



Effects of the electrochemically grown hydrous oxide on the hydrogen electrode reaction on iridium electrode



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ABSTRACT

The hydrogen electrode reaction was studied on iridium electrodes covered by a hydrous oxide film in acid solution. The $\text{IrO}_x \cdot n\text{H}_2\text{O}$ film was prepared by the application of repetitive cyclic voltammetry and it was characterized by the charge of the broad voltammetric peak at 0.97 V. It was observed for charges lower than $720 \mu\text{C cm}^{-2}$ a slight increase of both, the H_{UPD} electroadsorption and the steady state limiting current of hydrogen oxidation, with respect to Ir metal. For higher oxide charge values, both variables decrease while a small anodic peak appears at 0.65 V. This behaviour was explained on the basis of the formation of two types of Ir oxide depending on the film thickness and the water concentration profile, which changes the site where the hydrogen reaction takes place.

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1. Introduction

The iridium electrode, unlike the rest of the noble metals, has a great ability to form thick films of hydrous oxides [1–8]. It is known that when it is subjected to a repetitively linear cyclic voltammetry perturbation in 0.5–1 M H_2SO_4 solution between a lower potential E_1 near zero (vs. RHE) and an upper potential $E_2 \geq 1.40$ V at sweep rates comprised in the range 0.04–0.15 V s^{-1} [1–6], a thick layer of hydrous oxide ($\text{IrO}_x \cdot n\text{H}_2\text{O}$) is formed. This film is also obtained by the application of a square wave potential signal, between the same potential limits or with lower values of E_2 [7,8]. The oxide layer is visualized in a potentiodynamic profile as a reversible couple in the potential region comprised between 0.7 V and 1.2 V, with a current peak at 0.96 V. Moreover, the film obtained exhibits a markedly different behaviour with respect to the other noble metals. The most important characteristics are: (i) oxide layer grows with the increase of the number of applied potentiodynamic cycles (triangular sweep or square wave), it is amorphous, its stoichiometry is undefined and it is inhomogeneous in depth. It can reach a thickness equivalent to hundreds of adsorbed oxygen monolayers, as it can be derived from the charge involved in the oxidation/reduction process [6]. (ii) Oxide exhibits highly reversible redox behaviour, being the cathodic peak almost a mirror image of the anodic peak [1–8]. This redox couple corresponds to the transition $\text{Ir}^{+3}/\text{Ir}^{+4}$ of oxide species [9–12], while it is not observed any reduction process to Ir metal yet under hydrogen evolution

[13]. Moreover, a small peak can be observed at approximately 0.65 V [1–7]. (iii) Hydrous Ir oxide exhibits electrochromism, originated in the proton flow to or from the oxide layer during the oxidation/reduction process [10,11,14]. (iv) The process of adsorption/desorption of underpotentially deposited hydrogen (H_{UPD}) still takes place although the electrode surface is completely covered by the iridium hydrous oxide. It only disappears when the oxide film reaches significantly high thickness values [15]. On the other hand, it is well known that the inhibition of the H_{UPD} adsorption sites is always accompanied by a decrease in the reaction rate of the hydrogen evolution [16,17], although the surface sites involved are different. All these aspects emphasize the role played by the Ir electrode pretreatment on its electrocatalytic activity towards hydrogen electrode reaction (HER). It has been already studied on iridium electrodes on both overpotential regions, that corresponding to the hydrogen evolution reaction and that where the hydrogen oxidation reaction takes place [18,19]. The electrode was previously subjected to a thermal treatment under hydrogen atmosphere in order to ensure that the reaction took place on metallic iridium. On the other hand, G. Bronöel and M. Haim [20] studied the hydrogen oxidation on an Ir electrode previously subjected to 200 voltammetric cycles between $0.03 \leq E / \text{V}$ (vs. RHE) ≤ 1.40 in sulphuric acid solution. Although the authors did not include a voltammogram of the cycled electrode, it should be covered by the hydrous oxide film and therefore the results obtained cannot be compared with those recorded on Ir metal.

Taking into account that the voltammetric cycling technique, widely used as electrode pretreatment, produces on iridium the formation of an

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irreducible oxide layer, the objective of the present work is the analysis of the influence of the oxide growth process on the hydrogen electrode reaction in acid solution.

2. Materials and methods

2.1. Electrode preparation

The iridium electrodes were prepared via sputtering on a glassy carbon (GC) substrate from an iridium target (Goodfellow) in an argon atmosphere (0.1 mbar), using a sputter coater Emitech K500X, operated at 30 mA during 4 min. The glassy carbon (SPI) substrate was previously mirror polished and subjected to ultrasonic cleaning in ultra-pure water for 5 min and then was voltammetrically characterized to ensure a clean and reproducible deposition surface. In order to have an initial surface free of oxide, the iridium electrodes were annealed in a tubular furnace at 600 °C during 30 min in hydrogen atmosphere and then cooled in the same environment.

The development of the oxide layer was carried out following the procedure proposed by J.O. Zerbino et al. [3]. It consisted in the application of repetitive cyclic voltammetry between $-0.07 < E$ (vs. RHE) / V < 1.66 at a sweep rate of 0.15 V s^{-1} . The thickness of the resulting oxide layer was modified varying the time of cycling.

2.2. Electrochemical measurements

All the electrochemical experiments were carried out in a three electrode cell. The electrolyte solution was 0.5 M H_2SO_4 . The reference electrode was a hydrogen bubble electrode in the same solution (RHE), located inside a Luggin-Haber capillary tube. The counter electrode was a platinum wire of high area, located in a separate compartment in order to avoid contamination. Ultra pure water (resistivity 18.2 M Ω) was employed for cell rinsing and solution preparation. The working electrode was mounted in a Teflon holder, with a geometric exposed area of 0.167 cm² and connected to a rotating disc device. The rotation rate was varied between $900 \leq \omega \leq 3600$. The electrodes were electrochemically characterized via cyclic voltammetry between 0.0 and 1.3 V at 0.1 V s^{-1} under nitrogen atmosphere after the thermal treatment under H_2 as well as after the growth of the oxide layer. All experiments were carried out at room temperature (295 K).

2.3. Electrode characterization

The surface morphology of the electrodes was characterized by Atomic Force Microscopy (AFM), using an Agilent 5400 microscope operated in tapping mode and the images were processed with the software WSxM 6.2. EDS spectra were also obtained with a Microscope Phenom World ProX operated at 15 kV for superficial composition determination.

The amount of adsorption sites accessible to the reaction intermediate species on the Ir metal surface when it is covered by a hydrous oxide layer was evaluated through the charge of H_{UPD} obtained by cyclic voltammetry.

2.4. Evaluation of the current-overpotential dependence

The current (I) - overpotential (η) curves of the hydrogen electrode reaction on the hydrous iridium oxide electrode were evaluated under continuous hydrogen bubbling to ensure the solution saturation, through the application of a potential program and the acquisition of the current response at different rotation rates. These measurements were carried out using a potentiostat Wenking POS2, connected to a PC via an Advantech PCI1710HG interface and operated with the software Labview®. Once the working electrode reached the equilibrium potential ($0.0 \pm 0.002 \text{ V}$ vs. RHE), the potential program was applied, which consisted in 3 s at 0.0 V, followed by 5 s at the desired

overpotential value. In this last period, readings of the current value were made each 0.01 s and the mean value of the current data measured in the last second was assigned to the step overpotential. Then the program was repeated for each η value, which was varied in the range $-0.015 \leq \eta / \text{V} \leq 0.30$. Four rotation rates were employed, varied between $900 \leq \omega / \text{rpm} \leq 3600$.

3. Results

3.1. Electrode characterization

Fig. 1 shows the voltammograms corresponding to the Ir electrode before (a) and after (b) the application of the procedure for the formation of the hydrous oxide layer. The voltammetric profile shown in curve (a) corresponds to that expected for metallic iridium [1,13,21], where it can be observed the peaks corresponding to electroadsorption/desorption of H_{UPD} . Moreover, the voltammogram of the same electrode covered by a thick oxide layer is depicted in curve (b). It can be appreciated the presence of a wide anodic peak centred at 0.96 V and at almost the same potential value the corresponding cathodic reduction peak. It can be also observed a small anodic peak located at 0.65 V, but the corresponding cathodic peak is not found. When the anodic limit of the potentiodynamic sweep is set immediately after this peak (0.70 V) it can be appreciated a quasi reversible response, which cannot be perceived in the extended voltammogram. As it has been already mentioned, this voltammetric profile is typical of the Ir electrode covered by a thick layer of hydrous oxide [1–7,15]. Moreover, it can be noticed the disappearance of the peaks corresponding to the adsorption/desorption of H_{UPD} . The variation of the charge of these peaks with the thickness of the oxide layer will be analysed later.

Fig. 2 shows the AFM image obtained for iridium electrode before (a) and after (b) the formation of the hydrous oxide layer. It can be observed in micrograph (a) that Ir electrode is constituted by nanoparticles of approximately 50 nm diameter. The EDS analysis shows only the presence of carbon (substrate) and iridium. The surface covered by the oxide layer (micrograph (b)) shows a smoother morphology with loss of definition of the nanoparticles due to the development of the oxide film. The corresponding EDS profile shows peaks of C, Ir and O.

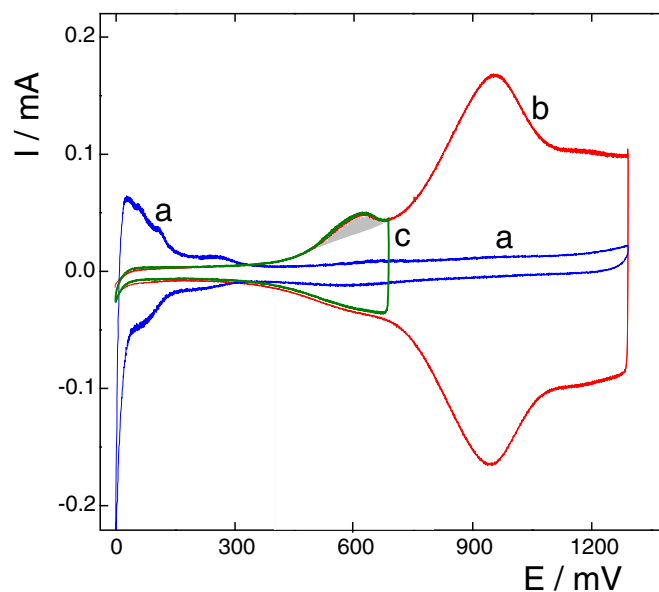


Fig. 1. Voltammetric profile of the Ir electrode run at 0.1 V s^{-1} in 0.5 M H_2SO_4 . (a) Ir metal; (b) Ir oxide electrode; (c) upper potential limit 0.7 V.

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