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Dedicated to Professor Valer Fărcăşan at his 85th anniversary

GALVANOSTATIC H_2O_2 ELECTROSYNTHESIS ON RETICULATED GLASSY CARBON ELECTRODE

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ABSTRACT. The influence of experimental parameters (electrolyte concentration, current density and air flow rate) on the current efficiency and specific energy consumption for H_2O_2 electrosynthesis by cathodic reduction of oxygen on reticulated glassy carbon electrode was investigated. The optimum results, consisting in high H_2O_2 concentration and current efficiency associated with low specific energy consumption, were obtained at 0.392 mA cm^{-2} current density and 60 l h^{-1} air flow rate when a 1 M NaOH solution was used as electrolyte.

Keywords: H_2O_2 electrosynthesis, partial oxygen reduction, reticulated glassy carbon electrode.

INTRODUCTION

The pulp and paper industry remains a promising market for H_2O_2, primarily due to environmental concerns over chlorine based processing [1, 2]. Thus, the use of hydrogen peroxide has become an attractive alternative. Among the various ways of producing hydrogen peroxide, the synthesis by partial electroreduction of dissolved oxygen in alkaline media [3]:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + HO^- \qquad \varepsilon^\circ = -0.065\ V \qquad (1)$$

has received much attention. However, this reaction has limited applicability due to the low oxygen solubility, the low reaction rate and the reduction of oxygen to HO^- [3]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4\ HO^-, \qquad \varepsilon^\circ = -0.401\ V \qquad (2)$$

Carbonaceous materials are often selected as electrode materials because of their intrinsic electrocatalytic properties for the partial electroreduction of the dissolved oxygen. The high porosity of carbonaceous materials as well as the possibility to fabricate them at desired porosity (e.g. the reticulated carbon electrode) assure a high active surface necessary to increase the reaction rate for H_2O_2 electrosynthesis (expressed for the volume unit of the electrochemical reactor).

The low solubility of O_2 in aqueous solutions determines a low mass transfer limiting current density and requires the use of a 3D electrode. The reticulated glassy carbon electrode has an exceptionally high void volume, a high surface area combined with self-supporting rigidity, a low resistance to fluid flow, a

good resistance to very high temperatures in non-oxidizing environments and is very inexpensive compared to solid glassy carbon [4, 5]. The reticulated glassy carbon may easily be machined into various geometric shapes and mounted in various cell configurations. Holes, tubes, disks or rings are also produced [5, 6].

In this context, the aim of the present work was to investigate the influence of different experimental parameters (electrolyte concentration, current density and air flow rate) on the current efficiency and specific energy consumption for H_2O_2 electrosynthesis process by cathodic reduction of oxygen from NaOH alkaline solutions, on reticulated glassy carbon electrode.

EXPERIMENTAL SECTION

Chemicals

The electrolyte was a NaOH aqueous solution (*Lachema, Czech Republic*) of different concentrations: 1 M, 2 M or 4 M.

The quantity of H_2O_2 obtained during the electrosynthesis process was measured by titration with a 0.0117 N $KMnO_4$ solution.

Experimental equipment

The experimental set up used for H_2O_2 galvanostatic electrolysis on reticulated glassy carbon electrode is presented in fig 1.

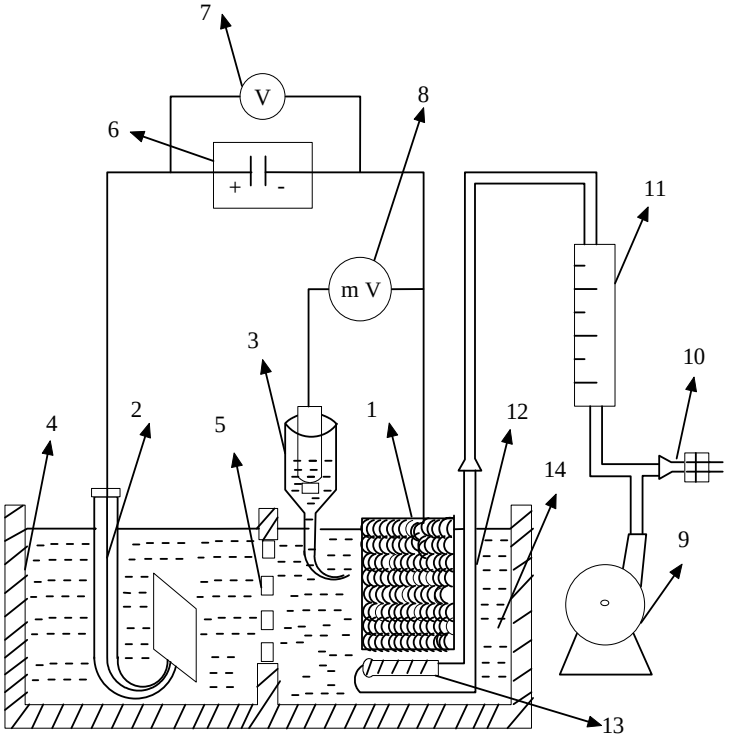

Fig. 1. The experimental set up for galvanostatic electrolysis.

The set up for galvanostatic electrolysis was composed from: 1- reticulated glassy carbon electrode as cathode; 2 - Pt as anode; 3 - saturated calomel electrode (SCE) as reference electrode; 4 - plexiglass electrosynthesis cell (2 compartments, working volume: 2 x 150 ml); 5 - ion exchanging membrane, Nafion® type; 6 - d.c. power source; 7 - voltmeter; 8 - digital milivoltmeter; 9 - air pump; 10 - tap to adjust the air flow rate; 11 - flow rate meter; 12 - air bubbling; 13 - frit; 14 - electrolyte solution (NaOH).

The specific surface of the cathode was 17 cm^2/cm^3. The cathode volume was 7.5 cm^3, which corresponds to a real active surface of the cathode of $17 \cdot 7.5 = 127.5$ cm^2.

RESULTS AND DISCUSSION

In order to determine the current efficiency and the specific energy consumption, preliminary, the experimental quantity of H_2O_2 was evaluated and the theoretical quantity of the electrosynthesized H_2O_2 was calculated.

The experimental quantity of H_2O_2 (m_{exp,H_2O_2}), obtained from the electrosynthesis process, was evaluated according to the following relation:

$$m_{exp,H_2O_2} = C_{KMnO_4} \cdot V_{KMnO_4} \cdot \frac{V_{NaOH}}{V_{sample}} \cdot E_{H_2O_2} \quad (g) \qquad (3)$$

where: C_{KMnO_4} is the normal concentration of the $KMnO_4$ solution; V_{KMnO_4} is the permanganate volume used for the titration (ml); V_{sample} is the sample volume from the cathodic compartment (ml); V_{NaOH} is the electrolyte volume from the cathodic compartment (ml), $E_{H_2O_2}$ is the equivalent of H_2O_2.

The theoretical quantity of H_2O_2 (m_{th,H_2O_2}) was calculated based on Faraday's law:

$$m_{th,H_2O_2} = I \cdot t \cdot E_{H_2O_2} \cdot \frac{1}{F} \quad (g) \qquad (4)$$

where: I is the current intensity (A), t is the time of electrosynthesis (s), F is the Faraday constant (96500 C).

The current efficiency of the electrosynthesis process was calculated as the ratio of the experimental and theoretical quantities as H_2O_2:

$$r_F = \frac{m_{exp,H_2O_2}}{m_{th,H_2O_2}} \cdot 100 \quad (\%) \qquad (5)$$

On the other hand, the energy consumption (W) and the specific energy consumption (W_s) were calculated as follows:

$$W = E_B \cdot I \cdot t \qquad (W\ s) \qquad (6)$$

$$W_s = \frac{W}{m_{exp,H_2O_2}} \qquad (kWh/kg\ H_2O_2) \qquad (7)$$

where: E_B represents the cell voltage (V); the meaning of the other symbols has been already presented.

The first experiment was made at constant current density (i = 0.196 mA cm^{-2}) and at constant air flow rate (Q_{air} = 25 l h^{-1}) for three different concentrations of the NaOH electrolyte (1, 2 and 4 M). The obtained results are presented in fig 2.

It can be observed from fig. 2 that the H_2O_2 concentration increases in time for all electrolyte concentrations. However, the increase of NaOH concentration leads to a slower increase of the H_2O_2 concentration. On the other hand, when the electrolyte concentration increases a decrease of the current efficiency corresponding to the electrosynthesis process (fig. 2 B) and, obviously, an increase of the specific energy consumption (fig. 2 C) were observed, due to the decrease of air solubility [3]. This means that it is better to use moderate concentrations of electrolyte in order to obtain a high current efficiency and low energy consumption.

Next, the influence of the current intensity on the H_2O_2 concentration, current efficiency and specific energy consumption obtained at different moments of the electrosynthesis process in NaOH 1M was studied (fig. 3).

The experimental results show that when the current density increases the reaction rate increases and, consequently, a larger quantity of hydrogen peroxide is obtained (fig. 3A). The current efficiency of the process exhibits a flattened maximum at a current intensity of ~ 50 mA. Above this value, the current efficiency decreases, probably due to the side cathodic reaction (hydrogen evolution reaction or complete oxygen reduction to HO^-) (fig. 3B). In the range of high values of current intensities (I > 40 mA) the specific energy consumption reaches a plateau (fig. 3C).

Further, the influence of the air flow rate on the process parameters at two values of the current intensities, 25 and 50 mA, was investigated (fig. 4). Three values of air flow rate were used: 25, 40 and 60 l h^{-1}.

The experimental results show that at 50 mA the increase of the air flow rate has a favourable effect on the H_2O_2 concentration, as well as on the current efficiency and specific energy consumption (fig. 4). Thus, as it can be observed in figure 4 at a current intensity of 50 mA the increase of the air flow rate involves an increase of H_2O_2 concentration and current efficiency, while the specific energy consumption decreases. The best values for the current efficiency were obtained at an air flow rate of 60 l h^{-1}, while the specific energy consumption presents convenient values.

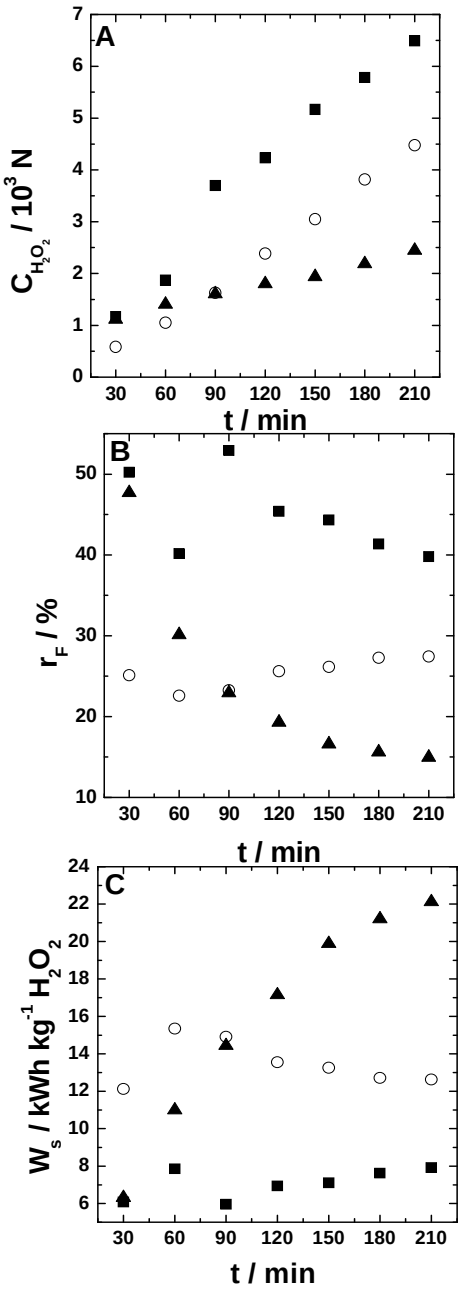

Fig. 2. Evolution of H_2O_2 concentration (A), current efficiency (B) and specific energy consumption (C) during the H_2O_2 electrosynthesis for different NaOH electrolyte concentrations (■ = 1M; ○ = 2M; ▲ = 4M). Experimental conditions: i = 0.196 mA cm^{-2}; Q_{air} = 25 l h^{-1}; room temperature.

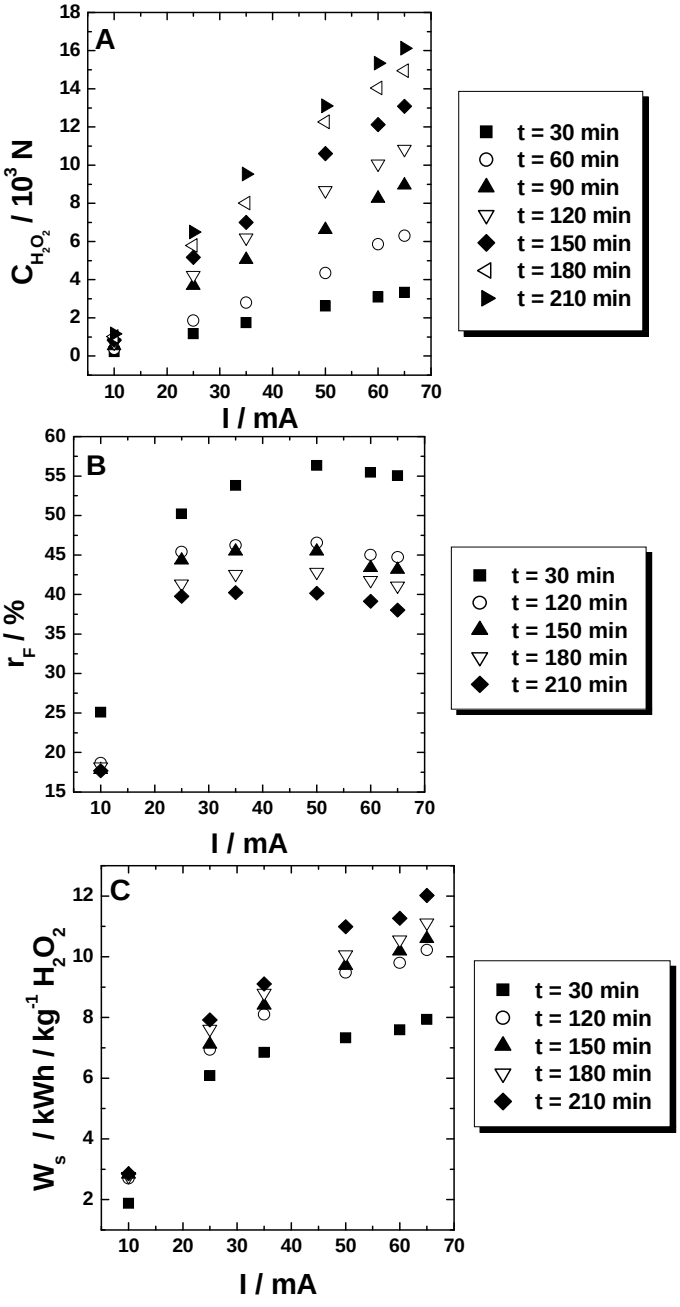

Fig. 3. Influence of the H_2O_2 concentration (A), current efficiency (B) and energy consumption (C) on the current intensity, at different moments of the H_2O_2 electrosynthesis process.
Experimental conditions: electrolyte, 1M NaOH; Q_{air} = 25 l h^{-1}; room temperature.

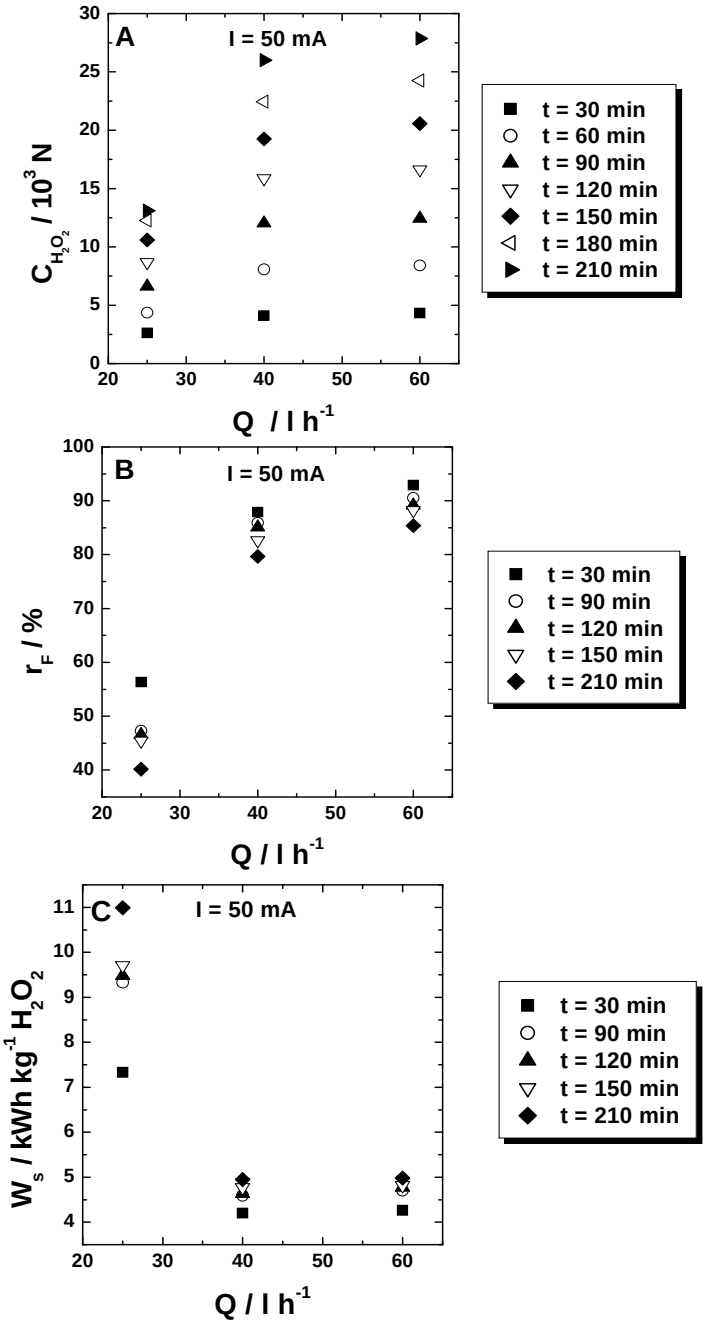

Fig. 4. The dependence of H_2O_2 concentration (A), current efficiency (B) and energy consumption (C) on the air flow rate, at different moments of the electrolysis process. Experimental conditions: electrolyte, NaOH 1M; ambient temperature.

CONCLUSIONS

The study of the H_2O_2 electrosynthesis process by cathodic reduction of oxygen on reticulated glassy carbon electrode in alkaline electrolyte allows formulating the following conclusions:

- The best results (high values of H_2O_2 concentrations and current efficiencies associated with low specific energy consumption) were obtained for a current density of 0.392 mA cm^{-2} and an air flow rate of 60 l h^{-1} when a 1M NaOH solution was used as electrolyte.
- The increase of the current efficiency with the current density and air flow rate is limited by the inherent increase of the specific energy consumption [7].

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