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High performance gold-supported platinum electrocatalyst for oxygen reduction

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Abstract

High performance gold-supported Pt electrocatalyst for the reduction of oxygen was prepared by replacing Cu adlayers, deposited potentiostatically on Au, with Pt at open-circuit potential in a 0.1 M HCl solution containing K_2PtCl_6. Auger Electron Spectroscopy and Atomic Force Microscopy reveal the surface modification. The kinetics of oxygen reduction on this platinum modified electrode was studied by the rotating-disc electrode technique. The activity of the electrode is lower than the activity of a smooth Pt electrode in the negative potential scan, but it is significantly higher in the positive scan. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Au substrate; Copper electrodeposition; Displacement deposition; Platinum; Oxygen reduction; Catalytic activity

1. Introduction

Considering the importance of the activity of the electrocatalysts used as cathodes and/or anodes for the performance of fuel cells, it is not surprising that intensive work has been done during the last decades to improve the catalytic activity of existing electrocatalysts and to develop new, better ones. For the cathodic reaction, which is the reduction of oxygen, platinum is the best electrocatalyst both in acid and alkaline fuel cells. Numerous studies have been reported in the literature [1–8] on the reduction of oxygen on supported Pt electrocatalysts. Very recently, it was found by Kokkinidis et al. [9,10] that Pt can be deposited on titanium very easily by immersing a titanium electrode, immediately after its mechanical polishing, in a hexachloroplatinic acid solution, as a result of a displacement reaction taking place between Ti and $PtCl_6^{2-}$ ions. In the case of the oxygen reduction [10], it was found that the catalytic activity was always smaller compared to that of a smooth Pt electrode. The low activity of the Pt/Ti electrode was attributed to the irreversible oxidation of the titanium surface. The effect of oxides of the background metal on the catalytic activity of the Pt clusters deposited in this way can be avoided if one can deposit Pt on metals that are not easily oxidized, such as noble metals. However, spontaneous deposition of Pt on noble metals is not thermodynamically possible. Therefore, the idea arose to deposit a less noble metal electrochemically first and, then, to replace it by platinum. Following this procedure we deposited Pt on Au by replacing Cu deposits. Copper was previously deposited potentiostatically on a gold substrate electrode. The replacement reaction took place at open-circuit potential by immersing the Cu/Au electrode in a solution of $0.1\ M\ HCl + 10^{-3}\ M\ K_2PtCl_6$. Very recently, Brankovic et al. [11] have also reported that submonolayers of Pt can be deposited spontaneously on Au(1 1 1) by replacement of upd monolayers of Cu. In this paper we present preliminary experiments on the reduction of oxygen showing that the Pt/Au electrode exhibits an excellent catalytic activity for the 4-electron reduction of O_2 in acidic solutions.

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2. Experimental

The electrochemical measurements were performed with an Autolab (Eco Chemie) PGSTAT 30 potentiostat with a Scan-Gen module connected to a three-electrode cell. The working electrode was an Au rotating-disc electrode (EDI – Tacussel, 2 mm in diameter). A Radiometer Ag/AgCl (saturated with KCl) electrode, connected to the working electrode compartment by a Luggin bridge and a Pt grid served, respectively, as the reference and the counter electrode. The working electrolyte was 0.1 M $HClO_4$ (Merck, suprapure) saturated with oxygen at 1 atm. All solutions were prepared with MilliQ pure water. The other reagents were HCl 36% (Merck, suprapure), $CuSO_4$ (Merck, ACS reagent) and K_2PtCl_6 (Alpha Aesar, Johnson Matthey GmbH). The cell was thermostated at 22 °C. All potentials in this paper are referred to the RHE.

The deposition of Pt onto the gold disk electrode is performed in several steps, as follows:

1. Removal of the Pt clusters from the previous experiment by immersing the electrode in aqua regia (33% $HNO_3 + 66\%$ HCl) for ca. 5 min.
2. Polishing with silicon carbide grinding paper (Struers) followed by an alumina–water slurry (EMS 1 μm and 50 nm). After each polishing step, the electrode was sonicated in Millipore water.
3. Electrochemical activation of the electrode in 0.1 M $HClO_4$ by cycling at a rate of 2 V s^{-1} between −0.13 and +1.87 V vs. RHE until the CV obtained is consistent with the behaviour of a polycrystalline gold electrode at a scan rate of 50 mV s^{-1}.
4. Overpotential deposition of Cu from a solution of 0.1 M $HClO_4 + 10^{-2}$ M $CuSO_4$ by applying a potential step from 0.77 to −0.03 V vs. RHE during 60 s ($t_{\mathrm{Cu,dep}} = 60$ s).
5. Replacement of Cu with Pt at open-circuit potential by immersing the Cu/Au electrode in a solution of 0.1 M $HCl + 10^{-3}$ M K_2PtCl_6. The replacement (or immersion) time was kept constant, $t_{\mathrm{Pt,repl}} = 3$ min.

The deposition of Pt on Au according to this procedure was fairly reproducible on the basis of the electrochemical behaviour.

Gold films epitaxially grown on glass, supplied by Metallhandel Schröder GmbH, were used for the preparation of the samples for AES and AFM. These gold substrates were annealed at 700 °C for 6 h prior to the experiment and kept in MilliQ 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 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 pixels for all images.

3. Results and discussion

The displacement reaction during which the copper layer is replaced with platinum proceeds according to the overall reaction

$$2Cu^0/Au + PtCl_6^{2-} \rightarrow Pt^0/Au + 2Cu^{2+} + 6Cl^- \qquad (1)$$

The driving force for this displacement mechanism is the positive difference between the equilibrium potential of platinum in contact with its complexes and the equilibrium potential of the opd metal adlayer. Hence, the copper atoms on the surface are oxidized by the platinum complexes and are displaced by platinum atoms. Through this mechanism, the amount of metal deposited is determined by the stoichiometry of the redox reaction.

3.1. AES study

Since the amount of platinum on the copper modified gold surface is quite low, the samples were not sputtered prior to the analysis. On the basis of a charge of 390 μC cm^{-2} for the reduction of a monolayer of copper [12], a rough estimation leads to about 200 monolayers of copper on the Au substrate prior to the exchange with platinum. The maximum loading of platinum can, therefore, be estimated from the amount of copper deposited. For the present modified electrode a maximum platinum loading of 40 μg cm^{-2} can be expected. It is noteworthy that all the surveyed samples revealed the presence of residual copper on the surface, regardless the exchange time with platinum. Fig. 1 shows a typical AES spectrum obtained after replacement of copper with platinum on the gold electrode. For quantification purposes, the main Auger transitions for copper are detected at kinetic energies of 920 eV (Cu1), 840 eV (Cu2) and 775 eV (Cu3), whereas for platinum, the main transitions can be found at energies of 70 eV (Pt1), 200 eV (Pt2) and 280 eV (Pt3). However, on the Pt/Cu/Au modified surfaces the Auger transitions for platinum overlap with transitions related to other metals. At 70 eV there is an overlap of Pt1 and a low energy copper transition; at 200 eV, an Auger transition of chlorine is interfering with the platinum signal. Moreover, carbon, which cannot be avoided since the sample was not sputtered prior to analysis, is masking the Pt3 transition. Hence, for quantification, high energy transitions for platinum (1980 and 1960 eV) were used and the primary electrons energy increased from 3 to 10 keV. Since the thickness of the copper deposits largely exceeds the free

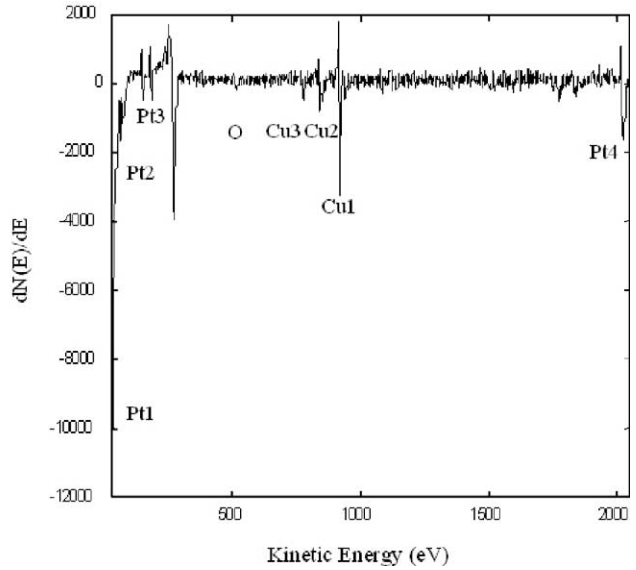

Fig. 1. AES spectrum for the system Pt–Cu/Au ($t_{\mathrm{Cu,dep}} = 60$ s). $t_{\mathrm{Pt,repl}}$(s): 120.

inelastic mean path of the electrons, no transitions relative to the gold substrate were observed. Using relative sensitivity coefficients for copper and platinum at 10 keV electron beam energy, it is possible to obtain a relative ratio between copper and platinum on the surface. Copper on the surface amounts to 46% after 30 s of the metal displacement reaction. It decreases to 20% after 120 s and after 180 s the surface composition is about 16% in copper. The amount of copper drops as the displacement reaction proceeds, but it is expected to reach a constant value at high replacement times, since the displacement reaction can only take place as long as copper atoms are in direct contact with platinum complexes. When all the copper is covered with platinum, the displacement rate is expected to drop to zero. Since a significant bimetallic interaction or a possible alloying between copper and platinum cannot be excluded [13], the data presented in this section should be considered as semi-quantitative results since the relative sensitivity coefficients used in all calculations are measured for pure metals.

3.2. AFM study

Several samples were examined by Atomic Force Microscopy. Image A, in Fig. 2 shows the structure of the bare gold surface after annealing in a furnace for 6 h. The different regions present on the surface are extending over a few micrometers and the boundaries between regions are very regular. Image B in Fig. 2, on the other hand, shows the morphology of the metal particles on the surface after 180 s exchange of Cu with platinum.

As can be seen, the metal clusters are almost uniformly spread on the Au substrate and expose quite a rough surface. The size of the particles is about 50–100 nm in diameter, after a replacement time of 180 s. The size and shape distribution is quite homogeneous. It is most probable that these metal particles are the result of the agglomeration of smaller particles.

3.3. Oxygen reduction on Pt/(Cu)/Au

Oxygen reduction was selected as a probe for the assessment of the catalytic activity of the modified Pt/(Cu)/Au surface. Fig. 3 shows current–potential curves obtained over a range of rotation rates (500–3000 rpm) recorded for the reduction of oxygen in 0.1 M $HClO_4$ on Pt/(Cu)/Au electrodes prepared according to the

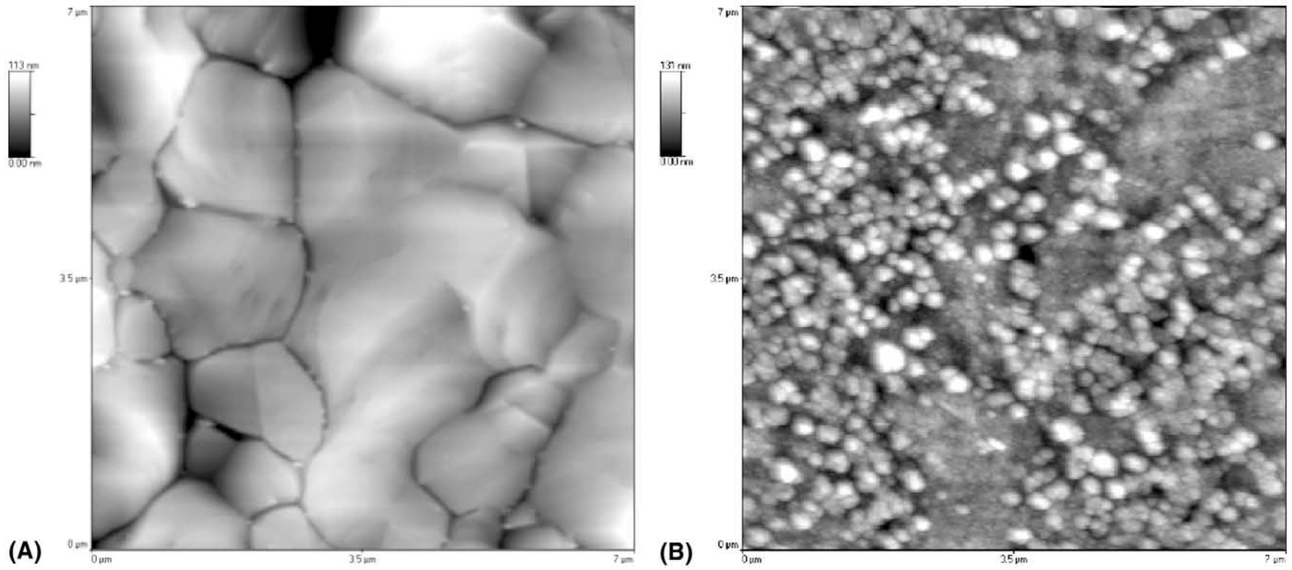

Fig. 2. AFM contact mode images of (A) bare Au and (B) Au covered by Cu deposit ($t_{\mathrm{Cu,dep}} = 60$ s). $t_{\mathrm{Pt,repl}}$(s): 180.

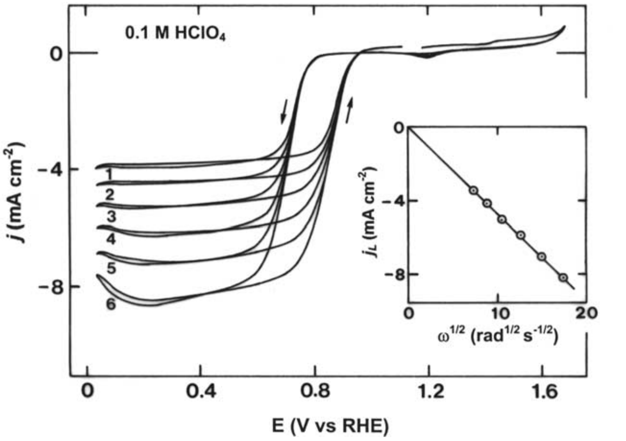

Fig. 3. Current–potential curves for oxygen reduction on Pt/Au ($t_{\mathrm{Cu,dep}} = 60$ s, $t_{\mathrm{Pt,repl}} = 180$ s) rotating-disc electrodes in O_2-saturated 0.1 M $HClO_4$ ($\mathrm{d}E/\mathrm{d}t = 20$ mV s^{-1}). Rotation frequency f = (1) 8.33; (2) 12.5; (3) 18.33; (4) 25; (5) 33.33; (6) 50 Hz. The inset shows plot of j_L vs. $\omega^{1/2}$ ($\omega = 2\pi f$).

experimental procedure described previously. The cyclic voltammogram of the Pt/(Cu)/Au electrode in O_2-free 0.1 M $HClO_4$ solution presents both peaks of the reduction of Pt-oxides and Au-oxides, indicating that the Au surface is not fully covered by platinum. The active area of the Pt clusters has been roughly estimated from the hydrogen adsorption/desorption peaks observed in the CV curves. The limiting currents 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 microparticles 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 equations should be the geometric area of the Au-disc (0.0314 cm^2) and not the exposed area of the Pt clusters. The inset of Fig. 3 shows the j_l, versus $\omega^{1/2}$, where j_l is referred to the geometric surface area of the Au-disc substrate electrode.

From the slope $\mathrm{d}j_L/\mathrm{d}\omega^{1/2} = 4.78 \times 10^{-4}$ A cm^{-2} rad$^{-1/2}$ s$^{1/2}$, the number of electrons transferred was evaluated by means of the Levich equation; using values of $v = 8.93 \times 10^{-3}$ cm^2 s^{-1}, $D_{O_2} = 1.93 \times 10^{-5}$ cm^2 s^{-1} [14] and $c_{O_2} = 1.22 \times 10^{-6}$ mol cm^{-3} [14], the number of electron found equals 4.

A remarkable hysteresis can be observed between the forward and backward scan. This behaviour shows that there is a significant change in the catalytic activity of reduced and oxidized platinum clusters spread on the Au substrate. It is important to note that the catalytic activity of reduced Pt/(Cu)/Au surfaces is much higher than the activity of a smooth polycrystalline Pt electrode (see below) and, of course, much higher than the activity of the Au substrate where O_2 undergoes a 2-electron reduction at even higher overpotentials than on smooth platinum. The halfwave potentials of the reduction waves (positive scan) on Pt/(Cu)/Au measured at different rotation rates are ca. 100 mV more positive than those measured for smooth Pt 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. [15] and Marković et al. [16] in a perchloric acid solution at the same rotation rates. It should 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 plots reported in Fig. 4, kinetic currents were calculated by means of the equation

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{b\omega^{1/2}}, \tag{2}$$

where I is the measured current, ω is the electrode rotation rate, I_k is the kinetic current given by

$$I_k = nFSk_c c_{O_2} \tag{3}$$

and b is the Levich slope

$$b = 0.62nFSc_{O_2}(D_{O_2})^{2/3}v^{-1/6}. \tag{4}$$

Koutecky–Levich plots for various potentials yield straight lines with intercepts corresponding to the kinetic currents I_k, which gives the reaction rate constant k_c. In addition, the slope of the straight lines allows us to assess the number of electrons involved in the oxygen reduction reaction. The value of k_c derived from the Koutecky–Levich plots is 55.0×10^{-2} cm s^{-1} at a potential of 0.65 V vs. RHE and 5.21×10^{-2} cm s^{-1} at 0.8 V vs. RHE. It should be noted that in this calculation the geometric surface area of the Au disc was taken into

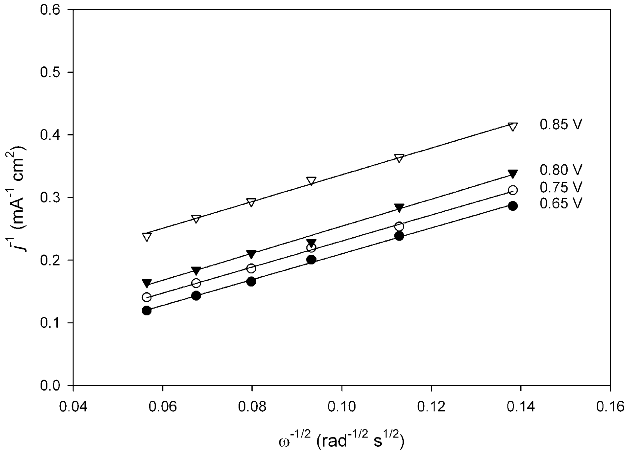

Fig. 4. Koutecky–Levich plots for oxygen reduction in O_2-saturated 0.1 M $HClO_4$ on Pt/Au ($t_{\mathrm{Cu,dep}} = 60$ s $t_{\mathrm{Pt,repl}} = 180$ s) electrodes ($\mathrm{d}E/\mathrm{d}t = 20$ mV s^{-1}).

account and not the real surface area. However, if one considers the electrode area estimated from the hydrogen adsorption–desorption peaks obtained in an oxygen-free solution, k_c amounts to 3.17×10^{-2} cm s^{-1} at 0.8 V, a value about 20% higher than that reported for Pt (1 1 0), the most active face at the same potential [17].

The Tafel behaviour in the mixed kinetic-diffusion control region was also examined by using mass-transport corrected currents. The Tafel sloped obtained at $f = 1500$ rpm 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 plays a decisive role on the kinetics of oxygen reduction.

For the purpose of comparison we have recorded the polarization curves for O_2 reduction on smooth Pt and Pt particles spread on platinum. The two electrodes exhibit practically similar catalytic activity and, moreover, the curves are only slightly dependent on the potential sweep direction. On the other hand, the activity of Pt particles spread onto the gold surface depends strongly on the potential sweep direction. It is lower than the activity of smooth Pt in the negative going sweep, but it is markedly higher in the positive sweep. This behaviour tends to indicate the existence of Pt particle–Au substrate interactions. The significant hysteresis on the polarization curves shows that the oxygen reduction reaction is much faster on a reduced than on an oxidized surface of the Pt adlayer. The difference in the catalytic activity of reduced and oxidized surface is a characteristic property for Pt and many other metal electrodes. However, such a large difference between the positive going and the negative going sweep was never observed in the past for the reduction of oxygen on platinum and Pt based electrocatalysts. This behaviour is certainly associated with the Pt–OH formation and reduction since Pt–OH causes inhibition of the O_2 reduction [18]. Finally, the stability of the catalytic activity of the Pt/(Cu)/Au for the O_2-reduction was examined by continuous cycling of the potential. During the first 10–12 cycles there is no decrease in the catalytic activity, but as the cycling went on, a progressive slight decrease in the catalytic activity was observed for the reduced surface of the Pt particles. The diffusion of Cu atoms through the Pt film to the surface of platinum cannot be totally excluded. Moreover, it is known that Cu(upd) adatoms inhibit the reduction of oxygen on platinum [19,20].

4. Conclusion

The preliminary data presented in the present paper indicate that the modified Pt(Cu)/Au electrodes have a significant catalytic activity towards the reduction of oxygen. This study indicated that the catalytic activity is a function of the potential scanning direction. This dependence is probably an indication that Pt–OH formation is affecting the kinetics of the oxygen reaction. On one hand, the modified electrode is less active than polycrystalline platinum during the negative going scan but on the other hand it exhibits a significantly higher activity in the positive going sweep. Bimetallic interaction or surface alloying is probably responsible for the modification of the Pt–OH formation and reduction since there is a shift of the Pt oxide reduction peak of about 100 mV to less positive values. Further investigations are planned in order to provide a consistent explanation (for example, comparison of electroless deposition of Pt versus direct plating).

Finally, the general displacement reaction

$$2Cu^0/Au + PtCl_6^{2-} \rightarrow Pt^0/Au + 2Cu^{2+} + 6Cl^-$$

is probably one of more reactions that actually can take place during the dissolution of the copper layer. A possible disproportionation of platinum complexes and the thermodynamic stability of copper (I) complexes in high Cl^- concentrations are likely to complicate the exchange process proper. The platinum loading of this modified electrode is very low and its activity as good if not better than a bulk catalyst. At this stage, the RDE measurements were not able to discriminate between a direct 4e$^-$ reduction of oxygen or a possible reduction involving a fast catalytic decomposition of H_2O_2 [21]. Further investigation will be carried out in order to fully understand the exchange mechanism and the catalytic behaviour of the modified electrode.

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