	0.37	224	0.26	139	0.42	256	0.23	-	-	459	0.13
0.05	100	0.59	265	0.22	100	0.59	287	0.21	549	0.11	293	0.20
0.1	122	0.48	263	0.22	91	0.65	307	0.19	310	0.19	324	0.18
0.5	130	0.45	274	0.22	146	0.40	318	0.19	-	-	-	-
1	168	0.35	290	0.20	171	0.35	366	0.16	-	-	-	-

"b_1" corresponds to the tafel slope for the potential lower than -0.13 V vs. SHE, while the "b_2" refers to tafel slope for the potential higher than -0.13 V vs. SHE (See Figs. 4a, 4b, 4c). The values of αn_1 and αn_2 are estimated from the Eq. 1.

The reaction order for the OH^- is deduced by the plots between log j vs. the log C_{OH} at a constant potential in Figs. 4d, 4e and 4f. From the analysis of the curves (Figs. 4a, 4b and 4c), two Tafel zones were obtained. The first zone is more cathodic potentials (E< -0.13 vs. SHE), and the second Tafel zone with the potentials from -0.13 to 0.13 V vs. SHE, which has a high slope values with the value of αn around 0.2 (Table 2). From the log j vs. log C_{OH-} plot (Figs. 4d, 4e and 4f), the reaction order with respect to OH^- concentration is obtained around 0.5 for Au(1 1 1) and Au(2 1 0), and around 0.2 for Au(1 0 0) in the potential range from -0.23 to -0.15V.

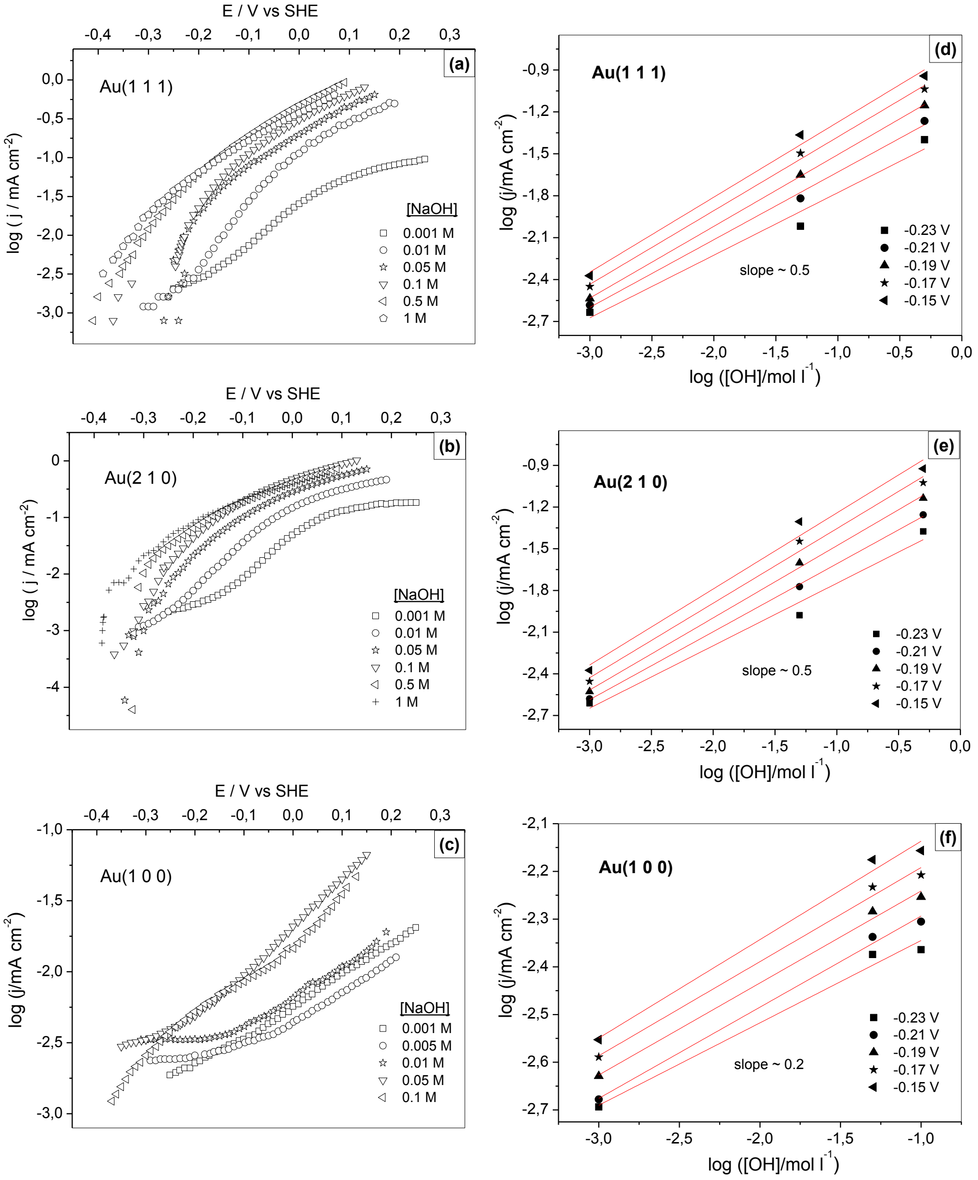

Figure 4. Tafel slopes of Au(1 1 1) (a), Au(2 1 0) (b), and Au(1 0 0) (c) electrodes for different OH^- concentration. $C_{EtOH} = 1$ M for (a) and (b), $C_{EtOH} = 0.1$ M for (c), and reaction order plots (log j vs. log $[OH^-]$) of Au(1 1 1) (d), Au(2 1 0) (e), and Au(1 0 0) (f) electrodes at a given value of potential. Sweep rate: 5 mV s^{-1}.

Fig. 5 shows the variation of the peak currents with different OH^- concentrations. At the peak current, the reaction order for OH^- is deduced around 0.2 for Au(1 0 0) and Au(2 1 0), and 0.4 for Au(1 1 1); however, there is no significant change in the reaction order for Au(1 1 1) electrode either in 0.1 M EtOH (Fig. 5b) or in 1 M EtOH solution (Fig. 5d). Noticeably, there is a decrease in the reaction order of OH^- from 0.5 to 0.2 with increasing electrode potential on Au(2 1 0). It seems that the enhanced surface defects on this electrode lead to the increase in the adsorption of OH^-, thus decreased in the influence of the bulk concentration of OH^-. The different reaction order at the peak current density was also observed with the methanol oxidation on Pt-Pd/C electrocatalyst in alkaline medium, suggesting that different reaction process occurs in two different potential regions [24]. In the case of Au(1 0 0), however, there is no change in the reaction order of OH^- with the increasing potential.

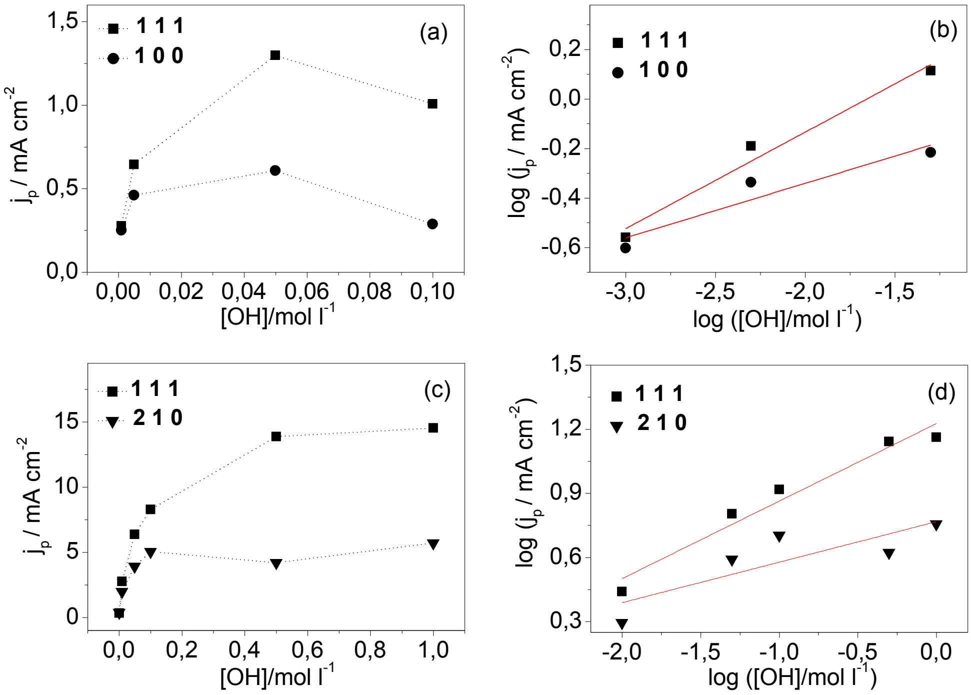

Figure 5. Plot of peak currents vs. OH^- concentration in 0.1 M EtOH (a) and 1 M EtOH solution (c) and, corresponding fitted lines on the log-log scale (b) and (d), respectively. Sweep rate: 5 mV s^{-1}.

It is well known that the adsorption of poisoning intermediates coming from the oxidation of ethanol leads to the deactivation of the electrode surface. Thus, the amount of the adsorbed poisoning species accumulated on the surface can be evaluated by the ratio of the forward anodic peak current density (I_f) to the reverse anodic peak current density (I_b), I_f/I_b. In this sense, the effect of the solution pH on the ratio of the forward anodic peak current density (I_f) to the reverse anodic peak current density (I_b) was investigated using ethanol concentration of 1 M (Fig. 6). The maximum I_f/I_b value of Au(2 1 0) is close to 2.5, higher than that of Au(1 1 1) at pH 12, and is decreased with increasing pH until 13, indicating that ethanol is more efficiently oxidized with little accumulation of carbonaceous residues on this surface. A similar trend is observed for Au(1 1 1), and the maximum I_f/I_b value is also achieved at pH 12. A remarkable phenomenon is that there is no change in the I_f/I_b value at the pH range between 13 and 14. The comparison of I_f/I_b value for Au(h k l) at the solution pH 14, which is also depicted in the inset of Fig. 6.

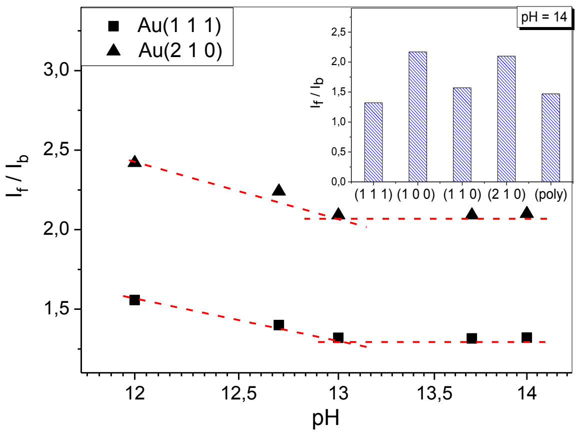

Figure 6. Effect of pH on the forward and backward peak current ratio (I_f/I_b) for the oxidation of 1 M EtOH on Au(1 1 1) and Au(2 1 0) electrodes, scan rate 50 mV s^{-1}. Inset is the comparison of the I_f/I_b value for the different Au(h k l) electrodes at pH 14.

On the basis of analyzing the kinetic parameters for the ethanol oxidation reaction in alkaline media, a possible surface adsorption-reaction mechanism on Au(h k l) would be as follows, where the oxidation of ethanol is controlled by diffusion and adsorption step takes part in the rate determining process (r.d.s.).

$$\mathrm{Au} + \mathrm{OH}^-_{\mathrm{sol}} \leftrightarrow \mathrm{Au(OH)}_{\mathrm{ads}} + \mathrm{e}^- \tag{1}$$

$$\mathrm{Au(OH)}_{\mathrm{ads}} + \mathrm{OH}^-_{\mathrm{sol}} \rightarrow \mathrm{AuO} + \mathrm{H_2O} + \mathrm{e}^- \tag{2}$$

$$\mathrm{Au(OH)}_{\mathrm{ads}} + \mathrm{CH_3CH_2OH} \xrightarrow{\mathrm{r.d.s.}} \mathrm{Au(CH_3CH_2O)}_{\mathrm{ads}} + \mathrm{H_2O} + \mathrm{e}^- \tag{3}$$

$$\mathrm{Au(CH_3CH_2O)}_{\mathrm{ads}} + \mathrm{OH}^-_{\mathrm{sol}} \rightarrow \mathrm{product} + \mathrm{H_2O} + \mathrm{e}^- \tag{4}$$

Supposing that the adsorbed OH on the surface and ethanol molecules present in the solution are involved in the rate determining step (Eq. 3), and in a subsequent step, the rapid reaction between adsorbed ethoxy species and the solution OH^- ions leads to the oxidation product (Eq. 4). Therefore, the rate of reaction (Eq. 3) could be expressed as:

$$r = k\,\theta_{\mathrm{OH}}[\mathrm{EtOH}]\exp(\alpha FE/RT) \tag{5}$$

where θ_{OH} is the surface coverage with adsorbed OH, [EtOH] is the concentration of ethanol in the solution, k is a rate constant, and α is the transfer coefficient.

The fractional surface concentration of OH^- can be related to the bulk concentration of OH^- using an adsorption isotherm in the simplest form:

$$\theta_{\mathrm{OH}}/(1-\theta_T) = K[\mathrm{OH}]^n \tag{6}$$

where K is the adsorption coefficient, θ_T is the surface coverage of all adsorbed species and n is the reaction order with respect to OH^-.

If Eq. (6) is substituted for Eq. (5) the reaction rate becomes as follows:

$$r = k\,K[\mathrm{OH}]^n[\mathrm{EtOH}](1-\theta_T)\exp(\alpha FE/RT) \tag{7}$$

4. CONCLUSION

In the present study, the mechanism of the ethanol oxidation reaction on Au(h k l) electrodes in alkaline media was studied using the cyclic voltammetry. The effect of some experimental parameters such as the ethanol and OH^- concentration in the solution was evaluated. At low potentials, the Tafel slope was around 120 mV dec^{-1}, whereas at high potentials the Tafel slopes increased over 300 mV dec^{-1} as the mechanism of the ethanol oxidation affected by the formation of surface oxides on the gold electrodes. The kinetics of the ethanol oxidation on Au(h k l) was determined by the OH^- surface coverage, which depends on the electrode potential.

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