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Keyword: electrochemical flow-by reactor; hydrogen peroxide; gas diffusion electrodes; organic redox catalysts;Published Date: 7/1/2020Page.152-170Vol 8 No 07 2020DOI: https://doi.org/10.31686/ijier.vol8.iss7.2463

Hydrogen Peroxide Production in an Electrochemical Flow-by Reactor using Gas Diffusion Electrodes Modified with Organic Redox Catalysts

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Abstract

This paper presents a proposal to use an electrochemical flow-by reactor for hydrogen peroxide electrogeneration using cathodes formed from the incorporation of organic redox catalysts (2ethylanthraquinone, 2-tert-butylanthraquinone, alizarin, and azobenzene) in the structure of gas diffusion electrodes. These electrodes help circumvent the low solubility of oxygen in aqueous solutions. Organic redox catalysts, which typically contain quinone or azo groups in their structure, were added to the electrode mass in a 10% proportion. The electrodes were used to study the electrogeneration of hydrogen peroxide in situ, in an acid medium (0.1 mol L^{-1} H₂SO₄ and 0.1 mol L^{-1} K₂SO₄, pH 1), inside an electrochemical flow-by reactor. Comparative analysis among the different catalysts indicated that the best electrode for hydrogen peroxide electrogeneration was the gas diffusion electrode modified with 10% of 2ethylanthraquinone. With an underflow rate of 200 L h⁻¹, hydrogen peroxide was formed with a maximum yield of 998.12 mg L⁻¹ after 2 h at -2.0 V vs Pt//Aq/AqCl, for which the energy consumption was 11.21 kWh kg⁻¹. The use of the electrochemical flow-by reactor was much more efficient, in that it yielded higher concentrations of hydrogen peroxide with extremely low energy consumption, compared to that obtained when using an electrochemical cell. In addition, for ensuring appropriate usage of the electrodes, optimizing their potential for the maximum generation of hydrogen peroxide, and obtaining the highest efficiency for the reduction of oxygen, a fuzzy algorithm was developed to help support the user's decision.

Keywords: electrochemical flow-by reactor; hydrogen peroxide; gas diffusion electrodes; organic redox catalysts; fuzzy logic decision support

1. Introduction

Concern about the environment, especially regarding the increasing contamination and pollution levels, has fueled studies on the prevention and control of pollutants. In recent years, many processes have been tested to increase the efficiency of treatment of resistant effluents. Among them, advanced oxidative processes, which are based on the generation of the hydroxyl radical ('OH), have high oxidizing powers, and can promote the degradation of several pollutants in a short time [1-3]. In this context, the use of hydrogen peroxide (H_2O_2) is an advantage, as it is one of the most versatile oxidants known. It is superior to chlorine, chlorine dioxide, and potassium permanganate. H_2O_2 can be converted to a hydroxyl radical by catalysis, with a reactivity lower than that of only fluorine [4].

Among the procedures studied for the production of H_2O_2 , one involves the use of gas diffusion electrodes (GDEs), which, because of their structure, favor contact between the reagents, facilitate rapid removal of the reaction products, and easily transport the current to the electrode [5]. The use of a GDE, in addition to cathodically generating a highly oxidant species *in situ*, such as H_2O_2 , allows one to modify the cathodic reaction in industrial anode processes (such as chlorine generation or effluent treatment). This typically manifests in the evolution of hydrogen during the oxygen reduction reaction. This preferential cathodic reaction exchange, possible only with the use of a GDE as a cathode, displaces the cathode equilibrium potential toward the direction of a more positive potential, implying a decrease of the same order in the potential difference between the cathode and the anode [6].

The production of H_2O_2 in a GDE is based on the reduction of oxygen in an aqueous medium. This type of electrode is not subject to limitations imposed by the concentration of the gas in the medium, or by the diffusion of the O_2 molecules from the interior of the solution to the surface of the electrode, as in conventional electrodes.

There has been immense interest to modify GDEs with organic redox catalysts in order to increase the generation of H_2O_2 . Modification of the carbon surface by quinones can be performed to establish the relationship between the structure and catalytic activity for the reduction of O_2 and in particular, for the production of H_2O_2 [7].

Many of these studies used electrodes modified with a quinone or azo group, and the results showed an increase in the speed of the O₂ reduction reaction and a better yield of H₂O₂. 2-ethylanthraquinone, when used as a catalyst for the GDE, increased the H₂O₂ formation rate in an electrochemical cell and reduced the overpotential for oxygen reduction by 400 mV when compared to the performance of a non-modified electrode [6]. Azobenzene, when used as a catalyst, also improved the efficiency of H₂O₂ production in an electrochemical cell but reduced the overpotential for oxygen reduction by 300 mV less negative compared to that using a non-modified electrode [8]. Experiments using GDEs modified with 2-ethylanthraquinone, 2-tert-butylanthraquinone, or azobenzene carried out in an electrochemical cell have proven promising for the use of GDEs toward *in situ* H₂O₂ electrogeneration [9]. In addition to a considerable amount of H₂O₂ electrogenerated in an acidic medium, these electrodes required less energy, as the H₂O₂ electrogeneration reaction overpotential shifts to less negative values compared to non-modified GDEs [9].

In this study, an electrochemical flow-by reactor was used to monitor the electrochemical efficiency of oxygen reduction and consequently, to increase the yield in the production of H_2O_2 *in situ*. For this

purpose, GDEs modified with 10% organic redox catalysts (2-ethylanthraquinone, 2-tertbutylanthraquinone alizarin, and azobenzene) were used as the cathode. Further, to enable the appropriate use of the electrodes for the maximum generation of H_2O_2 and to obtain the best efficiency in the reduction of oxygen, a fuzzy algorithm was developed. This algorithm was applied to support the decision for the selection of the electrode and potentials, taking into account the feasibility of operation using the experimental results herein.

The proposed fuzzy decision support system follows the methods presented by Erozan [10] to manage the maintenance activities of critical components in manufacturing systems, and those by Gallab et al. [11] to quantify the risks associated with maintenance activities, by coupling the risk analysis method with fuzzy logic. This branch of artificial intelligence allows the transfer of knowledge generated in the experiments, to a decision system that clearly defines the correct selection parameters necessary to obtain greater efficiency in the results, toward their application in the treatment of resistant effluents.

2. Materials and Methods

2.1 Chemicals

An electrochemical flow-by reactor was constructed using a set of two polypropylene plates containing the cathode and anode (both with a geometric area of 20 cm²), according to the scheme shown in Figure 1. These plates were separated by a 2 mm-thick inert rubber spacer. The recirculation system used 1.0 L of the supporting aqueous electrolyte (pH 1) containing H₂SO₄ (0.1 mol dm⁻³) and K₂SO₄ (0.1 mol dm⁻³), which was pumped into the reactor by a peristaltic pump. A recirculation system ensured that the electrolyte was pumped at a controlled and constant flow through the reactor (200 L h⁻¹). The reservoir contained a refrigeration system that maintained the carrier electrolyte at a temperature of 20 °C. The reactor was then coupled to an Autolab PGSTAT-30 potentiostat/galvanostat with a high-current module (BSTR-10), in which linear voltammetry and electrolysis at constant potential were performed.



Figure 1. Schematic representation of electrochemical flow-by reactor with gas diffusion electrode and dimensionally stable anode

Printex 6L was used to construct the GDEs according to methods described previously [6-9]. The GDE was modified with 10% (w/w) of organic redox catalysts (2-ethylanthraquinone (EAQ), 2-tertbutylanthraquinone (BAQ), alizarin (ALZ), and azobenzene (AZO)) to yield modified gaseous diffusion electrodes (MGDEs) [6-9]. These electrodes (GDE or MGDE) were used as cathodes. The anode used was dimensionally stable (DSA[®]-Cl₂ from De Nora do Brazil Ltda). A pseudo-reference Pt//Ag/AgCl system positioned on the face of the cathode was also used [12].

The electrodes were subjected to initial conditioning. This involved the application of a potential of -2.0 V vs Pt//Ag/AgCl for 30 min in the presence of N₂ at a pressure of 0.2 bar. This was followed by linear voltammetry (30 scans) performed in the range of -0.5 to -4.0 V vs Pt//Ag/AgCl, at a scan rate of 20 mVs⁻¹, in the presence of N₂ and again in the presence of O₂. The voltammetric response allowed better visualization of the processes of O₂ reduction and H₂O₂ decomposition, in less negative potentials, thus providing the range of potentials for the realization of electrolysis.

The *in situ* electrochemical production of H_2O_2 was achieved by the reduction of O_2 , through electrolysis in the GDE or MGDE for 2 h in the electrochemical flow-by reactor, under a constant flow of O_2 (P = 0.2 bar) at the backside of the electrode. The interval for conducting the electrolysis was defined as -1.5 V \leq -3.0 V *vs* Pt//Ag/AgCl, based on the voltammetry performed.

Samples were collected at 10 min intervals and the H_2O_2 production was quantified spectrophotometrically using a UV-Vis spectrophotometer (UV Mini-1240 UV-VIS Spectrophotometer SHIMADZU). For this procedure, it was necessary to react to the samples collected with (NH₄)₆Mo₇O₂₄.4H₂O 2.4 mmol dm⁻³ in H₂SO₄ 0.5 mol dm⁻³ [13].

2.2 Fuzzy Logic Algorithm

As stated by Gallab et al. [11], fuzzy logic is based on the theory of fuzzy sets developed by Zadeh [14], and is a generalization of the classical set theory. This technique provides flexibility for reasoning and considers inaccuracy, subjectivity, uncertainty, imprecision. It also provides wide opportunities for working with imprecise linguistic data by defining rules and membership functions in sets called "fuzzy sets" [15].

Gallab et al. [11] also state that the fuzzy sets theory is applicable when assessing indicators for which there is no conventional model for estimating and measuring, or if the model is too complex.

This theory, presented by Zadeh [16, 17], is the most suitable formalism to qualitatively describe linguistic variables. According to Lamrani and Tkiouat [18], fuzzy inference is a formulation process for converting a given input data combination scenario into a single output data using fuzzy logic and involves the association function, fuzzy logic operators and if-then rules.

According to the guidelines outlined by Dernoncourt [15], the choices made by the designer of a fuzzy system, such as defining the membership functions and the decision matrix, are based mainly on the advice of the expert or statistical data.

In this work, a fuzzy logic system was established as per the following steps:

i) Fuzzyfication, which uses the inputs as parameters. The inputs were obtained from the types of electrodes and from the possible values of potentials available in the potentiostat/galvanostat, converted to pertinence functions;

- Fuzzy inference system, which considers one base of rules established by experts and an inference engine to assess the degree of relevance of each of the variables in each proposed scenario, and then infers the triggering of the rules governing the system;
- iii) Defuzzification (used to provide a fuzzy output numerical value obtained from the fuzzy output membership values and the fuzzy numerical value represents the center of gravity of the fuzzy output possibility distribution that shows the expected efficiency electrogeneration of H_2O_2).

Gallab et al. [11] list the steps to build the algorithm framework:

- Select the key indicators that affect the dependent variables;
- Create fuzzy sets for both independent and dependent variables, and then use the membership functions to specify the degree of truth up to which each variable belongs in a certain fuzzy set;
- Establish the inference rules in the system;
- Generate the output fuzzy set of the dependent variables based on the independent variables and the inference rules. A numerical value of the output fuzzy set is then calculated by the defuzzification operation;
- Use the model results to make a decision.

The fuzzy logic algorithm was built as per the steps above. The Mathworks software tool "MatLab", with 'Electrode Type' and 'Potential' data, and controllers based on fuzzy concepts, were used to decide H_2O_2 productivity. As a starting point, the data categorized as 'Electrodes' and 'Potentials' were translated into fuzzy variables.

When working with data in classical systems, one must consider the truth function, which assigns to each variable the truth value 1 (true) or 0 (false). Let v be a function defined from the set of variables (V) for the set binary $\{0, 1\}$, that is:

 $v: V \rightarrow \{0; 1\}$ v(p) = 0 or v(p) = 1, for variable p

In non-classical situations, the fuzzy valuation function carries the variables for the closed interval [0, 1]. This implies that a variable 'p' can have $\mu f(p) = 0.8$, thus assigning it a degree of membership of 0.8 of its occurrences. As 0.8 is closer to 1 than to 0, semantically, this denotes that the event or data bound to the variable 'p' has a high chance of occurring. Formally, the fuzzy valuation (μf) is given by $\mu_f: V \rightarrow [0, 1]$

$$\mu_f(\mathbf{p}) = \mathbf{a}, \mathbf{a} \in [0, 1]$$

In terms of the variables for the potentials and electrodes, the function was modeled according to Figures 2.a and 2.b.



Figure 2. Fuzzyfication of the variable (A) electrode and (B) potential.

In Figure 2.a, the abscissa axis represents the types of electrodes and the ordinates represent the degrees of pertinence of the respective electrodes. The data used are as follows:

- i) GDE: 0.1 (Params: [-0.225 -0.025 0.118 0.194])
- ii) EAQ: 0.3 (Params: [0.2 0.3 0.4])
- iii) BAQ: 0.5 (Params: [0.4067 0.5 0.59])
- iv) ALZ: 0.7 (Params: [0.6 0.7 0.79])
- v) AZO: 0.9 (Params: [0.8 0.9 1 100])

Similarly, in Figure 2.b the x-axis denotes the values of the potentials (1.5, 2.0, 2.5, and 3.0) and the y-axis their respective degrees of pertinence.

- i) V1 = 1.5 (Params: $[1 \ 1 \ 1.6 \ 2]$)
- ii) V2 = 2.0 (Params: [1.5 2 2.5])
- iii) V3 = 2.0 (Params: [2 2.5 3])
- iv) V4 = 2.0 (Params: [2.5 3 3.657 4.157])

From these input data, the fuzzy controller will determine the desired output values in the system, namely, the GDE productivity, EAQ productivity, BAQ productivity, ALZ productivity, and AZO productivity. The scheme is illustrated in Figure 3.



Figure 3. Generalized Fuzzy system for H₂O₂ production.

The fuzzy controller performs the decision making process through a set of rules formalized from the experience of a subject specialist. The method of inference adopted was the one proposed by Mamdani and Assilian [19], the most commonly used fuzzy inference technique.

For our purposes, the explicit tables with the data acquired from the experiments guided the basis of rule construction. They are as follows:

R₁: If (Potential is V1) and (Electrode is GDE) then (PROD GDE is BAD) R₂: If (Potential is V2) and (Electrode is GDE) then (PROD GDE is GOOD) R₃: If (Potential is V3) and (Electrode is GDE) then (PROD GDE is AVERAGE) R₄: If (Potential is V4) and (Electrode is GDE) then (PROD GDE is REGULAR) R₅: If (Potential is V1) and (Electrode is EAQ) then (PROD EAQ is MEDIA) R₆: If (Potential is V2) and (Electrode is EAQ) then (PROD EAQ is EXCELLENT) R₇: If (Potential is V3) and (Electrode is EAQ) then (PROD EAQ is GOOD) R₈: If (Potential is V4) and (Electrode is EAQ) then (PROD EAQ is GOOD) R₉: If (Potential is V1) and (Electrode is BAQ) then (PROD BAQ is BAD) R₁₀: If (Potential is V2) and (Electrode is BAQ) then (PROD BAQ is MEDIA) R₁₁: If (Potential is V3) and (Electrode is BAQ) then (PROD BAQ is GOOD) R₁₂: If (Potential is V4) and (Electrode is BAQ) then (PROD BAQ is REGULAR) R₁₃: If (Potential is V1) and (Electrode is ALZ) then (PROD ALZ is REGULAR) R₁₄: If (Potential is V2) and (Electrode is ALZ) then (PROD ALZ is EXCELLENT) R₁₅: If (Potential is V3) and (Electrode is ALZ) then (PROD ALZ is GOOD) R₁₆: If (Potential is V4) and (Electrode is ALZ) then (PROD ALZ is MEDIA) R₁₇: If (Potential is V1) and (Electrode is AZO) then (PROD AZO is REGULAR) R₁₈: If (Potential is V2) and (Electrode is AZO) then (PROD AZO is GOOD)

R₁₉: If (Potential is V3) and (Electrode is AZO) then (PROD_AZO is EXCELLENT) R₂₀: If (Potential is V4) and (Electrode is AZO) then (PROD_AZO is MEDIA)

The metric used to classify attributes BAD, REGULAR, AVERAGE, GOOD and EXCELLENT is given by:

- i) BAD: Productivity (mg L^{-1}) \leq 370
- ii) REGULAR: $371 \le$ Productivity (mg L⁻¹) ≤ 525
- iii) AVERAGE: $500 \le$ Productivity (mg L⁻¹) ≤ 655
- iv) GOOD: $657 \le$ Productivity (mg L⁻¹) ≤ 825
- v) EXCELLENT: $830 \le$ Productivity (mg L⁻¹) ≤ 1000

3. Results and Discussion

Figure 4 compares the voltammetric behavior of the GDE and MGDE with O₂ (0.2 bar), flowing through the backside of the electrode. Although poorly defined, it is possible to observe thresholds that are related to the reduction reactions of O₂ forming H₂O₂ (O₂ + 2 H⁺ + 2 e \rightarrow H₂O₂), probably occurring in the range of -1.25 to -2.5 V vs Pt//Ag/AgCl, and the decomposition reaction of this product (H₂O₂ + 2 H⁺ + 2e \rightarrow 2 H₂O) after -2.5 V vs Pt//Ag/AgCl.

Note that the current values range from nearly zero to approximately -1.25 V vs Pt//Ag/AgCl. From this potential, an increase in current related to the beginning of the reduction reaction of O₂ occurs. This increase is more accentuated for the GDE modified with ALZ and BAQ. This increase in current implies the beginning of the O₂ reduction reaction in less negative overpotentials, and indicates that the MGDE will present a greater efficiency in generating H₂O₂ when compared to the GDE.



Figure 4. Linear voltammograms obtained using an electrochemical flow-by reactor with a gas diffusion

electrode (GDE) and modified gas diffusion electrodes (MGDE) pressurized with oxygen (0.2 bar). Acidic medium (1.0 L of 0.1 mol L⁻¹ K₂SO₄ in 0.1 mol L H₂SO₄, pH 1) supplied at flow rate of 200 L h⁻¹. $v = 20 \text{ mV s}^{-1}$ and T = 20 ⁰C.

As described, electrolysis was carried out at a constant potential for 2 h, and the samples were collected at 10-min intervals to analyze the H_2O_2 production by UV-Vis spectrophotometry. Figure 5 shows the H_2O_2 production versus time using the GDE and MGDE. In all cases, the H_2O_2 concentration increased linearly as a function of time.





Figure 5. Concentration of hydrogen peroxide formed as a function of time using an electrochemical flow-by reactor with a gas diffusion electrode (GDE) and modified gas diffusion electrodes (MGDE) pressurized with oxygen (0.2 bar). Acidic medium (1.0 L of 0.1 mol L⁻¹ K₂SO₄ in 0.1 mol L H₂SO₄, pH 1) supplied at flow rate of 200 L h⁻¹ and T = 20 °C. (A) GDE; (B) MGDE with 10% EAQ; (C) MGDE with 10% ALZ; (D) MGDE with 10% BAQ and (E) MGDE with 10% AZO.

An initial increase in the H₂O₂ concentration up to -2.0 V vs Pt//Ag/AgCl for the GDE (Figure 5A) and for the MGDE with EAQ and BAQ was observed (Figure 5B and 5D). For the MGDE with ALZ and AZO, this increase extended to -2.5 V vs Pt//Ag/AgCl (Figure 5C and 5E). Beyond these potentials, the efficiency of production began to decrease due to the decomposition of the electrogenerated H₂O₂ with H₂O formation. The hydrogen evolution reaction was also responsible for this decrease as it tended to be more pronounced, competing with the H₂O₂ formation reaction. In terms of performance, it was observed that the use of the MGDE resulted in higher H₂O₂ production, independent of the nature of the added catalyst. Thus, the MGDE was comparatively more efficient than the GDE.

An important electrochemical parameter is the energy consumption (EC), which was calculated from the cell potential monitored during electrolysis [20]. Table 1 shows a comparative analysis of the EC during H_2O_2 production in the different electrodes studied, and the maximum concentration of H_2O_2 obtained.

| cathodes | E (V) | H ₂ O ₂ (mg L ⁻¹) | EC (kWh kg ⁻¹) |
|--------------|-------|---|----------------------------|
| GDE | -2.0 | 765.29 | 29.32 |
| MGDE 10% EAQ | -2.0 | 998.12 | 11.21 |
| MGDE 10% BAQ | -2.0 | 885.33 | 16.62 |
| MGDE 10% ALZ | -2.5 | 804.95 | 19.27 |
| MGDE 10% AZO | -2.5 | 899.15 | 20.18 |

Table 1. H2O2 production and energy consumption (EC) obtained after 2 hours of electrolysis using theGDE or MGDE cathodes.

The results presented in Table 1 show that the modification of the electrodes with organic redox catalysts resulted in an increase in the H_2O_2 production efficiency, with lower energy consumption, compared to the unmodified electrode (GDE). Therefore, the use of the MGDE with EAQ (10% (w/w)) resulted in better catalytic efficiency and lower EC at all studied potentials.

Comparing the results shown in Table 1 with the results obtained in experiments performed in the electrochemical cell [9], it can be concluded that the use of the electrochemical flow-by reactor was much more efficient. It resulted in higher concentrations of H_2O_2 with significantly lower EC, even at a higher optimum potential.

The implementation of the decision algorithm is described in Figure 3. First, the algorithm takes the two input linguistic variables and assigns them a membership to one or more linguistic terms based on the membership functions. Once each of the input linguistic variables is assigned membership, the step size output is determined via the "if . . . then" rule base as shown in Figure 5. The rule base was created through the data obtained in the experiments. With the aid of the MatLab software tool, the results were obtained from the input data (type of electrode and potential applied).

a) The GDE electrode (0.1) and all available potentials in another type of modeling of Figure 5 are shown in Figure 6 and 7.



Figure 6. Pertinence function associated with the first output variable (GDE).



Figure 7. Result obtained of triggering the base rules considering the potentials 1.5, 2.0, 2.5 and 3.0V (GDE).

The values obtained were very close to those generated in the experiment according to Figure 5. Numbers 1, 2, 3, and 4 refer to the rules used in the process by the controller, i.e., R1, R2, R3, and R4.

b) The EAQ electrode (0.3) and all available potentials in another type of modeling of Figure 5 are shown in the Figure 8 and 9.



Figure 8. Pertinence function associated with the first output variable (EAQ).



Figure 9. Result obtained of triggering the base rules considering the potentials 1.5, 2.0, 2.5 and 3.0V (EAQ).

c) The BAQ electrode (0.5) and all available potentials in another type of modeling of Figure 5 are shown in the Figure 10 and 11.



Figure 10. Pertinence function associated with the first output variable (BAQ).



Figure 11. Result obtained of triggering the base rules considering the potentials 1.5, 2.0, 2.5 and 3.0V (BAQ).

d) The ALZ electrode (0.7) and all available potentials in another type of modeling of Figure 5 are shown in the Figure 12 and 13.









e) The AZO electrode (0.9) and all available potentials in another type of modeling of Figure 5 are

shown in the Figure 14 and 15.



Figure 14. Pertinence function associated with the first output variable (AZO).



Figure 15. Result obtained of triggering the base rules considering the potentials 1.5, 2.0, 2.5 and 3.0V (AZO).

Despite being a software tool that works with uncertainties, the results obtained by the scenarios inputted in the developed algorithm of inference were analogous to those obtained experimentally. For future work, we aim to transpose the algorithm of this system into windows desktop application developed in Microsoft Visual Studio Rapid Application Development (RAD) and in the form of an application on an Android platform developed in the integrated development environment Android Studio.

4. Conclusions

All MGDEs presented a superior yield of H_2O_2 in relation to the GDE. The GDE modified with 10% of 2-ethylanthraquinone showed better performance. Under a flow rate of 200 L h⁻¹, H_2O_2 was formed with a maximum yield of 998.12 mg L⁻¹ after 2 h at -2.0 V vs Pt//Ag/AgCl and 11.21 kWh kg⁻¹ energy consumption.

In general, the results demonstrated the immense potential of the MGDE with organic catalysts in an electrochemical flow-by reactor for the electrogeneration of H_2O_2 . The process showed a high catalytic efficiency with lower energy consumption.

To provide decision support to users, a fuzzy algorithm with an inference engine based on the Mamdani and Assilian [19] method was developed to help decide the productivity of H_2O_2 by entering the values of only two inputs (electrode type and potential).

It was observed that the knowledge obtained by the expert in the execution of the experiment could be fully transferred to a fuzzy inference algorithm, thus eliminating the need for new queries or experiments, and automating the scenario selection process that presents the best result in terms of H_2O_2 productivity through the availability of electrode type and the potential generated from the potentiostat/galvanostat.

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Conflicts of interest

The authors declare no conflict of interest.

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