



Electrochemical ozone production using electrolyte-free water for environmental applications



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ABSTRACT

Oxide fine-mesh electrodes composed of lead dioxide doped with Fe^{3+} (OFM-Fe-PbO₂) were prepared by electrodeposition onto a stainless-steel fine-mesh support in order to obtain fluid-permeable electrodes for an electrochemical filter-press reactor. These electrodes were used in electrochemical ozone production (EOP) carried out during the electrolysis of electrolyte-free water in order to obtain an environmentally friendly technology for the “in situ” water treatment. SEM images of electrodes prepared using different electrodeposition conditions showed the formation of well-defined crystalline grains, which uniformly covered the metallic wires of the support. X-ray analysis revealed that the formation of a β -PbO₂ phase is more pronounced than the α -PbO₂ phase. A maximum EOP current efficiency of 10%, obtained at $j = 1.5 \text{ A cm}^{-2}$, corresponding to a rate for the ozone generation of 1.58 g h^{-1} and a specific electric energy consumption of 0.250 kWh g^{-1} , was attained for the OFM-Fe-PbO₂ electrode formed using the electrodeposition bath containing 1.0 mM Fe^{3+} . The performance of the electrochemical reactor was evaluated during long-term galvanostatic electrolysis ($t = 60$ days, $j = 1.0 \text{ A cm}^{-2}$ and 24°C), during which it was verified that the reactor voltage (U) and EOP current efficiency (Φ_{EOP}) were both stable. The robustness of the SPE filter-press electrochemical reactor allied to a moderate EOP current efficiency indicated that the OFM-Fe-PbO₂ electrode (1.0 mM Fe^{3+}) is promising for in situ ozone production from the electrolysis of electrolyte-free water.

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1. Introduction

Ozone is an environmentally friendly oxidant used in various applications regarding water and wastewater treatments [1]. Ozonation can also be used in the purification of water loops used in the pharmaceutical and semiconductor industries, the wood pulp bleaching process, treatment of textile wastewaters and so forth [1–3].

As ozone is a highly reactive gas under ordinary conditions, it must be generated on site [1–6]. In most cases, on-site ozone generation is carried out by means of dielectric barrier discharge (also called the Corona process) [1,2]. The main drawback presented by the Corona technology is that the energy efficiency decreases rapidly as we try to increase the ozone generation rate [2].

Ozone can also be generated using electrochemical reactors, whereby water electrolysis carried out under appropriate

conditions enables the ozone–oxygen gaseous mixture to be generated in aqueous medium [1,2,4–12]. The process, known as electrochemical ozone production (EOP), is very important for some specific niche applications, as in the case of the ultra-purification of water used in pharmaceutical and semiconductor industries, where the use of ultra-purified water is mandatory [4–6].

The main advantage presented by EOP is the high concentration achieved in the gaseous phase (O_2/O_3), which can range from approximately 4–35 wt.% [2–6,12–14]. As discussed by Da Silva et al. [2,4,5], EOP is gaining popularity for small/medium ozone applications, owing to features that are not achieved with the Corona technology. For instance, the development of electrochemical reactors that can operate in electrolyte-free water permitted the direct application of ozone into water streams, thereby considerably minimizing the drawbacks associated with mass transport from the gas to the condensed phase (e.g., the ozone solubilisation process) and the release of undesirable by-products (e.g., NO_x in Corona devices) during ozone generation [2–6].

Most of the anodes for the EOP process are composed of lead dioxide (PbO₂) that is either pure or doped with different elements

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[4,6,12,13]. These anodes can exhibit a very good overall performance for ozone generation under long-term operation conditions (e.g., a moderate current efficiency allied to a very high resistance to corrosion/erosion at very high current densities) [4–6]. In addition, this electrode material is very cheap.

The electrocatalytic activity of PbO₂ electrodes for the oxygen and/or oxygen–ozone evolution reactions, as well as its stability in acidic solutions, can be modulated by the incorporation of dopants in the crystal lattice, which can be achieved by adding the dopant into the electrodeposition bath [10–14]. As recently reported by Rosestolato et al. [14], doping PbO₂ with Fe³⁺ and Co²⁺ yields anodes that resist corrosion up to relatively high anodic potentials/currents; this extends the anode lifetime by decreasing amorphisation of the electrocatalyst and its partial detachment caused by a high pressure of O₂ formed inside the pores during water electrolysis. This is an important result since stability of electrodes is as important as their electrochemical activity for practical applications.

Potential environmental problems regarding the possible contamination of the treated water is disregarded, as the stability of lead dioxide in an SPE reactor inhibits the solubilisation of Pb⁴⁺ ions [5,6].

The electrochemical generation of ozone was reviewed by Christensen et al. [15] in 2013. Among other issues, they discussed the very high current efficiencies already obtained for the generation of ozone using the Ni/Sb-SnO₂ anode, that is, current efficiencies up to 50% (equivalent to 18 kWh kg⁻¹ O₃) were reported when employing Ni/Sb-SnO₂ anodes with platinised Ti mesh cathodes housed in a divided glass cell utilising a Nafion[®] membrane from Dupont as the separator and 0.5 M H₂SO₄ as the electrolyte.

However, these very high current efficiencies were only obtained for small/moderate current densities ($j \approx 10\text{--}40 \text{ mA cm}^{-2}$), owing to the chemical instability of the anode material. As a result, the ozone generation rate, expressed in grams of ozone per unit time, is less than those obtained for the PbO₂-based anodes reported in Ref. [6]; therefore, the important figure-of-merit for electrochemical reactors denoted as the space–time yield is about 8–10 times higher in the case of PbO₂-based anodes when compared to the available data for the Ni/Sb-SnO₂ anodes.

The objective of the present work is to report the fabrication and characterisation of a robust electrochemical ozoniser developed for several different environmental applications involving the “in situ” water treatment of the electrolyte-free water by means of the application of oxide fine-mesh electrodes composed of undoped (OFM-PbO₂) and doped lead dioxide (OFM-Fe-PbO₂) supported on a stainless-steel fine-mesh substrate.

2. Experimental

2.1. Anode preparation for the SPE filter-press reactor

The lead dioxide (PbO₂) layer supported on a surface of a stainless-steel fine-mesh substrate [AISI-316 from Steel Mesh Co. (Brazil); $A_G = 20 \text{ cm}^2$, $\varnothing = 0.05 \text{ mm} \times 0.05 \text{ mm}$ and $\varepsilon = 0.2 \text{ mm}$] was used to obtain an oxide fine-mesh lead dioxide electrode (OFM-PbO₂), presenting a three-dimensional structure that was prepared by electrodeposition in an all-glass undivided cylindrical electrochemical cell ($V = 0.25 \text{ dm}^3$), where the substrate was symmetrically disposed at a distance of $\approx 2.0 \text{ cm}$ between two graphite counter electrodes ($A_G = 20 \text{ cm}^2$). The substrate was previously etched for 5 min in a boiling HNO₃ solution (0.5 mol dm⁻³) in order to increase its surface roughness. Then, the PbO₂ layer was electroformed at 60 °C under galvanostatic conditions ($j = 20 \text{ mA cm}^{-2}$ and $t = 1.0 \text{ h}$) from an acidic aqueous solution (0.01 mol dm⁻³ HNO₃) containing 0.2 mol dm⁻³ of Pb(NO₃)₂. In the

case of the doped lead dioxide layers (e.g., OFM-Fe-PbO₂), salt containing Fe³⁺ ion was added to the above-mentioned electrolytic bath in order to obtain the following concentrations for the ion: 1, 10 and 100 mmol dm⁻³. Electrodes were prepared in triplicate to check the reproducibility of the experimental findings. Electrodeposition was carried out using an OS-4000 power source (3A/30V) from ICEL (Brazil). Vetec (Brazil) “purum p.a.” products were used throughout.

2.2. Cathode preparation for the SPE filter-press reactor

A stainless-steel fine-mesh (AISI-304: $A_G = 20 \text{ cm}^2$, $\varnothing = 0.05 \text{ mm} \times 0.05 \text{ mm}$ and $\varepsilon = 0.05 \text{ mm}$) supplied by Steel Mesh Co. (Brazil) was used as the cathode.

2.3. Membrane electrode assembly and the SPE filter-press reactor

A system comprising oxide fine-mesh electrodes, solid polymer electrolyte (SPE) and perforated current collectors was assembled using a specially designed cell housing made of acrylic, in which the oxide fine-mesh electrodes were pressed against the SPE (Nafion[®] 324–Dupont) using a clamping system [4]. Fluid manifolds (water distribution channels) were machined into the intermediate acrylic plates to facilitate the supply of water to the SPE/electrode interface (active zones for electrolysis).

To obtain the desired configuration for the SPE cell, a stainless-steel mesh (AISI-304: $A_G = 20 \text{ cm}^2$, $\varnothing = 0.2 \text{ mm} \times 0.2 \text{ mm}$ and $\varepsilon = 0.2 \text{ mm}$) was placed between the electrodes (anode and cathode) and the perforated current collectors, which was also made of stainless-steel (AISI-304). These auxiliary stainless-steel meshes were used to propitiate a uniform distribution of pressure on the membrane electrode assembly (MEA), since the “sandwich” (collector/mesh/anode/SPE/cathode/mesh/collector) was compressed through springs fixed at the edges of the perforated current collectors [4]. A pressure of 0.5 kgf cm⁻² was applied by fastening spring-loaded screws (a clamping system) that were fixed in the perforated current collectors in order to promote an adequate mechanical/electrical contact at the electrode/SPE/H₂O interface. This procedure ensured adequate compression of the SPE, providing the necessary conditions for the zero-gap configuration.

The mechanisms of ionic and electron conduction in an SPE filter-press cell using electrolyte-free water are different from those in conventional electrochemical cells that utilise liquid electrolytes [4,16,17]. In this case, hydrated hydrogen ions (H⁺·x H₂O) are the carriers inside the SPE that move through channels, passing from one fixed sulfonic acid group to the adjacent one (a Grotthuss-like mechanism). Thus, during electrolysis, the hydrated hydrogen ions generated at the anode/SPE/H₂O (three-phase) interface move inside the SPE towards the cathode, where they recombine with electrons, resulting in the hydrogen evolution reaction (HER). Clearly, electrons originating from the anode pass through the external circuit to the cathode. Therefore, there is no pH change in the regions neighbouring the anodic active centres of the membrane electrode assembly (MEA) during the EOP, as 100% of the generated protons are transported in the hydrated form by the SPE in order to establish the electroneutrality of the entire electrochemical system.

Reinforced Nafion[®] 324 (Dupont, Brazil) was pre-treated by immersing it into boiling 50 v/v% HNO₃ solution for 30 min and then in boiling deionised water for 2 h to provide adequate hydration of the membrane [16,17].

Fig. 1 shows the experimental setup used in the present study, in which the electrolysis of electrolyte-free water was carried out by recirculation through a plug-flow batch reactor at a volumetric flow rate (Q) of 23.6 cm³ s⁻¹.

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