INFLUENCE OF CURRENT AND KIND OF GAS ON THE HYDROGEN PEROXIDE GENERATION IN THE WATER SOLUTIONS

L. Nemcova[1], F. Krcma[1], A. Nikiforov[2,3], Ch. Leys[2]

[1]*Brno University of Technology, Faculty of Chemistry, Purkynova 118, 61200, Brno, Czech Republic*
[2]*Ugent, Department of Applied Physics, Jozef Plateaustraat 22B, 9000 Gent, Belgium*
[3]*Laboratory of Non-Linear Plasma Processes, Institute of Solution Chemistry RAS, Academicheskaya 1, 153045 Ivanovo, Russia*
E-mail: krcma@fch.vutbr.cz

This contribution presents results of underwater electric discharge created in the bubbles in NaH_2PO_4. $2H_2O$ solution. This discharge configuration is relatively new one and fully combines both gas and liquid phase discharges. The gas bubbles are introduced into the system by thin stainless steel capillary that plays simultaneously a role of HV pin electrode; water solution of low conductivity up to 0.05 mS is grounded. Thus the HV pin electrode is covered by thin gas layers and the discharge is generated in the gas phase in pin to plane configuration. The discharge streamers (plasma channels) generated in the gas phase are long enough (up to 1 cm) and thus they introduce into the liquid phase and further propagate in it. The streamer length as well as their density is growing with increase of the applied voltage. The AC voltage between 2.0–3.0 kV was used in the contemporary experiment. Discharge current was varied from 20 to 30 mA, lower currents of 10 mA and 15 mA didn't allow stable discharge operation though some streamers were observed. The hydrogen peroxide generation was studied in the time evolution; the applied voltage and discharge current were the other studied parameters. Amount of generated peroxide was more or less directly proportional to the supplied energy. Four different gases (Air, Ar, He and N_2) were used for the bubble generation. Air was the most effective for the hydrogen peroxide generation, the lowest production was observed in nitrogen bubbles. This experimental result should be explained by addition of the molecular oxygen into the system that can recombine with hydrogen atoms generated by the discharge if Air was introduced. On the other hand, in case of nitrogen, a non negligible part of energy can be carried out by various metastable excited states.

Key words: underwater discharge, hydrogen peroxide, gas bubbles

1. Introduction

Underwater electrical discharges have attracted substantial attention as a new and effective alternative method for the treatment and sterilization of solutions as well as surface treatment of various materials. In general, underwater discharges can be divided into two groups based on the method of plasma ignition. Pulsed discharges are generated by high voltage pulses with durations of a few nanoseconds to microseconds with currents up to kA. The second group consists of dc or ac discharges generated in vapour bubbles. During the past two decades, research on electrical discharges in electrically conductive liquids or above these liquids´ surfaces has been focused on getting a better understanding of the pre-breakdown and breakdown phenomena in water and on several applications in water such as degradation of hazardous organic compounds, killing of microorganisms, chemical synthesis, medicine and biomedical engineering. Underwater discharges are effective sources of radicals and active particles: OH, H, O, HO_2, hydrogen peroxide, ozone, UV radiation and shock waves. An essential advantage of such systems is the possibility to combine plasma-induced effects with the highly selective chemical processes occurring in solutions. The destruction of organic compounds is initiated by reactions with hydroxyl radicals, hydrogen peroxide and ozone, if gaseous oxygen is introduced into the system [1, 2].

Hydroxyl radicals

OH radical is characterized by high reactivity with organic compounds and one of the highest redox potential (2.80 V). High value of redox potential guarantees non-selective behaving in oxidative reactions. Hydroxyl radicals are able to react with any organic substance which is presented in solution and therefore OH radicals belong to the most important particles which are generated by electric discharge. Moreover, the OH radical generation by underwater discharges is very effective.

Hydrogen peroxide

Hydrogen peroxide is versatile chemical and strong oxidant with a standard electrode potential of 1.763 V at pH 0 (Eq.1) [1].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^0 = 1.763V \tag{1}$$

While main industrial applications of H_2O_2 are bleaching of textiles and paper, important environmental applications are the removal of inorganic and organic pollutants from wastewater. The use of H_2O_2 as ·OH generating agent in advanced oxidation processes (AOPs) such as ozonation ($O_3/H_2O_2/UV$), hydrogen peroxide photolysis (UV/H_2O_2) and Fenton processes (Fe^{2+}/H_2O_2) improves its effectiveness in industrial technologies [3].

In the present work, the spectrophotometric determination of hydrogen peroxide by the reaction with metavanadate in acidic medium (vanadate method) was used because the H_2O_2 compound gives with metavanadate yellow colored peroxovanadium complex (Eq.2) [4]. (při jaké vlnové délce?)

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow VO_2^{3+} + 3H_2O \tag{2}$$

2. Experimental technique

The principal scheme of the experimental set-up for the generation of the underwater discharge in gas bubbles is presented in Figure 1. The discharge reactor consists of discharge camber (volume 1 L), on the bottom of which the glass capillary (the inner diameter of 1.2 mm, length of 50 mm) is placed. Liquid is connected to ground potential through a shunting resistance of 100 Ohm by stainless steel electrode placed at the upper part of the chamber. The plasma-solution reactor is cooled in order to avoid thermal destruction of hydrogen peroxide at temperatures above 70 °C [5]. The metallic tube with diameter of 0.5 mm is placed inside the glass capillary and it is used as the HV electrode. The gas (Ar, He, Air or N_2) is applied through this metallic tube in order to produce bubbles. Gas flow in the system is supplied by mass flow control system (MKS 4000). Flow rate of used gases is fixed at 200 sccm in all experiments. The electric discharge is located directly on the surface of the metallic tube inside of bubbles. The DC power supply for the discharge sustaining is connected to the reactor through a ballast resistor of 30 kΩ. The applied voltage is varied from 1.7 to 2.7 kV.

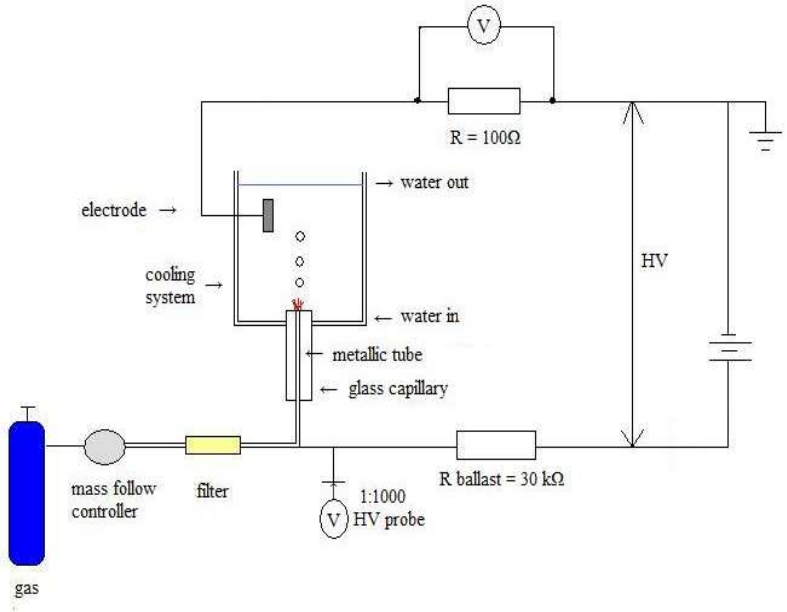

Fig. 1. Experimental set-up.

3. Results and discussion

The hydrogen peroxide was generated in the reactor during 20 minutes. The initial conductivity of NaH_2PO_4 . $2H_2O$ solution was kept in all experiments at 50 µS/cm. The gases He, Ar, Air and N_2 were alternated in the experiments while the other conditions remained constant. The applied voltage in the range 1.7–2.7 kV allowed discharge currents of 10–30 mA. Figure 2 shows hydrogen peroxide generation at the discharge current of 10 mA in all used gases. On Figures 3 and 4 we can see kinetic curves for hydrogen peroxide generation at 20 and 30 mA, respectively. The hydrogen peroxide generation at the lowest current of 10 mA is not effective because plasma is not stable operating and thus the described dependences are not smooth curves. At the higher currents, the discharge operates regularly and the hydrogen peroxide production is nearly directly proportional to the time of discharge operation; the saturation effect can be seen at the latest times (the same see in [6]). The H_2O_2 amount is nearly directly proportional to the applied current (concentration increases from 4.8 mmol/l at current of 20 mA to 8.9 mmol/l at 30 mA in argon). The initial hydrogen peroxide production rates were calculated from the linear (initial) parts of time dependencies and they are shown in table 1. The highest production rate was observed in Air bubbles, probably due to reaction of atomic oxygen (generated by dissociation of oxygen molecules from Air) with atomic hydrogen generated by water dissociation. In the other gases the peroxide production was within the experimental error interval nearly similar.

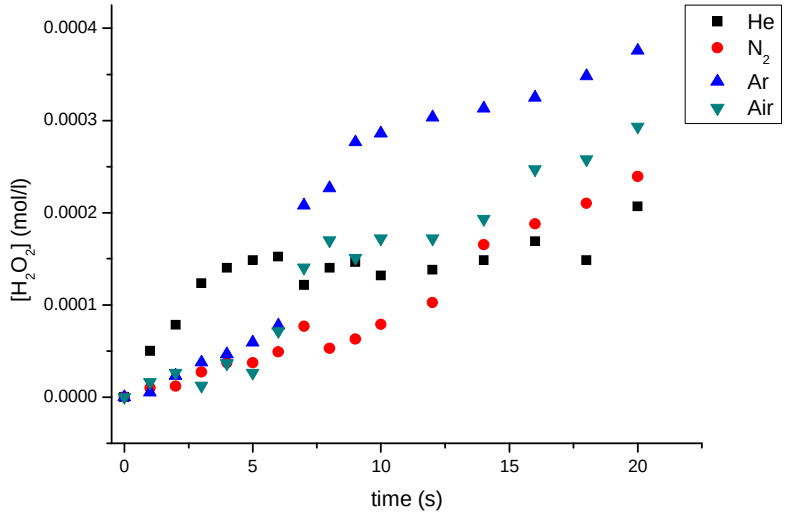

Fig. 2. Hydrogen peroxide generation at the current of 10 mA.

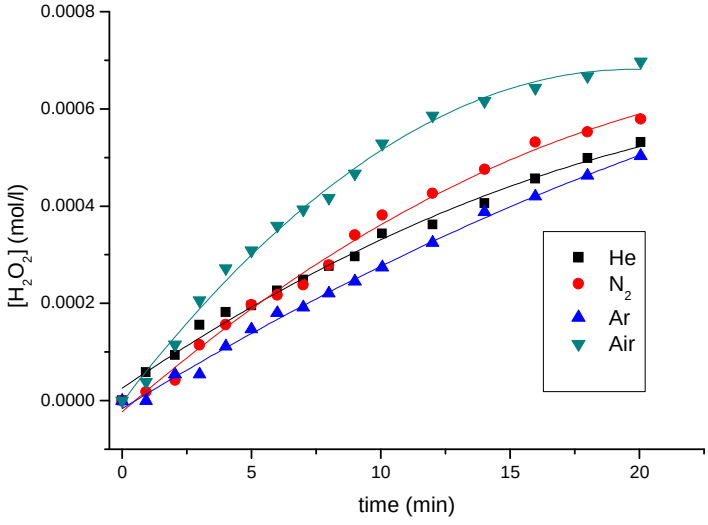

Fig. 3. Hydrogen peroxide generation by using 20 mA.

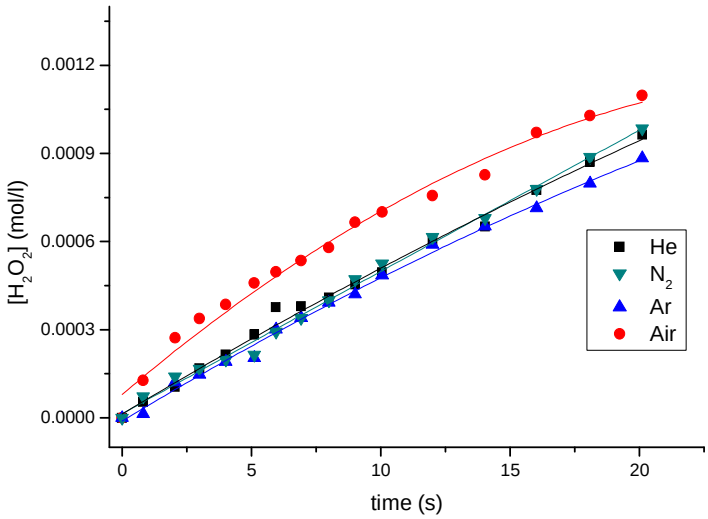

Fig. 4. Hydrogen peroxide generation by using 30 mA.

Tab. 1. Initial rate of hydrogen peroxide formation as a function of discharge current

Current [mA]	**Initial hydrogen peroxide production rate [mmol/l·s]x10^{-4}**			
	He	*Ar*	*N_2*	*Air*
15	3.3	3.6	3.8	4.2
20	4.2	3.7	5.0	5.8
25	5.8	6.1	6.3	6.7
30	8.3	8.3	6.8	8.3

4. Conclusion

This work has been focused on chemical efficiency of the electric discharge generated inside the bubbles in water solution. The influence of the used gas (Air, He, Ar, N_2) and the discharge current on the effectiveness of H_2O_2 production were studied. We observed that concentration of H_2O_2 during discharge operation was linearly proportional to the discharge current. It was also nearly independent on the used gas kind, only in air some hydrogen peroxide production enhancement was determined. The current less than 10 mA was not applicable, because plasma was not stable and thus hydrogen peroxide was generated irregularly.

5. References

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