Galvanostatic oxidation of formaldehyde-methanol solutions on $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrodes using a filter-press cell

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Abstract

The galvanostatic oxidation of methanol-containing formaldehyde solutions, under conditions of simultaneous oxygen evolution, in 0.5 M H_2SO_4 acid was studied using a $Ti/Ru_{0.3}Ti_{0.7}O_2$ dimensionally stable anode ($DSA^®$), in a filter-press cell. The reaction products detected were $HCOOH$, CO_2 and CO_3^{2-}. The CO_3^{2-} species is formed from the oxidation of $HCOOH$ and subsequently decomposes in solution to CO_2. Conversely CO_2 is also formed electrochemically from the electrooxidation of formaldehyde and methanol. A mechanism, which considers the 'active' and 'non-active' nature of the electrode, is suggested. First-order kinetics, with respect to the variation of formaldehyde and methanol, are displayed and two linear regions observed. This is interpreted as being due to the presence of the reaction products of oxidation inhibiting the oxidation of formaldehyde at the electrode surface. Further, a mechanism is proposed considering the species present in solution.

1. Introduction

Formaldehyde is an extremely important industrial material being used in the manufacture of resins and as a C1 building block for the syntheses of larger molecules [1] and as such it can be widely encountered in industrial waste discharges. Formaldehyde, with formic acid, can be encountered as the product of methanol oxidation in fuel cells and other systems. Formaldehyde is highly reactive chemical and tends to polymerise in the presence of acids such as H_2SO_4 [2]. As a result commercial formaldehyde is generally marketed as a 37% solution containing 8–15% methanol as a stabilizer. In this context the study of the electrooxidation of formaldehyde in the presence of methanol would be of importance in understanding the reaction processes taking place in such systems.

Dimensionally stable anodes ($DSA^®$) are promising materials for many electroorganic applications and have been classified as 'active' or 'non-active' [3, 4], depending on the electrode material. Active electrodes mediate the oxidation of an organic species via the formation of higher oxides of the metal, (MO_{x+1}), where there is a higher oxidation state available (e.g., RuO_2 or IrO_2). This leads to selective oxidation. Non-active electrodes present no higher oxidation state available and the organic species is directly oxidized by an adsorbed hydroxyl radical, giving complete combustion (e.g., SnO_2 or PbO_2). However, no electrode can be said to be completely active or non-active and generally a small amount of 'active' behaviour can be observed on principally 'non-active' electrodes and vice versa.

Burke and Murphy [5] observed that during the electrooxidation of methanol the concentration had an effect on the selectivity of the reaction. O'Sullivan [6] concluded that the oxidation of formaldehyde occurred via Ru(VI) and Ru(VII) higher oxide species electrogenerated at the electrode surface. The oxidation of formaldehyde was observed to proceed via formic acid to carbonate at higher potentials [6], whereas the galvanostatic oxidation of formaldehyde was proposed to lead to the formation of CO_2 via formic acid [7].

The use of a filter-press cell with electrolyte flux enables the simulation of an industrial process on a laboratory scale, be it with a view to electrosynthesis [8] or effluent treatment. Thus, a study of the electrochemical oxidation of formaldehyde–methanol solutions at a $DSA^®$ type electrode with the dual aim of simulating a prospective industrial treatment process and understanding the mechanistic processes involved is presented.

2. Experimental details

A two-compartment filter-press cell was used with a $Ti/Ru_{0.3}Ti_{0.7}O_2$ $DSA^®$ anode (nominal area, 14 cm^2) and a stainless steel plate cathode (area 14 cm^2), mounted using $Viton^®$ and $Teflon^®$ spacers of varying thickness and electrolyte flow was provided by a peristaltic pump, as described elsewhere [7]. The cell parameters, namely

cell volume, current density and electrolyte flux were determined in initial experiments in two different ways: (i) *cyclic voltammetry*, by comparing the anodic charges obtained for a series of voltammograms under different cell parameters (cell volume and electrolyte flux). The parameters that gave the maximum anodic charge were subsequently employed. The cell volume was determined at 4.45 cm³ and the flux through the cell at 9 cm³ min⁻¹ (20 rpm). Where these parameters were employed the term 'procedure 1' is used; (ii) *controlled electrolysis*, by determining the maximum quantity of formic acid and CO_2 formed as a function of differing cell volume, electrolyte flux and current density, during electrolysis of 1 h. The cell volume was determined at 5.78 cm³, the flux through the cell at 32 cm³ min⁻¹ (100 rpm) and the current density at 40 mA cm⁻². Where these parameters are used the term 'procedure 2' is used.

The cell volume was adjusted by varying the number of Viton® and Teflon® spacers. Both sets of determined parameters were compared under prolonged electrolysis conditions at 40 mA cm⁻².

All electrolyses were carried out at a constant current density of 40 mA cm⁻², under conditions of simultaneous oxygen evolution, in 0.5 M H_2SO_4 using a stabilised current power source (Tectrol). The gases liberated passed through two traps (250 cm³ each) containing $Ba(OH)_2$ (10 M and 5 mM, respectively). The amount of CO_2 liberated was calculated from the measured change in the pH of the solutions of $Ba(OH)_2$ due to the formation of insoluble $Ba(CO_3)$.

Analyses of the reaction products were performed using HPLC (Shimadzu LC-10AD VP) with an ion exchange column (HPX-87H, Bio-Rad). The eluent was 3.33 mM H_2SO_4. The electrolysis products were identified using an ultraviolet detector (Shimadzu SPD-10A VP) at $\lambda = 210$ nm (for HCOOH) in conjunction with a refractive index detector (RID-10A) (for CH_3OH, H_2CO and CH_3OH). Products were identified by comparing the retention times against those for pure reference materials obtained from Mallinckrodt: formaldehyde 37 wt % (containing methanol, 12.51 wt %) and formic acid, 94.3 wt %, used without further purification.

The cyclic voltammetric measurements were carried out in 0.5 M H_2SO_4 using a potentiostat (EG&G/PAR model 273). The potentials in this study are referred to the $Hg/Hg_2SO_4/SO_4^{2-}$ (MSE) reference electrode.

Nitrogen gas was passed constantly through the system to remove CO_2, but was turned off when the instantaneous current efficiency (ICE) was measured. Values for the ICE and the initial electrochemical oxidation index (EOI) were obtained by the oxygen flow-rate method [9].

3. Results and discussion

Galvanostatic electrolysis of solutions of formaldehyde (0.1 and 0.01 M) in H_2SO_4 (0.5 M) at 40 mA cm⁻² yielded the initially observed products of formaldehyde,

formic acid and carbon dioxide under the cell parameters determined by both procedures 1 and 2. The term 'yield' refers to the carbon balance, and considers all the species (methanol, formaldehyde, formic acid and CO_2) identified in the reaction mixture.

3.1. Electrooxidation of formaldehyde

The electrolysis, over 9 h, of 0.1 M H_2CO under procedure 1 conditions resulted in a yield of 92% by totalling the formaldehyde, formic acid, CO_2 and methanol present, Figure 1. Under procedure 2 conditions the overall yield was 88%. The values of the calculated yields are shown in Table 1. In previous work Motheo et al. [7] reported yields of at least 98% for the oxidation of formaldehyde using reagents free of methanol.

The difference in the applied parameters for procedures 1 and 2 is manifested by a difference in the quantity of CO_2 produced during electrolysis (Figure 2 and Table 1). From Figure 2 it can be seen that initially CO_2 production increases rapidly and subsequently falls, agreeing with previous reports [7] for galvanostatic oxidation of formaldehyde. The variation of the organic species (CH_3OH, H_2CO and HCOOH) in the reaction mixture, for the conditions established by procedure 2, varied little from that observed under those of procedure 1. This indicates that flux and cell volume have little influence on the overall rate of oxidation of methanol/formaldehyde to formic acid.

The calculated yields for the electrooxidation of 0.01 M H_2CO for procedures 1 and 2 were 99 and 94% (4.5 h electrolysis), respectively. This follows the

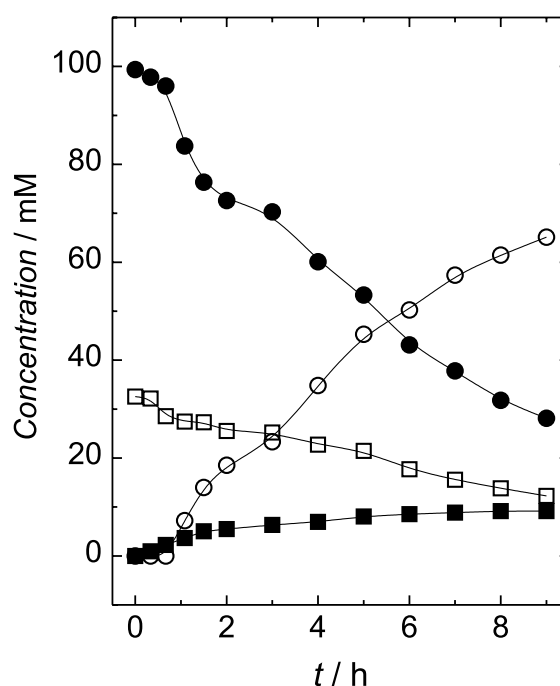*Fig. 1.* Dependence of the concentration of reactants with the electrolysis time for the oxidation of 0.1 M H_2CO in 0.5 M H_2SO_4 at 40 mA cm⁻²; (●) H_2CO (□) CH_3OH and products; (○) HCOOH (■) CO_2. Flux 9 cm³ min⁻¹. Cell volume: 4.45 cm³.

Table 1. Production of CO_2 and overall yield determined for the electrolysis at a $Ti/Ru_{0.3}Tiu_{0.7}O_2$ electrode of formaldehyde and formic acid under procedures 1 and 2 conditions

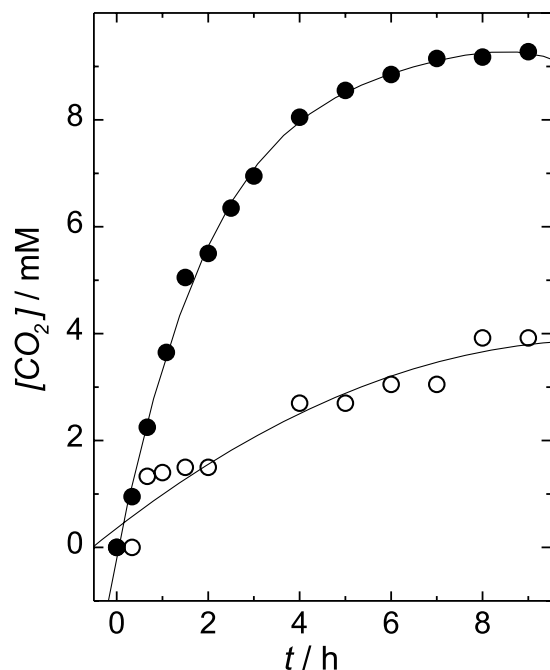|	Procedure 1				Procedure 2			
	CO_2 produced /mM	CO_2 produced /%	Carbon balance/%	Initial EOI	CO_2 produced /mM	CO_2 produced /%	Carbon Balance/%	Initial EOI
H_2CO (0.10 M)	9.45	7	92	0.84	3.93	2.7	88	0.71
H_2CO (0.01 M)	4.35	30	99	–	1.26	9.5	94	–
HCOOH (0.05 M)	1.50	3	56	0.06	1.48	3.0	55	0.06

Fig. 2. Production of CO_2 during the electrolysis at 40 mA cm^{-2} of 0.1 M H_2CO in 0.5 M H_2SO_4 by: (●) procedure 1 and (○) procedure 2.
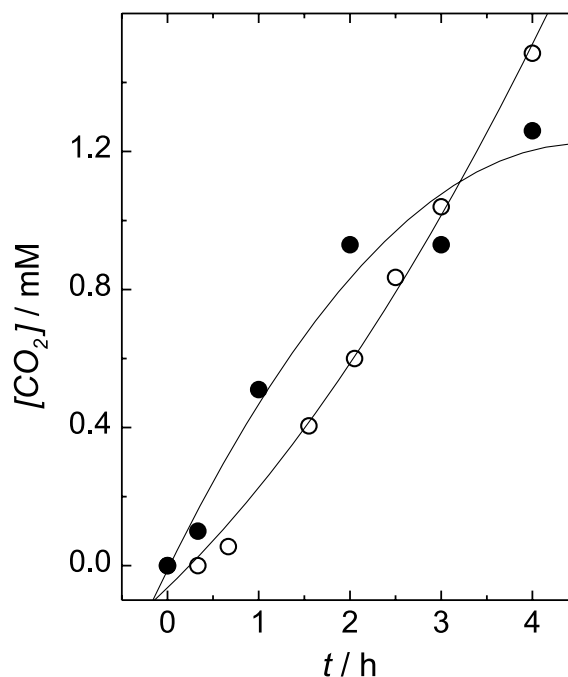

Fig. 3. Production of CO_2 during the electrolysis at 40 mA cm^{-2} by procedure 2 of (○) 0.05 M HCOOH and (●) 0.01 M H_2CO in 0.5 M H_2SO_4.

same pattern as observed for the higher concentration where the changing of the parameters resulted in a fall in the calculated yield.

The production of CO_2 followed the same pattern as observed for the 0.1 M formaldehyde (Figure 3). At lower concentrations, the amount of CO_2 produced, as a proportion of the total organic content, is greatly increased (Table 1). For electrolysis of 0.01 M H_2CO under procedure 1 conditions the quantity of CO_2 produced is 9.45% compared to 4.35% for 0.1 M. As seen for the higher concentration, the quantity of CO_2 produced falls with the change in cell parameters, this time to 3.93% overall. Burke and Murphy [5] observed variation in the formation of CO_2 from methanol solutions with concentration and suggested that such a phenomenon indicates that the oxidation of methanol to CO_2 proceeded via the adsorption of an OH_{ads} species at the electrode surface, which was inhibited at higher concentrations. In this case, such a process would be hindered by the increased concentrations of formaldehyde. According to this hypothesis, the variation of cell volume and flux through the cell would also have an

effect on the rate of •OH adsorption and thus influence the production of CO_2 in the same manner.

3.2. *Electrooxidation of 0.05 M formic acid*

During the study of the electrooxidation of 0.05 M HCOOH (the principal reaction product of H_2CO oxidation), a rapid fall in the overall yield to 55% over 4.5 h of electrolysis at 40 mA cm^{-2} was observed. This loss suggested that a quantity of other undetected specie(s) was being produced. This led to the consideration of the possibility of the formation of CO_3^{2-} as a product of the oxidation of HCOOH at an elevated surface oxide of Ru, as previously reported by O'Sullivan and White [6]. This hypothesis was tested by adding a small amount of a solution of $Ca(OH)_2$ to the reaction mixture and a white precipitate was observed to form. This indicated the presence of dissolved CO_2 or CO_3^{2-} in the reaction mixture. As nitrogen gas was passed through the system during the electrolysis it is considered unlikely that the precipitate was due to the presence of CO_2. Thus a mechanism involving the

oxidation of HCOOH to the carbonate on $Ti/Ru_{0.3}$-$Ti_{0.7}O_2$ electrodes under galvanostatic conditions must be considered. This would account for the extreme fall in the yield. During the oxidation of HCOOH, evolution of CO_2 was observed (Table 1) but with a different form compared to that observed for formaldehyde (Figure 3).

3.3. Mechanistic considerations

From the results presented above two observations can be made. First, the percentage yields for formaldehyde display a pattern, where the yield under conditions in procedure 1 is consistently higher than that for procedure 2, with the exception of HCOOH. It was suggested above, in agreement with the literature [6], that HCOOH is oxidized to CO_3^{2-}, present as H_2CO_3. The low presence of the CO_3^{2-} species meant that it was not detected in the analysis of the products by HPLC under the conditions used and this would result in a fall in the calculated yield. Where the quantity of CO_2 produced is high, as for procedure 1, the yield is higher due to the fact that more products are identified. For procedure 2 the lower tendency to form CO_2 results in a lesser-calculated yield as more formaldehyde is oxidized to the carbonate via formic acid.

Secondly, in contrast to formaldehyde, the quantity of CO_2 produced from HCOOH remains constant for both procedures 1 and 2 (at ~3%), and both follow the same trend with a slow initial evolution followed by rapid increase with time after approximately 1 h 40 min (Figure 3). It can be postulated, by comparison with the evolution of CO_2 from solutions of formaldehyde, that CO_2 evolution from solutions of HCOOH proceeds via a different mechanism. This would be an addition to the work by Motheo et al. [7] where a simple mechanism for the oxidation of formaldehyde to CO_2 via HCOOH was considered. This would correspond to an 'active' path according to Comninellis and de Battistti [3]. The shape of the curve for CO_2 formation from the oxidation of HCOOH suggests that CO_2 is produced as a secondary product by the decomposition of the carbonate in solution.

It would then follow that the formation of CO_2 from the oxidation of methanol and formaldehyde (Figure 2) occurs via a second pathway, giving rise to a two-pathway mechanism (Equation 1):

$$CH_3OH/H_2CO \begin{array}{c} \nearrow^2 CO_2 \\ \searrow_1 CO_3^{2-} \end{array} \qquad (1)$$
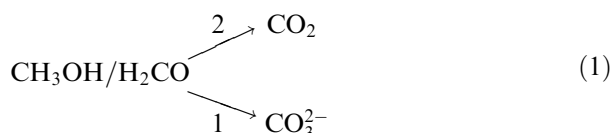
Such mechanisms have been proposed for the oxidation of methanol on more traditional materials such as Pt [10]. In this case one pathway leads to CO_2 while the other leads to CO_3^{2-}.

Such a possibility can be described by the active and non-active nature of the electrode as proposed by Cominellis and de Battistti [3]. No electrode can be
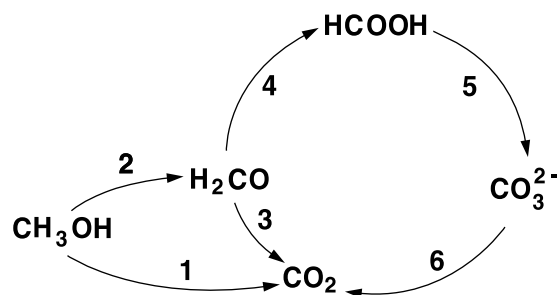

Fig. 4. Scheme representing the galvanostatic oxidation of formaldehyde and methanol at a $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode in 0.5 M H_2SO_4. Paths 1 and 3: 'non-active' route; paths 2, 4 and 5: 'active' route; path 6: decomposition.

classified as completely active or non-active. In this way, the complete combustion of methanol or formaldehyde to CO_2 at $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrodes would occur via a non-active mechanism, but its oxidation to HCOOH would occur via an active route. The mechanistic considerations discussed above are represented in Figure 4 where paths 1 and 3 represent the complete oxidation to CO_2 by a non-active route and paths 2, 4 and 5, the selective oxidation by an active route. Path 6 represents the simple decomposition of CO_3^{2-} to CO_2.

3.4. Kinetic considerations

The variation of the concentration of formaldehyde, under procedure 1, displays first order kinetics, with two distinct areas (Figure 5). The first area occurs in the
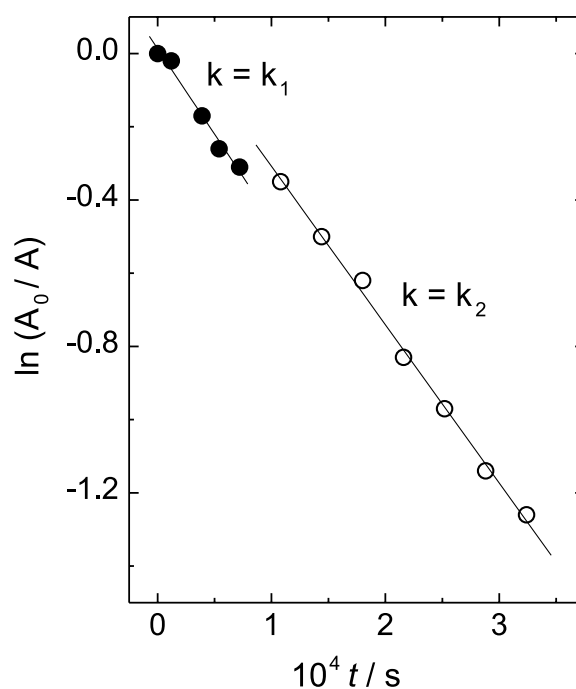

Fig. 5. First order plot for the variation in the concentration of formaldehyde under procedure 1 (cyclic voltammetry) conditions showing two distinct regions, (A_0 = initial concentration and A = actual concentration).

Table 2. Values of k_1 and k_2 obtained by procedures 1 and 2 for the oxidation of formaldehyde, methanol and formic acid at a Ti/$Ru_{0.3}Tiu_{0.7}O_2$ electrode

Compound	Procedure	k_1/s^{-1}	k_2/s^{-1}
Formaldehyde (0.1 M)	1	4.85×10^{-5}	4.33×10^{-5}
	2	–	4.77×10^{-5}
Methanol (0.03 M)	1	3.44×10^{-5}	3.45×10^{-5}
	2	–	3.88×10^{-5}
Formic acid (0.05 M)	1	4.40×10^{-5}	2.97×10^{-5}
	2	4.68×10^{-5}	2.66×10^{-5}
Formic acid (Variation during initial stages of electrolysis)	1	1.35×10^{-4}	
	2	2.38×10^{-4}	

range of 0–2 h 30 min (9000 s) and then there is a shift to the second area after this time. For the second area the value of k is lower, which, with the shift in position indicates a change in the mechanism. Two areas can also be seen for methanol, but with the same value of k (Table 2). Analysis of the first order plots achieved under procedure 2 conditions shows that only one area can be observed for both methanol and formaldehyde (Figure 6).

For procedure 1, these observations can be explained by considering the presence of the initial species in the reaction medium (H_2CO and CH_3OH) and their subsequent oxidation products (as shown in Figure 4). Initially, as H_2CO and CH_3OH are oxidised to HCOOH at the electrode surface, the reaction proceeds at a given rate, with $k = k_1$. The increase in the concentration of
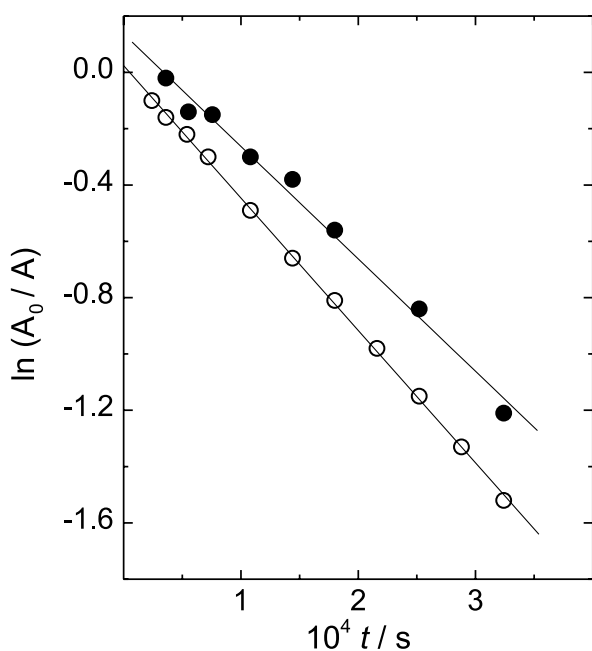

Fig. 6. First order plot for the variation in the concentration of (○) formaldehyde and (●) methanol under procedure 2 (controlled electrolysis) conditions, the two distinct regions are absent, (A_0 = initial concentration and A = actual concentration).

HCOOH lowers the rate of oxidation of formaldehyde, with $k = k_2$, and affects the mechanism after about 2 h 30 min. This would, in fact, make k_1 a hybrid of the rate constants of oxidation via active and non-active sites, and thus gives a higher value. The value of k_2 would be that of the variation of formaldehyde reacting at active sites, being first order.

The variation of the concentration of HCOOH during the electrolysis of formaldehyde (under procedure 1 conditions) initially shows first-order dependence, but after about 2 h 30 min this breaks down. Under procedure 2 conditions this first order dependence in the variation of HCOOH is seen for less time at 1 h 30 min (5400 s) and the value of k is increased compared to procedure 1. This indicates that the rate of oxidation/consumption of HCOOH (in the presence of H_2CO and CH_3OH) under procedure 1 is slower than that for procedure 2 whereas the opposite is observed for both H_2CO and CH_3OH where the overall value of k is increased.

It is clear from Table 2 that the change in the cell parameters affects the rate of the reaction. It is probable that changes to a higher cell flux and greater cell volume in procedure 2 favours the reaction of H_2CO and CH_3OH over HCOOH, thus lowering the rate of HCOOH oxidation in their presence. The formation of CO_2 is inhibited with the change in reaction conditions possibly due to the inhibition of the formation of an OH_{ads} species [5], as was observed by varying the concentrations of formaldehyde in this paper. This can now be rationalised as the inhibition of the formation of non-active sites on the electrode surface and subsequently the complete oxidation of methanol or formaldehyde. For this reason only one area is observed in the first-order plots for procedure 2 conditions with only one value of k seen (Figure 6). Overall, the same behaviour was seen for electrolysis of 0.01 M formaldehyde as for the higher concentrations (Table 2).

Direct electrolysis of 0.5 M HCOOH again shows two distinct linear regions, with two different values of k. It is seen that $k_1 < k_2$, and this can be explained by considering the presence of CO_3^{2-} inhibiting the electrode reaction, when an equilibrium is reached after a certain time. Procedure 2 shows a faster initial formation of carbonate compared to procedure 1, but the second phase shows a comparative decrease, probably due to a faster initial formation of CO_3^{2-} inhibiting HCOOH oxidation to a greater extent later on.

The fact that the flow rate results in different values of k for all organic species shows that the reaction is mass transfer controlled, indicating the importance of cell parameters.

Cyclic voltammograms (Figure 7) of Ti/$Ru_{0.3}Ti_{0.7}O_2$ in 0.1 M H_2CO show no passivation of the electrode surface over 40 cycles indicating that the formation of an inhibiting film is not the cause of the fall in CO_2 production. Values for the measured E_{cell} increased rapidly over the first 30 min from ~2.50 V until reaching an equilibrium at ~2.60 V, also indicating the
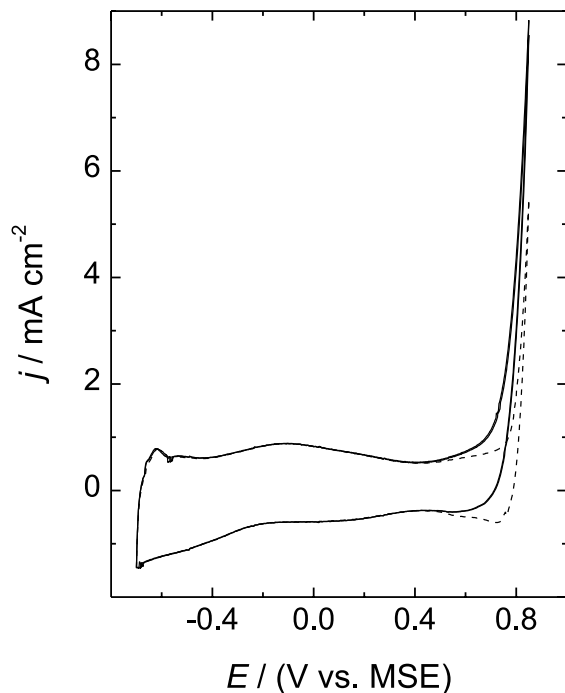
Fig. 7. Cyclic voltammograms of Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ in 0.5 M H$_2$SO$_4$ (dashed line) and 0.5 M H$_2$SO$_4$ with 0.1 M H$_2$CO (solid line) after 40 cycles. Scan rate 20 mV s^{-1}.

absence of a resistive film. The potential of the working electrode followed the same pattern, increasing rapidly during the initial stages of the experiment to remain constant at ~1.17 V. The voltammograms show typical DSA type behaviour: the broadness of the peaks is attributed to the heterogeneous nature of the oxide layer with the presence of an organic species shifting the onset of the OER to negative values [7].

3.5. *Instantaneous current efficiency*

A measure of the current efficiency at any instant in time can be obtained by calculating the 'instantaneous current efficiency' (ICE) [9]. In this case the ICE was obtained by the oxygen flow-rate method [9] as

$$ICE = \frac{V_0 - V_t}{V_0} \qquad (2)$$

where V_0 is the flow-rate of O$_2$ in the absence of the organic and V_t in the presence of the organic.

The average current efficiency can be described as the 'electrochemical oxidation index' (EOI):

$$EOI = \frac{\int_0^\tau (ICE)dt}{\tau} \qquad (3)$$

where τ is electrolysis time when the ICE is almost zero. Following details given by Stucki and Kotz, the initial value of the ICE can be described as the initial EOI [11] (i.e., EOI $\sim$ ICE).

The values for the initial EOI are displayed in Table 2. For formaldehyde it can be claimed that, procedure 1

gives a higher initial EOI value compared to procedure 2, which corresponds to a higher efficiency of organic oxidation. Although this contradicts the overall efficiency increase for procedure 2 over procedure 1, it can be explained by considering the possible inhibition of non-active sites, discussed above, and the subsequent lower formation of CO$_2$. The initial EOI for HCOOH is the same for both procedures. For 0.01 M H$_2$CO the EOI was difficult to measure due to the low concentration of the organic and values are not shown in Table 2.

4. Conclusions

The electrochemical oxidation of formaldehyde at a Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode using a filter-press cell was presented. The results indicate that:

(i) The electrooxidation of formaldehyde proceeds via two different mechanisms: active and non-active. The non-active mechanism results in the complete combustion of formaldehyde to carbon dioxide, whereas the active mechanism results in a selective oxidation, via formic acid, to carbonate with CO$_2$ evolution only seen as a result of carbonate decomposition. This would differ from previous results, where CO$_2$ was thought to be produced via formic acid.

(ii) First-order plots show that the formaldehyde concentration falls with first-order dependence. Two distinct areas (procedure 1) are shown, characterized by k_1 and k_2, where $k_1 > k_2$ owing to the fact that k_2 is a hybrid value incorporating both active and non-active values of k. After almost 9000 s the formation of HCOOH inhibits the reaction at non-active sites and subsequently $k = k_2$ which corresponds to the reaction of formaldehyde or methanol at solely active sites. A higher flow-rate (procedure 2) inhibits the formation of non-active sites reducing the formation of CO$_2$ and provides a value of k resulting from the reaction at non-active sites. A higher flow rate also inhibits the oxidation of HCOOH. This illustrates the importance of reaction conditions in a filter-press cell (flow rate, cell volume).

(iii) First order plots for methanol show the same two distinct linear regions, but with the $k_1 \sim k_2$ indicating that the rate of methanol oxidation is not affected by its oxidation products. It has been shown that the inclusion of the methanol present in formaldehyde solutions is of great importance when calculating the yield to avoid an overestimate and also helps provide a clear picture of the disappearance of species in the reaction.

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