Oxidation of carboxylic acids in water at IrO$_2$–Ta$_2$O$_5$ and boron doped diamond anodes

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ARTICLE INFO

Article history:
Received 24 February 2011
Received in revised form 29 August 2011
Accepted 3 September 2011

Keywords:
Electrochemical incineration
Carboxylic acids
BDD
Iriddium anode
AOPs
Oxidation of organics

ABSTRACT

A detailed study was dedicated to the anodic oxidation of three carboxylic acids (namely, oxalic, formic and maleic acid) with the objective to evaluate in a systematic way the effect on the oxidation of carboxylic acids of numerous relevant parameters, including the nature and the concentration of the carboxylic acid, the alimentation regime (potentiostatic vs. amperostatic), the current density and the working potential values, the flowdynamic regime, the temperature and the nature of the electrode material. It was observed that the effect of some operative parameters strongly depends on the nature of the electrode and of the carboxylic acid. As an example, the efficacy of abatement decreased in the order oxalic > formic > maleic at iridium anodes while an opposite trend was observed at diamond anodes (formic ~ maleic > oxalic), thus confirming that different oxidant agents are involved at these two electrodes. Also the effect of the temperature depends on both the nature of the acid and of the anode. On the other hand, for all electrodes and substrates, higher current efficiencies were obtained when most part of the process was under the kinetic control of the oxidation reaction, i.e., when low current densities and high flow rates were imposed. A detailed study on the effect of concentration was performed. It was found that higher concentrations of carboxylic acids enhanced the current efficiency at all kinetic regimes. A comparison between potentiostatic and amperostatic electrolyses was also carried out.

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1. Introduction

Recent researches have demonstrated that electrochemical methods offer an attractive alternative to traditional routes for treating wastewaters containing toxic or refractory organic pollutants [1,2]. Both oxidation and reduction routes were used for the treatment of organic compounds in water [2–4]. Oxidation processes allow the conversion of organic pollutants to carbon dioxide (electrochemical “incineration” or “combustion”) (Eq. (1)), to non toxic compounds or to biocompatible organics, that can be treated in a conventional biological process.

\[ C_mH_n + 2mH_2O \rightarrow mCO_2 + (n + 4m)H^+ + (n + 4m)e^- \] (1)

Combined processes are more difficult to optimize. Therefore, the development of a single oxidation process that allows the treatment of wastewaters without the necessity of a post-treatment stage is more often pursued by researchers.

Carboxylic acids are common intermediates of the chemical and electrochemical oxidation of several compounds. They are rather stable [5–9] and are often mineralized at longer times with respect to the starting substrates [10,11]. Thus, in advanced oxidation processes (AOPs), various carboxylic acids (usually oxalic, formic, acetic and maleic) are formed as final intermediates and their slow mineralization by means of hydroxyl radicals prolongs the treatment time increasing economic costs. Brillas et al. [12] have shown that the degradation rates of carboxylic acids change with their nature and with employed AOP. In particular oxalic acid (OA) is more resistant with respect to formic acid (FA) and maleic acid (MA) both at anodic oxidation on BDD and in electro-Fenton processes.

As far as the electrochemical oxidation is concerned, the abatement of various carboxylic acids proceeds usually with quite low current efficiencies and dramatically depends on the nature of the anodic material [6,8,13–15]. The groups of Rodrigo and Comninellis independently studied the electrochemical oxidation of some carboxylic acids at BDD [5,7,16]. In particular Weiss et al. [16] have shown that the oxidation of maleic acid proceeds with the simultaneous formation of both formic and oxalic acids. Some studies were recently dedicated to the anodic oxidation of oxalic acid, thus allowing to evaluate in detail the effect of the electrode material, the reactor configuration and of other several operational parameters [8,13–15,17,18] on the electrochemical oxidation of this organic compound. Very in deep studies were furthermore devoted to the oxidation of acetic acid at BDD [30]. On the other hand, both oxalic and acetic acids are known to present very specific behaviors with respect to other organic acids. Thus, oxalic acid presents a relatively
low reactivity towards hydroxyl radicals, thus giving rise to different oxidation routes with respect to most of organics [6,8] while acetic acid adsorbs on a BDD surface resulting in a very singular auto-inhibition effect [30].

In this paper a quite detailed study was dedicated to the oxidation of three carboxylic acids (namely, oxalic, formic and maleic acid) with the objective to evaluate in a systematic way the effect on the oxidation of carboxylic acids of numerous relevant parameters, including the nature and the concentration of the carboxylic acid, the almentation regime (potentiostatic vs. amperostatic), the current density and the working potential values, the flowdynamic regime, the temperature and the nature of the electrode material, thus allowing the optimization and a better understanding of the process. As anode materials, two very different electrodes were used: the Ti/IrO$_2$–Ta$_2$O$_5$ (DSA–O$_2$) which is quite stable and not particular expensive but known to present a quite low oxygen overpotential and the boron doped diamond (BDD) which conversely presents a high oxygen overpotential and is probably one of the more promising materials for the electrochemical incineration [2,19]. Formic, maleic and oxalic acids were chosen as model compounds for two main reasons. First, they are formed as final intermediates for the oxidation of numerous substrates. Second, their oxidation is expected to present very different behaviors. Oxalic acid is known to present a relatively low reactivity towards hydroxyl radicals and is likely to be involved, on various electrodes, in a direct anodic oxidation process. Conversely, formic and maleic acid easily react with hydroxyl radicals and maleic acid is reported to be adsorbed on various anode materials.

2. Materials and methods

Electrolyses were performed in two different systems: system I was constituted of a bench-scale batch divided or undivided glass cell, equipped with a Saturated Calomelane Electrode (SCE) reference electrode, a Ti/IrO$_2$–Ta$_2$O$_5$ or a BDD-Nb thin sheet anode (wet surface area 4.5 cm$^2$) and a nickel cathode. Anodic solution was stirred by a magnetic stir bar. A cation-exchange membrane Nafion 324 was used as separator. The volume of electrolytic solution was 60 mL both in the undivided cell and in each compartment of the divided electrochemical glass reactor. System II, previously described in detail [13], was constituted of a batch continuous recirculation reaction system operated in undivided configuration and loaded with 250 mL of electrolytic solution. The cell was equipped with a BDD-Nb thin sheet or a Ti/IrO$_2$–Ta$_2$O$_5$ anode (surface area 9.14 cm$^2$) and one nickel cathode. Amel 2055 potentiostat was used for electrolyses. Chronoamperometric measurements were performed by an Autolab PGSTAT12. All potentials quoted in this work are referred to SCE. Each experiment at BDD was performed after polarization of the electrode at 3.0 V for at least 10 min.

Samples of the electrolytic solution were periodically taken and analyzed during the electrolyses to evaluate the performances of the process in terms of conversion of the acid during the different stages of the experiments. Carboxylic acid concentrations were evaluated by liquid chromatographic analyses, as previously reported [13]. For some experiments, the trend of the oxidative process was monitored by measuring the chemical oxygen demand (COD); for this kind of analyses an Avantes fiber–optic SD2000 dual spectrometer equipped with a DH2000 light source was used. The supporting electrolyte was in most cases composed by 0.035 M Na$_2$SO$_4$ (Janssen Chimica) and H$_2$SO$_4$ (Sigma Aldrich). All these chemicals were analytical grade. BDD and Iridium anodes were supplied by Condias and De Nora S.p.A. (Milano, Italy), respectively. The thickness of the stagnant layer in the adopted conditions was estimated through a typical limiting-current essay as previously reported [13]. A value of 10$^{-5}$ cm$^2$ s$^{-1}$ was used for the diffusion coefficient.

3. Results and discussion

3.1. Influence of the nature of the anodic material and of the carboxylic acid

3.1.1. Chronoamperometric measurements

According to the literature, carboxylic acids are usually not oxidized in the range of stability of water at both diamond and iridium anodes. Thus, the electrochemical incineration of these compounds is carried out at the potentials of oxygen evolution. Prior to electrochemical incineration experiments, chronoamperometric measurements were recorded in background solutions containing Na$_2$SO$_4$, in the absence and in the presence of different concentrations of oxalic, formic and maleic acids at 25°C in acidic solutions at 1.5 and 1.7 V vs. SCE at IrO$_2$–Ta$_2$O$_5$ anodes and at 2.4 and 2.7 V for BDD. As shown in Fig. 1, at DSA anodes a very different response was observed for the investigated acids. As previously reported in literature, in the case of oxalic acid, an increase of the steady-state current was observed upon enhancing its concentration, at both examined polarization potentials, thus showing that this carboxylic compound is significantly oxidized at iridium anodes in the range of potential of oxygen evolution. A quite different picture was observed for formic and maleic acids. The current decreased in the presence of formic acid as a possible consequence of preferential adsorption phenomena involving the formic acid or an intermediate product which may hinder the water discharge. For maleic acid, concentrations higher than 20 mM were necessary to observe a very small increase of the current density. This behavior, considering that 12 and 2 electrons are necessary for the complete oxidation of maleic and oxalic acid, respectively, may suggest that the unsaturated dicarboxylic acid presents a very low reactivity at iridium anodes.

The chronoamperometric behavior of several carboxylic acids (namely, oxalic, formic, maleic, acetic and succinic acid) at BDD was previously studied in detail in the range of potential of oxygen evolution at room temperature [20]. For low acid concentrations ([OR]$^0$) and high working potentials, current densities changed approximately linearly with [OR]$^0$. Moreover plots of current densities as a function of the chemical oxygen demand COD, were quite similar for all the investigated acids with the exception of OA which gave rise to higher current densities. The behavior observed for most of the investigated carboxylic acids was explained by assuming that, at high potentials in the low concentration range, the oxidation of the organic by hydroxyl radicals generated from the water oxidation is so fast that the rate determining step is the mass transport of the acid from the bulk of the solution to the anodic surface. For high acid concentrations and/or low potentials, the linear variation is often loosed and a decrease of the current density usually occurred upon increasing [OR]$^0$, as shown in Fig. 2 for the oxidation of maleic acid at 2.4 V. At higher potential a similar trend was observed but an higher concentration of MA was necessary to have a current decrease. This is probably due to the fact that when concentrations of the carboxylic compounds are too high and/or low potentials are used, the rate of generation of hydroxyl radicals is not sufficient to oxidize all of the molecules transported to the anode, thus allowing the occurrence of lateral reactions, including direct anodic oxidation and adsorption phenomena. In this context it is useful to remember that adsorption of MA at BDD was previously observed at BDD anodes by cyclic voltammetric studies by Weiss et al. [16]. Oxalic acid gave rise to higher current densities than other tested acids. This was probably due to the fact that this acid is involved in a slow reaction with hydroxyl radicals.
in the presence of maleic acid, the electrolyses were prolonged to achieve an appreciable variation of the COD.

In the case of formic and oxalic acids, the oxidation product was carbon dioxide and no appreciable formation of by-products was detected. Thus, a comparable decrease of COD and of the concentration of the acids was observed. A different picture was observed in the case of the maleic acid. Indeed, in this case, the electrolyses gave rise, both at iridium and diamond anodes, to a very fast decrease of the carboxylic acid concentration but to a slight change of the COD as a consequence of the cathodic reduction of MA to succinic acid. To overcome this drawback the electrolyses of MA were repeated in a divided cell in system I, under similar operative conditions in terms of current density and thickness of the stagnant layer.

As shown in Fig. 3, the abatement of the COD obtained by anodic oxidation dramatically depends on the nature of both the anode and the acid. At BDD, high and similar abatements of the COD were obtained for FA and MA (Fig. 3a). For the latter, according to the studies of Weiss et al. [16], the oxidation proceeded with the formation of formic acid as the main intermediate and of small amounts of oxalic acid, whose concentrations showed an increase in the first part of the electrolysis followed by a marked decrease in the last stages of the experiment. Also the formation of very small amounts of malonic and fumaric acid was detected. The electrolyses of solutions of OA at BDD gave a lower abatement of COD for the same amount of charge passed with respect to the other acids (Fig. 3a). FA and MA are likely to be involved at BDD in a very fast indirect oxidation by means of free or weakly adsorbed hydroxyl radicals electrogenerated by the oxidation of water [20]. In this frame, one has to observe that OA is considerably less reactive towards hydroxyl radicals than many other organic substrates such as many benzene derivatives and other carboxylic acids [21]. Thus, the oxidation mediated by hydroxyl radicals is expected to be less favored and oxalic acid is likely to be involved, at least at low pH, in a direct electrochemical oxidation at the anodic surface [13,20].

At iridium anodes, a very different behavior was observed. A slight higher abatement of COD was observed for OA with respect to FA. When maleic acid was used, in agreement with chronamperometric measurements, very low abatements of both COD (see Fig. 3b) and acid concentration were observed. Thus, after the passage of an amount of charge corresponding to about 1.4 Qth, a reduction of COD of only about 10% was obtained. Also when the passed charge was increased to about 3.2 Qth the overall abatement was as low as 20% with a current efficiency of 5%. Similar
results were previous found by other authors. Quite interestingly, Li et al. [22] found that the oxidation of phenol at Ru oxide proceeded with the formation of MA which remained in the solution for a very long time. Moreover Bock and MacDougall showed, that the performances of iridium anodes in the oxidation of maleic acid decrease with the passed charge probably as a result of irreversible interactions between the anodic surface and MA and/or its oxidation products [23].

As shown in Fig. 3, a higher abatement of COD was observed at BDD for all the investigated acids. This is in line with the fact that non-aromatic organic acids are reported in the literature to be quite resistant to the degradation at transition metal oxide anodes such as Pt, Ir and Ru based ones, their oxidation often representing the key step for the abatement of more complex molecules such as phenol or quinone derivatives [23–27].

Furthermore, the rate of abatement decreased as follows: OA > FA ≫ MA at iridium anodes while an opposite trend was observed at diamond anodes (FA > MA > OA). These data confirm that different oxidant agents are involved at BDD and DSA anodes. Thus, at active electrodes, such as IrO₂ based anodes, water oxidation involves the formation of chemisorbed oxygen (see Eqs. (2)–(4)) that, according to literature [24,25], is consumed in the oxidation of organic compounds with the formation of selective oxidation products (Eq. (4)) and in an easy oxygen evolution (Eq. (5)). On the contrary, at diamond anodes, free or weakly adsorbed hydroxyl radicals are generated (Eq. (6)) which are expected to have a stronger oxidizing power and to cause often a complete combustion of organics (Eq. (7)).

\[
\begin{align*}
\text{MO}_x + \text{H}_2\text{O} & \rightarrow \text{MO}_x(\text{OH}) + \text{H}^+ + e^- \\
\text{MO}_x(\text{OH}) & \rightarrow \text{MO}_x+1 + \text{H}^+ + e^- \\
\text{MO}_{x+1} + \text{RH} & \rightarrow \text{MO}_x + \text{RHO} \\
\text{MO}_{x+1} & \rightarrow \text{MO}_x + 0.50\text{O}_2 \\
\text{BDD} + \text{H}_2\text{O} & \rightarrow \text{BDD}^{*(\text{OH})} + \text{H}^+ + e^- \\
\text{BDD}^{*(\text{OH})}_n & + \text{RH} \rightarrow \text{BDD} + \text{CO}_2 + \text{H}_2\text{O} \\
\text{BDD}^{*(\text{OH})}_n & \rightarrow \text{BDD} + 0.50\text{SO}_2 + \text{H}^+ + e^-
\end{align*}
\]

Furthermore, in the case of oxalic acid, a direct anodic oxidation process is likely to be involved whose competition with oxygen evolution necessarily depends on the nature of the electrode material. In particular, according to literature, the anodic oxidation of OA is likely to require an adsorption step to take place [8]. Ferro at al. [6] reported a very low effect of OA on cyclovoltammetric curves recorded at Ti/IrO₂–Ta₂O₅. Authors justified this phenomenon in terms of a poor catalytic activity of IrO₂ towards the anodic oxidation of OA or to a preferential interaction between active sites and hydroxyl radicals, which would result in the hindrance of OA adsorption.

A very low effect of OA addition on quasi-steady polarization was observed also at fluorine-terminated BDD. On the other hand, measured currents were doubled at strongly and mildly oxidized BDD [6]. In this context one has to observe that we have used an oxidized BDD (see Section 2) that could justify the relatively high abatements of OA observed in our experiments.

3.2. Influence of the temperature

The effect of temperature on the anodic incineration of OA was widely investigated by the group of De Battisti in the presence of several anodes [8], by our group for the case of DSA–O₂ ones [15] and by Canizares et al. [5] for BDD. According to literature data, the effect of the temperature on the abatement of OA strongly depends on the nature of the anodic material. Indeed, an increase of the temperature gave rise to a slight change of the OA abatement at BDD [5,8] and to a drastic increase at IrO₂ based anodes [8,15]. Conversely, Saracco et al. [31] found that the oxidation of Cumaric acid was favored by higher temperatures at Pt/Ti, PbO₂, and Ru/Ti. In this work we wanted to extend the study to FA and MA performing a set of chronoamperometric measurements and electrolyses at BDD and iridium anodes at 25 and 50 °C. With all investigated acids the chronoamperometric response of BDD was substantially not affected by the temperature for most of investigated conditions (Fig. 4). At iridium anodes a slight effect of the temperature was observed for MA (Fig. 1b and c). Conversely, in the case of the oxidation of OA and FA, a more marked increase of the current density with the acid concentration was observed at the highest investigated temperature, thus probably indicating that, for these anode–organic couples, higher values of temperature favor the oxidation processes with respect to the oxygen evolution.

For what concern the amperostatic electrolyses, at BDD the incineration of formic acid was only slightly enhanced by an increase of the solution temperature (see Fig. 5a). A similar result was obtained for oxalic acid [5,8]. On the other hand, at iridium oxide anodes, a strong increase of the abatement was observed by working at 50 °C for both acids (Fig. 5b). These data indicate, according to Martinez-Huitle et al. [8], that the rate determining steps for OA and FA oxidation and for oxygen evolution reaction at iridium oxide anodes are different as indicated by their different temperature sensitivity that is attributed to differences in the
activation energies of the rate determining steps. More relevant, these results show that the incineration of OA and FA can be carried out successfully at IrO$_2$-Ta$_2$O$_5$ anodes with very high conversions and current efficiencies CE which are at least comparable to that obtained at BDD. This result is very interesting since 50 °C are easily achievable on applicative scale and DSA anodes are widely industrially used, very stable as confirmed also in our study (performances were unchanged after several days of continuous operations), less expensive than Si-BDD and allowed a significant reduction of cell potentials (2.5–3.1 V) with respect to BDD (3.2–4.7 V).

Unfortunately the efficacy of temperature enhancement with DSA electrodes is not general as when experiments were performed in the presence of MA, a very low abatement was obtained also at 50 °C (Fig. 5b), further confirming the high stability of this organic towards anodic oxidation at oxide electrodes, as previously found in chronoamperometric experiments.

3.3. Influence of current density and flow dynamic regime on the performances of the process

The influence of flow rate and current density on the oxidation of OA at BDD was previously investigated by various authors [6–9,13–15]. The effects of the current density and of the hydrodynamic conditions, according to our previous studies, are strongly interrelated and must be considered together [13,15].

From a theoretical point of view, when the abatement of organic pollutants takes place by direct anodic oxidation or by reaction with electrogenerated hydroxyl radicals (”direct processes”), the oxidation processes is localized on the anode surface or in a thin reaction layer adjacent to the electrode surface with a thickness dramatically lower than that of the diffusion layer. Thus, electrogenerated hydroxyl radicals are expected to be converted in “adsorbed oxygen” at active electrodes such as iridium ones or to exist as weakly physical adsorbed or free species that can diffuse through a very thin portion of the diffusion layer, due to their very high reactivity, at non-active electrodes such as BDD. It follows that the oxidation process, in the absence of species that can oxidize the organics in the bulk of the solution or in large portion of the diffusion layer (such as active chlorine generated by chloride ions oxidation), can be considered as a surface or a pseudo-surface process [28,29]. When the rate of the mass transfer of the organic to the anodic surface is dramatically lower than the rate of oxidation, the concentration of the pollutant at the anodic surface/reaction layer $C^0$ is close to zero and the oxidation process is under mass transfer control. This case arises, for an amperometric process, when the limiting current density $i_{lim} = nFk_m[RH]^n \ll i_{app}$ ICE$^0$ (where $n$ is the number of electrons exchanged for the anodic oxidation of RH to carbon dioxide or to stable products, $F$ is the Faraday constant (96,487 mol$^{-1}$), $[RH]^n$ and $k_m$ are the bulk concentration and the mass transfer coefficient of the organic RH), respectively. $i_{app}$ is the applied current density and ICE$^0$ the instantaneous current efficiency for the oxidation of RH at oxidation reaction control (under adopted operative conditions), e.g., when $[RH]^n \ll C^0 \leq CE$ ICE$^0$ (where $C^0 = i_{app}/(nFk_m)$) [18,29]. Please consider that under these conditions the flowdynamic conditions, imposed by the flow rate, are expected to affect the mass transfer coefficient and as a consequence the abatement of the organics. Furthermore, under mass transfer control, the oxidation rate is not controlled by applied current density. Thus higher current densities do not affect the abatement of the organic for a given time but result in lower $CE$s.

Conversely, when $i_{lim} \gg i_{app}$ ICE$^0$, mass transfer is significantly faster with respect to oxidation rate, $C^0$ is very close to the bulk concentration $C^0$ and the process is under reaction oxidation control. Under these conditions, the flowdynamic conditions are not expected to affect the abatement of the organics while a higher current density should determine lower times of the treatment [18,29].

To evaluate the effect of the current density on the performances of the process at different hydrodynamic regimes, some experiments were carried out in the presence of FA or OA at pH
of 2, changing the flow rate (from 0.2 to 1.2 L/min) and the current density (from 1 to 39 mA/cm²) at both diamond and iridium based anodes. Experiments were carried out up to a passed charge close to the value Qth necessary for the complete oxidation of the acid computed for a process with a current efficiency of 100%. The first experiment was performed at BDD in the presence of a quite low initial concentration of FA (10 mM), a high current density (39 mA/cm²) and a low flow rate (0.2 L/min) (see Table 1, entry 1). In these conditions, C1 is significantly higher than the initial concentration of FA. Thus, the process is expected to take place under mass transfer kinetic control since the beginning. The applied current density was dramatically higher with respect to iₘₐₓ for all the electrolysis, thus giving rise to a very low abatement as a consequence of the fact that most of the charge passed was used for the parasitic evolution of oxygen. When the experiment was repeated at lower current densities, the abatement rapidly increased but it was necessary to wait for a longer time of the electrolysis to reach Qth (see Table 1, entries 1–3). According to the simple theoretical picture above mentioned, the flow rate did not affect the process at low current densities when the process was under oxidation reaction control (e.g., [OA][C]) (see Table 1, entries 3 and 4) but resulted in a strong increase of the abatement of the acid at high current densities when the process was mainly under kinetic or mass transfer control (see Table 1, entries 2 and 5). One experiment was repeated with a higher initial concentration of FA of 100 mM working at 39 and 0.2 L/min (see Table 1, entry 7). In these conditions, the initial and the final concentration of FA are, respectively higher and lower than C1 so that a mixed kinetic regime is expected for the larger part of the experiment. Thus, an increase of the abatement could be achieved by lowering the current density and increasing the flow rate (see Table 1, entries 7 and 8).

As reported in Table 1 (entries 9–11), when selected experiments were repeated at DSA a similar effect of current density and flow rate was observed even if slight lower abatements were obtained with respect to BDD under analogous operative conditions.

Similar results were also achieved in the case of OA (Table 2). As an example, for a concentration of [OA] lower than C1 for a large part of the experiment, the abatement readily increased upon enhancing the flow rate and decreasing the current density (see Table 2, entries 1 and 2) while for [OA] ≫ C1, the abatement achieved for a given value of the charge passed was not affected by these two parameters (see Table 2, entries 4–6).

The effect of current density on the abatement of maleic acid and the formation of FA and OA as by-products was studied by performing a set of electrolyses in a divided cell at different current densities (from 1 to 25 mA/cm²). As shown in Fig. 6, at low current densities for a process that takes place mainly under oxidation reaction kinetic control, no significant effect of current density is observed (see triangle and circles in Fig. 6a). Conversely, for high current densities when the process takes place under mass transfer control, the abatement of MA with the charge passed decreased with i (see empty and filled squares in Fig. 6a).

Higher concentration of by-products was observed for low current densities when the process is under oxidation reaction control.

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### Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th><a href="mM">FA</a></th>
<th>Electrode</th>
<th>I/A (mA/cm²)</th>
<th>Flow rate (L/min)</th>
<th>Conversion (%)</th>
<th>Charge passed (Q/Qth)</th>
<th>Time passed (min)</th>
<th>C1 (mM)</th>
<th>iₘₐₓ for the residual concentration (mM/cm²)</th>
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### Table 2

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<th>Entry</th>
<th><a href="mM">OA</a></th>
<th>Electrode</th>
<th>I/A (mA/cm²)</th>
<th>Flow rate (L/min)</th>
<th>Conversion (%)</th>
<th>Charge passed (Q/Qth)</th>
<th>Time passed (min)</th>
<th>C1 (mM)</th>
<th>iₘₐₓ for the residual concentration (mM/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>BDD</td>
<td>39</td>
<td>0.2</td>
<td>17–20</td>
<td>1.25</td>
<td>27</td>
<td>50.5</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>BDD</td>
<td>17</td>
<td>1.2</td>
<td>45–47</td>
<td>1.35</td>
<td>67</td>
<td>9.9</td>
<td>8.3</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>BDD</td>
<td>39</td>
<td>0.2</td>
<td>64–66</td>
<td>1.0</td>
<td>228</td>
<td>50.5</td>
<td>27.8</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>BDD</td>
<td>39</td>
<td>1.2</td>
<td>77–79</td>
<td>1.0</td>
<td>230</td>
<td>23.2</td>
<td>35.0</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>BDD</td>
<td>17</td>
<td>0.2</td>
<td>77–79</td>
<td>1.0</td>
<td>533</td>
<td>21.6</td>
<td>17.4</td>
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<tr>
<td>6</td>
<td>100</td>
<td>BDD</td>
<td>17</td>
<td>1.2</td>
<td>79–83</td>
<td>1.0</td>
<td>533</td>
<td>9.9</td>
<td>34.6</td>
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<tr>
<td>7</td>
<td>50</td>
<td>BDD</td>
<td>17</td>
<td>1.2</td>
<td>69–73</td>
<td>1.0</td>
<td>266</td>
<td>9.9</td>
<td>24.3</td>
</tr>
</tbody>
</table>

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*a* Amperostatic electrolyses in system II. System solvent supporting electrolyte (SSE): Water, Na₂SO₄, H₂SO₄, T = 25 °C. Qth, charge necessary for a total conversion of FA with a CE = 100%. V = 250 mL.

*b* C1 = iₘₐₓ/(2FD/I).

*c* iₘₐₓ = nFκmA[RH] computed for the residual concentration of FA at the end of the electrolysis.

d Initial concentration of oxalic acid.
concentration under mass transfer control regime was studied by various authors. On the other hand, it is difficult to found in the literature data on the effect of the organic concentration on the performances of the process when a fast mass transfer kinetics is involved. More precisely, this latter condition was usually investigated at BDD anodes under conditions where the current efficiency of the process is close to 100% so that no appreciable effect of the organic pollutant concentration can be expected. Thus, we have performed here a focused investigation with the aim of studying the effect of the organic concentration on the performances of the process both for fast and slow mass transfer kinetics. Let us first consider the case of processes under mass transfer control. To examine this situation, the values of the initial concentration and of the current densities were selected to have an initial $\text{OR}^0 > C^*$ (e.g., the applied current density $i_{\text{app}}$ was higher than the initial limiting current density $i_{\text{lim}}$). As shown in Table 1 (entries 1 and 6) and in Fig. 7a for the case of FA, an increase of the initial concentration resulted, for all the investigated carboxylic acids, in a drastic enhancement of the conversion achieved for the same value of the ratio $Q/Q_{\text{th}}$, as a result of the higher gradient of the organic concentration between the bulk and the electrolytic surface which drove a faster mass transport. Let us consider now the case of some electrolyses performed with both initial and final values of $\text{OR}^0$ higher than $C^*$ to have a process kinetically controlled by the reactions at the electrolytic surface during all the electrolysis. As shown in Table 1 (entries 11 and 12) and in Fig. 7b, in the case of the oxidation of FA at Ir anodes, for experiments performed with $C_0$ of 100 and 10 mM, the current efficiency of the process was lower than 100% and significantly increased upon enhancing the concentration of the organic. For BDD anodes, a different picture was observed. Thus, at 0.1 and 0.05 M initial concentration of the FA, current efficiencies were very close to 100% for a large part of the experiment so that the effect of the organic concentration could not be clearly appreciated (Fig. 7c and Table 1, entries 8 and 13). On the other hand, when the experiment was performed with an initial concentration of FA of 10 mM, conversions decreased appreciably, thus allowing to detect the effect of the organic concentration (Fig. 7c and Table 1, entry 4). A similar investigation was also performed in the case of the oxidation of OA at BDD carried out under the kinetic control of the oxidation reaction (see Table 2, entries 6 and 7) working at initial concentrations of 50 and 100 mM. The effect of the concentration was evident also at these high concentrations (Fig. 7d), as a result of the lower oxidant ability of BDD for OA with respect to FA.

3.5. Influence of the working potential

Some of the authors have previously observed that the oxidation of OA is favored by a potentiostatic alimentation vs. an amperostatic one and by lower working potentials. As above mentioned, OA oxidation at BDD is expected to take place by direct anodic oxidation while most of organics are likely to be degraded at diamond anodes by hydroxyl radicals [13]. Hence, a set of electrolyses was here performed under potentiostatic alimentation in the undivided bench-scale batch cell (system I) at different applied potentials $E$ at BDD in the presence of a solution of FA to evaluate the role of the potential for an organic which is expected to be oxidized by BDD/•OH). As reported in Table 3, higher values of $E$ resulted in a lower abatement of FA for the same amount of charge passed (Table 1), as a result of mass transfer limitations. Hence, the utilization of low values of the working potential should be preferred to obtain high current efficiency. On the other hand, experiments performed at the less positive potentials present the drawback of lower current density values that imply longer electrolysis time. During potentiostatic electrolyses a slight but continuous decrease of current density occurred as a result of the consumption of the
Fig. 7. Trend of dimensionless concentration $C/C^0$ vs. dimensionless passed charge for amperostatic electrolyses of FA at BDD (a and c) and IrO$_2$-Ta$_3$O$_5$ (b) and of OA at BDD (d). $C^0$ is the initial organic concentration. For (a), $C^0=10$ (■) and $36$ mM (□) (experimental conditions reported in Table 1, entries 1 and 6, respectively). For (b), $C^0=10$ (■) and $100$ mM (□) (experimental conditions reported in Table 1, entries 4, 13 and 8, respectively). For (c), $C^0=50$ (■) and $100$ mM (□) (experimental conditions reported in Table 1, entries 7 and 6, respectively). Electrolyses of oxalic and formic acid performed in system II, undivided cell. SSE: water, Na$_2$SO$_4$, H$_2$SO$_4$ (pH = 2). $T=25$ °C. Qth, charge necessary for a total conversion of the acid with a CE = 100%.

Table 3
Electrochemical abatement of formic acid: potentiostatic experiments.*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alimentation mode</th>
<th>Working potential (V)</th>
<th>Initial and final $i/A$ (mA/cm$^2$)</th>
<th>Conversion (%)</th>
<th>Time passed (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Potentiostatic</td>
<td>2.6</td>
<td>14–10</td>
<td>68–72</td>
<td>146</td>
</tr>
<tr>
<td>2</td>
<td>Potentiostatic</td>
<td>2.75</td>
<td>21–17</td>
<td>58–62</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>Potentiostatic</td>
<td>3.0</td>
<td>27–21</td>
<td>48–52</td>
<td>n.d.</td>
</tr>
<tr>
<td>4</td>
<td>Potentiostatic</td>
<td>3.3</td>
<td>25–23</td>
<td>43–47</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>Potentiostatic$^b$</td>
<td>3.3</td>
<td>22–20</td>
<td>32–36</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>Amperostatic</td>
<td>2.74</td>
<td>20</td>
<td>48–53</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

* Electrolyses performed in system I. [FA] = 10 mM. System solvent supporting electrolyte (SSE): Water, Na$_2$SO$_4$, H$_2$SO$_4$. $T=25$ °C. Qth = 1.9 charge necessary for a total conversion of FA with a CE = 100%. Anode: BDD.

$^b$ Electrolysis performed without magnetic stirring.

acid. Thus, when the FA concentration was reintegrated, current density raised to the initial values. To explain this behavior one can suppose that, at high potentials in the low concentration range, the oxidation of the organic by hydroxyl radicals generated from the water oxidation is so fast that the rate determining step is the mass transport of the acid from the bulk of the solution to the anodic surface (see Section 3.1.1). Thus, when the experiment performed at 3.3 V was repeated in the absence of magnetic stirring, lower current densities and abatements were obtained (see Table 3, entries 4 and 5). Quite interestingly, when two experiments were performed with similar initial values of the current density and anode potential under potentiostatic (Table 3, entry 2) and amperostatic (Table 3, entry 6) mode, a lower abatement was obtained in the galvanostatic electrolysis. This is likely to be due to the fact that during amperostatic electrolyses, a gradual increase of the potential with the charge passed takes place, to compensate the diminution of the acid concentration, thus giving rise to lower current efficiencies with respect to the potentiostatic experiment performed with the same initial current density/working potential.

4. Conclusions

In this paper a detailed study was dedicated to the oxidation of three carboxylic acids (namely, oxalic, formic and maleic acid) with the objective to evaluate in a systematic way the effect on the oxidation of carboxylic acids of numerous relevant parameters, thus allowing the optimization and a better understanding of the process. It has been demonstrated that the effect of some operative parameters on the process dramatically depends on both the nature of the electrode and of the carboxylic compound. Higher abatements were obtained at BDD with respect to DSA anodes for all the adopted carboxylic compounds. The rate of abatement decreased in the order OA > FA > MA at iridium anodes while an opposite trend was observed at diamond anodes (FA ∼ MA > OA), thus indicating that different oxidant agents are involved at these two electrodes. An increase of the temperature did not affect significantly the conversion of oxalic and formic acid at BDD but resulted in a drastic increase of the abatement at DSA anodes. Conversely, very poor abatements of maleic acid were obtained at DSA both
at 25 and 50 °C. Higher current efficiencies were obtained when most part of the process was under the kinetic control of the oxidation reaction, i.e., when low current densities and high flow rates were imposed. In particular when the oxidation reaction was under kinetic control of the oxidation reaction, no effect of flow rate or current density was observed which, otherwise, dramatically influence the process when a mass transfer control occurs. Incineration of carboxylic acids was also favored by high concentrations of the organic both for a process under mass transfer and oxidation reaction kinetic control. Potentiostatic regime gave higher abatements than amperostatic ones and higher potentials resulted in lower current efficiencies.

Acknowledgement

Università di Palermo is acknowledged for financial support.

References