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On mechanistic differences in methanol oxidation in basic medium induced by the activation of gold electrodes

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A comparative study of methanol oxidation on normal and polycrystalline gold electrodes activated by square wave potential sweep in a basic medium has been performed. The differences in kinetic parameters obtained can be attributed to changes in the bond energy of OH on both forms of gold, whereas the corresponding changes in intensity obtained are the consequence of the change in the surface area induced by the activation.

1. Introduction

The efficient conversion of the chemical energy contained in fuels into electrical energy by means of fuel cells is a much-studied topic in electrochemistry. In order to obtain the conversion of the chemical energy contained in methanol with a minimal entropy production, i.e. under application of a minimum overpotential, different electrocatalysts have been used [1–4].

The most studied catalyst has been platinum. As a metal with a relatively low percentage d-band character, platinum is a good catalyst for reaction mechanisms in which adsorption is a slow process [5]. Thus, it induces the dissociation of the H atom on the same carbon where the hydroxyl group is located. The energy necessary for the dissociation is compensated by the high adsorption energy of hydrogen atoms on the platinum surface.

Methanol also oxidizes on gold electrodes in a basic medium but oxidizes little in an acid medium on the same electrode, which is typical behaviour for alcohols on gold electrodes [6]. On the other hand, Arvia and co-workers [7] have reported the change in activity and 'electrocatalytical' properties of electrodes as a consequence of dissolution and recrystallization processes that take place after application of certain potential–time programmes.

A comparison between the results obtained for methanol oxidation on gold electrodes in a basic medium, with and without activation, has been reported in this paper. Both activated and unactivated gold electrodes do not show any oxidation of methanol in an acid medium throughout the potential range studied.

2. Experimental details

The working electrode consisted of a polycrystalline gold plate (of area 1 cm^2 and 99.999% pure grade). A gold wire (0.5 mm thick) rolled into a spiral was used as a counter electrode. The half cell $Hg–Hg_2SO_4–K_2SO_4$ (salt) was used as a reference electrode. A three-compartment thermostated electrochemical cell was used, in which the compartment separation was made by means of a G-3 glass frit. The reference electrode compartment was placed close to the working electrode surface (≈ 2 mm) by means of a Haber–Luggin capillary.

Solutions were prepared with doubly distilled water and Merck (p.a.) reagents ($HClO_4$, H_2SO_4, KOH, KF and CH_3OH). Temperature was maintained at 25.0 ± 0.2° C, except in the experiment for the determination of activation energy, where temperatures were measured with the same accuracy. Solutions were deaerated by means of N_2 stirring, and during the experiments

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a continuous flow of nitrogen was passed over the solution. The working electrode was treated before each experiment by dipping it in a hot 3 : 1 $HNO_3 : H_2O$ mixture and rinsing with distilled water.

The voltammetric response of the electrode in 1 M $HClO_4$ obtained after application of a repetitive triangular potential sweep at $v = 0.2\,V\,s^{-1}$ between oxygen and hydrogen evolution was taken as a standard, in order to be sure that an electrode of the same activity was always being used. In order to increase the activity of the working electrode, the following treatment was applied. The working electrode was electropolished by application of 50 Hz a.c. at 10–15 V in 8 M H_2SO_4. It was then repeatedly rinsed with distilled water and finally placed in a 1 M $HClO_4$ solution for 1 h.

In order to obtain electrode anodization, square wave potential sweep (SWPS) in 1 M $HClO_4$ solution was used. The potential was pulsed between a low value of $E_l = -0.045$ V (MSE) and an upper value of 2.056 V (MSE) $\leqslant E_u \leqslant$ 3.256 V (MSE) at a frequency of 4 kHz for a period of 3 min. The low and upper potentials were maintained for a time of $\tau_l = 0.1$ ms and $\tau_u = 0.15$ ms during each pulse. The value of E_u falls in a potential range in which a thick oxide layer is formed on the gold surface. The SWPS activation of the electrode was stopped at E_u and the gold oxide layer was eliminated by electroreduction induced by a cathodic potential sweep at $v = 0.01\,V\,s^{-1}$.

The change in activation of the electrode carried out by the SWPS method was attributed to an increase of the actual area of the electrode surface, and was determined as the ratio between the charge of electroreduction for gold oxides during the cathodic sweep in a voltammogram taken at $v = 0.2\,V\,s^{-1}$ after applying the SWPS treatment and the same charge obtained at the same sweep rate after a normal (repetitive triangular potential sweep) RTPS treatment.

The potential was controlled by means of a Brucker Mod. 310 potentiostat (with a response time of 20 μs and an accuracy of 0.1%). A PAR Mod. 175 function generator was used for this work.

3. Results

3.1. *Unactivated gold electrodes*

Fig. 1 shows a typical voltammogram for the

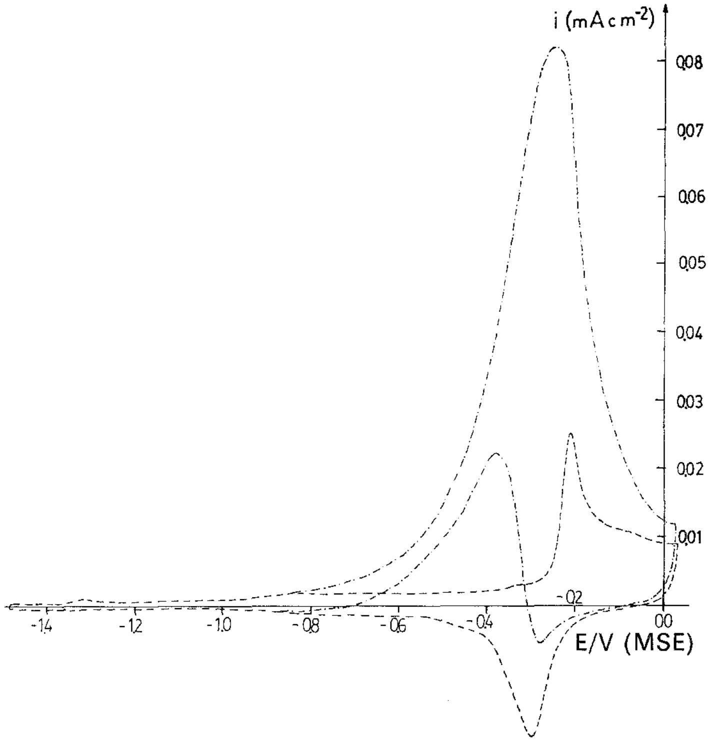

Fig. 1. Plot of i (mA cm^{-2}) versus E (V versus MSE) for 0.5 M methanol in 1 M KOH, $v = 5\,mV\,s^{-1}$. The dashed curve represents the voltammogram of gold in 1 M KOH in the absence of methanol for an unactivated electrode; $T = 25$°C.

oxidation of methanol on an unactivated standard polycrystalline gold electrode in a basic medium. It can be seen that oxidation starts at potential values where the gold electrode in a basic medium is partially covered with OH^- ions. The peak maximum appears at $E_P = -0.25$ V (MSE) and this value does not change with the methanol concentration (in the range 0.1 to 2 M). The current diminishes rapidly with increasing potential value since in this potential range the oxide layer starts to form. I_P increases proportionally with methanol concentration (adsorption should not be the determining step in the mechanism), and grows with the pH value. A growing pH value gives rise to a more cathodic E_P. For high methanol concentrations (from 1.25 M at 2 M), a potential sweep made at $v = 5\,\mathrm{mV\,s^{-1}}$ does not give rise to any reduction peak during the cathodic scan, due to the direct reduction of the oxide layer by the organic substance. When the concentration of methanol decreases and the sweep rate increases, a cathodic peak appears corresponding to the electrochemical reduction of the gold oxides. During the cathodic sweep, after oxide reduction, an anodic peak is recorded, appearing at the same potential range at which the peak for methanol oxidation in the anodic scan appears. E_P for this anodic peak slightly shifts towards more cathodic potentials with decreasing methanol concentrations.

Fig. 2 shows the Tafel slopes obtained under quasi-stationary conditions (*I–E* curves recorded at $v = 5\,\mathrm{mV\,s^{-1}}$) for the oxidation of methanol at pH = 14, $T = 25°$ C and at various methanol concentrations. There is no significant change in the slope with methanol concentration and the average obtained is 271 mV per current decade, with an α_{an} value of 0.22.

Fig. 3 shows the plot of log i versus log C_{MeOH} with the potential as parameter. From the plot, a reaction order of 1 with respect to the methanol concentration is obtained. This value is independent of the potential in the range -0.35 to -0.65 V (MSE).

Fig. 4 shows the Tafel slopes as a function of pH recorded under similar conditions to the above for a methanol concentration of 0.5 M. The value of b is 271 mV per decade, and is constant over the pH range 10.5 to 14. Every current was obtained by subtracting the contribution of the double-layer current to the total value of i. From the log i versus log C_{OH^-} plot (Fig. 5) a reaction order of 0.5 with respect to OH^- concentration is deduced in the potential range -0.48 V to -0.3 V (MSE) and in the pH range 11.5 to 13.5. This reaction order is independent of the potential value in the pH range studied.

Fig. 6 shows log i versus T^{-1} (K^{-1}) plots at different potential values. The temperature range was 4 to 50° C. A potential-dependent activation energy value is deduced. A value of the apparent activation energy, $\Delta H^{\neq}$, extrapolated to the E_{zcp} of gold (taken as $E_{zcp} = -0.9$ V MSE) of $+80\,\mathrm{kJ\,mol^{-1}}$, is obtained. Likewise, from the intercept of the log i versus

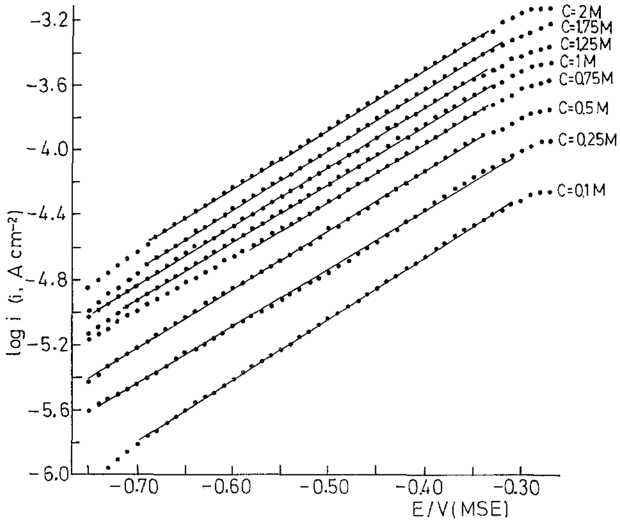

Fig. 2. Tafel slopes at different methanol concentrations in 1 M KOH for an unactivated electrode where $v = 5\,\mathrm{mV\,s^{-1}}$, $T = 25°$ C.

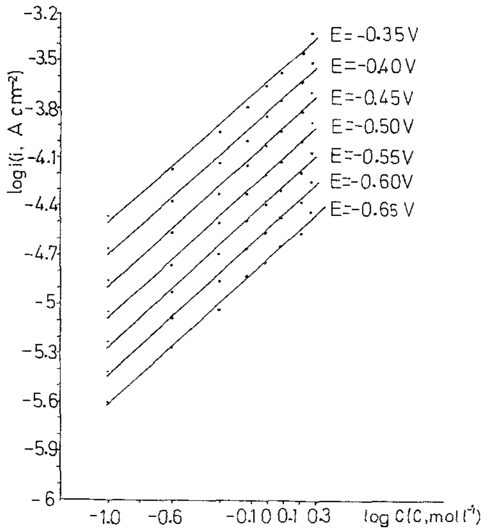

Fig. 3. Dependence of log i on C_{MeOH}, at constant potential, in 1 M KOH for an unactivated electrode.

T^{-1} curve, a value for $\Delta S^{\neq}$ of $-276\,J\,mol^{-1}\,K^{-1}$ is deduced. From the $\Delta H^{\neq} = f(E)$ and $\Delta S^{\neq} = f(E)$ plots (Figs 7, 8), a plot for $\Delta G^{\neq} = f(E)$ can be obtained (Fig. 9).

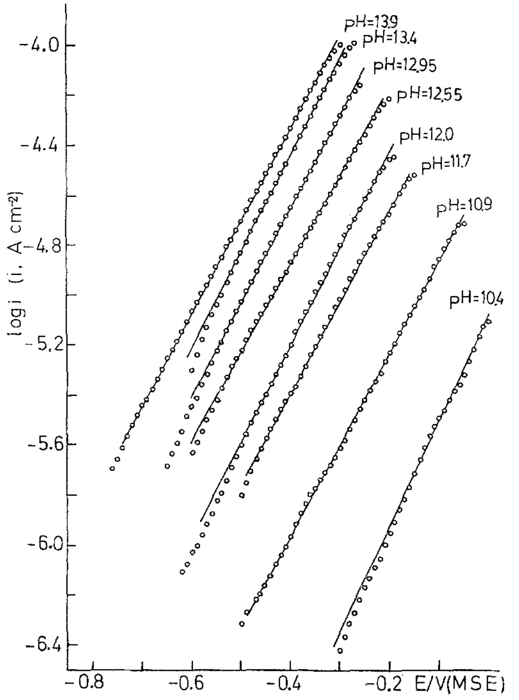

Fig. 4. Tafel slopes at different pH values for an unactivated electrode. $C_{MeOH} = 0.5\,M$; $v = 5\,mV\,s^{-1}$; $T = 25°C$.

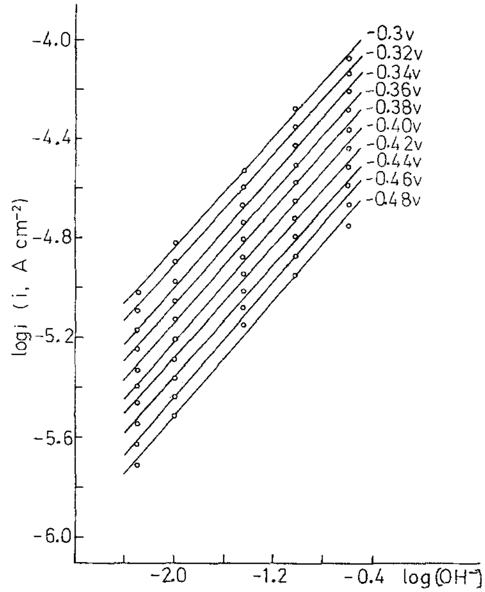

Fig. 5. Dependence of log i on C_{OH} at constant potential in $C_{MeOH} = 0.5\,M$ for an unactivated electrode where $v = 5\,mV\,s^{-1}$, $T = 25°C$.

3.2. *Activated electrodes*

After applying the SWPS treatment, an increase in the 'electrocatalytic' activity of the electrode was observed. When measured in acid solution, the activity of the electrode was 20 times that of the unactivated electrode. On introducing the electrode, activated as previously described, into a basic solution, a significant loss of activity was detected. An electrode initially 20 times more activated than an unactivated one, in an acid solution, resulted in a behaviour in basic solution as if it were only eight times more activated. The activity of the electrode is measured as a coefficient, R, which results from the relationship between the reduction charge for gold oxides taken from a voltammogram for an activated electrode in acid (or basic) medium (in absence of organic substance) and the reduction charge for gold oxides taken from a voltammogram for an unactivated electrode under the same conditions (acid or basic solution) (Fig. 10).

The form of the voltammogram for methanol oxidation on an activated gold electrode in a basic medium was very similar to that shown in Fig. 1, except that currents were around six times higher.

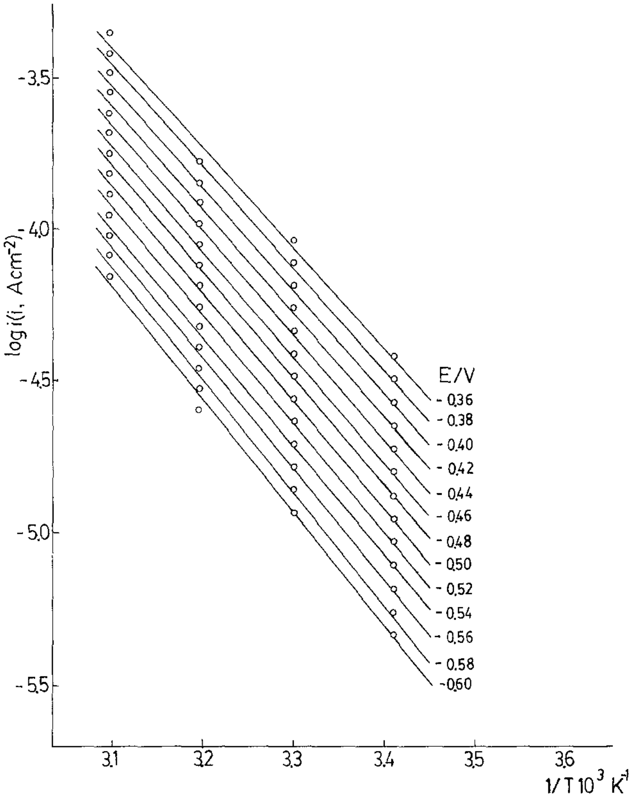

Fig. 6. Dependence of log i on $1/T$ at a constant potential. $C_{\mathrm{MeOH}} = 0.5\,\mathrm{M}$ in 1 M KOH; $v = 5\,\mathrm{mV\,s^{-1}}$.

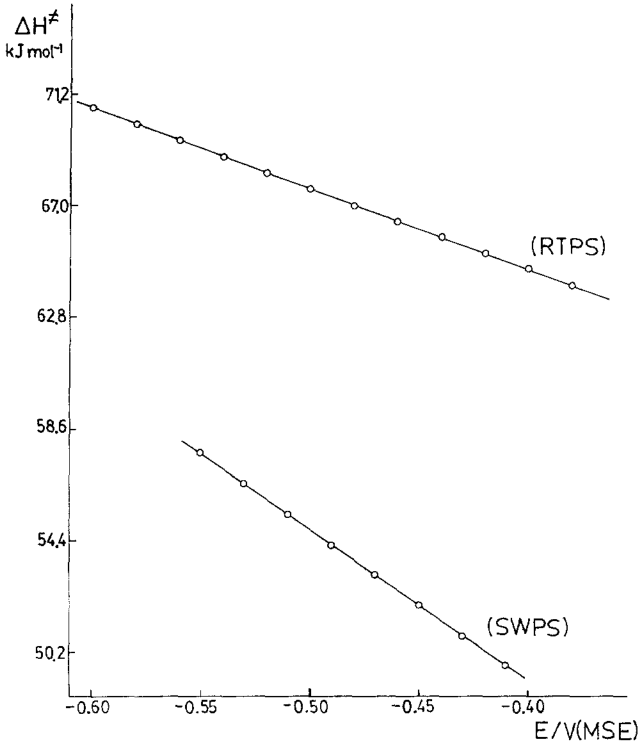

Fig. 7. Variation of ΔH with the potential for an unactivated electrode (RTPS) and for an activated electrode (SWPS).

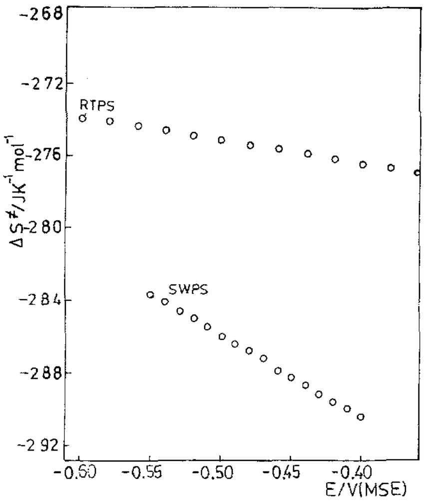

Fig. 8. Variation of ΔS with the potential for an unactivated electrode (RTPS) and for an activated electrode (SWPS).

The potential value at which the maximum current on an activated gold electrode is obtained is close to that for an unactivated electrode. The dependencies of i_P on methanol concentration and sweep rate are similar to those obtained for unactivated electrodes. Likewise, the changes in E_P, induced by changing methanol concentration, sweep rate and OH^- concentration, are similar to those described for an unactivated electrode for both anodic peaks (that obtained during the anodic scan and that recorded during the cathodic one).

The value deduced for the Tafel slopes in the case of an activated gold electrode at pH = 14, $T = 25°$ C and different methanol concentrations is 230 mV per current decade in the potential range -0.52 to -0.35 V (MSE). The reaction order with respect to methanol concentration was deduced to be 1 (for concentrations varying from 0.5 to 1.5 M). Likewise, a reaction order of 0.30 with respect to OH^- concentration was deduced. This value is almost constant in the pH range 11.5 to 13.5 and for potential values between -0.5 and -0.3 V (MSE). Likewise, a log $i = f(1/T)$ plot leads to a potential-dependent apparent activation energy. The $\Delta H^{\neq}$ value, measured at $E = -0.9$ V (MSE) is 77.5 kJ mol^{-1}, and at $E = -0.40$ V (MSE) is 49.3 kJ mol^{-1} (see Fig. 7). Values of $\Delta S^{\neq}$ and $\Delta G^{\neq}$ can also be obtained as previously explained, and Figs 8 and 9 show a plot of their variation with E.

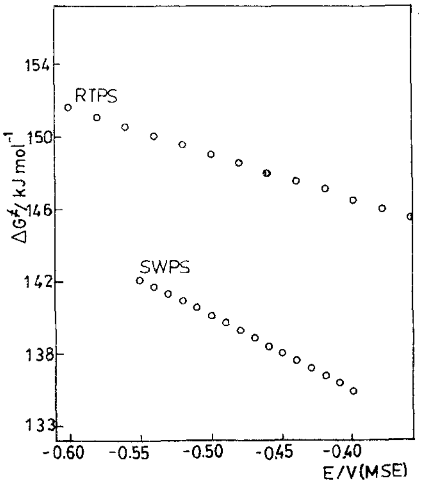

Fig. 9. Variation of ΔG with the potential for an unactivated electrode (RTPS) and for an activated electrode (SWPS).

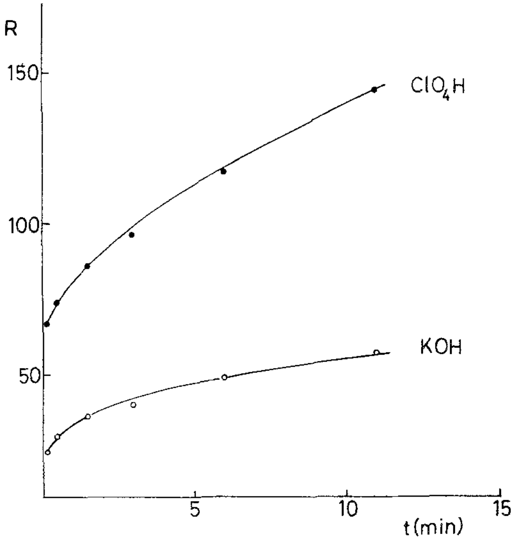

Fig. 10. Dependence of R on t (min) in different media. ●, 1 M $HClO_4$; ○, 1 M KOH, $T = 25°$ C.

4. Discussion

From the above results, the following experimental rate equations can be given.

For unactivated electrodes:

$$i_u = nFk_u C_{MeOH} C_{OH^-}^{0.5} \exp\,[\alpha_u FE/RT] \tag{1a}$$

For activated electrodes:

$$i_a = nFk_a C_{MeOH} C_{OH^-}^{0.3} \exp\,[\alpha_a FE/RT] \tag{1b}$$

The second equation is valid whichever activity of the electrode is considered. In Equations 1a and 1b, subscripts u and a refer to unactivated and activated electrodes, respectively, whereas α_u and α_a represent the anodic transfer coefficients obtained from the Tafel slopes for methanol oxidation on unactivated and activated electrodes, respectively; α_u is 0.22 and α_a 0.26.

A theoretical treatment of the reaction sequence proposed as a reaction mechanism would have to give a rate equation corresponding to the experimental equation. The proposed mechanism must also agree with the following experimental facts.

(i) Methanol oxidation does not take place significantly in acid solutions. This means that OH coverage on gold should play an important role as a substrate for methanol adsorption. This adsorption takes place by formation of hydrogen bridges between the alcohol and the Au–OH coverage [8]. On the other hand, the linearity obtained in the dependence between i_p and methanol concentration, indicates that adsorption of methanol on the OH coverage is not a rate-determining step. In fact, the formation of hydrogen bonds is not to be linked to any activation energy barrier. This supposition means that the adsorption step on both unactivated and activated electrodes is rapid.

(ii) For both unactivated and activated electrodes, the apparent activation energy has a similar value of around 70 kJ mol^{-1}. Such a high apparent activation energy seems to indicate the breaking of a chemical bond as a rate-determining step. Values of the apparent activation energy can be obtained from the rate equation written in the following way:

$$\begin{aligned}\ln i = {} & \ln [nFk(k_b T/h)\, C_{\mathrm{MeOH}} C^{\alpha}_{\mathrm{OH^-}}] \\ & + \Delta S^{\neq}/R - (\Delta H^{\neq} - \alpha F E)/RT \end{aligned} \tag{2}$$

Potential-dependent values of $\Delta S^{\neq}$ of around $-276\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for RTPS gold electrodes and of around $-288\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for SWPS-activated gold electrodes are obtained. These values indicate a high increase in order in the activated complex. The reactants are initially in solution: OH$^-$ ions and methanol molecules. When OH$^-$ ions adsorb on the gold surface there is a change from translational to vibrational degrees of freedom, characterized by $\Delta S^{\neq}_{\mathrm{OH}} < 0$. Methanol adsorbs on the OH coverage, giving rise to a higher decrease in the $\Delta S^{\neq}$ value. The $\Delta S^{\neq}$ value reported for methanol oxidation on platinum in an acid medium [9] is around $-221\,\mathrm{J\,mol^{-1}\,K^{-1}}$, a little smaller than that obtained in this work in which an OH$^-$ adsorption on the gold surface has also to be taken into account.

According to the above experimental facts, the following reaction mechanism is proposed for both unactivated and activated electrodes:

Step 1

$$\mathrm{Au + OH^- \rightleftharpoons AuOH} + \delta e$$

(Formation of the OH coverage on gold and partial charge transfer: $\delta < 1$.)

Step 2

$$\mathrm{(CH_3OH)_{sol} + AuOH \rightleftharpoons (CH_3OH)_{ads}}$$

(Adsorption of methanol on the Au–OH coverage previously formed.)

Step 3

$$\mathrm{(CH_3OH)_{ads} + OH_{ads} \longrightarrow H_2O + (\underset{\cdot}{C}H_2OH)_{ads}}$$

(Reaction between an adsorbed methanol molecule and one adsorbed OH. This reaction takes place with the breaking of a chemical bond and is thought to be the rate-determining step.)

Step 4

$$\mathrm{(\underset{\cdot}{C}H_2OH)_{ads} \rightleftharpoons \underset{+}{C}H_2OH} + e$$

(Electron transfer reaction.)

Step 5

$$\begin{aligned}\mathrm{(\underset{+}{C}H_2OH)_{sol} + OH^-_{sol}} & \mathrm{\rightleftharpoons HO{-}CH_2{-}OH} \\ & \mathrm{\rightleftharpoons HCHO + H_2O}\end{aligned}$$

Further steps may lead to an oxidation of methanol to methanoic acid and eventually to CO_2 and water.

With step 3 as the rate-determining step, observing that it consists of an OH desorption reaction and supposing that in the OH coverage there is an interaction between adsorbate particles (Temkin model [6]), the rate of step 3 can be written as follows:

$$v_3 = k_3 \Gamma_A \exp[-(1 - \gamma_{OH}) g_{OH} \theta_T / RT] \tag{3}$$

where Γ_A represents the surface concentration of methanol adsorbed on the AuOH coverage. From step 2, in equilibrium, $\Gamma_A = K_2 C_A$ (Equation 4) where K_2 represents the equilibrium constant for step 2 and C_A the methanol concentration in solution.

In order to obtain an expression for the exponential factor in Equation 3 it is necessary to make use of step 1. It has been supposed that the OH coverage follows a Temkin isotherm with the transfer of less than an electron from each OH^- ion adsorbed. A quantitative expression for step 1 in equilibrium is:

$$\exp[-g_{OH} \theta_T / RT] = K_1 C_{OH^-} \exp[\delta FE/RT] \tag{4}$$

where $\delta < 1$ and represents the fractional charge transfer from OH^- ions to the electrode, and K_1 is the equilibrium constant for step 1. From Equation 5 the following equation can be obtained:

$$\exp[-(1 - \gamma) g_{OH} \theta_T / RT] = K_1^{1-\gamma} C_{OH}^{1-\gamma} \exp[(1 - \gamma) \delta FE/RT] \tag{5}$$

By substituting Equations 4 and 6 in Equation 3,

$$v_3 = K_1^{1-\gamma} K_2 K_3 C_A C_{OH}^{1-\gamma} \times \exp[(1 - \gamma) \delta FE/RT] \tag{6}$$

Equation 7 represents the theoretical rate equation deduced from the reaction sequence given and is valid for both activated and unactivated gold electrodes. In order to test the validity of the proposed mechanism, Equation 7 has to be compared with the experimental rate equation.

5. Comparison between experimental and theoretical rate equations

5.1. *Gold electrodes after RTPS treatment*

The experimental (Equation 1a) and the theoretical rate equation (Equation 7) are equal when the experimental reaction order with respect to OH^- concentration coincides with $1 - \gamma$. For that case,

$$Z_{OH^-} = 0.5 = 1 - \gamma_{RTPS}$$

and therefore $\gamma_{RTPS} = 0.5$.

For both exponential terms to be equal,

$$\alpha_u = 0.22 = (1 - \gamma_{RTPS}) \delta_{RTPS}$$

and substituting $\gamma_{RTPS} = 0.5$ gives $\delta_{RTPS} = 0.44$.

5.2. *Gold electrodes after a SWPS treatment*

The calculation proceeds, again comparing the experimental to Z_{OH^-} (reaction order) value with the exponent of C_{OH^-} in the theoretical rate equation. Thus:

$$Z_{OH^-} = 0.30 = 1 - \gamma_{SWPS}$$

and

$$\gamma_{SWPS} = 0.70$$

Comparing the exponential terms in Equation 1b with that in Equation 7:

$$\alpha_a = 0.26 = (1 - \gamma_{SWPS}) \delta_{SWPS}$$

and by using γ_{SWPS} previously deduced, $\delta_{SWPS} = 0.87$.

Measurements of Tafel slopes made using gold electrodes of different degrees of activation show that δ_{SWPS} is independent of the activation. Therefore, if there is not an essential change in the reaction mechanism from activated to unactivated gold electrodes, it is necessary to admit a change in the value of γ and δ. The fact that $\delta_{SWPS} > \delta_{RTPS}$ would indicate that the OH coverage on the activated gold electrode would be more intensively adsorbed than on the unactivated one. According to step 1 in the mechanism, the higher amount of charge transferred gives rise to an Au–OH coverage more polarized, resulting in stronger hydrogen bridges between the coverage and methanol molecules and making step 3 easier and therefore the reaction rate greater. This fact is also found in the different values for the apparent activation enthalpy: 77 kJ mol^{-1} for activated versus 80 kJ mol^{-1} for unactivated electrodes. One explanation for this change in the fraction of charge transfer induced by the activation procedure developed by Arvia and co-workers

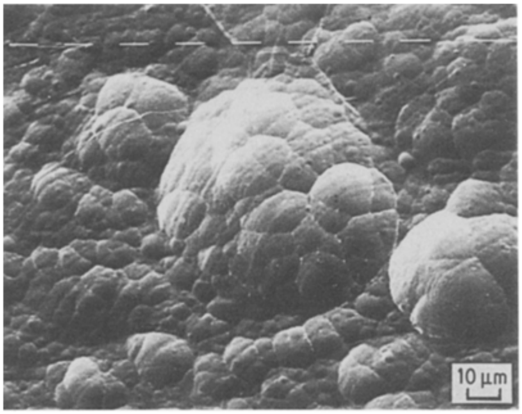

Fig. 11. SEM photograph of a gold surface after RTPS treatment.

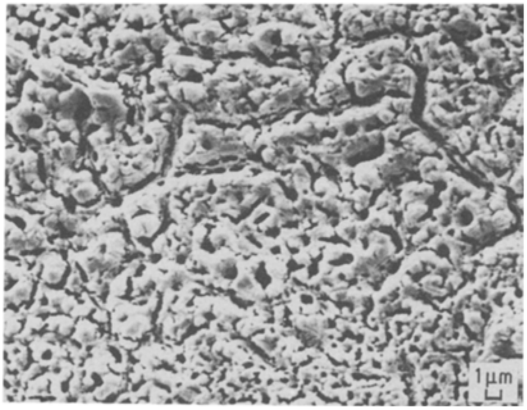

Fig. 13. SEM photograph of the electroreduced gold surface after SWPS treatment. $R = 100$.

[7] is a change in the ratio of microfacets in the gold polycrystalline surface towards a higher proportion of (1 1 1) microcrystals. This change should also have an effect on the adsorption energy of the OH_{ads} as well as on the fractional charge transferred. Fig. 11 shows the SEM micrographs of a gold electrode before activation and after being activated to two different degrees. The micrographs show an increase in the electrode area as the electrochemical results confirm.

6. Conclusions

Activation of a gold electrode according to the method reported by Arvia and co-workers [7] influences the reaction mechanism for the oxidation of methanol in basic medium only with respect to the OH coverage formation. The changes of Tafel slopes and reaction orders can be attributed to differences in charge transfer during the OH^- coverage formation and to the resulting change in the chemical bond strength between gold and OH coverage. The higher currents obtained on activated electrodes are due to an increase in electrode area confirmed by SEM.

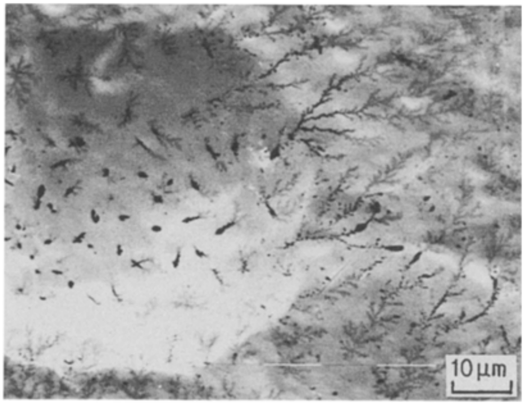

Fig. 12. SEM photograph of an electroreduced gold surface after SWPS treatment. $R = 20$.

Acknowledgement

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