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Current efficiency and mass transfer effects in electrochemical oxidation of C1 and C2 carboxylic acids on boron doped diamond electrodes

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A B S T R A C T

The oxidation of acetic, glycolic, glyoxylic, oxalic and formic acid has been studied on boron doped diamond electrodes. Our voltammetry study on rotating disk electrodes highlights clear differences between the carboxylic acids (formic, oxalic, glyoxylic and glycolic acid) that can be oxidized via a direct electron transfer (DET) and acetic acid which can presumably solely be oxidized by •OH radicals formed in the region where water oxidation takes place. In glycolic and glyoxylic oxidation oxalic acid is the main intermediate formed. Surprisingly, glyoxylic acid could not be detected as an intermediate in the glycolic acid oxidation. Chronoamperometric experiments confirm that all compounds except acetic acid react further to CO_2, which could be deduced from the electron balances. It was shown that formic, oxalic, glyoxylic and glycolic acid can be selectively oxidized at 2.3 V vs. Ag/AgCl with high current efficiencies, below or close to mass transfer limiting rates. At higher potentials (2.4 V and 2.5 V) simultaneous water electrolysis results in lower current efficiencies. At these potentials the conversion rates can exceed the limiting rates, which might be attributed to effects related to water oxidation (i.e. O_2 evolution and •OH radical formation).

1. Introduction

The purification of wastewater in the chemical industry is important to ensure future availability of clean water. The removal of organics from waste streams has been reported for many toxic compounds such as phenol [1], 4-chlorophenol [2] and benzene [3]. The final stage of these processes is often the oxidation of carboxylic acids to CO_2. For example, C1 and C2 carboxylic acids have been found as end-products and/or (accumulating) intermediates in electrochemical and wet air oxidation processes [3–5]. Electrochemical oxidation on boron doped diamond (BDD) electrodes has shown to be an effective method to oxidize carboxylic acids [6,7]. BDD electrodes have been proven to perform better than more common electrode materials such as Pt, because of its characteristics such as a wide potential window and a high anodic stability [8]. For example, it has been reported that glycolic acid cannot be completely converted to CO_2 on platinum electrodes acid [9]. Given the importance of carboxylic acid removal in wastewaters it is needed to broaden current knowledge of oxidation processes on BDD. This work extends the research of the electrochemical oxidation of carboxylic acids, more specifically the oxidation of acetic, glycolic, glyoxylic, oxalic and formic acid on boron doped diamond electrodes. An important research question we want to answer is to see whether it is possible to oxidize these

compounds with a good current efficiency (hence avoiding water electrolysis), while at the same time being close to mass transfer limitation. If these two requirements are met, it should be possible to design the electrochemical oxidation wastewater oxidation process on an industrial scale.

Different oxidation mechanisms have been reported for the oxidation of carboxylic acids on BDD. In the region prior to water oxidation, compounds can react via a direct electron transfer mechanism (DET). This mechanism has been shown for the oxidation of different compounds, such as phenol, oxalic acid and formic acid [10–12]. It has been shown that carboxylic acids on BDD can also be oxidized by •OH radicals formed via water oxidation [6,13,14]. In addition, alternative oxidation mechanisms have been proposed, such as the oxidation of carboxylic acids by (radical) species formed in the oxidation of sulphate [7,15].

The electrochemical oxidation of formic on BDD electrodes has been shown by several studies by means of cyclic voltammetry. In the presence of formic acid a (pseudo) plateau was observed close to the oxygen evolution region [16–18] indicating mass transfer limitations. In our previous work we showed that the reaction slows down during the oxidation process, as evidenced with chrono-amperometry experiments [19]. This difference was attributed to a surface modification at the elec-
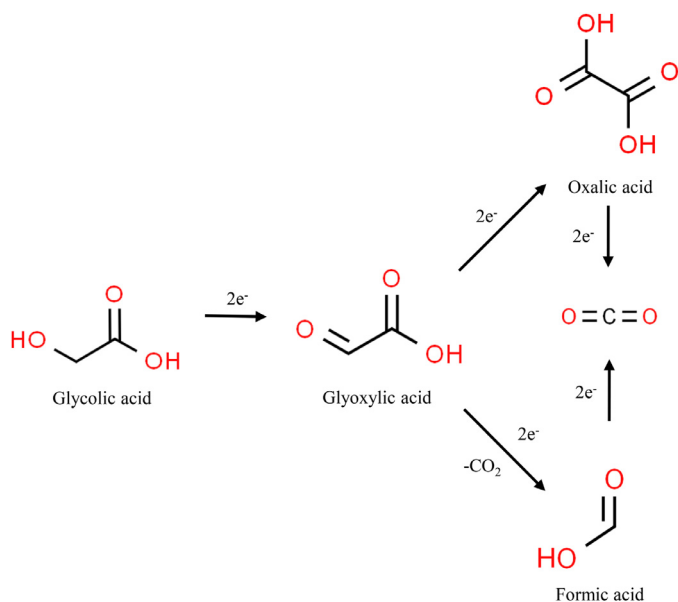
Fig. 1. Oxidation pathway of glycolic acid based on reaction mechanisms suggested in literature [22–25].

trode. Furthermore, we found that formic acid and formate can be selectively oxidized in a chrono-amperometry experiment with a current efficiency of ~100% at 2.3 V vs Ag/AgCl while being almost completely mass transfer limited.

Oxalic acid showed an increased current before oxygen evolution [6,7], but, no apparent plateau. These studies further showed low current efficiencies (<35%) for the oxidation of oxalic acid in galvanostatic experiments [6,7]. No intermediates have been found in the oxidation of formic and oxalic acid. It is generally accepted that oxalic acid and formic acid react in a 2-electron oxidation to CO_2 [7,12,20,21].

In the oxidation of glyoxylic and glycolic acid the formation of intermediates should be taken into account to evaluate the efficiency of the process. A number of studies suggest that photo-degradation, enzymatic and/or electrochemical oxidation of glycolic acid yields glyoxylic acid, which further reacts to oxalic and formic acid and ultimately to CO_2 [22–26]. Fig. 1 depicts this suggested reaction mechanism. The overall reactions of glyoxylic acid and glycolic towards CO_2 are oxidations that involve 4 and 6 electron transfers respectively. To our knowledge, no cyclic voltammetry of glyoxylic acid and glycolic acid on boron doped diamond has been reported.

A larger number of intermediates has been reported in the oxidation of acetic acid. Kapalka et al. suggested that the oxidation of acetic acid proceeds via the formation of methanol, methyl acetate and ethane.

This suggested reaction mechanism is based on a DEMS study [27] and is shown in Fig. 2. The main product was found to be CO_2, which is an 8-electron oxidation from acetic acid. Additionally, the formation of formic acid was suggested despite the fact that the DEMS study was unable to detect it [27]. Gandini et al. found low amounts of formic acid and traces of oxalic acid during the electrochemical oxidation of acetic acid on BDD [14], which has also been suggested by other authors [20,21,28]. Although these studies did not describe these pathways in detail, others have shown that methanol oxidation proceeds via formic acid towards CO_2 on electrodes such as PtRu and gold [29–31]. These steps have been added to the reaction pathway in Fig. 2. The galvanostatic oxidation of acetic acid on BDD has shown to be slower in comparison to formic and oxalic acid [6]. Voltammetry studies showed that no peak is observed before the water oxidation region in the presence of acetic acid [6,32].

Although reaction mechanisms for the oxidation of these C1 and C2 carboxylic acids have been suggested in literature and galvanostatic electrolysis has shown some intermediate formation during the scope of the reaction, there is still considerable ambiguity with regard to the selectivity and intermediate formation in the oxidation of carboxylic acids at different potentials. Also, there has been limited research on the effect of mass transfer. This study investigates the oxidation of acetic, glycolic, glyoxylic, oxalic and formic acid on BDD and aims to further elucidate the reaction pathways. In contrast to previously reported work on the oxidation of carboxylic acids on BDD, this study describes the oxidation on rotating disk electrode experiments and chrono-amperometry experiments in a two-compartment flow cell. Both set-ups were used because of the well-defined mass transfer.

2. Materials and methods

The following chemicals were used without further purification: formic acid (99–100%, VWR chemicals), oxalic acid (Acros organics, 98%), acetic acid (Sigma Aldrich, 100%), sodium sulphate (99.8%, VWR chemicals), glycolic acid (Alfa Aesar, 98%), glyoxylic acid solution (50% solution in water, Merck), sulphuric acid (95–97%, Merck) sodium phosphate dibasic (≥99.5%, VWR), sodium phosphate monobasic (100%, VWR), sodium hydroxide (0.1 M, Merck) and methylacetate (Alfa Aesar, 99%).

Buffer solutions of 0.5 M Na_2SO_4 were prepared and adjusted to pH 2 by the addition of sulphuric acid. The starting concentration of the carboxylic acids was 5 mM. All experiments were performed at room temperature.

An Autolab PGSTAT 30 potentiostat was used for the electrochemical measurements. All experiments were performed with an Ag/AgCl reference electrode (Qm713X, Prosense).

DIACHEM® (Condias) boron doped diamond electrodes were used in the electrochemical experiments. These oxygen-terminated electrodes [33] have a boron content of 500–8000 ppm, which gives an electrical
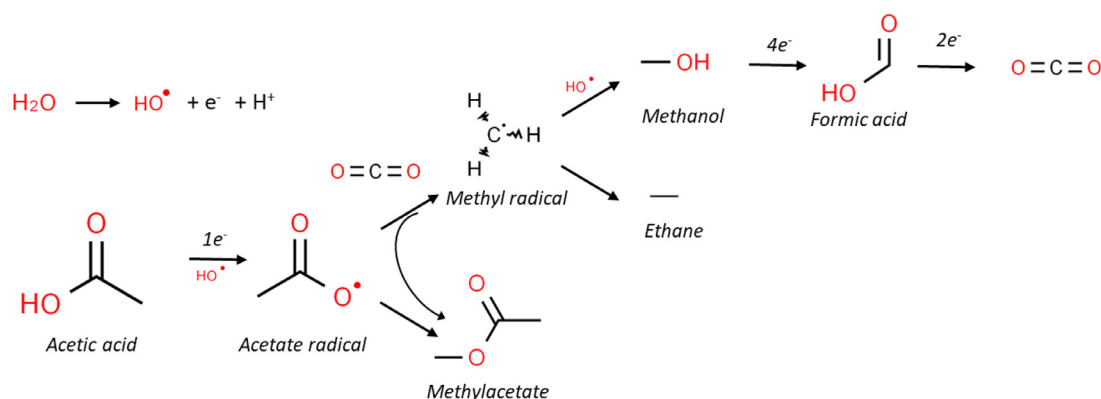

Fig. 2. Oxidation pathway of acetic acid, based on reaction mechanisms suggested in literature [14,27,29–31].

resistivity of 0.1-0.05Ω cm [34]. The diamond film thickness was approximately 5 μm for the electrodes in the flow reactor. More details on the characteristics of these electrodes and the characterization of BDD electrodes in general can be found in [35–37].

Experiments were performed with an electrode rotator (MSR, Pine research instrumentation Inc.) and rotating disk electrodes (E4TQ change disk Tip, Pine research instrumentation). The rotation rate of the electrode was varied between 50 and 1800 RPM. A boron doped diamond disk (5 mm diameter, DIACHEM®, Condias) and a platinum mesh (8.0•3.0 cm) were used as working and counter electrode respectively. The working volume of the cell was 70 mL.

A divided flow cell (Micro Flow Cell, Electrocell) was used to perform chrono-amperometric experiments. The boron doped diamond (DIACHEM®, Condias) and nickel electrodes were separated by a Nafion 117 membrane (Electrocell) with an inter electrode gap of 8 mm (4 mm on each side of the membrane). On both electrodes (9.5•4.6 cm), a square of 10 cm^2 was in contact with the solution. The anolyte (150 mL, starting volume) and catholyte (130 mL, starting volume) were pumped through the reactor and recirculated to the vessels using a peristaltic pump for the catholyte side and a gear pump for the anolyte side. The reference electrode was connected to the flow path of the electrolyser to minimize ohmic losses. Samples of 1.5 mL were taken from the anolyte vessel at 5 min intervals.

To determine carboxylic acid concentrations, measurements were performed with high-performance liquid chromatography (HPLC) using a Shimadzu shim-pack C18 column (250•3.0 mm, 5 μm) equipped with a pre-column. The temperature was 60 °C, the injection volume was 1 μL for oxalic acid and 5 μL for acetic, glyoclic and formic carboxylic acids. The flow rate of the mobile phase (0.01 M H_3PO_4) was 0.5 mL min^{-1}. The determination of glyoxylic acid was performed using a RHM-Monosaccharide H$^+$ (8%, 150 • 7.8 mm) Phenonomenex column. A mobile phase of 0.5 mM H_2SO_4 was used (flow rate: 0.8 mL min^{-1}). The oven temperature was set to 70 °C, and 5 μL of each sample was injected.

3. Data analysis

3.1. Conversion, selectivity and yield

The conversion of the carboxylic acids in the chrono-amperometry experiments was defined as

$$X_i = \frac{N_{i0} - N_i}{N_{i0}} \tag{1}$$

in which Xi is the conversion (-) of compound i, N_i and N_{i0} are the number of moles of compound i (mol) at time t and time $t = 0$ respectively.

The selectivity of the intermediates formed in the oxidation of carboxylic acids was calculated using:

$$S_j = \frac{N_j}{N_{i0} - N_i} \tag{2}$$

in which S_j is the selectivity of intermediate j and N_j is the number of moles of intermediate j (mol) formed.

The selectivity and conversion were used to calculate the yield:

$$Y_j = X_i \cdot S_j \tag{3}$$

where Y_j is the yield of compound j.

3.2. Current efficiency

The current efficiency is defined as the charge that is used in the desired reaction over the total charge:

$$CE = \frac{q_j}{q_{tot}} \cdot 100\% \tag{4}$$

where CE is the current efficiency, q$_{tot}$ is the total charge (Coulomb) and q$_j$ charge in the reaction of compound i to j (q$_j$). The latter can be calculated using:

$$q_j = N_j \cdot n_j \cdot F \tag{5}$$

in which F is the Faradays constant (96,485 C/mol) and n_j the number of electrons in the formation of the intermediate.

3.3. Mass transfer

To assess the effect of mass transfer on the oxidation of the carboxylic acids, it was decided to compare the rate of mass transfer towards the electrode and the conversion rate of the carboxylic acids at the electrode. The mass transfer rate of the carboxylic acids towards the electrode was calculated using:

$$MT = k_L \left(c_{i,b} - c_{i,s} \right) \tag{6}$$

in which MT is the rate of mass transfer (mol m^{-2} s^{-1}) k_L, the mass transfer coefficient (m s^{-1}) and c the concentration of the oxidized compound (mol m^{-3}) in the bulk and surface (subscripts b and s respectively). The bulk concentration was measured at set intervals (as described in the previous section). In case of mass transfer limitations, the surface concentration is 0. The mass transfer coefficient was calculated using:

$$k_L = \frac{Sh \, D}{l} \tag{7}$$

in which, Sh is the dimensionless Sherwood number, D the diffusion coefficient (m^2 s^{-1}) and l the characteristic length (m).

The Sherwood correlation below has been established for the Electrocell [38] used in this work:

$$Sh = 1.05 Re^{0.44} Sc^{0.33} \tag{8}$$

where Sh, Re and Sc are the dimensionless Sherwood number, Reynolds number, Schmidt number respectively.

The mass transfer rate was compared to the conversion rate that was normalized to the surface area of the electrode, which was defined as:

$$r_2 = \frac{m}{A \, t} \tag{9}$$

where r$_2$ is the conversion rate of the starting compound (mol m^{-2} s^{-1}), m the number of moles of compound converted (mol), A is the electrode surface (m^2) and t is the time (s).

4. Results

4.1. Formic, oxalic and acetic acid

Fig. 3 shows the cyclic voltammograms in the presence of formic, oxalic and acetic acid on a rotating disk BDD electrode at 200 and 1800 RPM. As we have previously reported, for formic acid a pseudo-plateau can be observed at 2.1 V (vs Ag/AgCl), the height of which depends on the rotational speed. Lower current densities are observed in the case of oxalic acid, which slightly increase at higher rotational speed. Acetic acid is not oxidized prior to water oxidation. The results suggest that formic and oxalic acid are oxidized by a direct electron transfer (DET) mechanism, because increased current densities are observed prior to water oxidation. It has previously been suggested that acetic acid cannot be oxidized via the DET mechanism [36], which could explain the absence of current density measured before water oxidation.

It is interesting to note that for formic acid and oxalic acid the current densities in the backward scan are lower than in the forward scan. In our previous work we have suggested that this decreasing reactivity might be related to a reversible change in surface groups at higher potentials, which influences the oxidation by the DET mechanism [19]. As a result, the current densities observed in chrono-amperometry experiments are lower than expected based on the forward scan in the voltammetry experiments. Fig. 3 suggests that a similar process could occur for oxalic acid. For acetic acid this effect is not observed.

The chrono-amperometry experiments of formic, oxalic and acetic acid in a parallel plate flow reactor at different potentials are shown in
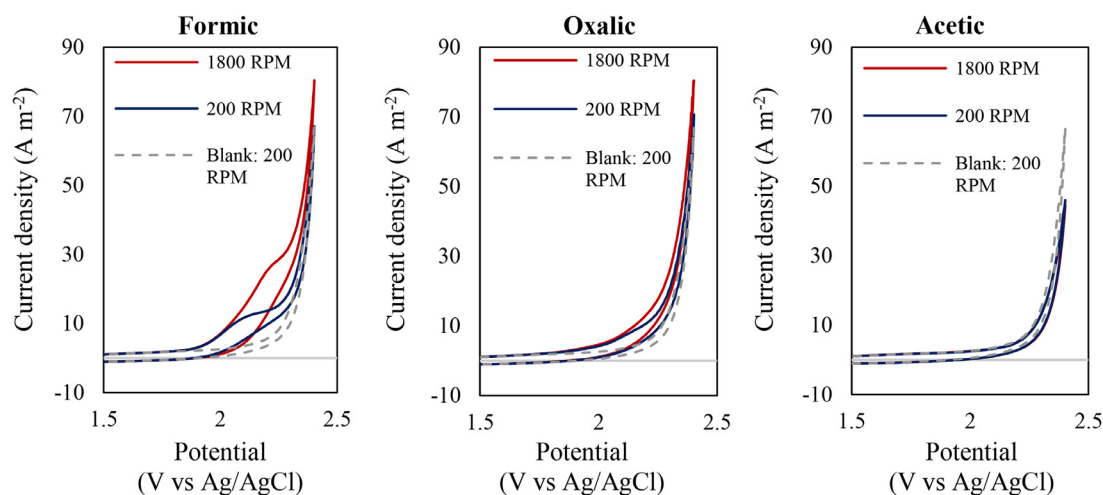
Fig. 3. Cyclic voltammetry in the presence of 5 mM formic acid, oxalic acid and acetic acid on rotating BDD electrodes (0.2 cm^2) at different rotation rates. Scan rate: 0.05 V s^{-1}. Solution: 0.5 M Na$_2$SO$_4$ + H$_2$SO$_4$ (pH 2).
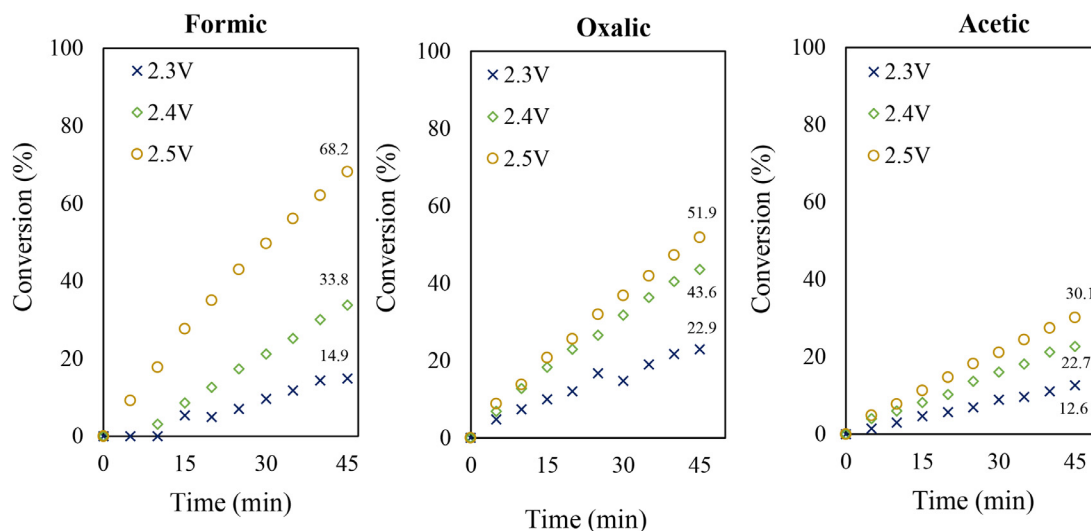

Fig. 4. Oxidation of 5 mM formic, oxalic and acetic on a BDD electrode (10 cm^2) in an Electrocell parallel plate flow cell at various potentials (vs Ag/AgCl): 2.3 V (x), 2,4 V (◊) and 2.5 V (o). Solution: 0.5 M Na$_2$SO$_4$ + H$_2$SO$_4$ (pH 2). Electrolyte flow rate: 20 L h^{-1}.

Fig. 4. The current densities measured in these experiments can be found in the supporting information. At 2.3 V vs Ag/AgCl similar conversions are observed for formic and acetic acid, while the oxidation rate of oxalic acid is slightly higher. This is in apparent contrast with the cyclic voltammetry experiments where acetic acid oxidation is much slower and confirms that the oxidation rate of formic acid and oxalic acid are slowed down during oxidation. This is also in line with the observed currents, which are lower than in the forward scan in the cyclic voltammetry (see supporting info). At higher potentials the oxidation rates increase more significantly for formic and oxalic acid than for acetic acid. These results are in line with previously reported experiments; for example the galvanostatic experiments of Aquino de Queiroz et al., who showed that the oxidation of formic and oxalic acid is faster in comparison to acetic acid oxidation [6].

No intermediates could be detected during the course of the reaction for oxalic, formic and acetic acid. Based on the reaction mechanism in Fig. 1 it is assumed that both formic acid and oxalic acid oxidize directly to CO$_2$ without the formation of intermediates. Contrary to expectations, intermediates were also not found in the oxidation of acetic acid. It is most likely that in the oxidation of acetic acid some intermediates are formed that were not found using HPLC. For

instance, according to the DEMS study of Kapalka et al. 43% of the total current (at 2.65 V vs Ag/AgCl) could be attributed to the oxidation of acetic acid to CO$_2$, whereas the remaining current was ascribed to the formation of methanol, ethane and methyl acetate (as shown in Fig. 2). Although in our work we were capable of detecting methyl acetate in the HPLC, we did not observe it. This makes the formation of methanol or ethane more likely (which could not be detected by the HPLC method used). This can be supported by the fact that in additional experiments at higher concentrations (0.2 M) of acetic acid, minor amounts of formic acid have been detected (results can be found in the supporting information), which is the product formed in the oxidation of methanol.

The assumption that the carboxylic acids of interest are completely converted to CO$_2$ on BDD can be verified by examining the electron balance of the experiments. Fig. 5 relates the electrical charge passed based on the measured current density and time with the conversion of the reactant multiplied by Faraday's constant. The slope of the graph is equal to the number of electrons per molecule of reactant converted.

It can be seen that in the oxidation of oxalic and formic acid at 2.3 V ~2 electrons are used, which is equal to the number of electrons needed for the conversion to CO$_2$. This implies that oxalic acid and formic acid
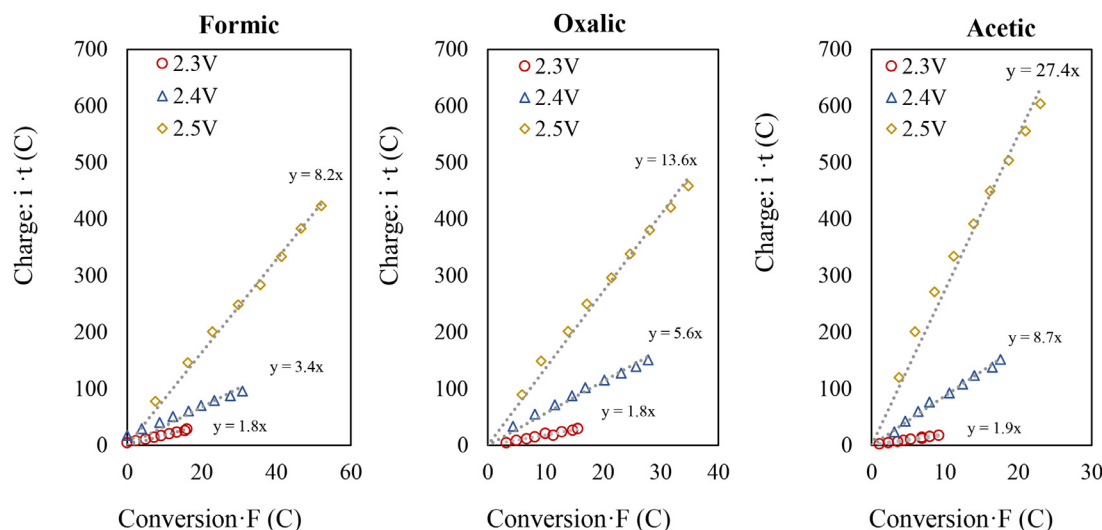
Fig. 5. Charge passed based on Faradays law ($q = m \cdot F$) versus the electrical charge passed ($q = i \cdot t$). The amount of mol oxidized (m) is based on the measured degradation of the carboxylic acid. Data based on oxidation of 5 mM formic, oxalic and acetic acid on a BDD electrode (10 cm2) in an Electrocell at different potentials (vs Ag/AgCl): 2.3 V (o), 2.4 V (△) and 2.5 V (◇). Solution: 0.5 M Na_2SO_4 + H_2SO_4 (pH 2). Electrolyte flow rate: 20 L h^{-1}.

are selectively oxidized to CO_2 and that water oxidation does not yet occur at a significant rate. It means that the current efficiencies are close to 100%. Higher numbers of electrons are observed in the oxidation at 2.4 V and 2.5 V, which can be explained by concurrent water oxidation. At these potentials the current efficiencies decrease significantly to respectively 61.6% and 22.3% for formic acid and 36.4% and 15.2% for oxalic acid.

Although the oxidation of acetic acid to CO_2 is an 8-electron reaction (reaction 5), Fig. 5 suggests that only 2 electrons are involved per acetic acid molecule in the oxidation reaction at 2.3 V. As suggested before this is probably due to intermediates that are formed, but were not detected. The reaction mechanism in Fig. 2, suggests that these 2 electrons could lead to the formation of methyl acetate, ethane or methanol. Given that methyl acetate was not detected, its most likely that ethane or methanol are formed according to:

$$2\,CH_3COOH \rightarrow C_2H_6 + 2\,CO_2 + 2e^- + 2H^+$$

$$CH_3COOH + H_2O \rightarrow CH_3OH + CO_2 + 2H^+ + 2e^-.$$
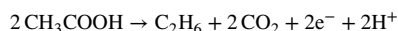
The increasing numbers of electrons at 2.4 V (8.7) and 2.5 V (27.4) could be related to the formation of more intermediates, water oxidation, or full oxidation of acetic acid to CO_2. We can therefore not conclude whether full oxidation of acetic acid to CO_2 takes place or not and more detailed analysis is needed.

An important aspect that needs to be considered in electrochemical experiments is the effect of mass transfer, which is generally evaluated by calculating the limiting current density. This calculation requires a number of electrons that is involved in the oxidation of each carboxylic acid. This is possible for formic and oxalic acid, which react in 2-electron transfers to CO_2, as shown in the previous paragraph. However, for acetic, glyoxylic and glycolic acid (which are discussed in the next section), the formation of intermediates complicates the calculation of the limiting current density. It has therefore been decided to compare the limiting transfer rate of the carboxylic acids to the electrode (Eq. (6)) to the conversion rate (Eq. (9)).

Fig. 6 shows the comparison of the limiting mass transfer rate to the conversion rate for the oxidation of formic, oxalic and acetic acid at different potentials. At 2.3 V the theoretical mass transfer rates are higher compared to the conversion rates for formic, oxalic and acetic acid. This shows that the selective oxidation (close to 100% current efficiency) that takes place at this potential is mainly limited by kinetics and not yet limited by mass transfer. At higher potentials the oxidation

rates are closer to or even exceed the mass transfer limitation rates for oxalic (2.4 V and 2.5 V) and formic acid (2.5 V), but this comes at the price of decreased current efficiency (see Fig. 5). In our previous work we have suggested that conversion rates that exceed the mass transfer rate could be related to O_2 bubble formation or the diffusion of •OH radicals, which are both linked to water oxidation. It can be speculated that •OH radicals formed could diffuse to the bulk of the solution [7]. In this situation the carboxylic acids react in the bulk of the solution as well as on the electrode surface. On the other hand, the oxygen bubbles formed at higher potentials might induce an increased mixing effect. Multiple studies have shown improved mass transfer at the working electrode as a result of gas evolution at the counter electrode [39–41]. A similar effect could explain the improved mass transfer of the carboxylic acids in this study.

4.2. Glyoxylic and glycolic acid

Fig. 7 shows the cyclic voltammograms of glyoxylic and glycolic acid at 200–1800 RPM. Both glyoxylic and glycolic acid show increased current densities prior to water oxidation, which suggest DET mechanisms. The observed current densities are higher compared to the oxidation of acetic, formic and oxalic acid shown in Fig. 3. The voltammograms show a clear dependence on rotation rate suggesting mass transfer limitations. Similar to formic acid, the current densities observed in the backward scan are lower compared to the forward scan, which is most significant in the oxidation of glycolic acid. The comparison of glyoxylic and glycolic oxidation in the forward scan shows higher current densities for glycolic acid. However, the backward scan shows comparable current densities for glyoxylic and glycolic acid (comparison can be found in the supporting information).

Fig. 8 shows the conversion of glyoxylic and glycolic acid and the formation of intermediates at varying potentials in a parallel plate flow cell. The conversion of glyoxylic and glycolic acid is comparable at 2.3 V at 2.4 V, which is in line with the current densities observed in the backward scan of the cyclic voltammograms. The oxidation rate of glycolic acid is higher at 2.5 V compared to glyoxylic acid. Oxalic acid was found to be the main intermediate formed in all glycolic and glyoxylic acid experiments. Furthermore, minor amounts of formic acid are formed at 2.5 V in the oxidation of glycolic acid, which is not observed in the oxidation of glyoxylic acid. Interestingly, glyoxylic acid formation is not
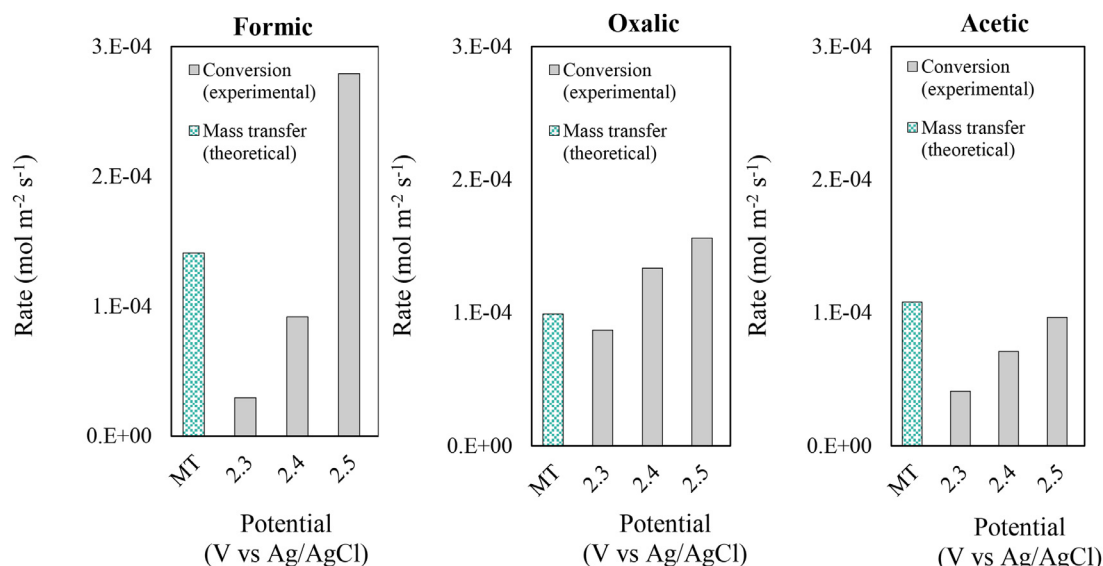
Fig. 6. Comparison of the mass transfer limiting rates (MT, dotted column) to the initial conversion rates in the oxidation of formic, oxalic and acetic at various potentials vs Ag/AgCl (solid grey columns). Data based on oxidation on a BDD electrode (10 cm2) in an Electrocell. Solution: 0.5 M Na_2SO_4 + H_2SO_4 (pH 2). Electrolyte flow rate: 20 L h^{-1}. Diffusion coefficients for acetic: $1.25 \cdot 10^{-9}$ cm2 s^{-1} [42], formic: $1.52 \cdot 10^{-9}$ cm2 s^{-1} [42] and oxalic acid: $1.33 \cdot 10^{-9}$ cm2 s^{-1} (estimated using a modified Wilke-Change equation [42,43], as shown in supporting information). Mass transfer based on starting concentration of the carboxylic acids (5 mM), Reynolds number: 259 and Sherwood numbers: 108, 113 and 115 for formic, oxalic and acetic acid respectively. The conversion rate is based on the initial datapoints ($t = 0$ to $t = 15$).
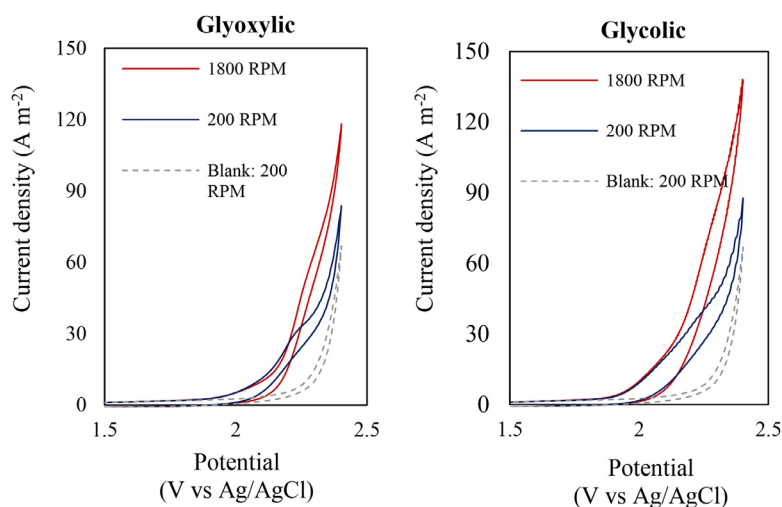

Fig. 7. Cyclic voltammetry in the presence of 5 mM glyoxylic (left) and glycolic acid (right) on rotating BDD electrodes (0.2 cm2) at 200 and 1800RPM. Scan rate: 0.05 V s^{-1}. Solution: 0.5 M Na_2SO_4 + H_2SO_4 (pH 2).

observed in the glycolic experiments, in contrast to what would be expected based on the reaction mechanism presented in Fig. 1.

The comparison of the formation of oxalic acid in the glyoxylic acid oxidation at different potentials shows that the selectivity towards oxalic acid in the oxidation of glyoxylic acid is slightly higher at 2.3 V (51%), compared to 2.4 V (31%) and 2.5 V (37%). Comparing Figs. 8–4 show that the oxidation rates of oxalic acid and glyoxylic acid are similar for 2.4 V and 2.5 V, whereas the oxidation of oxalic acid is slower at 2.3 V. This could explain the higher accumulation of oxalic acid at this potential. Yet, we do not see the same effect in the oxidation of glycolic acid, where the amount of oxalic acid after 40 min is respectively 37%, 51% and 28% at 2.3 V, 2.4 V and 2.5 V. It is further interesting to note the formation of formic acid at 2.5 V in the oxidation of glycolic acid, which is not observed at lower potentials. It might be the case that higher overpotentials are required for the C–C cleavage in glycolic acid that results in formic acid, which has for example been shown in the oxidation of ethylene glycol on Pt and Au [9].

The fact that glyoxylic acid was not detected in the oxidation of glycolic acid cannot be explained by comparison of the individual oxidation rates. The individual reaction rate at 2.5 V is lower for glyoxylic acid in comparison to glycolic acid and therefore one would expect the accumulation of glyoxylic acid in the reaction. This suggests that if glycolic acid reacts via glyoxylic acid towards oxalic acid (the most logical pathway), the glyoxylic formed at the electrode directly reacts further towards oxalic acid and does not enter the solution. Similar results have been reported for the oxidation of glycolic acid on platinum electrodes with the difference that glycolic acid cannot be completely converted to CO_2. The main intermediate of glycolic acid oxidation on Pt was found to be oxalic acid and less than 2% of the intermediates was glyoxylic acid [9], which is in line with our results on BDD.

Comparing the yield of oxalic acid to the conversion of the starting compound (glycolic or glyoxylic acid) shows that more moles of starting compounds are oxidized than moles of oxalic acid are formed. This could be explained by the formation of CO_2 (which was not measured)
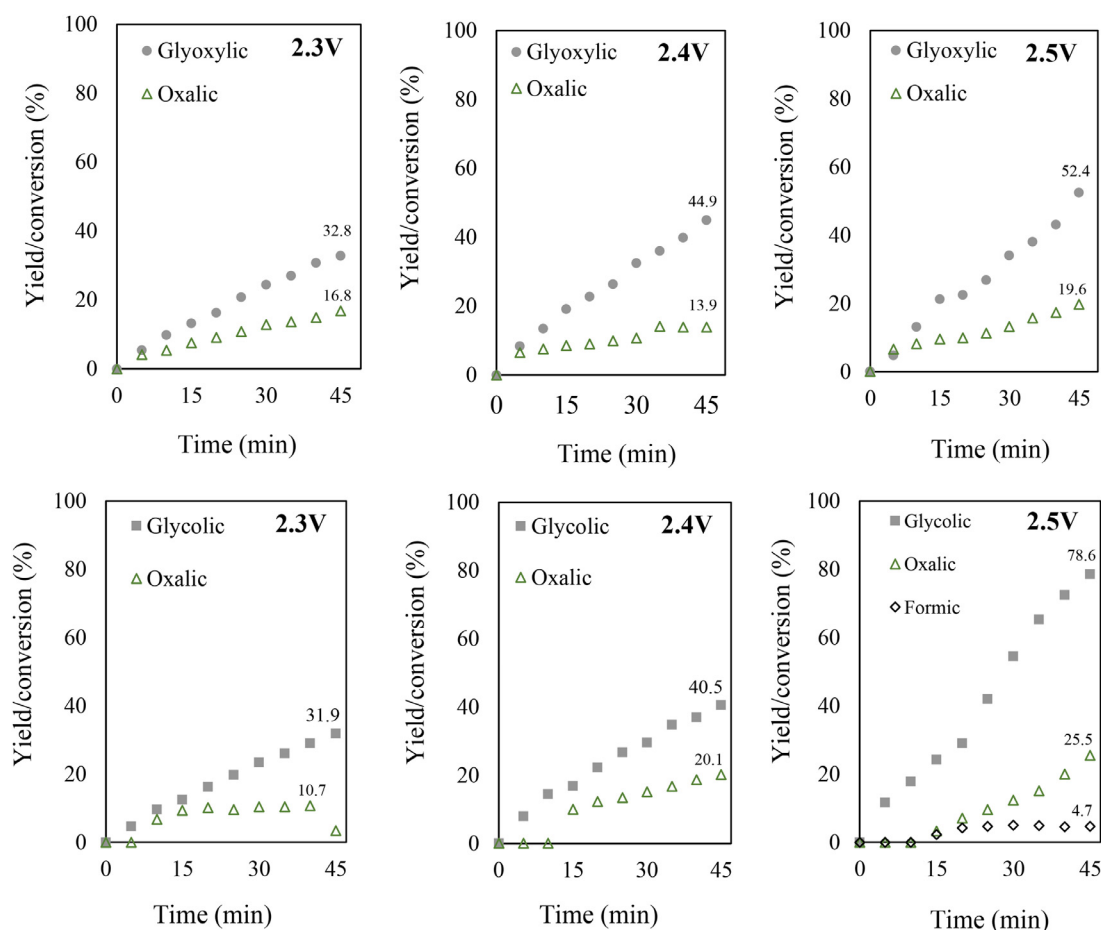
Fig. 8. Conversion of 5 mM glyoxylic acid (■) and glycolic acid (◆) and formation of intermediates (oxalic acid: Δ and formic acid: -) at various potentials (vs Ag/AgCl): 2.3 V (left), 2.4 V (center) and 2.5 V (right) on a BDD electrode (10 cm2) in an Electrocell. Solution: 0.5 M Na_2SO_4 + H_2SO_4 (pH 2). Electrolyte flow rate: 20 L h^{-1}.

or the presence of undetected intermediates. The former explanation is most likely and consistent with previous findings in the literature. Most studies report a minor formation of intermediates and suggest that carboxylic acids completely convert to CO_2. For example, in the oxidation of succinic acid ($C_4H_6O_4$) on BDD, minor mole fractions of oxalic (10%), formic acid and glyoxylic acid (<4%) were detected [22]. Similarly, small amounts of formic acid and oxalic were formed in the oxidation of maleic acid ($C_4H_4O_4$) on BDD [44].

The assumption that glyoxylic and glycolic acid convert to CO_2 was verified by the electron balances. The electrical charge passed based on the measured current density and time was compared to the charge calculated based on the conversion. The latter is calculated using Faradays law based on the yield of oxalic acid ($n = 2$ or 4 for glyoxylic and glycolic respectively) and the assumption that the remaining part is converted to CO_2 ($n = 4$ or 6 for glyoxylic and glycolic respectively). Fig. 9 compares the charge measured ($i•t$) to the charge based on the conversions of glyoxylic and glycolic acid and the yield of oxalic and formic acid ($m•n•F$).

The comparison shows that at 2.3 V the measured charge is comparable to the charge calculated based on the conversion for glyoxylic and glycolic acid. This calculation confirms the assumption that the remaining fraction at this potential can be attributed to CO_2 formation. The water oxidation is most likely still negligible at this potential, which was also seen for formic and oxalic acid oxidation. This means that these compounds can be oxidized with close to 100% current efficiency at 2.3 V. Increasing the potential shows that there is a significant gap between the measured charge and the charge calculated based on the

conversion, which can be attributed to water oxidation at 2.4 and 2.5 V. The current efficiencies at 2.4 V (20% and 19%, for glyoxylic and glycolic respectively) and 2.5 V (12% for both glyoxylic and glycolic acid) decrease as a result of significant water oxidation.

Fig. 10 compares the conversion rates (Eq. (9)) to the limiting mass transfer rates (Eq. (6)) for glyoxylic and glycolic acid oxidation. At 2.3 V the conversion rate is close to or above the limiting rates for both compounds. It is interesting to note that Fig. 9 suggests that glyoxylic and glycolic acid can be selectively oxidized, while the conversion rates are close to the mass transfer limiting values as shown in Fig. 10. At higher potentials the experimental values exceed the limiting current densities, similarly to formic, oxalic and acetic acid oxidation. These results suggest that there is an enhanced mass transfer effect, which has been discussed in the previous section.

In the context of industrialization of this process it is important to select the optimum potential for the oxidation of the carboxylic acids. For a cost-effective process, one would like to operate at a potential where the reaction has a high current efficiency, full conversion to CO_2 and is close to mass transfer limitation in order to be able to operate the reactor at high current densities. This work has shown that formic acid can be selectively oxidized at 2.3 V, although it is not completely mass transfer limited at this potential. The selective oxidation of oxalic acid takes place close to the mass transfer limiting value at 2.3 V. The oxidation of glycolic and glyoxylic acid can be oxidized with high current efficiencies at 2.3 V. Although these compounds are not completely converted to CO_2 conversion, the oxalic acid that is formed should not be problematic as its easily oxidized on BDD. Finally, the acetic acid
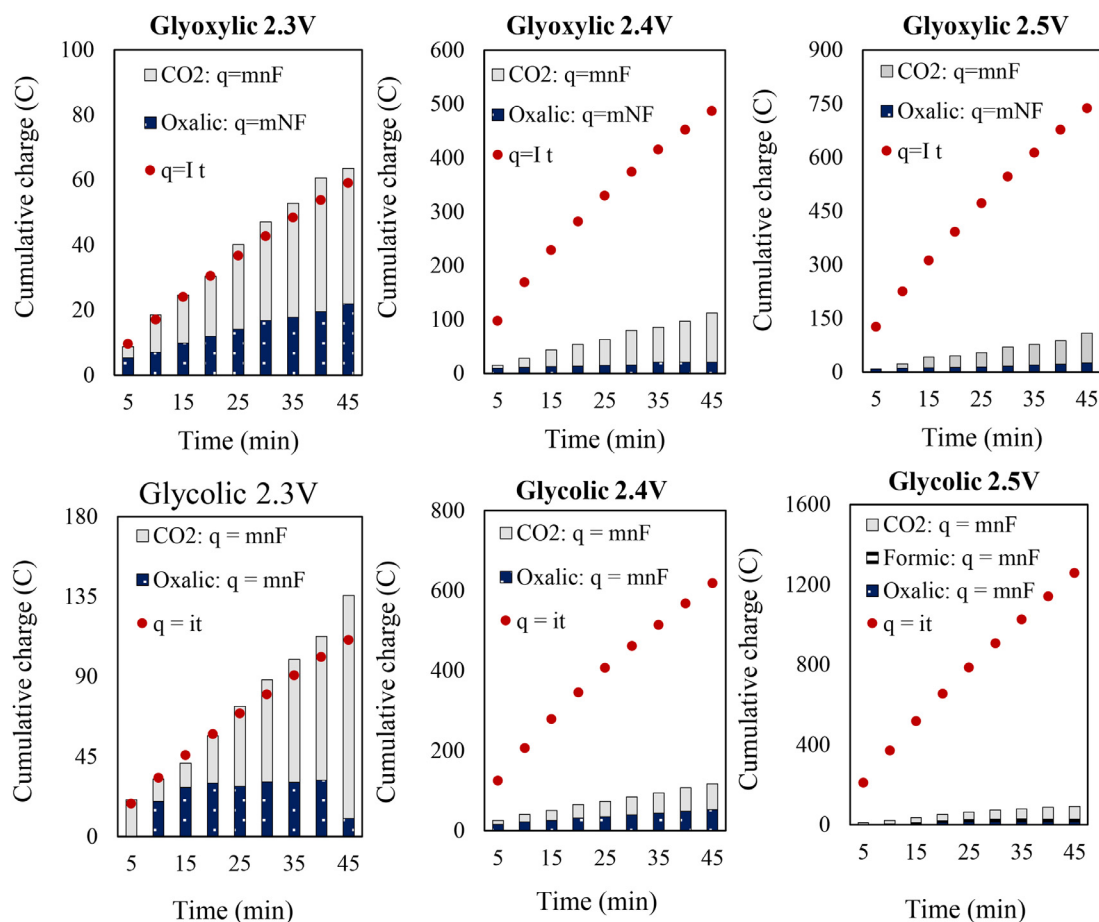
Fig. 9. Comparison of the charge based on the observed current densities ($\bullet$, $q = i \bullet t$) to the charge calculated based on Faradays law (stacked columns, $q = m \bullet n \bullet F$). The latter is a combination of the conversion to oxalic acid (dotted column, $n = 2$ or $n = 4$, for glyoxylic and glycolic respectively) and the assumption that the remaining fraction is converted to CO_2 (solid column, $n = 4$ or $n = 6$, for glyoxylic and glycolic respectively). Data based on oxidation of 5 mM glyoxylic and glycolic acid on a BDD electrode (10 cm^2) in an Electrocell. Solution: 0.5 M Na_2SO_4 + H_2SO_4 (pH 2). Electrolyte flow rate: 20 L h^{-1}.
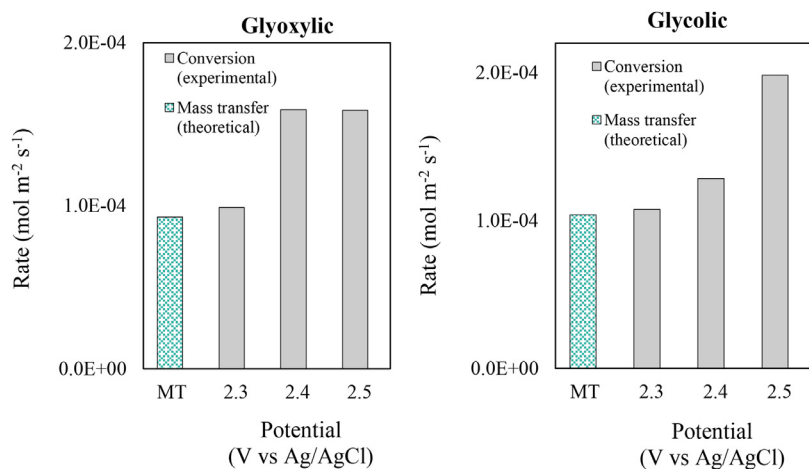

Fig. 10. Comparison of the mass transfer limiting rates (MT, dotted column) to the initial conversion rates in the oxidation of 5 mM glyoxylic and glycolic at various potentials vs Ag/AgCl (solid columns). Data based on oxidation on a BDD electrode (10 cm2) in an Electrocell. Solution: 0.5 M Na_2SO_4 + H_2SO_4 (pH 2). Electrolyte flow rate: 20 L h^{-1}. Diffusion coefficients for glyoxylic acid: $1.23 \bullet 10^{-9}$ cm^2 s^{-1} and glycolic acid $1.27 \bullet 10^{-9}$ cm^2 s^{-1} (estimated using a modified Wilke-Change equation [42,43], shown in supporting information). Mass transfer based on starting concentration of the carboxylic acids (5 mM), Reynolds number: 259 and Sherwood numbers: 116 (glyoxylic) and 115 (glycolic). The conversion rate is based on the initial datapoints ($t = 0$ to $t = 15$).

cannot be selectively oxidized to CO_2 on BDD. This might be related to the fact that acetic acid solely reacts with $\bullet$OH radicals, while the other carboxylic acids can also react via the DET mechanism.

5. Conclusion

We have presented the oxidation of formic, oxalic, glyoxylic, glycolic and acetic acid on boron doped diamond electrodes to gain better un-

derstanding on the selectivity, intermediate formation and mass transfer effects. The cyclic voltammograms showed that formic, oxalic, glyoxylic and glycolic acid react via a direct electron mechanism that occurs prior to water oxidation. Acetic acid is not oxidized prior to water oxidation, but seems to need $\bullet$OH radicals to be oxidized. The backward scans of the cyclic voltammograms show a decreasing reactivity, which might be linked to a modification of surface groups on the electrode. This effect significantly decreased the oxidation rates of the carboxylic acids,

especially formic and glycolic acid. Chrono-amperometry experiments in a parallel plate set-up showed that formic acid and oxalic acid react in 2-electron transfer reactions towards CO_2 without the formation of intermediates. The intermediate formed in the oxidation of acetic acid is most likely methanol and/or ethane. The oxidation of glycolic acid and glyoxylic acid proceeds via the formation of oxalic acid. The carboxylic acids can be oxidized at a high current efficiency in the parallel plate flow reactor below or close to mass transfer limited rates at 2.3 V (vs Ag/AgCl). At higher potentials the current efficiencies significantly decrease due to simultaneous water oxidation. At these potentials conversion rates exceed the mass transfer limiting values, which is most likely related to water oxidation effects; i.e. $^\bullet$OH radicals that diffuse to the bulk of the solution and/or oxygen bubbles improving mixing near the electrode.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ceja.2021.100093.

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