A review on the electrochemical production of chlorine dioxide from chlorates and hydrogen peroxide

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Abstract

Chlorine dioxide is one of the most interesting oxidants because it combines a strong capacity of oxidation with low formation of hazardous byproducts such as chlorinated organics during its application. Because of that, it is widely used in disinfection of drinking water and, currently, it is aimed to be used in the disinfection of COVID19 from surfaces and buildings. Although it is usually produced by the chemical interaction of chlorite with hypochlorite/chlorine or hydrochloric acid, one interesting alternative for its production is the combination in strongly acidic media of chlorate and hydrogen peroxide. Both compounds are known to be efficiently manufactured with electrochemical technology, opening the possibility of a complete electrochemical process to produce this important oxidant. This review summarizes the recent progress in the electrochemical production of the two raw materials, as well as the complete electrochemical production of chlorine dioxide, not only paying attention to the scientific literature but, most importantly, to recent patents, trying to see in which TRL are each of the technologies and what are the elements of the value chain required for a complete implementation of the technology.

Keywords

Electrochemical production; chlorate; hydrogen peroxide; chlorine dioxide

Highlights

- Chlorine dioxide can be efficiently produced from hydrogen peroxide and chlorate in acidic media
- Hydrogen peroxide production can be improved operating at high pressure and with special cell design
- Cathode has a primary influence on the production of hydrogen peroxide
- In situ electrochemical production of chlorine dioxide is feasible
- Low TRL of hydrogen peroxide production becomes the bottleneck of the electrochemical production of chlorine dioxide

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1. Introduction

Production of oxidants is a topic of the major interest for our Society. They are used in many different applications, ranging from their use as reagents in the production of many chemicals to the removal of hazardous anthropogenic pollutants contained in industrial wastes, or to the disinfection of water, where they can be used to remove not only pathogenic bacteria but also other hazardous species like viruses or fungi.

Although several important oxidants are produced using chemical technologies (e.g. hydrogen peroxide is mostly produced by the anthraquinone method), the electrochemical technology has demonstrated to be the most interesting for the production of a wide range of powerful and useful oxidants. Thus, chlorine, which is the most important oxidant nowadays, not only in the industry but also in disinfection, is produced by the very well-known chloralkaline process, in which the development of mixed metal oxides (MMO) anodes in the late sixties of the twentieth century was a real turning point. Their robustness, and the promotion in the oxidation of chlorides to chlorine with respect to the competing oxygen evolution side reaction, have allowed to obtain really high current efficiencies[1]. Several decades later of the development of MMO electrodes, other interesting electrode materials, in special the boron-doped diamond coatings, demonstrated their ability to produce efficiently many other interesting oxidants[2]. Thus, species, which were difficult to be produced up to that moment by chemical or electrochemical methods, were started to be successfully manufactured and, nowadays, the good results obtained are motivating that many of them are undergoing important research effort in order to enlarge their technology readiness level (TRL) up to levels in which the full value-chain could be completed, approaching fast to their potential commercialization.

The most important family of oxidants produced with the diamond coating electrodes are the peroxo-species[3], characterized by the presence of the functional group -O-O- and which includes peroxosulfates[4], peroxophosphates[5], peroxocarbonates[6] and peroxoacetates[7]. In addition, these new powerful electrodes can promote the oxidation of chloride, not only to chlorine but also to chlorates and perchlorate[8]. These later species, from the thermodynamic point of view, are very powerful oxidants, although their action is very limited at room temperature because of kinetic considerations and it is only promoted when the temperature is raised, where they may have important uses as explosives. Other important oxidants that are produced with these new electrodes includes perbromates[9] and ferrates[10], which are extremely difficult to be produced

with other electrochemical technologies. Also, it is worth to highlight ozone, which can be generated efficiency, especially using special cell designs, being very efficient the use of PEM electrolyzers for its production, according to recent studies [11].

Anyway, chlorine remains as the star of the oxidants and chloralkaline industry has nowadays a huge importance. However, because of the important chemistry with organics, chlorine has many drawbacks related to the impact on environment and health, and the development of efficient processes for the production other oxidants is a real necessity[12, 13]. This becomes an acute problem, because very few alternatives appear as realistic for the disinfection of water. Among them, chlorine dioxide emerges as the most promising[14], although sometimes its use is overvalued and, even in the present COVID19 pandemic, it has been proposed not only its efficient application as a solution for killing the virus on surfaces or in air, but also its use as medicine which, in addition to be very dangerous for human health, it has no scientific sense. Also, the formation of chlorite can become a serious drawback, although it can be managed easily according to the existing experience. Thus, chlorine dioxide is known to be one of the most important disinfectants, very appreciated in Water Treatment Facilities (WTF) because it avoids the formation of organochlorinated species[15]. Typically, in WTFs, is made on site, by combination of chlorite and hypochlorite/chlorine or hydrochloric acid[16-18]. However, alternatively, it can be rendered by reaction of chlorate with methanol, sulfur dioxide or hydrogen peroxide. Here, is where a niche of opportunity appears for electrochemical technology because the anodic transformation of chloride to chlorate is a well-known process, as well as the cathodic production of hydrogen peroxide from oxygen.

This review focuses on the production of chloride dioxide from this two precursors, shedding light on the recent knowledge about the production of each of the two reagents and their combination, by summarizing the expertise published or patented in the last five years. This information will be discussed at the light of the technology readiness level, to point out how far is the technology for the full-scale applicability.

2. Electrochemical production of sodium chlorate.

Chlorate is currently considered as a commodity, and it is produced industrially by electrochemical oxidation of concentrated brines of sodium chloride (over 300 g dm^{-3}) at high temperatures (over 60ºC) and acidic pHs in non-divided cells, with efficiencies that are over 90% when dichromate is added in the feeding brine

formulation. Technology is fully optimized and cell voltages in the nearness of 3.0V, and current densities in the range 1500-4000 A m^{-2}, are applied with specific energy consumptions near 5 kWh per kg of chlorate produced. Industrial facilities do not only consist of the electrochemical cells but they also have a pre-electrochemical treatment consisting of brine purification to remove different impurities contained in the sodium chloride raw material (fluoride, sulfates, calcium, …) and a post-electrochemical treatment consisting of the surplus hypochlorite removal (using heat and hydrogen peroxide), crystallization of the chlorate, centrifugation and drying. The electrochemical cell can integrate or, alternatively, should be connected to a chemical reactor, where the slow chemical chlorate formation takes place. Cooling is necessary to regulate temperature because of the important amounts of heat dissipated. Reaction system is rather complex, consisting of a sequence of several electrolytic and chemical processes. The first stage is the oxidation of chloride to chlorine (eq 1) which competes with the oxidation of water to form oxygen (eq 2). Although historically different types of anodes were used for this process, since the last quarter of the past century use of suitable formulations of mixed metal oxides have demonstrated to be the key to allow a promotion of the first reaction, reaching outstanding efficiencies. On the cathode, the main reaction is the reduction of water to form hydrogen and hydroxyl ions (eq 3). These ions promote the disproportionation of chlorine to chloride and hypochlorite (eq 4), which later continued with further disproportionation reactions up to the formation of chlorate (eq 5). Alternatively, the electrochemical oxidation of hypochlorite to chlorate is also feasible (eq 6), being promoted with anodes such as the diamond coatings which, in turn, do not stop oxidizing in this point but also can continue up to the formation of perchlorates (eq 7). Role of hydroxyl radicals in these two later processes seems to be very important according to recent studies [19].
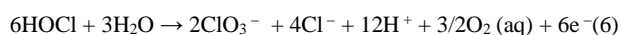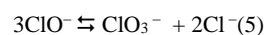
$$2\,Cl^- \rightarrow Cl_2(aq) + 2e^- \quad (1)$$

$$2H_2O \rightarrow O_2(aq) + 4\,H^+ + 4e^- \quad (2)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \quad (3)$$

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O \quad (4)$$

$$3ClO^- \leftrightarrows ClO_3^- + 2Cl^- \quad (5)$$

$$6HOCl + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2O_2\ (aq) + 6e^- \quad (6)$$

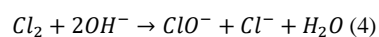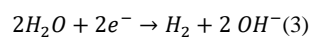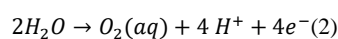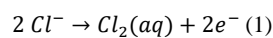$$2ClO_3^- + H_2O \rightarrow 2ClO_4^- + 2H^+ + 2\,e^- \quad (7)$$

Table 1 shows some of the recent progress regarding this process. It is important to consider that most of them are related to fundamental studies at very low TRL, trying to develop new electrodic materials, avoid or promote the formation of perchlorate or, simply, to elucidate the role of dichromate on the efficient production of chlorates. Also, to prevent the formation of chlorates during the treatment of water or wastewater containing chlorides, which has been found to be a major problem for a safe supply of disinfected water or for a proper reclaiming of wastewater. Evaluation of the production of chlorates with anodes consisting of diamond coatings has also been a very important point of concern, and comparisons of the performance of these novel electrodes with different formulations of metal mixed oxides (MMO) has attracted the interest of researchers. However, although this new electrode has demonstrated a much higher oxidation capacity, production of perchlorates has been found as a major drawback and MMO still remains as the reference electrode to produce chlorates.

Table 1. Recent works related to chlorate production

Objective / Technology evaluated	Electrolyte composition / electrode type /operation conditions	Main conclusions drawn	Ref.
Determination of the speciation of electrochemically generated chlorine-related species on the $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode / Understanding the chloride mediated oxidation of real effluents/ Not related to chlorate production but on chlorine speciation during wastewater treatment.	Aqueous solution containing NaCl (1.25 g L^{-1}) / $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode/ Current densities ranging from 25 to 75 mA cm^{-2}	. Oxygen evolution inhibition depends predominantly on the specific electrochemical species formed (Cl_2, HClO, ClO^-, chlorite, chlorine dioxide). The elimination of organic matter was achieved ranging from 80% to 86%.	[20]
Elucidation of the mechanisms of perchlorate (ClO_4^-) formation from chlorate (ClO_3^-) on boron-doped diamond (BDD) film anodes by use of a rotating disk electrode reactor.	Reaction rates for ClO_3^- removal and ClO_4^- formation were measured at constant potential conditions by use of a rotating disk electrode (RDE) experimental setup / Ultrananocrystalline BDD films p-silicon substrates/ Rates of ClO_4^- formation were determined as functions of the electrode potential (2.29 – 2.70 V/ standard hydrogen electrode, SHE) and temperature (10 – 40 °C).	Combination of direct electron transfer and hydroxyl radical oxidation with a measured apparent activation energy of 6.9 ± 1.8 kJ mol^{-1} at a potential of 2.60 V/SHE/ ClO_4^- production rates were zero order with respect to ClO_3^- concentration.	[21]

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The electrochemical generation of several oxidative species was studied at the surfaces of five commercial boron-doped diamond anodes with different doping levels (100 –8000 ppm)/ All materials evaluated were characterized by linear sweep voltammetry, cyclic voltammetry, electrochemical impedance spectroscopy, contact angle, and scanning electron microscopy, as well as by bulk electrolysis/	The electrolyte solution was prepared by 3.0 g L^{-1} Na_2SO_4 or 3.7 g L^{-1} of NaCl and H_2SO_4 0.5 mol L^{-1}/ BDD anodes/ CV measurements were performed at the potential limits of $-0.7 - +1.1$ V with a scan rate of 100 mV s^{-1} in a solution of $[Fe (CN)_6]^{3-}/^{4-}$ 0.01 mol L^{-1} in 0.1 mol L^{-1} Na_2SO_4. Linear sweep voltammetry experiments were performed in the potential interval of $0.0 - 2.7$ V.	Low boron doping favors the formation of hydroxyl radicals, while higher doping levels favor the direct oxidation of sulfate and chloride on the surface of the diamond electrodes.	[22]
The behavior of RuO_2 and DSA anodes in hypochlorite oxidation is compared to outline limitations of the anode performance in the chlorate process/ Comparison of the voltammetric and DEMS (electrochemical mass spectrometery) characteristics.	Solution based on 0.1 M $NaClO_4$ electrolyte (30 mM of hypochlorite/hypochlorous acid)/ Nanocrystalline ruthenium dioxide (RuO_2) and DSA ($Ti_{0.7}Ru_{0.3}O_2$) anodes/ All experiments were carried out at polarization rate of 5mV/s in the potential range between 0.3 to 1.3 V vs. Ag/AgCl.	The catalytic hypochlorite decomposition observed for DSA represents a serious barrier for the chlorate process, outlining the need of further optimization of the industrial grade anode for the chlorate process.	[23]
Assessment of the viability of the electrochemical production of perchlorate from such high concentration of the raw materials/ The valorization of brines, with concentrations like those produced by reverse osmosis or electrodialysis processes, by electrolysis with diamond anodes is evaluated.	Solutions of NaCl (with target concentrations ranging from 1.0 to 2.0 M and an additional test at 5.0 M) / BDD was used as the anode and stainless steel was used as the cathode/ The anolyte consisted of different solutions of sodium chloride with concentrations ranging from 1.0 to 5.0 M, and the catholyte consisted of 1.0 M solutions of sodium hydroxide.	It is possible to transform more than 80% of the initial chloride concentration into perchlorate, with current efficiencies higher than 70%, regardless of the initial concentration of sodium chloride contained in the brine.	[8]
Provide relevant information to better understand the fundamental mechanisms of chloride electro-chlorination and oxidation processes in BDD / A semi-quantitative analysis of various volatile species produced during the electrolysis of highly saline water at BDD electrode has been conducted by differential electrochemical mass spectrometry (DEMS) using the dual thin layer flow through cell.	Sodium chloride (99.9% ChemSolute) was used as main component of the water matrix to prepare synthetic seawater (0.6M NaCl) / BDD working electrode/ Potential step experiments were conducted holding at 0 V vs. Ag/AgCl in the supporting electrolyte with the desired pH for 60 s, then stepped to 3 V vs. Ag/AgCl for 100 s (steady state current transients). Afterwards, the potential was stepped back to 0 V.	The quantification of released species highlighted that the evolution of chlorine corresponds to a ca. 80% of the current efficiency, which is a significant contribution to the overall electro-chlorination process.	[24]

Influence of the electrode materials and technical cells for chlorate and perchlorate formation potential under laboratory- and technical-scale conditions/ Electrochemical Water Activation or Inline Electrolysis (IE).	Natural and synthetic water samples with chloride contents between 20 mg dm^{-3} (0.56 mmol L^{-1}) and 250 mg L^{-1} (7.04 mmol L^{-1})/ Room temperature, at current densities between 10 and 571 A m^{-2}/ Three MMO electrodes with active coatings on Ti sheets and the BDD material were studied with a rotating anode.	Only one MMO material showed chlorate formation in the laboratory experiments, whereas in technical cells, in all four cases, chlorate was detected, but perchlorate was not found on MMO anodes.	[25]
Evaluation of electrocatalytic materials which can be used as efficient cathode to produce sodium chlorate.	The materials consist of nanocrystalline iron aluminide alloys doped with catalytic species such as Ru.	Contrary to the previously reported Ti$_2$RuFe catalytic material, these new electrocatalysts do not absorb hydrogen and, are more stable during the hydrogen evolution reaction.	[26]
Evaluation of the role and importance of chromium (VI) in the chlorate manufacturing process/ Sodium chlorate is industrially produced by electrolysis of an aqueous salt solution, in which chromium (VI) constitutes an important excipient component.	Cell voltage (V) 2.9–3.7; Current density (kA m^{-2}) 1.5–4; Temperature (ºC) 65–90; NaCl concentration (g dm^{-3}) 70–150; NaClO$_3$ concentration (g dm^{-3}) 450–650; NaClO concentration (g dm^{-3}) 1–5; Na$_2$Cr$_2$O$_7$ concentration (g dm^{-3}) 1–6; Electrolyte pH 5.5 – 7.0; Electrode distance (mm) ~3.	There is no way to efficiently run chlorate electrolysis without the addition of chromium (VI). It is shed light on the role of chromium.	[27]
Elucidation of the role of chromate. Results were validated with data from bench scale and pilot plant trials.	Trials were made in a 500 mL batch reactor in the ranges 70–80∘C, 5.0–7.7 mol/L ionic strength, 0–5 g/L Na$_2$Cr$_2$O$_7$ and pH 5.8–7.	The fraction of chlorate formed by chromate catalysis depends primarily on the dichromate concentration but also on pH and other operation parameters. Under industrial operation conditions, it is reasonable to assume that 30–70% of the chlorate is formed by chromate catalysis.	[28]
Evaluation of the influence of several treatments (oxidation with potassium permanganate, chlorine dioxide and sodium hypochlorite, coagulation/flocculation with ferric chloride and aluminum sulfate, filtration and adsorption onto activated carbon) on chlorine dioxide consumption and on chlorite and chlorate formation in the final oxidation/disinfection stage/ Not related to electrochemistry but results with great applicability.	Laboratory scale employing water samples collected from the DWTP of Cremona (Italy).	The chlorine dioxide demand is high when sodium hypochlorite or potassium permanganate are employed in pre-oxidation. On the other hand, chlorine dioxide leads to the highest production of chlorite and chlorate.	[29]
Photoanodic chlorine generation and chlorate formation were investigated using a nanoporous TiO$_2$ photo-electrode	The electrochemical experiments were performed by biasing a TiO$_2$ anode with a potential of 1.0 V vs. SCE with 7.4 mW/cm^2 UV illumination. A 100 mL test solution	Chlorine formation increased over time finally reaching a steady-state concentration of 42 mg/L in 45 rain. On the other hand, chlorate formation was observed after only 5 min	[30]

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	containing 1.0×10^{-2} M NaCl was used in each compartment.	irradiation and increased over time.	
The characteristics of chlorate (ClO_3^-) and perchlorate (ClO_4^-) formation were studied during the electrolysis of water containing chloride ions (Cl^-).	Concentration of Cl^- (6 – 30 mg L^{-1}), 10 mM t-BuOH and 0.17 mM $Na_2S_2O_3$ / the anode and cathode, were made of the same material, using an undivided Pt/Ti plate electrode/ Current density (192 to 270 mA cm^{-2}); applied voltages (25 – 30 V); electric conductivity was adjusted to 250 mS cm^{-1} using NaCl and K_2SO_4; water temperature 20 (±2 ºC); pH was adjusted in 3.6, 5.5, 7.2, 8.0 and 9.0	The direct oxidation reaction rate of Cl^- to ClO_3^- was 13%. The key formation pathways of ClO_3^- and ClO_4^- were studied using kinetic model development.	[31]
The products of the oxidation at BDD anode of chloride ions in aqueous solutions were identified during galvanostatic electrolyses performed in a filter-press reactor operating both in batch and continuous mode	Solution contained 100 ppm of chloride ions/ Boron doped diamond (BDD) anode/ Anodic current density values ranging from 2.5 to 7.6 mA cm^{-2} / Solutions containing 200 mg dm^{-3} of SO_4^{2-} as supporting electrolyte and different amount of Cl^- ranging from 50 to 2500 mg dm^{-3}.	Low chloride concentrations electrolysis with BDD anode produce a mixture of powerful oxidant: low current density, high mass transfer conditions and low residence time were found as optimal conditions to maximize the concentration of oxidants and minimize the concentration of chlorates.	[32]

Anyway, it is worth to take in mind that production of chlorates is nowadays at a very high TRL. That is, the most important aspects are fully develop by process engineers in the industry for the full-scale production, which is a really-mature technology. Consequently, they are not in the primary focus on academic researchers but of researchers of private companies aiming to improve the efficiency of the processes and this type of progress is not typically disseminated but preserved in order to give a commercial advantage in the competitivity of companies.

3. Electrochemical production of hydrogen peroxide

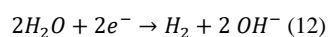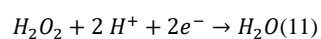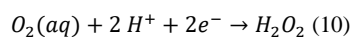Although hydrogen peroxide can be formed electrochemically on the surface of the anode by oxidation of water (eq 8), the harsh oxidation conditions generated on this surface and in its nearness leads to further oxidation of this oxidant molecule to other more oxidized species (oxygen and even ozone) and, hence, it is not considered as an efficient pathway to explain its generation.

$$2H_2O \rightarrow H_2O_2 + 2\,H^+ + 2e^- \ (8)$$
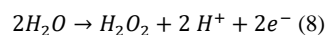
Alternatively, it can also be generated by decomposition of other anodically formed species, such as peroxosulfate, which can either be not only electrochemical but also chemical, specially promoted by operation at high temperatures (eq 9)

$$H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2 \ (9)$$
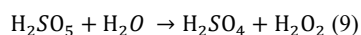
However, the reduction of oxygen on the surface of the cathode, summarized in equation 10, is known to be the key reaction involved in the production of this oxidant and this reaction competes with the further reduction of this oxidant to water (eq 11) and with the reduction of water to hydrogen (eq 12).

$$O_2(aq) + 2\,H^+ + 2e^- \rightarrow H_2O_2 \ (10)$$

$$H_2O_2 + 2\,H^+ + 2e^- \rightarrow H_2O \ (11)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \ (12)$$

Depending on the cathodic potential, the production of hydrogen peroxide can be promoted with respect to the formation of the other two competing species. In fact, this reaction is known to be very sensitive to many factors and in order to reach high rates for the production of hydrogen peroxide the system should include the development of 1) highly catalytic cathodic surfaces which allows the efficient transformation of oxygen into hydrogen peroxide[33], 2) pressurization to improve the solubility of oxygen and, hence, decrease mass transport limitations[34], 3) improve gas-liquid contact and minimize compression energy consumption by using jet aeration[35, 36] and 4) improve the mechanical design of the cell by using a flow-through cathode and minimize the ohmic resistance by including microfluidic strategy[36, 37]. This way, efficiencies nearly 100% can be reached. These values are very competitive but, event that, the anthraquinone method remains to be the most used nowadays and many efforts has still to be made to fill in the complete value chain of this alternative production in particular trying to obtain formulations for the cathode stable enough as to be applied industrially. Table 2 supports all these conclusions by summarizing the recent progress found in the literature regarding hydrogen peroxide production.

Table 2. Recent works related to hydrogen peroxide production

Objective / Technology evaluated	Electrolyte composition / electrode type /operation conditions	Main conclusions	Ref.
Evaluation of electrocatalysts produced from ceria high aspect ratio nanostructures (CeO_2 HARN) supported on black carbon (Vulcan XC-72) in different mass proportions of CeO_2 HARN (1%, 2.5%, 4%, 5.5% and 10%) by examining the oxygen reduction reaction (ORR) in alkaline medium (1 mol L^{-1} NaOH) for the electro-generation of H_2O_2.	1 mol L^{-1} NaOH saturated with O_2 / Vulcan XC-72 and Pt/C E-TEK/ The CeO_2 HARN were prepared via a hydrothermal method and were supported on Vulcan XC-72 via an impregnation method.	The CeO_2 HARN/C-based electrocatalysts is promising for in situ H_2O_2 electro-generation via electrochemical advanced oxidation processes. The catalyst containing 1% CeO_2 HARN shows more promising results and contains a low metallic oxide load supported on the carbon, increasing its cost-benefit.	[38]
A nitric acid modified graphite / polytetrafluoroethylene (PTFE) composite cathode with exterior hydrophobic film was fabricated for cost-effective electro-generation of hydrogen peroxide (H_2O_2).	250 mL of 0.1 M Na_2SO_4 and flow rate of 2.0 L min^{-1} by an air pump to feed O_2 / utilizing HNO_3 modified graphite/polytetrafluoroethylene cathode with exterior hydrophobic film/ Mass graphite/PTFE binder ratio (1:1 – 4:1); pH (3.0 – 9.0) and current density (3.0-15 mA cm^{-2}).	With the 2 M HNO_3 modification rendered, H_2O_2 electro-generation was improved. The exterior hydrophobic film on the as-prepared graphite/PTFE cathode endowed the cathode with strong hydrophobic stability.	[39]
The effect of pressure on the electrochemical generation of hydrogen peroxide was studied in undivided cells changing the pressure from 0 to 30 relative bar and the current density from 1 to 100 mA cm^{-2}	50 mM Na_2SO_4 / undivided cells on carbon felt electrodes with carbon black + PTFE mixture Current densities within the range 1 – 100 mA cm^{-2}.	Under the best conditions (30 bar and 100 mA cm^{-2}), concentrations up to 225 mM together with the highest production rate (1.84 mmol H_2O_2 cm^{-2} h^{-1} and 98.9 % CE) in an electrolytic system fed with air are reported.	[34]
Cathode modification to support efficient H_2O_2 electro-generation via the reduction of dissolved anodic O_2. Graphite felt (GF) is in situ anodically modified by electrode polarity reversal technique in an acid-free, low conductivity electrolyte.	An electrolyte of 50mM Na_2SO_4 or a simulated groundwater that consists of 5mM Na_2SO_4 and 0.3mM $CaSO_4$ were used. For electrochemical modification, the GF electrode served as an anode while the Ti/MMO electrode served as a cathode/ An undivided electrochemical batch reactor was used for H_2O_2 generation and GF modification. The oxygen was in situ supplied by the Ti/MMO anode because oxygen supplied by external pure O_2 or air aeration usually achieves an extremely low O_2/air utilization efficiency (< 0.1%).	The modified GF exhibits a significantly higher activity towards O_2 reduction (up to 183.3% higher H_2O_2 yield is obtained). The modified GF can produce H_2O_2 at a high yield under neutral pH and low current intensity by the modified GF (35% of the charge need to produce the same amount by unmodified GF).	[40]

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Proof of concept of a new cell for the in-situ electrochemical production of H_2O_2 from oxygen reduction reaction	50 mM Na_2SO_4 / In both electrochemical cells, a modified carbon felt (CF) electrode was used as the cathode/ The new cell incorporates a venturi-based jet aerator to supply atmospheric oxygen without additional energy consumption to a 3D flow-through modified carbon felt (CF) cathode.	Suitable design with higher efficiency that a flow-by cell with a gas diffusion cathode under similar conditions.	[35, 41]
Testing of a highly effective composite acetylene black – PTFE cathode consisting of a sheet active core and a damp-proof coating has been developed.	Air as O_2 source in Na_2SO_4 solution of 0.05 M. / composite acetylene black–PTFE cathode Current densities: 12, - 48 mA cm^{-2}/ Three – electrode undivided cell	The cathode use not only O_2 dissolved in the electrolyte but also O_2 in air bubbles as O_2 source for the electro-generation of H_2O_2.	[42]
Preparation of a hydrophobic cathode equipped with cracks for gas transfer	0.1 mol/L Na_2SO_4; MO of 105 mg/L / porous hydrophobic acetylene black cathode/ Applied current density= 300 to 700 mA/cm²; Electrolysis time = 30 min.	Cracks can avoid the formation of bubbles in the porous electrode which is favorable to gas transmission. The reaction is almost not affected by the content of dissolved oxygen and the gas flow with this structure. The H_2O_2 concentrations up to 14.4 mmol/L after 30 min electrolysis with current efficiency beyond 90% are obtained.	[43]
Electrosynthesis of polypyrrole/multi-walled carbon nanotube (MWCNT) nanocomposites with different concentration of MWCNT on graphite cathode for the electro-generation of H_2O_2 by reducing dissolved oxygen	0.1 mol L^{-1} Na_2SO_4 / graphite cathode modified with electrochemically synthesized polypyrrole /MWCNT nanocomposite/ Optimum operation conditions are 0.55 V (vs. SCE) and pH= 3 after 10 min electrolysis.	The cathode modified with nanocomposite with 2.5% w/w MWCNT (GPM-2.5) showed highest electrocatalytic activity.	[44]
A simple chemical method using hydrazine hydrate as the main reagent was firstly used to modify graphite felt as cathode for production of hydrogen peroxide	Different concentration of hydrazine hydrate ranging from 5 to 20% were studied/ Chemically modified graphite felt cathode / Electrofenton tests were carried out using p-Np (initial concentration 50mg/L) as model pollutant, and 0.05 M Na_2SO_4 as supporting electrolyte /	The optimum concentration of the hydrazine hydrate was 10%, and the yield of H_2O_2 was as 2.6 times as that without modification under the same conditions.	[45]

Polyacrylonitrile-based carbon fiber brush (PAN-CFB) cathode was used to electro-generate hydrogen peroxide (H_2O_2) via oxygen reduction reaction (ORR) and to degrade phenol in electro-Fenton system.	Na_2SO_4 solution containing phenol of 100mg L^{-1}, $FeSO_4 \cdot 7H_2O$ was added to supply Fe^{2+} / Ti/IrO_x – TiO_2/IrO_2 mesh anode and PAN-CFB cathode/ Applied current (50 to 300mA), cathodic potential (-0.5 to -1.2 V), electrolyte concentration (0.03–0.5 mol L^{-1}) and volume (2 to 1 L) as well as electrode distance (1 – 5 cm).	PAN-CFB cathode generated H_2O_2 efficiently (current efficiency at 300mA>90%), showing high selectivity regardless of the electrolyte.	[46]
A novel acetylene black-PTFE cathode for electro-generation of hydrogen peroxide (H_2O_2) was fabricated using acetylene black powder (ABP) as catalyst, PTFE as binder.	Na_2SO_4 of 0.05 M and air-feeding flowrate of 2 L min^{-1}, the average H_2O_2 generation rate reached 58.9 mg $L^{-1}h^{-1}cm^{-2}$ during 150 min / Effective acetylene black-PTFE cathode with PTFE film/ Solution pH (3–11), applied current density (5–20 mA cm^{-2})/ Two-electrode undivided cell fed with air at 2 L min^{-1} in Na_2SO_4 solution of 0.05 M.	High activity of for the electro-generation of H_2O_2 with air feed, at pH 3 and the current density of 20 mA cm^{-2} the average H_2O_2 generation rate reaching 58.9 mg L^{-1} h^{-1} cm^{-2} during 150 min of electrolysis and the current efficiency being 92.7%.	[47]
A modified Vulcan XC72 carbon with $WO_{2.72}$ NPs ($WO_{2.72}$/Vulcan XC72) was used for the preparation of the GDE.	$WO_{2.72}$ NPs were supported on Vulcan XC72 and Printex 6L carbons at a mass ratio of 1:100 (W:C) to evaluate the electrocatalytic activity for ORR and H_2O_2 electro-generation/ The $WO_{2.72}$/Vulcan XC72 GDE cathode was combined with a Pt or boron-doped diamond (BDD) anode for the decolorization of 0.260 mM Orange II azo dye solutions by electrochemical advanced oxidation processes.	This catalyst is a promising candidate for application in EAOPs.	[48]
GDEs were constructed using carbon black either unmodified or modified with Ta_2O_5 nanoparticles. The properties of Ta_2O_5/C for the electrocatalysis of oxygen reduction by rotating ring-disk electrode is evaluated.	Nanostructured gas diffusion electrode.	The current efficiency for H_2O_2 electro-generation on Ta_2O_5/C catalyst is 83.2% whereas carbon black exhibits 65.3%. The modified GDE produces 27.9 mg $L^{-1}$of H_2O_2, while the unmodified GDE generates 19.1 mg $L^{-1}$of H_2O_2.	[49]
New air-diffusion cathode containing CoS_2 nanoparticles to enhance the H_2O_2 electro-generation.	Applied current density of 100 mA cm^{-2} for the removal of tetracaine.	The successful treatment of tetracaine at pH 3.0 and 100 mA cm^{-2} demonstrated the viability of the manufactured CoS_2-based cathode.	[50]

	Na$_2$SO$_4$ aqueous solution (5g/L) was used as the supporting electrolyte. Prior to the electrolysis, oxygen (96% purity) was bubbled near the cathode at a flow rate of 0.5 L/min for 10 min, and then oxygen was reduced at a constant current of 100mA for 90 min, with a constant stirring rate of 300 rpm.	The H$_2$O$_2$ production of three GFs at 90 min were 18.67 mg/L, 32.13 mg/L and 37.47 mg/L, respectively, compared to only 3.24 mg/L by the original GFs.	[51]
A modified GFs was used as cathode, a graphite plate as anode			

Thus, opposite to the production of chlorates, fundamental research in the production of hydrogen peroxide is very active and there are many fundamental works related to the optimization of operation conditions (e.g. use of higher pressures or lower temperatures) or to the formulation of new cathodes to make the process more efficient and to try to approach the efficiency of the widely applied chemical process. However, it is important to increase dramatically the TRL of these studies, in particular regarding the cathode stability and catalytic behavior, so there is still gap for further research in this topic over the next years.

4. **Production of chlorine dioxide from chlorate and hydrogen peroxide**

Although typically chlorine dioxide is produced by the chemical combination of chlorite and hypochlorite/chlorine or hydrochloric acid, in this review we are focusing on the production of this reagent from two species that can be easily produced onsite by electrochemical technology. The reaction shown in equation (13) requires strong acidic media and produces oxygen as byproduct

$$ClO_3^- + ½\, H_2O_2 + H^+ \rightarrow ClO_2(aq) + \frac{1}{2}O_2 + H_2O \qquad (13)$$
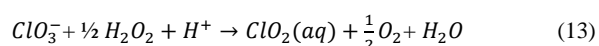
Regarding this reaction, and its alternatives in which methanol of sulfur dioxide are used as reductants of chlorate to produce the chlorine dioxide, there are many works published recently. The most relevant data of various of the most interesting are summarized in Table 3, where it can be seen, that formation of chloride dioxide is very efficient, but a good adjustment of operation conditions should be done. Also, that hydrogen peroxide exhibit advantages over the use of methanol in terms of a more sustainable solution, which avoid the formation of hazardous species such as formaldehyde. Not least important the possibility of preparing portable solutions which can help to expand the use of chloride dioxide for the disinfection of buildings.

Table 3. Scientific works related to chemical chlorine dioxide production

Objective / Technology evaluated	Reagents (concentration)/ electrode type	operation conditions	Main conclusions	Ref.
Cleaner production process for producing sodium chlorite by reducing sodium chlorate with hydrogen peroxide in the presence of sulfuric acid.	Temperature: $50 - 70$ ºC; Concentration of sulfuric acid: $4 - 5.5$ mol L^{-1}; concentration of sodium chlorate: $400 - 650$ g L^{-1} and molar ratio of hydrogen peroxide to sodium chlorate $0.5 - 0.7$.	Ambient air is used to mix the reaction liquid and to dilute the generated chlorine dioxide. The generated chlorine dioxide is introduced to and absorbed through a series of three absorbers.	Sodium chlorate conversion to sodium chlorite of $95 - 100\%$. Waste acid in the chlorine dioxide generator is dramatically reduced with recycling in the new process. The by-produced sodium sulfate in sulfuric acid is minimized and reclaimed.	[52]
Determine if formaldehyde and carbon dioxide are formed in the methanol-chlorate process.	0.05 M by diluting neat methanol, 0.25 M sodium carbonate solution, solution of $C0_2$ in sulfuric acid was generated by injecting 0.5 mL of the labeled sodium carbonate solution into a 4.5-mL solution of 2.8 M sulfuric acid.	Formaldehyde is detectable at mild oxidative conditions, including ambient temperature and low chlorate to methanol ratio/ Carbon dioxide was detected at conditions in the range of commercial operation but not under the mild conditions used to detect formaldehyde.	Adding a low concentration of chlorine to the reaction solution increased the production of carbon dioxide at ambient temperature.	[53]
Description of a portable chlorine dioxide (ClO_2) generation system to decontaminate buildings contaminated with B. anthracis spores.	Development and field testing of a mobile chlorine dioxide generation system for the decontamination of buildings contaminated with Bacillus anthracis	The system functioned satisfactorily	Measurement of ClO_2 levels at the generator outlet showed that the desired production rate was not achieved.	[54]
Evaluation of the production and stability of chlorine dioxide (ClO_2) in organic acid solutions and its effectiveness in killing Bacillus cereus spores	100 or 50 μg/ml in organic acid solutions	Sodium chlorite (5000, 10,000, or 50,000 μg/ml) was added to 5% acetic, citric, or lactic acid solution, adjusted to pH 3.0, 4.0, 5.0, or 6.0, and held at 21 °C for up to 14 days.	The amount of ClO_2 produced was higher as the concentration of sodium chlorite was increased and as the pH of the acid solutions was decreased. The stability in production of ClO_2 was enhanced by increasing the pH of the organic acid solutions.	[55]
Determination of the optimum conditions for the production of gaseous chlorine dioxide (ClO_2) from aqueous ClO_2 ($HCl+NaClO_2$) (useful information for designing a sanitization program using gaseous ClO_2 under various environmental conditions).	$NaClO_2$ (50,000-500,000 mg/mL)	Reaction of 1 N HCl with various concentrations of $NaClO_2$ (50,000- 500,000 mg/mL)/ Effects of relative humidity (RH; 43, 85, and 100%) and temperature (4, 12, and 25ºC).	It was observed that the concentration of gaseous ClO_2 was increased as RH was decreased, or the temperature was increased. Finally, it was confirmed that the amount of gaseous ClO_2 was highly correlated (R^2 =0.9546 - 0.9992) with the volume of aqueous ClO_2.	[56]
The effect of adding hydrogen peroxide on a methanol-based chlorine dioxide generation process was studied.	3 mol/L H_2SO_4, 70 °C, 0.97 mol/L $NaClO_3$, total reducing agent 0.01 mol/L	In a continuous generator at 6 mol/L H_2SO_4 acidity under atmospheric pressure, by substituting 10% of the methanol with hydrogen peroxide of an equivalent reducing strength, the	Chlorine dioxide generation is increased and that chlorine, usually present as a byproduct in the chlorine dioxide solution, can be largely eliminated when hydrogen	[57]

		generation rate of chlorine dioxide is doubled.	peroxide is present as a co-reducing agent.	
Evaluation of reaction mechanisms during the manufacturing of chlorine dioxide from the reduction of sodium chlorate with hydrogen peroxide.	In each experiment, measured amounts of hydrogen peroxide, sulfuric acid and water were first added to the reaction flask and equilibrated to the bath temperature.	The side-reaction rate was compared with the rate that chlorine dioxide is produced under a typical set of industrial conditions: 80 °C, 2 M sulfuric acid, 3.4 M sodium chlorate and 3.2 M sodium sulfate.	At the cited industrial conditions, the reaction model predicts that chlorine dioxide is consumed by the side-reaction at about 0.8%-1.5% of the rate at which it is produced.	[57]
The development of chlorine containing species during the hydrogen peroxide-based chlorine dioxide generation process has been determined.	reaction condition of 60°C, 0.0025 mol/L H_2O_2, 0.45mol/L $NaClO_3$, and 2 mol/l H_2SO_4	Accordingly, two distinct phases, namely the induction period and the steady-state phase, were identified.	It is demonstrated the viability of the reaction between chloric acid and chlorous acid, which is responsible for the generation of chlorine dioxide in the hydrogen peroxide-based ClO_2, process	[58]
Chlorine dioxide formation by reduction of sodium chlorate with hydrogen peroxide in aqueous sulfuric acid/ The rate of reaction was studied in both batch and well-mixed reactors over ranges of temperature and reactant concentrations which bracket conditions of commercial interest.	2 M sodium chlorate and 2.6 M sulfuric acid	The rate data were correlated by a power law model in which an acidity function H- was used to characterize the acidity of sulfuric acid.	The rate model reasonably predicted transient chlorine dioxide production rate data gathered in a commercial plant trial. The rate model should provide a useful tool for design.	[59]
The reaction between sodium chlorate and sodium chloride in presence of aqueous sulfuric acid is studied	Well stirred reactor at various temperatures and molar concentrations of chlorate, chloride	Reaction has been found first and second order with respect to chlorate and chloride concentration, respectively.	The temperature dependence of the reaction is also investigated and pre-exponential Arrhenius parameter as well as activation energy are determined. ClO_2/Cl_2 ratio is markedly affected by chlorate to chloride ratio.	[16]
Reaction paths governing chlorine dioxide formation from solutions of sodium chlorate, sulfuric acid, hydrogen peroxide and sodium chloride were examined.	2M H_2SO_4, 2M $NaClO_3$, 0.1M H_2O_2 and 0.01M NaCl Temperature 25°C	At conditions of this study, the rate of the chloride-chlorate path predominated and was enhanced by hydrogen peroxide, reaching an upper limit as hydrogen peroxide concentration was increased.	Chlorine dioxide was formed by two paths: the reduction of chlorate by hydrogen peroxide and the reduction of chlorate by chloride.	[60]
Reaction between chlorous acid and hypochlorous acid in sulfuric acid solution was studied.	The concentrations of sulfuric acid, hypochlorous acid and chlorous acid were, 4.5 mol/L, 0.5 mmol/L and 1.0 mmol/L, respectively.	Under the conditions of 0.5 mmol/L hypochlorous acid, 1 mmol/L chlorous acid , 4.5 mol/L sulfuric acid, and 25°C, within 30 seconds of reaction time, it was found that in the reaction solution there were 0.64 mmol/L chloric acid and 0.58 mmol Cl, and HOCl	It was found that chlorine dioxide is generated only if chloride is present.	[61]

However, the production of chlorine dioxide using electrochemical technology has also been the target of many other studies, such as those shown in Table 4, where it can be seen that MMO electrodes remains as the most important choice of anode and that production of chlorine dioxide using chlorite is the most widely

electrochemical systems studied. It is important to highlight that 1) despite of the industrial production of chlorate by electrochemical technology and the promising results obtained by the electrogeneration of hydrogen peroxide and 2) the most sustainable pathway to produce chlorine dioxide as compared with other routes, there are no works trying to integrated both processes. This means that there is still a very important gap in the scientific knowledge to be fulfilled with the integration of the anodic production of chlorate and the cathodic production of hydrogen peroxide.

Table 4. Scientific works related to electrochemical chlorine dioxide production

Objective / Technology evaluated	Reagents (concentration)/ electrode type	operation conditions	Main conclusions	Ref.
The effect of the feed flow rate, initial feed pH, the concentration of NaCl salt, the concentration of $NaClO_2$ precursor, and the applied current on the generation of ClO_2 was studied using IrO_2-coated–Ti as the anode.	Feed solution containing a mixture of $NaClO_2$ and NaCl was directly introduced into the electrolytic cell assembly, and ClO_2 generation experiments were performed by single-pass system without recirculation.	Feed solution flow rate $= 10 – 150$ ml min^{-1}; feed solution pH 2.3 – 5.0; NaCl concentration $= 0 – 169.4$mM; $NaClO_2$ concentration $= 0 –7.7$mM; applied current $= 100 –1200$mA.	The constant current electrolysis of NaCl – $NaClO_2$ mixture solution by single-pass arrangement offers an easy way for on-line generation of ClO_2 gas in solution.	[62]
Problems of chlorine dioxide formation and reactions during and after electrolysis. First results are presented, which were obtained in synthetic and real drinking waters using titanium anodes with IrO_2/RuO_2 coatings	Discontinuous electrolysis experiments were performed using activated titanium anodes containing IrO_2 and RuO_2	The influence of chloride concentration up to 250 mg L^{-1}, current density (up to 500Am^{-2}) and other parameters on ClO_2 formation is shown.	Chlorine dioxide is efficiently produced	[14]
Evaluation of the effect of voltage, anolyte, catholyte, and pH on the production of ClO_2 by an electrolytic method	The $NaClO_2$ was selected as the compositions of anolyte/ Titanium anode containing noble metals and geometry grid to increase its activation	Working voltage: 6 V, 8 V, 10 V, and 12 V; Catholyte (NaOH): 0 %, 0.1 %, 0.3 %, 0.5 %, and 0.7 %; Anolyte (NaCl): 2 %, 4 %, 6 %, 8 %, and 10 %; Anolyte ($NaClO_2$): 0.5 %, 1 %, 2 %, 4 %, and 6 %; pH value (anolyte): 2, 7, and 12.	The maximum concentration and purity of the ClO_2 were 302.01 mg/L and 91 %, respectively, with a mixture of 2 % sodium chloride (NaCl) and 6 % sodium chlorite ($NaClO_2$).	[63]
Evaluation of the electrolytic generation of dissolved chlorine dioxide from an un-buffered solution of sodium chlorite and sodium chloride mixture in an un-divided electrochemical cell set-up with RuO_2-coated-Ti anode and Pt-coated-Ti cathode under constant current mode.	Mixture of $NaClO_2$ and NaCl / The anode and cathode were 2mm thick mesh type RuO_2/Ti and Pt/Ti plates, respectively.	Feed solution flow rate = 10 to 150 mL/min; feed solution pH = 2.3 to 9.4; NaCl concentration = 0 to 170mM; $NaClO_2$ concentration = 0 to 7.7mM; current = 100 to 1200mA (8.4 to 101.4 mA/cm^2 of effective surface area).	Experiments were conducted by performing single pass experiments, with no circulation. The current efficiency and the power Consumption were calculated for the optimized conditions and compared with IrO_2 electrode of our previous investigation.	[64]
A titanium anode coated in ruthenium generates the largest amount of active	The electrode plate uses a titanium plate as the cathode, and the anode plate uses a grid-formed	Sodium chlorite is added into the brine and an electrolysis reaction is performed at 40 ℃ and 12 V for batch operation.	During continuous electrolysis, when the inflow rate for the anode electrolyte is increased to 120 mL min^{-1},	[65]

chlorine (chlorine dioxide) during the electrolysis of brine in seawater desalination plants	titanium plate as the substrate.		ClO_2 is produced at a constant concentration of 60 mg L^{-1} after 30 minutes.	

Anyhow, if the results published in scientific journals are interesting, it is worth to point out that the information available from patents is even more exciting, because it reflects the real interest in the spreading of the technology to allow its commercialization. Some of the recent patents are shown in Table 5, where it can be seen (two first rows) that chemical production of chlorine dioxide still remains to be a topic of interest for companies and that there is also interest from companies to produce electrolytically chloride dioxide, although the chlorite method, as it happens with the scientific literature, focusses still the main interest, perhaps because of the ease of the technology.

Table 5. Several recent patents related with the chemical and electrochemical production of chlorine dioxide

Year / Title	Field of the invention /justification	Summary of the invention (as in the patent document)	Ref.
2013 / Production of chlorine dioxide release material	Process to produce chlorine dioxide release materials Chlorine dioxide generating system that is suitable for industrial applications	"Process for the production of a chlorine dioxide release material comprising the steps of: a) admixing a metal chlorite salt solution or suspension and a dehydrating agent; b) admixing a dry and/or anhydrous acid source capable of donating protons to chlorine dioxide generation reactions, with said metal chlorite salt and dehydrating agent to a mixture."	[66]
2015 / Process to produce chlorine dioxide	Process to produce chlorine dioxide, which allows the generation of chlorine dioxide gas at a selected pressure. The present invention is to provide an efficient process for producing chlorine dioxide at sub-atmospheric pressure that is suitable for applications in which chlorine dioxide gas is used.	"Process for the continuous production of chlorine dioxide comprising generating chlorine dioxide in an aqueous reaction medium in a reaction vessel (1) maintained at sub-atmospheric pressure, bringing gaseous chlorine dioxide from said reaction vessel to an absorption tower (7) and contacting it therein with a flow of water to form an aqueous solution containing chlorine dioxide, bringing said aqueous solution containing chlorine dioxide to a stripper (12), blowing a gas through said aqueous solution of chlorine dioxide in the stripper to strip off from 10 to 100% of the chlorine dioxide entering the stripper and form a gaseous chlorine dioxide product."	[67]
2014 / Process and combined plant of production of chlorine dioxide for water treatment through desinfection	Process and a combined plant of production of chlorine dioxide for water treatment through disinfection. The process and the plant allow to overcome the limits of the solutions according to the prior art and to obtain the technical results previously described.	"Water treatment combined plant, comprising at least one electro-chlorinator (1) for producing sodium hypochlorite in solution, a first reaction chamber (4) to which sodium hypochlorite coming from said electro-chlorinator (1) and an acid solution coming from a first storage tank (13) and dosed by means of a first dosing section (2) arrive and from which a chlorine solution comes out, a second reaction chamber (5) to which said chlorine solution coming from said first reaction chamber (4) and a sodium chlorite solution arrive, coming from a second storage tank (14) and dosed by means of a second dosing section (3) and from which a chlorine solution dioxide comes out and an injection point (9) of said chlorine solution dioxide in a water treatment section."	[68]
2010/ Method for producing chlorine dioxide	Process for the production of chlorine dioxide by the reaction of chlorine and chlorite. Chlorine dioxide can be produced	"Chlorine is generated electrochemically in a first process step from a saturated sodium chloride solution, wherein sodium hydroxide solution and hydrogen gas are generated in a cathode chamber, and chlorine is generated in an anode chamber, and, in a second process step, the generated	[69]

	economically and with comparatively little effort.	chlorine is reacted in a reactor with sodium chlorite with the addition of an acid to form chlorine dioxide."	
2016 / Chlorine dioxide production device and chlorine dioxide production method	A device and a method for producing chlorine dioxide by electrolyzing anolyte solution containing chlorite with using a diaphragm electrolytic cell having an anode chamber and a cathode chamber.	"A device and a method for generating chlorine dioxide by implementing an electrolytic treatment while supplying an amount of anolyte solution containing chlorite and an amount of catholyte solution containing e.g. sodium hydroxide, sodium chloride etc. to an anode chamber and a cathode chamber respectively of a diaphragm electrolytic cell."	[70]

In this context, the development of more robust methods for the production of hydrogen peroxide and the finding of the conditions in which both electrochemical processes can be integrated may become a turning point for the development of the technology.

5. Conclusions

From this work, the following conclusions can be drawn:

- Chlorate production is at a very high TRL but there is still scientific interest in testing novel electrodes such as the diamond coatings to improve performance. Also, it is of interest the complete understanding of the role of chromium in the efficient production of chlorates and the ways to promote or prevent chlorate formation during the electrolysis of aqueous solutions containing chloride.

- Hydrogen peroxide production by electrochemical methods is at a lower TRL and many studies are being conducted trying to find optimum operation conditions, suitable cell designs and specially good formulations of the cathode material, trying to attain suitable electrocatalytic properties and high robustness. Large efforts should be made in the recent years to make this process competitive.

- Chloride dioxide can be produced chemically from the reduction at strongly acidic media of chlorates. However, according to most of the scientific literature and patents the production from chlorite is preferred and there should be made a great scientific effort to cover the gap with the integration of electrochemical production of chlorates and hydrogen peroxide.

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