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Comparative electrochemical behaviour of CO_2 on Pt and Rh electrodes in acid solution

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Abstract

The electroformation of adsorbed species on Pt and Rh from CO_2 dissolved in aqueous 0.5 M H_2SO_4 and the influence of adsorbed species on the hydrogen evolution reaction (HER) were examined for smooth and columnar structured Pt and smooth and rhodized Rh electrodes at 25°C. Different electrosorbed species resulting from the adsorption of CO_2 on Rh were found. The electro-oxidation of these adsorbates on Rh takes place over a potential range larger than that for adsorbates on Pt, overlapping the potential range of electroformation of the O-containing layer. A part of the reduced CO_2 adsorbates on Rh behaves as CO-like adsorbates. The presence of adsorbed species from CO_2 influences differently the stationary HER current potential curves for both types of Pt and Rh electrodes. In the range of low current density (cd), the Tafel slope for Pt is -0.030 V decade^{-1}. Conversely, the presence of a chemisorbed species on Rh changes the Tafel slope for the HER in the range of low cd from -0.030 V decade^{-1} for CO_2-free solutions to -0.120 V decade^{-1} for CO_2-saturated solution. These changes are explained by a modification in the rate-determining step of the HER produced by chemisorbed species.

Keywords: CO_2 electrochemistry; Acid solutions

1. Introduction

A few decades ago the formation of a "reduced" carbon dioxide adsorbate (r-CO_2) on Pt in acids was found, in particular when the electrode–CO_2 interaction took place in the potential range of H-atom electrosorption [1]. The formation of r-CO_2 adsorbates was of special interest for the electro-oxidation of those organics which could be used as potential fuels in electrochemical energy conversion devices. More recently, the study of the structure and the electrochemical behaviour of r-CO_2 adsorbates was undertaken to establish the reaction pathways related to the production of valuable organics from CO_2 electroreduction [2,3], a process involving waste material whose accumulation in the atmosphere has been the subject of extensive discussion and concern [4].

Pt and Rh are active electrocatalysts for a number of reactions in aqueous and non-aqueous solutions, but they differ in their behaviour for H-atom electrosorption, and CO_2 electroreduction and electro-oxidation [5–9]. These differences can be related to the fact that Rh catalysts are very active for the selective synthesis of a number of organic compounds from CO and H_2 [10,11]. Otherwise, the formation of CO_2 adsorbates is largely favoured on H-adsorbing metals such as Pt and Rh, in contrast to Ir, Ru and Os [12]. Similar types of adsorbate are formed probably on Pd electrodeposits as CO_2 electrochemical reduction also takes place on this metal in alkaline solution [13]. Therefore, to understand the electrocatalytic differences between Rh and Pt it is interesting to study comparatively the electro-oxidation characteristics of both r-CO_2 adsorbates and the hydrogen evolution reaction (HER) on these metals in CO_2-free and in CO_2-containing acid solutions,

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including the possible influence of surface topography, working with smooth and rough electrode surfaces.

2. Experimental

Runs were made using four different working electrodes (we), namely smooth polycrystalline (pc) Rh, rhodized (rd) Rh, smooth polycrystalline (pc) Pt and columnar structured (cs) Pt. Electrochemical roughening, an electrochemical technique which has been described extensively in previous publications [14], was employed to prepare the cs-Pt we. The procedure consisted basically of the accumulation of a thick hydrous Pt oxide layer built up by applying a fast square wave potential routine to a pc-Pt electrode in acid, followed by electrochemical reduction of the hydrous Pt oxide layer by a linear potential scan. The value of R, the roughness factor of the cs-Pt we, was defined by the H-adatom voltammetric charge ratio involving the charge measured before divided by the charge determined after cs-Pt formation [14]. For these electrodes values of R up to 70 were used.

Preparation of the rd-Rh we was done by electrolysis from a 2% $RhCl_3$ in 0.1 M HCl aqueous solution. For these electrodes the value of R was in the range $10 \leq R \leq 33$. In this case, R was determined from the H-electroadsorption charge ratio measured at the voltammetric current minimum which appeared between the H-electrosorption current peak potential and the HER threshold potential [15]. The value of q_H, the charge of H adatoms evaluated by this procedure, was a fraction of the H-adatom monolayer charge [15], i.e. $q_H = 0.59$ monolayer, where the H-adatom monolayer charge density was taken as $q_{H,ml} = 0.210$ mC cm^{-2}.

The we potential E was measured against a $Hg|Hg_2SO_4|0.5$ M H_2SO_4 reference electrode (MSE) (E_{MSE}/(vs. SHE) = 0.660 at 25°C), although in the text all potentials are given on the standard hydrogen electrode scale (SHE). A Pt gauze was employed as counterelectrode.

The electrolyte solution was aqueous 0.5 M H_2SO_4 prepared from 98% H_2SO_4 (Merck, p.a.) and Milli-Q* water. Reduced CO_2 adsorbates were produced by keeping the we immersed in the CO_2-saturated solution at a potential which was preset somewhere in the H-atom electrosorption potential range.

The electroformation of CO_2 adsorbates and their subsequent electro-oxidation were studied on Rh in a way similar to that previously reported for rough Pt [6]. Accordingly, the we was potential cycled between 0.01 V and 1.46 V in 0.5 M H_2SO_4; then, after saturating the solution with CO_2, the potential was stepped to E_{ad} for different adsorption times t_{ad}. Adsorption equilibrium was reached for $t_{ad} = 10$ min. Finally, the potential was stepped to 0.26 V. Subsequently, a voltammetric scan from 0.26 V to 1.15 V was run in 0.5 M H_2SO_4 at potential scan rates in the range 0.001 V s^{-1} $\leq v \leq$ 0.20 V s^{-1}. Voltammetry and potentiostatic polarization data were obtained with conventional circuitry. Voltammograms and polarization curves are displayed as E vs. j plots, where j stands for the real current density.

All the experiments were performed at 25°C.

3. Results

3.1. Voltammetric data

As reported in previous publications [6,7], r-CO_2 adsorbates on Pt in acids are formed in the range 0 V $\leq E \leq$ 0.4 V which is related to the formation of H-adatoms (region I). The voltammogram for the electro-oxidation of r-CO_2 on pc- and cs-Pt electrodes in aqueous 0.5 M H_2SO_4 exhibits a complex current peak which is scarcely sensitive to the we topography (Fig. 1). This current peak, which is observed even at the highest v covered by this work, indicates the presence of at least two r-CO_2 adsorbates. The relative current contribution of these adsorbates depends on E_{ad}, t_{ad} and v.

Electro-oxidation voltammograms of r-CO_2 adsorbates formed on cs-Pt for constant E_{ad} and increasing t_{ad} (Fig. 1) show that E_p, the current peak potential, moves positively and q_{ox}, the electro-oxidation real charge density, increases with t_{ad}. Further, a current peak in the potential range 0.7–0.8 V is observed. The value of q_{ox} resulting from these voltammograms reaches a maximum value when $E_{ad} \approx 0.12$ V (Fig. 2).

For Rh, similar experiments indicate that in this case region I extends over the range 0 V $\leq E \leq$ 0.3 V where the H-adatom electrosorption reactions take place. For values

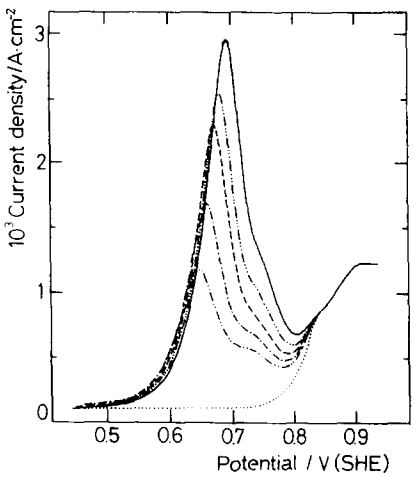

Fig. 1. j/E voltammogram of the electro-oxidation of r-CO_2 adsorbates formed on cs-Pt ($R = 26$) at $v = 0.05$ V s^{-1}, $E_{ad} = 0.06$ V; t_{ad} is (———) 300 s, (-·-·-) 120 s, (- - -) 60 s, (-··-) 30 s, (-·-·-) 15 s (· · ·) baseline voltammogram in the absence of CO_2. Current densities are referred to the electrode real surface area before the columnar structure preparation process; 25°C.

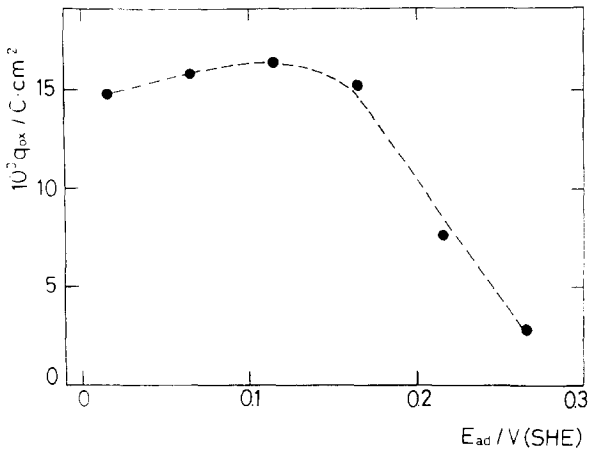

Fig. 2. r-CO_2 electro-oxidation charge density vs. E_{ad}; t_{ad} = 300 s, cs-Pt electrode (R = 70). Charge densities are referred to the real area of the Pt electrode before the columnar structure preparation; 25°C.

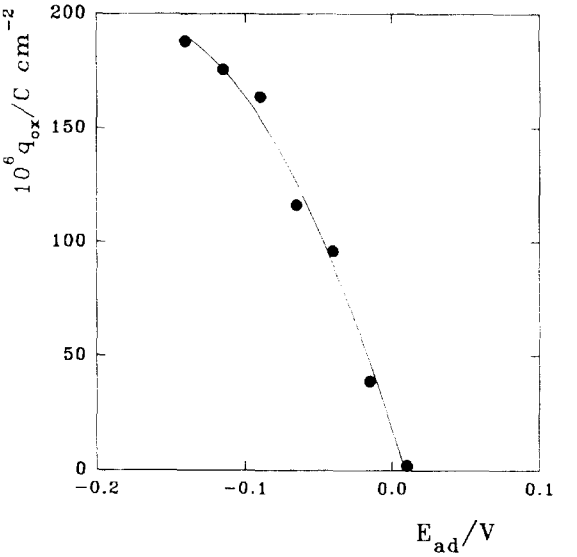

Fig. 4. r-CO_2 electro-oxidation charge density vs. E_{ad}; t_{ad} = 300 s, pc-Rh electrode, 0.5 M H_2SO_4, 25°C.

of E_{ad} in the range 0.01 V $\leq E_{ad} \leq -0.15$ V, and for t_{ad} values in the range 0 s $\leq t_{ad} \leq$ 300 s, the electrosorption of CO_2 begins at potentials below approx. 0.1 V, in good agreement with data previously reported from radio-tracer measurements [9].

Single sweep electro-oxidation voltammograms for r-CO_2 adsorbates on pc-Rh run from E_{ad} upwards (Fig. 3) are, in principle, comparable with those obtained for cs-Pt (Fig. 1). However, for Rh, the electro-oxidation potential of r-CO_2 adsorbates, which starts at ca. 0.2 V below that of Pt, extends over a range which largely overlaps the O-electroadsorption potential range.

The r-CO_2 main electro-oxidation voltammetric peak on pc-Rh becomes sharp at low values of v (Fig. 3). For $E_{ad} = -0.14$ V and $t_{ad} = 200$ s, the voltammogram shows a negative shift of E_p as v is decreased from 0.01 V s^{-1} to 0.001 V s^{-1} (Fig. 3). A similar shift of E_p has also been observed for all Pt electrodes [6]. At a constant v, the value of E_p for pc-Rh is very close to that already found for cs-Pt [7].

Otherwise, to attain for pc-Rh a value of q_{ox} similar to that resulting from cs-Pt, it was necessary to set $E_{ad} < 0$ V as it results from comparison of data shown in Figs. 2 and 4, after considering that for cs-Pt, $R = 70$. Likewise, the value of q_{ox} increases as E_{ad} is decreased (Fig. 4) showing that for $E > 0.06$ V, almost no formation of r-CO_2 species takes place on pc-Rh in acid.

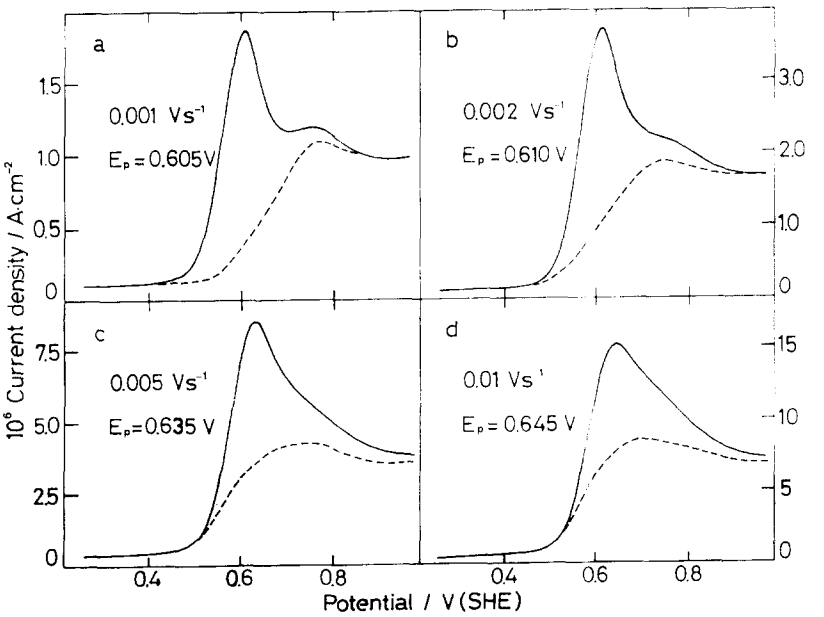

Fig. 3. Electro-oxidation voltammograms of r-CO_2 adsorbates run at different v; $E_{ad} = -0.14$ V, $t_{ad} = 200$ s. Dashed lines refer to CO_2-free 0.5 M H_2SO_4; pc-Rh electrode, 25°C.

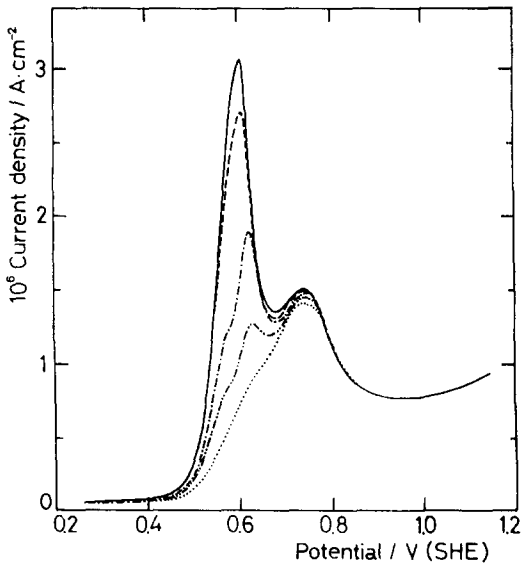

Fig. 5. Electro-oxidation voltammograms of r-CO_2 adsorbates formed at different E_{ad}; $v = 0.001$ V s^{-1}, $t_{ad} = 300$ s; E_{ad} is (———) −0.14 V, (- - -) −0.09 V, (-·-) −0.04 V, (-···) −0.015 V. The dotted line refers to the absence of CO_2; pc-Rh electrode, 0.5 M H_2SO_4, 25°C.

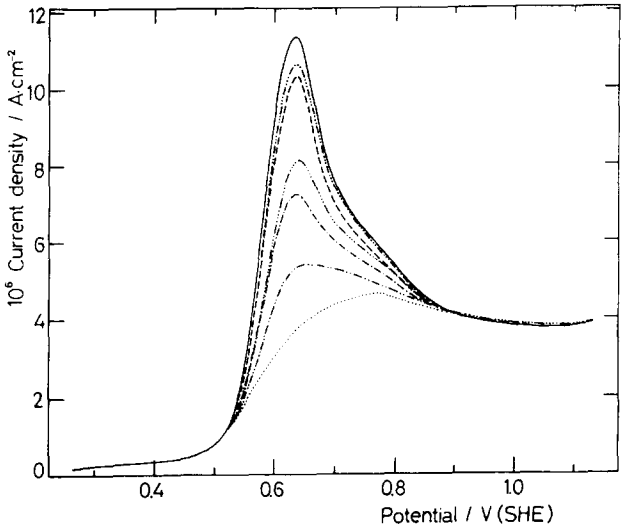

Fig. 6. Electro-oxidation voltammograms of r-CO_2 adsorbates formed at different E_{ad}; $v = 0.005$ V s^{-1}, $t_{ad} = 300$ s; E_{ad} is (———) −0.14 V, (-·-·-) −0.115 V, (- - -) −0.09 V, (-·····) −0.065 V, (-··-) −0.04 V, (-···-) −0.015 V. Dotted line refers to the absence of CO_2; pc-Rh electrode, 0.5 M H_2SO_4, 25°C.

Furthermore, the voltammogram at $v = 0.001$ V s^{-1} for the electro-oxidation of r-CO_2 adsorbates formed at values of E_{ad} in the range $-0.015\ \text{V} \leq E_{ad} \leq -0.14$ V and $t_{ad} = 300$ s on pc-Rh, shows that in the potential range of the main current peak, a first current contribution appears as a shoulder at ca 0.57 V, and a second contribution appears at ca 0.61 V (Fig. 5). These two contributions involve a charge value equivalent to values of θ_{CO2}, the degree of surface coverage by r-CO_2 species, in the range $0 \leq \theta_{CO2} \leq 1$. The value $\theta_{CO2} = 1$ was taken arbitrarily for $q_{ox} = 0.210$ mC cm^{-2}. It should be noted that in these experiments no current peak splitting can be distinguished either for $\theta_{CO2} \rightarrow 1$ or for $v > 0.001$ V s^{-1}.

For r-CO_2 electro-oxidation on pc-Rh the value of E_p also depends on E_{ad} (Figs. 5 and 6), and from the corresponding values of q_{ox} it results that the largest θ_{CO2} appears when $E_{ad} = -0.14$ V and $t_{ad} = 300$ s. These results are in contrast with those already reported for Pt, where the largest value of θ_{CO2} was found for $E_{ad} = 0.1$ V [7].

3.2. Polarization curves for the HER at Pt and Rh

The distinct features of r-CO_2 adsorbates formed on Rh and Pt in aqueous 0.5 M H_2SO_4 were also reflected through their influence on the stationary HER polarization curves at both pc- and rd-Rh and pc- and cs-Pt electrodes.

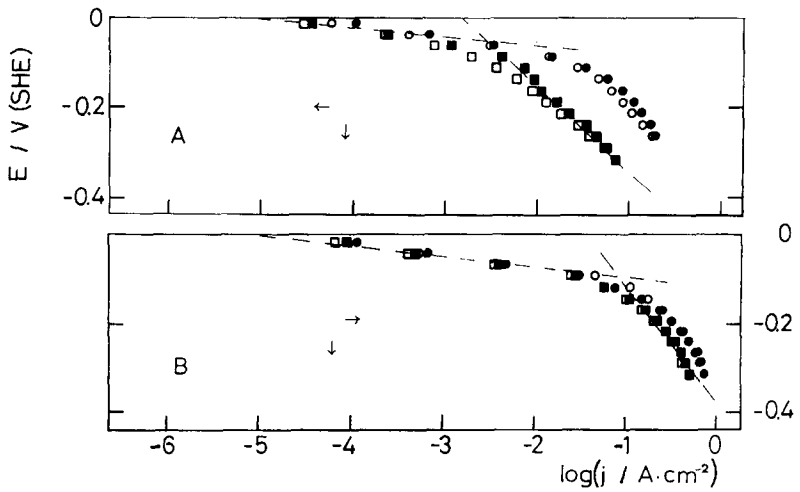

Fig. 7. (a) Tafel plots for the HER on pc-Pt in the presence and absence of CO_2 in solution. (●) From 0.4 V to −0.3 V, N_2 saturated solution. (○) From −0.3 V to 0.4 V, N_2 saturated solution. (■) From 0.4 V to −0.35 V, CO_2 saturated solution. (□) From −0.35 V to 0.4 V, CO_2 saturated solution. (b) Tafel plots for the HER on cs-Pt ($R = 75$) in the presence and in the absence of CO_2 in solution. (●) From 0.4 V to −0.3 V, N_2 saturated solution. (○) From −0.3 V to 0.4 V, N_2 saturated solution. (■) From 0.4 V to −0.35 V, CO_2 saturated solution. (□) From −0.35 V to 0.4 V, CO_2 saturated solution. Current densities are referred to the real area of the Pt electrode before the columnar-structure preparation process; 0.5 M H_2SO_4, 25°C.

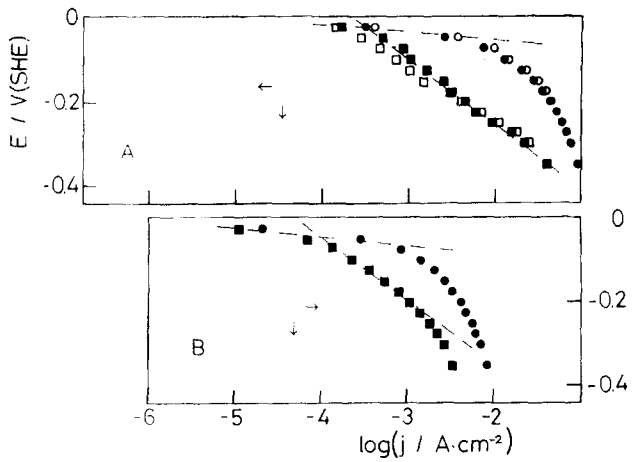

Fig. 8. (a) Tafel plots for the HER on pc-Rh in the presence and in the absence of CO_2 in solution. (●) From 0.4 V to −0.3 V, N_2 saturated solution. (○) From −0.3 V to 0.4 V, N_2 saturated solution. (■) From 0.4 V to −0.35 V, CO_2 saturated solution. (□) From −0.35 V to 0.4 V, CO_2 saturated solution. (b) Tafel plots for the HER on rd-Rh in the presence and in the absence of CO_2 in solution. (●) From 0.4 V to −0.3 V, N_2 saturated solution. (■) From 0.4 V to −0.35 V, CO_2 saturated solution,; 0.5 M H_2SO_4, 25°C.

In CO_2-free solution and in the absence of r-CO_2 adsorbates, the stationary E vs. log j plot for either pc- (Fig. 7(A)) or cs-Pt (Fig. 7(B)) can be described in terms of two distinguishable potential ranges (regions II and III). Region II, in the range 0 V ≤ E ≤ −0.1 V, corresponds to the potential range where the HER takes place. It is characterized by the Tafel slope $b_T = -0.030$ V decade^{-1}. Region III from $E < -0.1$ V downwards, involves the HER influenced by the formation of H_2 bubbles and, in this region $b_T \approx -0.180$ V decade^{-1}.

Similar polarization curves run for pc-Pt in CO_2-saturated solution show a decrease in current in regions II and III compared with those polarization curves recorded in CO_2-free solution. On the assumption that the decrease in cathodic current is caused by r-CO_2 adsorbate surface blockage, this effect for $E < -0.1$ V would appear when $\theta_{CO2} = 0.82$. This figure for θ_{CO2} agrees fairly well with that previously reported for both pc- and cs-Pt [6], but it is smaller than that resulting from rd-Rh under comparable conditions.

For cs-Pt immersed in CO_2-saturated solution the small shift in the HER polarization curve would correspond to $\theta_{CO2} \approx 0.25$, a figure which contrasts with $\theta_{CO2} = 0.85$, the saturation value of θ_{CO2} previously reported [6,7]. This apparent discrepancy in θ_{CO2} for pc- and cs-Pt suggests that for the latter, under stationary conditions, only a fraction of the overall surface is accessible to reactants. Presumably this fraction corresponds to tip domains of the columnar topography, i.e. to a fraction of the true electroactive surface [16].

The HER stationary polarization curve for Rh electrodes (Fig. 8) in CO_2-free solution involves two distinguishable regions as well. The polarization curve in region II, i.e. 0 V to −0.1 V, fits a reasonable Tafel relationship with $b_T \approx -0.030$ V decade^{-1}. Finally, in region III, which covers from −0.1 V downwards, the polarization curve also exhibits a rather poor Tafel behaviour with $b_T \approx -0.180$ V decade^{-1}.

For both pc-Rh (Fig. 8(A)) and rd-Rh (Fig. 8(B)) electrodes in CO_2-saturated solution, it appears that, at a constant E, polarization curves shift towards smaller values of j compared with those obtained in CO_2-free solution, and region II tends to approach a single straight line with the single slope $b_T \approx -0.120$ V decade^{-1}. Seemingly, r-CO_2 adsorbates on Rh, in contrast to Pt, modify considerably the kinetics of the HER for $E < -0.05$ V. For Rh, the value of θ_{CO2} for $E < -0.1$ V, which would be associated with the change in behaviour of the polarization curve, is $\theta_{CO2} > 0.94$.

Finally, polarization curves resulting from either decreasing or increasing the potential stepwise tend to coincide, although the current obtained in region I is generally higher when E is shifted positively.

4. Discussion

4.1. Possible adsorbates formed on Pt and Rh from CO_2 dissolved in 0.5 M H_2SO_4

The anodic stripping voltammograms of r-CO_2 adsorbates and the influence these adsorbates exert on the HER on Rh and Pt in aqueous 0.5 M H_2SO_4 show some noticeable differences, which can be considered by looking first at the characteristics of r-CO_2 adsorbates on Rh and Pt.

The formation of r-CO_2 adsorbates from the CO_2-containing solution on both Pt and Rh results from the interaction between the metal surface covered either partially or completely by H-adatoms, and CO_2 in the solution, although the presence of H-adatoms appears to be a necessary but not a sufficient condition for anchoring CO_2 on these metals [17]. However, the reactivity of CO_2 differs depending on whether strongly or weakly bound H-adatoms are involved [6,7], as can be deduced from the anodic stripping peak multiplicity for the corresponding adsorbates [7,18]. Therefore, although seemingly the behaviour of Rh and Pt for r-CO_2 adsorbate formation is qualitatively comparable, the potential for the highest yield of r-CO_2 adsorbates on Rh is more negative than that for Pt, and the electro-oxidation of r-CO_2 adsorbates on Rh is less clearly defined because of the overlapping of the early stages of O-electroadsorption which occurs at potentials below that for Pt.

However, anodic stripping voltammograms of r-CO_2 adsorbates on Rh in acid recorded at 0.001 V s^{-1} make possible the distinction of at least two forms of r-CO_2 adsorbate as on Pt [6]. For the latter, r-CO_2 adsorbates have been described as ensembles consisting of Pt sites, H-adatoms and trapped CO_2 species [6]. The electro-oxidation of these ensembles produces in part adsorbed CO

species, as shown recently by "in situ" FTIR spectroscopy [19]. Adsorbed species of the same type should be related to the current contribution which appears in r-CO_2 electro-oxidation on Rh in acid [9].

Otherwise, the fact that the highest value for θ_{CO2} on Rh is obtained at values of E_{ad} more negative than that for Pt, i.e. at values of E_{ad} where the HER already takes place, and the ability of Rh to break the CO bond to catalyse hydrogenation reactions [10,11], suggest that the r-CO_2 adsorbates formed on Rh differ from those produced on Pt. Furthermore, the negative shift of the value of E_{ad} related to the maximum value of θ_{CO2} correlates with the fact that sulphate anions are more strongly bonded to Rh than to Pt [20]. Therefore, for Rh the formation itself of H-adatoms required for H-bond-linked CO_2 adsorbate formation takes place in a potential range which is shifted negatively with respect to that for Pt.

From analysis of the voltammograms, it is likely that r-CO_2 adsorbates on Rh will involve some new adsorbed species produced at relatively high negative potentials where the formation of precursors involved in the electroreduction of CO_2 itself may take place. This reaction would either interfere or compete with the HER. This new adsorbed species could be related to those adsorbed residues involved in the electro-oxidation of formic acid as the cyclic voltammograms of r-CO_2 and CHO_2H adsorbates on Rh tend to resemble each other [21–23]. In fact, the electro-oxidation current contribution found at lower potentials, which is enhanced when $E < -0.05$ V, can be related to those current peaks recorded for the voltammetric electro-oxidation of CO and CHO_2H on Rh in acid [9]. Thus, for both pc-Rh [24] and rd-Rh [22] the voltammetric oxidation of adsorbed CO exhibits a single sharp anodic current peak covering a potential range which largely overlaps the initial stages of Rh(OH) formation [24]. Likewise, the electro-oxidation of CHO_2H on Rh also involves the formation of a main adsorbate which is electro-oxidized in the same potential range related to the r-CO_2 adsorbate [22,23]. Therefore, it seems reasonable to admit that the presence of two closely located current peaks for (r-CO_2) electro-oxidation on Rh could be related to a CO-type adsorbate as the tightly bound C-containing adsorbed residue, and a weakly bound r-CO_2 adsorbate.

However, for Rh at $E < -0.05$ V (region II), the CO adsorbate can also be partially electroreduced according to a reaction such as

$$Rh(CO) + H^+ + e^- \rightarrow Rh(r\text{-}CO) \quad (1)$$

Reaction (1) would produce a rather large coverage of the Rh surface by the r-CO adsorbate, i.e. an adsorbate which may be considered as a precursor for the formation of organics from the electroreduction of CO_2 on Rh. In fact, the voltammetric electro-oxidation of (r-CO) (Fig. 3) tends to be closer to that of species resulting from CHO_2H adsorption on Rh rather than on other molecules such as methanol [9].

In principle, the preceding interpretation can be supported by thermodynamic data. Thus, the potential range related to the formation of CO adsorbates in region I can be compared with the half-cell potential for the reduction of CO_2 to CO according to [25,26]

$$CO_2(g) + 2H^+(aq) + 2e^- = CO(g) + H_2O(l) \quad (2)$$

which is E_r (vs. SHE) = −0.104 V. Therefore, as has been concluded recently for Pt and Pd [3,13], the formation of r-CO_2 as a co-adsorbate for $E > -0.10$ V should be also considered as an underpotential electroadsorption on Rh, although the process is positively shifted for Pt compared with Rh.

The formation of r-CO species and reduced species from r-CO_2 in region II, for $E < -0.1$ V, becomes thermodynamically feasible as the half-cell potentials for the formation of species such as CHO_2H and CH_2O, from CO_2 and H^+-ion according to the following reactions

$$CO_2(g) + 2H^+(aq) + 2e^- = CHO_2H(aq) \quad (3)$$

$$CO_2(g) + 4H^+(aq) + 4e^- = CH_2O(g) + H_2O(l) \quad (4)$$

are E_r (vs. SHE) = −0.114 V [25,26], and −0.028 V [26,27] respectively. For reaction (3) the value E_r (vs. SHE) = −0.196 V has also been reported [27]. It should be noted that a change in the phase of the products would change slightly the value of E_r for reactions (3) and (4). Nevertheless, although the above values of E_r for the various CO_2-containing species are small, overpotentials on Rh and Pt are probably larger owing to the formation of adsorbed intermediates on the electrode surface.

4.2. The kinetics and probable mechanism of the HER on Rh in CO_2-containing aqueous 0.5 M H_2SO_4

At a constant H_2 gas pressure, H^+-ion activity and temperature, the potential determining reaction for Rh and Pt in acid solution at zero current density (cd),

$$2H^+(aq) + 2e^- = H_2(g) \quad (5)$$

is in equilibrium. For these metals reaction (5) proceeds through the reversible electrosorption of H-atoms which takes place in region I, whereas the HER occurs in region II.

Let us first consider those processes taking place in region I, i.e. in the H-adatom reversible electrosorption potential range. In CO_2-free acid solution, the Rh surface in region I is largely covered by SO_4^{2-}/HSO_4^- ions which adsorb reversibly on Rh in acid [20,28]. Then, H-adatom electrochemical formation would involve the following competitive potential-dependent adsorption equilibrium:

$$x\mathrm{Rh}(SO_4^{2-}/HSO_4^-) + yH^+ + ye^- = (x-y)\mathrm{Rh}(SO_4^{2-}/HSO_4^-) + y\mathrm{Rh(H)} + ySO_4^{2-}/HSO_4^- \quad (6)$$

where the parentheses stand for adsorbed species, and x and $(x-y)$ are the fractions of the Rh surface covered by sulphate anions, and y is the fraction of Rh covered by H-adatoms, respectively, with the ratio x/y decreasing as the applied potential is shifted negatively.

However, in a CO_2-containing solution, r-CO_2 adsorbates are formed on an electrode surface which is already partially covered by H-adatoms by a reaction such as

$$y'\mathrm{Rh(H)} + \mathrm{CO_2} \rightarrow y'\mathrm{Rh(r\text{-}CO_2)} \quad (7)$$

where $y' < y$. Furthermore, in region I a reduction in (r-CO_2) species by H-adatoms appears to be possible yielding CO-type adsorbed species. This process can formally be represented by

$$y''\mathrm{Rh(r\text{-}CO_2)} + 2y''\mathrm{Rh(H)} \rightarrow y''\mathrm{Rh(CO)} + y''\mathrm{H_2O} + 2y''\mathrm{Rh} \quad (8a)$$

and H-adatoms are replenished according to the reaction

$$2y''\mathrm{Rh} + 2y''\mathrm{H^+} + 2y''\mathrm{e^-} = 2y''\mathrm{Rh(H)} \quad (8b)$$

where $y'' < y' < y$, and y' and y'' denote the fraction of the Rh surface covered by (r-CO_2) and (CO) respectively. Reaction (8b) would be influenced by anion adsorption as indicated by reaction (6).

For the sake of simplicity, the r-CO_2 adsorbate ensemble could be represented as ($2HCO_2$) [29] and it decomposes on Rh yielding CO-type adsorbates as described for Pt and Pd [17] in the same solution. Therefore, in the presence of CO_2 three types of adsorbate would coexist on Rh in the acid solution in region I, namely (H), (r-CO_2) and (CO), the latter being the dominant species, as can be concluded from FTIRS data [17]. These adsorbates would account for the presence of two current contributions owing to (r-CO_2) and (CO) in the anodic stripping voltammogram depicted in Fig. 5, which has also been observed for Pd and Pt [17]. Voltammetric data also show a large overlapping of the electro-oxidation potential range of these adsorbates [22,23].

Let us consider now the HER which takes place in region II. In the absence of CO_2, the HER polarization curves for both Rh and Pt fit Tafel lines, the slope of which depends on the cd range. Thus, in the low cd range, $b_T \approx -0.030$ V decade^{-1}, i.e. a value very close to the $-2.303\ RT/2F$ ratio at 25°C, irrespective of the direction of stepping the potential. Likewise, in the high cd range, $b_T \approx -0.180$ V decade^{-1}.

The value $b_T \approx -0.030$ V decade^{-1} has been related to a reaction pathway involving two consecutive steps, namely a fast discharge of H^+ ions followed by a slow combination of two H-adatoms yielding H_2 [30,31]. In this case, a Langmuir adsorption isotherm has been assumed for H-adatoms.

When CO_2 is present in the solution there is an increase in the cathodic overvoltage for the HER, particularly for pc-Pt, and pc-Rh and rd-Rh. In addition, there is a clear change in the Tafel slope for the HER on Rh in the low cd range, whereas the values of b_T for Pt in the low and high cd range, and for Rh in the high cd range, appear to be independent of the presence of CO_2. Unfortunately, at higher cathodic overpotentials ($E < -0.1$ V) it is virtually impossible to separate the influence of CO_2 and the interference of H_2 bubbling in the HER polarization curves.

The entire influence of CO_2 on the Tafel plot for the HER is mitigated appreciably on cs-Pt. The influence of CO_2 in this case is probably due to a considerable blockage of the cs-Pt surface leaving only tip domains as active surface areas for the HER. In this case, the absence of hysteresis in the polarization curves run by stepping the potential forwards and backwards would indicate that the surface blockage owing either to (r-CO_2), (CO) or H_2 in voids remains approximately the same in the entire HER potential range.

The influence of CO_2 on the HER polarization curve for Rh already begins at 0 V, i.e. at a potential lower than that for Pt. In this case, the presence of CO_2 leads to a Tafel region with a considerable increase in b_T as it approaches $b_T \approx -2RT/F$ even in the low cd range. These facts are consistent with the shift of the polarization data shown in Figs. 7 and 8. Further, for Rh the maximum q_{ox} value results for $E_{ad} = -0.14$ V and $t_{ad} = 300$ s. Seemingly, at this potential the interference of sulphate anion adsorption on Rh becomes negligible [20], favouring (r-CO) formation. The presence of a high surface coverage of Rh by (r-CO) adsorbates would mean that in region II the HER is hindered, as results from the shift in b_T from -0.030 V decade^{-1} in the CO_2-free solution to $b_T = -0.120$ V decade^{-1} in CO_2-containing solutions. Following the conventional reaction pathway proposed for the HER under a Langmuir adsorption for adsorbed reaction intermediates, this change in b_T can be related to a shift in the rate-determining step for the HER from the H-adatom combination step (Tafel step) to the first electron transfer step (Volmer step). This shift is probably favoured by the fact that, as concluded from tracer experiments, the j_0 (Volmer step)/j_0 (Tafel step) ratio is 1 or thereabouts [32].

From the above interpretation it can be concluded that the increase in the degree of surface coverage by (r-CO) on Rh modifies the kinetics and mechanism of the HER by decreasing the degree of surface coverage by those species acting as intermediates in the HER [31], and by shifting the rate-determining step in the HER pathway from the H-adatom combination step to the first electron transfer step.

In conclusion, the difference in the behaviour of Rh and Pt towards their interaction with CO_2 in the electrochemical environment is to some extent comparable with that already found for these metals in contact with CO_2 in the gas phase [33–36].

5. Conclusions

The electrosorption of CO_2 for Pt commences at ca. 0.3 V and attains a maximum at ca 0.1 V, whereas for Rh it

begins at ca. 0 V and increases steadily to attain the maximum coverage at ca. −0.15 V. This negative shift in the adsorption potential for Rh correlates with the greater adsorbability of sulphate anions on Rh as compared with Pt.

Adsorbed species formed from the underpotential electroadsorption of CO_2 on Rh and Pt in acid solution can be ascribed to a reduced form of absorbed CO_2 and a CO-type adsorbate, the latter appearing as the predominant surface species. For Rh in the HER potential range a new adsorbed species is formed which is probably related to a reduced form of adsorbed CO. Accordingly, there is an indirect effect of sulphate anion adsorption via H-adatoms on the electrochemical behaviour of CO_2 on Rh and Pt in acid.

The presence of CO_2 adsorbates on Pt produces an increase in the cathodic overvoltage particularly in the high cd range. The Tafel slope for the HER in the low cd range is $b_T = -0.030$ V decade^{-1}, irrespective of the presence of CO_2 in the solution. The Tafel slope for the HER on Rh increases from $b_T = -0.030$ V decade^{-1} for CO_2-free acid solution to $b_T = -0.120$ V decade^{-1} for CO_2-containing solution.

The change in the Tafel slope for the HER on Rh in acid suggests a change in the rate-determining step in the HER pathway. In the absence of CO_2 a Tafel mechanism under a Langmuir isotherm for the reaction intermediates accounts formally for the HER kinetics, whereas in the presence of adsorbates produced from CO_2 a Volmer mechanism can explain the kinetics of the system.

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