

Screening Process for Activity Determination of Conductive Oxide Electrodes for Organic Oxidation

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Um método modificado para o cálculo da carga faradaica normalizada (q_{fN}) é proposto. O método envolve a simulação de um processo de oxidação, por voltametria cíclica, empregando potenciais na região da reação de desprendimento de oxigênio (RDO). Este método é aplicável a espécies orgânicas, cuja oxidação não é manifestada por um pico de oxidação definido em eletrodos de óxidos condutores. A variação de q_{fN} para eletrodos de composição nominal $Ti/Ru_xSn_{1-x}O_2$ ($x = 0,3; 0,2$ e $0,1$), $Ti/Ir_{0,3}Ti_{0,7}O_2$ e $Ti/Ru_{0,3}Ti_{0,7}O_2$, na presença de diferentes concentrações de formaldeído foi investigada. Foi observado que eletrodos contendo SnO_2 são os mais ativos frente à oxidação de formaldeído. Subseqüentemente, para investigar a aplicabilidade do modelo proposto, eletrólises galvanostáticas (40 mA cm^{-2}) de formaldeído foram efetuadas em duas concentrações distintas ($0,10$ e $0,01 \text{ mol dm}^{-3}$). Os resultados estão de acordo com o modelo proposto e indicam que este novo método pode ser usado para determinar a atividade relativa de eletrodos de óxido. De acordo com trabalhos prévios, pode ser concluído que não somente a natureza do material eletrodico, mas também a espécie orgânica em solução e a sua concentração são fatores importantes a serem considerados na oxidação de espécies orgânicas.

A modified method for the calculation of the normalized faradaic charge (q_{fN}) is proposed. The method involves the simulation of an oxidation process, by cyclic voltammetry, by employing potentials in the oxygen evolution reaction region. The method is applicable to organic species whose oxidation is not manifested by a defined oxidation peak at conductive oxide electrodes. The variation of q_{fN} for electrodes of nominal composition $Ti/Ru_xSn_{1-x}O_2$ ($x = 0.3, 0.2$ and 0.1), $Ti/Ir_{0.3}Ti_{0.7}O_2$ and $Ti/Ru_{0.3}Ti_{0.7}O_2$ in the presence of various concentrations of formaldehyde was analyzed. It was observed that electrodes containing SnO_2 are the most active for formaldehyde oxidation. Subsequently, in order to test the validity of the proposed model, galvanostatic electrolyses (40 mA cm^{-2}) of two different formaldehyde concentrations (0.10 and 0.01 mol dm^{-3}) were performed. The results are in agreement with the proposed model and indicate that this new method can be used to determine the relative activity of conductive oxide electrodes. In agreement with previous studies, it can be concluded that not only the nature of the electrode material, but also the organic species in solution and its concentration are important factors to be considered in the oxidation of organic compounds.

Keywords: DSA®, aldehydes, oxidation, normalized faradaic charge

Introduction

Dimensionally stable anodes have been used extensively in electro-organic chemistry in the last decade, especially as prospective materials for the treatment of waste materials. The general mechanism proposed by Comninellis¹ discriminates between “active” and “non-active” materials where both mechanisms occur *via* the initial formation of $\bullet OH_{ads}$. It is said that “active” materials (e.g. RuO_2) promote

a selective oxidation *via* the formation of higher oxides, which, in turn, oxidize the organic species. On the other hand, “non-active” materials (e.g. SnO_2) do not present higher oxidation states and the $\bullet OH_{ads}$ interacts directly with the organic species to promote complete oxidation to CO_2 . It should be noted, however, that the mechanism described¹ does not consider the adsorption of the organic molecule on the electrode surface. According to the proposed scheme¹ the electrode material can be varied to suit a determined process, for example waste treatment would be more rewarding with a “non-active” material whereas electro-

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synthesis would require an “active” material. However, it has been shown that not only the electrode material, but also the type of organic species present,² its concentration^{3,4} and the solvent/supporting electrolyte used⁵ can play an important role. It is interesting to note that often a trial and error approach is employed when choosing oxide materials for electro-oxidation reactions.

In this study a screening process for determining the activity of oxide electrodes for the oxidation of formaldehyde is presented. Electrodes of the following compositions were used: Ti/Ru_xSn_{1-x}O₂ (x = 0.3, 0.2 and 0.1), Ti/Ir_{0.3}Ti_{0.7}O₂ and Ti/Ru_{0.3}Ti_{0.7}O₂. The screening method involves the variation of the organic concentration and calculation of the resultant effect on the voltammetric charge. The results obtained are then compared to results obtained during the galvanostatic oxidation of formaldehyde.

It is the aim of this paper to demonstrate that it is not necessarily the nature of the electrode material, but also the organic species and its concentration determine the activity. It is hoped that such a “screening process” will aid in the choice of electrode material for a given organic reaction.

Experimental

A two-compartment filter-press cell, separated by an ion exchange membrane (IONAC AM 3470), was used with a conductive oxide anode (nominal area, 14 cm²) and a stainless steel plate cathode (area 14 cm²) as described elsewhere.^{3,6}

The Ti/Ru_xSn_{1-x}O₂ electrode was prepared in the laboratory by the standard technique of thermal decomposition of the appropriate mixtures of precursor salts (0.2 mol dm⁻³ SnCl₂ and RuCl₃·nH₂O) dissolved in 1:1 HCl (v/v). For the Ti/Ir_{0.3}Ti_{0.7}O₂ electrode the precursor salts were IrCl₃ and TiCl₄ (both 0.2 mol dm⁻³) dissolved in 1:1 HCl (v/v). The calcination of the electrode was performed at 400 °C under a flux of oxygen (5 cm³ min⁻¹). After each addition of chloride precursors the electrode was calcinated for 10 min. When the desired mass was achieved the electrode was calcinated at 400 °C for a further hour. The electrode of nominal composition Ti/Ru_{0.3}Ti_{0.7}O₂ was obtained commercially from De Nora, Brazil.

The cyclic voltammetry measurements were carried out in 0.5 mol dm⁻³ H₂SO₄ using a potentiostat (EG&G/PAR model 273). The potentials in this study are referred to the mercury sulfate electrode (MSE).

Acetaldehyde (CH₃CHO 99%) and propionaldehyde (CH₃CH₂CHO 98%) were obtained from Merck and used without further purification. The other reagents: formaldehyde (H₂CO 37% solution with 12.5% methanol), sulfuric acid (H₂SO₄ 98%), formic acid (HCOOH 94.8%),

were obtained from Mallinckrodt and also used without further purification.

Experimental procedure

The concentration of the organic species was varied in the range of 0.01 to 0.50 mol dm⁻³. For each concentration voltammograms were recorded in the potential range of -0.40 to 1.00 V vs. MSE at sweep rates of 20 to 500 V s⁻¹. Although it is not common that such high anodic potentials are used in the study of oxide electrodes, in this study the aim was to imitate the conditions encountered during galvanostatic electrolysis (*i.e.* under conditions of simultaneous oxygen evolution).¹ The anodic charge (q_A) was determined by integration of the anodic component of the voltammogram, as will be described in the following section.

Results and Discussion

Cyclic voltammetry: normalized faradaic charge (q_{FN})

There is often some difficulty when comparing the catalytic properties of distinct electrode materials. Differences in electrode morphology can lead to misleading results. With this in mind, it is important to eliminate morphological differences when, for example, studying the oxidation of organic compounds.

The anodic voltammetric charge (q_A/mC cm⁻²) is generally considered a measure of the electroactive area of conductive oxides.⁴ The value of q_A is a consequence of different factors that include the mobility of the supporting electrolyte ion, the potential sweep rate as well as the preparation method.⁴ q_A is calculated in the potential region where the decomposition of water does not occur (normally 0.4 to 1.4 V vs. RHE). In acid media, in accordance with equation 1, the value of q_A is the result of proton exchange with the electrolyte and the capacitive charge (pseudo-capacitive charge).⁶



Thus, q_A can be considered the active area available for H⁺ exchange with the solution. This active area can include sites that are positioned in the less accessible internal regions of the oxide layer. When interpreting the results of organic oxidation, it can be difficult to obtain a relation between the value of q_A and the observed catalytic activity. Indeed, it has been suggested that the reaction of organic species occurs solely at the more easily accessible sites on the oxide surface.⁵ This is due to the larger size

of the organic molecules that limits their diffusion to the electrochemically active sites to which the smaller H^+ has access. Hence a large q_A value is no guarantee of increased catalytic activity for organic oxidation.

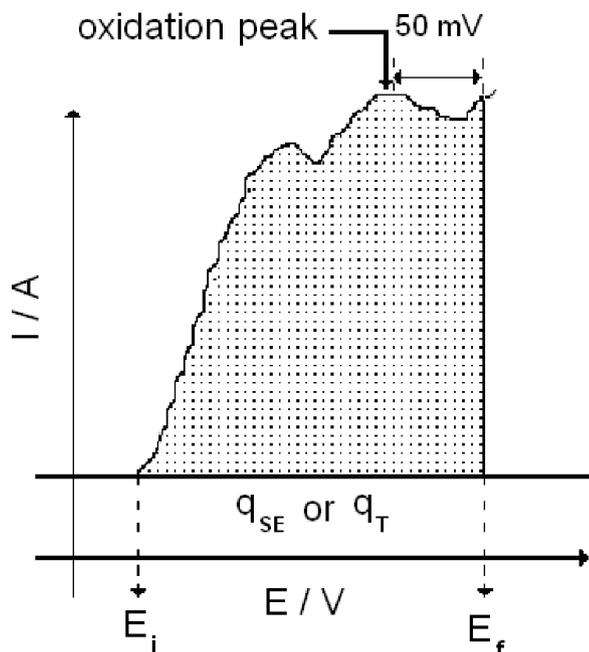


Figure 1. Method of calculation of the normalised faradaic charge (q_{fN}) presented in literature. Information taken from information provided in reference 5.

The normalized faradaic charge (q_{fN})⁵ is a parameter that can be used to provide an idea of catalytic activity of different materials. The value of q_{fN} is determined by calculating the charge of the anodic component of the voltammogram that corresponds to the oxidation peak (q_T) and subtracting from this the charge over the same potential interval solely in the presence of the supporting electrolyte (q_{SE} , see Figure 1). Thus the faradaic charge (q_f), which is the charge associated with the oxidation of the organic species, is determined according to the following relationship:

$$q_T - q_{SE} = q_f \quad (2)$$

The normalized faradaic charge is then calculated according to:

$$q_f / q_A = q_{fN} \quad (3)$$

This gives a value in which the morphological effects have been eliminated and thus permits the comparison of the global catalytic activity of distinct electrode materials. However, it should be noted that the oxidation of organic

species at conductive oxide electrodes is not always manifested in the form of a distinct peak. In fact, oxidation is often represented by the dislocation (anodically or cathodically) of the current associated with the oxygen evolution reaction (OER) and thus the method presented by Zanta *et al.*⁵ is difficult to apply.

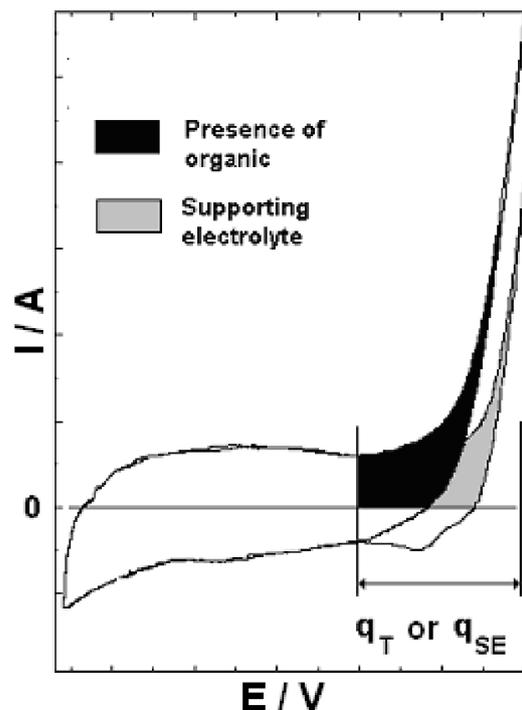


Figure 2. Illustration of the modification of the method proposed in reference 5.

In this study, a modification of the method of determination of q_{fN} for oxidation of organic species, which is not manifested in the form of a clear peak, is proposed. Thus, the determination of q_{fN} was achieved by establishing the potential at which oxidation of the organic takes place ($E > 0.5$ V vs. MSE at high organic concentrations). With this in mind, the anodic potential limit was set at 1.0 V, which is sufficiently positive to result in copious oxygen evolution. Thus, the charge was calculated from 0.5 V to 1.0 V in the absence of the organic species and denoted q_{SE} (*i.e.* the charge due to the supporting electrolyte). In the presence of the organic species the charge was then calculated over the same potential range and denoted as q_T . The value of q_f and q_{fN} were calculated as previously described in equations 1 and 2. The calculation is represented schematically in Figure 2.

In this manner, a modified method for comparing the catalytic activity of different electrode materials, which considers simultaneous oxygen evolution,¹ is presented here.

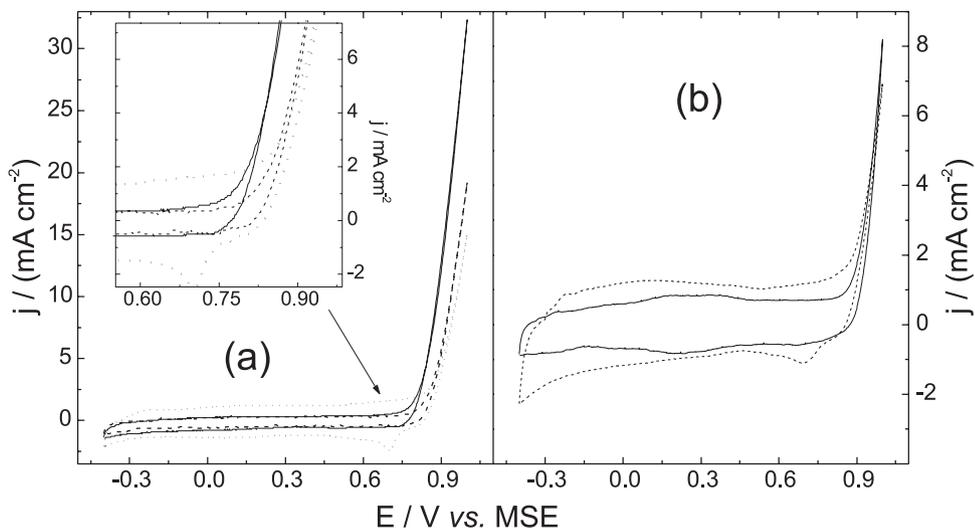


Figure 3. Cyclic voltammograms in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ of the electrodes employed. (a) Electrodes of composition $\text{Ti/Ru}_x\text{Sn}_{1-x}\text{O}_2$: $x = 0.3$ (dotted line), 0.2 (solid line) and 0.1 (dashed line). (b) $\text{Ti/Ir}_{0.3}\text{Ti}_{0.7}\text{O}_2$ (solid line) and $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ (dashed line). $v = 20 \text{ mV s}^{-1}$.

Cyclic voltammetry in absence of organic species

The voltammograms in 0.5 mol dm^{-3} sulfuric acid are shown in Figure 3. The anodic charge ($q_A / \text{mC cm}^{-2}$, calculated in the region of water stability, -0.20 to 0.50 V vs. MSE) has the order $\text{Ti/Sn}_{0.1}\text{Ti}_{0.9}\text{O}_2 > \text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2 > \text{Ti/Ir}_{0.3}\text{Ti}_{0.7}\text{O}_2 > \text{Ti/Sn}_{0.3}\text{Ti}_{0.7}\text{O}_2 > \text{Ti/Sn}_{0.2}\text{Ti}_{0.8}\text{O}_2$. The magnitude of q_A is considered a measure of the electro-active area of the electrode⁶ and hence might be considered an indicator of the overall catalytic power of a given material.

Typically, the effect of increasing the sweep rate is manifested by a decrease in the value of q_A . This is attributed to the exclusion of less easily accessible sites located in the inner part of the electrode.⁷ It was observed that the electrodes containing SnO_2 present a much more accentuated decrease in the anodic charge than the $\text{Ti/Ir}_{0.3}\text{Ti}_{0.7}\text{O}_2$ or $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ electrode.

Cyclic voltammetry in presence of formaldehyde

The addition of formaldehyde to the electrolyte results in typical DSA[®] type behavior for all electrodes in the presence of this organic species (Figure 4).^{3,8,9} This is exemplified by an increase in the value of the anodic charge in the potential region above 0.5 V vs. MSE and an increase in the current associated with the oxygen evolution reaction (OER). The effect of increasing the concentration of formaldehyde is manifested by a quasi-linear increase in the magnitude of q_{FN} for all electrodes.

The behavior of q_{FN} with H_2CO concentration for the electrodes with nominal compositions $\text{Ti/Ir}_{0.3}\text{Ti}_{0.7}\text{O}_2$, $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and $\text{Ti/Ru}_{0.3}\text{Sn}_{0.7}\text{O}_2$ is presented in Figure 5.

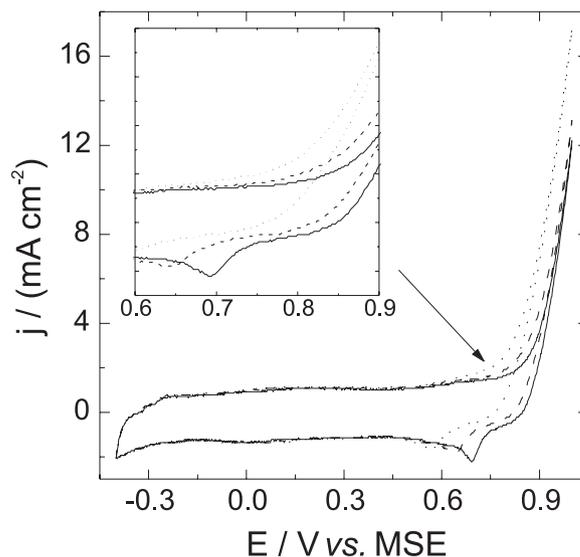


Figure 4. Cyclic voltammograms of the $\text{Ti/Ru}_{0.3}\text{Sn}_{0.7}\text{O}_2$ electrode in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 0.00$ (solid line); 0.05 (dashed line); 0.20 (dotted line) $\text{mol dm}^{-3} \text{ H}_2\text{CO}$. $v = 20 \text{ mV s}^{-1}$.

Analysis of Figure 5 would indicate the following order of activity (considering the final values of q_{FN} at $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{CO}$):



This indicates that any prospective process for the oxidation of formaldehyde would be more fruitful if electrodes of nominal composition $\text{Ti/Ru}_x\text{Sn}_{1-x}\text{O}_2$ are used. The reaction orders presented above will be tested and verified for galvanostatic electrolyses in a later section of this paper.

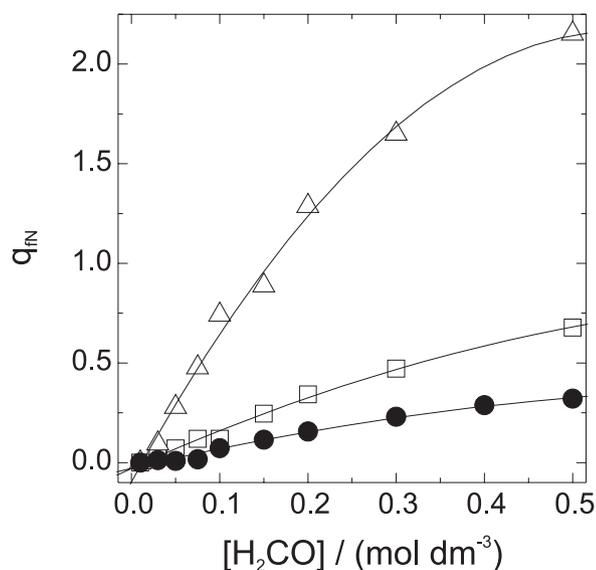


Figure 5. Variation of q_{IN} with H_2CO concentration: (●) $Ti/Ru_{0.3}Ti_{0.7}O_2$; (□) $Ti/Ir_{0.3}Ti_{0.7}O_2$; (△) $Ti/Ru_{0.3}Sn_{0.7}O_2$.

When the results obtained are considered together with the work of Zanta *et al.*,⁵ it is interesting to consider the behavior of Ti/RuO_2 electrodes in non-aqueous solvents, where the possibility of forming $MO(S)$, instead of the $MO(OH)$ observed in water, is suggested.⁵ At higher currents an oxidation process was observed, which was attributed to the oxidation of the solvent.⁵ If the current associated with OER increases with formaldehyde concentration, as observed in this study, the mechanism of oxidation must follow a direct electron transfer step between the formaldehyde and the electrode. In this light it is probable that the formation of some kind of $MO(H_2CO)$ species is involved, which is then oxidized by a direct mechanism:



This kind of mechanism does not fall within that presented by Comninelliis,¹ as the mechanism does not consider interaction of the organic species with electrode. The hypothesis presented here is supported by the fact that in previous studies in this laboratory we have shown that the OER current increases in the presence of formaldehyde.³ However, O_2 production in fact decreases,³ indicating that the current increase is not associated with O_2 production. Thus, considering the direct electron transfer mechanism, the rate of O_2 evolution is decreased, however, the mechanism probably remains the same.

Effect of electrode material and organic concentration

Up to this point it has been shown that the difference in the electrode material heavily affects the global catalytic

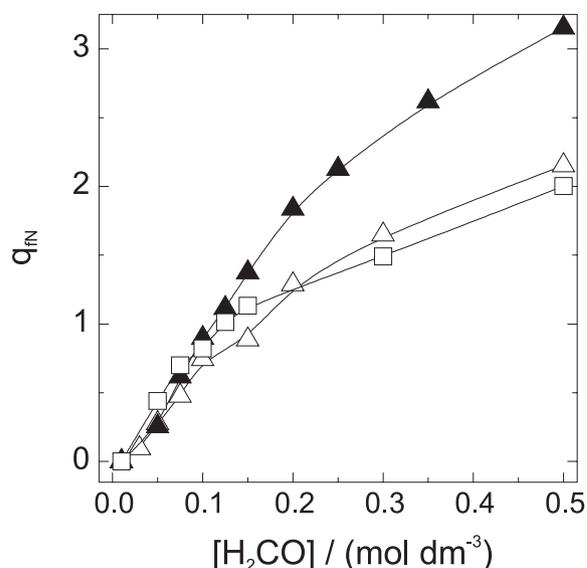
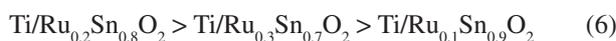


Figure 6. Variation of q_{IN} with H_2CO concentration for electrodes of nominal composition $Ti/Ru_xSn_{1-x}O_2$: (□) $Ti/Ru_{0.1}Sn_{0.9}O_2$; (▲) $Ti/Ru_{0.2}Sn_{0.8}O_2$; (△) $Ti/Ru_{0.3}Sn_{0.7}O_2$.

activity for oxidation. If the series of electrodes of nominal composition $Ti/Ru_xSn_{1-x}O_2$ are compared with each other, the behavior seen in Figure 6 for formaldehyde is observed. A cursory glance at Figure 6 would indicate the following sequence of activity (considering the final values of q_{IN} at $0.5 \text{ mol dm}^{-3} H_2CO$):



However, if the data in Figure 6 is separated in to low ($0.01\text{-}0.05 \text{ mol dm}^{-3}$) and high ($0.10\text{-}0.50 \text{ mol dm}^{-3}$) concentration domains, the behavior shown in Figure 7 is observed.

Table 1. Variation of $q_{fN} / [R]$ ($\text{dm}^3 \text{ mol}^{-1}$)

Electrode	Low	High
$Ti/Ru_{0.3}Ti_{0.7}O_2$	0.0018	0.0012
$Ti/Ru_{0.1}Sn_{0.9}O_2$	0.0110	0.0025
$Ti/Ru_{0.2}Sn_{0.8}O_2$	0.0064	0.0049
$Ti/Ru_{0.3}Sn_{0.7}O_2$	0.0069	0.0034
$Ti/Ir_{0.3}Ti_{0.7}O_2$	0.0006	0.0006

The slopes calculated from the data in Figure 7 are given in Table 1. It apparent that the electrodes present different activities in different concentration ranges. At low concentrations the electrode with nominal composition $Ti/Ru_{0.1}Sn_{0.9}O_2$ presents the greater increase in q_{fN} , whereas at higher concentrations the greater increase is seen for the electrode $Ti/Ru_{0.2}Sn_{0.8}O_2$. Thus, considering the values

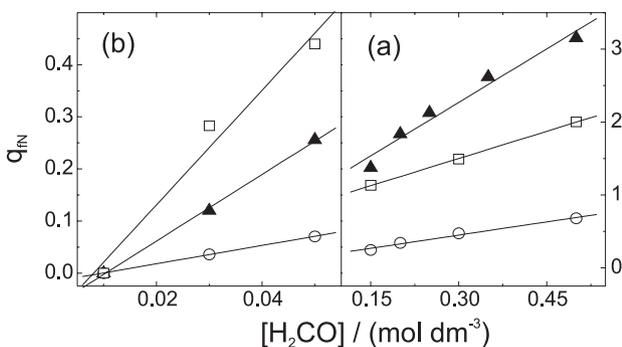
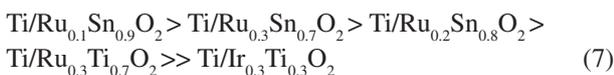


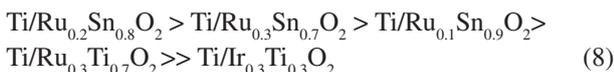
Figure 7. Variation of q_{IN} at (a) low and (b) high concentrations with H_2CO concentration: (○) $Ti/Ru_{0.3}Ti_{0.7}O_2$; (●) $Ti/Ir_{0.3}Ti_{0.7}O_2$; (□) $Ti/Ru_{0.1}Sn_{0.9}O_2$; (▲) $Ti/Ru_{0.2}Sn_{0.8}O_2$.

presented in Table 1 it is possible to suggest the following order of activity for formaldehyde oxidation:

Low concentrations:



High concentrations:



These orders of activity suggest that different concentrations might require different materials for optimization of a given process. This is important as industrial waste discharges can vary in concentration depending on the nature of the manufacturing process.

Galvanostatic electrolysis

By comparing the variation of q_{IN} for different electrodes, it is possible to establish a sequence that predicts the order

of activity for different oxide electrodes. The measurements were obtained under conditions of simultaneous oxygen evolution, which permits the simulation of a galvanostatic oxidation process.

The galvanostatic oxidation of formaldehyde-containing solutions was performed at 40 mA cm^{-2} in order to compare with previous studies performed in this laboratory.^{3,8} Two different concentrations were investigated, one in the higher concentration domain (0.10 mol dm^{-3}) and the other in the lower range (0.01 mol dm^{-3}), in order to compare the results obtained in the previous section.

The only detected products of formaldehyde oxidation were formic acid and CO_2 . Figure 8 presents the concentration-time profile of the oxidation of a 0.10 mol dm^{-3} formaldehyde solution as a function of time for all the electrodes studied. The decrease in the formaldehyde concentration presents pseudo 1st order kinetics and the

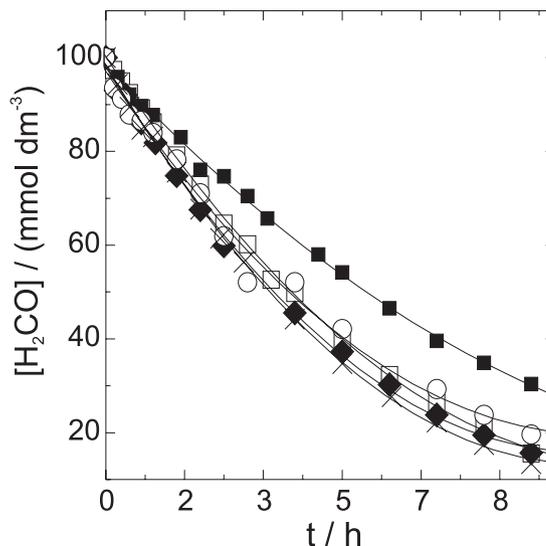


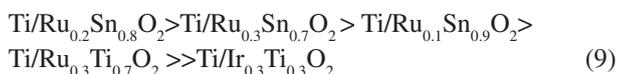
Figure 8. Concentration-time profile obtained during oxidation (40 mA cm^{-2}) of a 0.10 mol dm^{-3} formaldehyde solution. (■) $Ti/Ir_{0.3}Ti_{0.7}O_2$; (○) $Ti/Ru_{0.3}Ti_{0.7}O_2$; (X) $Ti/Ru_{0.2}Sn_{0.8}O_2$; (□) $Ti/Ru_{0.3}Sn_{0.7}O_2$; (◆) $Ti/Ru_{0.1}Sn_{0.9}O_2$.

Table 2. Data obtained during the oxidation of formaldehyde solutions

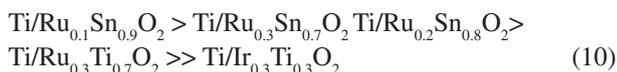
Electrode	$[H_2CO] / (\text{mol dm}^{-3})$	$K_{ox} (\ln[A/A_0]) / (10^{-5} \text{ s}^{-1})$	$k_{carb} / (10^{-4} \text{ mmol dm}^{-3} \text{ s}^{-1})$	$CO_2 / (\text{mmol dm}^{-3})$
$Ti/Ru_{0.3}Ti_{0.7}O_2$ (industrial)	0.01	6.41	3.10	0.58
	0.10	4.88	24.65	3.11
$Ti/Ir_{0.3}Ti_{0.7}O_2$	0.01	4.09	3.00	0.82
	0.10	3.62	20.70	1.99
$Ti/Ru_{0.3}Sn_{0.7}O_2$	0.01	7.52	3.30	0.56
	0.10	4.86	37.00	2.90
$Ti/Ru_{0.2}Sn_{0.8}O_2$	0.01	6.47	3.80	0.61
	0.10	5.21	42.80	3.00
$Ti/Ru_{0.1}Sn_{0.9}O_2$	0.01	8.58	5.50	0.65
	0.10	4.95	28.40	4.06

k_{carb} : Rate of formation of respective carboxylic acid.

values of the constants (k_{ox}) are presented in Table 2. Analysis of the values presented in Table 2 for higher concentrations gives the following order of reaction:



This sequence of reaction is the same as that presented in Figure 7. Following the same method for lower concentrations:



which is the same as Figure 8.

It should be noted that the reaction sequence can be applied to the data presented in Table 2 only in the case of the rate of formaldehyde disappearance and formic acid formation. The activity for formation of CO_2 is not predicted by the reaction sequence given. This indicates that the variation of q_{FN} can only be applied considering the predominant reaction that occurs (and subsequently the formation of any relatively stable product), but not to the formation of secondary products and so on.

The results obtained indicate that it is possible to predict the activity of oxide electrodes towards galvanostatic oxidation.

Conclusions

A relatively quick and easy method, which employs cyclic voltammetry, for the “screening” of electrode materials for a given reaction has been presented. The method involves the simulation of an oxidation process by employing potentials that enter the region of the oxygen evolution reaction. A modified method for the calculation of the normalized faradaic charge (q_{FN}) is presented. Although the calculation of q_{FN} has already been described in the literature, the current modification enables the method to be applied to organic species whose oxidation is not manifested by a defined oxidation peak at conductive oxide electrodes. It is hoped that the method presented enables a rapid triage of electrode materials before any

time consuming electrolysis assays are performed. It is suggested that the oxidation of formaldehyde may occur via direct electron transfer at the electrode surface mediated by the formation of an $\text{MO}(\text{H}_2\text{CO})$ species indicating that not only the nature of the electrode material, but also the organic species in solution and its concentration are important factors to be considered in the oxidation of organic compounds. This can be important as any one given prospective treatment process might be optimized by the use of a certain electrode material, whereas another process would require the use of another.

Acknowledgments

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