

The study of H₂O₂ generation by DC diaphragm discharge in liquids

Z. STARÁ, F. KRČMA

Faculty of Chemistry, Brno University of Technology,
Purkyňova 118, 612 00 Brno, Czech Republic

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The contribution gives results of hydrogen peroxide generation obtained in the DC diaphragm discharge in water solutions. Chemical active species, such as hydroxyl radicals and hydrogen peroxide are produced by the discharge. The dependencies of hydrogen peroxide concentration on high voltage (magnitude and polarity), material of electrodes and dielectric diaphragm are studied for one electrolyte (NaCl) used for initial solution conductivity. The used dielectric diaphragms differ in material and they have various thickness.

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Key words: hydrogen peroxide generation, diaphragm discharge, discharge in liquids

1 Introduction

The discharges generated in liquids have a special position among plasma sources. Various active chemical species such as hydroxyl radicals, hydrogen and oxygen radicals, hydrogen peroxide etc. are produced by this kind of discharge [1]. These active species initiate many further chemical reactions. Therefore the processes taking place in these discharges can be applied in fields of water treatment. Especially the destruction of various organic pollutants dissolved in water and specific reactions in liquid phase are actually the main research fields of discharges in liquids [1, 2, 3]. Another purpose of the discharge in liquids can be surface treatment of textile fibres. Plasma generated by the discharge can modify the hydrophilic or hydrophobic properties of textile, according to the initial discharge conditions. The textile materials could be either natural or synthetic [4]. The common discharge configurations are point-to plane [1] and coaxial [2], several experiments were done in diaphragm (electrode-less) configuration [3]. During almost all of these experiments, a pulsed high voltage in the range from about 10 to 20 kV was used to create the discharge. The present contribution focuses on the diaphragm discharge created using the non-pulsed DC high voltage with tension of about 2 kV only. The diaphragm discharge creates in a small pin-hole in the dielectric diaphragm, which is placed between the two electrodes, as it is described below. The nature of this discharge type is assumed the similar as in the other configurations for that the processes were reviewed recently in [5].

2 Experimental

A special discharge reactor was used in experiments (see Fig. 1). It consists of two chambers – a negative one with a cathode and a positive part with an anode. The plane electrodes made of stainless steel or of titanium covered by platinum (2.5 μm) were arranged in the distance of 4 cm symmetrically with respect to the dielectric diaphragm, that

divided the reactor into two parts. A small pinhole (initially of 0.25 mm) was localised in the centre of the dielectric diaphragm. Various materials (PET, PTFE, PES, POM–C) were used as a dielectric diaphragm and they also had different thickness, varied from 0.05 to 1.00 mm. To generate high voltage and to create the discharge, a non-pulsed DC high voltage source was used. The applied high voltage tension was varied from 1.4 kV to 2.8 kV and two magnitudes of the serial resistance (5.5 k Ω and 88 k Ω) were used to modify the discharge current. Due to considerable heating of the reactor by the discharge and by the Joule heating of the electrolyte and also to prevent the destruction of the hydrogen peroxide, two cooling boxes with ice were installed in both parts of the reactor. This system kept the temperature under 15 °C during all the experiments. To ensure the homogeneous conditions in the whole volume of the liquid, a mixing system was adjusted in the reactor. The demineralised water containing NaCl electrolyte was used to obtain the defined initial conductivity of the solution.

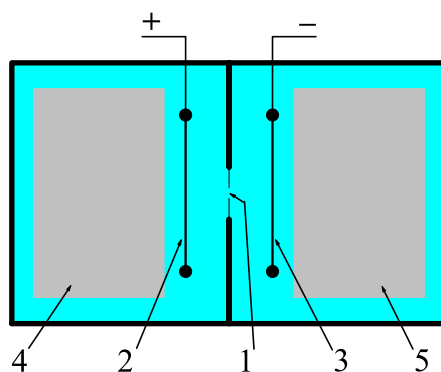
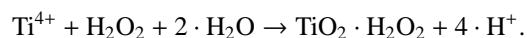


Fig. 1. A scheme of the discharge reactor: 1 – diaphragm with pinhole, 2 – cathode, 3 – anode, 4, 5 – cooling boxes.

The hydrogen peroxide was determined spectrophotometrically using the specific reaction with titanyl ions in presence of the sulphuric acid (the titanium reagent):



The created peroxotitanyl complex gave a yellow colour with the maximum absorbance at 407 nm [5]. The absorbance intensity was depended on the amount of the hydrogen peroxide according to the equation [6]:

$$y = 0.4596 \cdot x,$$

where y means absorbance and x is the concentration of the hydrogen peroxide. The samples were taken from the both parts of the reactor and the sampling time was estimated on 5 minutes. H_2O_2 concentration produced by the discharge was increased almost linearly in

time, therefore it could be described by the following equation:

$$c_{\text{H}_2\text{O}_2,t} = k_{\text{H}_2\text{O}_2} \cdot t,$$

where $c_{\text{H}_2\text{O}_2,t}$ means concentration of hydrogen peroxide, $k_{\text{H}_2\text{O}_2}$ is the rate constant of the H₂O₂ production and t is discharge duration.

3 Results

The hydrogen peroxide generation by the diaphragm discharge was studied and its dependence on the discharge conditions was investigated. The influences of applied voltage (its polarity and magnitude), material of the electrodes, used dielectric diaphragm (material and thickness) on the H₂O₂ production were observed. The amount of hydrogen peroxide increases almost about linearly with discharge duration. The rate constants of H₂O₂ production were calculated for each measurement and compared with another experiments.

The hydrogen peroxide production is significantly higher in the chamber with the cathode than in the positive part of the reactor (see Fig. 2). The conductivity of NaCl solution increases during the time, especially in the positive part of the reactor (see again Fig. 2). The conductivity increase is caused dominantly by the electrode material destruction as it was pointed before [6]. The saturation, in both hydrogen peroxide concentration and conductivity, can be observed when the discharge is running for a longer time.

The dependence of the H₂O₂ generation on the applied voltage tension is shown in Fig. 3. The concentration of hydrogen peroxide increases about linearly with the increasing voltage. During the discharge a special phenomenon was observed [7]. The discharge did not burn regularly and it did not show strictly non-pulsed voltage and current. The direct electric measurements demonstrated the real character of the discharge. It was established as quasi-pulsed [7]. The cause of this phenomenon is that the discharge is created in the bubbles of boiling liquid in the pin-hole, which are appearing in the discharge area, and therefore the breakdowns on these bubbles are very irregular.

Two different serial resistances were used to modify the discharge current, 5.5 kΩ and 88 kΩ. These resistances gave the discharge current of the average value 200 mA and 25 mA, respectively at 5 mM NaCl solution at voltage of 3.5 kV. So the mean discharge power had various magnitude, too, and, of course, it had a significant influence on H₂O₂ production. The difference is perceptibly seen in Fig. 4. The lower serial resistance allows much higher current and therefore the discharge power was much higher, too. The hydrogen peroxide generation is about proportional to the discharge power.

The comparison of hydrogen peroxide generation by the discharge in dependence on difference electrodes material is shown in Fig. 5. It can be seen, when the stainless-steel electrodes are used the hydrogen peroxide generation is more effective than the platinum electrodes are used. The H₂O₂ concentration had saturated after shorter time in the case of the iron electrodes. This effect could be caused by possible chemical reactions catalyzed by ferric or ferrous ions. The influence of the electrode material on hydrogen peroxide generation will be an object of further study including electrodes made also from different materials.

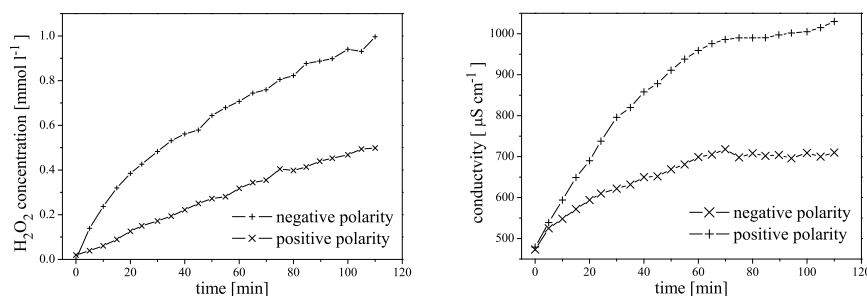


Fig. 2. Production of hydrogen peroxide (left) and conductivity (right) in time (2.8 kV, 5 mM NaCl, 163 mA, PET diaphragm).

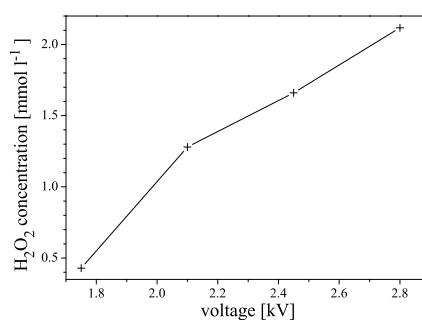


Fig. 3. Hydrogen peroxide concentration after 60 minutes of the discharge treatment as a function of the applied voltage (3 mM NaCl, PET diaphragm, negative polarity).

Six different types of the dielectric diaphragm were used in experiments up to now: polyethylenterephthalate (thickness of 0.25 mm), polyester (0.05 and 0.19 mm), polytetrafluoroethylene (Teflon, 0.50 and 1.00 mm) and Acetal Co-Polymer (Ertacetal C, 1.00 mm). The comparison of H₂O₂ generation at such different conditions is shown in Tab. 1. The most suitable materials for hydrogen peroxide generation in our experiments were PET of 0.25 mm thickness and PES of 0.19 mm. The Teflon diaphragm (PTFE) of both thicknesses was inconvenient because although this material has high chemical and thermal stability its hardness is lower. It had mechanically corroded by the discharge treatment quite easily, the pinhole in the diaphragm had enhanced its diameter rapidly (during a few minutes) and therefore the discharge could not be created for the time allowing rate coefficient calculation by these conditions. This result shows that it is necessary to take into account either chemical (inercy for the radicals and light emitted from the discharge) either physical (thickness, hardness, temperature stability) properties of the diaphragm material. The thickness of diaphragm is of course one of the main parameters that have an influence on the peroxide generation. If the diaphragm is thin lower voltage is sufficient to create the discharge but the discharge volume is relatively small (the discharge is located domi-

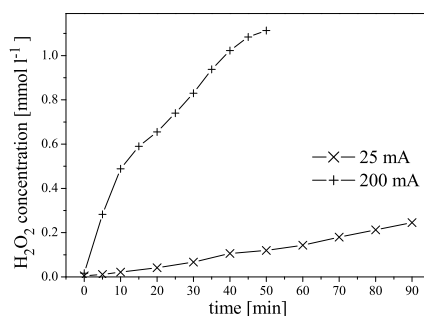


Fig. 4. The comparison of the H_2O_2 production by the discharge at different current (2.8 kV, 5 mM NaCl, PET diaphragm, stainless steel electrodes, negative polarity).

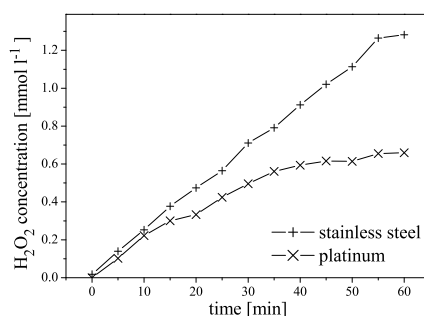


Fig. 5. The influence of the electrodes material on the hydrogen peroxide production (1.75 kV, 5 mM NaCl, PET diaphragm, negative polarity).

nantly in the hole at our experimental conditions). On the other hand, the thick diaphragm the discharge volume is large but the higher applied voltage is necessary for the discharge creation. The further study will be focused on exact study of dielectric diaphragm thickness on the H_2O_2 production.

Table 1. The rate constants of hydrogen peroxide production for various types of the dielectric diaphragm (1.75 kV, 5 mM NaCl, stainless steel electrodes).

Material	Thickness [mm]	Rate constant [$mmol\cdot l^{-1}\cdot s^{-1}$]
PET	0.25	3.750×10^{-7}
PES	0.05	1.167×10^{-7}
PES	0.19	3.600×10^{-7}
PTFE	0.50	unmeasurable
PTFE	1.00	unmeasurable
POM-C	1.00	4.667×10^{-8}

4 Conclusions

Hydrogen peroxide generation by the DC diaphragm discharge in water solutions was investigated and presented in this contribution. The influence of the discharge conditions on the H_2O_2 production was studied, especially the dependence on the applied high voltage, material of the used electrodes and on the dielectric diaphragm properties (its material and thickness). The rate constants of the hydrogen peroxide generation were calculated for each experiment. The highest production of H_2O_2 was observed in the negative part of the discharge reactor, it grew about linearly in time up to one hour and increased proportionally with increasing voltage, too. The higher discharge current modified by the serial resistance enhances the hydrogen peroxide production proportionally to the average total discharge power. In the case of titanium electrodes covered by platinum, H_2O_2 concentration was lower and became earlier saturated than in the case of stainless steel electrodes. The most effective materials of the diaphragm were PET of 0.25 mm thickness and PES of 0.19 mm thickness, the Teflon diaphragm could not be used due to its fast destruction by the discharge.

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