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Effect of the Pt/Ru intermetallic boundary on the carbon monoxide electrooxidation: Excess electrocatalytic activity

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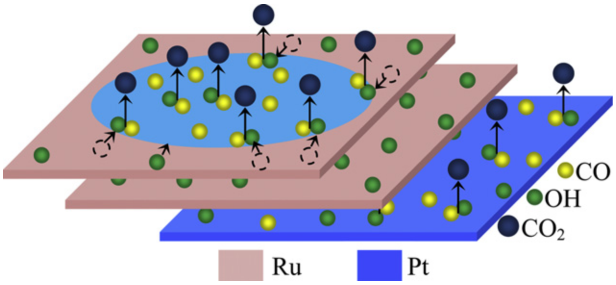
HIGHLIGHTS

- ► Study of the carbon monoxide oxidation reaction on Pt, Ru and Pt/Ru electrodes.
- ► Evaluation of the contribution to the reaction of the intermetallic region on Pt/Ru.
- ► Quantification of such contribution through the excess electrocatalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

The carbon monoxide oxidation reaction was studied on smooth Pt, Ru and Pt/Ru (Ru partially covered by Pt islands) rotating disc electrodes on acid solution saturated with CO gas ($P_{CO} = 1$ atm) through steady state measurements. The current density vs. overpotential plot of the Pt/Ru electrode shows a profile qualitatively similar to the sum of both curves corresponding to pure Pt and Ru. On this basis, the excess electrocatalytic activity was defined as the difference between the current densities of the bimetallic electrode and those corresponding to the pure metals, which allowed evaluating the contribution of the intermetallic region to the reaction. It was verified that this property depends on overpotential, defining two ranges of positive excess values, $0.6 \leq \eta/V < 0.82$ and $0.88 < \eta/V \leq 1.0$, separated by the range $0.82 \leq \eta/V \leq 0.88$, where the contribution of the boundary region is negligible. A simple model was developed, which explains the experimental results on the basis of the spillover of the adsorbed reaction intermediates, while the reaction between adsorbed species on both sides of the intermetallic edge is not feasible.

1. Introduction

The oxidation of adsorbed carbon monoxide (CO_{ad}) on Pt and bimetallic Pt–M electrodes has been widely studied, because of its role played in polymer electrolyte membrane fuel cells (PEMFC) [1–15]. It is well known that platinum has a large affinity towards the adsorption of CO, inhibiting the CO electrooxidation reaction, and therefore higher overpotentials are needed for the occurrence of this reaction. In order to weaken CO–Pt bonding or provide the adsorbed hydroxyl species (OH_{ad}) from oxyphilic surface atoms, binary electrocatalysts Pt–M were developed, being Ru the most widely employed as M metal [5–7,11–15]. The role of the second metal, particularly Ru, was studied on alloys [12,13], as well as on Pt (or Ru) surfaces partially covered, or decorated, by Ru (or Pt) islands [14,15]. In this context it can be mentioned the works of Gasteiger et al., who used polycrystalline Pt/Ru alloys of different compositions, prepared by arc melting of the pure metals under an argon atmosphere [12,13]. Other authors employed Ru-decorated Pt

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single crystal surfaces as model electrocatalysts, obtained by electrodeposition as well as spontaneous deposition [6]. Another way to obtain model Pt/Ru electrocatalyst, developed by Brankovic et al., consists in the spontaneous deposition of Pt submonolayers on the Ru(0001) surface [15,16]. They obtained columnar shaped Pt clusters covering from submonolayer to multilayer depending on the concentration of Pt ions and on the time of immersion. This method was also applied to deposit Pt submonolayers on Ru nanoparticles supported on Vulcan XC-72 carbon [16,17]. In all cases it was found a larger CO tolerance with respect to Pt. The effect of the intermetallic boundary region was analyzed on the basis of the current–potential curve obtained by the application of the voltammetric stripping of CO adsorbed at low potentials [18–23]. The stripping voltammogram shows two peaks, one at $0.4 \le E\,(\text{vs. RHE})/\text{V} \le 0.6$ called preignition peak and the other, located at more anodic potentials, called ignition peak. Koper et al. considered that the first peak corresponds to the CO oxidation on Ru while the second one to the reaction taking place on Pt [18,19]. On the other hand, Lu et al. proposed that the reaction takes place on both sides of the edge of the Ru island [21,22]. Finally, Roth et al. indicated that the preignition peak corresponds to the CO oxidation on the intermetallic region and the second peak was assigned to the oxidation of the CO that diffused towards such region [23]. It should be noticed that these peaks show the CO_{ad} oxidation in absence of a readsorption process from solution. Thus, despite the numerous works published on this subject, the contribution of the intermetallic boundary region has not been clearly determined yet and still remains an incompletely resolved issue.

In order to analyze the contribution of the intermetallic region a model electrode should be used, where the edge between Pt and Ru is clearly defined. In the present case, a Ru electrode partially covered by Pt islands is employed. An aprioristic analysis of the expected response for the CO electrooxidation on this electrode indicates that it should exhibit contributions of Pt and Ru themselves in the surface regions far from the intermetallic boundary as well as a specific contribution corresponding to this boundary region.

On this basis, the aim of the present work is the evaluation of the contribution of the intermetallic region to the CO oxidation reaction, starting from the measurement of the polarization curves on steady state on Pt/Ru electrodes, as well as on pure Pt and Ru electrodes. Thus, the difference between the current densities of the bimetallic electrode and those corresponding to the pure metals will define a property that can be called an “excess electrocatalytic activity”, which allows the quantification of the contribution of the intermetallic boundary region to the electrocatalytic activity of the Pt/Ru electrode to the CO oxidation. An explanation of this contribution is also proposed, on the basis of the spillover of the adsorbed reaction intermediates.

2. Experimental

2.1. Electrodes preparation and characterization

The working electrodes were rotating discs of polycrystalline platinum 99.99% (Radiometer analytical) and ruthenium 99.95% (MaTecK GmbH) with a geometric area of 0.07 cm^2. They were mechanically polished with emery paper of different grit sizes and then alumina powder up to 0.05 μm, followed by sonication in ultra-pure water for 5 min. In order to obtain the bimetallic electrode, a rotating disc of polycrystalline ruthenium was immersed in a deoxygenated 0.1 mM H_2PtCl_6 + 0.5 M H_2SO_4 solution during a period of time ranging between $5 \le t/\text{min} \le 20$, following the procedure described elsewhere [16], although all the results shown correspond to $t = 10$ min, unless otherwise stated. The morphology of the deposit was analyzed by AFM observations in the tapping mode, obtained in a microscope AFM/STM Agilent Technologies model 5400. The electrochemical characterization was carried out by cyclic voltammetry at 0.05 V s^{-1} in 0.5 M H_2SO_4 solution saturated with nitrogen gas and at 25 °C.

2.2. Evaluation of the CO oxidation

The experimental determination of the dependence $j(\eta)$ for the carbon monoxide oxidation reaction was carried out in a three electrodes cell specially built for the use of a rotating electrode and with a particular design of the gas saturator. The working electrodes were the polycrystalline Pt and Ru discs and the bimetallic Pt/Ru prepared as it is described in the previous item. They were rotated through the use of a rotating disk Radiometer EDI 10K. The counterelectrode was a platinum helical wire of large area. The electrolytic solution was 0.5 M H_2SO_4, prepared with ultra-pure water (PureLab, Elga LabWater). Measurements were carried out at 25 °C under ultra high purity 99.9% CO gas (10 ppm O_2, 30 ppm CO_2) bubbling at 1 atm, ensuring a continuous saturation of the electrolyte. The applied overpotentials were controlled with respect to a reversible hydrogen electrode in the same solution (RHE). Taking into account that the CO used contains 30 ppm of CO_2, the value of the theoretical equilibrium potential of the CO oxidation reaction with respect to the RHE can be calculated ($E^e = -0.025$ V) [24].

The first type of experimental determinations to study the CO oxidation was a slow potentiodynamic sweep run at 0.01 V s^{-1}, which was applied to the three types of electrodes studied, Pt, Ru and Pt/Ru. The determination of the experimental current–overpotential dependences for the reaction on steady state was carried out on these electrodes, through the application of a potential program consisting in holding the potential at 0.2 V during 3 min, followed by successive steps, each with duration of 3 min. On the basis of the behaviour observed on the slow potentiodynamic sweep, the ranges of overpotentials employed in the steady state measurements were adopted: $0.5 \le \eta/\text{V} \le 1.2$ for Pt and $0.4 \le \eta/\text{V} \le 1.0$ for Ru and Pt/Ru. During the potentiostatization at a given overpotential, the current value was measured each 0.1 s and the mean value of the last 10 s was assigned to this overpotential to ensure that the steady state current was reached. The current densities are referred to the geometric area (0.07 cm^2), unless otherwise stated. Immediately after these measurements, the Ru and Pt/Ru electrodes were subjected to the electrochemical characterization by cyclic voltammetry described above in order to verify that the electrode surface was not modified.

3. Results

3.1. Electrode surface morphology

The surface morphology of the working electrodes were analyzed by atomic force microscopy operating in the tapping mode. Fig. 1 shows the AFM image corresponding to the Ru surface before the Pt deposition. It can be observed that the surface is fairly smooth, which is verified by the corresponding profile plot depicted in the inset of Fig. 1.

A similar image was obtained for the Pt electrode, subjected to the same surface treatment. The Pt/Ru electrode obtained by spontaneous deposition of Pt on Ru shows a surface morphology (Fig. 2) characterized by the presence of smooth hemispherical particles, which height can be estimated by the corresponding profile (Fig. 2, inset), varying between 15 and 70 nm. It can be appreciated from Fig. 2 that the ruthenium area exposed to the electrolyte solution is significantly lower than the original. From