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A Microgravimetric Study of Simultaneous Adsorption of Anions and Copper on Polycrystalline Pt Surfaces

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A deposição em subtensão de Cu foi estudada em quatro diferentes eletrólitos ácidos, por meio de medidas simultâneas de voltametria cíclica e microgravimetria, usando uma microbalança eletroquímica de cristal de quartzo. A influência dos ânions na formação da monocamada de Cu foi determinada. Entre os três picos de dessorção observados, encontrou-se que o primeiro é muito sensível à natureza do anion presente em solução. Este comportamento foi relacionado com o baixo recobrimento da superfície da Pt com os ad-átomos, na faixa de potenciais correspondente, que resulta apenas em interações muito fracas entre os ad-átomos de Cu. A monocamada é composta de uma primeira camada de Cu adsorvido sobre Pt e uma segunda camada de ânions adsorvidos sobre os ad-átomos de Cu, com cada ânion ocupando dois ad-átomos adjacentes, com exceção do Cl^-, que se depositou na forma de um ânion para cada ad-átomo de Cu. Esta estrutura forma, conseqüentemente, uma bi-camada. A modificação dos perfis dos massogramas e voltamogramas pelo acréscimo do Cl^- no eletrólito de perclorato também foi analisada.

The underpotential deposition of Cu was studied in four different acid electrolytes by simultaneous measurements of cyclic voltammetry and microgravimetry using a electrochemical quartz crystal microbalance. The influence of anions on the Cu monolayer was determined. Among the three desorption peaks observed, the first was found to be very sensitive to the nature of the anion present in solution. This was related to the low coverage of the Pt surface by ad-atoms, in the respective potential range, which yields a weak interaction between the Cu ad-atoms. The monolayer is composed of a first layer of Cu adsorbed on Pt and a second layer of anions adsorbed on the Cu ad-atoms, with each anion occupying two adjacent Cu atoms, with the exception of the Cl^- anion which was deposited on only one Cu ad-atom. This structure consequently forms a bi-layer deposit. The modification of voltammetric and massogram profiles by adding Cl^- to the perchlorate electrolyte was also analyzed.

Keywords: underpotential deposition, ad-atom, quartz crystal microbalance, massogram, anions, adsorption

Introduction

The underpotential deposition of metals has been intensively studied, on both polycrystalline and single crystal surfaces of different substrates,[1] using a wide variety of techniques. The techniques that have been employed include scanning tunneling and atomic force microscopy,[2-4] X-ray diffraction,[5,6] X-ray absorption spectroscopy,[7,8] electrochemical quartz crystal microbalance[9-12] amongst others. The great importance of metal deposition processes has made UPD the subject of several review papers.[1,13,14]

Among the very large amount of published work, Cu UPD is one of the most studied systems. Cu UPD has been studied on either polycrystalline[10,15-17] or on single crystal[18-20] electrodes. As the atomic radius of Cu is smaller than that of Pt or Au (the most common substrates), the Cu ad-atom occupies only one active site on these materials.[15,21] Due to this, the deposited monolayer presents very well defined properties.

In this way, the well-defined Cu monolayer becomes a very convenient probe to discuss the effect of anion co-adsorption, since it can promote alterations in the ad-atom structure. It is not surprising that a large number of published papers have been dedicated to the subject, either on Pt[19,22-25] or on Au.[26-29] However, in order to

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optimize the monolayer organization and highlight any possible alteration due to anion adsorption, previous studies have mainly focused on single crystal surfaces. The major importance of this subject is discussed by Lipkowski and co-workers[26] in terms of the effect of anions in the ordering of deposited metal ad-atoms and in the promotion of the UPD process. In particular, the deposition of copper on gold electrodes has become the most exhaustively investigated UPD reaction. Kolb and co-workers[30] were the first to show that anions play a significant role in the electrodeposition of copper. Several subsequent studies provided convincing evidence that, particularly, sulfate ions co-adsorb with the deposited copper ad-atoms and that such co-adsorption accelerates the Cu deposition reaction[31] and affects both the ordering[32] and the oxidation state of the metal ad-atoms.[33] Further studies with radiochemical techniques also demonstrated that sulfate and chloride adsorption on Cu-covered polycrystalline Au electrodes is significantly enhanced by co-adsorbed copper.[34] Evidence for analogous influences of Cu and anion co-adsorption on Pt [111] are also available.[35,36]

To some extent, the highly organized nature of single crystal surfaces is very convenient for studying the effects of anions and the co-adsorption of metallic ad-atoms. However, for many practical applications, single crystals present difficulties that hinder their utilization. In this way, the behavior of anions and metallic ad-atoms on polycrystalline surfaces is also very interesting, even if it is true that there is an the increased level of complication associated with the disordered nature of such surfaces. In this way, the objective of this work is to investigate, using an electrochemical quartz crystal microbalance, the co-adsorption in acid medium of Cu and anions such as sulfate, perchlorate, phosphate and chloride, on a polycrystalline Pt surface.

Experimental

The experimental details have been presented in a recent communication.[37] In addition, CuO (Merck PA) was used to prepare the 5.0×10^{-5} mol L^{-1} + 0.5 mol L^{-1} ($HClO_4$, H_2SO_4, HCl or H_3PO_4 Merck PA) electrolytes.

At-cut quartz crystals with fundamental frequency of 9 MHz were used as the working electrodes. Each crystal had a 0.2 cm^2 circular area of Pt surface. Using the total charge density for the UPD H desorption on Pt, it was possible to calculate an electrochemical area of 0.35 cm^2, which was used throughout this work.

The experimental voltammetric data were analyzed with the aid of Origin (Microcal Inc.) software.

Results and Discussion

The strong influence exerted by the anion during Cu UPD on polycrystalline Pt, can be observed from the alterations promoted in the voltammetric profiles obtained in the different electrolytes used (Figure 1). In Figure 1, the effect of adding CuO (5×10^{-5} mol L^{-1}) to 0.1 mol L^{-1}

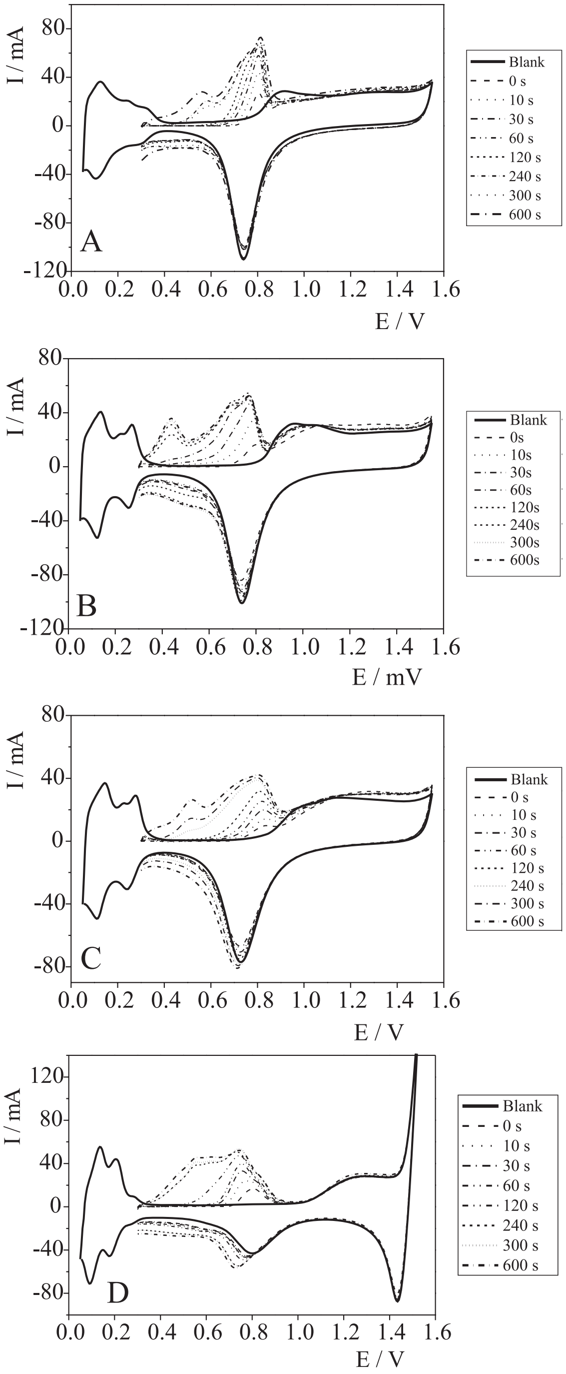

Figure 1. Cyclic voltammograms for polycrystalline Pt electrode in an electrolyte containing CuO (5×10^{-5} mol L^{-1}) + 0.1 mol L^{-1}: (A) $HClO_4$, (B) H_2SO_4, (C) H_3PO_4 and (D) HCl. Sweep rate = 0.1 V s^{-1}. Solid lines correspond to the steady state response for the blank solution.

of (a) $HClO_4$, (b) H_2SO_4, (c) H_3PO_4 and (d) HCl, at a potential sweep-rate of 0.1 V s^{-1}, can be observed. The corresponding full lines are associated with the response of the electrode in pure electrolyte, without any Cu^{2+}. For the other lines, Cu ad-atoms were deposited at 0.3 V for the deposition times indicated. Analysis of the voltammetric profile for Cu UPD on polycrystalline Pt in H_2SO_4 solution has previously been reported.[38] The four peaks observed can be attributed to the different energetic states of Cu_{ads} and are associated to lateral repulsion interactions.[39] At the deposition potential used here, no evidence for bulk Cu deposition was obtained.

Voltammetric analysis

In order to analyze the UPD processes in the four electrolytes studied here, a deconvolution procedure was applied to each anodic branch in the voltammograms presented in Figure 1. On the basis of a mathematical treatment proposed by Armand and Clavilier,[40,41] the Cu UPD voltammetric response can be described by a Frumkin-Fowler isotherm that yields symmetrical voltammetric peaks. These symmetrical peaks are very well represented by the Gaussian equations used by the deconvolution program included in the Origin software. This program decomposes the experimental data into a set of individual peaks with Gaussian forms. The peak position (E_p), the peak height (I_p) and the half-peak width ($\Delta E_{1/2}$) are the parameters to be optimized. The minimization of the deviation between calculated and experimental values is evaluated by the chi-square method, as described in the software package.

Using the method described above, the observed voltammetric forms were decomposed into the components presented in Figure 2 (for each electrolyte) as the respective dotted lines, using, as baselines, the double-layer currents observed in the voltammogram for the blank solution. The sum of these peaks (for each case), represented by the full lines, is completely coincident with the respective experimental curves. The voltammetric form in all electrolytes, except in the case of HCl, present four dissolution peaks, like those discussed for H_2SO_4. In HCl only three anodic peaks were observed. In this way, the influence of the electrolyte anions seems to be restricted to the area and position of each peak. These values are collected in Table 1, together with the half-peak width. From Table 1 it is evident that changing the anion causes differences in either the peak potential and the half-peak width values. However, the only parameter that varies in a continuous manner is $\Delta E_{1/2}$ for the first peak, which increases continuously with the growing strength of interaction between each anion and the electrode surface. The UPD Cu species associated with Peak 1 presents the lowest Cu-Cu lateral interaction due to the low coverage of such ad-atoms (θ_{Cu} (Peak 1) ≈ 0.3). Thus, there is plenty of space for anion adsorption on the Pt substrate and, consequently, it is possible to observe the strongest Cu-anion lateral interaction.

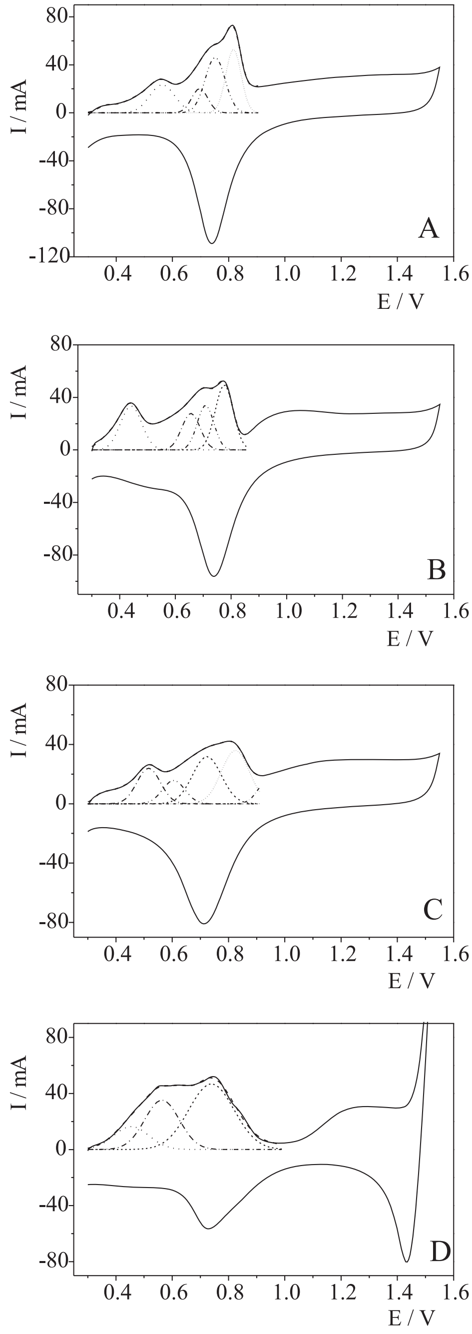

Figure 2. Deconvoluted Cu UPD responses for the voltammetric profiles obtained under the experimental conditions specified in Figure 1.

Finally, it can also be observed that, in the presence of Cl^-, the total anodic charge for Cu desorption increases

Table 1. Peak parameters for Cu UPD on polycrystalline Pt electrodes in several electrolytes

	Peak 1	Peak 2	Peak 3	Peak 4
		$HClO_4$		
Q / (μC cm^{-2})	129.90	148.12	52.45	94.31
E_p / (V)	0.815	0.750	0.695	0.561
$\Delta E_{1/2}$ / (V)	0.060	0.085	0.066	0.101
		H_2SO_4		
Q / (μC cm^{-2})	142.30	91.48	83.00	110.81
E_p / (V)	0.776	0.706	0.653	0.439
$\Delta E_{1/2}$ / (V)	0.070	0.069	0.073	0.089
		H_3PO_4		
Q / (μC cm^{-2})	154.01	138.67	50.80	86.60
E_p / (V)	0.821	0.719	0.603	0.515
$\Delta E_{1/2}$ / (V)	0.114	0.127	0.092	0.102
		HCl		
Q / (μC cm^{-2})	293.99	-	168.85	80.21
E_p / (V)	0.737	-	0.559	0.450
$\Delta E_{1/2}$ / (V)	0.183	-	0.139	0.146

to 543.05 μC cm^{-2}, meaning 1.3 monolayers are deposited. This can be the result of strong Cu^{2+} and Cl^- interactions, which change the UPD potential to values closer to that of bulk deposition.

Microgravimetric analysis

In order to analyze the adsorption of non-electroactive species (*i.e.* the anions) on the electrode surface during Cu UPD, the mass variation of the working electrode was studied simultaneously with the voltammetric sweep. The results are collected in Figure 3, where the dotted lines correspond to the electrolyte response in each acid medium and the full lines the response after adding CuO (5×10^{-5} mol L^{-1}) to each electrolyte. The mass responses corresponding to the blank solutions have been analyzed in a recent communication.[37] It was observed that, in the range of Cu UPD potential explored here, anions adsorb only slightly on polycrystalline Pt surfaces. The maximum coverage and the nature of species adsorbed were found to be: 0.07 monolayer for $ClO_4^-.2H_2O$, 0.07 for $HSO_4^-.2H_2O$, 0.19 for HPO_4^{2-} and 0.11 for Cl^-.

The mass variations promoted by adding CuO (5×10^{-5} mol L^{-1}) to each of the four electrolytes and holding the potential at 0.3 V for 600 s to allow for a full monolayer of Cu_{ads}, are presented in Figure 3. In Figure 3A stands for 0.1 mol L^{-1} $HClO_4$, (B) H_2SO_4, (C) H_3PO_4 and (D) HCl. In the positive potential sweep (Figure 3A), in 0.1 mol L^{-1} $HClO_4$ + 5×10^{-5} mol L^{-1} CuO, in the potential range between 0.3 and 0.85 V, a mass loss of 200 ng cm^{-2} can be

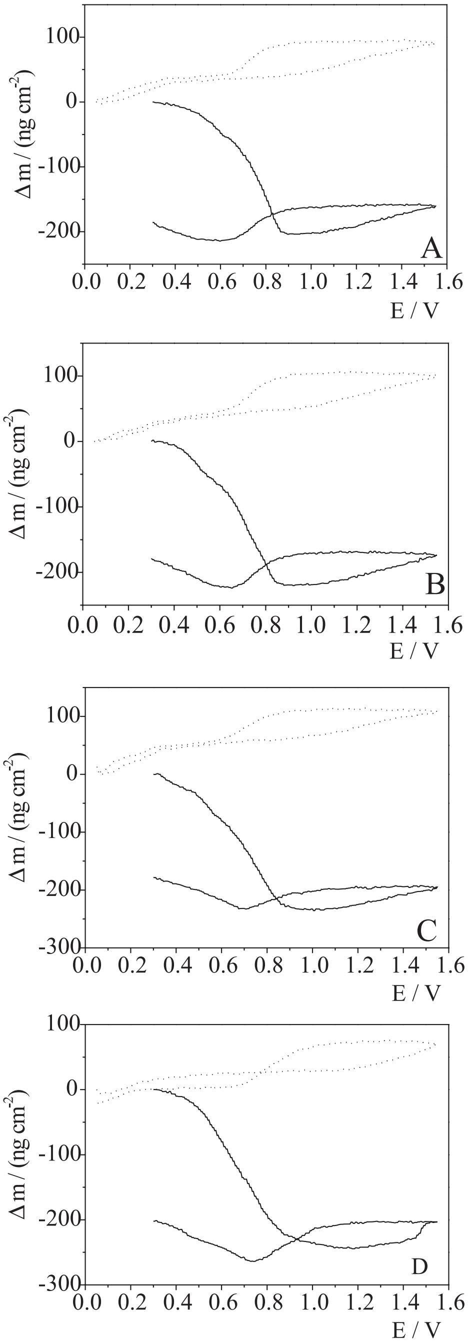

Figure 3. Massograms for Cu UPD obtained in CuO (5×10^{-5} mol L^{-1}) + 0.1 mol L^{-1}: (A) $HClO_4$, (B) H_2SO_4, (C) H_3PO_4 and (D) HCl at 0.1 V s^{-1}. Dotted lines correspond to the blank responses.

observed, which is larger than the value calculated for a complete Cu monolayer. The theoretical calculation of the electrode mass loss after the desorption of Cu_{ads} is performed considering the atomic mass of Cu (*i.e.* 63.5), the number of active sites (atoms) on the polycrystalline Pt surface (3 × 10^{15}) and the factor to convert atomic mass units to ng (1.66×10^{-24}). The product of these factors and the electrochemical area of the electrode result in a mass loss of 137 ng cm^{-2}. This being considered, with the dissolution of the Cu monolayer there is an excess mass loss of 63 g cm^2. Simultaneously, the dissolution of the Cu monolayer can be followed by the associated cyclic voltammetric charges. Thus, as shown before, a value of 420 μC cm^{-2} (as calculated by the sum of all peaks for $HClO_4$ in Table 1) demonstrates that a full Cu_{ads} monolayer is being desorbed from the electrode surface (in a two-electron oxidation process). In conclusion, there is an excess mass loss of 63 ng cm^{-2} that should be explained.

In the negative potential range associated with Cu UPD, the only possibility for the excess mass loss is associated with the difference between anion coverage on the Cu surface and on the Pt surface. It has already been demonstrated[37] that on bare Pt surfaces, the maximum amount of ClO_4^- adsorbed reaches 0.07 of a monolayer and has an associated mass variation of only 20 ng cm^{-2}. In this way, a 0.28 monolayer (four times) on the Cu ad-layer is necessary to justify an excess mass loss of 60 ng cm^{-2} during Cu oxidation, considering that 0.07 will reabsorb on the free Pt surface. To consider a variation in the amount of water molecules during Cu dissolution is difficult because water is adsorbed on all surfaces (Cu_{ads}, anions and Pt) so its contribution to the mass variation should be very small.

In order to gain further insight in to the possibility discussed above, the Δm *vs* ΔQ plot was constructed based on the voltammetric and microgravimetric responses presented in Figure 3 (Figure 4). Such relationships are derived from the mass balance and Faraday's Law:

$$\Delta m_{total} = n_{Cu}M_{Cu} + n_{ClO_4^-}M_{ClO_4^-} \qquad (1)$$

$$\Delta Q_{total} = n_{Cu}Z_{Cu}F \qquad (2)$$

where M is the molar mass of each species, n the number of moles and Z the number of electrons transferred. Considering that each perchlorate ion occupies two adsorption sites on the Cu monolayer ($n_{ClO_4^-} = 0.5n_{Cu}$) and that there is only a fractional anion coverage on the Cu monolayer (x), the division of (1) by (2) yields:

$$\left(\frac{\Delta m}{\Delta Q}\right)_{exp} = \frac{1}{F}\left(\frac{M_{Cu}}{Z_{Cu}}\right) + \frac{x}{2F}\left(\frac{M_{ClO_4^-}}{Z_{Cu}}\right) \qquad (3)$$

The experimental value obtained from Figure 4 for the slope of Δm *vs.* ΔQ is 4.1×10^{-4} g C^{-1}. Inserting this and the other values in equation 3, it is possible to calculate the fractional coverage of perchlorate anions on the Cu monolayer. The value obtained was 0.31, which means that 62% of Cu ad-atoms are bonded with ClO_4^- (since each anion is adsorbed on two ad-atoms). In this way, the oxidation of Cu ad-atoms also promotes desorption of 0.31 of a monolayer of perchlorate anions. Desorption of a full perchlorate anion monolayer should result in a mass loss of approximately 216 ng cm^{-2} (as discussed before

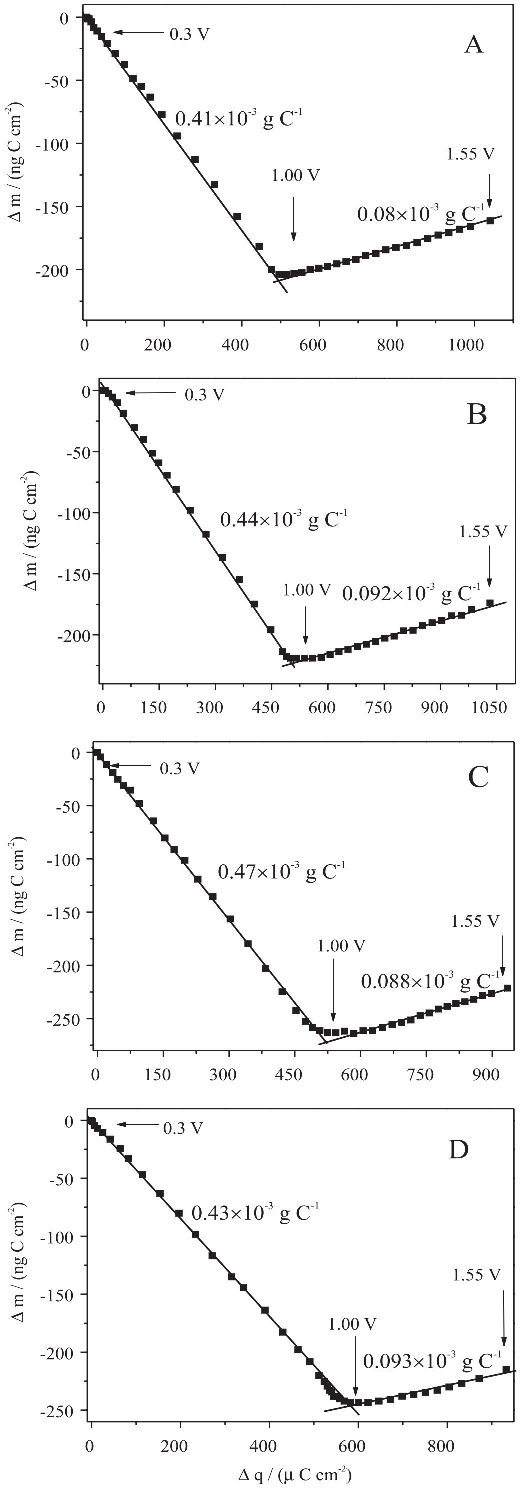

Figure 4. Δm *vs.* DQ plots obtained from the voltammograms showed in Figure 1 and from the massograms presented in Figure 3.

Table 2. Mass variations and Cu UPD coverage factors for the different anions under study

Anions	$\Delta m^{a}_{observed}$ / (ng cm^{-2})	Excess Δm / (ng cm^{-2})	($\Delta m/\Delta Q$) / (g C^{-1})	θ^{max} (Pt) Reference 37	$\theta^{observed}$ (Cu)
ClO_4^-	200	63	4.10×10^{-4}	0.07	0.31
HSO_4^-	220	83	4.30×10^{-4}	0.07	0.39
HPO_4^{2-}	225	88	4.35×10^{-4}	0.19	0.42
Cl^-	220	42	4.30×10^{-4}	0.11	0.55

[a]The theoretical Δm for a complete Cu monolayer is 137 ng cm^{-2} for the first three anions and 178 ng cm^{-2} for Cl^-.

for Cu UPD). Thus, the desorption of 0.31 of a monolayer would be responsible for a decrease of 65 ng cm^2 in the electrode mass, which explains the excess mass loss observed for Cu_{ads} oxidation.

The same analyses were also performed for the three other electrolytes used and the results are collected in Table 2. Of course, the adsorption of a Cl^- ion should occur at only one Cu ad-atom.

Electrochemical response in $HClO_4$ after the addition of Cl^-

Since Cu UPD in the electrolyte that contained Cl^- presented results that were significantly different from the others, the effect of adding chloride to the ClO_4^- electrolyte was also investigated. The effect on the voltammetric and microgravimetric responses of adding varying concentrations of Cl^- to the electrolyte that contained CuO (5×10^{-5} mol L^{-1}) + $HClO_4$ (0.1 mol L^{-1}), is presented in Figure 5.

The strong influence exerted by Cl^- on Cu UPD at polycrystalline Pt can clearly be observed in Figure 5. The voltammetric profile changes from that characteristic of Pt in ClO_4^- (b) to that in Cl^- (g). Moreover, the preferential inhibition of Peaks 1 and 2, at approximately 0.8 V, can be clearly observed. The initial steps of Cu deposition are influenced by chloride. However, the coverage of the Pt surface with adsorbed Cl^- is not high (θ_{max} = 0.11)[37] and, thus, the blockage of surface sites by Cl^- during Cu deposition can not be considered as a reason for the behavior observed. The only other alternative is the association of Cu^{2+} with Cl^- ions in solution, which results in the formation of a complex structure. The change in free energy of the depositing species shifts the potential to more negative values. This can also explain the increase in the monolayer charge, since the interactions of such species and the surface should be stronger than in other electrolytes. The total oxidation charge values varied from 420 μC cm^{-2} (typical for ClO_4^-) to 543 μC cm^{-2} (for Cl^-) as observed before. The influence of chloride is also observed in the formation and reduction of platinum oxide, in the positive potential region.

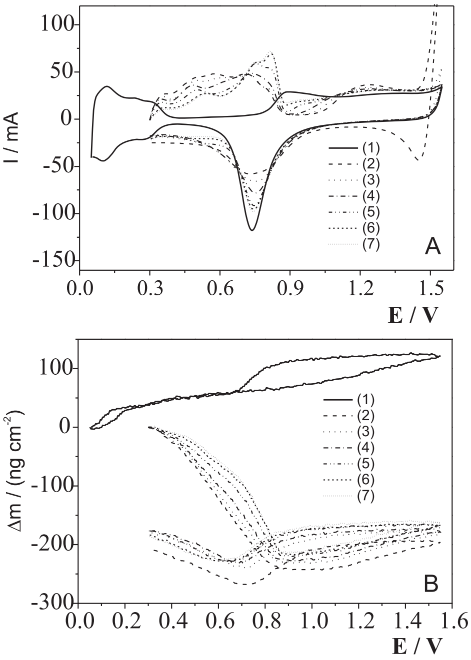

Figure 5. First cyclic voltammograms (A) and massograms (B) for the blank solution (1) and for Cu UPD obtained in CuO (5×10^{-5} mol L^{-1}) + $HClO_4$ (0.1 mol L^{-1}), with successive additions of Cl to the electrolyte: (2) 10^{-2}, (3) 10^{-3}, (4) 10^{-4}, (5) 10^{-5}, (6) 10^{-6} and (7) 10^{-7} mol L^{-1}. Sweep rate = 0.1 V s^{-1}.

The microgravimetric experiments presented the same behavior as the voltammograms. The loss of mass, observed between 0.3 and 0.85 V becomes sharper with the Cl^- content, in agreement with the inhibition of Peaks 1 and 2 for Cu UPD. The loss of mass increases from 200 to 220 ng cm^{-2}, as discussed before. The addition of Cl^- to the perchlorate electrolyte promotes the effects already observed for the pure electrolyte.

Conclusions

Two important conclusions can be drawn from the results presented and discussed in this paper. The first one is related to the enhanced sensibility of one of the Cu UPD peaks to the nature of the anion present in the electrolyte. The oxidation peak related to the desorption of the last portion of Cu monolayer on the Pt surface (Peak

1 in the voltammograms of Figure 2) had their half-peak width and charge affected by the nature of the supporting electrolyte, as shown in Table 1. Following the discussion of the voltammetric results, this sensibility is associated with the absence of Cu-Cu lateral interactions at a stage of low Pt surface coverage with UPD atoms. In this way, the substitution of electrolyte by those containing anions with higher intensity of adsorption, *i.e.*, ClO_4^-, HSO_4^-, HPO_4^{2-} and Cl^-, in this order, makes the first UPD peak increase and have higher a voltammetric charge associated with its desorption. As discussed in a previous communication,[39] the increasing coverage of the Pt surface with Cu results in proportionally stronger lateral interactions between ad-atoms. On such a surface, the presence of strongly adsorbed anions can inhibit Cu-Cu lateral interactions, allowing that the deposition of Peak 1 species occurs to a large extent, so increasing the voltammetric charge associated with it.

The second conclusion is concerned with the bi-layer nature of copper and anion coverage on the Pt surface. The microgravimetric results indicate that the copper monolayer adsorbed on the Pt surface is covered to a large extent by the respective anion. Each perchlorate, sulfate or phosphate ion is adsorbed on two ad-atoms. In this way, a highly ordered surface is obtained during Cu UPD on polycrystalline Pt in the presence of such anions.

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