Article

The Oxidation of Formaldehyde on High Overvoltage DSA Type Electrodes

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Neste trabalho a oxidação eletroquímica do formaldeído é estudada sobre eletrodos dimensionalmente estáveis preparados por decomposição térmica de precursores (correspondentes cloretos). Foram utilizados como eletrodos de trabalho: $Ti/Ir_{0.3}Ti_{0.7}O_2$, $Ti/Ru_{0.3}Ti_{0.7}O_2$ e $Ti/Ir_{0.2}Ru_{0.2}Ti_{0.6}O_2$. As eletrólises foram realizadas galvanostaticamente em uma célula do tipo filtro prensa em soluções 0,5 mol L^{-1} H_2SO_4 com concentração inicial de formaldeído de 100 mmol L^{-1}. A concentração de formaldeído decresce rapidamente com o tempo de eletrólise sendo que o eletrodo ternário (Ir + Ru + Ti) é o que apresenta maior atividade catalítica. O ânodo contendo somente Ir, apesar de maior carga superficial é o de menor atividade eletrocatalítica. Para a oxidação de ácido fórmico, formado pela oxidação de formaldeído, a presença de Ir na composição do ânodo não favorece o processo, sendo o ânodo contendo somente Ru o mais efetivo para este processo.

The electrochemical oxidation of formaldehyde is studied on dimensionally stable anodes prepared by thermal decomposition of precursors (the corresponding chlorides). The working electrodes used were: $Ti/Ir_{0.3}Ti_{0.7}O_2$, $Ti/Ru_{0.3}Ti_{0.7}O_2$ and $Ti/Ir_{0.2}Ru_{0.2}Ti_{0.6}O_2$. The electrolyses were performed galvanostatically in a filter press cell with 0.5 mol L^{-1} H_2SO_4 solutions with initial formaldehyde concentration equal to 100 mmol L^{-1}. The concentration of formaldehyde decreases fast with the electrolysis time, with the ternary anode (Ir + Ru + Ti) presenting the best performance for this step. The anode containing only Ir, despite presenting the higher superficial charge, is the one with the lowest electrocatalytic activity. For the formic acid oxidation step, the presence of iridium in the anode composition does not promote the process, the anode containing only ruthenium being the most effective for this step.

Keywords: *formaldehyde, electrooxidation, DSA, oxides*

Introduction

Around the world there is an increasing preoccupation with the cleanness of the environment. Wastewater, coming mainly from industrial effluents, is full of inorganic and/or organic contaminants which have to be treated in order to be considered harmless. In the case of organic substances, one of the possible treatments is electrochemical oxidation leading to, whenever possible, a total "combustion" process which will produce carbon dioxide as the only product. The effectiveness of this kind of treatment depends on many variables, such as for example, the pH of the medium, the current density level and the nature of the electrode material.

Dimensionally stable anode (DSA) type electrodes have been used for many years as stable anodes in the chlor-alkali industry[1]. These electrodes were generally based on RuO_2/TiO_2 mixtures deposited on a metallic substrate (usually titanium). Later, modified DSA type electrodes incorporating iridium oxides were investigated for the oxygen evolution reaction[2,3] and also with other metals[4-6], in order to modulate their properties and to increase their service life. More recently, DSA type electrodes have been used for the oxidation of some organic molecules that constitute water pollutants, notable phenols[7], as well as for the electrolysis of sea water[8,9].

As pointed out in many publications, an indirect electrochemical oxidation may take place *via* surface mediators at

metal oxide electrodes[10,11]. For this case, Comninellis and co-workers[12] developed a theoretical model to describe, in a quantitative way, the efficiency of the oxidation reaction that takes place together with oxygen evolution at oxide electrodes. The analysis performed by the authors is specific for oxide electrodes for which the potential of the surface redox couple is higher than the thermodynamic potential for oxygen evolution. Oxide electrodes are very interesting because proper selection of the material allows a good degree of selectivity. Also, the combination of more than one metal oxide is known to show synergistic effects toward electron transfer reactions.

Presently, there is much interest in studying the oxidation of small organic molecules that can be considered as model molecules and, at the same time, are connected to interesting environmental problems. Formaldehyde is one of these molecules that is present in many technological processes such as in the textile industry, and which is normally discarded without previous treatment. The oxidation of formaldehyde on fuel cell type electrodes[13] and even on single crystals[14] has been the object of recent publications. So, it may be of interest to see if formaldehyde can be oxidized at DSA type electrodes.

In this work, the oxidation of formaldehyde is studied on three different DSA type oxide electrodes, in order to determine the effect of the electrode composition and also to verify the possibility of synergistic effects with the incorporation of different oxides in the electrode.

Experimental

Three different oxide electrodes were used for the electrolysis: $Ti/Ir_{0.3}Ti_{0.7}O_2$, $Ti/Ru_{0.3}Ti_{0.7}O_2$ and $Ti/Ir_{0.2}Ru_{0.2}Ti_{0.6}O_2$. The titanium supported (14 cm^2 plates) oxide layers were prepared by thermal decomposition of precursors in isopropylic alcohol and applied by brushing on the metallic support. The solvent was evaporated at low temperature (80 - 90ºC) and the dried layer heated at 450ºC for 5 min. in a 5 L min^{-1} O_2 flux in a preheated oven. These steps were repeated until the desired oxide thickness (2 µm nominal) was reached. An one hour final annealing at the same temperature and O_2 flux completed the procedure. This Ti-support pretreatment and the electrode mounting are described elsewhere[15,16].

Electrochemical (voltammetry and electrolysis) experiments were performed in a filter press cell (flow cell, Electrocell AB), as shown schematically in Figure 1. The anolyte (100 mmol L^{-1} solution of formaldehyde in 0.5 mol L^{-1} H_2SO_4) and the catholyte (0.5 mol L^{-1} H_2SO_4) were circulated separately by a Masterfler® peristaltic pump. Two compartments were separated by an ion exchange

membrane (IONAC AM 3470). The galvanostatic electrolyses were performed using a galvanostat/potentiostat (Wenking Model HP 88). The flat plate DSA electrodes were used as working electrodes and the stainless steel plate as counter electrode. The cyclic voltammograms were obtained by using a $Hg/Hg_2SO_4/SO_4^{-2}$ (MSE) reference electrode which was connected, via a sodium sulfate solution, to an extension of the IONAC membrane used to separate the cell compartments.
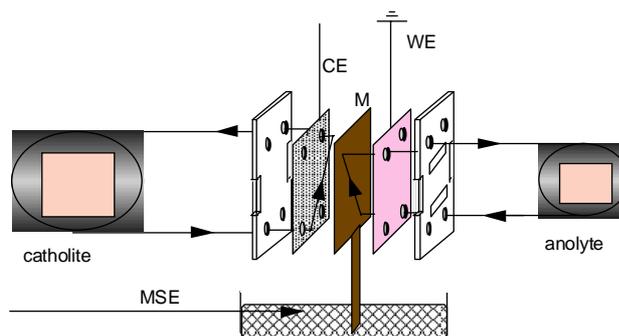

Figure 1. Scheme of the filter press cell where WE: working electrode; CE counter electrode; MSE: $Hg/Hg_2SO_4/SO_4^{-2}$ reference electrode; M: membrane.

Analysis of the reaction products was carried out during the electrolysis by High Performance Liquid Chromatography (HPLC). This apparatus was composed of an isocratic pump (Knauer HPLC Pump 64) and an ion-exchange column (HPX-87H, from Bio-Rad). The eluent was a dilute solution of sulphuric acid (3.33 mmol L^{-1} H_2SO_4) at a flow rate of 0.6 cm^3 min^{-1}. After separation at room temperature, the electrolysis products were successively detected with an UV detector (Applied Biosystems 785A) working at $\lambda = 210$ nm, and a refractometer (Spectra-Physics SP8430). The chromatograms were recorded on a two-channel integrator (D 2500 Merck). The nature of the organic compounds was determined by comparing their retention times with those for pure reference products under the same analysis conditions.

All the solutions were prepared from ultra-pure water (Millipore Milli-Q System) and Merck reagents (formaldehyde, formic acid, sodium hydroxide and sodium carbonate). Before each experiment, the solutions were deaerated with ultra-pure nitrogen (U Quality from L'Air Liquide). All the experiments were performed at room temperature.

Results and Discussion

Cyclic voltammetry

Figure 2 presents the voltammograms of the three different electrodes in a 0.5mol L^{-1} H_2SO_4 solution in the absence and in the presence of 100 mmol L^{-1} of formaldehyde cover-

ing mainly the double layer potential region. The behaviour observed is typical of thermally prepared oxide layer electrodes[2-6] with the surface oxidation potential range presenting a displacement to more positive values when in the presence of the organic substance. The broadness of the peaks can be understood in terms of a large heterogeneity in the surface sites, as proposed by Trasatti and Kurzweil [17]. However, by comparison of the three voltammograms, one can see that for the oxides containing iridium in their compositions the displacement is bigger. Additionally, the activity of the electrodes, estimated by the voltammogram area follows the order: $(Ru + Ti) < (Ir + Ru + Ti) < (Ir + Ti)$. Both observations are characteristic of the presence of iridium oxide, as shown in the literature[18].
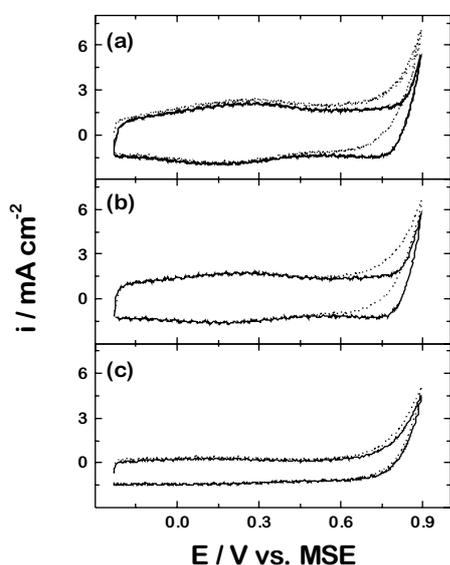

Figure 2. Cyclic voltammogram of DSA type electrodes in a 0.5 mol L^{-1} H_2SO_4 in the absence (dashed line) and presence (full line) of 0.1 mol L^{-1} formaldehyde. (a) $Ti/Ir_{0.3}Ti_{0.7}O_2$; (b) $Ti/Ru_{0.2}Ir_{0.2}Ti_{0.6}O_2$; (c) $Ti/Ru_{0.3}Ti_{0.7}O_2$. $v = 50$ mV s^{-1}.

Formaldehyde behavior in acidic medium

In order to determine the formaldehyde concentration as a function of the electrolysis time, it was used the HPLC technique with a refraction index detector. To establish the standards for the chromatograms two solutions were used: 100 mmol L^{-1} of formaldehyde in water and 100 mmol L^{-1} of formaldehyde in 0.5 mol L^{-1} H_2SO_4 aqueous solution. As illustrated in Figure 3, in acidic medium the detected formaldehyde concentration is approximately 30% of the concentration detected when it is dissolved in pure water. This discrepancy is related to the different forms in which formaldehyde is present in the solution. In a pure aqueous solution, up to 99% of formaldehyde is present as the hydrate (HCHO. H_2O). However, a cyclic trimeric form called trioxane

can be formed through a reaction of the formaldehyde in acidic medium[19]. Thus, the experimental observations described above can be interpreted in terms of the detection of the hydrate form in single aqueous medium while, in acid medium, only one third of the formaldehyde is in the hydrate form and the rest is in the trimeric form.
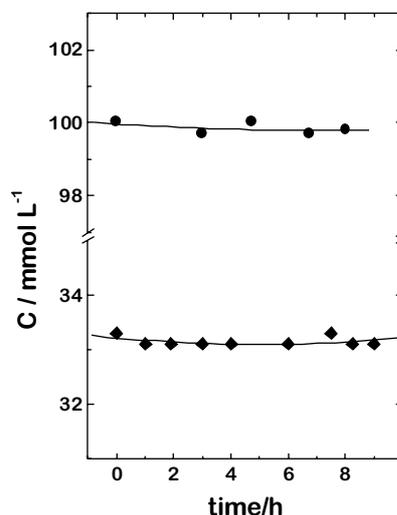

Figure 3. Dependence of formaldehyde concentration detected by HPLC with time in the following systems: (●) 100 mmol L^{-1} in water; (◆) 100 mmol L^{1} in 0.5 mol L^{-1} H_2SO_4.

Electrolyses

The electrolyses were performed at constant current (40 mA cm^{-2}) and anolyte samples were taken at several times during the experiment. By the chromatographic results it was possible to observe the concentration variation of formaldehyde, as well as the formation of formic acid which was identified as the direct product of formaldehyde electrooxidation. An example of these results is shown in Figure 4 for the electrolysis of formaldehyde using a Ti / $Ir_{0.3}Ti_{0.7}O_2$ anode. One can see that the concentration of formaldehyde decreases fast reaching a value below detection in less than 5 h of electrolysis. In the same time period of time the concentration of formic acid increases and reaches a plateau. After four h of electrolysis the concentration of formic acid starts decreasing.

In the anodic compartment outlet of the cell a trap containing a sodium hydroxide solution was placed in order to determine the CO_2 formed in the reaction through the concentration of carbonate formed. These determinations were performed before and after the electrolyses by using the HPLC technique and sodium carbonate standard solutions. For all electrolyses the mass balance, considering the three detected components with the formaldehyde in the hydrate form, gave results which reached at least 98% of the total mass. The small difference with the total was considered as
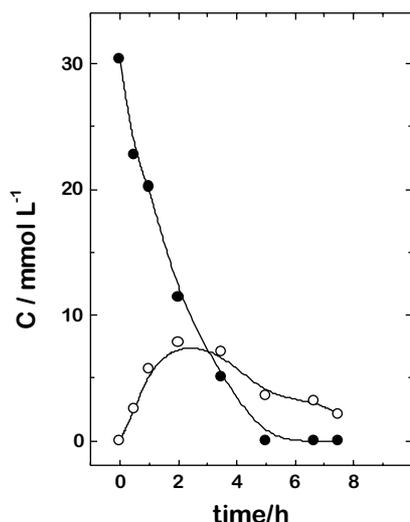
Figure 4. Dependence of (●) formaldehyde and (○) formic acid concentration with electrolysis time at 40 mA cm^{-2} in an aqueous solution of 0.5 mol L^{-1} H$_2$SO$_4$ containing 100 mmol L^{-1} of formaldehyde and using a Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode.

due to some CO_2 lost in the system tubing. However, for all the electrode materials tested, the detectable products in solution were formic acid and carbon dioxide formed through the possible reactions:

Scheme 1
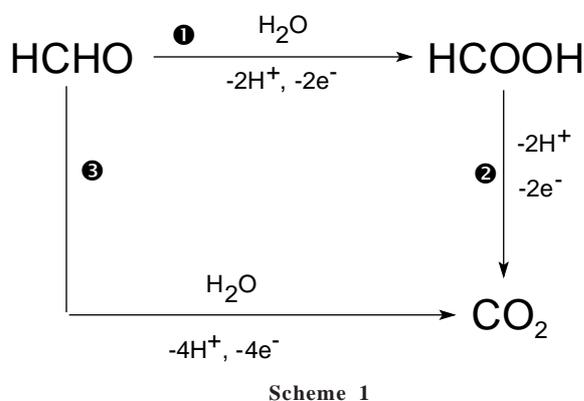
In order to analyze the influence of the anode composition, the curves of formaldehyde concentration as a function of the electrolysis time, for the different anodes used, are presented in Figure 5. It is possible to observe that the curve corresponding to the ternary oxide anode (Ru + Ir + Ti) is the lowest one, which indicates that the consumption of formaldehyde is faster. On the other hand, the curves corresponding to the binary oxides are almost coincident, being practically impossible to distinguish between their activities. As a first approximation, this difference in the activity between binary and ternary oxides, just for the step involving the disappearance of formaldehyde, can be interpreted as due to synergistic effects.
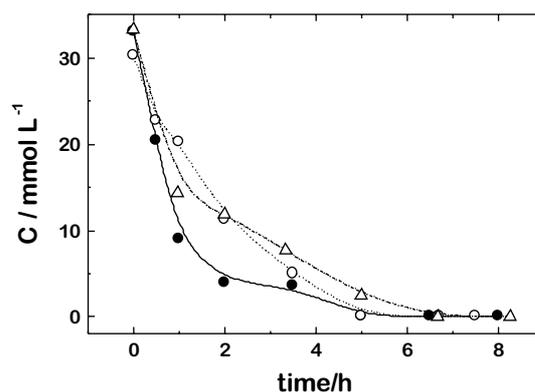

Figure 5. Dependence of formaldehyde concentration with electrolysis time at 40 mA cm^{-2} from an aqueous solution of 0.5 mol L^{-1} H$_2$SO$_4$ containing 100 mmol L^{-1} of formaldehyde and using: (○) Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$; (△) Ti/Ir$_{0.3}$Ti$_{0.7}$O$_2$; (●) Ti/Ru$_{0.2}$Ir$_{0.2}$Ti$_{0.6}$O$_2$.

Following the same procedure, the curves of formic acid concentration as a function of the electrolysis time, for the different anodes, are shown in Figure 6. In this case, the influence of the anode material is much stronger than in the case of the oxidation of formaldehyde, with the activity varying as: (Ir + Ti) < (Ru + Ir + Ti) < (Ru + Ti).
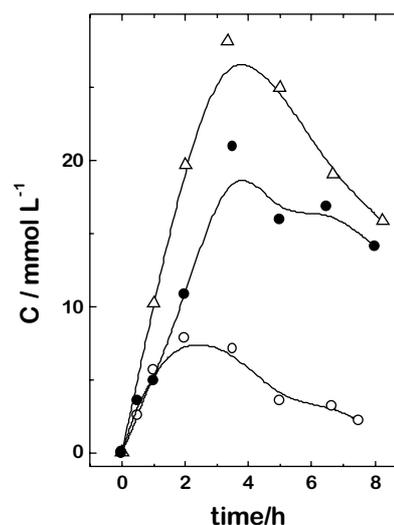

Figure 6. Dependence of formic acid concentration with electrolysis time at 40 mA cm^{-2} from an aqueous solution of 0.5 mol L^{-1} H$_2$SO$_4$ containing 100 mmol L^{-1} of formaldehyde and using: (○) Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$; (△) Ti/Ir$_{0.3}$Ti$_{0.7}$O$_2$; (●) Ti/Ru$_{0.2}$Ir$_{0.2}$Ti$_{0.6}$O$_2$.

A similar behavior can also be seen in Figure 7, where the increase of the amount of carbon dioxide, in percentage (calculated from the mass balance), is shown as a function of the electrolysis time.

From the above observations, it appears that the oxidation of formaldehyde to formic acid step (see Scheme 1, reaction 1) is the *rds* of the total oxidation process on (Ru + Ti) oxide. On the other hand, the *rds* on (Ir + Ti) and (Ir + Ru
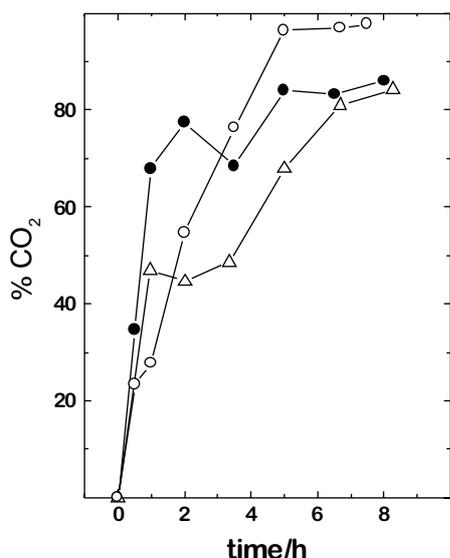
Figure 7. Variation of calculated carbon dioxide concentration (in percentage) with the electrolysis time for the systems using the electrodes: ($\bigcirc$) $Ti/Ru_{0.3}Ti_{0.7}O_2$; ($\triangle$) $Ti/Ir_{0.3}Ti_{0.7}O_2$; ($\bullet$) $Ti/Ru_{0.2}Ir_{0.2}Ti_{0.6}O_2$.

Scheme 2.

+ Ti) oxides seems to be the oxidation of formic acid to carbon dioxide (reaction 2 in Scheme 1). Additionally, there is no experimental evidence for the formation of carbon dioxide directly from formaldehyde, as is represented in Scheme 1 by reaction 3.

The oxidation of formaldehyde on DSA type electrodes only takes place under conditions of simultaneous oxygen evolution, that is, on a surface fully covered by a higher metal oxide[20]. It is likely that this oxide plays a key role in the oxidation process. From the results of this work, it is proposed a general mechanism for the oxidation of formaldehyde with simultaneous oxygen evolution, in acid medium, shown in Scheme 2.

Under the experimental conditions imposed to promote the faradaic processes involving formaldehyde oxidation, it is assumed that chemisorptive active sites act as heterogeneous mediators. Thus, the necessary oxygen transfer is mediated by the higher metal oxides electrogenerated at the surface of the electrode, (MO_x)-OH or (MO_x)-O. These models must obviously consider simultaneous oxygen evolution as pointed out in steps 1-3 in Scheme 2.

It can be assumed that the electroactive chemisorptive sites can either be decomposed by evolving molecular oxygen, via reaction 3, or intermediate the oxidation of formaldehyde to formic acid, steps 4 and 5, and also intermediate the oxidation of formic acid to carbon dioxide, reactions 6 and 7. The nucleophilic attack of the activated sites, (MO_x)-O, leads to the O-adsorbed species via the possible intermediates generated in steps 4 and 6, and in sequence leading to a free formic acid and carbon dioxide,
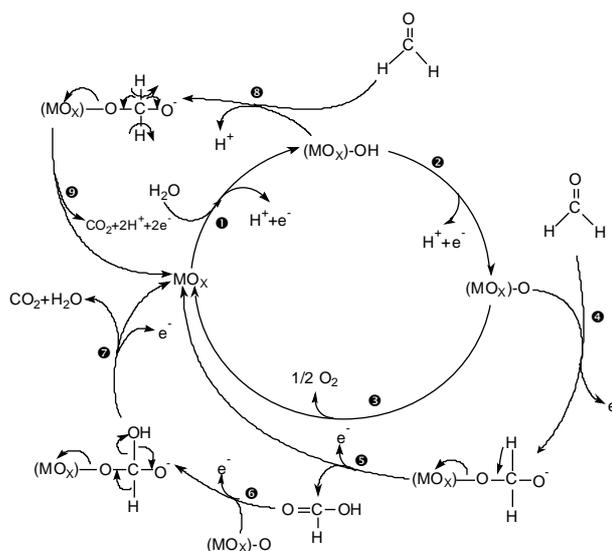
steps 5 and 7, respectively. The possible direct oxidation of formaldehyde to carbon dioxide involves the hydroxyl species, (MO_x)-OH, and can be rationalized through the reactions 8 and 9. All the above mentioned processes take place simultaneously with competing molecular oxygen electrogeneration.

Conclusions

The main observations made during this work are as follows:

Prolonged electrolysis permits to identify formic acid, carbon dioxide and molecular oxygen (as a side product) during the oxidation of formaldehyde on DSA type electrodes.

The consumption of formaldehyde is faster on the ternary alloy oxide, (Ir + Ru + Ti), while the binary oxides, (Ru + Ti) and (Ir + Ti), show no difference in activity.

The variation of formic acid concentration with the electrolysis time is much more dependent on the anode material than in the case of the formaldehyde consumption. The activity for the oxidation of formic acid to carbon dioxide varies according to the sequence: (Ru + Ti) > (Ir + Ru + Ti) > (Ir + Ti).

The proposed *rds* for (Ru + Ti) oxide is the formation of formic acid, while for (Ir + Ti) and (Ir + Ru + Ti) oxides the *rds* is carbon dioxide formation.

A general mechanism was proposed based on the experimental evidences and considering the competing molecular oxygen electroformation, that generates the chemisorptive active sites to act as an heterogeneous mediator.

Acknowledgments

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