Investigation of formic acid oxidation on Ti/IrO2 electrodes

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Abstract
A model has been proposed according to which the voltammetric charge involved in the Ti/IrO2 electrodes is due to two contributions: a faradaic contribution due to surface redox activities at the IrO2 coating and a non-faradaic contribution due to the charging of electrical double layer (\(q_{dl}^∗\)). The later \(q_{dl}^∗\) has been proposed as a tool for the estimation of the relative surface area of the Ti/IrO2 electrodes.

Differential electrochemical mass spectrometry (DEMS) measurements using H\(_2\)\(^{18}\)O has demonstrated that we are dealing with an active electrode in which the surface redox couple IrO3/IrO2 acts as mediator in the oxidation of formic acid (FA).

From the voltammetric measurements using different IrO2 loading and FA concentrations, the kinetic parameters of FA oxidation via the surface redox couple IrO3/IrO2 have been determined.

Finally a model has been proposed considering that FA oxidation at Ti/IrO2 anodes is controlled by mass transfer. The good agreement between the experimental results and the model indicates that the surface reaction between FA and the electrogenerated IrO3 is a fast reaction.

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1. Introduction

Thin film conductive coating deposited on an inert substrate has been widely investigated as anode material for chlorine evolution [1], oxygen evolution [1] and oxidation of organic compounds [2–4].

Concerning organics oxidation it has been found that frequently electrochemical oxidation of some organics in aqueous media occurs, without any loss in electrode activity, only at high potentials with concomitant evolution of O\(_2\) [5,6]. Furthermore it has been found that the nature of electrode material influences strongly both the selectivity and the efficiency of the process [7–9].

In order to interpret these observations a comprehensive model for anodic oxidation of organics in acid medium, including competition with oxygen evolution has been proposed [7–9]. This model permits to distinguish between two limiting cases: ‘active’ and ‘non-active’ anode. Fig. 1 illustrates the reaction scheme in acid medium (e.g. HClO\(_4\)), where M designates an active site at the anode surface. In all cases, the initial step is the discharge of water molecules to form adsorbed hydroxyl radicals (Eq. (1)):

\[
M + H_2O \rightarrow M(\cdot OH) + H^+ + e^-
\]

The electrochemical and chemical reactivity of the adsorbed hydroxyl radicals depends strongly on the nature of electrode material used. Two extreme classes of electrodes can be defined: ‘active’ and ‘non-active’ electrodes:

(a) At ‘active’ electrodes there is a strong electrode (M)–hydroxyl radical (\(\cdot OH\)) interaction. In this case, the adsorbed hydroxyl radicals may interact with the anode with possible transition of the oxygen from the hydroxyl radical to the anode surface, forming the so-called higher oxide (Eq. (2)). This may be the case when higher oxidation states on the surface electrode are available above the thermodynamic potential for oxygen evolution (1.23 V vs SHE).

\[
M(\cdot OH) \rightarrow MO + H^+ + e^-
\]

The surface redox couple MO/M can act as mediator in the oxidation of organics at ‘active’ electrodes (Eq. (3)). This reaction is in competition with the side reaction of oxygen evolution due to the chemical decomposition of the higher oxide (Eq. (4)):

\[
MO + R \rightarrow M + RO
\]

\[
MO \rightarrow M + (1/2)O_2
\]
Fig. 1. Scheme of the electrochemical oxidation of organic compounds on ‘active’ anodes (reactions (1)–(4)) and on ‘non-active’ anodes (reactions (1), (5) and (6)). (1) Water discharge to hydroxyl radicals; (2) formation of the higher metal oxide; (3) partial (selective) oxidation of the organic compound, R, via the higher metal oxide; (4) oxygen evolution by chemical decomposition of the higher metal oxide; (5) combustion of the organic compound via hydroxyl radicals; (6) oxygen evolution by electrochemical oxidation of hydroxyl radicals [7–9].

The oxidation reaction via the surface redox couple MO/M (reaction (3)) may result in the partial (selective) oxidation of organics. This anodic oxidation process has been reported as redox catalysis. (b) At ‘non-active’ electrodes there is a weak electrode (M)–hydroxyl radical (*OH) interaction. In this case, the oxidation of organics is mediated by hydroxyl radicals (Eq. (5)), which may result in fully oxidized reaction products such as CO2.

\[
\text{M}^*\text{OH} + R \rightarrow \text{M} + m\text{CO}_2 + n\text{H}_2\text{O} + \text{H}^+ + e^- \tag{5}
\]

This reaction is in competition with the O2 evolution (Eq. (6)) side reaction (through formation of H2O2 as intermediate) to O2 without any participation of the anode surface:

\[
\text{M}^*\text{OH} \rightarrow \text{M} + (1/2)\text{O}_2 + \text{H}^+ + e^- \tag{6}
\]

The distinction between ‘active’ and ‘non-active’ behavior and the underlying mechanistic explanation are supported by several experimental observations, including measurement of the concentration of reactive intermediates in the oxygen evolution reaction, such as hydroxyl radicals produced by discharge of water [10].

In this work the active character of the IrO2 (Ti/IrO2) electrode for the anodic oxidation of formic acid (FA) has been demonstrated using differential electrochemical mass spectrometry (DEMS) measurements. Furthermore from the voltammetric measurements obtained using different IrO2 loading and FA concentrations the kinetic parameters involved in the oxidation of FA has been determined. Finally a model of FA oxidation competing with oxygen evolution at ‘active’ type anodes has been proposed.

2. Experimental

The Ti/IrO2 working electrodes were prepared by thermal decomposition at 500 °C of a H2IrCl6 (99.9%, ABCR) precursor aqueous solution deposited on disc-shaped titanium supports, which were previously treated in boiling 1 M oxalic acid (≥97%, Fluka) solution.

DEMS measurements are carried out in a thin layer flow through cell, where the faradaic reactions take place, and the mass spectrometric compartment. In a typical DEMS experiment, the ionic currents related to the electrogenerated volatile products are recorded in parallel to the faradaic current during the voltammetric sweep. More informations concerning DEMS measurements are given elsewhere [11].

Electrochemical measurements were carried out in a single-compartment, three-electrode cell (50 ml) using an Autolab PGSTAT 30. The working electrode was Ti/IrO2 (with different IrO2 loading) of 0.785 cm2 geometric area, the counter electrode was a Pt wire, and the reference electrode was Hg/Hg2SO4/K2SO4 (sat.) (MSE: 0.65 V vs. SHE). All tests were performed in 1 M HClO4 supporting electrolyte at 25 °C.

In the bulk electrolysis experiments, a one compartment electrolytic flow cell has been used. Electrolysis has been carried out under galvanostatic conditions using Ti/IrO2 anode and zirconium cathode with an inter-electrode gap of 10 mm. Both electrodes were disks (90 mm diameter) with a geometric area of 63 cm2 each. The thickness of the diffusion layer under the used hydrodynamic conditions has been estimated from the limiting current measurements using the Fe(CN)64−/3− redox couple (d = 36.5 mm), then the mass transfer coefficient kₘ for the oxidation of formic acid has been calculated using the relation (Eq. (7)):

\[
k_m = \frac{D_{FA}}{\delta} \tag{7}
\]

where kₘ is the mass transfer coefficient for the oxidation of formic acid (m s⁻¹), DFA is the diffusion coefficient of formic acid (m² s⁻¹) and δ is the diffusion layer thickness (m).

3. Results and discussion

3.1. Measurement of the voltammetric charge involved in the IrO2 electrodes

Cyclic voltammetry in the potential window of water stability has been usually used for the evaluation of the electrochemical activity of the Ti/IrO2 electrodes. In fact the voltammetric charge q* obtained by integration of the voltammetric curves has been reported to be related with both the morphology and to the active surface area of the coating.

In this work the influence of potential window and potential scan rate on q* have been investigated in order to evaluate the conditions under which q* is in fact related with the active surface area of the IrO2 coating.

3.1.1. Influence of the potential window

Fig. 2 shows cyclic voltammograms obtained with a Ti/IrO2 electrode at four scan rates using different potential windows. This figure shows that the anodic current between 0.25 and 1.35 V vs. SHE is not dependent on the fixed upper limit (1.05 or 1.35 V vs. SHE) when the lower cut-off was fixed at 0.25 V vs. SHE, while it is clearly higher when the lower cut-off potential was set to −0.05 V vs. SHE. Furthermore it has been found that the ratio between the anodic and the cathodic charges are close to unity for all the investigated potential windows and scan rates (results not shown). These results show clearly that the charging–discharging process is reversible, however some slow processes are involved in the potential region between −0.05 and 0.25 V vs. SHE.

3.1.2. Effect of scan rate

Fig. 3 shows the variation of the voltammetric charge q* with scan rate obtained with different loadings in 1 M HClO4 at 25 °C corresponding to the potential window between −0.05 and 1.35 V vs. SHE.

This figure shows that the voltammetric charge for all investigated loadings and potential windows decreases with the scan rate, furthermore, q* increases with increasing electrode loading.
Similar results were obtained for the three potential windows used for the cyclic voltammetry measurements presented in Fig. 2.

The decrease of the charge with scan rates was explained by two main approaches.

The first approach proposed by Ardizzone et al. [12] is based on the accessibility to the active sites of the electrode and was studied further by Da Silva et al. [13]. The decrease of the voltammetric charge with the scan rate has been explained by the exclusion of the inner part of the electrode due to the slow diffusion of protons through the porous structure of the electrode. The voltammetric charge has been attributed to the redox surface couples according to the faradaic reaction as follows:

$$\text{IrO}_x(\text{OH})_y + \delta \text{H}^+ + \delta \text{e}^- \overset{\text{cathodic}}{\rightarrow} \text{IrO}_{x-\delta}(\text{OH})_{y+\delta} \overset{\text{anodic}}{\rightarrow}$$

(8)

The second approach is that proposed by Sugimoto et al. [14]. This approach is based on the presence of mainly two types of capacitances: The double layer capacitance, (non-faradaic fast process), which dominates at high scan rates and a redox surface capacitance (faradaic slow surface process), which mainly contributes only at low scan rates. The decrease of the voltammetric charge with the scan rate is explained by the slow behaviour of the redox surface process resulting in its exclusion at high scan rates.

In a recent paper it has been found that the apparent activation energy $E_a$ for the charging processes decreases with increasing scan rate approaching zero activation energy at high scan rates. This has allowed us to consider a model according to which the voltammetric charge is due to two contributions [15].

The first one is due to a slow process with low activation energy ($2.4 \text{kJ mol}^{-1}$) related to the diffusion of protons within the IrO$_2$ coating inducing surface redox activities. This charging process dominates at low scan rates and depends on the square root of scan rate. The second process is a fast (instantaneous) contribution with near-zero activation energy and is related with the charging of the electrical double layer ($\tilde{q}_{dl}$). This charging process dominates at high scan rates and is scan rate independent [15].

In this work the approach is to use $\tilde{q}_{dl}$ as a tool for the estimation of the relative surface area of the investigated Ti/IrO$_2$ electrodes. In order to estimate $\tilde{q}_{dl}$, very high scan rates should be used. However this can be obtained graphically using a relation (Eq. (9)) similar to those proposed by Ardizzone et al. [12]:

$$q^*(\nu) = q_{dl}^* + \text{const} \left( \frac{1}{\nu^{1/2}} \right)$$

(9)

In fact, plotting $q^*$ as a function of $1/\nu^{1/2}$ gives straight lines; the intercept of these straight lines on the $1/\nu^{1/2}$ axis gives $q_{dl}^*$ for the different investigated IrO$_2$ loadings (Fig. 4).

The variation of the obtained $q_{dl}^*$ with the IrO$_2$ loading is given in Fig. 5. The direct proportionality between $q_{dl}^*$ and the IrO$_2$ loading demonstrated the power of $q_{dl}^*$ as a tool for the estimation of the relative surface area of the IrO$_2$ coating.
3.2. Differential electrochemical mass spectrometry measurements (DEMS)

In order to demonstrate that IrO₂ is an active electrode involving surface IrO₃/IrO₂ redox couple for the oxidation of formic acid (model organic compound), two series of DEMS measurements have been carried out.

(a) Labelling of the IrO₂ coating with ¹⁸O:

The DEMS measurements have been carried out in 1 M HClO₄ containing 10% (w/w) H₂¹⁸O. Several successive cycle voltammetric (CV) scans (10 mV s⁻¹) were performed between 0 and 1.6 V (vs. SHE). Fig. 6 shows the measured gas phase concentrations of ¹⁶O₂ (m/z = 32) and ¹⁶O¹⁸O (m/z = 34) obtained during the first six successive CV scans as well as the predicted one from the concentration of marked water (H₂¹⁸O) in the electrolyte. The increase of ¹⁶O¹⁸O (m/z = 34) and the concomitant decrease of ¹⁶O₂ (m/z = 32) after each scan before reaching a steady state after four cycles, proves directly that the oxide layer has been labelled with ¹⁸O, i.e. the ¹⁶O from the lattice has been replaced by ¹⁸O from H₂¹⁸O according to the reactions (Eq. (10)):  

\[
\text{IrO}_2 + H_2^{18}O \rightarrow \text{Ir}^{16}O^{16}O^{18}O + 2H^+ + 2e^- \\
2\text{Ir}^{16}O^{16}O^{18}O \rightarrow 2\text{Ir}^{16}O^{16}O^{16}O^{18}O + 16O_2 
\]

(b) Reaction of the labelled IrO₂ (Ir–¹⁶O–¹⁸O) with formic acid:

In these DEMS measurements, the cell containing the labelled IrO₂ (Ir–¹⁶O–¹⁸O) was first carefully washed several times with regular water then the cell was filled with a solution of 2 mM HCOOH in 1 M HClO₄/H₂¹⁶O.

Fig. 7 shows a typical DEMS experiment obtained with this labelled electrode. This figure shows clearly the formation of C¹⁶O¹⁸O (m/z = 46), which proves clearly that the labelled IrO₂ (Ir–¹⁶O–¹⁸O) indeed participated in the oxidation of the formic acid according to the reactions (Eq. (11)):  

\[
\text{Ir}^{16}O^{18}O + H_2^{16}O \rightarrow \text{Ir}^{16}O^{16}O^{16}O^{18}O + 2H^+ + 2e^- \\
\text{Ir}^{16}O^{16}O^{18}O + \text{HC}^{16}O^{16}OH \rightarrow \text{Ir}^{16}O^{16}O^{16} + \text{C}^{16}O^{18}O + H_2^{16}O 
\]

More details indicating that oxygen from the IrO₂ lattice indeed participates, in both oxygen evolution and organics oxidation, are given elsewhere [16,17].

3.3. Electrochemical measurements

Fig. 8 shows the influence of FA concentration in 1 M HClO₄ on the voltammetric curves (10 mV s⁻¹) obtained using Ti/IrO₂ electrodes with different loadings.

In order to determine the kinetic parameters of FA oxidation on Ti/IrO₂ anodes from these voltammetric measurements, a comprehensive model is presented based in the fact that the surface redox couple IrO₃/IrO₂ is involved in both oxygen evolution and FA oxidation.

Three reactions have been considered in this model:

(a) Electrochemical oxidation of surface IrO₂ to IrO₃ via hydroxyl radicals according to the global reaction (Eq. (12)):

\[
(k_{-1}
\text{IrO}_2)_s + H_2O \overset{k_{1}}{\rightleftharpoons} (\text{IrO}_3)_s + 2H^+ + 2e^- 
\]

(b) Chemical oxidation of the adsorbed formic acid (FA) by the electrogenerated IrO₃ according to the global reaction (Eq. (13)):

\[
(\text{IrO}_3)_s + \text{(HCOOH)}_{ad} \overset{k_c}{\rightarrow} (\text{IrO}_2)_s + \text{CO}_2 + H_2O 
\]
Fig. 7. DEMS measurements using labelled iridium oxide Ir^{16}O^{18}O in 2 mM HCOOH/1 M HClO_4 regular water solution. Potential scan rate: 10 mV s^{-1}; T: 25 C. (A) Faradaic current densities ($J_f$) obtained from the cyclovoltammetric measurements. (B) Ionic current density ($J_i$) obtained from the mass spectrometer response for $m/z=46$ (C^{18}O^{16}O).

(c) Oxygen evolution via decomposition of surface IrO_3 according to the global reaction (Eq. (14)):

$$\text{(IrO}_3)_n \xrightarrow{k_{dec}} \text{(IrO}_2)_n + (1/2)\text{O}_2$$

Both reactions (13) and (14) have been considered to be heterogeneous chemical reaction regenerating the reduced state (IrO_2), at the surface of the electrode.

The rate of IrO_3 electrogeneration (Eq. (12)) is given by (Eq. (15)):

$$r_{\text{IrO}_3} = \frac{j}{n F} = \gamma_{3D} k_1 \Gamma_0 (1 - \Theta) - \gamma_{3D} k_{-1} \Gamma_0 \Theta$$

And the corresponding current density is given by (Eq. (16)):

$$j = \gamma_{3D} n F \Gamma_0 [k_1 (1 - \Theta) - k_{-1} \Theta]$$

With $\gamma_{3D}$ is the three-dimensional roughness factor defined by

$$\gamma_{3D} = \frac{A_{\text{real}}}{A_g}$$

where $j$ is the current density (relative to the geometric area) (A m^{-2}), $\Gamma_0$ is the density of IrO_2 active surface sites (mol m^{-2}), $\Theta$ is the fractional surface covered by IrO_3, $k_1$, $k_{-1}$ are the electrochemical rate constant for the forward and the backward reactions (Eq. (12)), respectively (s^{-1}), $n$ is the number of involved electrons in reaction (12) ($n=2$), $A_{\text{real}}$ is the real (wetted) electrode surface area (m^2) and $A_g$ is the geometric (projected) electrode surface area (m^2).

The rate of the chemical oxidation of FA by IrO_3 (reaction (13)) is given by Eq. (18):

$$r_{\text{oxid}} = \gamma_{3D} k_c \Gamma_0 \Theta C_{\text{ad}}$$

where $k_c$ is the chemical rate constant (m^3 mol^{-1} s^{-1}) and $C_{\text{ad}}$ is the concentration of the adsorbed FA at the surface of the electrode (mol m^{-3}).

The rate of decomposition of surface IrO_3 to oxygen (Eq. (14)) is given by the reaction (Eq. (19)):

$$r_{\text{dec}} = \gamma_{3D} k_{dec} \Gamma_0 \Theta$$

Fig. 8. Steady state polarization curves using Ti/IrO_2 electrodes with different loadings: (a) 0.35 mg cm^{-2}, (b) 0.87 mg cm^{-2}, (c) 1.75 mg cm^{-2} and (d) 3.5 mg cm^{-2} and for different concentration of formic acid in 1 M HClO_4 supporting electrolyte: (1) 0 mM, (2) 195.33 mM, (3) 387.78 mM, (4) 577.4 mM, (5) 764.25 mM and (6) 948.41 mM. T = 25 C.
where $k_d$ is the decomposition rate constant of the higher oxide IrO$_3$ ($s^{-1}$).

Considering steady-state conditions the fractional surface coverage of IrO$_3$ is obtained (Eq. (20)):

$$
\Theta = \frac{k_0^f}{k_1^f + k_{-1}^f + k_c C_{FA} + k_d}
$$

(20)

From Eqs. (16) and (20) considering that $C_{FA} = C_{FA}^{bulk} = C_{FA}$ and $n = 2$ we obtain:

$$
\frac{1}{j} = \frac{1}{2\gamma_{1D}Fk_1^fT_0} \left[ \frac{k_c C_{FA}}{k_1^f + k_{-1}^f + k_c C_{FA} + k_d} \right]
$$

(21)

Since it is difficult to determine from this relation the kinetic parameters of the model, the reciprocal of both sides of this relation has been taken (Eq. (22)).

$$
\frac{1}{j} = \frac{1}{2\gamma_{1D}Fk_1^fT_0} + \frac{k_1^f + k_{-1}^f + k_d}{2\gamma_{1D}Fk_1^fT_0 k_c C_{FA}}
$$

(22)

According to this equation, the plotting of the inverse of current density ($1/j$) against the inverse of FA bulk concentration ($1/C_{FA}$) should be linear.

In fact from the data of Fig. 8, the plot of $1/j$ against $1/C_{FA}$ gives straight lines for all the investigated IrO$_2$ loadings (Fig. 9). From this figure the intercept on the $1/j$ axis will give $1/2\gamma_{1D}Fk_1^fT_0$ according to Eq. (22).

In order to calculate the transfer coefficient $\alpha$ and the apparent standard rate constant ($k_1^{e,0}$)$_{ap}$ (defined by Eq. (23)) of the electrochemical reaction (mol m$^{-2}$ s$^{-1}$) for all the investigated loadings, the intercepts in Fig. 9 have been plotted against the overpotential (considering that $E_0 = 1.3$ V vs. SHE [3] for reaction (12)) and are given in Fig. 10:

$$
(k_1^{e,0})_{ap} = \gamma_{1D}k_1^{e,0}T_0
$$

(23)

From the slope of the obtained straight lines in Fig. 10, the transfer coefficients $\alpha$ for the different IrO$_2$ loadings have been calculated (Table 1) using the relation (Eq. (24)):

$$
k_1^f = k_1^{e,0}\exp\left(\frac{\alpha nF}{RT}\eta\right)
$$

(24)

where $n$, $F$, $R$, $T$ have their usual meaning.

Furthermore from the intercept of the straight lines in Fig. 10 the apparent standard rate constants ($k_1^{e,0}$)$_{ap}$ have been determined and plotted as a function of $q_{dl}^*$ (Fig. 12). The $q_{dl}^*$ values have been obtained from Fig. 5.
Table 1 shows that the transfer coefficient $\alpha$ is almost loading independent. This is contrary to the apparent standard rate constants $(k_{1}^{e,0})_{ap}$ which increase with increasing loading $(q_{dl})^{*}$, having a tendency to reach a plateau. The fact that the transfer coefficient $\alpha$ is almost loading independent and $(k_{1}^{e,0})_{ap}$ is loading dependent is predictable as $\alpha$ is an intensive quantity (related with the intrinsic electrocatalytic properties of IrO$_2$) contrary to $(k_{1}^{e,0})_{ap}$ which is an extensive quantity involving geometric factors.

As two electrons are involved in reaction (12), the $\alpha$ value is approximately 0.5; which is the theoretical value for one electron transfer reaction involved in the rate-determining step of the process.

Working at high overpotentials (>1.45 V vs. SHE) and neglecting the side reaction of oxygen evolution $(k_{a} = 0)$ due to the fact that the background current of OER has been subtracted from the formic acid oxidation I–V curves, and neglecting as well the backward reaction of the electrochemical oxidation of the surface $(k_{–1}^{e,0} = 0)$, Eq. (22) is transformed to Eq. (25).

$$\frac{j}{J_{0}} = \frac{1}{2Fk_{1}^{e,0}C_{FA}}$$

(25)

where $(k_{1})_{ap}$ is the apparent rate constant of reaction (14) (m s$^{-1}$) defined by

$$(k_{1})_{ap} = \rho_{DL} I_{0} k_{c}$$

(26)

From the background-subtracted I–V curves (due to oxygen evolution) of Fig. 8, the inverse of the current density has been plotted against the inverse of FA concentration and this for the different investigated IrO$_2$ loadings (Fig. 11). From the slope of the obtained straight lines the apparent rate constants $(k_{1})_{ap}$ for the reaction (13) have been calculated. The obtained $(k_{1})_{ap}$ values for different loadings are given in Fig. 12.

Fig. 11 shows that both the apparent standard rate constant $(k_{1}^{e,0})_{ap}$ for the electrochemical reaction (Eq. (12)) and the apparent rate constant $(k_{1})_{ap}$ for the chemical reaction (Eq. (13)) follow the same tendency towards the IrO$_2$ loading.

3.4. Bulk electrolysis

A model for the electrochemical oxidation of formic acid (FA) on Ti/IrO$_2$ anodes has been developed for a batch recirculation reactor system under galvanostatic conditions. This model is based on the reactions presented in the previous chapter and given by Eqs. (12)–(14).

The main assumption in this model is that the global rate of the electrochemical oxidation of FA is a fast reaction and it is controlled by the current or by mass transport of FA to the anode surface depending on the difference between the applied and the limiting current. Under these conditions, the limiting current density for the electrochemical oxidation of FA under given hydrodynamic conditions can be written as

$$j_{lim}(t) = 2Fk_{m}[FA]_{0}$$

(27)

where $j_{lim}$ is the limiting current density for FA oxidation (A m$^{-2}$), $F$ is the Faraday constant (C mol$^{-1}$), $k_{m}$ is the mass transport coefficient (m s$^{-1}$) given by Eq. (7) and $[FA]_{0}$ is the FA bulk concentration (mol m$^{-3}$).

At the beginning of electrolysis ($t = 0$) the initial limiting current density $(j_{lim}^{0})$ is given by

$$j_{lim}^{0} = 2Fk_{m}[FA]_{0}$$

(28)

where $[FA]_{0}$ is the initial FA concentration.

Under galvanostatic conditions, two different operating regimes are defined: at $j_{ap} < j_{lim}$. The electrolysis is controlled by current (current control regime) and at $j_{ap} < j_{lim}$. It is controlled by the mass transfer (mass transport control regime).

Where $j_{ap}$ is the applied current density under galvanostatic operation mode.

3.4.1. Electrolysis under current control ($j_{ap} < j_{lim}$)

In this operating regime, the current efficiency is 100% and the rate of FA oxidation is constant and can be written as

$$r = \lambda \frac{j_{lim}^{0}}{4F}$$

(29)

where $\lambda$ is the dimensionless current density defined as

$$\lambda = \frac{j_{ap}}{j_{lim}^{0}}$$

(30)

where $j_{ap}$ is the applied (working) current density in galvanostatic mode.
The evolution of formic acid concentration with time, in this operating regime \( j_{ap} < j_{lim} \), is given by

\[
[FA]_t = [FA]_0 \left( 1 - \frac{\lambda A_{km} t}{V_R} \right)
\]

(31)

where \( A \) is the anode area (m²), and \( V_R \) (m³) is the volume of reservoir in a batch recirculation reactor system.

This behaviour persists until a critical time \( (t_{cr}) \), at which the applied current density is equal to the limiting current density, which corresponds to

\[
[FA]_{cr} = \lambda [FA]_0
\]

(32)

where \([FA]_{cr}\) is FA concentration at the critical time.

Substituting Eq. (32) in Eq. (31) the critical time is obtained (Eq. (33)).

\[
t_{cr} = \frac{1 - \frac{\lambda}{\lambda} \frac{V_R}{Akm}}{R}
\]

(33)

3.4.2. Electrolysis under mass transport control \( (j_{ap} < j_{lim})\)

When the applied current exceeds the limiting one, the secondary reaction of oxygen evolution takes place. This results in a decrease of the instantaneous current efficiency (ICE) of FA oxidation.

In this regime the FA concentration decreases exponentially with time (Eq. (34)):

\[
[FA]_t = \lambda [FA]_0 \exp \left( -\frac{A_{km}}{V_R} t + 1 - \frac{\lambda}{\lambda} \right)
\]

(34)

The instantaneous current efficiency (ICE) for the oxidation of FA can be defined as

\[
ICE = \frac{j_{lim}}{j_{ap}} = \frac{[FA]_0}{\lambda [FA]_0}
\]

(35)

Thus, from Eqs. (34) and (35), ICE is now given by

\[
ICE = \exp \left( -\frac{A_{km}}{V_R} t + 1 - \frac{\lambda}{\lambda} \right)
\]

(36)

In order to verify the validity of this model, the anodic oxidation of FA has been performed under galvanostatic conditions and the concentration of FA has been followed during electrolysis.

Fig. 13a shows the evolution of FA concentration during electrolysis under galvanostatic conditions (157 mA cm⁻²) of a 0.85 M FA solution in 1 M HClO₄ at 50 °C and the current efficiency of the reaction is reported in Fig. 13b.

The fact that there is a good agreement between the proposed model and the experimental results demonstrates that the reaction between formic acid and electrogenerated IrO₃ (Eq. (13)) is a fast reaction, which was the main assumption of our model.

4. Conclusions

In this work the influence of IrO₂ loading on the oxidation of organic compounds, using formic acid as a model, has been investigated for the first time in the best of our knowledge. The main conclusions of this work are:

- A model has been proposed according to which the voltammetric charge involved in the charging–discharging process of the Ti/IrO₂ electrode is due to two contributions: the first contribution is due to a faradaic process involving surface redox activities and the second is a fast (instantaneous) contribution with zero activation energy due to the charging of the electrical double layer.
- Differential electrochemical mass spectrometry (DEMS) measurements using H₂¹⁸O have demonstrated that we are dealing with an active electrode in which the surface redox couple IrO₃/IrO₂ acts as mediator in the oxidation of formic acid.
- From the voltammetric measurements using different IrO₂ loadings and FA concentrations, it has been found that the apparent kinetic parameters of FA oxidation via the surface redox couple IrO₃/IrO₂ are strongly dependent on IrO₂ loading.
- A model has been proposed considering that formic acid oxidation at Ti/IrO₂ anodes is controlled by mass transfer. The good agreement between the experimental results and the model indicates that the surface reaction between formic acid and the electrogenerated IrO₃ is a fast reaction.

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