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Characterization and kinetic study of a nanostructured rhodium electrode for the hydrogen oxidation reaction

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HIGHLIGHTS

- Preparation and characterization of nanostructured rhodium electrodes.
- Kinetic study of the hydrogen oxidation reaction.
- Correlation of experimental results through a unique set of kinetic parameters.
- Reaction takes place under both Tafel–Volmer and Heyrovsky–Volmer routes.

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ABSTRACT

The hydrogen oxidation reaction was studied on a nanostructured rhodium electrode at different rotation rates. The electrode was prepared via sputtering on a glassy carbon disc support and it was characterized by X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and cyclic voltammetry, which allowed verifying the nanostructured morphology and the absence of any phase other than metallic rhodium. The real surface area was evaluated by CO stripping voltammetry. Experimental current density (j) – overpotential (η) curves of the hydrogen oxidation reaction were obtained in the range $-0.015\ \text{V} \le \eta \le 0.25\ \text{V}$ at different rotation rates in sulphuric acid solution. They were correlated by kinetic expressions derived from the Tafel–Heyrovsky–Volmer mechanism and thus the kinetic parameters were evaluated. It was verified that over this overpotential region the reaction proceeds through the simultaneous occurrence of the Tafel–Volmer and the Heyrovsky–Volmer route.

1. Introduction

The hydrogen oxidation reaction (*hor*) has received considerable attention in relation to the development of the H_2–O_2 proton exchange membrane fuel cell (PEMFC) [1]. Therefore, the elucidation of the factors that define the electrocatalytic behaviour for this reaction is essential for the development of new and cheaper electrode materials. Kinetic studies of the hydrogen electrode reaction have been carried out on different metals preferably in the cathodic overpotentials range, which corresponds to the hydrogen evolution reaction (*her*) [2]. Starting from these results, it has been established that platinum has the highest electrocatalytic activity, as it can be derived from its position on the top of the volcano curve, which relates the exchange current density (j_o) with the adsorption free energy of the reaction intermediate [3–6]. On the other hand, the number of kinetic studies of the *hor* is significantly less, most of them carried out on Pt, on smooth electrodes [7–10] as well as on supported nanoparticles [11–13]. Among the scarce kinetic data of the *hor* on other noble metals, it can be cited the evaluation of the kinetic parameters on Pd [14,15], Ru [16] and Ir [17].

There are only a few studies of the hydrogen electrode reaction on rhodium. The first antecedent corresponds to an evaluation of the equilibrium polarization resistance [18]. Another work measured the exchange current density and the Tafel slope (b) for the *hor* as a function of hydrogen partial pressure [19]. These experimental kinetic parameters were also measured for the *her* on acid solution [20]. More recently this reaction was studied by faradaic impedance, including the hydrogen absorption process [21]. Therefore, there has been no report about kinetic studies of the hydrogen oxidation reaction on Rh electrodes. On this context, the present work deals with the evaluation of the elementary kinetic parameters of the Volmer-Heyrovsky-Tafel mechanism on nanostructured Rh electrodes through the correlation of experimental current density (j) vs. overpotential (η) curves, measured in

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sulphuric acid solution under steady state and controlled mass transport conditions.

2. Experimental details

2.1. Electrode preparation

The working electrodes were prepared via sputtering on a glassy carbon (GC) substrate from a rhodium target provided by Goodfellow Corp. in an argon atmosphere (0.1 mbar), using a sputter coater Emitech K500X, operated at 30 mA during 4 min. Previously to Rh deposition, the glassy carbon (SPI-Glas^{TM} 25) substrate was mirror polished and subjected to ultrasonic cleaning in ultrapure water for 5 min and then was voltammetrically characterized to ensure a clean and reproducible deposition surface.

2.2. Electrode characterization

The surface morphology of the Rh electrodes was characterized by Atomic Force Microscopy (AFM). AFM images were obtained using a multi-technique Agilent microscope model 5400, operated in tapping mode and processed with the software WSxM 6.2.

The Rh electrode was also physicochemically characterized by X-ray Photoelectron Spectroscopy (XPS) using a multitechnique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with pass energy of 30 eV; a Mg Ka X-ray source was operated at 200 W and 12 kV. The working pressure in the analysing chamber was less than 5.9×10^{-7} Pa. The XPS analyses were performed in the spectral region corresponding to Rh 3d core level. The data treatment was performed with the Casa XPS program (Casa Software Ltd., UK).

2.3. Electrochemical measurements

All the electrochemical measurements were performed in a three electrodes cell specially built for the use of a rotating electrode and with a particular design of the gas saturator at 298 K. The electrolytic solution was 0.5 M H_2SO_4, prepared with ultra-pure water (PureLab, Elga LabWater). The working electrode was mounted in a teflon holder, with an exposed geometric area of 0.07 cm^2. It was rotated through the use of a rotating disk Radiometer EDI 10K system. Furthermore, a large area platinum wire acted as counter electrode and a hydrogen electrode in the same solution (RHE) was used as reference electrode. The working electrode was electrochemically characterized by cyclic voltammetry using a potentiostat-galvanostat Wenking POS2 controlled by an interface Advantech PI1710HG and the software Labview 8. The voltammograms were obtained at 0.1 V s^{-1} in nitrogen saturated solution between 0.0 and 1.3 V.

The electrocatalytic activity towards the hydrogen oxidation reaction was evaluated through the current (I) − overpotential (η) response in hydrogen saturated solution. The polarization curves were obtained at different rotation rates in the range $900 \le \omega$/rpm ≤ 4900. A potential program was applied, which initiated with a 3 s step at 0.0 V, followed by a 5 s step to the desired overpotential value. In this last period, readings of the current value were made each 0.1 s and the mean value of the current data measured in the last 2 s was assigned to the step overpotential. Then the program was repeated for each η value, which was varied in the range $-0.015 \le \eta/\mathrm{V} \le 0.25$. The electrolyte solution was renewed after each experiment.

Finally, the real area of the electrode was determined by CO stripping voltammetry. CO adsorption was carried out in an auxiliary cell in a CO saturated solution, holding the electrode potential at 0.05 V during 15 min. Then, the voltammetric stripping was carried out at 0.05 V s^{-1} in nitrogen saturated solution between 0.0 and 1.3 V.

3. Results and discussion

3.1. Morphological and physicochemical characterization

The surface morphology was analysed by AFM (Fig. 1). It can be observed that the Rh layer, deposited by sputtering on a glassy carbon substrate, consists of uniformly distributed nanoparticles. In order to estimate the particle size, the height profile was analysed in different places on the electrode surface. Two of them are illustrated in the inset of Fig. 1. The average height of the nanoparticles obtained from these profiles is ranging between 2 and 6 nm.

The physicochemical characterization of the Rh electrode was carried out by XPS analysis. Fig. 2 illustrates the spectrum in the range of binding energy comprised between 303 and 318 eV (continuous line). It can be observed two peaks located at 307.0 eV and 311.8 eV respectively, which are in agreement with the values reported for $3d_{5/2}$ and $3d_{3/2}$ signals of metal rhodium [22]. The deconvolution of these peaks is also shown (dotted lines).

3.2. Electrochemical characterization and real area evaluation

Fig. 3 shows the voltammetric profile of the nanostructured Rh electrode obtained in 0.5 M H_2SO_4 solution at 0.05 V s^{-1} under nitrogen bubbling. The electrode was previously subjected to a CO adsorption carried out in an auxiliary cell in a CO saturated solution at 0.05 V during 15 min. The first cycle corresponds to the stripping of the adsorbed CO, where it can be observed a sharp peak at approximately 0.725 V. The complete electrooxidation of the adsorbed CO is produced in this first anodic sweep, as it can be verified through the second voltammetric cycle, which reproduces the blank voltammogram of metallic rhodium in this electrolyte

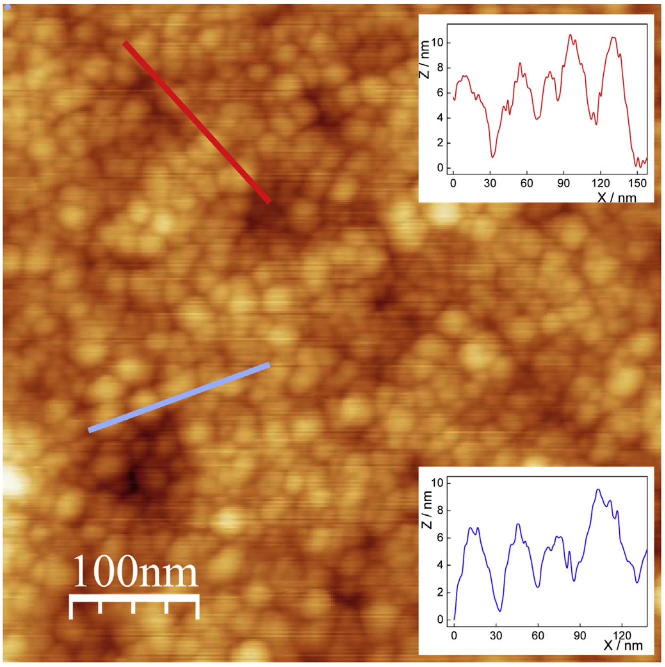

Fig. 1. AFM image of the nanostructured Rh electrode. Insets: height profiles.