



# Kinetics of the hydrogen oxidation reaction on nanostructured rhodium electrodes in alkaline solution



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## HIGHLIGHTS

- Kinetic study of the hydrogen oxidation reaction in alkaline solution.
- Nanostructured rhodium supported on glassy carbon.
- Experimental polarization curves at different rotation rates.
- Tafel-Heyrovsky-Volmer mechanism and Frumkin type adsorption.
- Reaction proceeds mainly through the Tafel-Volmer route.

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## ABSTRACT

The hydrogen oxidation reaction was studied on a nanostructured rhodium electrode at different rotation rates in alkaline solution. The electrode was prepared via sputtering on a glassy carbon disc support and it was characterized by atomic force microscopy and cyclic voltammetry. The real surface area was evaluated by CO stripping voltammetry. Experimental current density ( $j$ ) – overpotential ( $\eta$ ) curves of the hydrogen oxidation reaction were obtained in the range  $-0.015 \leq \eta/V \leq 0.40$  at different rotation rates ( $900 \leq \omega/\text{rpm} \leq 4900$ ). The resulting curves were correlated by kinetic expressions derived from the Tafel-Heyrovsky-Volmer mechanism with a Frumkin type adsorption of the reaction intermediate and the kinetic parameters were evaluated. It was verified that over this overpotential region the reaction in alkaline solution proceeds mainly through the Tafel-Volmer route. These results were compared with those previously obtained in acid solutions.

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## 1. Introduction

In the last decade there was a marked increase in the interest in the hydrogen oxidation reaction (HOR), which led to numerous experimental studies on different electrode materials in acid solutions [1–8]. There was also advances in the derivation of theoretical expressions for the interpretation of the experimental dependences of the current density ( $j$ ) on overpotential ( $\eta$ ), under the kinetic mechanism of the Tafel-Heyrovsky-Volmer [9–11]. Starting from these equations, the kinetic parameters (equilibrium reaction rates of the elementary steps and equilibrium surface coverage) were evaluated on different noble metals [12–16]. Conversely, the hydrogen oxidation reaction in alkaline solution

has not received similar attention, being scarce the published works [17–20]. In the particular case of rhodium electrodes, it cannot be found any kinetic study of the hydrogen oxidation reaction in alkaline medium. 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 vs. overpotential curves, measured in 0.1 M NaOH solution under steady state and controlled mass transport conditions.

## 2. Experimental details

### 2.1. Electrode preparation and characterization

The working electrodes were prepared via sputtering on a glassy carbon substrate from a rhodium target in an argon atmosphere.

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The preparation details can be found elsewhere [16]. 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 electrode was also characterized electrochemically by cyclic voltammetry carried out in a three electrodes cell. The electrolytic solution was 0.1 M NaOH (Merck pro analysis), prepared with ultrapure water (PureLab, Elga LabWater). The working electrode was mounted in a teflon holder, with an exposed geometric area of 0.07 cm<sup>2</sup> (*A<sub>g</sub>*). Furthermore, a large area platinum wire acted as counter electrode, located externally to the cell to avoid contamination from platinum electrodisolution. A hydrogen electrode in the same solution (RHE) was used as reference electrode, placed in a holder connected to a Luggin capillary of 0.2 mm diameter, located in the centre and at a distance of 0.2 mm of the working electrode surface. This configuration ensures that the ohmic effects are negligible in the experimental conditions and that the hydrodynamics of the rotating electrode is not affected. Cyclic voltammetry was carried out using a potentiostat-galvanostat Wenking POS2 controlled by an interface Advantech PI1710HG and the software Labview 8. The voltammograms were obtained at 0.05 V s<sup>-1</sup> in nitrogen saturated solution between 0.0 and 1.3 V.

The real area of the electrode was determined by carbon monoxide stripping voltammetry. CO adsorption was carried out in an auxiliary cell in a CO saturated solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> (Merck pro analysis) holding the electrode potential at 0.05 V (vs. RHE) during 15 min. Then, the voltammetric stripping was carried out at 0.05 V s<sup>-1</sup> in nitrogen saturated solution between 0.05 and 1.3 V.

## 2.2. Hydrogen oxidation measurements

The experimental determination of the dependence  $j(\eta)$  for the hydrogen oxidation reaction on steady state was carried out in the cell described above. Five rotating rates ( $\omega$ ) was employed in the range  $900 \leq \omega/\text{rpm} \leq 4900$ , using a rotating disc equipment (Radiometer EDI 10000). The electrolyte solution was NaOH 0.1 M, which was subjected to a continuous and efficient hydrogen bubbling at  $P = 1$  atm. The counter electrode was a large area Pt electrode. The applied overpotential was varied in the range  $-0.015 < \eta/V < 0.40$ , controlled against a hydrogen electrode reference in the same electrolyte solution. A potential program was applied in order to obtain the steady state polarization curves. It was 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  $\eta$  value. The electrolyte solution was renewed after each experiment, which were carried out at 25 °C.

## 3. Results and discussion

### 3.1. Electrode characterization and real area evaluation

Fig. 1 shows the voltammetric profile of the nanostructured Rh electrode in 0.1 M NaOH solution at 0.05 V s<sup>-1</sup> under nitrogen bubbling in the potential range  $0.0 < E/V < 1.3$  vs. RHE. It can be appreciated in the anodic scan the profile corresponding to the hydrogen desorption located between 0.1 and 0.3 V, immediately followed by the electroadsorption of OH and other rhodium hydroxylated species. The cathodic sweep shows the peak corresponding to the electroreduction of such species at approximately 0.37 V, which is strongly overlapped with the peaks corresponding to the hydrogen electroadsorption, due to the late disinhibition of

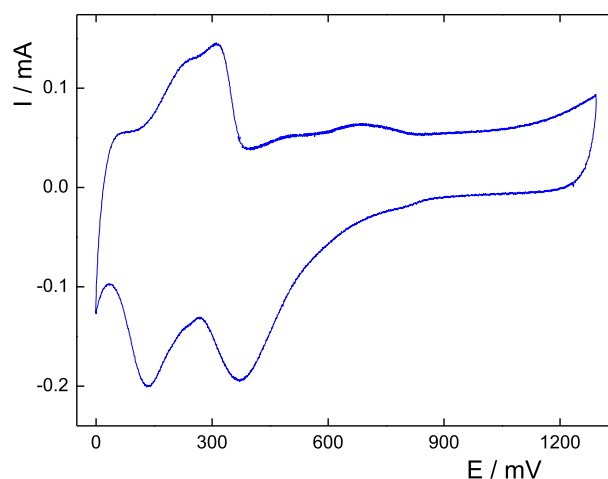


Fig. 1. Voltammogram of the Rh electrode in 0.1 M NaOH at 0.05 V s<sup>-1</sup> and 298 K.

the adsorption sites occupied by the Rh oxide [21,22]. The potentiodynamic profile is similar to that corresponding to electrodeposition Rh in 1 M KOH solution [21].

The voltammetric charge corresponding to the electrooxidation of the adsorbed CO in acid solution was used for the determination of the real electrode area (Fig. 2). 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 solution [16,23,24]. The voltammetric charge corresponding to the electrooxidation of the adsorbed CO was evaluated as the difference between the first and second cycle in the potential range  $0.40 < E/V < 1.3$ , resulting a value equal to 0.301 mC. Taking into account that the voltammetric charge of one CO monolayer is equal to 0.2877 mC cm<sup>-2</sup> [16], the electroactive area (*A<sub>e</sub>*) of the Rh electrode is 1.043 cm<sup>2</sup>. Moreover, as the reaction under study has a strong diffusion contribution, which depends on the geometric area, meanwhile the kinetic reaction takes place on the real surface area, the relationship between both values is an important parameter for the correct analysis of the reaction. This relationship, called active area factor ( $f_{aa} = A_e/A_g$ ), is in this case equal to 14.69.

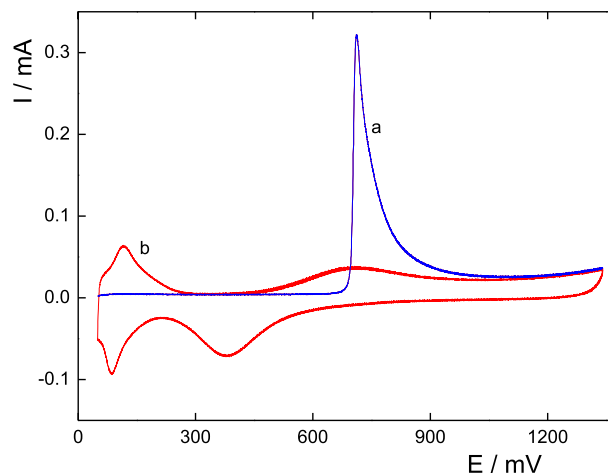


Fig. 2. Voltammetric stripping of adsorbed CO on the Rh electrode. (a) First cycle; (b) Second cycle. 0.05 V s<sup>-1</sup>; 0.5 M H<sub>2</sub>SO<sub>4</sub>, 298 K.

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