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Oxygen reduction at platinum modified gold electrodes

M. Van Brussel^{a,1}, G. Kokkinidis^{a,1,2}, A. Hubin^{b,1}, C. Buess-Herman^{a,1,*}

^a Faculté de Sciences, Service de Chimie Analytique et Chimie des Interfaces, Université Libre de Bruxelles, CP 255, Boulevard du Triomphe, B-1050 Brussels, Belgium

^b Department of Metallurgy, Electrochemistry and Materials Science, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium

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Abstract

The reduction of oxygen has been studied on polycrystalline gold electrodes modified by platinum deposited spontaneously from an aqueous K_2PtCl_6 solution via the displacement of copper or lead adlayers. The change in the surface composition and morphology has been checked by XPS, AES and AFM data. The kinetic results have shown that such electrodes may present a higher catalytic activity compared to bulk platinum electrodes during a scan where the potential is made more positive and is thus clearly expressed by an hysteresis in the CV curves. The displacement of copper and lead deposits gave similar amplitudes of the hysteresis but the modified electrodes obtained via a lead deposit present a better stability upon cycling in acid solutions. The observed behaviour can be correlated to the modification of the M–OH formation and reduction on noble metals. \bigcirc 2003 Elsevier Ireland Ltd. All rights reserved.

Keywords: Au electrode; Displacement deposition; Platinum; Oxygen reduction; Catalytic activity

1. Introduction

Regarding its application in various technological areas, the reduction of oxygen is since many years the subject of intensive research [1]. In aqueous solutions, oxygen reduction is a multi-electron reaction that may proceed according to two overall pathways: a direct four-electron reduction and a peroxide pathway that involves a two-electron reduction leading to peroxide as intermediate which can undergo further reduction or decomposition. The high dissociation energy of the O– O bond (494 kJ mol⁻¹) is responsible for the fact that the four-electron reduction is observed only on some metals while hydrogen peroxide with a dissociation energy of 146 kJ mol⁻¹ can more easily be reduced on many surfaces [2,3].

E-mail address: cbuess@ulb.ac.be (C. Buess-Herman).

¹ ISE Member.

On Pt electrodes, which are the most active pure metal surfaces, the oxygen reduction follows predominantly the direct four-electron mechanism. As a result, the preparation of supported platinum electrocatalysts has received increasing attention in order to produce cheap and/or efficient cathodes.

So far, only a limited amount of work has been performed on the deposition of platinum from platinum salt solutions at open-circuit potential. Electroless deposition of Pt on freshly cleaved HOPG [4–6] involves the reaction of incompletely oxidized functionalities existing at defects on the graphite surface and is therefore difficult to control properly. Kokkinidis et al. [7,8] have shown recently that the deposition of Pt takes place on freshly polished titanium at open-circuit through a displacement reaction between Ti(0) and dissolved Pt(IV). However, it was found that the activity of the modified electrode for the oxygen reduction was smaller compared to that of a smooth platinum electrode.

Platinum overlayers on an $Au(1 \ 1 \ 1)$ substrate have also been grown under UHV conditions and their reactivity has been studied using CO as a probe molecule [9]. Surprisingly, the Au substrate has increased the Pt overlayer reactivity. The authors explain

^{*} Corresponding author. Tel.: +32-2-650-2939; fax: +32-2-650-2934.

² On leave from Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, Greece.

the results on the basis of a simple model in which the change in the CO binding energy is directly proportional to the shift of the d-band of the metal overlayer. According to this model, the increased activity of the $Pt/Au(1 \ 1 \ 1)$ system should be expected for other adsorbates and reactions.

Very recently, we have reported preliminary experiments relative to the performance of a gold-supported platinum electrocatalyst [10] for oxygen reduction. Since spontaneous deposition of Pt can be achieved by a displacement reaction between the platinum ions and a metal less noble than Pt, we have adopted the procedure where Pt is deposited on Au by replacing Cu deposits. Such a procedure was recently applied by Brankovic et al. [11] for the formation of submonolayers of Pt by displacement of Cu upd monolayers on Au(1 1 1). Recently, the electrodeposition of platinum from $PtCl_6^2$ or $PtCl_4^2$ solutions has also been achieved on gold single crystal substrates and characterized by cyclic voltammetry, STM and EQCM [12–15].

In the present paper we have examined the surface modification and the activity for oxygen reduction in acid and alkaline media of several platinum modified gold electrodes which differ by the amount of copper deposited in the opd region on a polycrystalline gold substrate. Better insight into the activity of the modified electrodes is also provided by varying the substrate and the nature of the displaced metal.

2. Experimental

2.1. Electrodes and electrolytes

The electrochemical measurements were performed with an Autolab (Eco Chemie) PGSTAT 30 potentiostat equipped with a Scan-Gen module connected to a threeelectrode cell. The working electrode was gold or a platinum rotating-disc electrode (EDI Tacussel, 2 mm in diameter). The rotating speed was controlled with a Controvit unit from Tacussel. A Radiometer Ag/AgCl (saturated with KCl) electrode, connected to the working electrode compartment by a Luggin bridge and a Pt grid served as the reference and the counter electrode, respectively. The working electrolyte was 0.1 M HClO₄ or 0.1 M NaOH saturated with oxygen at 1 atm. The cell was thermostated at 22 °C. All potentials given in this paper are referred to the RHE.

The electrolyte solutions were prepared from Milli-Q water (Millipore 18 M Ω cm) and HClO₄ or NaOH (Merck, suprapure). The other reagents were HCl 36% (Merck, suprapure), CuSO₄ (Merck, ACS reagent), Pb(ClO₄)₂ (Aldrich), O₂ 3.5 (Messer) and K₂PtCl₆ (Alpha Aesar, Johnson Matthey GmbH).

2.2. Deposition of Pt on Au

The deposition of Pt onto the gold disk electrode is performed according to an experimental procedure described previously [10].

The overpotential deposition of Cu from a solution of 0.1 M HClO₄+10⁻² M CuSO₄ was performed by applying a potential pulse of controlled duration. The various deposition times ($t_{Cu,dep}$) were 3, 10, 40, 60 and 120 s. The initial potential was $E_i = +0.77$ V and the final potential $E_f = -0.03$ V vs. RHE.

The displacement of Cu by Pt at open-circuit potential was carried out by immersing the Cu/Au electrode in a solution of 0.1 M HCl $+10^{-3}$ M K₂PtCl₆ during 180 s.

In order to gather more information on the displacement reaction and on the electrochemical behaviour of the modified surfaces, two additional procedures were devised to determine a possible influence either from the gold substrate or from the displaced metal. The first procedure involves the replacement of the gold substrate with a platinum one. The second experiment is performed by using a lead adlayer deposited on gold instead of the copper adlayer. Since the driving force for the displacement reaction is the potential difference between the two electrochemical systems, the displacement reaction can take place provided that the redox potential of the displaced metal is lower than the redox potential of the hexachloroplatinate/platinum system. For the deposition of Pt on gold by displacement of a lead adlayer, the overpotential deposition of Pb from a solution 0.1 M HClO₄+ 10^{-2} M Pb(ClO₄)₂ was also performed by applying a potential pulse of controlled duration. The deposition time $(t_{Pb,dep})$ was 60 s while the immersion time of the electrode in the hexachloroplatinate solution was 180 s. The initial potential was $E_i = +$ 0.77 V and the final potential $E_{\rm f} = -0.33$ V vs. RHE.

2.3. Preparation of samples for AES, XPS and AFM studies

Gold films epitaxially grown on glass, supplied by Arrandee GmbH, were used for the preparation of the samples for AES, XPS and AFM. These gold substrates were annealed at 700 °C for 6 h prior to the experiment and kept in Milli-Q water to avoid contamination.

The AES measurements were performed on a PHI-590 equipment. The spectra were acquired with electron beam energies of 3 and 10 keV. Relative sensitivity coefficients were derived from a copper-platinum reference sample under the same experimental conditions. The detector used was a CMA analyser (resolution set at 0.3%). The operational pressure in the analyser chamber was 10^{-9} Torr.

The XPS measurements were performed using a VG-CLAM II analyser and a dual anode (Mg/Al) X-ray source powered at 300 W. The anode used for all spectra was the Mg anode. The spectra are reported in binding energy mode, with a pass energy ranging from 100 to 25 eV, depending on the experiment.

The microscope used for the AFM study was a TopoMetrix Discoverer TMX 2000, operating in contact mode. The tip was TopoMetrix manufactured, (ref. number 1520-00-A) with a spring constant of 0.03 N m⁻¹. Resolution is 400×400 points for all images.

3. Results and discussion

For the sake of clarity, all the platinum modified gold electrodes are labelled as follows:

 $Pt/(Me_{xs})/Au$

where, Me is the displaced metal and xs represents the deposition time in seconds of the metal to be displaced. The Pt/(Me)/Au label should be regarded as a general label for platinum modified gold electrodes obtained by Me adlayer displacement.

The cyclic voltammogram obtained with a modified electrode in oxygen-free 0.1 M $HClO_4$ (Fig. 1) shows typical features for both polycrystalline gold and platinum.

3.1. Oxygen reduction on Ptl(Cu)|Au for different deposition times in acidic medium

Rotating-disc voltammograms for oxygen reduction were recorded on Pt/(Cu)/Au modified electrodes where the deposition time, and consequently, the amount of copper deposited, was changed while the displacement time was kept constant. The deposition times were 3, 10, 40, 60 and 120 s. Fig. 2A and B clearly show that the catalytic activity for oxygen reduction does not only depend on the potential sweep direction but also on the amount of copper deposited on the surface. Fig. 2 clearly shows that the halfwave potential for oxygen



Fig. 1. Cyclic voltammogram of a Pt/(Cu_{60s})/Au modified electrode in oxygen-free 0.1 M HClO₄ (dE/dt = 50 mV s⁻¹). Initial potential is indicated by the arrow.



Fig. 2. Current-potential curves for oxygen reduction recorded (A) in the negative and (B) in the positive potential sweep direction on Pt/ (Cu_{xs})Au rotating-disc electrodes in O₂-saturated 0.1 M HClO₄ (d*E*/d*t* = 20 mV s⁻¹). Rotation rate 1100 rpm. Deposition time *x* (s): (1) 3; (2) 10; (3) 40; (4) 60; (5) 120. The insets A and B show mass-transport corrected Tafel plots.

reduction increases as the amount of copper is increased, until it reaches a maximum value for Pt/(Cu_{60s})/Au. If the amount of copper is further increased, the halfwave potential decreases. Using values of the kinematic viscosity, $v = 8.93 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, [16] the O₂ diffusion coefficient, $D_{O_2} = 1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [16] and the oxygen concentration, $c_{O_2} = 1.22 \times 10^{-6} \text{ mol cm}^{-3}$ [16] the Levich analysis of the rotating-disc voltammograms for oxygen reduction yielded a four-electron reduction wave for all but the Pt/(Cu_{3s})/Au electrode, where the number of electrons is equal to 3.6. This latest observation is an indication that the amount of platinum is in this particular case too low to achieve limiting currents at the level of a four-electron reduction. The curves recorded for the $Pt/(Cu_{40s})/Au$ and the $Pt/(Cu_{60s})/$ Au electrodes display a remarkable hysteresis between the forward and backward scans. The potential difference between the positive and the negative scan for the Pt/(Cu_{60s})/Au electrode amounts to almost 200 mV. This unusual behaviour is not recorded on bulk platinum. Both the $Pt/(Cu_{40s})/Au$ and the $Pt/(Cu_{60s})/Au$ samples have a higher catalytic activity when compared to polycrystalline platinum [1], but the $Pt/(Cu_{60s})/Au$ electrode shows the most promising behaviour towards oxygen electroreduction.

The limiting currents in Fig. 2 are well expressed over a wide potential range. It seems that there is no influence of Pt distribution and loading on the limiting current. This is due to the fact that the spherical diffusion zones corresponding to the Pt particles overlap and as a result of this the diffusion of oxygen on the Pt/(Cu)/Au surface is equivalent to the planar diffusion to the whole surface. Therefore, the area-term in the Levich equation should be the geometric area of the Au-disc (0.0314 cm^2) and not the exposed area of the Pt clusters. This is, however, not the case in the kinetic study where the real area of the electrode must be taken into account.

The halfwave potentials of the reduction waves (positive scan) on Pt/(Cu_{60s})/Au measured at different rotation rates are ca. 100 mV more positive than those measured for smooth Pt [1] and comparable (or slightly less negative) than those estimated from the polarization curves, reported for the most active Pt(1 1 0) face by Perez et al. [17] and Markovic et al. [18] in a perchloric acid solution at the same rotation rates. It should, however, be noted that $E_{1/2}$ values can be considered only as a qualitative criterion for the catalytic activity, since $E_{1/2}$ is known to depend on the real area of the electrodes.

A kinetic analysis of the current-potential curves was made in the mixed kinetic-diffusion control region. From the Koutecky-Levich analysis, kinetic currents were calculated by means of the equation

$$\frac{1}{i} = \frac{1}{i_{\rm k}} + \frac{1}{b\omega^{1/2}} \tag{1}$$

where *i* is the measured current, ω is the electrode rotation rate, *i*_k is the kinetic current given by

$$i_{\rm k} = nFAkc_{\rm O_2} \tag{2}$$

where A is the area of the electrode and b is the Levich slope:

$$b = 0.62nFAc_{0,}(D_{0,})^{2/3}v^{-1/6}$$
(3)

Koutecky–Levich plots for various potentials yield straight lines with intercepts corresponding to the kinetic currents i_k , which give the reaction rate constants k. The slope of the straight lines allows us to assess the number of electrons involved in the oxygen reduction reaction. The number of electrons involved is consistent with the Levich analysis. The values of k derived from the Koutecky–Levich analysis are reported in Table 1. The indicated values of k are, however, reported using the geometric area of the Au electrodes. If the real surface is taken into account, the derived values of k are smaller, and in the specific case of Pt/(Cu_{60s})/Au it was reported previously that the value of k at 0.8 V vs. RHE was 5.21×10^{-2} cm s⁻¹ using the geometric area and 3.17×10^{-2} cm s⁻¹ using the real surface area estimated from the hydrogen upd in oxygen-free HClO₄. It must be emphasized that the latter value is higher than the reported value of Pt(1 1 0) [17,18], the most active face in the same experimental conditions.

The Tafel behaviour in the mixed kinetic-diffusion control region was also examined by using masstransport corrected currents. The insets of Fig. 2 shows the Tafel slopes obtained at 1500 rpm for the Pt/(Cu_{60s})/ Au electrode. The slopes were -65 mV dec^{-1} for the negative scan and -76 mV dec^{-1} for the positive scan. These values are very close to the value of -60 mV dec⁻¹, indicating Pt–OH formation and reduction play a decisive role on the kinetics of oxygen reduction. Table 1 displays Tafel analysis data for other Pt/(Cu)/Au electrodes.

The significant hysteresis on the polarization curves for the $Pt/(Cu_{40s})/Au$ and the $Pt/(Cu_{60s})/Au$ shows that the oxygen reduction reaction is much faster on a reduced than on an oxidized surface of the Pt adlayer. The Tafel data suggests that this hysteresis is related to the formation of Pt–OH and its possible modification by the substrate. The possible effect of the gold substrate is further discussed in Section 3.4.

To complete the study of Pt/(Cu)/Au electrodes in acidic medium surface analysis techniques were used. The displacement of the copper adlayer by platinum was confirmed. However, the displacement time of 180 s is not enough to replace the whole copper adlayer with platinum. Auger and XPS measurements confirmed the presence of residual copper on all samples. This observation indicates that although the displacement reaction is quite fast, the rate eventually drops to zero as

Table 1 Kinetic parameters for oxygen reduction on Pt/(Cu_{xs})/Au in 0.1 M HClO₄ (T = 22 °C)

$t_{\mathrm{Cu,dep}}(\mathbf{s})$	Tafel analysis				Koutecky-Levich analysis (positive sweep)		
	Negative sweep		Positive sweep		0.65 V	0.80 V	п
	$b \text{ (mV dec}^{-1})$	$10^9 j_0 (\mathrm{A \ cm^{-2}})$	$b \text{ (mV dec}^{-1})$	$10^7 j_0 (\mathrm{A \ cm^{-2}})$	$10^2 k (\mathrm{cm \ s}^{-1})$		
3	-104	3.0	-150	2.2	0.33	_	3.6
10	-92	1.1	-122	0.9	1.03	-	4.1
40	-77	0.58	-122	10.3	6.22	-	4.1
60	-65	0.14	-76	1.9	55.0	5.21	4.0

the reaction can only take place as long as copper is in contact with the platinum containing solution. As the reaction proceeds, the copper adlayer is covered by deposited platinum until no exchange sites are left available.

AES experiments indicate that the amount of deposited platinum increases as the displacement reaction proceeds. Fig. 3A–D show a series of Auger spectra recorded at different immersion times for the Pt/(Cu_{60s})/Au electrode. The amount of platinum increases, however, the derived quantitative data show a decrease in the exchange rate, which is consistent with the displacement reaction mechanism.

Fig. 4A and B show the surface morphology of the Pt/ (Cu_{60s})/Au modified electrode, at different resolutions. The modified surface exposes metallic particles homogeneously dispersed on the surface. The size distribution of these particles is quite narrow. On Fig. 4A it appears that most particles exhibit a more or less spherical shape with a 100 nm radius. Upon closer inspection, (Fig. 4B) it appears that each the particles consists in an agglomeration of metallic particles of much smaller dimensions, in a particular grape-like structure. The rather rough surface of these metallic particles probably explains part of the increased catalytic activity.

Finally, the stability of the Pt/(Cu_{60s})/Au electrode was examined by continuously cycling at 1500 rpm. Fig. 5 shows no decrease in the catalytic activity in the first cycles, but as the cycling went on, a progressive slight decrease in the catalytic activity was observed at the positive branch of the hysteresis. After potential cycling, AFM reveals that the surface morphology is completely different (Fig. 4C). Roughness data were calculated by means of Eq. (4) for different images.

$$Ra = \frac{1}{N} \sum_{i=1}^{N} \left| Z_i - \left[\frac{1}{N} \sum_{i=1}^{N} Z_i \right] \right|$$
(4)

Ra values are decreased by $\pm 50\%$ after potential cycling. Although the electrooxidation of the surface is known to increase the roughness of the surface, it appears that in this particular case, the potential cycling led to a flattening of the metallic particles on the surface. The decrease in catalytic activity as the cycling goes on is most likely related to the change in surface morphology.



Fig. 3. AES spectra for the system Pt/(Cu_{60s})/Au at different immersion times. (A) 0 s; (B) 60 s; (C) 120 s; (D) 180 s.



Fig. 4. AFM contact mode images of $Pt/(Cu_{60s})/Au$ at low resolution (A), high resolution (B), AFM contact mode images of $Pt/(Cu_{60s})/Au$ after continuous potential cycling in O₂-saturated 0.1 M HClO₄ ($dE/dt = 20 \text{ mV s}^{-1}$) (C) and AFM contact mode image of $Pt/(Pb_{60s})/Au$.

The underlying copper layer was possibly partially dissolved during the potential cycling, which explains the change in morphology. Metallic nanoparticles are also known to change their shape upon potential cycling [19].



Fig. 5. Continuous potential cycling showing the deactivation of the $Pt/(Cu_{60s})/Au$ electrode for the reduction of oxygen in O₂-saturated 0.1 M HClO₄ (d*E*/d*t* = 20 mV s⁻¹). Rotation rate 1500 rpm. The inset shows the full voltammogram (first cycle) and its part, which is demonstrated in the figure.

3.2. Oxygen reduction on $Pt/(Cu_{60s})/Au$ in alkaline medium

The kinetics of oxygen reduction on Au-supported Pt electrocatalysts were also studied in aqueous 0.1 M NaOH solution. Fig. 6 shows current-potential curves for oxygen reduction on the Pt/(Cu_{60s})/Au electrode as a function of the rotation rate. Very stable polarization curves were obtained. After 4 h of continuous cycling of the potential at 20 mV s⁻¹ in the range between 1.67 and 0.03 V vs. RHE, the halfwave potentials remained constant for both cathodic and anodic sweep directions. An hysteresis is also present in the region of potentials where the surface is covered by OH_{ads} and O_{ads}, but the potential difference between the forward and backward scan is much lower than in the case of acid solutions.

The limiting current varies linearly with $\omega^{1/2}$ (inset A in Fig. 6). The number of electrons involved in the reaction mechanism was estimated from the Levich slope; it was found equal to four. Kinetic analysis in the mixed kinetic-diffusion control region is also presented in Fig. 6 (inset B) in the form of Tafel plots corrected for the mass-transport. Tafel slopes at low currents were found to be -65 and -62 mV dec⁻¹ in the cathodic and anodic sweep direction, respectively. At high currents, the Tafel slope increases to about -90 mV dec⁻¹ in both sweep directions. The Tafel slopes



Fig. 6. Current-potential curves for oxygen reduction on Pt/(Cu₆₀₈)/Au rotating-disc electrode in O₂-saturated 0.1 M NaOH ($dE/dt = 20 \text{ mV s}^{-1}$). Rotation rate (rpm): (1) 500; (2) 750; (3) 1100; (4) 1500; (5) 2100; (6) 3000. The insets show: (A) plot of j_L vs. $\omega^{1/2}$ ($\omega = 2\pi f$). (B) Mass-transport corrected Tafel plots (1) in the negative and (2) in the positive potential sweep direction at 1500 rpm.

obtained seem to be in line with the Tafel slopes of -60 and -120 mV dec^{-1} reported for smooth Pt in alkaline solutions, indicating some similarity between oxygen reduction on smooth and Au-supported Pt electrocatalysts. Unlike the acidic medium, there was no significant deactivation of the electrode upon cycling.

3.3. Oxygen reduction on Pt/(Pb_{60s})/Au in acidic medium

Additional experiments, in which the copper adlayer was replaced by a lead adlayer were performed. The lead adlayer was deposited potentiostatically at -330 mV vs. RHE for 60 s. The displacement was carried out during 180 s. Fig. 4D shows a AFM image of the same surface. The morphology is roughly the same as that obtained for a 60 s copper deposit followed by an exchange of 180 s. Metallic particles are uniformly spread on the substrate and have a radius of about 50–100 nm. Closer

inspection of these particles reveals grape-like structures similar to those reported for a copper adlayer. This seems to indicate that the surface morphology does not depend significantly on the nature of the displaced metal.

Fig. 7 shows the recorded rotating-disc voltammograms for the $Pt/(Pb_{60s})/Au$ modified electrode in acid solution for oxygen reduction. The curves are similar to those reported for the $Pt/(Cu_{60s})/Au$ modified electrodes. There is a significant hysteresis of about 200 mV between the positive going scan and the negative going scan. The remarkable similarity between the polarization curves recorded on the copper based electrodes and the lead based electrodes confirms the fact that the nature of the displaced metal does not have an important effect on the behaviour of the electrode.

One peculiar feature of the potential hysteresis is that the potential difference between the positive and negative going sweeps depends on the vertex potentials of the



Fig. 7. Comparison between the polarization curves of oxygen reduction obtained in O₂-saturated 0.1 M HClO₄ on Pt/(Pb_{60s})/Au at low positive end potential and high positive end potential. (dE/dt = 20 mV s⁻¹). Rotation rate: 1500 (rpm).

experimental procedure. If the positive end of the voltammogram is decreased, the width of the hysteresis is also decreased but the positive branch is unaffected. On the other hand, the negative end potential of the cyclic voltammogram has no effect on the electroche-

mical behaviour of the electrode when the cycling is performed. Hysteresis phenomena have been reported earlier for the formation and reduction of oxide films on noble metals [20]. The present hysteresis for oxygen reduction can therefore be correlated to the character-



Fig. 8. Comparison between the recorded XPS spectra of $Pt/(Pb_{60s})/Au$ before and after continuous potential cycling. Mg-Anode, pass-energy: 50 eV, step 0.20 eV, dwell 50 ms.

istics of the oxide formation and reduction on the modified electrode. If the electrode is not polarized too positively before reducing the oxygen, the onset of oxygen reduction in the negative going scan takes place at a more positive potential since the amount of surface OH is lower than in the case where the electrode is oxidized. In the case of noble metals, the difference of pathway in formation from that in reduction of the oxide film is generally explained by the presence of a place-exchange mechanism involving the metal and the OH and O species. Such mechanism can be expected to be modified when distinct metal atoms are present at the electrode surface.

XPS measurements performed onto the $Pt/(Pb_{60s})/Au$ modified electrode, both before and after potential cycling reveal that the amount of lead on the electrode decreases as it dissolves upon cycling. Fig. 8 shows two XPS spectra recorded before oxygen reduction and after 12 potential cycles. The amount of Pb decreases and consequently the relative surface concentration of platinum increases. Moreover, when compared to XPS spectra recorded on $Pt/(Cu_{60s})/Au$ modified electrodes, the amount of deposited Pt is roughly the same, regardless if lead or copper was used. The dissolution of the remaining metal while cycling, among other effects, probably explains why there is a progressive deactivation of the surface as the oxygen reaction proceeds.

3.4. Oxygen reduction on $Pt/(Cu_{60s})/Pt$ and polycrystalline platinum in acidic medium

Fig. 9 shows the recorded cyclic voltammograms for oxygen reduction on polycrystalline platinum and on a $Pt/(Cu_{60s})/Pt$ electrode. On polycrystalline platinum,



Fig. 9. Comparison between the polarization curves of oxygen reduction obtained in O₂-saturated 0.1 M HClO₄ on (—) Pt/(Cu_{60s})/Au and (---) Pt/(Cu_{60s})/Pt and a bare Pt rotating-disc electrodes (d*E*/d*t* = 20 mV s⁻¹). Rotation rate 1500 rpm.

there is no significant hysteresis between the positive and the negative going scan, the electrochemical behaviour for oxygen reduction being otherwise the same. On the other hand, the replacement of the gold substrate by a polycrystalline platinum one, yields a typical polycrystalline platinum curve. This observation is an indication that indeed the gold substrate plays a role in the oxygen reduction reaction. Additional evidence supporting this hypothesis is given by Fig. 10, which shows an AFM image of the $Pt/(Cu_{60s})/Pt$ electrode. The morphology as well as roughness of the surface is identical to those reported in Fig. 4A and D. The remarkable catalytic activity can thus not be ascribed to the surface roughness only. Possible complex bi-metallic interactions and/or electronic effects are responsible for this particular activity. More sensitive XPS measurements are going to be carried out in order to detect a possible surface alloying.

4. Conclusions

The study of the oxygen reduction on a polycrystalline gold electrode modified by the spontaneous deposition of platinum through replacement of a copper or lead deposit has shown that such electrodes may present an increased catalytic activity compared to bulk platinum electrodes. The high electrocatalytic activity is observed only when the O₂ reduction takes place during a back potential scan and is thus clearly expressed by an hysteresis in the CV curves. The results obtained at constant time of immersion of the electrode into a platinum salt solution have shown that the activity is dependent on the amount of platinum displacing copper and that a maximum in activity is reached. XPS and AES data have revealed that the displacement reaction was not complete in the various experimental conditions used but a quantitative determination of the platinum content was not achieved in this work since, prior to the exchange, the deposition of copper has involved charges which were in some instances equivalent to more than 100 monolayers.

The importance of the role of the displaced metal has been investigated by performing experiments with lead instead of copper. The displacement of copper and lead deposits gave similar results and in particular the amplitude of the hysteresis is not significantly dependent on the nature of the displaced metal.

The increased activity revealed through the hysteresis cannot be attributed to an increase of the roughness of the deposit. Deposition of platinum on a massive platinum electrode following exactly the same procedure did not give rise to the presence of an important hysteresis in the CV curves for oxygen reduction and AFM images reveal similar deposit morphology on a gold and a platinum substrate.



Fig. 10. AFM contact mode image of Pt/(Cu_{60s})/Pt.

We suggest thus that the platinum modified gold electrode must present sites which have different geometric and energetic characteristics. Oxygen reduction on bare platinum is known to involve the adsorption of O_2 which is favourably binded to the surface according to a twofold bridge site. The presence of a gold substrate may lead to a modification of the kinetic of the initial stages of oxide formation and reduction.

The distinct feature observed in NaOH and HClO₄ solutions is indicative of the intervention of the change in M–OH formation. The deactivation observed by cycling in acid media with the modified electrode resulting from the copper deposit replacement is probably due to the diffusion of remaining Cu atoms through the Pt film since it is known that copper upd layers unlike lead cause an inhibition of the oxygen reduction rate [21–23].

Further work is required to have a better insight into the formation of M-OH and the chemisorption of O_2 on these platinum modified electrodes.

Finally, the procedure used in this work may be extended to produce multimetallic electrodes such as platinum–ruthenium modified gold electrodes which can be easily obtained by displacement of a lead adlayer deposited on gold. Such a procedure offers the advantage of depositing both metals at the same time on the substrate which may lead to a better homogeneity and a possible higher activity of the modified surface.

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