Research Article

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Towards the production of chlorine dioxide from electrochemically *in-situ* produced solutions of chlorate

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Abstract

BACKGROUND: This work focuses on the electrochemical production of chlorate solutions for direct use and integration in the manufacture of chlorine dioxide (ClO_2), from the perspective of manufacturing portable ClO_2 electrochemical generators.

RESULTS: Chlorate production was evaluated from the oxidation of sodium chloride (NaCl) contained in brackish solutions (20 g L^{-1}) and brines (200 g L^{-1}) in single chamber flow electrochemical cells. Efficiency in chlorate ion (ClO_3^-) production increased with temperature and NaCl concentration, but the use of brackish solutions led to a higher quality product, as compared to the brines, with lower concentration of chlorine and hypochlorous acid. To evaluate the production of ClO_2, samples corresponding to two different qualities of the electrogenerated solutions underwent stripping to exhaust chlorine, before being mixed with hydrogen peroxide (H_2O_2) and sulfuric acid. Results showed that using a chlorate solution obtained from the electrolysis of 20 g L^{-1} NaCl solution at 50 mA cm^{-2} and passing 57.35 Ah L^{-1}, a maximum concentration of 33.3 mmol L^{-1} ClO_2 could be attained, which corresponds to a maximum conversion of 48.75%.

CONCLUSIONS: Efficiency of the synthesis depends on both the purity of chlorate and the H_2O_2/ClO_3^- ratio. This confirms that *in-situ* electrogenerated chlorate can be used to manufacture ClO_2, but there are still many gaps to be overcome and further work must be carried out to optimize the production of the desired oxidant in a portable ClO_2 device.

Keywords: chlorate; chlorine dioxide; electrolysis; mixed-metal oxide; operation parameters

INTRODUCTION

The search for efficient disinfectants is a topic of major interest nowadays within a context in which this necessity is becoming more and more important because of the emergence of new problems.[1] Chlorine dioxide (ClO_2) is widely used as an oxidizer and disinfectant for diverse applications such as pulp bleaching, water purification, grease bleaching, medical treatment, sanitation, food processing, aquaculture, and even for the removal of pollutants such as phenols from industrial wastewater.[2,3] Its great potential in diverse applications has triggered the improvement of the conventional synthesis method and one of the most interesting approaches is that based on the chemical reduction of sodium chlorate in concentrated acid solutions with different reducing agents.[4–6] Sodium chlorate is a very well-known and powerful oxidant, becoming explosive when activated at high temperatures.[5] It is considered a commodity and its first industrial uses date back to the beginning of the 20th Century,[7] although its extensive production commenced only in the late 1960s.[8,9]

Quality of chlorate can be of extreme importance for obtaining a high efficiency in the production of ClO_2, and one of the challenges that must be faced nowadays in the formation of this important oxidant is the *in-situ* production of the reagents. It is important to bear in mind that in the industrial production of chlorates, the electrochemical process is only a small part of the whole process, and purification is of extreme importance and includes several unit operations with exigent operation procedures. Hence, directly obtaining solutions with high content of chlorates without further purification stages could be of a great relevance in the development of *in-situ* production of ClO_2. The supporting electrolyte used as reagent can become a key input, in particular the concentration of chlorate precursors which it contains, because the surplus reagents may not only have an impact

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on the production efficiency of ClO_2, but also become important in the later regeneration of the reagent for further production of chlorates, for developing a more sustainable process. In addition, formation of chlorate from the electrooxidation of chloride [Eqn (1)], depends strongly on the anodic material, as well as on the operation conditions (current density or potential applied and temperature).[10] This reaction competes with the oxidation of water to form oxygen [Eqn (2)]. Meanwhile, on the cathode electrode, it is well-known that the main reaction is the reduction of water to form hydrogen and hydroxyl ions [Eqn (3)], and these ions are known to contribute to the disproportionation of chlorine to chloride and hypochlorite [Eqn (4)], which is a first step in the chemical [Eqn (5)] and electrochemical [Eqn (6)] formation mechanisms of chlorate. The first mechanism also is known to be positively influenced by temperature and pH also is known to play an important role on the overall efficiency.

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \tag{1}$$

$$2H_2O \rightarrow O_{2(aq)} + 4H^+ + 4e^- \tag{2}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O \tag{4}$$

$$3ClO^- \leftrightarrow ClO_3{}^- + 2\,Cl^- \tag{5}$$

$$6HOCl + 3H_2O \rightarrow 2ClO_3{}^- + 4Cl^- + 12H^+ + 3/2O_2 + 6e^- \tag{6}$$

Over the last century, many studies have investigated the production of chlorine species using mixed metal oxide (MMO) anodes, demonstrating that it is a really complex process, which is influenced not only by the catalytic features of the MMO coatings, but also the operation conditions. In this context, ruthenium oxide/titanium (RuO_2/Ti) presents low overpotential for the oxygen evolution reaction (OER) and because of that, RuO_2/Ti-based mixed oxide electrodes have been investigated widely as electrocatalysts for the OER and chlorine evolution reactions. Relevant works were made by the research group of Avaca regarding sol–gel derived $Ru_xIr_{1-x}O_2$ coatings.[11,12] It also is interesting to highlight the mechanistic works made by the research group of Zeradjanin regarding the competition between the oxygen and chlorine evolution reactions at RuO_2-coated Ti electrodes. More recently, the use of other anodic materials has drawn the interest of researchers and among them, the harsh oxidation conditions produced during electrolysis of boron-doped diamond (BDD) anodes have pushed the research on this topic, although it has been found that oxidation with this type of anodes does not stop with the production of chlorates, but in the generation of perchlorates.[7,13,14] Hence, studies about the influence of the operation conditions on the selectivity of this reaction remain a topic worthy of study.

In industrial processes, electrolysis is only one of the stages of the production of chlorates and the purification of the product integrates many unit operations that, unfortunately, would be very difficult to be integrated in portable ClO_2 generators. Thus, to the best of the authors' knowledge, integration of the direct electrolytic production of chlorates (without purification stages) with the chemical dosing of hydrogen peroxide (H_2O_2) has not yet been explored. Consequently, there is still an important gap in the scientific knowledge with many potential applications. In this context, it is expected that the formation of ClO_2 may depend on the concentration of chlorates contained in the electrochemically manufactured solution and on the relationship between H_2O_2 and chlorates, because the redox chemistry of chlorine involves many species which are highly interrelated[15-17] necessitating taking extreme care over the operation conditions and procedures.[18]

Considering this background, the present work evaluates the electrochemical production of chlorate-rich solutions for direct use as reagents, together with H_2O_2, for the production of ClO_2, with the final aim of advancing in the development of portable ClO_2 generators. To this end, this study did not use industrial processes developed in the chloralkaline industry; rather, it explored *in-situ* production for direct use. The raw materials used in this production (such as brackish solutions or brines) were evaluated along with the required operation current density and temperature. The product then was mixed with H_2O_2 and acidified with sulfuric acid (H_2SO_4) to produce ClO_2. Based on this, we analyzed the key points involved in the efficient generation of this important oxidant and subsequent steps in the development of portable devices.

MATERIALS AND METHODS

Chemicals

Sodium chloride (NaCl) with anticaking (F.C.C.) food grade, H_2O_2 (33% w/v) and H_2SO_4 (90–91%) were purchased by Panreac (Castellar del Vallès, Barcelona, Spain), Labbox (Vilassar de Dalt, Barcelona, Spain) and Merk (Darmstadt, Germany), respectively. Sodium carbonate (analytical grade, ≥99.0%) and acetone supplied from Merk were used as the mobile phase for ion chromatography. Titanium (IV) oxysulfate (1.9–2.1%) also was purchased from Merk and used as an indicator for H_2O_2. Other chemicals employed in several analyses were analytical grade and supplied from Scharlab. Double deionized water (Millipore Milli-Q system, resistivity 18.2 MΩ cm at 25 °C) was used to prepare all solutions.

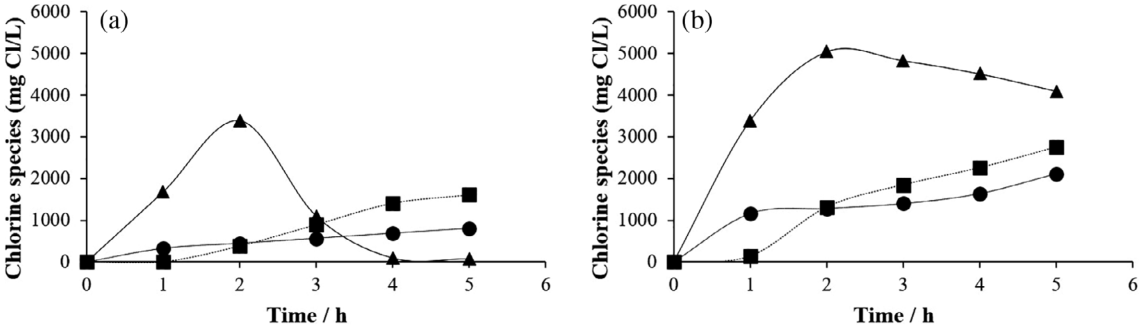

Figure 1. Production of hypochlorite (▲), chlorate (■) and chlorite/ClO_2 (●) during the electrolysis (discontinuous mode) of brines of NaCl 20 g L^{-1} (a) and 200 g L^{-1} (b) concenetrations at 60 °C with a current intensity of 3.9 A (50 mA cm^{-2}).

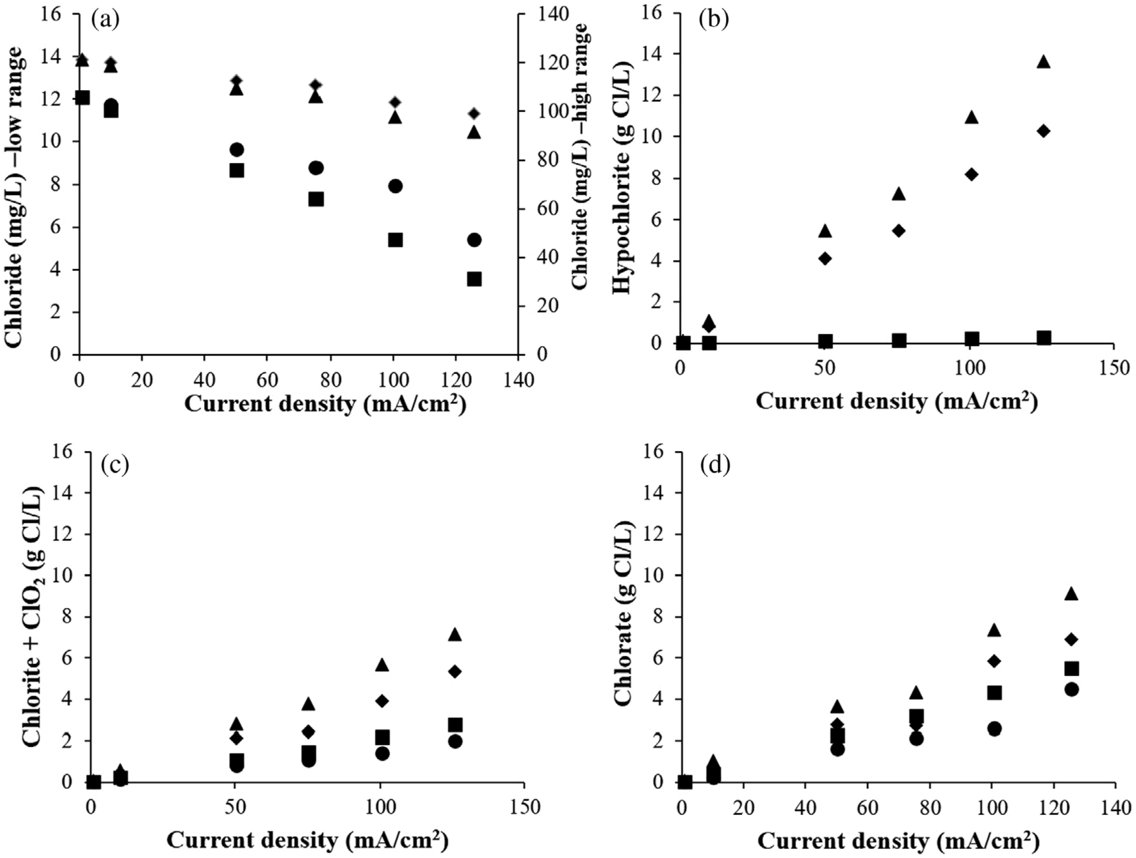

Figure 2. Changes in the concentration of chloride (a), hypochlorite (b), chlorite and ClO_2 (c) and chlorate (d) after 5 h of electrolysis (discontinuous mode) of 20 g L^{-1} NaCl solutions at 60 °C (●) and 80 °C (■) and 200 g L^{-1} NaCl brines at 60 °C (◆) and 80 °C (▲).

Electrochemical cell

Electrolysis assays were performed in a commercial single compartment electrochemical cell using a solution containing NaCl (20 g L^{-1} or 200 g L^{-1}) as supporting electrolyte. Circular MMO (based on RuO_2/Ti and supplied by Ti anode®) and circular stainless steel (AISI 304) were used as anode and cathode, respectively. The geometric area was 78 cm^2 for both electrodes and the interelectrode gap between the two was 9 mm. The experiments were carried out at constant current (galvanostatic conditions) and discontinuous mode. The current densities applied in the different test ranged from 1 mA cm^{-2} to 125 mA cm^{-2} at temperatures of 60 and 80 °C. The volume treated was 0.25 L and the electrolysis time was 5 h. No corrosion of the anode was observed during the tests on the surface or in the solution composition. In order to test the feasibility of the electrogenerated chlorate in the generation of ClO_2, additional electrolysis assays were performed in the same cell using 0.25 L electrolyte with 20 g L^{-1} NaCl at 50.0 mA cm^{-2} and 50 °C in semicontinuous mode (by feeding the electrochemical cell with 18 mL h^{-1} electrolyte). The collected samples subsequently were used for the generation of ClO_2.

Chlorine dioxide assays

Two samples were taken from the outlet at electrolysis times of 90 min (Sample 1, S1) and 300 min (Sample 2, S2) and used for the generation of ClO_2. To remove the presence of chlorine/hypochlorite, these samples were previously stripped with air. 10 mL of each sample (S1 and S2) were mixed with 4 mL of commercial H_2O_2 (33 000 mg L^{-1}) and 25 mL H_2SO_4 (5 mol L^{-1}) in a glass reactor (0.250 L), which were completely closed. The mixture was kept at a constant temperature of 68 °C (with thermostatic bath) and under gentle stirring conditions (350 rpm). Samples of the liquid and gas phase were taken periodically to quantify the evolution of ClO_2.

Characterization methods

Chlorite, chlorate and hypochlorite were determined by a titration method. This method is based on the procedure proposed by

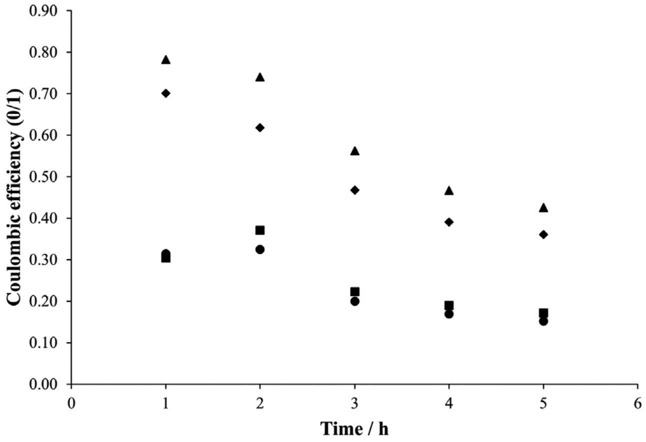

Figure 3. Time course of the current efficiency during the electrolysis (discontinuous mode) of NaCl solutions at 9.8 A ▲ T = 80 °C, C_0 = 200 g L^{-1}; ◆ T = 60 °C, C_0 = 200 g L^{-1}; ■ T = 80 °C, C_0 = 20 g L^{-1}; ● T = 60°C, C_0 = 20 g L^{-1}.

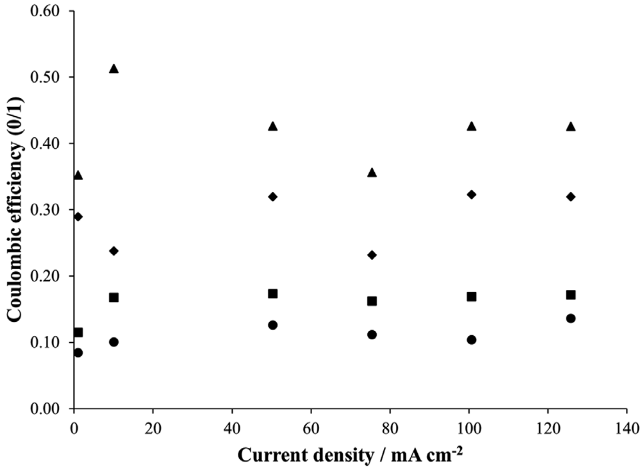

Figure 4. Coulombic efficiency of the oxidation of chloride (▲) $T = 80°C$, $C_0 = 200\ g\ L^{-1}$; (◆) $T = 60\ °C$, $C_0 = 200\ g\ L^{-1}$; (■) $T = 80\ °C$, $C_0 = 20\ g\ L^{-1}$; (●) $T = 60\ °C$, $C_0 = 20\ g\ L^{-1}$.

Marco A.E. *et al.*[19] First, the available chlorine was removed from the samples collected in electrolysis using H_2O_2. Then, to obtain the concentration of chlorite and chlorate, the samples were reacted with potassium iodide (KI) at pH 2 (for chlorite measurement) and at a strongly acidic pH (for chlorate measurement). Finally, the solutions were titrated with sodium thiosulfate. Moreover, hypochlorite was measured by titration at basic pH with 0.001 M arsenic trioxide (As_2O_3) in 2 mol L^{-1} sodium hydroxide (NaOH). To obtain a more accurate measurement of the chlorate concentration in the ClO_2 assays, a Metrohm Compact Ion Chromatograph Flex was used. The mobile phase consisted of 85:15 v/v 3.6 mM Na_2CO_3/Acetone solution and flowed at 0.8 mL min^{-1} through a Metrosep A Supp 7. The injection volume was 20.0 μL. The evolution of the H_2O_2 concentration could be monitored spectrophotometrically due to the complex formed between H_2O_2 and Ti^{2+}[20] using a UV-1700 Shimadzu Spectrophotometer at a wavelength of 410 nm. In the ClO_2 reactor, the chlorine species were monitored by spectrophotometry using an Agilent 300 Cary series UV–visible spectrophotometer. The wavelengths of chlorite, hypochlorous acid, chlorine and ClO_2 were detected at 230, 323, 310 and 360 nm, respectively.[4] Regarding the gas phase, air was used to strip gases from the reaction media. On the one hand, 5 mL stripped gas was bubbled in a solution containing 10 mL water and the solution was immediately measured spectrophotometrically. On the other hand, another 5 mL stripped gas was bubbled in a solution containing 10 mL KI (1 g L^{-1}) producing the transformation of iodide to iodine and the iodine solution was titrated with sodium thiosulfate.

RESULTS AND DISCUSSION

Production of chlorate solution

Figure 1 compares the production of oxidized chlorinated species when a highly concentrated solution of NaCl (20 g L^{-1}) and a brine of the same salt (200 g L^{-1}) were electrolyzed for 5 h at 50 mA cm^{-2} in discontinuous operation mode by recycling continuously the electrolyte between a reservoir tank and the electrochemical cell.

It is important to note that the concentration of chlorite increases before that of the chlorates (as expected) but it does not reach a maximum during the electrolysis period, meaning that its formation continues even after the complete disappearance of hypochlorite. However, the concentration of chlorate was higher than that of chlorite. At the end of the tests, the concentrations of chlorate were 1.62 and 2.76 g L^{-1} for the brackish solution and the brine, respectively, although in the first case it accounted for 13.32% of the total chlorine and in the second for only 2.27%.

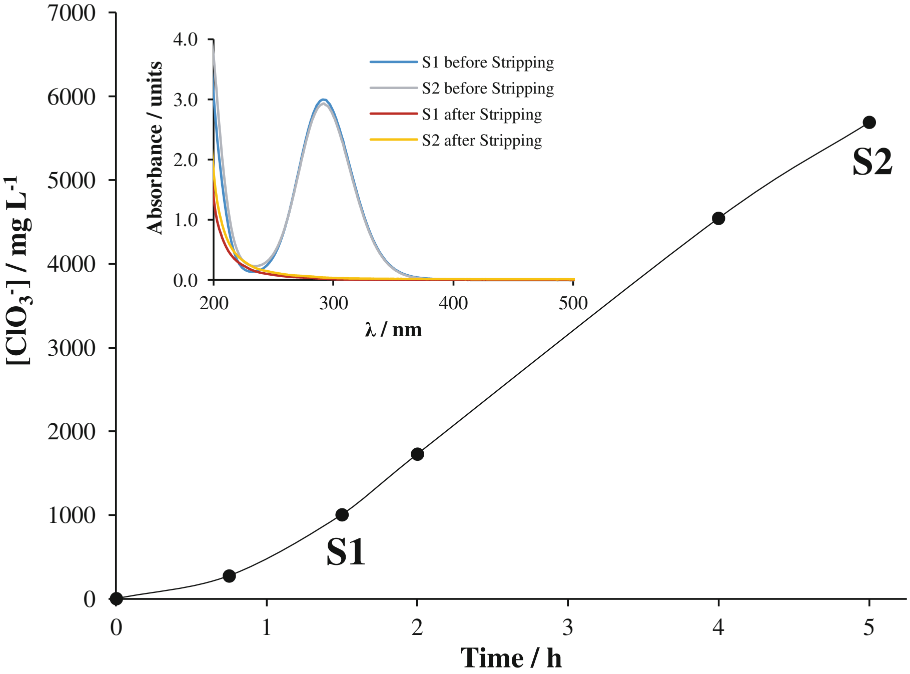

Figure 5. Production of ClO_3^- during the electrolysis (semicontinuous mode) of 20 g L^{-1} NaCl. $j = 50$ mA cm^{-2}, $T_{Electrolysis} = 50$ °C. The inset panel shows UV–visible spectra of samples S1 and S2 before and after the stripping process showing exhaustion of the concentration of hypochlorite/chlorine.

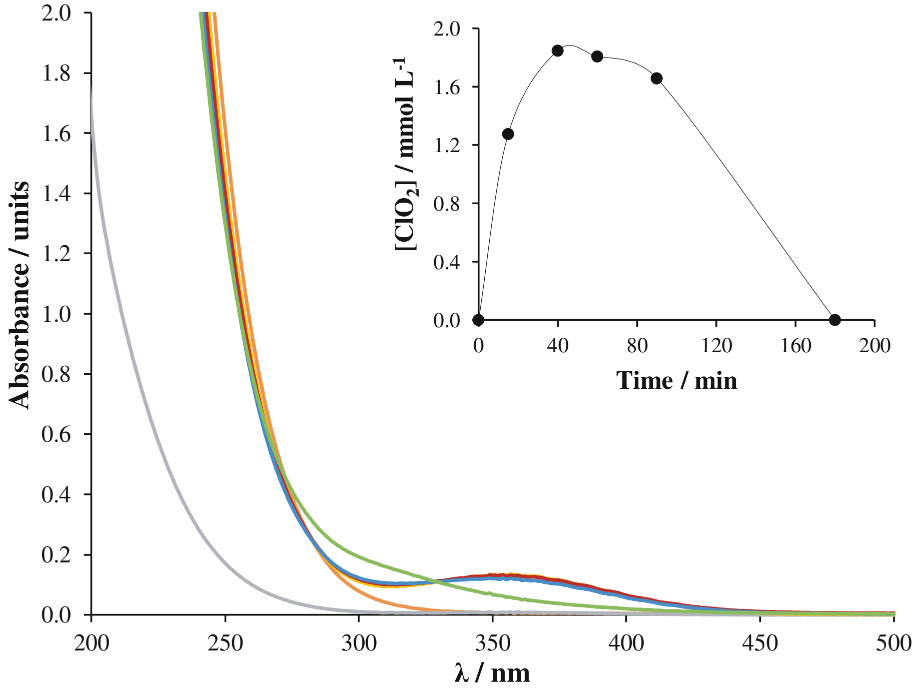

Figure 6. Changes in the UV–visible spectra in liquid phase during ClO_2 production test from electrochemically produced chlorate of sample S1. (▬) 0 h, (▬) 15 min, (▬) 40 min, (▬) 60 min, (▬) 90 min and (▬) 180 min. Inset panel shows the concentration of ClO_2 produced in the system during the reaction.

Figure 2 shows the effect of current density on the speciation of chlorine after 5 h of electrolysis. As expected, because of the higher electric charge passed, the higher the current density, the higher the progress of the oxidation. In addition, a positive effect of temperature also was noticed. There was a very important reduction in the concentration of the chlorides during the electrolysis of the solution, down to values at which it is still not limiting the rate of the processes as indicated by the linear decay. This was not the case in the electrolysis of the brine, where huge concentrations of chloride remained unreacted at the end of the tests. At the highest current density and temperature tested, the concentrations of chlorate after 5 h of operation were, for the brackish solution and the brine, 5.51 and 9.14 g L^{-1}, respectively, which correspond to 45.43% and 7.53% of the total chlorine

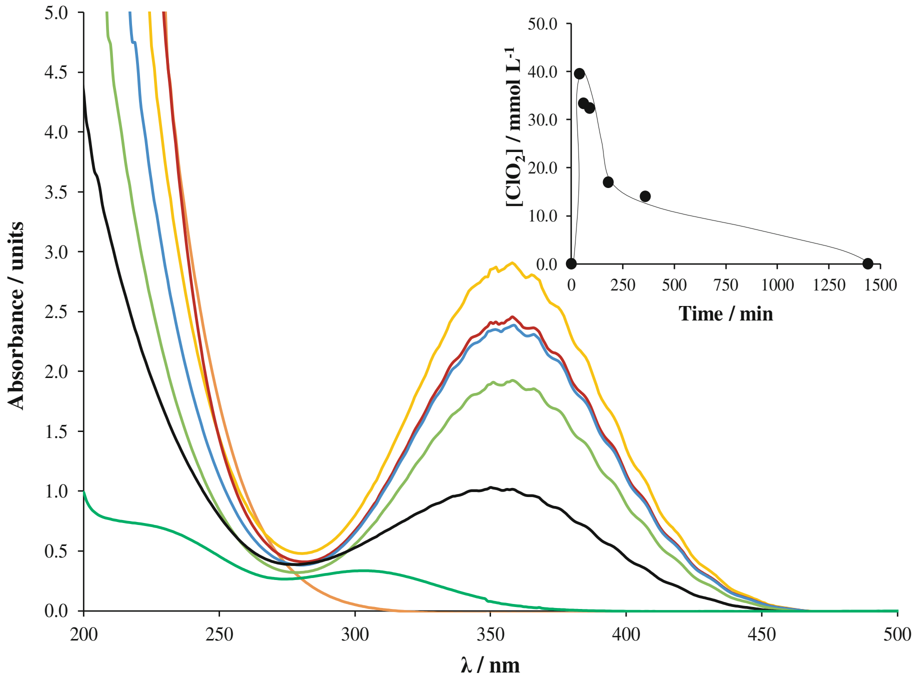

Figure 7. Changes in the UV–visible spectra in liquid phase during ClO_2 production test from electrochemically produce chlorate of sample S2. (▬) 0 h, (▬) 40 min, (▬) 60 min, (▬) 90 min, (▬) 180 min, (▬) 360 min and (▬) 1440 min. Inset panel shows the concentration of ClO_2 produced in the system during the reaction.

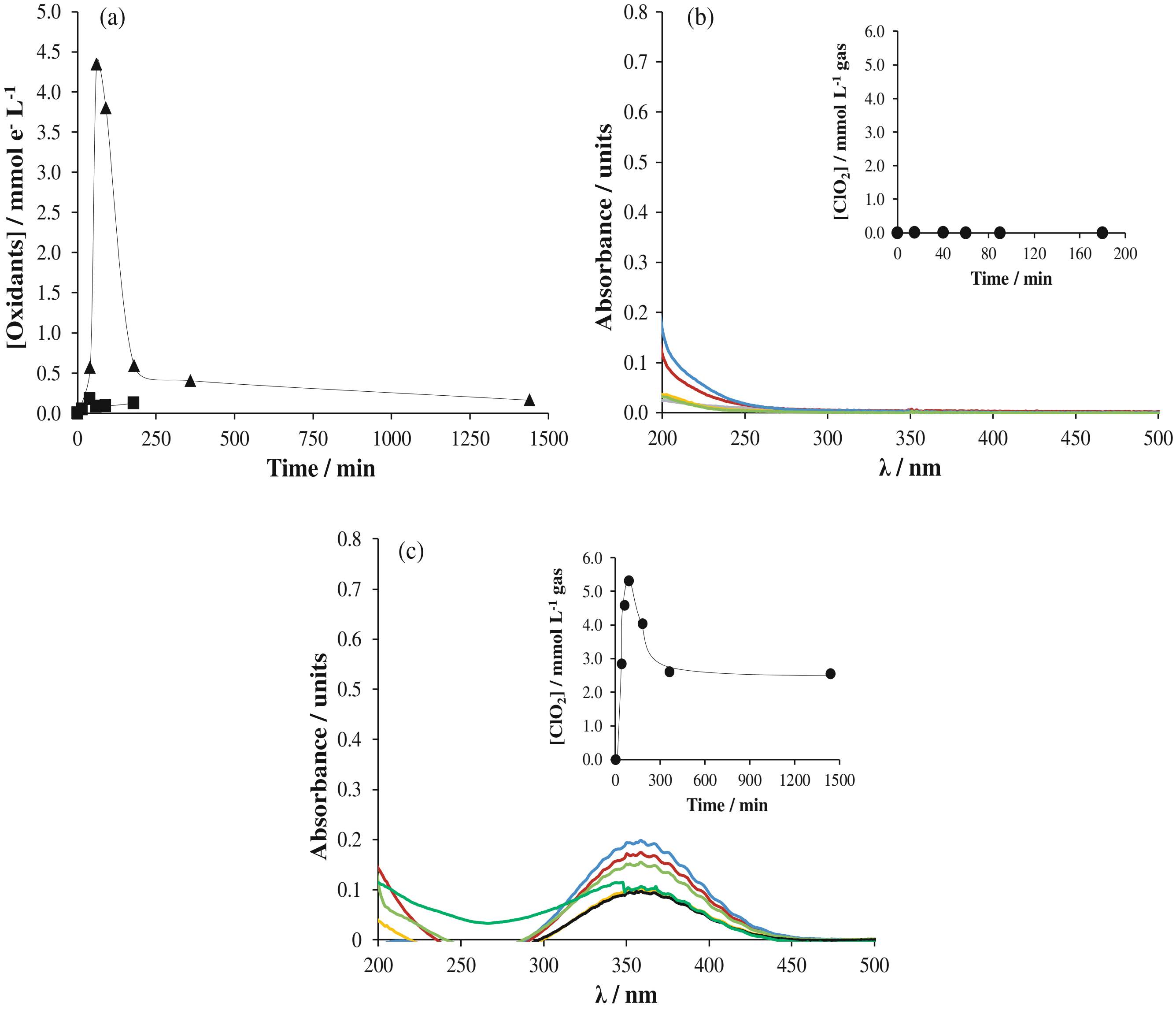

Figure 8. (a) Evolution of oxidants in gas phase during ClO_2 production from electrochemically produced chlorate of samples S1 (■) and S2 (▲). Changes in the UV–visible spectra in gas phase during ClO_2 production test from electrochemically produced chlorate of samles S1 (b) and S2 (c). (▬) 15 min, (▬) 40 min, (▬) 60 min, (▬) 90 min and (▬) 180 min, (▬) 360 min and (▬)1440 min. In (b) and (c), inset panels show the concentration of ClO_2 produced in the system during the reaction.

present in the initial raw material solution. In the same tests, the production of chlorite was 2.75 and 7.12 g L^{-1}, representing 22.69% and 5.87% of the chlorine. Hence, conversion of chloride into species susceptible to forming ClO_2 is 68.12% for the brackish solution and only 13.4% for the brine. This means that operating with brine allows a higher concentration of chlorates to be obtained, but into a liquid in which the purity is much lower.

Current efficiency is a very important parameter for chlorate production. Changes in the total values are shown in Fig. 3; as seen, during all tests, this parameter decreases continuously from maximum values of ≈80%, attained at the beginning of the electrolysis of the brine at high temperatures, down to 15%, obtained at the end of the electrolysis of the solution at 60 °C. Because the concentration of chloride is not limiting the efficiency (even in the electrolysis of the solution), this decrease in efficiency must be explained in terms of the interaction of the oxoanions of chlorine with other species, such as H_2O_2 formed cathodically, as pointed out in previous works of our group.[11,21,22]

The effect of current density on efficiency is very low, almost negligible as compared to that of temperature and concentration of salt in the electrolyte. This confirms that there is not a real competition between the chlorine and the oxygen evolution reactions within the operation conditions evaluated. Figure 4 shows the global coulombic efficiency after 5 hs of operation as a function of the current density, where average values of 11.0 ± 1.9, 16.0 ± 2.2, 28.7 ± 4.2 and 41.7 ± 5.9% for the electrolysis of the concentrated solutions at 60 and 80 °C and the brines at 60 and 80 °C, respectively, demonstrate an improvement of the current efficiency of 21.67% when increasing concentration, and 8.96% when increasing temperature.

Use of electrogenerated chlorate to produce chlorine dioxide

In order to check the feasibility of using directly electrochemically produced chlorate solutions in the production of ClO_2, chlorates were manufactured in the same cell operated in semicontinuous mode by feeding the electrochemical cell with 18 mL h^{-1} of a 20 g L^{-1} NaCl solution at 50 °C maintaining a current density of 50 mA cm^{-2}. Two samples were taken at applied current charges of 21.11 Ah L^{-1} (S1) and 57.35 Ah L^{-1} (S2). As shown in Fig. 5, chlorate concentrations of both samples were 1000 mg L^{-1} (S1) and 5700 mg L^{-1} (S2). Then the samples were stripped with air to remove chlorine/hypochlorite. The inset of Fig. 5 shows that the absorption peaks at 300 nm [associated to the mixture of chlorine (310 nm) and hypochlorous acid (323 nm)] disappear after the stripping. This confirms their exhaustion and that the reagent produced electrochemically contains only chlorates and chlorites (the shoulder near 200 nm correspond to the overlapping of the peaks of chlorate 200 nm and the absorption peak of chlorite at 230 nm). Because of our objective of simplicity, no other purification stages were applied.

Thus, after stripping with air, samples (10 mL) from S1 and S2 were mixed with H_2O_2 (4 mL, 33 000 mg L^{-1}) and H_2SO_4 (25 mL, 5 mol L–1) to produce ClO_2. The cocktail of oxidants formed during electrolysis is very complex and the addition of reagents to chemically quantify each oxidant can interfere with the results; hence, the reaction was assesse spectrophotometrically. Figures 6 and 7 show the UV–visible spectra recorded at different reaction times and the concentrations of ClO_2 (in the inset). ClO_2 absorbs at 360 nm and as seen, the concentration was strongly related to the amount of chlorate oxidized (the quality of the reagent used was different in S1 and S2) and time. ClO_2 is exhausted because of the stripping with air of the reaction mixture and the further progress in its reduction by H_2O_2 [Eqn (7)].

$$ClO_3^- \overset{H_2O_2}{\rightarrow} ClO_2 \overset{H_2O_2}{\rightarrow} ClO_2^- \overset{H_2O_2}{\rightarrow} ClO^- \qquad (7)$$

Thus, H_2O_2 reduces chlorates to ClO_2 in a first step and then the reaction may follow down to the production of chlorite or hypochlorous acid/hypochlorite if excess H_2O_2 is contained in the reaction mixture. The important light absorption in the range 200–300 nm attests to the formation of chlorite, which presents an absorption oxidation peak at 230 nm. This chlorite anion is contained in the initial samples because it is a product of the electrolysis of NaCl and it is not stripped by air. However, its concentration increased over the experimental time as it demonstrated by the shift of the curve to higher wavelengths. In most samples the concentrations were as high as to mask the peaks, but this peak was clearly observed in the spectra taken at 1440 min as shown in Fig. 7 (with S2), as well as the peak corresponding to hypochlorous acid (323) and chlorine (310 nm) that were not observed in the other spectra recorded. Thus, it is important to point out that after the chemical reaction tests, in the case of the sample S1 all chlorate was exhausted and 1641.7 mg L^{-1} H_2O_2 still remained in the reaction mixture, and this explains the complete depletion of ClO_2.

Meanwhile, during the processing of S2, the final concentration of chlorates was 41.3 mg L^{-1} and that of H_2O_2 was only 344.3 mg L^{-1}, which also explains the higher presence of ClO_2 and its final disappearance at the end of the tests.

The species formed in the reaction tanks were desorbed with bubbled air and the stripped gaseous streams, containing ClO_2, were collected in tanks containing 10 mL KI (1 g L^{-1}) to evaluate its oxidation capacity and in tanks containing 10 mL water to quantify the stripped oxidants. The oxidation capacity of these streams is shown in Fig. 8(a). These results highlight the important differences observed between the use of the two qualities of chlorate (S1 and S2). In addition, Fig. 8(b) and (c) show the UV–visible spectra of samples collected in tanks with water. The peak corresponding to ClO_2 (especially for reagent 2) is clearly visible and spectra indicate that the gas flow did not contain chlorite or hypochlorous acid.

Hence, results demonstrate that ClO_2 can be produced from the mixture of product of the electrolysis of NaCl (in which hypochlorite is stripped) with commercial H_2O_2. Formation of ClO_2 depends on the concentration of chlorates produced. However, this production depends importantly on the ratios between H_2O_2 and chlorates because ClO_2 is an intermediate in the reduction of chlorates and not the final product, and excess of H_2O_2 leads to the progress of the reaction down to undesirable oxidant species.

CONCLUSIONS

From this work, the following conclusions can be drawn:

- Chlorate can be produced efficiently from the oxidation of NaCl contained in brackish solutions (20 g L^{-1}) and brines (200 g L^{-1}) in single chamber flow electrochemical cells. Efficiencies depend on the operation conditions and concentration of NaCl, but brine is preferred for use in the production of ClO_2 because of the better quality of the reagent solution produced.
- Global coulombic efficiency does not depend importantly on the current density and average values of 11.0 ± 1.9, 16.0 ± 2.2, 28.7 ± 4.2 and 41.7 ± 5.9% were obtained for the electrolysis of the concentrated solutions at 60 and 80 °C and the brines at 60 and 80 °C, respectively, pointing out an improvement of current efficiency of 21.67% when increasing concentration and 8.96% when increasing temperature.
- Operating at 126 mA cm^{-2} and 80°C, 5.51 and 9.14 g L^{-1} chlorate were obtained after 5 h of operation for the brackish solution and the brine, respectively, which corresponded to 45.43% and 7.53% of the total chlorine present in the solution. In the same tests, the production of chlorite was 2.75 and 7.12 g L^{-1}, which represented 22.69% and 5.87% of the chlorine. Hence, conversion of chloride into species susceptible to form ClO_2 was 68.12% for the solution and only 13.4% for the brine, confirming that the brackish solution produces a better reagent.
- Air stripping can be used to remove hypochlorous acid/chlorine from the electrolyte. After 60 min, hypochlorous acid was shifted to chlorine and both were fully exhausted from the liquid.
- Electrochemically produced chlorates can be used to produce ClO_2 by reaction with H_2O_2 in extremely acidic media. Formation of ClO_2 depends on the concentration of chlorates in the electrolyzed solution and, in turn, this production depends importantly on the ratios between H_2O_2 and chlorates. ClO_2 behaves as an intermediate in the reduction of chlorates to chlorine and not as the final product, and excess of H_2O_2 leads to the progress of the reaction down to undesirable oxidant species.
- Chloride dioxide leads to the formation of a gaseous stream with a high oxidation capacity. Stripping of ClO_2 from the reaction media may promote its use as gaseous reagent with important applications in the treatment of VOCs and odors.
- A maximum concentration of 33.3 mmol L^{-1} was obtained starting from a solution containing 68.26 mmol L^{-1} indicating that the maximum conversion obtained was 48.75%. This maximum conversion was obtained at the beginning of the test and then concentrations decreased because of the formation of chlorite and chlorine from the reduction of ClO_2 with H_2O_2. This confirms that these chlorate solutions obtained *in-situ* electrochemically

can be used to manufacture ClO_2, but further work has to be carried out to optimize production of the desired oxidant.

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DECLARATION OF COMPETING INTEREST

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

AUTHOR STATEMENT

Conceptualization: AM, CS, EVDS and MAR; methodology: AM; validation: CS, EVDS and MAR; formal analysis: AM and MKSM; investigation: AM and MKSM; resources: CS and MAR; data curation: AM and MKSM; writing-original draft: AM; writing-review and editing: CS, EVDS and MAR; supervision: CS and MAR; project administration: MAR; funding acquisition: MAR.

REFERENCES

1. Herraiz-Carbone M, Cotillas S, Lacasa E, Canizares P, Rodrigo MA and Saez C, Removal of antibiotic resistant bacteria by electrolysis with diamond anodes: a pretreatment or a tertiary treatment? *J Water Process Eng* **38**:101557 (2020).
2. Jonnalagadda SB and Nadupalli S, Chlorine dioxide for bleaching, industrial applications and water treatment. *Indian Chem Eng* **56**: 123–136 (2014).
3. Vogt, H., Balej, J., Bennett, J.E., Wintzer, P., Sheikh, S.A., Gallone, P. *et al*. *Ullmann's Encyclopedia of Industrial Chemistry*. (2000).
4. Monteiro MKS, Moratalla Á, Sáez C, Dos Santos EV and Rodrigo MA, Production of chlorine dioxide using hydrogen peroxide and chlorates. *Catalysts* **11**:1478 (2021).
5. Qian Y, Chen Y, Jiang Y and Zhang L, A clean production process of sodium chlorite from sodium chlorate. *J Clean Prod* **15**:920–926 (2007).
6. Yin G and Ni Y, The effect of chloride on the HClO2 HOCl2 reaction in a 4.5 Mol/L sulfuric acid solution. *Can J Chem Eng* **76**:248–252 (1998).
7. Bergmann MEH, Iourtchouk T, Schmidt W, Hartmann J, Fischer M, Nüsske G *et al*., Laboratory- and technical-scale comparison of chlorate and perchlorate formation during drinking water electrolysis: a field study. *J Appl Electrochem* **45**:765–778 (2015).
8. Gomes ASO, Busch M, Wildlock M, Simic N and Ahlberg E, Understanding selectivity in the chlorate process: a step towards efficient hydrogen production. *ChemistrySelect* **3**:6683–6690 (2018).
9. Hong CC, Lenzi F and Rapson WH, The kinetics and mechanism of the chloride-chlorate reaction. *Can J Chem Eng* **45**:349–355 (1967).
10. Jung YJ, Baek KW, Oh BS and Kang J-W, An investigation of the formation of chlorate and perchlorate during electrolysis using Pt/Ti electrodes: the effects of pH and reactive oxygen species and the results of kinetic studies. *Water Res* **44**:5345–5355 (2010).
11. Mattos-Costa FI, de Lima-Neto P, Machado SAS and Avaca LA, Characterisation of surfaces modified by sol-gel derived RuxIr1−xO2 coatings for oxygen evolution in acid medium. *Electrochim Acta* **44**: 1515–1523 (1998).
12. Zeradjanin AR, Menzel N and Strasser P, Role of water in the chlorine evolution reaction at ruo2-based electrodes—understanding electrocatalysis as a resonance phenomenon. *ChemSusChem* **5**:1897–1904 (2012).
13. Sales Monteiro MK, Sales Monteiro MM, de Melo Henrique AM, Llanos J, Saez C, Dos Santos EV *et al*., A review on the electrochemical production of chlorine dioxide from chlorates and hydrogen peroxide. *Curr Opin Electrochem* **27**:100685 (2021).
14. Santos GOS, Eguiluz KIB, Salazar-Banda GR, Sáez C and Rodrigo MA, Understanding the electrolytic generation of sulfate and chlorine oxidative species with different boron-doped diamond anodes. *J Electroanal Chem* **857**:113756 (2020).
15. Crump B, Ernst WR and Neumann HM, Influence of H2O2 on a chloride-dependent reaction path to chlorine dioxide. *AIChE J* **44**:2494–2500 (1998).
16. Pillai KC, Kwon TO, Park BB and Moon IS, Studies on process parameters for chlorine dioxide production using IrO2 anode in an undivided electrochemical cell. *J Hazard Mater* **164**:812–819 (2009).
17. Szabó M, Lihi N, Simic N and Fábián I, Potential catalysts for the production of NaClO3 in the decomposition of HOCl. *Chem Eng Res Des* **169**: 97–102 (2021).
18. Burke M, Tenney J, Indu B, Hoq MF, Carr S and Ernst WR, Kinetics of hydrogen peroxide-chlorate reaction in the formation of chlorine dioxide. *Ind Eng Chem Res* **32**:1449–1456 (1993).
19. Aieta EM, Roberts PV and Hernandez M, Determination of chlorine dioxide, chlorine, chlorite, and chlorate in water. *J Am Water Work Assoc* **76**:64–70 (1984).
20. Eisenberg G, Colorimetric Determination of hydrogen peroxide. *Ind Eng Chem Anal Ed* **15**:327–328 (1943).
21. Moratalla Á, Araújo DM, Moura GOMA, Lacasa E, Cañizares P, Rodrigo MA *et al*., Pressurized electro-Fenton for the reduction of the environmental impact of antibiotics. *Sep Purif Technol* **276**: 119398 (2021).
22. Rodríguez-Peña M, Pérez JAB, Llanos J, Saez C, Barrera-Díaz CE and Rodrigo MA, Understanding ozone generation in electrochemical cells at mild pHs. *Electrochim Acta* **376**:138033 (2021).