



# Ultra-low platinum coverage at gold electrode surfaces: A different approach to the reversible hydrogen reaction



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## ARTICLE INFO

### Article history:

Received 17 June 2016

Received in revised form 16 September 2016

Accepted 20 September 2016

Available online 21 September 2016

### Keywords:

Gold electrode

Platinum ad-atoms

Active site

Hydrogen reaction

Rotating electrode

Diffusion

Adsorption

Electron transfer

Butler-Volmer formalism

## ABSTRACT

The hydrogen reversible reaction (HRR) with ultra-low concentrations of platinum sites supported on a gold substrate is studied with decreasing amounts of active sites (estimate coverage range from 0.006 to  $10^{-5}$ ) at a rotating electrode in a 0.5 M  $H_2SO_4$  solution. These particular experimental conditions allow the voltammetric study of the HRR without diffusion limitation in the whole range of potential. In the absence of a more precise determination of the amount of platinum surface sites, a method is given to compare results obtained from distinct experimental runs. Once eliminated the contribution of gold to the current recorded, it becomes possible to normalize the currents in the entire range of platinum coverage. It shows that below 0.2 V, the normalized HER and the HOR currents are linearly connected to the amount of active sites. At higher potentials the normalized currents indicate a systematic decrease of the efficiency of the active sites for HOR that deviates from linearity when their surface concentration decreases. Around the reversible potential, the voltammetric profiles obey to the Butler-Volmer formalism. The conditions of its applicability are discussed. The simulation of the experimental current allows the determination of the partial oxidation and reduction currents. The simulated reduction current is then compared to the HER current recorded in a solution without dissolved hydrogen and saturated with argon. The close fit of the two responses gives evidence for the possibility to have access to HER kinetic data free of diffusion. Finally a comparison is made between results obtained at ultra-low content of platinum active sites with pure platinum as well as for an intermediate coverage of gold with platinum.

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## 1. Introduction

In a previous work [1] it was reported how a clean gold electrode, a well characterized and non-active material for hydrogen oxidation reaction (HOR) stays inactive when cycled in an acidic solution free of platinum group metal (PGM) impurities. It was shown that it became active for this reaction after successive polarization cycles if the solution contained platinum cations even at a concentration as low as  $10^{-10}$  to  $10^{-9}$  M. In this case a progressive activity of gold for the HOR was observed when using the well known protocol of electrochemical activation. Resulting CVs are then comparable to those reported in previous works and interpreted by their authors as an intrinsic activity of the gold electrode surface for the HOR due to the formation of gold active sites in a particular surface structure induced by the electrochemical treatment [2–4]. From the experiments reported in ref. [1], the observation of HOR activation at gold electrode is attributed to the presence at

the gold surface of an active impurity, in most cases platinum, or other platinum metals previously present in the cell in hardly detectable amount in the solution. The presence of impurity of this kind may be commonly the case in electrochemical experiments when platinum is routinely used as constitutive element of electrochemical cells despite the risk of contamination already recognized in 1965 [5], mentioned several times latter [6,7] and also discussed in relevant review articles [8 and references therein]. Once determined the chemical origin of the activation of the gold electrode, it may be taken advantage of the particular profile of the hydrogen reversible reaction (HRR), showing substantial and fundamental differences from that generated by a platinum electrode in acidic medium. The main feature of an ultra-low surface concentration of platinum on gold is to push away the effect of hydrogen diffusion on the limitation of the reaction current when this system is used as rotating disc electrode (RDE) more efficiently than under other conditions [9,10]. This is due to the large inversion of the value of the ratio between the amount of reactive sites at the surface to the amount of reactant entities available on the solution side of the interface when compared to a platinum electrode. It results a wide potential range where the reaction appears under the control of the overpotential with a well-marked voltammetric profile of Butler-Volmer type around the equilibrium potential [1]. In contrast to alkaline

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<sup>1</sup> Professor Aldaz has intensively participated to the various steps of this work. Unfortunately his death did not allow him to know the complete version of the manuscript that contains all the ideas he discussed and nothing unknown from him.

solutions [11,12], this type of profile is never observed in acidic solutions with a platinum electrode [12] or a gold electrode with higher coverage in platinum sites [13] or when mass transport is increased by using a nanosized platinum electrode [9]. This particular situation gives the opportunity for a determination of the kinetic parameters controlling the HRR without diffusion effect of molecular hydrogen reactant. The success of this approach depends on a strict control of the surface of the gold substrate in platinum adatoms content during the recording of the intensity-potential curve of the hydrogen reaction under potentiodynamic regime. In conflict with this requirement, the cyclic voltammograms (CV) reported in ref. [1] were recorded previously during the accumulation of the platinum sites on gold surface. Nevertheless a stationary CV profile was reached. This finding was interpreted as an exact balance between the amount of sites created by deposition during the cycle and the amount lost in the same. If this mechanism may explain the achievement of the stationary conditions, it becomes possible to study the hydrogen reaction during the stripping of the platinum sites in a solution free of platinum ions eliminating the risk of a deposition of platinum in a cycle. A comparison of the results obtained during the formation and the elimination of the active sites would be useful in validation of the results obtained with an extreme dilution of active surface sites. Starting from a gold electrode with an ultra-low platinum coverage, the aim of this work is the study of the hydrogen reaction when decreasing amounts of platinum result from applied cycles until the complete loss of the electrode activity for the HOR. The so-called protocol of activation, in this case, works as a deactivation process by anything else than its cleaning properties.

## 2. Experimental

The experimental setup is the same than that used in the previous study [1]. Very briefly, two electrochemical cells were used (denoted respectively cell 1 and cell 2) with gold counter-electrodes checked free of platinum. The use of a hydrogen electrode as reference electrode was carefully controlled and designed to avoid any contamination of the solution contained in the compartment where the electrode is tested. Both cells were filled initially with the same solution 0.5 M H<sub>2</sub>SO<sub>4</sub> in equilibrium either with an argon or a hydrogen atmosphere. In the last case, the absence of residual oxygen whose reduction wave on gold occurs below 0.5 V has to be ascertained. In cell 2, minute amounts of platinum were introduced by applying some polarization cycles to a platinum bead (usually 10–20 cycles) within the limits of hydrogen and oxygen evolution (from 0.05 to 1.5 V). The resulting content in platinum in cell 2 is between 10<sup>-10</sup> M and 10<sup>-9</sup> M. (for more details see ref. [1]). Solutions with similar concentrations were prepared with platinum salt yielding comparable results but not used in the present work to preserve the cleanliness of the system under investigation. Polarization curves were performed and recorded in potentiodynamic regime with an Autolab PGSTAT302N (Metrohm B.V.) system. The experimental protocol for the formation of platinum sites on the gold surface in cell 2 was described in ref. [1] as a preliminary experimental step. The present study begins once the rotating gold electrode in cell 2 has reached a stationary activity for hydrogen reaction corresponding to a stationary equilibrium between the amount of platinum deposited and dissolved during one CV between -0.1 and 1.75 V vs RHE. This electrode is then transferred to the solution free of platinum (cell 1), where it is taken advantage of the existence of a potential dissolution window of the active sites to follow the hydrogen reaction changes with decreasing amounts of active sites. Thus, in contrast to a solution containing platinum ions (cell 2) [1], it exists in a given cycle a region negative of the platinum deposition potential (0.7 V vs NHE [14]) where the amount of deposited platinum could be stable during the potential sweep, particularly around the hydrogen reversible potential. This last point together with the wider range in platinum surface concentration explored in this work, constitute a drastic difference with the conditions

previously evaluated during platinum sites growth [1] to justify the present approach.

On the other hand, it has been also shown in [1] how the diffusion of hydrogen as limiting reaction process could be avoided at relatively low rotation rate thus eliminating the geometric constraint of the use of a rotating disc electrode. For sake of convenience, the plane gold surface, with hanging meniscus configuration, used in [1] was replaced in the present work by a spherical gold bead with a diameter of 1.9 mm, as a rotating electrode, with its entire surface immersed into the solution.

In the absence of a precise knowledge of the ultra-low concentration in active sites of platinum at the gold surface, the best way to evaluate or to compare the activity between various experimental runs or with various electrodes is to adjust the HRR currents in the same proportion as the amounts of charge required for the reduction of a monolayer of gold oxide formed in defined conditions. These two data are available on the same CV i.e. for the same area of contact with the solution. In this respect, grounded on the charge required for oxide reduction as proposed in [8], comparison of the electrode areas in contact with the solution for different experimental runs will be obtained by measuring, between 1.5 and 0.9 V vs RHE, the total charge evolved for the reduction of the gold surface oxide in a cycle including the HRR and with an upper potential limit of 1.75 V vs RHE. This will be useful in any attempt to compare the results reported in [1] with the present ones and also it avoids the need to know the exact area corresponding to the response of the electrode in contact with the solution including some roughness effects [8,15]. This protocol will be applied in the following for the construction of Fig. 5.

## 3. Results

### 3.1. The stationary platinum coverage

Fig. 1 shows the stationary CVs reached in cell 2 with a platinum concentration around 4.5 · 10<sup>-10</sup> M in 0.5 M H<sub>2</sub>SO<sub>4</sub> as described in [1]. This stationary state for a given solution composition is essentially under the control of the sweep rate, the potential limits and the rotation programme. The stability of the voltammetric profile over the whole potential range, for several cycles, indicates the achievement of a dynamic equilibrium for platinum at the gold surface. During the recording of the CVs, the conditions of rotation were changed to minimize the effects of all kind of impurities. Thus, the stationary CVs shown in Fig. 1 were recorded without electrode rotation in the negative-going sweep until the sharp increase of the current at about 0.14 V corresponding to the activation of the rotation (1500 rpm) maintained in the subsequent positive sweep and stopped at the end of the HOR around 0.8 V. A first attempt at an interpretation of the profile of the positive-going sweep

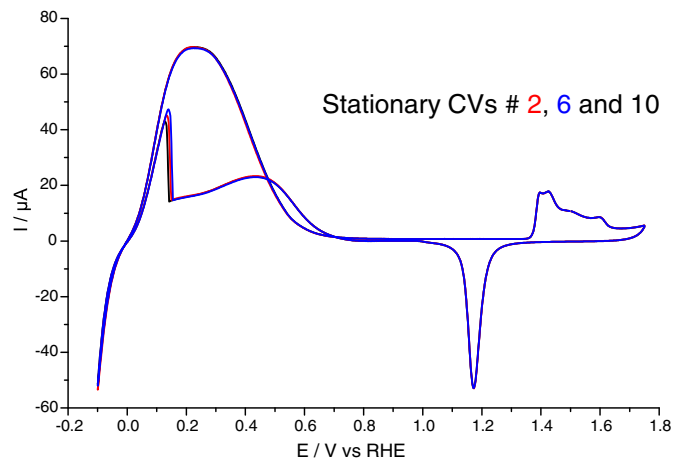


Fig. 1. Stationary CVs of adsorbed platinum active sites on a gold electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> saturated with H<sub>2</sub> gas in cell 2 at a scan rate of 50 mV s<sup>-1</sup>.

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