

## SOLAR POWERED PEM ELECTROLYSER USED AS OZONE GENERATOR FOR TERTIARY WATER TREATMENT

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*This paper presents an autonomous system used for tertiary water treatment. The system is based on a modified fuel cell and employs Ti electrodes for the electrochemical generation of ozone. Nafion 117 membrane was used as electrolyte. The ozone concentration generated using this system was higher than the one needed for water disinfection.*

**Keywords:** ozone, Ti electrodes, autonomous system

### 1. Introduction

In the recent years, water treatment has gained attention as a result of rapid population growth and increased drinking water demand and due to the fact that more than 884 billion people lack access to clean drinking water [1]. Among water treatment processes, tertiary water treatment may be considered the most important step as disinfection inactivates pathogens [2, 3], some of them responsible for waterborne diseases. Usually, tertiary treatment implies the use of chlorine-based compounds (gaseous chlorine, hypochlorite acid, chlorine dioxide) [2, 4]. Although the chemical treatment may be effective, unwanted side reactions take place between the disinfecting agent and the substances (mainly organic compounds) present in water [4] which lead to the so-called disinfection by-products [5-11]. In the recent years, studies have been focusing on new, environmentally friendly disinfection methods [12]. Among these, ozonation is one of the most suitable methods [2, 13].

Ozonation is used intensively in water treatment as it produces no harmful by-products, as opposed to chlorination [2, 13]. Moreover, ozone acts as a disinfecting agent as well as an oxidizing agent. Ozone has an oxidation potential of 2.07V [13-17].

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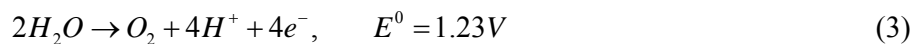
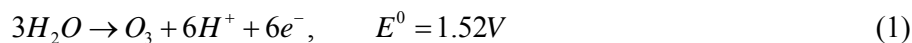
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Ozone has been proven to be an effective disinfectant, often better than chlorine-based compounds [3]. Ozone is known to remove colour, taste and odour from drinking water [18]. Studies proved the efficiency of ozone in the removal of some pharmaceuticals [18, 19], estrogens [19] and progesterone [18], endocrine disruptors [20], caffeine [18] and for the degradation and discolouration of atrazine [21], Reactive Orange 122 [22], Orange-13 and Blue-19 [23]. Among the pathogens responsible for waterborne diseases, ozone has proven effective in the destruction of *Escherichia Coli* [12], *Giardia lamblia* [16], *Encephalitozoon intestinalis* [24], *Bacillus subtilis* and *Aspergillus brasiliensis* [25]. In some cases, ozone proved to be a much more potent disinfectant than free chlorine [24].

The major drawback of ozone disinfection arises from ozone short half-life (15 minutes at 25°C) [14, 16, 26] and higher capital costs [2]. Moreover, prior to ozonation, the water must be treated in order to remove the particulate material, as microorganisms may attach to it and cause a drop in the process efficiency [3].

Among the generation methods, Corona discharge and electrolysis are the most common methods for ozone generation [4, 15]. The latter has several advantages compared to Corona discharge and it is the most used method. Among the advantages, one mentions the fact that ozone is generated in the aqueous media [27] and the concentration of ozone is higher than the one obtained in the Corona discharge [15]. Moreover, as opposed to Corona discharge, which requires high voltage, the electrolytic process requires relatively low voltage (usually over 1.8 V) [26]. As drawbacks of the electrolytic process, one mentions high energy consumption [15] and the complexity of the system [27]. Among the parameters that influence the electrolytic process, one highlights the nature of electrode material [12, 13] and operating parameters, the applied voltage being of a paramount importance [12].

The reactions that describe the electrochemical generation of ozone and the associated standard electrode potentials are given by Eq. (1) and (2) [4, 13, 14, 28-32]. During the electrolysis of water, ozone is generated at the anode and hydrogen gas is produced at the cathode. The ozone generation reaction is a side reaction, as the main reaction taking place at the anode is oxygen evolution reaction, which is thermodynamically favoured (Eq. 3) [4, 13-15, 28-32]



Another drawback of the electrolytic generation of ozone arises from the stability of the electrode material. Electrodes should have oxygen over potential [13, 27]. Studies have proven that such electrodes are those made of platinum

[13], boron-doped diamond [30], PbO<sub>2</sub>-loaded Pt screens [26], Ti/ $\beta$ -PbO<sub>2</sub> [21, 33], silicon/titanium oxide/platinum/titanium dioxide (Si/TiO<sub>x</sub>/Pt/TiO<sub>2</sub>) [13, 14], Pt-TaO<sub>x</sub>/Ti [28], Ni-Sb-SnO<sub>2</sub>/Ti [29] and tantalum oxide [34].

The aim of this paper is to present the experimental results of ozone generation using a PEM (proton exchange membrane, namely Nafion 117) electrolyser based on perforated Ti electrodes.

## 2. Experimental part

The electrochemical generation of ozone was accomplished using an autonomous system based on a modified reversible PEM fuel cell used as electrolyser. The electrodes were made of perforated Ti sheets and hydrated activated Nafion membrane. One has collected only the ozone gas in a gas collector filled with tap water. Hydrogen gas was discharged in the air.

In the present study, one has used Ti electrodes instead of Pt electrodes as previous studies have shown that the Nafion membrane may be damaged by the oxidation of the Pt anode to form Pt oxides, such as PtO<sub>2</sub>. During the oxidation of the Pt anode, ionic species can be formed and released from the Pt anode surface. These species pass through the membrane and concentrate on the cathode side of the Nafion 117 membrane. The reduction of these species by hydrogen causes the decomposition of the Nafion 117 membrane [32]. Although Ti also forms a layer of TiO<sub>2</sub>, it has a better mechanical resistance and it is not subjected to poisoning, as it is the case of Pt.

The dissolved ozone concentration was measured using disposable ozone test strips.

One has generated ozone at 7 current densities ranging from 200 A·m<sup>-2</sup> to 800 A·m<sup>-2</sup>. The experiments were conducted at constant current. The necessary voltage was supplied by a power source. One has also generated ozone using a solar charger as power source, in order to provide autonomy to the process and to assess the system's ability to generate ozone when no power source is available.

The solar charger was tested at the beginning of the experiments using a standardised charging/discharging procedure for the evaluation of the rechargeable battery capacity. The charging and the discharging process took place at a constant current, namely 0.5 A and 0.33 A (the discharging current value was correlated with the manufacturer's initial information regarding the rechargeable battery capacity).

One has monitored the concentration of dissolved ozone at every 3 minutes. The total operating time was 30 minutes, as ozone has a short half life (approximately 15 minutes at 25°C) [26].

### 3. Results and discussion

Table 1 shows the concentration of ozone generated during the electrolytic process and the values of the operating parameters at 6 minutes after the beginning of the experiments. Tables 2 and 3 show the values of the same operating parameters at 15 minutes and at the end of the process.

In the initial stage of the research, the dissolved ozone was produced using a laboratory power rectifier that allowed a control over the supplied current (and implicitly current density) as well as over the applied voltage. The second experimental stage was concerned with the manufacturing of an autonomous system so that the ozone generator may be used in remote areas where the clean water sources are not easily reachable, nor the 220 V power grids (e.g. Danube Delta).

The results obtained in the case of the electrochemical generation of ozone in laboratory at voltages lower than 3V, for various electrolysis times (see Table 1 – 3) showed that the concentration of ozone does not vary significantly versus the applied voltage up to 2.9 V. The increase of the voltage above 2.9 V shows an increase of the generated dissolved ozone (the concentration doubles its value when the voltage is increased from 2.9 to 3.1V).

The ozone was also generated using an autonomous system. The choice of the solar charger took into consideration the experimental values of the ozone concentration.

The results of the testing procedure showed that the solar charger discharges after 80 minutes, during which time it may provide the necessary voltage for the electrolytic process to take place. The electrode surface directly in contact with Nafion membrane is  $13.72 \cdot 10^{-4} \text{ m}^2$ . The current density provided by the charger is 0.48 A (which corresponds to a current density of about  $350 \text{ A} \cdot \text{m}^{-2}$ ), while the output voltage is 2.74V. One should bear in mind the fact that during the testing procedure, the charger was completely covered in order to avoid its recharging. Therefore, the actual time it may operate in a discharging state may be improved provided that the system has access to the sunlight.

The system provides twice the necessary energy to power the system for 30 minutes electrolysis time. Moreover, the solar charger may operate the electrolyser even in the absence of Sun for at least 70 minutes before being recharged.

Table 1

**Dissolved ozone concentration obtained after 6 minutes of electrolysis**

Current density ( $\text{A} \cdot \text{m}^{-2}$ )	Voltage (V)	Dissolved ozone concentration ( $\text{mg} \cdot \text{L}^{-1}$ )
200	2.2	0.05
300	2.4	0.05

400	2.7	0.05
500	2.8	0.05
600	2.9	0.05
700	3.1	0.10
800	3.1	0.10

Table 2

**Dissolved ozone concentration obtained after 15 minutes of electrolysis**

Current density ( $\text{A}\cdot\text{m}^{-2}$ )	Voltage (V)	Dissolved ozone concentration ( $\text{mg}\cdot\text{L}^{-1}$ )
200	2.2	0.05
300	2.5	0.05
400	2.7	0.10
500	2.8	0.05
600	2.9	0.10
700	3.0	0.10
800	3.1	0.10

Table 3

**Dissolved ozone concentration obtained after 30 minutes of electrolysis**

Current density ( $\text{A}\cdot\text{m}^{-2}$ )	Voltage (V)	Dissolved ozone concentration ( $\text{mg}\cdot\text{L}^{-1}$ )
200	2.2	0.10
300	2.5	0.10
400	2.6	0.10
500	2.7	0.10
600	2.9	0.10
700	3.0	0.10
800	3.0	0.10

**4. Conclusions**

The electrochemical generation of ozone was accomplished using an autonomous system based on a modified reversible PEM fuel cell used as electrolyser.

The results proved that the system provides a dissolved ozone concentration high enough to sterilise, inhibit and prevent microbial growth. The

operation time was 30 minutes to provide an excess of ozone, but this can be lowered if one may need only the threshold sterilisation concentration.

The solar charger used in the experiment discharges completely after more than one hour, thus one is able to conduct two set of experiments in one discharging cycle.

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