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KINETICS OF RHENIUM DIOXIDE DEPOSITION ON COLUMNAR STRUCTURED PLATINUM ELECTRODES

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Abstract

The kinetics concerning the early stage of the electrodeposition of rhenium dioxide on columnar-structured platinum electrodes from acid aqueous containing perrhenate ions was studied. The results demonstrate a zero-order kinetics obtained by holding the potential at two different values.

Keywords: Deposition, platinum electrodes, rhenium dioxide

INTRODUCTION

The electrodeposition of rhenium species on noble substrates has gained attention during the last years due to its possible application in binary electrodes [1-4]. The electrodeposition process on platinum can be achieved either by potentiostatic [5] or galvanostatic [6-9] procedures. In both cases, the early stages of the electrodeposition process result in the formation of a monolayer of rhenium species [5], but for longer times the development of multilayers takes place [9]. The multilayer rhenium-covered electrode consists of a mixture of rhenium oxides, as demonstrated by comparison of the voltammetric behavior of pure rhenium oxides and of the rhenium-covered electrode [9].

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The initial step of the electrodeposition of rhenium species on platinum electrodes leads to the formation of ReO_2 as the main reaction product [5-10]. Nevertheless, whether this reaction can be achieved by direct electron transfer (eq. 1) or through the participation of pre-adsorbed hydrogen atoms (H_{ad}) (eq. 2) is still a matter of discussion:

$$ReO_4^- + 4\,H^+ + 3e \rightarrow ReO_2 + 2\,H_2O \quad (1)$$

$$ReO_4^- + 3\,H_{ad} + H^+ \rightarrow ReO_2 + 2\,H_2O \quad (2)$$

The use of different metals shed some light on this issue. For gold electrodes, on which only minute amounts of hydrogen atoms can be adsorbed, electrochemical quartz microbalance studies showed that perrhenate electroreduction occurs at more negative potential values than that at which the hydrogen evolution reaction (HER) takes place [11-13], suggesting that H_2 was the reducing agent. On this electrode, metallic rhenium was identified as the electrodeposited species by SEM-EDS [12] and ellipsometry [13]. This case is suitable for a direct electron transfer mechanism (eq.1), which is reinforced by the fact that the industrial production of metallic rhenium is achieved by bubbling a stream of H_2 into an aqueous solution of perrhenate.

Furthermore, for Pt electrodes, a metal capable to adsorb hydrogen atoms, the second mechanism in which H_{ad} are postulated to reduce perrhenate ions (eq. 2) may be considered appropriated. Szabó and Bakos [8] found that ReO_2 electrodeposition on Pt could be achieved by the ionization of preadsorbed hydrogen atoms formed either in acid media or from methanol electrooxidation.

In order to acquire a deeper knowledge concerning the participation of H_{ad} in the early stages of rhenium species electrodeposition on Pt, two approaches have been essayed. First, the use of columnar-structured platinum electrodes (*cs*-Pt) which, because of their surface topography [14-17], allow an adequate handling of the variables related with mass transfer of perrhenate ions from the solution towards the electrode surface, and also of the surface sites available for both the rhenium species deposition and the electrosorption of hydrogen atoms. Second, a kinetic model involving the participation of H_{ad} has been tested to support the experimental findings. The experiments have been performed at two potential values located within the H-electrosorption potential domain.

EXPERIMENTAL

The columnar structured platinum working electrode, *cs*-Pt (real area 5 cm^2) was prepared from a polycrystalline Pt wire (Goodfellow, 99.999 %). The preparation technique consists of two stages [18-20]. The first one implies the

accumulation of a hydrous platinum oxide layer on the starting Pt electrode, through the application of a repetitive square wave potential routine at 4 kHz between 0.05 V and 2.40 V for a time *t*. The second stage involves the electroreduction of the hydrous oxide with a potentiodynamic sweep from 1.45 V down to 0 V at 0.001 V s^{-1} to produce the *cs*-Pt.

The supporting electrolyte was aqueous 1 M sulfuric acid prepared from T.J. Baker, ACS reagent with Millipore Milli-Q* Plus water. Aqueous rhenium-containing solutions, 10^{-3} M (working solution), were prepared by dissolving NH_4ReO_4 (Aldrich, 99 + %) in the supporting electrolyte.

A large area Pt wire and a reversible hydrogen electrode (RHE) were the counterelectrode and reference electrode, respectively. Potentials in the text are given on the RHE scale. All runs were performed at room temperature under nitrogen (99.998 %) atmosphere.

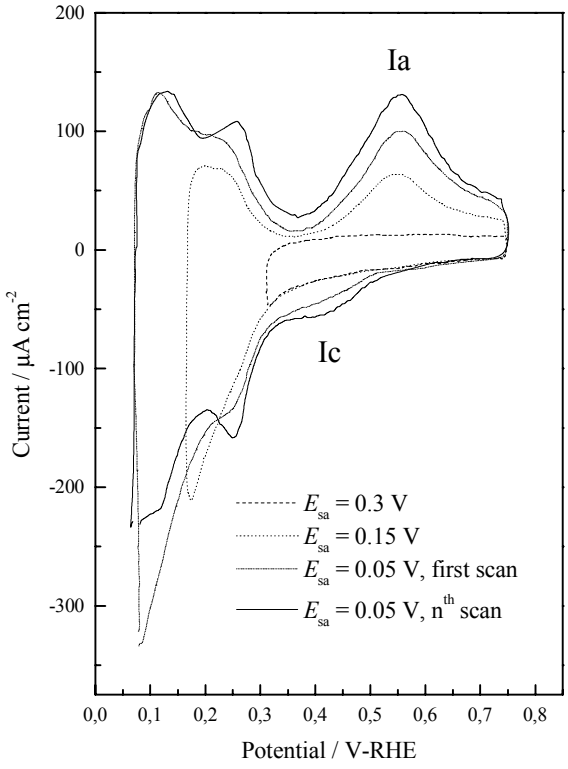

Fig. 1. Open window voltammograms for *cs*-Pt in 10^{-3} M aqueous perrhenate + 1 M H_2SO_4. $v = 0.10$ V s^{-1}, $A = 5$ cm^2

Triangular potential sweeps (TPS) from E_{sc} = 0.05 V to E_{sa} = 1.5 V, and TPS including a potential holding at E_h = 0.25 V and E_h = 0.15 V were performed, both applied for times (t_h) between 10 s and 180 s. The controlled hydrodynamic experiments were performed on *cs*-Pt ring-disc electrodes, prepared as mentioned above.

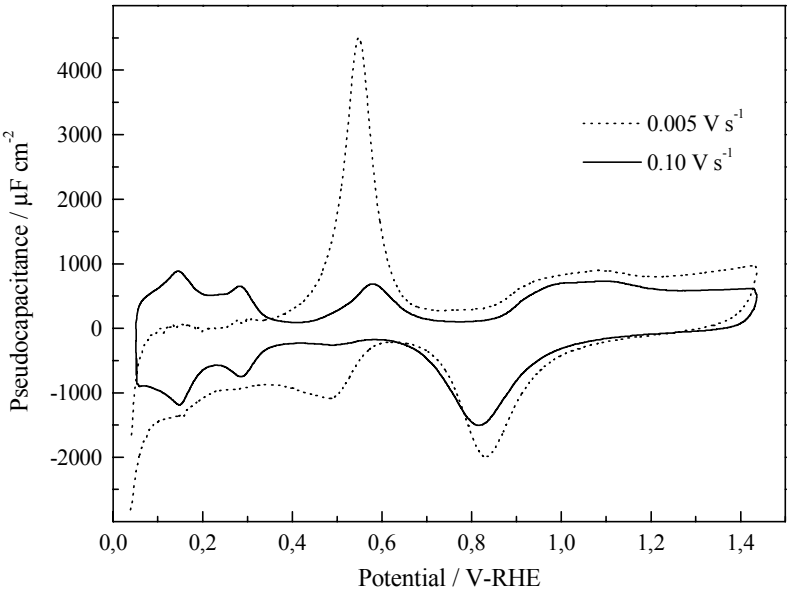

Fig. 2. Repetitive pseudocapacitance curves for the *cs*-Pt in 10^{-3} M NH_4ReO_4 + 1 M H_2SO_4. v = 0.005 and 0.10 V s^{-1}. A = 5 cm^2

RESULTS AND DISCUSSION

A clean *cs*-Pt electrode immersed in the working solution at 0.70 V and subjected subsequently to a potential cycling with a progressive decrease of the lower limit of the potential window (E_{sc}), show that no anodic current peak develops prior to E_{sc} = 0.25 V (Fig. 1). This result suggests that under potentiodynamic conditions the requirement to supply H_{ad} to form ReO_2 is fulfilled. However, if the same experiment is repeated but a potential cycling in the 0.05 to 1.5 V range is previously performed, an anodic current peak is

obtained independently of the value of E_{sc} (Fig. 1, full line). The anodic charge density related to the stripping of ReO_2 performed at 0.1 V s^{-1} resulted equal to (100 ± 10) μC cm^{-2}.

Moreover, regarding the surface topography of the *cs*-Pt electrode that may allow the occurrence of H_{ad} and/or ReO_2 deposition, depending on the potential sweep rate (v) at which the experiment is performed, it was thought about the necessity to found a suitable v permitting the development of the two reactions on the same electrode. Thus, the results indicate that either a coverage of a submonolayer of ReO_2 or a complete coverage by rhenium species at v = 0.1 V s^{-1} and 0.005 V s^{-1}, respectively, is achieved (Fig. 2). These findings can be explained taking into account the diffusion of perrhenate ions to the columnar topography of the electrode. At high v, perrhenate ions only reach the tips of the columns, leaving the voids free for hydrogen adsorption, while at lower v the voids are also filled with perrhenate ions and the reduction reaction can take place. Consequently, the amount of ReO_2 obtained under potentiodynamic conditions increases as v decreases.

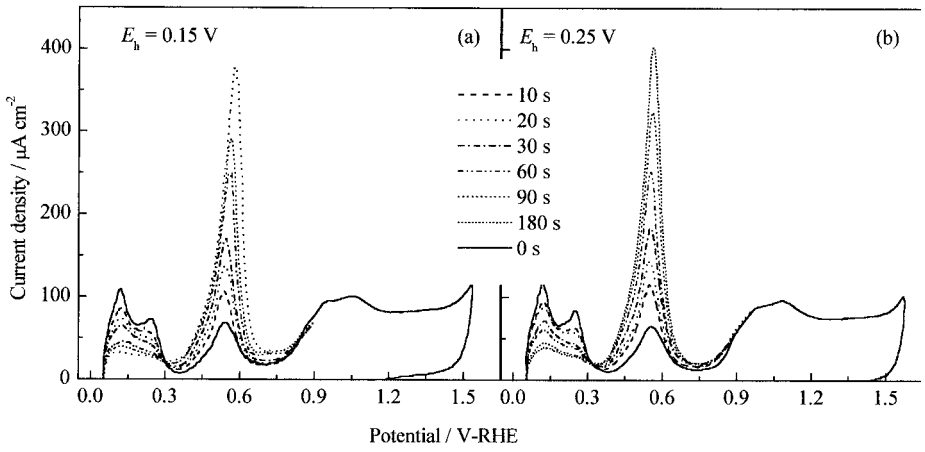

Fig. 3. Repetitive voltammogram for *cs*-Pt in 10^{-3} M aqueous perrhenate + 1 M H_2SO_4 (full line) and stripping curves after holding the potential at (a) E_h = 0.15 V and (b) E_h = 0.25 V, for 10 s ≤ t_h ≤ 180 s. A = 5 cm^2.

Once the experimental conditions to perform the potentiostatic deposition of rhenium species have been acquired, the study was carried out at two selected potentials (E_h). The cyclic voltammograms corresponding to the stripping of the ReO_2 formed on the *cs*-Pt electrode at E_h = 0.15 V and 0.25 V are shown in Figs 3a and b, respectively. The stabilized voltammograms in the working solution (t_h = 0) for both E_h (full line) show cathodic and anodic current peaks located at 0.46 V and 0.55 V, respectively. These current peaks result from the early stages in the electroformation and electrodissolution of adsorbed ReO_2 at a submonolayer level during the initial potential cycling [5]. The anodic charge density at t_h = 0 is equal to (100 ± 10) μC cm^{-2} for both E_h values. For a constant E_h, the anodic charge density related to the electrooxidation of ReO_2 to ReO_4^- increases with t_h, indicating that a larger quantity of ReO_2 has been formed. Accordingly, the charge density related to the H-electrosorption reaction decreases as t_h increases due to the blocking coverage of the *cs*-Pt surface by ReO_2 species. At E_h = 0.15 V, the anodic peak potential shifts towards positive values for t_h > 60 s, whereas for E_h = 0.25 V, no shift of the potential peak is observed in the whole t_h range. For E > 0.7 V, the ReO_2 species are completely stripped from the surface, as deduced from the undistorted O-electrosorption profile.

According to eq. 2, the kinetic equation related to the formation of ReO_2 can be written as:

$$\frac{dQ_{ReO_2}}{dt} = k[ReO_4^-][H^+]\theta_H^3 \qquad (3)$$

where k is the kinetic constant, Q_{ReO2} is the anodic charge density involved in the electrooxidation of ReO_2 to ReO_4^-, and θ_H is the degree of coverage of *cs*-Pt surface with H_{ad}. The value of θ_H depends on E_h, and it is constant for each E_h value because the H electrosorption reaction is very fast [21]. In addition, although H_{ad} are consumed while the reaction takes place, at $E \geq 0.15$ V the electrode surface has not yet achieved a complete coverage by these species, allowing the continuous renewal of H_{ad} as soon as they are consumed. Thus, at a fixed E_h all the factors at the right hand of eq. 3 are considered as constant ones.

Integration of eq. 3 leads to:

$$Q_{ReO_2} = Q^o_{ReO_2} + k'.t_h \qquad (4)$$

where Q^o_{ReO2} stands for the anodic charge density at t_h = 0, and $k' \equiv k[ReO_4^-][H^+]\theta_H^3$. This zero-order kinetic model explains why the reaction does not occur in a large extent in basic media [10], as both $[H^+]$ and θ_H decrease significantly with the increase of pH.

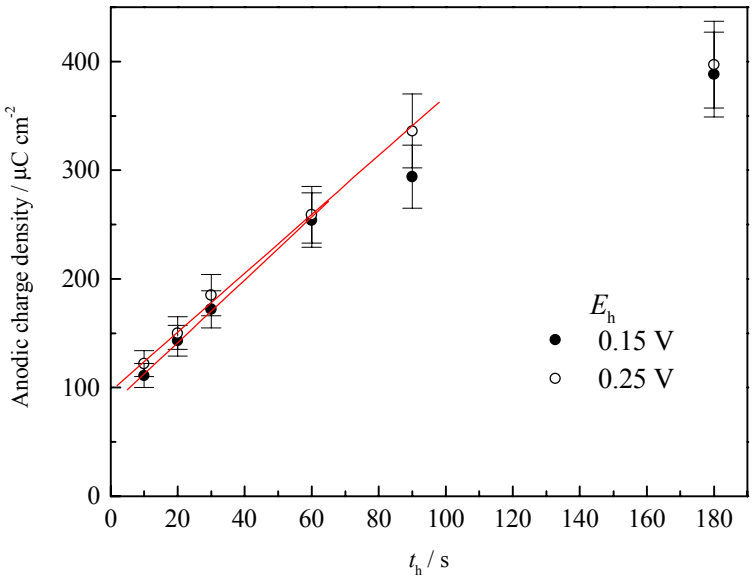

Fig. 4. Anodic charge densitiy *vs* t_h plot for E_h = 0.15 V and 0.25 V

The evolution of Q_{ReO2} with t_h is shown in Fig. 4. For E_h = 0.15 V, a linear relationship is obtained for $t_h \leq 60$ s, while for E_h = 0.25 V, the linear relationship is verified only for $t_h \leq 90$ s. The slopes of the linear ranges (k') are (2.9 ± 0.1) μC cm^{-2} s^{-1} and (2.7 ± 0.1) μC cm^{-2} s^{-1}, for E_h = 0.15 V and 0.25 V, respectively. The intercepts of Q_{ReO2} at t_h = 0, Q^o_{ReO2} are (83 ± 2) μC cm^{-2} and (97 ± 3) μC cm^{-2}, the latter being in close agreement with that found experimentally.

It should be emphasized that the t_h range in which eq. 3 is valid is larger for E_h = 0.25 V as compared with E_h = 0.15 V. This fact can be explained by taking into account that the only reaction occurring at E_h = 0.25 V is the one described by eq. 2, whereas at E_h = 0.15 V, two processes may be competing. In order to ascertain with this hypothesis, a rotating ring-disc electrode has been used to detect any soluble rhenium species that could have been formed. An anodic current is obtained when the ring potential is set at 0.60 V (Fig. 5), denoting the formation of a soluble species at 0.15 V, probably a Re(III)-soluble species

[22]. This fact explains for what reason the zero order kinetic model is accomplished by the data obtained at E_h = 0.15 V, although a slight departure between the predicted and the experimental values of Q^o_{ReO2} is observed.

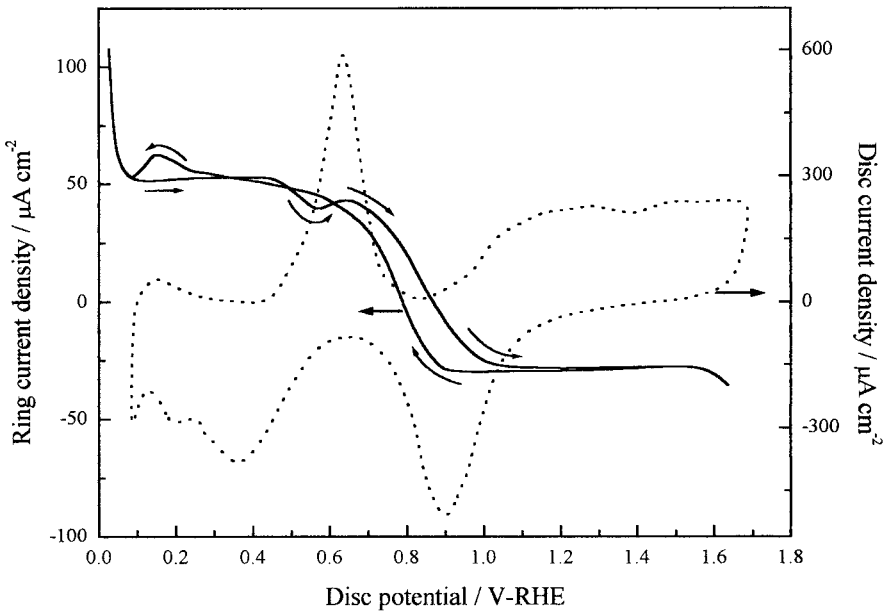

Fig. 5. Ring and disc current densities during the application of a triangular potential sweep to the ring at 0.10 V s^{-1} in the working solution. E_{ring} = 0.60 V, A_{disc} = 3.24 cm^2, A_{ring} = 0.76 cm^2

Moreover, the deviations detected from the proposed kinetic model deserve a particular consideration. These deviations are observed for t_h > 90 s at E_h = 0.25 V, and for t_h > 60 s at E_h = 0.15 V. At E_h = 0.25 V, this depart could be attributed to the formation of multilayers of adsorbed ReO_2 [9]. However, at E_h = 0.15 V, the formation of Re(III)-soluble species and its further oxidation to ReO_2 should account for the non-applicability of the kinetic model at an extended t_h range. The oxidation of Re(III)-soluble species during the positive going potential scan produces ReO_2 on the previously deposited ReO_2, probably in a multilayer fashion. In this sense, the anodic charge density increases,

preserving an almost constant value for the H-electrosorption charge density, explaining the deviations observed in Fig. 4. The formation of multilayers of adsorbed ReO_2 also agrees with the shift of the anodic peak potential observed in Fig. 3.

From the results presented in this work, the following conclusions can be drawn:

1. A kinetic model for the deposition of ReO_2 from acid aqueous containing perrhenate ions on *cs*-Pt electrodes was developed, which takes into account the participation of H_{ad} in the reduction process.
2. The kinetic model fits the experimental values obtained at E_h = 0.25 V, potential at which the reduction of perrhenate ion takes place (eq. 2).
3. Data obtained at E_h = 0.15 V fit the kinetic model, but the predicted values deviate slightly from the experimental ones. At this potential, a partial reduction of ReO_2 to Re(III)-soluble species occurs, which oxidizes to ReO_2 in the positive going potential sweep, accumulating in a multilayer fashion.
4. For prolonged t_h, a ReO_2 multilayer formation takes place, in accordance to other reports [9].

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