Diaphragm Discharge in Liquids: Fundamentals and Applications

Frantisek Krcma, Zdenka Stara, Jana Prochazkova
Faculty of Chemistry, Brno University of Technology, Purkynova 118, 612 00 Brno, Czech Republic
E-mail: krcma@fch.vutbr.cz

Abstract. Paper describes results of our research on DC diaphragm discharge creation in water solutions of electrolytes from the viewpoint of its principles, properties and applications. The thermal theory of discharge ignition in bubbles of evaporated solution has been confirmed by both high speed camera and sound records. Static current-voltage characteristics revealed a significant dependence of discharge breakdown on the solution conductivity. Determined breakdown parameters lay in the range of 900–1300 V and 40–100 mA, respectively, for NaCl solution conductivity varying from 150 to 1300 µS·cm⁻¹. Time resolved electrical characteristics showed a simultaneous appearance of current, voltage and sound oscillations as well as a light emission. Plasma diagnostics by optical emission spectroscopy confirmed formation of reactive species (hydroxyl, hydrogen and oxygen radicals) and excitation of metallic atoms presented in the solution. Moreover, rotational temperature was calculated from the obtained OH spectrum. Experiments focused on the diaphragm discharge applications are outlined in the paper. Results of hydrogen peroxide production, organic dye decomposition and treatment of humic acid solutions are compared from the viewpoint of experimental conditions.

1. Introduction

Electrical discharges generated in liquids are in an intensive research focus for a few last decades. Many scientists deal with various types of discharge configuration and several kinds of applied high voltage. The most frequent electrode geometry used for discharge creation is point-to-plane or coaxial [1–3] together with the application of DC pulsed voltage of about 20 kV. Other experiments in liquids have been carried out with capillary [4] or diaphragm discharge [5]. Discharge generation using AC voltage is also possible [6].

The diaphragm discharge, presented in this paper, is formed in reactor containing two electrodes (cathode and anode) separated by diaphragm in which the pin-hole is made. The DC high voltage is applied on the electrodes. Consequently, the high electric field between two planar electrodes is concentrated just in the pin-hole. If the electric field is sufficiently high, the discharge is formed in the bubbles of evaporated water in and/or near the pin-hole made in the diaphragm. Two kinds of plasma streamers of the opposite polarity are created in two parts of reactor separated each other by the insulating wall containing diaphragm, as it is shown in figure 1. The difference in properties of plasma channels propagating towards the electrodes is not only in their shape, but foremost in the velocity of electrons accelerated by the applied electric field and the energy dissipation in channels [7]. For better understanding of streamer propagation, there is an analogy between the generation of the diaphragm discharge and corona discharge in point-to-plate electrode configuration. The pin-hole behaves as a
point electrode of both polarities each one for two separated parts of the reactor. In the part with the plane cathode electrons are accelerated towards the positively charged pin-hole (like to the point anode) and the remaining positive space charge at the end of the streamer is further enhancing the electron velocity. Thus created streamers represent long plasma channels. This form of plasma is called in text as the “positive discharge”. Contrary to this, electrons propagating from the negatively charged pin-hole (like from the point cathode) towards the plane anode are dragged by the positive space charge and their velocity decreases. The final shape of negative streamers is represented by shorter bush-like plasma channels having a spherical shape and we called them the “negative discharge” [8], (see figure 1).

![Figure 1. Simplified scheme of diaphragm discharge formation: 1 – anode, 2 – cathode, 3 – negative plasma channels, 4 – positive plasma channels, 5 – electrolyte solution.](image)

Electrical discharges belong to the so-called Advanced Oxidation Processes (AOP’s) that can be utilized for different applications. Their main importance is in the formation of highly reactive species (especially radicals) and production of UV radiation. Subsequently, initiated processes lead to the excitation, ionization and decomposition of particles and compounds contained in treated solution. Thus methods based on electrical discharges are often used in water treatment, surface modification or other applications.

2. Experimental

2.1. Discharge reactor

A specially constructed batch discharge reactor was used in the study of diaphragm discharge formation, properties and applications (figure 2) [9]. The main chamber was divided by an insulating wall into two spaces with one electrode (stainless steel or platinum) in each part. A changeable diaphragm made of inert material (PET, thickness of 0.25 mm) was fixed in the centre of the barrier. Both electrode spaces were connected by a small orifice in the diaphragm (initial diameter of 0.2 mm) where the discharge was ignited. DC high voltage source providing constant power supply up to 300 W was used. Water solutions containing supported electrolyte (NaCl, NaBr, NaNO₃, Na₂HPO₄·12H₂O or Na₂SO₄; their concentration varied according to the needed conductivity) were split per 1.5 liters into both parts of the reactor. Addition compounds such as organic dyes (textile: Direct Red 79, Direct Blue 106, Direct Yellow 29, food: Acid Blue 74, Acid Red 14; initial concentration of 12–30 mg·l⁻¹) or humic acids (HUMIN-P 775, initial concentration of 35 mg·l⁻¹) were added when degradation effects of the discharge were investigated. Both mixing and cooling systems were used to keep experimental conditions homogeneous and constant during the whole process.
2.2. Plasma diagnostic and analytic methods
Breakdown moment of the diaphragm discharge as well as its further behaviour was studied from electrical characteristics (static and time resolved). For that purpose, two and four channel digital oscilloscope Tektronix TDS 1012B and TDS 2024B were used. Signals of discharge voltage (using the HV probe Tektronix P6015A), current, sound and emitted light were recorded. Plasma diagnostics was carried out by optical emission spectroscopy using the spectrophotometer Jobin Yvon Triax 550 in the range of 200–700 nm. Subsequently, rotational temperature was calculated from recorded OH radical spectra.

Detection of hydrogen peroxide generated by the discharge was done by colorimetric method using a specific titanium reagent. In the case of decomposition experiments, concentration of dyes and humic acids was determined by absorption spectroscopy. Moreover, fluorescence spectroscopy was carried out to obtain a humic index of treated humic solutions.

3. Results and discussion
3.1. Breakdown and formation of diaphragm discharge in electrolyte solution
According to the thermal theory of discharge initiation in liquid [8], breakdown appears in bubbles of evaporated water solution which is strongly heated by the applied electric field. To confirm this hypothesis in our device, series of photos from high speed camera was correlated with current and sound time resolved records. Obtained pictures showed on the bubble formation [10]. Moreover, determined amplitudes of sound closely corresponded to recorded current peaks (see figure 3). This sound effect could be related to the discharge creation represented by a rapid current increase.
3.2. Electric characteristics

Ignition of DC diaphragm discharge in electrolyte solutions highly depended on the initial conductivity of the liquid phase. Too low conductivity (adjusted by concentration of dissolved electrolyte) meant low amount of charge carriers and subsequently, weak current was insufficient for liquid heating and bubble creation. At the higher conductivities, the system resistance was lower and current was higher. Also the voltage drop in liquid was significantly smaller and thus the discharge breakdown was observed at lower voltage and higher current. Based on these assumptions, breakdown parameters (mean voltage and current) were determined from VA characteristics measured in electrolyte solutions of initial conductivity 50–1400 µS·cm⁻¹. A comparison obtained for two electrolytes (NaCl and KCl) is given in figure 4. It is obvious that in the middle range of tested conductivities (300–1300 µS·cm⁻¹) breakdown voltage was slightly decreasing with the increasing conductivity while breakdown current significantly increased with more or less the same trend in both electrolytes [10]. The extreme values of tested conductivities had a remarkable effect on breakdown appearance foremost due to the consequent discharge instability.

![Figure 4. Breakdown values of voltage (left) and current (right) as a function of solution conductivity. Comparison is given for two electrolytes (NaCl and KCl).](image)

An example of characteristics time evolution obtained in NaCl solution during the breakdown moment is demonstrated in figure 5. Increasing the input power into the reactor, voltage and current were slightly increasing and no light emission was recorded until the breakdown moment. Getting over this value, intensive peaks of current appeared together with light flashes while voltage mean magnitude remained more or less constant.

![Figure 5. Time resolved characteristics of diaphragm discharge. Given result represents simultaneous records of voltage, current and light signal during the breakdown moment in 4 mM NaCl solution.](image)
3.3. Optical diagnostics

Plasma properties were measured by optical emission spectroscopy in the range of 200–1000 nm. Strong emission of OH radicals as well as other reactive species (H and O atomic lines) was determined in the spectrum. Emission of metallic atoms coming from the dissolved electrolyte was observed, too. Figure 6 shows the dependence of sodium atomic line intensity on the concentration of NaCl electrolyte in the solution. The result that the Na intensity was directly proportional to the Na concentration in the solution can be applied as a determination method in the analytical chemistry [11]. Integral emission intensity of OH radicals remained constant over the whole tested concentration range. Additionally, rotational temperature was calculated from OH spectrum and its obtained magnitude was 500–900 K depending on the solution conductivity, applied power and electrolyte kind.

![Figure 6](image)

**Figure 6.** Emission intensity of Na atomic line (589 nm) and integral OH intensity over 305–315 nm as a function of electrolyte concentration (NaCl, input power of 160 W).

![Figure 7](image)

**Figure 7.** Left: Production of hydrogen peroxide by the diaphragm discharge in both electrode spaces (input power of 200 W, 4 mM NaCl). Right: Decomposition rate of the dye Direct Blue 106 achieved by the diaphragm discharge in both electrode spaces (input power of 170 W, 4 mM NaCl).

3.4. Example of applications

Diaphragm discharge generated in water solutions by constant DC voltage can be applied in more fields of utilization. The possibility of an excitation source for determination of metallic atoms in the solution has been already mentioned above [11]. Next useful process studied by our work is production of hydrogen peroxide [12]. Figure 7 (left) demonstrates its formation in both electrode spaces of the reactor. The second picture in figure 7 (right) represents the next discharge application for organic dye decomposition (the used textile dye Direct Blue 106). It is evident that electrode
polarity played a significant role in both processes. While H$_2$O$_2$ was formed with higher efficiency in the cathode space, decoloration of the dye went faster in the anode space [13]. Plasma treatment of humic solutions led to the enhancement of aliphatic components and decrease of aromatic substances [14,15].

4. Conclusion

Paper describes diaphragm discharge generated using constant DC voltage up to 4 kV in water solutions containing supported electrolytes. Confirmation of thermal theory as well as electric characteristics is presented and an influence of electrolyte (kind and concentration) is discussed. Plasma diagnostics by OES determined rotational temperature and formation of the main radicals (OH, H, O). Application of the discharge in dye and humic acid decomposition, hydrogen peroxide formation and metallic atoms determination is suggested, too.

Acknowledgments

This work was supported by the Czech Science Foundation, projects No. 202/03/H162 and No. 202/07/P371.

References

[1] Sun B, Sato M, Clements J S 2000 Oxidative processes occurring when pulsed high voltage discharges degrade phenol in aqueous solution Environ. Sci. Technol. 34 (3) p 509–513
[2] Sugianto A T, Ito S, Ohshima T, Sato M, Skalny J D 2003 Oxidative decoloration of dyes by pulsed discharge in water J. Electrostatics 58 p 135–145
[3] Sunka P, Babicky V, Clupek M, Lukes P, Simek M, Schmidt J, Cernak M 1999 Generation of chemically active species by electrical discharges in water Plasma Sources Sci. Technol. 8 (2) p 258–265
[4] De Baerdemaeker F, Simek M, Schmidt J, Leys C 2007 Characteristics of ac capillary discharge produced in electrically conductive water solution Plasma Sources Sci. Technol. 16 p 341–354
[5] Monte M, De Baerdemaeker F, Leys C, Maximov A I 2002 Experimental study of a diaphragm discharge in water Czech. J. Phys. 52 p D724–D730
[6] Manojlovic D, Ostojic D R, Obradovic B M, Kuraica M M, Krmanovic V D, Puric J 2007 Removal of phenol and chlorophenols from water by new ozone generator Desalination 213 p 116–122
[7] Kuzhekin I P 1995 Proc. 9th Int. Symp. High Voltage Eng. (Graz) p 8073–1
[8] Lukes P 2001 Water treatment by pulsed streamer corona discharge Ph.D. Thesis Prague
[9] Stara Z 2006 Study of chemical processes in electrical discharges in liquids Ph.D. Thesis Brno
[10] Stara Z, Krcma F, Prochazkova J 2008 Proc. 23rd SPPT (Prague) p 185
[11] Prochazkova J, Staraz Z, Krcma F 2006 Optical emission spectroscopy of diaphragm discharge in water solutions Czech. J. Phys. 56 p B1314–B1319
[12] Stara Z, Krcma F 2004 The study of H$_2$O$_2$ generation by DC diaphragm discharge in liquids Czech. J. Phys. 54 p C1050–C1055
[13] Stara Z, Krcma F, Nejezchleb M, Skalny J D 2008 Influence of solution composition and properties on organic dye removal in DC diaphragm discharge in water J. Adv. Oxid. Technol. 11 p 155–162
[14] Stara Z, Krcma F 2006 Treatment of humic acids solutions by DC diaphragm discharge Czech. J. Phys. 56 p B1351–B1356
[15] Halamova I, Stara Z, Krcma F 2008 Effects of diaphragm discharge in water solutions containing humic substances J. Phys., Conf. Series (Issue of IWSSPP conf. – submitted)