

Research Article

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Influence of electrode material on hydrogen peroxide generation by DC pinhole discharge

Abstract: In this work, several materials were studied as electrodes in a pinhole configuration of a DC plasma discharge to estimate their effect on the efficiency of the discharge, indicated by hydrogen peroxide production. Detection was carried out using a specific titanium reagent. This was combined with ICP-OES analysis of the final solutions to determine the difference between the amount of electrode material released during the discharge operation and electrolysis experiment carried out under the same conditions. It was found that from seven studied electrode materials, graphite gives the best results, while lower cost aluminum and titanium-zinc still work well. The most unsuitable materials were copper and brass; in these cases, no hydrogen peroxide was detected in the cathode part of the reactor. Results obtained by ICP analysis indicate that even in the case of brass, the absence of hydrogen peroxide is due to the presence of copper in the material. It probably affects both directly the phase of discharge creation and propagation and the decomposition reactions.

Keywords: hydrogen peroxide, underwater discharge, titanium reagent, electrode material, ICP-OES analysis

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1 Introduction

Plasma discharges generated in contact with or directly in conductive liquids have received great attention during last few decades. This is exhibited by the wide range of

their applications, ranging from water processing and destruction of hazardous compounds [1] to medical applications (e.g. enhancement of wound healing [2], lithotripsy of solid objects [3]) to synthesis of organic compounds [4] or nanostructures [5]. Most of the work in this field is conducted in water or water solutions. This medium is widely accessible and already utilized in various technologies.

Electrical discharges in liquids can be generated in various reactor configurations, when the intensity of applied electrical field reaches sufficiently high values (up to MV cm⁻¹ for water). The pinhole discharge is one of the suitable configurations for such plasma discharge generation. In this configuration, two electrode parts of the reactor are separated by a dielectric barrier with a small orifice. In pulse regime with a nano- or sub-nanosecond rising time, discharge breakdown appears directly in the liquid just in proximity to the pinhole. If slowly increasing DC voltage is applied, the discharge is ignited in bubbles generated by evaporation of the liquid in the pinhole. When high voltage DC is applied, plasma channels (streamers) of different shapes propagate from the pin-hole into the liquid on each side of the dielectric barrier (see Fig. 1 right) [6], depending on the electrode polarity. These streamer types differ especially in the energy dissipation originating from different electron velocities in plasma channels due to electron collisions with positive particles accelerating or decelerating electron avalanches [7]. The streamers' polarity also influences chemical reactions initiated in the liquid. The choice of pinhole configuration allows study of both polarities at the same time.

Main processes that can be observed during the discharge in liquids include bubble formation, propagation of plasma streamers, UV (and VIS) radiation, and shockwave formation [8]. Electrolysis in the system must be also taken into account within chemical processes [9]. The main active particles generated by the discharge in water solutions are OH, O and H radicals [10] that consequently initiate secondary chemical reactions.

One of diagnostic methods focused on characterization of the discharge efficiency is determination of hydrogen peroxide formed in liquids containing hydroxyl groups.

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The hydroxyl radical is among the most reactive species produced by the discharge in water solutions due to its very high oxidation potential (2.8 V). Therefore, it can be utilized in many subsequent processes. Hydrogen peroxide is the main stable product of the basic reaction chain and is formed primarily by the dimerization of two hydroxyl radicals. It does not have such high oxidation potential and although it can be consumed by side reactions, it is commonly used as a quantitative parameter of the discharge efficiency [8].

In this work, different materials were chosen to be used as electrodes in order to estimate their effects on hydrogen peroxide formation. These materials were: graphite, aluminum, stainless steel, platinum, copper, titanium-zinc and brass. The choice was driven by an attempt to cover materials with different properties.

For determination of hydrogen peroxide concentration, a specific titanium reagent was used. Titanium ions present in the reagent (Titanium(IV) oxysulfate/sulfuric acid solution) selectively react with hydrogen peroxide forming a yellow complex of pertitanic acid. Concentration of hydrogen peroxide in the initial solution is proportional to absorption of the complex solution at 407 nm [11]. Therefore, a simple UV-VIS measurement can be used to find the peroxide concentration.

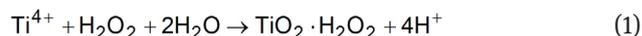
2 Experimental procedure

Two types of experiments were conducted. First, results of the plasmachemical process initiated by the pinhole discharge were studied. In the second type, the electrolytic process was studied under the same conditions. Each experiment was repeated three times, each time a new pair of electrodes was used, except for the case of graphite electrodes. Obtained results were in good agreement and were averaged for further evaluation. For experiments with the electric discharge, a polycarbonate batch reactor (see Fig. 1 left) was divided into two parts by a middle wall with a Shapal™-M nonporous ceramic diaphragm of 1-mm thickness. In the middle of the diaphragm, there was an orifice with a 1-mm diameter. Planar electrodes of chosen material were fixed symmetrically at a constant distance with respect to the diaphragm. Both electrodes were made of the same material. A positive DC voltage was applied to the anode while the other electrode was grounded and served as the cathode. A 5×8 cm area of the electrodes was immersed. Since the studied compound (hydrogen peroxide) is thermosensitive, a cooling system was included consisting of a stainless steel box in each

electrode part of the reactor. As a cooling medium, a mixture of water and ice was used. It was necessary to repeatedly renew the mixture by sucking away part of the water and adding new ice. The temperature of the bulk solution did not exceed 20°C. Higher temperatures can be expected in the vicinity of the diaphragm orifice leading to partial destruction of produced hydrogen peroxide. Homogenous conditions in whole volume of the solution were provided by a stirrer in each electrode part, which was powered by an electromotor with operating frequency of about 700 rpm. Solution of NaCl (4 mmol L⁻¹) in non-degassed distilled water with initial conductivity of 400 μS cm⁻¹ was used in all experiments. The solution was not buffered, so pH changed during the experiment – a rise could be observed in the cathode region and a drop occurred in the anode region. More details on the pH progress can be found in [12].

DC voltage up to 2 kV was supplied to the electrodes to get power of 100 W. This was reached at current values of around 55 mA. The main limiting part of the whole circuit is conductivity of the solution. Conductivity changes over time, differently in each electrode part of the reactor.

Total time of the experiment was 1 hour with a sampling time of 4 min. For testing sample preparation, 2 mL of solution were taken separately from each electrode part of the reactor and mixed with 1 mL of specific reagent in test-tubes. Hydrogen peroxide forms a yellow complex with titanyl ions, which is stable for at least six hours, according to reaction:



The determination of hydrogen peroxide concentration is possible by UV-VIS spectrometry. Absorbance of the complex was measured at 407 nm. Hydrogen peroxide concentration can be calculated from the value of absorbance. Straight-line calibration curve of the complex absorbance as a function of the peroxide concentration was estimated experimentally and the final calibration equation is as follows:

$$c_{\text{H}_2\text{O}_2} = 2.146 \cdot A_{407\text{nm}} (\text{mmol/l}) \quad (2)$$

The configuration of the reactor for electrolysis experiments differed in absence of the diaphragm. In that case, only the separating wall with a 10-mm-diameter opening was used. All the other conditions were kept the same. Experiment was conducted for 1 hour with a current of about 55 mA.

After both types of the experiment, the solutions were subjected to ICP-OES analysis in radial mode for metal

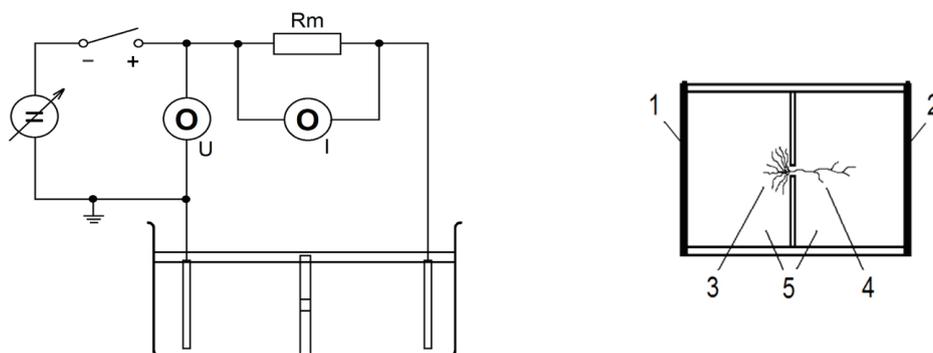


Figure 1: Left: Schematic configuration of the experimental reactor. Right: Formation of plasma streamers in the pin-hole during DC discharge. 1 – anode, 2 – cathode, 3 – negative streamer, 4 – positive streamer, 5 – electrolyte solution.

traces detection with respect to electrode polarity of the reactor parts. This enabled determination of the discharge effect on the release of the electrode material into the solution and thus its possible influence on hydrogen peroxide formation.

3 Results and discussion

The plasmachemical experiments showed strong dependency of discharge efficiency on the electrode material. Hydrogen peroxide concentration is higher in the cathode part in all cases, as has been reported before [13], except for copper and brass electrodes. Typical time dependency of concentration is shown in Fig. 2 for graphite electrodes. The increase of the concentration is essentially linear over the studied time period. After 60 minutes of the discharge, the hydrogen peroxide concentration reached 0.39 mmol L^{-1} in the cathode part and just over one third of this value, 0.15 mmol L^{-1} , in the anode part of the reactor. Comparison of hydrogen peroxide production in the cathode part of the reactor for studied electrodes is given by Fig. 3. It can be seen that the efficiency in hydrogen peroxide production is the highest for graphite electrodes followed by almost the same values for aluminum and titanium-zinc electrodes. Stainless steel electrodes were more effective than electrodes covered by platinum. Since there was no hydrogen peroxide detected in this reactor part when copper or brass electrodes were used, data for these electrodes are not present in the graph. A more detailed description and explanation for the findings is given below.

ICP analysis did not confirm any significant effect of the discharge on electrode erosion (see Fig. 4). It can be concluded that material release into the solution is driven only electrochemically. However in most cases, there are big differences between the solution composition in each

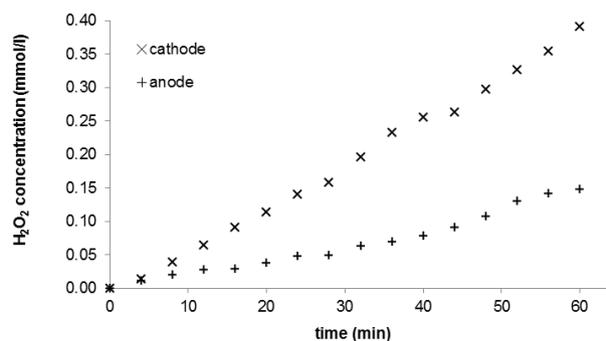


Figure 2: Typical time dependency of hydrogen peroxide concentration, graphite electrodes.

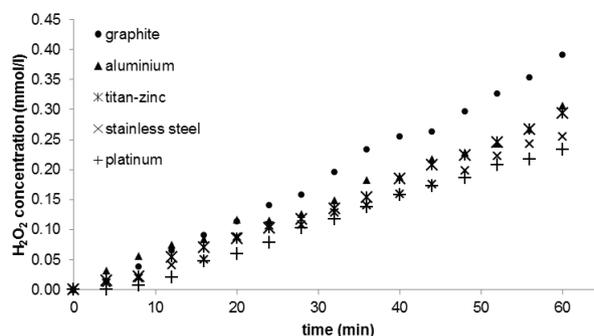


Figure 3: Comparison of hydrogen peroxide production, various electrodes.

electrode part, as can be seen in Fig. 4. For alloy materials – titanium-zinc and brass – the brackets indicate the determined element. In the case of titanium-zinc, no significant content of titanium was detected. The material released by electrolysis affects hydrogen peroxide production through the decomposing reactions more than any excessive material dissolved due to the presence of the discharge.

Initial production rate can be derived from the slope of the linear part of the time dependency of concentration.

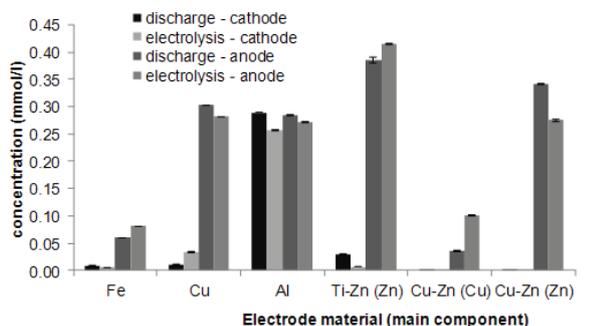


Figure 4: Comparison of metal amount detected by ICP analysis, various electrodes.

Table 1: Comparison of hydrogen peroxide production efficiency for different electrode materials.

Electrode material	$h_{\text{H}_2\text{O}_2}$ (gkW ⁻¹ h ⁻¹) cathode part	$h_{\text{H}_2\text{O}_2}$ (gkW ⁻¹ h ⁻¹) anode part	$h_{\text{H}_2\text{O}_2}$ (gkW ⁻¹ h ⁻¹) total
graphite	0.25	0.09	0.35
aluminium	0.20	0.09	0.29
titanium-zinc	0.19	0.07	0.26
stainless steel	0.17	0.05	0.22
platinum	0.16	0.07	0.23
copper	-	0.07	0.07
brass	-	0.03	0.03

Using this data, the efficiency of hydrogen peroxide production can be calculated as follows:

$$h_{\text{H}_2\text{O}_2} = \frac{dc_{\text{H}_2\text{O}_2}}{dt} \Big|_{t \rightarrow 0} (t_2 - t_1) M_{r(\text{H}_2\text{O}_2)} (P)^{-1} \quad (3)$$

where $\frac{dc_{\text{H}_2\text{O}_2}}{dt} \Big|_{t \rightarrow 0}$ is initial production rate, $(t_2 - t_1) = 60$ min, $M_{r(\text{H}_2\text{O}_2)}$ is the molecular mass of hydrogen peroxide in mg mmol⁻¹ and P is power in kW. Comparison of hydrogen peroxide efficiency obtained for different electrode materials is summarized in Table 1.

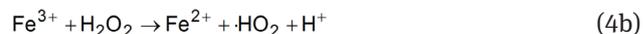
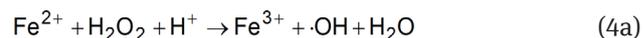
The order of metals based on hydrogen peroxide content follows the electrochemical potential row with one exception: the electrodes containing a significant proportion of copper (more detailed discussion see below). Electrochemical reactions on electrodes can lead to both reduction (cathode) and oxidation (anode) of H₂O₂.

Graphite proved to be the best choice for the electrode material. It did not show any visible damage after six hours of experiment or release any reactive particles into the solution, which would contribute to hydrogen peroxide decomposition. However, this material requires careful handling and may be costly.

Second best was aluminum. After several minutes of the experiment it started to show significant color changes depending on the electrode polarity, but ICP analysis did not show any differences in the number of released aluminum ions. This is given by the general material properties and can be explained by creation of an oxide layer that blocks further destruction of the material. Aluminum is the most active metal in the galvanic series used in this work.

Hydrogen peroxide concentration in the cathode part during the experiment with titanium-zinc electrodes practically copied the dependency obtained with aluminum electrodes. Even though titanium-zinc contains a small part of copper (up to 1% according to the manufacturer information), the restrictive effect of copper was not observed. This is an important finding mainly as it relates to the results for copper and brass electrodes, described below. Total H₂O₂ production was slightly lower.

Stainless steel, as one of the most often used materials, did not reach the values of the above-mentioned materials. The amount of iron detected by ICP was negligible in the cathode part. For bulk reactions, hydrogen peroxide should be destroyed in Fenton's reaction [14]:



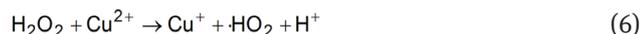
This reaction probably plays a bigger role in the anode part. The concentration of iron reached up to 0.1 mmol L⁻¹ (4 ppm) and the hydrogen peroxide concentration is the second lowest of all electrode materials.

H₂O₂ production obtained with platinum electrodes was a bit lower in the cathode part than that of the previously mentioned material, but it reached average values in the anode part. In total, the efficiency of platinum was higher than of stainless steel. This metal was not dissolved into the solution at any significant level in either electrode part to contribute to decomposition reaction of hydrogen peroxide. In the literature [15], surface reactions on the platinum electrodes were proposed that can withdraw sources of hydrogen peroxide or directly destroy it. Therefore, H₂O₂ production reaches lower values. The reactions can be written as:



Both remaining materials, copper and brass (an alloy of copper and zinc), have been reported as electrode

material before [16,17]. Surprisingly, when copper or brass electrodes were used in presented experiment, no hydrogen peroxide was detected in the cathode part of the reactor. Since no indications for such behavior were obtained for titanium-zinc electrodes, it can be assumed that copper is the responsible component. Concentration of H_2O_2 in the anode part with copper electrodes was comparable to other electrode materials, but with brass electrodes it reached only about half the value of pure copper. Content of copper was much higher in the solution from the anode reactor part; it reached the highest values of all studied materials. The diaphragm orifice is too small to allow significant mixing of the solutions from different electrode parts. Still, partial pumping effect may appear due to the discharge [18]. Copper ions can react with hydrogen peroxide in a way similar to Fenton's reaction. A complete set of reactions is called the Haber-Weiss reaction with the main step as follows [14]:



For copper containing electrodes, high catalytic effect of copper ions might be responsible for absence of hydrogen peroxide. Even though copper ions should be even more reactive in Fenton-like H_2O_2 destructive reactions than ferrous ions [14], the effect of such reaction should predominate in the anode part. The results show that the presence of the copper in electrode material probably influences directly the processes leading to the hydrogen peroxide creation, not only the decomposition reactions. No difference in discharge propagation was visible by naked eye. OES experiment was conducted to compare OH radical intensity for stainless steel and copper electrodes. It follows from the results that the intensity is much lower when copper electrodes are used. Therefore, a combined action of more parallel processes is probably the best explanation of the observed complete absence of hydrogen peroxide in the cathode part of the reactor.

4 Conclusions

This study aims to provide information on diaphragm reactor arrangement to enable comparison of efficiency and processes taking part in the system. Several materials were tested as electrodes in underwater diaphragm discharge in order to examine their influence on production of hydrogen peroxide. Also, differences between amounts of electrode material released into the solution during the experiment were compared for electrolysis and discharge operation.

It was shown that choice of electrode material can have significant influence on discharge efficiency. It was found by ICP analysis that the presence of the discharge does not contribute to material dissolution during the experiment in most cases, electrolysis playing the prevailing role. In the case of brass, zinc dissolution is slightly enhanced in contrast to suppression of copper release in experiments with discharge operation.

For H_2O_2 generation, the prevailing effect of electrochemical processes is strongly suggested by the results. Graphite proved to be the most effective material. Aluminum and titanium-zinc showed very similar results. The most often used material for planar electrodes in pinhole configuration is stainless steel. Anticipated Fenton reactions do not have a very strong effect. Platinum serves as an active surface for decomposition reactions of hydrogen peroxide; therefore the maximum values of its concentration were slightly below average.

In the cases of copper and brass, no H_2O_2 was detected in the cathode part, where higher concentration was expected than in anode part. It can be deduced that the presence of significant amount of copper in the electrode material leads to changes in the discharge propagation or promotes higher decomposition rate of H_2O_2 . The amount of hydrogen peroxide was comparable to other electrode materials in the anode part. The absence of hydrogen peroxide in cathode space is not given only by the concentration of metal component in the solution. An even higher amount of zinc was released into the solution during the experiment from titanium-zinc electrodes than the amount of copper was from either copper or brass electrodes.

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References

- [1] Manojlovic D., Ostojic D.R., Obradovic B.M., Kuraica M.M., Kršmanovic V.D., Puric J., *Desalination*, 2007, 213, DOI: 10.1016/j.desal.2006.05.059
- [2] Arjunan K.P., Friedman G., Fridman A., Morss Clyne A., *J. R. Soc. Interface*, 2011, 66, 9
- [3] Xu Z., *World J. Gastroenterol.*, 2006, 1, 12
- [4] Malik M.A., Ahmed M., Naheed R., Ghaffar A., *Plasmas Polym.*, 2003, 8, 4
- [5] Kim S., Sergiienko R., Shibata E., Hayasaka Y., Nakamura T., *Mater. Trans.*, 2010, 51, 8
- [6] Stara Z., Krcma F., Slavicek P., Aubrecht V., In: Schmidt J., Šimek M., Pekárek S., Prukner V., (Eds.), 28th International Conference on Phenomena in Ionized Gases, July 15 – 20 2007,

- Prague, Czech Republic, Ústav fyziky plazmatu AV ČR, Prague, Czech Republic, 2007, 1082-1085
- [7] Halamova I., Nikiforov A., Krcma F., Leys Ch., *J. Phys.: Conf. Ser.*, 2014, 516
- [8] Lukes P., PhD thesis, Institute of Plasma Physics, AS CR, Prague, CZ, 2001
- [9] Stara Z., Davidova J., Olexova B., Krcma F., Sural I., In: IEEE 35th International Conference on Plasma Science, 15-19 June 2008, Karlsruhe, Germany, IEEE Service Center, Piscataway, NJ, USA, 2008, 193
- [10] Bruggeman P., Leys Ch., *J. Phys. D: Appl. Phys.*, 2009, 42, 5, DOI: 10.1088/0022-3727/42/5/053001
- [11] Stara Z., PhD thesis, Brno University of Technology, Brno, CZ, 2006
- [12] Kozakova Z., Habilitation thesis, Brno University of Technology Brno, CZ, 2011
- [13] Krcma F., et al., *J. Phys.: Conf. Ser.*, 2010, 207, 1, DOI: 10.1088/1742-6596/207/1/012010
- [14] Halliwell B., Gutteridge J.M.C., *Biochem. J.*, 1984, 219
- [15] Hall S.B., Khudaish E.A., Hart A.L., *Electrochimica Acta*, 1998, 32, 5
- [16] Nikiforov A.Yu., Leys Ch., *Plasma Sources Sci. Technol.*, 2007, 16
- [17] Lee B.-H., Kim D.-S., Choi J.-H., *J. Electric. Eng. & Technol.*, 2010, 5, 2
- [18] De Baerdemaeker F., Šimek M., Leys Ch., Vestraete W., *Plasma Chem. Plasma Process*, 2007, 27