

ELECTROCHEMISTRY AND GREEN CHEMICAL PROCESSES: ELECTROCHEMICAL OZONE PRODUCTION

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After an introductory discussion emphasising the importance of electrochemistry for the so-called Green Chemical Processes, the article presents a short discussion of the classical ozone generation technologies. Next a revision of the electrochemical ozone production technology focusing on such aspects as: fundamentals, latest advances, advantages and limitations of this technology is presented. Recent results about fundamentals of electrochemical ozone production obtained in our laboratory, using different electrode materials (e.g. boron doped diamond electrodes, lead dioxide and DSA[®]-based electrodes) also are presented. Different chemical processes of interest to the solution of environmental problems involving ozone are discussed.

Keywords: ozone; electrochemistry; environment; green processes.

INTRODUCTION

Modern chemistry plays a key role in the improvement of quality of life around the world. However, these advances frequently came with an increase in contamination of the environment by toxic substances. Nowadays steps are being taken, mainly due to increasing economic, social, legal, and environmental pressures, to avoid further degradation. Therefore, the use of the so-called *Green Chemical Processes* where the “best available technology” not entailing excessive cost and aspiring to “performance without pollution” can be used in industrial processes is stimulated¹. We are now seeing momentum building around the green theme, where green products, processes, and technologies are deemed good for mankind. In this context, catalysis has and will continue to impact the discovery and development of environmentally attractive technologies and products².

As discussed in some contributions published in the IUPAC special topic issue, entirely dedicated to Electrochemistry and Interfacial Chemistry for the Environment³⁻⁹, electrochemical technology has an important role to play as part of an integrated approach to the avoidance and monitoring of pollution, process efficiency, cleaner processing, and modern techniques for electrical energy storage and conversion.

A fundamental reason for the importance of the electrochemical technology to minimise environmental problems is that it uses electricity as energy source. Of course, one must remember that when generated burning fossil components (e.g. coal, oil) a certain degree of environment contamination takes place mainly as CO₂ injected in the atmosphere. However, with respect to this issue, Brazil presents a more favourable situation since most of its electrical energy is generated in hydroelectric plants (although even this technology is not totally environmentally friendly).

Electrochemical technology can be used directly in several applications involving the removal and degradation of potential solid

and liquid pollutants from industrial wastes in water, soil and atmosphere¹⁰. Besides, this technology can also be used in the generation of very active oxidant species with proven efficiency in several green processes.

An environmental friendly oxidant should possess the following features¹¹: (i) reactive with compounds to be treated; (ii) neither produce nor leave undesirable by-products during the course of the reaction and (iii) readily available. A number of chemical oxidants are currently being used either as disinfectants for potable or swimming pool waters, or for the destruction of organic and inorganic chemical species found in wastewater. The most commonly used oxidants for the above purposes are: ozone, hydrogen peroxide, chlorine, chlorine dioxide, sodium and calcium hypochlorite, and potassium permanganate.

The benefits of generating oxidants electrochemically include¹¹: (i) close control of product yield and purity through control of applied current; (ii) elimination or minimisation of chemical by-product generation during oxidant synthesis; (iii) transport and storage of toxic and hazardous oxidants can be eliminated by producing them on site at an amount proportional to the waste concentration and (iv) electrochemical processes could have an economic advantage over traditional routes for oxidant generation, especially in small scale uses.

In particular, applications involving ozone have a number of advantages: it is a very strong oxidant ($E^0 = 1.51\text{V}$ (vs. RHE)); its decomposition leads to environmental friendly products (O₂); its instability ($t_{1/2} = 20\text{-}90$ min, depending on environment) requires it to be produced “on spot” reducing expenses and danger with transportation and storage. Ozone finds application in fields such as: water treatment, combustion of resistant organics, clean-up of effluents, bleaching of wood pulp^{2,10,11}.

Chlorine has long been used in the disinfection of water. It now seems that chlorinated hydrocarbons formed during the treatment may possess some carcinogenic action¹². For this reason chlorine is being replaced by ozone or hydrogen peroxide, whose production must thus be increased and improved. In the particular case of pulp and paper bleaching¹³, there is an increasing demand for alternatives (e.g. ozone) to chlorine dioxide (ClO₂). The substitution of chlorine

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dioxide by ozone as a bleaching agent permitted the development of the so-called totally chlorine free (TCF) bleaching technology¹⁴, reducing significantly the pollution burden and potential health hazard of chlorine derivatives of this industrial activity.

Several aspects related to ozone production and its applications were discussed in the 80's by Rice and Netzer¹⁵. Nowadays, ozone being an environmentally clean reagent with proven efficiency for several processes of technological importance, a crescent interest in electrochemical ozone production is observed¹⁶⁻⁴⁴.

The objective of this article is to revise and discuss fundamentals aspects as well applications of ozone production, giving especial attention to its electrochemical production. Green Chemical Processes where ozone can be employed are also discussed.

Ozone

According to Rideal⁴⁵, reports about ozone can be traced back to 1785 when van Marum, a Dutch physicist, found electric discharge in the air results in a characteristic ozone odour. In 1801 the same odour was observed during water electrolysis⁴⁵. However, ozone discovery was only officially announced by Schönbein⁴⁶, at the Academy of Munich, in 1840. The name "ozone" was derived by Schönbein from the Greek word "ozein", meaning "to smell".

In 1845 de la Rive and Marignac⁴⁷ obtained ozone by submitting pure dry oxygen to an electric spark. Later, investigations conducted by Hunt⁴⁸ on the oxidant properties of ozone permitted the author to postulate the ozone molecule is tri-atomic oxygen. Figure 1 shows the structure of the ozone molecule described by Bailey⁴⁹ as a resonance hybrid of the four canonical forms.

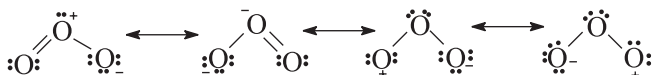


Figure 1. Structure of the ozone molecule as a resonance hybrid of the four canonical forms

As shown in Figure 1 ozone, O₃, is a triangular shaped molecule. Under ambient conditions it is an unstable gas possessing a very strong oxidation power and a characteristic sweet odour which is detectable in air (e.g. near copier machines) by most people at a concentration as low as 0.01ppm⁵⁰. Under normal conditions of temperature and pressure O₃ is moderately soluble in water (about 13 times higher than O₂). Its decomposition rate, producing O₂, strongly depends on the purity of the solvent phase, decreasing in the presence of impurities⁵¹. Ozone is the second most powerful oxidant molecule, exceeded in its oxidising power only by fluorine. Since ozone is a non-polluting oxidant (ozone is reduced to oxygen during oxidation of organics), its use far exceeds that of fluorine. In the mid 70's, ozone received a considerable amount of attention after it was shown that hydroxyl radicals are formed in ozonated water in the presence of either ultraviolet light, UV, or hydrogen peroxide¹¹. These hydroxyl radicals are oxidising agents⁵² far more powerful than ozone itself.

Ozone production using electric discharge and UV-absorption

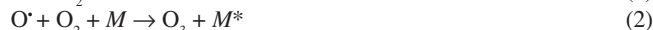
Ozone production by the corona discharge technology

The most important progress in ozone production was obtained by von Siemens⁵³ in 1857, when he developed an ozone generator tube based on the corona discharge process. Such process is based on the application of an alternating voltage between two electrodes

with dry air or oxygen passing in between. As a result of the electrical discharge, oxygen molecules decompose in O[•] which combines with O₂ resulting in O₃-formation. In the prototype developed by von Siemens about 3-8% of oxygen was converted to ozone. This type of ozone generator has subsequently served as a prototype for the majority of electric discharge generators⁵⁴.

Advances in the corona technology were obtained as a result of the investigation of the influence of the gas phase (oxygen) temperature on ozone yield⁵⁴. This study revealed an increase in O₃-concentration with decreasing temperature.

O₃ production in the corona technology can be described by next mechanism⁵⁵:



where *M* represents a molecule of an activated inert gas (e.g. N₂) serving the propose of removing the excess energy acquired during ozone molecule formation.

As shown by the above mechanism the reaction initiates when free electrons, having high energy (e⁻¹), collide with an oxygen molecule resulting in its dissociation. In the next step ozone is formed by a third order collision. As a result of energy absorption during collision the inert gas molecule turns into an excited molecule, M*. The importance for O₃ production of the activated inert gas inside the corona device was verified by Popovich *et al.*⁵⁶. Cromwell and Manley⁵⁷ and Rosen⁵⁸ showed O₃ production increases about 2-7% by adding 5 to 8 vol% of N₂ to the gas phase.

Simultaneously with ozone production a parallel route for ozone decomposition takes place when atomic oxygen or energised electrons react with an ozone molecule according to the following mechanism⁵⁵:



So, according to the above mechanisms, corona efficiency for O₃ production is the result of competition between steps (1)-(2) and (3)-(4). Literature data⁵⁴ show experimental factors affecting the corona efficiency for O₃ production are: temperature of the entering gas, oxygen content, presence of contaminants in the gas phase, ozone concentration, electric power and the gas flow.

The output from a modern corona-discharge system has been report to vary from 2 wt% for air as the input gas to 7 wt% for oxygen as the input gas⁵⁹. This low O₃-concentration is the main drawback presented by the corona technology. The specific energy consumption of classical ozonizers reported in the literature¹⁶ is around 14 Wh g⁻¹ for air and 6 Wh g⁻¹ for oxygen feed. However, a more recent study⁶⁰ reports a value of 5 Wh g⁻¹ for air.

Literature data⁶¹ show the use of corona technology in reactor systems for ozonation of organics in water can be optimised by: (i) reducing the amount of energy input and (ii) increasing the mass transfer rate of ozone gas into the aqueous phase. While the former depends on geometry of the corona, the latter depends on the mixing characteristics of the gas-liquid contactor used, the kinetics of ozone decay in water, and the number and size of bubbles produced. Optimisation of these parameters for different ozonation systems has been reported in the last ten years⁶⁰⁻⁶⁴. Suarasan *et al.*⁶⁰ presented an AC corona ozonation system using multi-point high-voltage electrodes as a means for direct ozonation of liquids. Shin *et al.*⁶¹ proposed an ozonation system which produces micro-bubbles having an average bubble diameter of 1.34-5.0x10⁻² mm. An increase of up to 40% in mass transfer rate was observed by these authors. The production of active species such as OH[•], H₂O₂, and O₃ in water and

aqueous solution has also been studied using the so-called pulsed-streamer corona discharge⁶². A combination of air stripping and pulsed corona has also been tested⁶³. Goheen *et al.*⁶⁴ report ozone generation in devices where a DC corona discharge is created between an electrode and the surface of a liquid.

Attempts have also been made to use advanced oxidation processes (AOP's)⁶⁵, such as the combination of ultraviolet (UV) light or hydrogen peroxide (H₂O₂) with standard corona ozonation systems, in order to increase the amount of hydroxyl radical (OH[•]), thus reducing the O₃-demand.

Photochemical ozone production

When irradiated by UV-light the O₂-molecule absorbs electromagnetic energy and can dissociate in two oxygen atoms. The oxygen atom can then combine with a neighbour O₂ molecule producing a ozone molecule, O₃.

Theoretically, the quantum yield of ozone production by irradiation of light at wavelengths, λ , shorter than 242 nm is 2.0, since each photon absorbed by an oxygen molecule will produce two oxygen atoms, each of which, in principle, can produce one ozone molecule⁶⁶:



However, the experimentally observed quantum yield is always lower than 2.0, in part, due to the reaction⁶⁶:



and, in part, to the photolysis of ozone by electromagnetic energy absorption⁶⁷:



where O[•](¹D) represents the excited electronic state of the oxygen atom called singlet.

The photochemical process requiring the least amount of energy will produce oxygen atoms in their lower energy state following next process⁶⁸:



where O₂ (³Σ_g⁻) represents the ground state of the oxygen molecule and O[•](¹P) represents the electronic state of oxygen atom called triplet. The energy involved in the above mentioned process corresponds to a wavelength of 242 nm. In practice it is very difficult to produce light of the appropriate wavelength ($\lambda \cong 242$ nm) to produce ozone from oxygen without the simultaneous presence of the longer and shorter wavelengths where ozone photolyses takes place ($200 \leq \lambda \leq 308$ nm) (see eq.8). Therefore, the experimentally observed quantum yield of ozone production is a balance between the yield of production (see steps 5 and 6) and the photolysis yield (see step 8). This balance obviously depends on the ratio of ozone-producing to ozone-consuming wavelengths present.

As already mentioned for the corona technology (see previous discussion), another factor affecting quantum yield of ozone formation is the presence of an inert body. Such process is represented as follows:



where *M* is any inert body present, such as: reactor wall, a nitrogen

molecule or a molecule of carbon dioxide. *M* acts removing the energy excess acquired during ozone molecule formation resulting in an excited inert body, *M*^{*}. Literature data show⁶⁹ the relative yields of ozone production at 185 nm, using as UV-source a low pressure mercury lamp at 1 atm total pressure and 0.25 atm of oxygen pressure, varies according to the inert gas used (e.g. CO₂, N₂, Ar) presenting values in the 0.5-1.0 interval. Calculations⁶⁹ show the ozone production rate achieved using a low-pressure mercury lamp ($\lambda = 185$ nm), considering 37% of the available UV-radiation is absorbed by oxygen to produce ozone, is 0.72 g kWh⁻¹. This production rate can be improved if the photochemical reactor wall is made of, or is coated with, a reflective material, such as polished aluminium.

Compared with the corona process (discussed in the previous section) photochemical ozone production is not a very efficient means of producing large amounts of ozone. However, UV-light is very suitable for producing ozone in small amounts e.g. for laboratories proposes, odour elimination, etc. A great attractive of photochemical ozone production is reproducibility due to the easy control of the rate of ozone production by controlling lamp source power.

Hybrid ozonation systems based on the combination of corona discharge technology combined with the simultaneous exposure of wastewater to UV-radiation has been developed for a variety of purposes, for instance, the destruction of polychlorinated biphenyls (PCB)⁷⁰ and phenol⁶¹.

Ozone production from water electrolysis

The low ozone concentration available using electric discharge in the gaseous phase (corona process) or UV-light absorption (photochemical process) technologies restricts ozone application in several Green Chemical Processes where a higher O₃-concentration is necessary^{11,71} (e.g. decomposition of resistant organic pollutants). To circumvent this difficulty various electrochemical processes for ozone production from water electrolysis were and are being investigated¹¹, originating the electrochemical technology called here *electrochemical ozone production*, *EOP*. The *EOP*-technology can generate far higher ozone concentrations than available conventionally⁴⁰, making possible the combustion of several resistant organic pollutants.

Stucki *et al.*³⁴ showed an electrochemical reactor for *EOP* can furnish optimum current yields in the order of 20% with a specific power consumption in the order of 65 Wh g⁻¹. Considering the technology available in the 80's, Foller and Goodwin⁷² concluded at that time *EOP* has "economic advantages" for ozone production rates less than 6.8 kg day⁻¹. Great advances have been made in *EOP* in the 90's using air depolarised cathodes in the electrochemical reactor⁴⁰.

Nowadays the rigid environmental legislation requiring the adoption of Green Chemical Processes has changed this unilateral point of view and strongly disregards economical aspects as a major limitation for the implantation of this technology which can significantly contribute to environment conservation.

Fundamentals of electrochemical ozone production

During electrolytic decomposition of water ozone is formed in the anodic compartment of the electrolytic cell according to the following half cell reaction⁷¹:



Oxidation of evolved oxygen could also possibly produce ozone according to:



However, up-to-now from a practical point of view only the process represented by eq.11 has been considered in the literature^{4,16,17,34,71}.

The oxygen evolution reaction, *OER*, always occurs simultaneously during *EOP* since it occurs preferentially over *EOP* due to its lower standard potential⁷¹:



As discussed recently by Da Silva *et al.*^{4,43}, although *OER* is a parallel reaction, this apparently “undesirable” process is necessary for *EOP*. Such argument is based on kinetic considerations since the partial coverage by adsorbed O_2 -molecule of the electrode surface acting as an intermediate for *EOP* directly affects the current efficiency of *EOP* (fraction of the current leading to ozone production). So, optimisation of *EOP* performance by a given electrode/electrolyte combination, is governed by partial inhibition of the *OER* and the formation of a more adequate O_2 and O^* -coverage of the electrode surface^{4,43}.

Three basic requirements for *EOP* are: (i) electrode material should present good conductance and a high anodic overpotential for *OER*; (ii) anions and cations from electrolyte should not engage in competitive reactions with *OER/EOP* and hydrogen evolution reaction, *HER*, respectively, and (iii) to avoid/minimise electrode wear, electrode material should present its highest oxidation state or be kinetically resistant to further oxidation.

The above considerations strongly restring candidates for electrode material and electrolyte. Literature data^{4,11,15-44} show most *EOP* investigations made use of Pt, glassy carbon, boron doped-diamond, PbO_2 and $\text{PbO}_2/\text{Ebonex}$ (Ebonex is a commercial material based on titanium suboxides) as electrode materials and H_2SO_4 , HClO_4 or H_3PO_4 solutions as electrolyte.

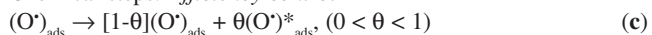
Different electrode mechanisms to describe the *OER/EOP* processes, taking into account different intermediates, can be found in the literature^{30,36,73}. However, these mechanisms do not permit a direct correlation between kinetic, surface adsorbed species and current efficiency for *EOP*. Recently Da Silva *et al.*⁴ proposed the following electrode mechanism for *OER/EOP* processes at inert electrodes (e.g. $\beta\text{-PbO}_2$), which permits a correlation between current efficiency for *EOP* and surface coverage by oxygen intermediates.

Mechanism for oxygen/ozone production at inert electrodes

Electrochemical steps: *Kinetic control*



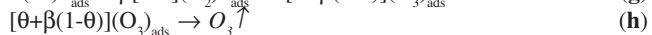
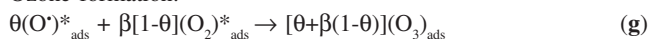
Chemical steps: *Efficiency control*



Oxygen evolution:



Ozone formation:



“ θ ” and “ β ” are the partial surface concentrations of the oxygenated intermediates describing the competition between the *OER* and *EOP* processes while “*” represents the surface concentration of the active centres leading to O_3 -formation.

Kinetic studies based on Tafel slope determination, $b(\equiv (\partial E/\partial \log j)_T)$ support primary water discharge (step (a)) as rate determining (rds) for the *OER/EOP* processes^{4,43,74-76}. In the above mechanism *EOP* occurs at high overpotentials ($E > 1.51 \text{ V(vs. RHE)}$), via steps (g) and (h), simultaneously with *OER* via step (f), respectively. Initially the electrochemical reaction proceeds via “electrochemical steps” (steps (a) and (b)) where the anodic current is sustained by the oxidation of the adsorbed water molecule, with concomitant release of two H^+ ions, resulting in an electrode surface covered by O^* having a very low interfacial pH. Continuation of the electrode process proceeds via “chemical steps”, which control the efficiency with respect to *EOP* and *OER* processes by means of a combination of the adsorbed intermediate species on the electrode surface (for more details see refs. 4 and 43). As demonstrated by Da Silva *et al.*⁴ the current efficiencies with respect to *OER*, Φ_{OER} , and *EOP*, Φ_{EOP} , processes are a function of the θ and β coverage according to:

$$\Phi_{\text{OER}} = [1-\beta][1-\theta] \quad (14)$$

$$\Phi_{\text{EOP}} = [\theta+\beta(1-\theta)] \quad (15)$$

Theoretical calculations⁴ show maximum Φ_{EOP} is obtained for θ and β -values tending towards unity. Under these conditions *ozone formation* (steps (g) and (h)) is favoured over *oxygen evolution* (step (f)). Accordingly, under these conditions *OER* is minimum, serving only as a source of adsorbed O_2 -species necessary for *ozone formation* at the electrode surface.

Eqs.14 and 15 clearly show that any experimental conditions optimising the partial coverages θ and β result in a direct improvement of the electrode performance for *EOP*.

Advances achieved in the electrochemical ozone production in the last decades

Since the discovery of ozone by electrolysis of sulphuric acid solutions in 1840 by Schönbein⁴⁶ approximately 25 publications have appeared until the 80's dealing with its electrolytic generation. During this long period technological progresses and profit prevailed over environmental concerns, causing an inhibition of the research involving *EOP* due to the costs related with this technology. However, as shown by the literature^{4,15-44} in the last decade rigid environmental legislation requiring as soon as possible the adoption of Green Chemical Processes has re-opened this prominent technological field.

Initially the first systematic studies involving ozone production from water electrolysis were conducted using platinum as electrode material and sulphuric acid solutions as supporting electrolyte. The use of a noble metal such as platinum in *EOP* studies is due to its high overpotential for the *OER* associated with its inertia during electrolysis even under drastic conditions of current density and interfacial potential.

The platinum/sulphuric acid system was exploited in two different ways: (i) using sulphuric acid solutions^{77,78} and current densities ranging between 50-100A cm^{-2} Φ_{EOP} -values of up to 27% were obtained at 0 °C; (ii) employing eutectic electrolyte compositions and very low temperatures ($<< 0 \text{ °C}$) Φ_{EOP} -values of up to 32% were reported^{79,80}. Literature data^{81,82} also report the use of a platinum anode/perchloric acid combination showing a Φ_{EOP} yield of 36% at -40 °C.

A significant advance in the *EOP* technology came with the use of PbO_2 as anode. The studies were conducted by three different groups of researchers: Semchenko *et al.*⁸³⁻⁸⁵; Fritz *et al.*⁸⁶ and Foller and Tobias^{17,18,39,40,72}.

For several reasons PbO_2 in its two crystallographic forms (α and β) is a very convenient electrode material for *EOP*: (i) it is rather cheap; (ii) supports high current densities without considerable wear;

(iii) presents Φ_{EOP} -values higher than those obtained at Pt electrodes for the same conditions of electrolyte and temperature.

Initially Semchenko *et al.*⁸³⁻⁸⁵ studied the electrolysis of phosphoric and perchloric acid reporting Φ_{EOP} -values of 13% (10-15 °C) and 32% (-15 °C), respectively. These authors observed an increase in Φ_{EOP} as a result of adding small quantities of fluoride ion to the electrolyte. Problems related with PbO_2 wear during *EOP* were observed by Semchenko *et al.*⁸³⁻⁸⁵ at that time. Foller and Tobias¹⁷ proposed PbO_2 wear is a result of a chemical/electrochemical dissolution mechanism operating under strong acid conditions. This inconvenient process was overcome by Kötzt and Stucki^{16,34} a few years later. These authors observed that the introduction of a solid polymer electrolyte membrane (*spe*) separating anode from cathode avoids the use of conventional acid electrolytes thus reducing significantly PbO_2 wear.

In the 70's, Fritz *et al.*⁸⁶ investigated phosphoric acid-based electrolyte systems reporting Φ_{EOP} -values of up to 13% at ambient temperatures. These authors also observed PbO_2 wear is suppressed in neutral buffered electrolyte.

Considerable advances in the *EOP* technology were obtained by Foller and Tobias^{17,18,40} investigating the influence of the addition of several different fluoro-anions to the electrolyte (e.g. F^- , BF_4^- , PF_6^-). These authors reported Φ_{EOP} -values of up to 53%, at $\beta\text{-PbO}_2$ electrodes at 0 °C, in 7.3 mol dm^{-3} HPF_6 . Fundamental studies conducted by Foller and Tobias¹⁷ using as anode Pt and PbO_2 and different fluoro-anions containing electrolytes, revealed a correlation between anion surface adsorption and Φ_{EOP} . Studies^{37,38} of *EOP* conducted in the 90's show the introduction of different ions, including fluoride anion, as doping agent into the PbO_2 coating also affects the Φ_{EOP} .

The use of glassy carbon as electrode material for *EOP* was investigated by Foller and Tobias⁷². These authors found pressed carbon black rapidly degrades while exhibiting CO_2 evolution as side reaction. Conventional graphite also undergoes wear during *EOP* as a result of c-axis swelling provoked by anion intercalation between its planes.

Advances in the fundamentals of *EOP* were recently achieved in our laboratory by Da Silva *et al.*⁴ when these authors showed that besides the nature of the electrode material, electrode morphology (e.g. porosity, roughness) also strongly influences *EOP* kinetics and Φ_{EOP} . On $\beta\text{-PbO}_2$ electrodes, depending on electrode morphology, BF_4^- can both act increasing or inhibiting *EOP*. Advances on the kinetics for *EOP* were also achieved^{4,36,73}. The electrode mechanism recently proposed by Da Silva *et al.*⁴ for *OER/EOP* processes at inert electrodes permits an adequate theoretical interpretation of the influence on Φ_{EOP} of the stability of intermediate oxygenated species adsorbed on the electrode surface (see previous discussion). In a recent study conducted by Da Silva *et al.*⁴³, involving the determination of the activation energy for both the *OER* and *EOP* processes it was shown that the presence of fluoro-anions in the electrolyte affects *EOP* indirectly by inhibiting the *OER* process in the high overpotential domain.

EOP studies at boron doped-diamond electrodes, BDDE, were also reported in the literature^{27,33}. This material presents a very high overpotential for *OER* associated with a high corrosion resistance. Considerable Φ_{EOP} -values in acid medium were found. A revision about conductive diamond electrodes and its application to electrochemical processes was recently published by Pleskov⁸⁷.

Factors affecting Φ_{EOP}

The main factors affecting *EOP* are: (i) chemical nature of the electrode material; (ii) electrode morphology; (iii) chemical nature of the electrolyte; (iv) current density; and (v) temperature of the

electrolyte. Therefore, to clarify the influence of these parameters on Φ_{EOP} we here present some contributions from our laboratory obtained in the last two years.

EOP current efficiency data presented in the following discussions were calculated according to the following equation^{4,43}:

$$\Phi_{\text{EOP}}/\% = [(A \cdot \dot{V} \cdot z \cdot F) / (\varepsilon \cdot l \cdot I_T)] \cdot 100 \quad (16)$$

where: A = Absorbance at 254 nm; \dot{V} = volumetric flow rate of ($\text{N}_2 + \text{O}_2 + \text{O}_3$) ($\text{dm}^3 \text{ s}^{-1}$); z = number of electrons ($n = 6$); ε = ozone absorptivity⁸⁸ at 254 nm ($3024 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$); l = optical path (10 cm); I_T = total current (*EOP* + *OER*) (Ampere); Φ_{EOP} = current efficiency for *EOP* (%); F = Faraday's constant (96485 C mol^{-1}).

Influence of the chemical nature of the electrode material on overpotential for *OER/EOP* processes

It was observed^{4,43,75,76} in several studies that depending on electrode material (e.g. $\text{DSA}^{\text{®}}$ ($\text{IrO}_2 + \text{Ta}_2\text{O}_5$; $\text{IrO}_2 + \text{Nb}_2\text{O}_5$), BDD and $\beta\text{-PbO}_2$), using the same conditions of current density, electrode potential and electrolyte, Φ_{EOP} -values strongly vary covering the 2-17% range. Figure 2 shows polarisation curves, E vs. j , for different electrode materials, recorded in the same base supporting electrolyte of 3.0 mol dm^{-3} H_2SO_4 at 0 °C.

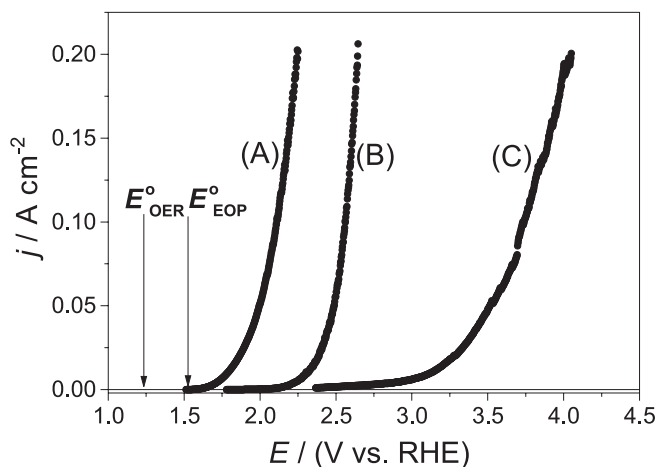


Figure 2. Polarisation curves, E vs. j , recorded under quasi-stationary conditions for different electrode materials: (A) $\text{Ti}/[\text{IrO}_2(0.5)+\text{Ta}_2\text{O}_5(0.5)]$; (B) $\beta\text{-PbO}_2$; (C) BDD. Electrolyte: 3.0 mol dm^{-3} H_2SO_4 , $T = 0$ °C. Arrow indicate the respective standard potentials

As illustrated in Figure 2 the onset of the *OER* strongly depends on the chemical nature of the electrode material. Contrary to the $\text{Ti}/[\text{IrO}_2(0.5)+\text{Ta}_2\text{O}_5(0.5)]$ electrode, where the *OER* initiates at relatively low overpotential, at $\beta\text{-PbO}_2$ and BDD electrodes the *OER* initiates far from its standard potential of 1.23V(vs. RHE). Such behaviour presented by the $\text{Ti}/[\text{IrO}_2(0.5)+\text{Ta}_2\text{O}_5(0.5)]$ electrode is due to the good electrocatalytic activity presented by IrO_2 (active component) for the *OER* process in acid medium⁸⁹.

Literature data⁸⁹ show conductive metallic oxides such as IrO_2 , RuO_2 are good catalysts for *OER*. As a result these oxides don't present good performance for *EOP*. Also, the existence of higher soluble oxidation states of these oxides leads, at the high overpotentials required for *EOP*, to accelerated electrode wear due to electrode corrosion⁹⁰. With electrode materials such as BDDE and $\beta\text{-PbO}_2$, which are considered "inert", the electrode materials simply acts as an electron sink during an anodic process and no considerable wear^{4,43} is observed even under drastic conditions of electrode

potential ($\sim 3.0V$ vs. RHE)) and current density ($\sim 1A\text{ cm}^{-2}$). Also, the absence of superior oxidation states (e.g. PbO_2 and BDDE) strongly reduces the electrocatalytic activity for *OER* increasing therefore indirectly the efficiency for *EOP*.

Influence of the electrode morphology and chemical nature of the electrolyte on Φ_{EOP}

The influence of electrode morphology (roughness/porosity) on Φ_{EOP} was recently investigated by Da Silva *et al.*⁴. Table 1 shows surface parameters as function of electrode preparation which were obtained following the methodology recently proposed by Da Silva *et al.*⁹¹.

Table 1. Surface parameters as function of electrode preparation

$\beta\text{-PbO}_2$ Electrode*	C_T mF cm^{-2}	C_E mF cm^{-2}	C_I mF cm^{-2}	φ
I	58	15	43	0.74
II	100	22	78	0.78

* $\beta\text{-PbO}_2$ deposition was done at constant anodic current: $j = 5\text{ mA cm}^{-2}$ (Electrode-I) or 20 mA cm^{-2} (Electrode-II) using a 40 min deposition time.

C_I , C_E , and C_T are the internal, external and total differential capacities, respectively. C_I and C_E respectively represent the contribution to the total film surface of the more internal (more difficult-to-access) and the more external (easy accessible) surfaces. φ is an intensive parameter defined as C_I/C_T , called the morphology factor⁹¹. Figure 3 exemplifies the influence of current density and electrode morphology on Φ_{EOP} , for different electrolytes, at 0°C .

As shown by Figure 3, with the exception of the BSE (both electrodes) and BSE + $0.03\text{ mol dm}^{-3}\text{ F}^-$ (at Electrode-I), significant improvements in current efficiency are observed in the presence of

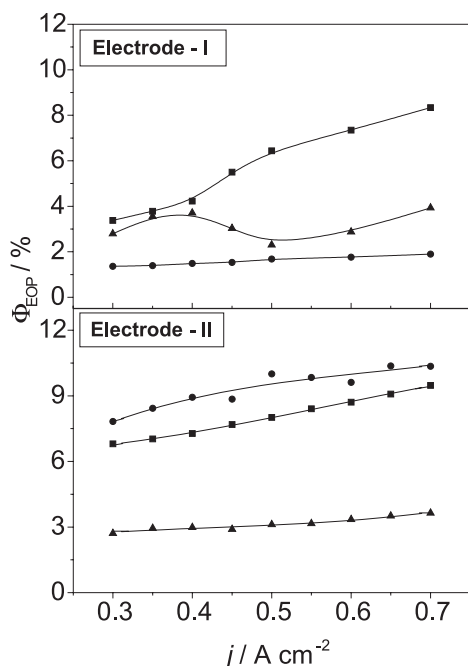


Figure 3. Influence of current density, j , on ozone efficiency, Φ_{EOP} , for different electrolytes and electrode morphology (Electrodes I and II). (\blacktriangle) BSE, $3.0\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$; (\bullet) BSE + $0.10\text{ mol dm}^{-3}\text{ HBF}_4$; (\blacksquare) BSE + $0.03\text{ mol dm}^{-3}\text{ NaF}$. $T = 0^\circ\text{C}$

fluoro-anions. Once a minimum Φ_{EOP} value is reached, gain in O_3 -production by further increasing the current density is only of minor importance. According to eq.15 such behaviour indicates a constant coverage by intermediates leading to *EOP*.

For the same electrolyte comparing the Φ_{EOP} -values at the two electrodes (see Fig.3), with the exception of BSE where approximately the same Φ_{EOP} -values are obtained, significant differences are observed in the presence of $0.03\text{ mol dm}^{-3}\text{ F}^-$ and $0.10\text{ mol dm}^{-3}\text{ BF}_4^-$. Since for the BSE Φ_{EOP} -values are not significantly affected by the electrode morphology, the effect observed in the presence of fluoro-anions cannot be explained by the change in surface area of the two electrode (see Table 1). An even more intriguing result is the effect of BF_4^- which, using the BSE as a reference, can act depending on electrode morphology as a promoter (Electrode-II) or inhibitor (Electrode-I) of the *EOP* process.

Influence of current density and temperature on Φ_{EOP}

The influence of the temperature on Φ_{EOP} depends on electrode material and nature of the electrolyte. Representative j vs. Φ_{EOP} curves for temperatures between 0 and 40°C are shown in Figure 4 for BSE containing $0.10\text{ mol dm}^{-3}\text{ HBF}_4$ at electrode-II. One can observe that Φ_{EOP} -values decrease with increasing temperature. This behaviour is normally found in investigations using temperature values $\geq 0^\circ\text{C}$ and can be understood considering the increase in the anodic potential with decreasing temperature combined with a lower O_3 decomposition rate when the temperature is decreased^{4,34}.

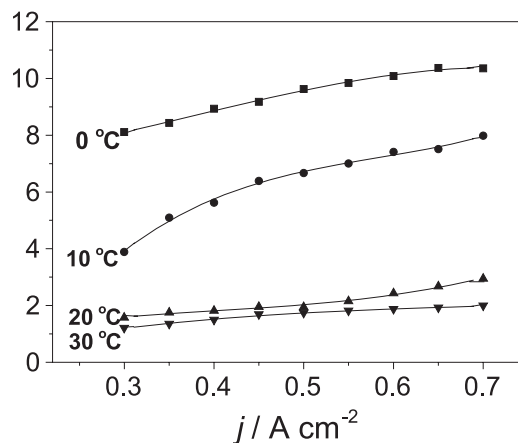


Figure 4. Influence of temperature on the Φ_{EOP} vs. j behaviour. Electrode-II. Electrolyte: $3.0\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$ containing $0.10\text{ mol dm}^{-3}\text{ HBF}_4$

Influence of electrode morphology and electrolyte on the polarisation curves obtained point-by-point

Figure 5 shows representative polarisation curves, at 0°C , for the different electrolytes investigated. All potentials were corrected for ohmic drop.

As shown in Figure 5 the influence of the fluoro-anions on the E vs. j profiles reveals to be dependent on electrode morphology. While in the case of the more compact coating (Electrode-I) the fluoro-anions cause an expressive effect on η over the complete current interval investigated, for the less compact coating (Electrode-II) the influence of the fluoro-anions is mainly verified at $j \leq 0.3\text{ A cm}^{-2}$.

The above results clearly establish a dependency between electrode morphology and Φ_{EOP} emphasising the need for a detailed investigation of the electrode preparation parameters in order to optimise Φ_{EOP} and reach a better understanding of the fundamental aspects involved.

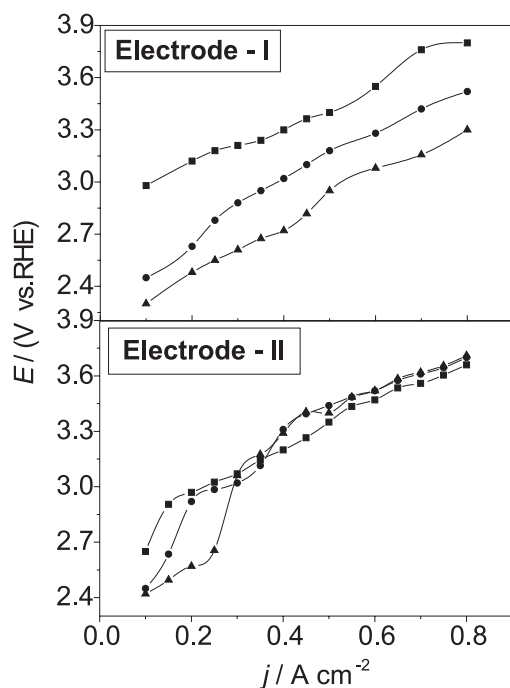


Figure 5. Dependence of the E vs. j profiles on electrolyte composition and electrode morphology (Electrodes I and II). E -values corrected for ohmic drop. Data points were taken point-by-point under galvanostatic polarisation. (\blacktriangle) BSE, $3.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; (\bullet) BSE + $0.10 \text{ mol dm}^{-3} \text{ HBF}_4$; (\blacksquare) BSE + $0.03 \text{ mol dm}^{-3} \text{ NaF}$. $T = 0^\circ\text{C}$

Status of the ozonation systems development

Among the various electrochemical EOP technologies, the solid polymer electrolyte, SPE , technology is particularly interesting^{16,22,26}, since it can operate in electrolyte-free water and hence allows *in situ* ozonation in water/effluent streams. This system, also called Membrel[®] process, is an example of the way EOP can be commercially relevant, with Japanese, French and Swiss companies offering products based on this approach⁴⁰.

In the SPE technology, porous electrodes are pressed onto a proton-exchange membrane (PEM) and pure water is electrolysed to produce a mixture of O_2 and O_3 on the backside of the anode and H_2 ^{16,34,92} or H_2O_2 ⁹³ on the cathode. Lead dioxide, PbO_2 , has been used as anode and the most widely employed PEM is Nafion[®]^{16,22,26,34}. Other membranes such as BAM[®] and DAIS[®]⁹⁴⁻⁹⁶ have been studied because of high Nafion[®] price. These membranes are perfluorinated sulphonic acid polymers, which perform as a separator and a solid electrolyte due to the highly acidic environment produced by the sulphonic acid groups. Thus, PEM exhibits excellent electrochemical and mechanical stability, high protonic conductivity, an appropriate electric conductivity and low gas permeability⁹⁷.

The SPE technology has the advantage of directly dissolving a high concentration of O_3 into water, and thus, to some extent, eliminates problems of contacting gas-phase ozone into wastewater (a usual problem for corona ozonizers)⁴⁰. A further advantage is that SPE cells can operate at several amps per square centimetre with typical thickness of a few millimetres. Thus a low ohmic drop is observed across the membrane resulting in lower electrical energy consumption⁹⁷. An especially attractive feature and a major advantage of the SPE technology is the possibility to operate at room temperature with high current efficiency for EOP . In fact, Stucki *et al.*^{16,34} observed Φ_{EOP} -values of about 18% at 30°C . Similar results were obtained by

Zhou *et al.*²⁶. In another investigation, Beaufils *et al.*⁹² reported Φ_{EOP} of 7% at 30°C . According to the authors, for similar experimental conditions (anolyte temperature, anode composition and current density), the cell configuration strongly influences EOP . This is certainly due to the rate of heat removal by different SPE cell designs, which affects the local anode temperature and consequently the rate of thermal O_3 decomposition.

With respect to corrosion stability of PbO_2 , two properties of the membrane cell design seem to be decisive. The electrolyte is convection-free thus preventing mechanical wear of the anode coating. Foller and Tobias¹⁷ proposed a chemical dissolution mechanism of PbO_2 when an interlayer having a very high proton activity builds up near the anode surface. In the case of the SPE cell, the absence of concentration gradients at the anode surface reduces drastically this dissolution. The small amount of PbO_2 that does dissolve is re-deposited immediately onto the surface because of unfavourable transport conditions for its removal from the electrode (absence of convection)¹⁷. Therefore, it was possible to operate SPE cells continually at 1 A cm^{-2} for more than 3 years³⁴.

Ozone reactors based on the SPE technology permit a wide variety of cell design configuration (water flux, current density, temperature) capable to promote high Φ_{EOP} and low electrical consumption compared to other electrochemical processes. Based on the significant advantages of the SPE technology, our laboratory initiated an investigation of these parameters in an ozone reactor.

Applications of Ozone in Green Chemical Processes

The removal of organics from wastewaters and effluents has become an increasingly important issue because of steadily increasing industrial activities. Important sources of contamination are the pulp and paper mill industry, the petrochemical industry, the food-processing industry, and runoff from urban areas.

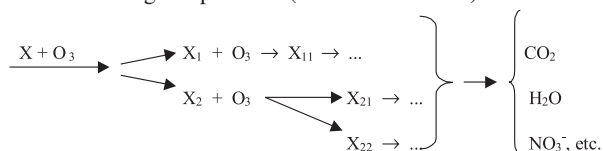
The first studies involving reactions between organics and ozone were conducted by Schönbein⁴⁶, Baumer⁹⁸ and von Gorup-Besanez⁹⁹. Wood, straw, corks, starch, humus, natural rubber, fats, alcohol, albumin, all are acted on by ozone. The bleaching effect produced by ozone on indigo was used by Schönbein⁴⁶ as a base of a method to quantitatively determine ozone concentrations. Ozone also has been applied as a selective disinfectant in brewing and cider manufacturing and additional uses include the production of oils, greases, dyes and soap¹⁰⁰. Details on the treatment of municipal/industrial effluents are also available¹⁰⁰.

Traditionally, chlorine dioxide, ClO_2 , has been a widely used and efficient bleaching agent of the wood pulp industry, causing, however, severe aggression to the environment^{14,16}. Since the 80's, in Norway¹⁰⁰, paper bleaching technology based on ozone has been developed to the commercial demonstration stage.

During degradation of organics only extended ozonation would lead to "full mineralization", i.e., to CO_2 , H_2O , NO_3^- , etc. For physical, technical or economical reasons, in practice, ozonation processes are stopped long before total mineralization. The rate expression for the removal of any organic pollutant is given by^{61,101}:

$$-d[X]/dt = k_{obs} \cdot [\text{O}_{3(aq)}] \cdot [X] \quad (17)$$

where X is the organic pollutant, k_{obs} ($= nk$) is the product of the actual rate constant and the stoichiometric factor, n , reflecting oxidation of daughter products (see scheme below).



Slow ozone reactions ($k_{\text{obs}} < 100 \text{ mol}^{-1} \text{ s}^{-1}$) are generally related to direct O_3 -reaction and depend on dissolved ozone concentration. These ozonations are usually not carried out with air-fed corona sources. When reaction rates are the rate limiting process, high available ozone concentration from *EOP* can be especially beneficial. Nevertheless, oxidations with ozone are often rapid and do not impose limitations on current commercial processes⁴⁰. The ozonation of phenol, chlorophenols, cresols, cyanide ion, sulphide ion, mercaptans and many amines present $k_{\text{obs}} \geq 10^4 \text{ mol}^{-1} \text{ s}^{-1}$. High electrochemical ozone concentration can also be of benefit in these cases, due to the possibility of using improved mass transfer rates, which means decrease capital costs.

In water, the direct reaction of dissolved ozone can hardly be separated from other reactions that arise from decomposition of aqueous ozone to secondary oxidants that are much more reactive than ozone itself¹⁰¹. Of all the secondary oxidants, the hydroxyl radical (OH^\bullet) plays a key role. These radicals can easily oxidise all types of organic contaminants and many inorganic solutes by a radical-type reaction. These radicals are immediately consumed on their formation and exhibit little substrate selectivity^{61,102}. Even organic substances that are known to be non-reactive with ozone or other oxidants, can be attacked by OH^\bullet .

In order to enhance the ozonation efficiency, efforts have been undertaken to increase the rate of its dissociation in aqueous solutions⁶¹. Advanced oxidation processes (AOP's) have been developed using UV-light or H_2O_2 , in addition to ozone, in order to accelerate its decomposition rate in water thus increasing the production of hydroxyl radicals (once ozone enters water, it becomes highly unstable and rapidly decomposes through a complex series of reactions initiated by OH^- -anions⁵⁹).

CONCLUSIONS

This article shows *EOP* is an environmental friendly technology with potential application in several Green Chemical Processes. Fundamental investigations of new electrode materials, having a higher overpotential for the *OER*, are highly desirable for the further advances in the *EOP* technology. Also, supporting electrolytes containing fluoro-anions surely improve the efficiency of the electrode process for O_3 -production including reducing energy consumption. Papers dealing with cell technology has appeared in the literature and show good performance for *EOP*. As seen here, there is no doubt that advances in electrochemical ozone generation technology allied with its favourable oxidant properties, certainly will stimulate even more its use in many different processes. Contrary to the corona technology, the electrochemical technology can generate higher O_3 concentrations, which are essential in "slow" oxidative reactions. Although operational costs of the corona technology is still lower than *EOP*, new technologies based on *SPE* cells are promising as an ozone source for many applications. As mentioned to reach a better understanding of *EOP* more detailed investigations are still necessary of such issues as electrode preparation parameters and anion adsorption phenomenon at the anode surface.

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