Study of gold-platinum and platinum-gold surface modification and its influence on hydrogen evolution and oxygen reduction

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Abstract: Surface modification of the electrodes was conducted from sulfuric acid solutions containing the corresponding metal–chloride complexes using cyclic voltammetry. Comparing the charges of the hydrogen underpotential deposition region, and the corresponding oxide reduction regions, it is concluded that a platinum overlayer on gold forms 3D islands, while gold on platinum forms 2D islands. Foreign metals present in an amount of up to one monolayer exert an influence on the change in reaction rate with respect to both hydrogen evolution (HER) and oxygen reduction (ORR) reactions. A platinum overlayer on a gold substrate increases the activity for HER and for ORR, compared with pure gold. These results can be understood in terms of a simple model, in which the change in the H and OH binding energies are directly proportional to the shift of the d-bond center of the overlayer. On the contrary, a gold layer on platinum slightly decreases the activity for both reactions compared with pure platinum.

Keywords: platinum, gold, modified electrodes, hydrogen evolution, oxygen reduction.

INTRODUCTION

The electrochemical evolution of hydrogen and the reduction of oxygen are reactions of considerable interest at the present time, especially in relation to the development of new electrode materials for energy conversion in fuel cells, metal–air batteries, water electrolysis, as well as from a fundamental point of view.[1,2] For both cathodic reactions, platinum is the best-known electrocatalyst in acid solutions. Moreover, Pt catalyzes meny other technologically important reactions.[3]

Unfortunately, the very high price of platinum requires new catalysts to be found for these reactions. Considering the importance of the activity of the

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electrocatalysts used as the cathode, 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. The study of electrodes modified with nanoparticles as catalytically active materials has received increased attention in recent years because of their important role in electrocatalysis.[4–10]

Although, Damjanović[11] over twenty years ago pointed out that enhancement of the activity of platinum in the ORR could be expected by surface modification of the Pt with Au, up to now, only a few studies of Pt–Au and Au–Pt nanoparticle-modified electrode systems have been reported.

Pedersen *et al.*[12] investigated the growth and reactivity of vacuum evaporated Pt on Au (111) in UHV using CO as the probe molecule. They suggested that an increased reactivity of the Au (111)-Pt system could be expected for other adsorbates and reactions as well.

Berg *et al.*[13] investigated the nucleation and growth of Au overlayers on the hexagonally reconstructed Pt(100) surface by scaning tunneling microscopy (STM) and photoelectron spectroscopy. They found that nucleation occurred preferably at the step edges intersecting the reconstruction rows. Islands also nucleate at structural defects in the surface. The STM images showed that Pt atoms are incorporated into the first monolayer of the Au islands, contributing to about 20 % of the island area. Growth of second monolayer islands starts well before completion of the first monolayer. High-resolution photoelectron spectroscopy measurements showed contributions to the Au 4f $_{7/2}$ core level spectrum from Au atoms in four different local environments in the surface: Au atoms at the Pt interface at (83.32 ± 0.02) eV binding energy, surface Au atoms with (1×1) symmetry at 83.50 ± 0.02) eV binding energy, surface Au atoms with a (1×7) symmetry at (83.63 ± 0.02) eV and bulk-like Au atoms at (83.87 ± 0.02) eV.

Waibel *et al.*[14] investigated the deposition of Pt onto unreconstructed Au (111) and Au (100) by cyclic voltammetry and *in-situ* STM from 0.1 M H_2SO_4+0.1 mM K_2PtCl_4. In both cases, a rather high overpotential for Pt deposition was observed, most probably due to the high stability of the $[PtCl_4]^{2-}$ complex. Nucleation of Pt starts mainly at defects, such as step edges for low deposition rates and three-dimensional clusters are formed. Due to the high overpotential, some nuclei appear also on the terraces at random sites.

Van Brussel *et al.*[15] investigated the performances of gold-supported Pt, prepared by replacing Cu adlayers, as catalysts for the ORR in 0.1 M $HClO_4$. The kinetics of the ORR on this platinum modified electrode was studied by the rotating disc electrode technique (RRDE). It was found that the activity of the electrode was lower than the activity of a smooth Pt electrode in the negative going potential scan, but significantly higher in the positive going scan.

El-Deab and Osaka[16] investigated the ORR at Au nanoparticles electrodeposited on Pt electrodes (Pt–Au electrodes) in 0.1 M KOH solution. Cyclic voltam-

metry and RRDE techniques were used in this investigation. It was found that the reaction pathway of the ORR to either HO_2^- or OH^- was highly dependent on the electrode potential and the Au surface coverage of the Pt electrode. The electrodes exhibited different electrocatalytic behavior in three potential regions: at $E > -300$ mV *vs.* SSC, the 2-electron reduction of O_2 to HO_2^- predominated, at $-300 > E > -500$ mV, the 4-electron reduction predominated, and at $E < -500$ mV, the 2-electron and 4-electron reduction pathways proceed concurrently. The increase of the surface coverage of Au on the Pt electrodes lead to a loss of activity of O_2 reduction to HO_2^-. This behavior was explained by the potential dependence of the amount and the nature of the adsorbed species on the Pt–Au electrode surface.

As pointed out, platinum is the best-known electrocatalyst for the ORR and the HER, while gold is less expensive but is a very poor catalyst, with good corrosion stability in acid solution. Hence, the aim of this work was to study surface modification of platinum by gold and gold by platinum and to determine in the change of the reaction rates of the hydrogen and oxygen reactions in dependence on the modification of the surface.

EXPERIMENTAL

All measurements were performed in a conventional three-compartment glass cell. The reference electrode was the saturated calomel electrode (SCE). All experiments were performed at a temperature $T = 300 \pm 1$ K. Pt ($A = 0.072$ cm^2) and Au ($A = 0.196$ cm^2) working electrodes were in a rotating disc configuration (RDE). The polycrystalline Pt and Au electrodes were polished with 0.1 and 0.05 μm Al_2O_3 slurries, followed by ultrasonic bath cleaning. From the coverage in the hydrogen underpotential deposition region, a roughness factor of 4.1 was calculated. Deposition of Pt on Au and Au on Pt were performed from 0.5 M H_2SO_4 containing 0.1 mM of H_2PtCl_6 and $HAuCl_4$ (dissolved in 0.1 M HCl to avoid hydrolysis), respectively. Cyclic voltammetry experiments ($v = 50$ mV s^{-1}) were conducted on deposited and characterized surfaces of platinum modified with gold (Pt–Au) and gold modified with platinum (Au–Pt), while the kinetics measurements were performed in a solution of 0.5 M H_2SO_4, prepared using bidistilled water.

In all experiments a potentiostat/galvanostat PAR M273 connected to a PAR 5301 lock-in amplifier, controlled by a computer through a GPBI PC2A interface, was used. EIS measurements were performed to determine the ohmic resistance of the electrolyte.

RESULTS

Deposition and characterization of the Pt deposits onto the Au electrode

Figure 1 shows cyclic voltammograms for a polycrystalline Au electrode in argon purged 0.5 M H_2SO_4 + 0.1 mM H_2PtCl_6 solution, as well as for an Au electrode in pure 0.5 M H_2SO_4 solution, starting from a potential of 1.2 V in the cathodic direction, at a sweep rate of 50 mV s^{-1}. The deposition of platinum started at a potential of about 0.4 V, reaching a limiting-like diffusion current density at ≈ 0.2 V. During the first sweep, the appearance of a hydrogen underpotential deposition, H_{upd}, region ($-0.25 < E < 0.05$ V), and a platinum-like oxide region ($E > 0.55$ V) indicated that deposition of metallic platinum had occurred on the covered Au surface. In the second (not shown), and in the third scan it was difficult to resolve
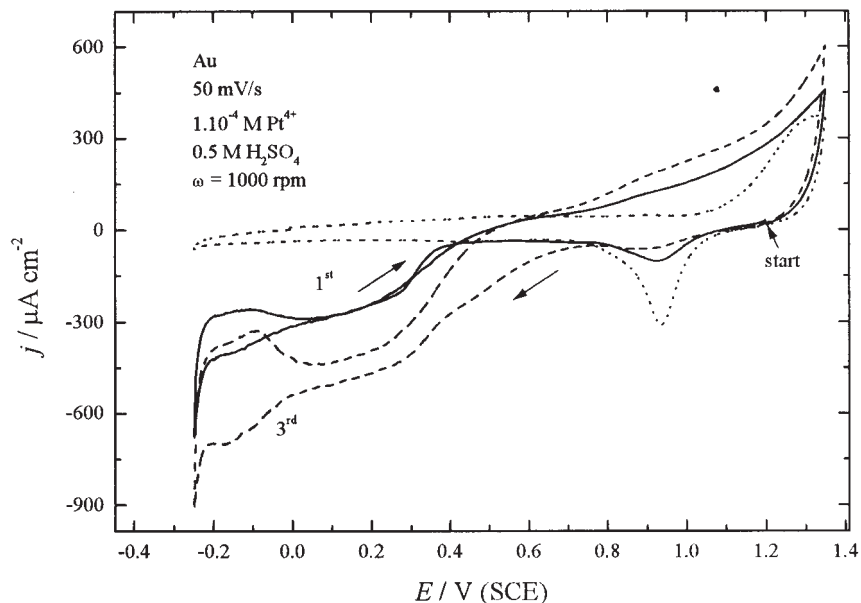
Fig. 1. First (–) and third (– – –) scan for a polycrystalline Au electrode in argon purged 0.5 M H$_2$SO$_4$+0.1 mM H$_2$PtCl$_6$, at a sweep rate of 50 mV s^{-1}, as well as for an Au (····) electrode in pure 0.5 M H$_2$SO$_4$.

where the platinum deposition on a Au covered surface started, due to the reduction of platinum oxide in the same potential region. A further increases of the H$_{upd}$, oxide region, and the appearance of a Pt double layer suggested that platinum deposition occurred during the cathodic scans. After the third scan, the electrode was washed and transferred to a cell with pure 0.5 M H$_2$SO$_4$ solution. The deposition of Pt on Au was fairly reproducible on the basis of the electrochemical behaviour of the Pt–Au electrodes.

The comparison of the cyclic voltammograms of bare Pt and Au electrodes with that of a Pt modified Au electrode in argon purged 0.5 M H$_2$SO$_4$ solution is shown in Fig. 2. The shapes of the cyclic voltammograms for bare polycrystalline Pt and Au electrodes in sulfuric acid solution are well established in the literature,[17,18] so they will not be discussed further here. The shape of the cyclic voltammogram of Au–Pt has the characteristics of both metals. In the cathodic direction, in the potential region of $0.8 < E < 1.1$ V, reduction of Au oxide was observed followed by the reduction of Pt oxide and the existence of a Pt–H$_{upd}$ region at negative potentials. In the anodic direction, the cyclic voltammogram is more like that of Pt, except there is some increase of oxide region above 0.8 V, due to the oxidation of uncovered Au surfaces.

In Table I, the charges under the current peaks characteristic for H$_{upd}$ deposition and for the reduction of PtOH and AuOH species for pure metals and gold modified by platinum are given, as well as the calculated values of the coverage with platinum.
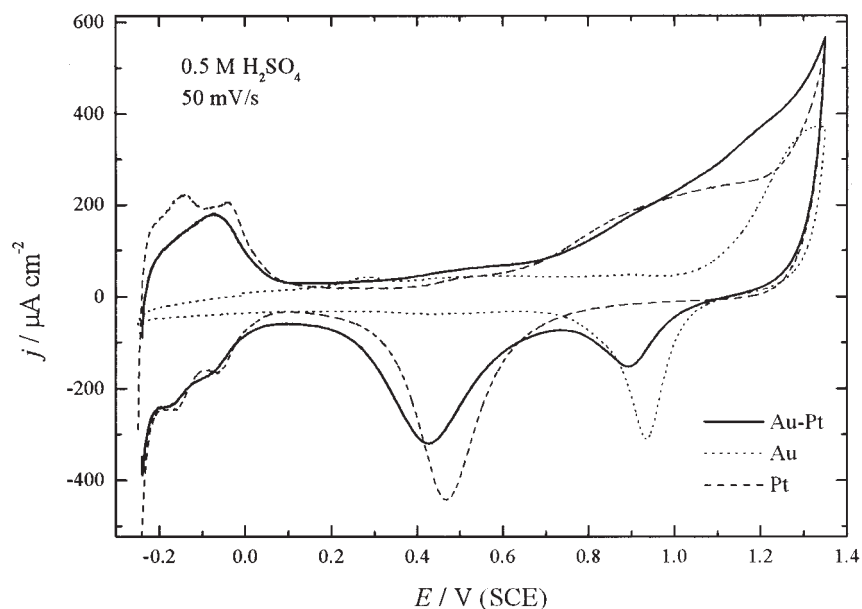
Fig. 2. Comparison of the cyclic voltammograms ($v = 50$ mV s^{-1}) of pure Pt and Au electrodes with that of a Pt modified Au electrode in argon purged 0.5 M H$_2$SO$_4$.

TABLE I. The values of the coverage of gold with platinum and relevant charges on Pt, Au and Au–Pt electrodes

	Q(H$_{upd}$)/μC cm^{-2}	Q(PtOH)/μC cm^{-2}	Q(AuOH)/μC cm^{-2}
Pt	980	1952	–
Au	–	–	868
Au–Pt	710	1589	590
θ(Pt)	0.72	0.81	0.32

From the H$_{upd}$ region, the active Pt sites on the Au electrode were 0.72 compared with those on a pure Pt electrode. Comparison of H$_{upd}$ region did not give the true coverage value. From the charge decrease of the Au–OH reduction peak on the Au–Pt electrode, compared with a pure Au electrode in the same potential region, the coverage with platinum was calculated to be 0.32. The platinum coverage on gold was estimated from the gold oxide reduction region, assuming that Pt deposition occurred through 3D nucleation, which is agreement with the conclusion given in the literature.[12,14]

The most important difference observed with the Au–Pt electrode compared with the pure metals is a broadening and a negative shift of the oxide reduction peaks of both metals. This could imply changes of the electronic properties of the surface, provoking stronger repulsive interactions between adsorbed oxygen containing species and increase of their binding energies, which is in compliance with

the UHV results given by Pedersen *et al.*[12]

Deposition and characterization of the Au deposits onto the Pt electrode

The cyclic votlammograms for a polycrystalline Pt electrode in an argon purged 0.5 M H_2SO_4+0.1 mM $HAuCl_4$ solution and that for a Pt electrode in a pure 0.5 M H_2SO_4 solution, starting from a potential of 1.2 V in the carthodic direction, at sweep rate of 50 mV s^{-1} are shown in Fig. 3. The deposition of gold started at a potential of about 1.0 V through two waves. It was observed that the charge of the H_{upd} region decreased during the cathodic sweep indicating that gold was deposited. In the anodic sweep, after H_{upd} region, deposition of gold continued up to a potential of ≈ 0.85 V. Above this potential, two shoulders and one peak at 1.2 V were observed. The nature of these features is not clear. They could be attributed to the oxidation of small amounts of Au^{1+} produced during the deposition or oxidation of chlorine anions (≈ 1 mM), which are present in the solution. These features were not observed in pure H_2SO_4 (see Fig. 4). During the second (not shown), and the third scan, a further decrease of the H_{upd} region, the reduction of platinum oxide and an increase of the gold oxide reduction peak ($E = 0.95$ V) were observed. After the third scan, the electrode was washed and transferred into a cell containing a pure 0.5 M H_2SO_4 solution.

The cyclic voltammograms of a pure Pt, a pure Au electrodes, as well as of a Au modified Pt surface are show in Fig. 4. The shape of the cyclic voltammogram of Pt–Au has characteristics similar to those of a Au–Pt modified surface.
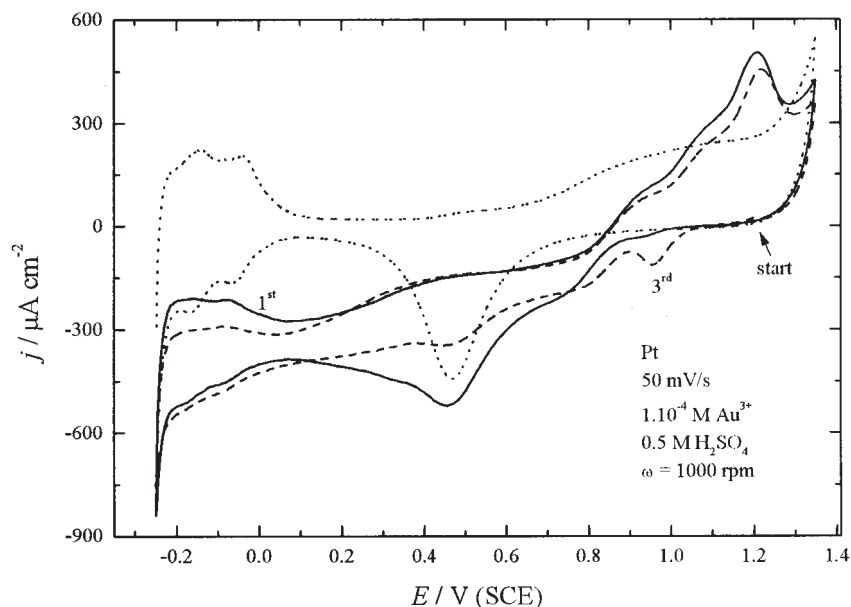

Fig. 3. First (–) and third (– – –) scan for a polycrystalline Pt electrode in argon purged 0.5 M H_2SO_4+0.1 mM $HAuCl_4$, at a sweep rate of 50 mV s^{-1}, as well as for a Pt ($\cdots$) electrode in pure 0.5 M H_2SO_4.
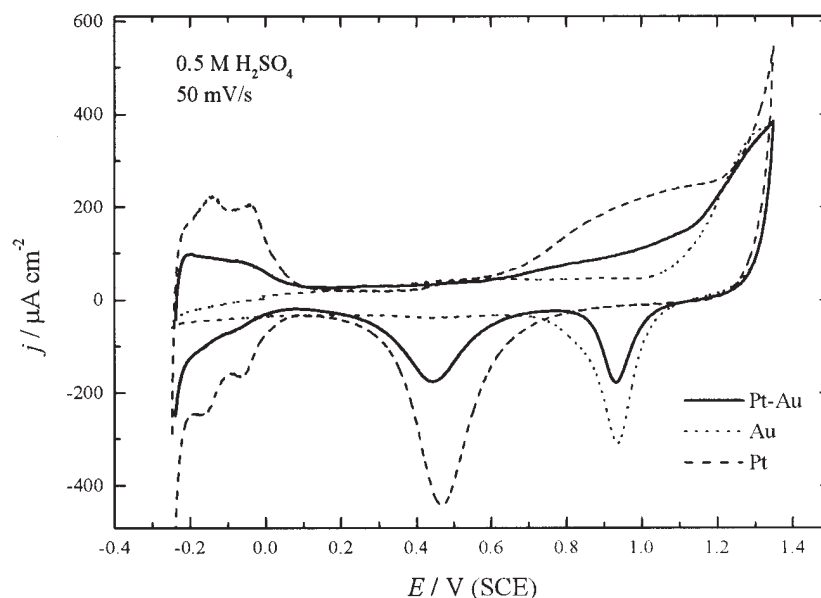
Fig. 4. Comparison of the cyclic voltammograms (ν = 50 mV s^{-1}) of pure Pt and Au electrodes with that of an Au modified Pt electrode in argon purged 0.5 M H$_2$SO$_4$.

The charges under the current peaks characteristic for H$_{upd}$ deposition and the reduction of PtOH and AuOH species for platinum modified by gold, as well as the calculated values of the coverage with gold are given in Table II.

TABLE II. The values of the coverage of platinum with gold and the relevant charges on an Au–Pt electrode

	Q(H$_{upd}$)/μC cm^{-2}	Q(PtOH)/μC cm^{-2}	Q(AuOH)/μC cm^{-2}
Pt–Au	502	1034	480
θ(Au)	0.51	0.53	0.45

The coverage of platinum with gold was estimated by comparing the charges for the gold/platinum oxide reduction regions and the H$_{upd}$ those of the pure metals. With all three methods the gold coverage was estimated to be $\approx 0.45 - 0.53$. It is reasonable to conclude from these results that Au deposition occurred through 2D nucleation and the formation of 2D Au islands on the Pt surfaces.

Hydrogen evolution and oxygen reduction reactions

Hydrogen evolution and oxygen reduction were selected as probes for the assessment of the catalytic activity of the modified electrodes.

Hydrogen evolution reaction. After electrochemical characterization of the electrodes, the electrolyte was saturated with pure argon and the hydrogen evolution reaction was examined applying a slow potentiodynamic sweep of 1 mV s^{-1} on all four surfaces, as shown in Fig. 5. The starting potential was $- 0.240$ V (SCE).
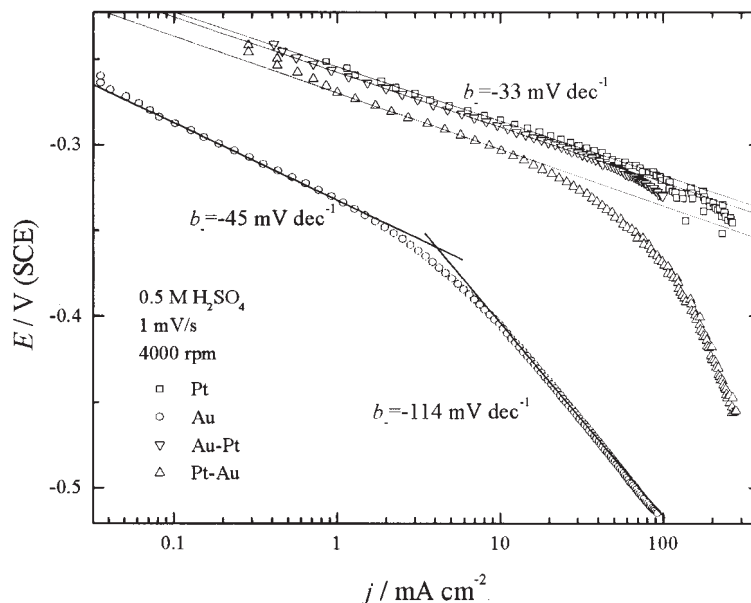
Fig. 5. Polarization curves (IR corrected) for the hydrogen evolution reaction on Pt, Au, Pt–Au
and Au–Pt electrodes.

For the pure Pt electrode, a single Tafel slope of –33 mV dec^{-1} and an exchange current density, j_0, of 0.33 mA cm^{-2} were obtained, which is in agreement with literature data for an "active platinum electrode".[19] In higher current density region (hcd), even with a high rotation rate of the electrode, the current was unstable due to the high rate of formation of hydrogen bubbles. The pure gold electrode exhibited two well-defined Tafel slopes, at lower current densities (lcd) –45 mV dec^{-1}, and –114 mV dec^{-1} at the higher current densities (hcd), with j_0 of ≈ 0.01 mA cm^{-2}.

The slope of –33 mV dec^{-1} for the Pt electrode is explained through Volmer–Tafel sequences with the Tafel step being the rate-determining step (rds). The two slopes for the gold electrode are explained with Volmer–Heyrovsky sequences with the Heyrovsky step being the rds. The change of the value of the slope occurs due to a change of hydrogen coverage with potential. It should be noted that in the negative going sweep (not shown), the lcd slope changes from -45 mV dec^{-1} to ≈ -60 mV dec^{-1}, indicating changes in the hydrogen coverage, θ_H, and adsorption conditions, which are explained by the surface diffusion of adsorbed hydrogen.[19] Therefore, it seems that the observed slopes in the lcd region are strongly dependent on the electrode pretreatment.

With the Au–Pt surface, a slope of –33 mV dec^{-1} and $j_0 = 0.25$ mA cm^{-2} were observed, indicating the same kinetics as with a Pt electrode, but the activities were $\approx 25\,\%$ smaller than with the pure Pt electrode. This result is in excellent agreement with data obtained of 0.72 active Pt sites on Au electrodes. Therefore, it seems that

Au does not influence the kinetics of the HER, and the high activity of Au–Pt electrodes for the HER is only due to the Pt overlayer.

The Pt–Au electrode has a Tafel slope of -33 mV dec^{-1} ($j_0 = 0.12$ mA cm^{-2}) up to a current density of ≈ 15 mA cm^{-2}. At higher current densities, the slope changes and a limiting-like current was observed. This current is not dependent on the rotation rate, and super-saturation with gaseous hydrogen is not be expected under 4000 rpm.[19] Therefore, the limiting-like current is most probably a reaction limiting curent of the Tafel step under conditions that $\theta_H \to 1$. The approximately ≈ 35 % activity of Pt–Au compared with pure Pt indicates that Au atoms suppressed the Tafel step on 10 to 15 % of the active Pt sites, which is expected bearing in mind that the gold coverage was $\approx 0.45 - 0.50$. On the basis of these results, it is difficult to differentiate which effect, electronic and/or geometric, plays a dominant role in the HER on a Pt–Au electrode.

Oxygen reduction reaction

The oxygen reduction reaction (ORR) on all the above-mentioned surfaces were investigated in solutions saturated with pure oxygen by applying a slow potential sweep of 1 mV s^{-1}. The starting potential for the cathodic scan was the equilibrium potential, established after cleaning the electrode by cycling the potential in the potential range from $- 0.3$ to 1.4 V. The results are shown in Fig. 6.
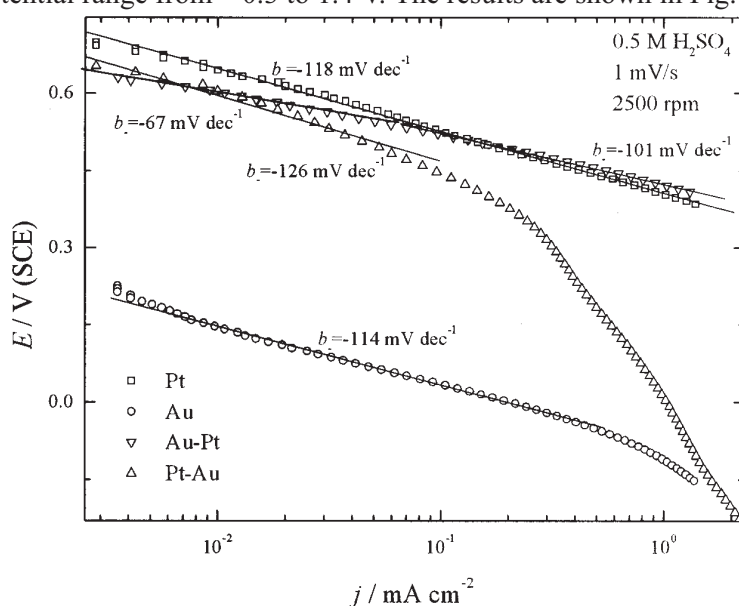

Fig. 6. Polarization curves for the oxygen reduction reaction on Pt, Au, Pt–Au and Au–Pt electrodes. Data for Pt and Au–Pt were corrected for diffusion effects.

On a pure Pt electrode, after corrections for diffusion effects, a single Tafel slope of -118 mV dec^{-1} over two and a half decades was obtained. The Au elec-

trode had dramatically smaller activities, with similar slopes of –114 mV dec^{-1}. The Au–Pt modified electrode is characterized by two slope, – 67 mV dec^{-1} in the lcd region and –101 mV dec^{-1} in the hcd region. The activity of the Au–Pt modified electrode compared with Pt is smaller in the lcd region, but in the hcd region it is even more active than pure Pt.

The ORR on a Pt–Au modified electrode is strongly dependent on the applied potential, with two separated reduction waves. Above ≈ 0.5 V, a Tafel slope of –126 mV dec^{-1} was observed (note: the polarization curve was not corrected for diffusion effects), after which two mixed activation–diffusion like regions had proceeded.

It is well known that the kinetics of oxygen reduction in acid solution is strongly dependent on the nature of the surfaces and products produced, whether H_2O or H_2O_2.

On pure polycrystalline Pt, a 4-electron direct path has been well established.[21] The first step in the overall reaction path is the adsorption of O_2 followed by the process of protonation as the rate-determining step. The single Tafel slope of –118 mV dec^{-1}, in the investigated current density region, means that interaction between the oxygen reduction intermediates $O_{2,ads}$ and Pt–OH can be neglected on a Pt surface.

On the contrary, on polycrystalline gold electrodes, the production of hydrogen peroxide as an intermediate (serial path) has been reported in numerous studies.[16,21,22] The value of the Tafel slope, close to –120 mV dec^{-1}, suggests that the rate-detemining step is the first electron-transfer reaction.

On a Au–Pt electrode, the Tafel slopes of ≈ – 60 and –100 mV dec^{-1} could be explained in the way given in previous papers,[23,24] where the significance of the coverage dependent pre-exponential and exponential energetic terms of the kinetic rate expression was indicated.

A slope of – 60 mV dec^{-1} was obtained if the exponential energetic part played a dominate role, which included interaction of the oxygen reduction inermediates $O_{2,ads}$ and Pt–OH and/or Au–OH species on the surfaces. On the other hand, a slope of –100 mV dec^{-1} was obtained if the coverage dependent pre-exponential factor played a dominant role. Therefore, in the lcd region, interactions of the adsorbed species are responsible for the slope of – 60 mV dec^{-1}, while in the hcd region, oxygen containing species remaining on the surfaces produce the slope of –100 mV dec^{-1}. These observations are in agreements with cyclic voltammetry experiments (Fig. 2). In this stage, without RRDE experiments, it is impossible to discuss the reaction pathway on this surface.

CONCLUSION

Platinum overlayer on gold and gold overlayer on platinum have been successfully deposited from sulfuric acid solutions containing the corresponding

metal–chloride complexes, using cyclic voltammetry. Comparing the charges of the hydrogen underpotential deposition region and the corresponding oxide reduction regions, it can be concluded that the platinum overlayer on gold forms 3D islands, while gold on platinum forms 2D islands. It was found that a platinum overlayer on a gold substrate dramatically increases the activities for HER and ORR, compared with pure gold. In the high current density region, Au–Pt electrodes show even higher activities than pure platinum, due to the changes of the adsorption conditions of the ORR intermediates. On the contrary, a gold layer on platinum slightly decreases the activity for both reactions compared with pure platinum. It is concluded that the kinetics of the HER on platinum was not affected by the gold overlayer, but a limiting reaction current density for the HER was observed above 15 mV cm^{-2}. The kinetics of the ORR changed and a platinum overlayer on a gold substrate increases the activities for this reaction since a gold layer on platinum slightly decreases the activity for this reaction. Due to the high price of platinum and the limited world reserves, it is reasonable to suggest that platinum modified gold electrodes in nano-scale technology could be potentially good replacements for pure platinum as catalysts for the oxygen reduction reaction, especially in low temperature fuel cells.

ИЗВОД

ПОВРШИНСКА МОДИФИКАЦИЈА ПЛАТИНЕ ЗЛАТОМ И ЗЛАТА ПЛАТИНОМ И ЊЕН УТИЦАЈ НА РЕАКЦИЈЕ ИЗДВАЈАЊА ВОДОНИКА И РЕДУКЦИЈЕ КИСЕОНИКА

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Површинска модификација платине златом и злата платином је извршена из раствора сумпорне киселине и одговарајућих хлоридних комплекса метала применом цикличне волтаметрије. Поређењем количине наелектрисања у области потпотенцијалне депозиције водоника и одговарајућих области редукције оскида чистих и модификованих електрода закључено је да платина на злату формира 3D, а злато на платини 2D острва. Активности овако модификованих површина за реакције издвајања водоника и редукције кисеоника у раствору сумпорне киселине поређене са активностима чистих метала. Електрода од злата модификована платином значајно увећава активност за обе испитиване рекације у поређењу са чистим златом. Са друге стране, електрода од платине модификована златом има незнатно мању активност у поређењу са чистом платином. Због ограничених ресурса и високе цене платине платина модификована златом може бити замена за чисту платину као добар катализатор за реакцију редукције кисеоника, посебно у горивим спреговима у области ниских температура.

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