

DC DIAPHRAGM DISCHARGE IN LIQUIDS: PROPERTIES AND APPLICATION

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Introduction

Electrical discharges generated in liquids have a special position among commonly investigated plasma sources. Comparing to the electric discharges initiated in the gas phase, discharge generation in liquids requires different conditions for its ignition, especially due to the important properties of the used liquid (water) such as dipole moment of water molecules, significantly higher density of particles than in gas, etc. [1]. Generation of electric discharge in gases has been an object of many studies focused on the application of different high energy sources and various electrode configurations. On the other hand, discharge creation in liquid, particularly in water, is limited to only a few suitable electrode geometries together with the application of a sufficient energy source. In all cases it is important to accumulate energy of the applied electric field on some edge or tip in the system. The most convenient and also by many authors the most investigated configuration is point-to-plane electrode geometry where the discharge is ignited using the DC pulsed high voltage [2, 3]. Further the coaxial, diaphragm or capillary configurations have been already studied [4-6]. Our work is focused on the generation of the diaphragm discharge when the DC non-pulsed high voltage is supplied into the reactor. Diaphragm discharge creates in a small pin-hole in the dielectric barrier dividing the whole reactor volume into two electrode spaces. When the DC high voltage is used for the discharge creation, two kinds of plasma channels (streamers) propagate from the pin-hole towards electrodes. These streamers differ not only in their shape but especially in their energy (due to the different kinetic energy of electrons) which strongly influences processes initiated by the discharge on both sides of the diaphragm [5, 7]. The main feature of the discharge generation in water is the formation of various reactive species (radicals, ions, oxidizing molecules) that can react with organic molecules of compounds dissolved in water and thus caused their decomposition. This paper describes both the moment of the discharge initiation and propagation in water solution of selected electrolyte and the crucial conditions of discharge application in the field of water treatment, particularly in the removal of organic dyes from water.

Experimental set-up

A simple batch discharge reactor was used in our experiments. Its total volume of approximately 3 litres was divided into two parts by the dielectric diaphragm made of some chemically inert as well as mechanically stable material (PET, thickness of 0.25 mm) with a small pin-hole in the centre (initial diameter of 0.4 mm). Two planar high voltage electrodes made of stainless steel were installed symmetrically on both sides of the diaphragm in the distance of 2 cm from the diaphragm. The discharge was created in the pin-hole of the diaphragm using the DC high voltage source which gave the non-pulsed voltage up to 4.5 kV [7, 8].

As the generation of the diaphragm discharge in water requires some minimal solution conductivity to ensure stable electric current in the system, used water solutions should contain supported electrolyte of definite concentration (NaCl). Based on this condition, particular conductivity of the solution was adjusted according to the concentration of electrolyte dissolved in deionised water in the range from 50 to 1400 $\mu\text{S}\cdot\text{cm}^{-1}$. In experiments investigating degradation processes initiated by

the diaphragm discharge, selected organic dyes (the most used one: Direct Red 79 – DR 79) in amount of approximately $15 \text{ mg}\cdot\text{l}^{-1}$ were added into the electrolyte solution. Static V-A characteristics of the discharge pre-breakdown and running were recorded by the ampermeter METEX M-4650CR and voltmeter UNI-T UT33B which were linked to the electric circuit with the discharge reactor and HV source according to the scheme given in Fig. 1. A digital fast camera (Olympus) was used for taking pictures of the discharge. The maximal speed sufficient for the discharge recording was up to 2 000 pictures per second.

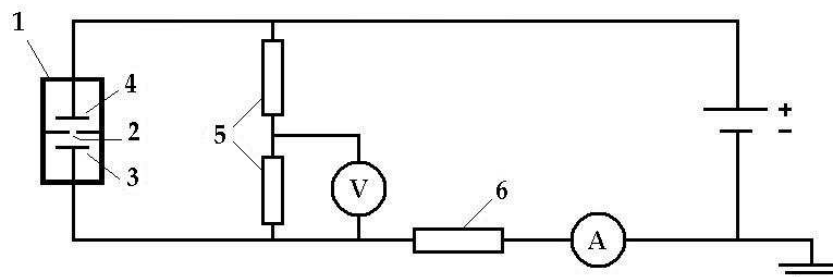


Fig. 1: Simplified scheme of experimental set-up: 1 – discharge reactor, 2 – dielectric diaphragm with pin-hole, 3 – grounded cathode, 4 – anode, 5 – resistances (ratio of division 1:33), 6 – source ballast resistance ($5.5 \text{ k}\Omega$).

Determination of organic dye concentration was carried out by absorption spectroscopy. Dye concentration was directly proportional to the absorption intensity of the dye solution measured at the appropriate fixed wavelength (DR 79: 506 nm). The whole UV-VIS absorption spectra of treated dye solutions were recorded, too. Chemical analysis of degradation products and by-products has not been properly developed in our contemporary experimental conditions yet.

Generation of diaphragm discharge in water

Diaphragm discharge was created in the vicinity of the small pin-hole in the dielectric diaphragm which divided the discharge reactor into two electrode spaces, each filled with a definite volume of electrolyte solution. Intensity of electric field between two planar electrodes accumulated just in the pin-hole. If the electric field was sufficient, the discharge was formed in the bubbles of evaporated water in and near the pin-hole of the diaphragm. These bubbles were nucleated due to the ohmic heating of the conductive liquid. The fact that creation of the discharge started originally in bubbles of water vapour (i.e. in the gas phase) was confirmed by records of the fast digital camera (velocity of about 2 000 pictures per second) where the bubble formation was clearly seen. These results show the relevance of the thermal theory describing the initiation of electric discharge in water [1]. If the DC high voltage was used for the discharge generation, two kinds of plasma streamers with the opposite polarity were created in two parts of reactor separated each other by the insulating wall containing diaphragm. The difference in plasma channels propagating towards the electrodes was not only in their shape (as it is given by the scheme and photo in Fig. 2), but foremost in the velocity of electrons accelerated by the applied electric field and energy dissipation in the channels [5]. For better understanding of streamer propagation, there was an analogy between the generation of the diaphragm discharge and corona discharge in point-to-plate electrode configuration. The pin-hole behaved as a point electrode of both polarities, each one for one separated part of the reactor. In the part with the plane cathode, electrons were accelerated towards the positively charged pin-hole (like to the point anode) and the remaining positive space charge on the end of the previous electron avalanche further enhanced the electron velocity. Thus created streamers represented long plasma channels and we called this part the “positive discharge” or “positive streamers”. On the other side, electrons propagating from the negatively charged pin-hole (like from the point cathode) towards the plane anode were dragged by the positive space charge remaining on the end of the previous electron avalanche and thus the electron velocity decreased. The final shape of negative streamers was represented by shorter plasma channels in a spherical shape and we called them the

“negative discharge” or “negative streamers” [1]. Positively charged ions in the system were attracted by the cathode but their propagation velocity was much slower than the velocity of electrons. Such dual character of the diaphragm discharge strongly influenced mainly chemical processes initiated by the discharge in water. More details about the diaphragm discharge creation you can also find in [7].

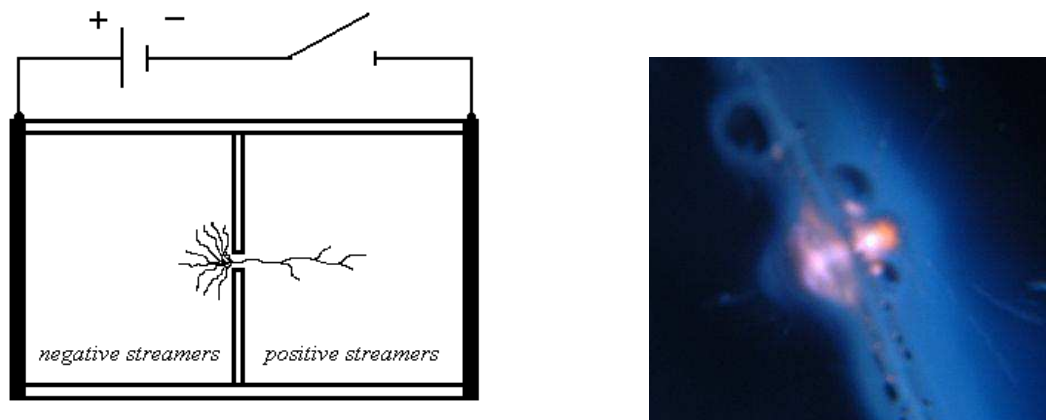


Fig. 2: Simplified scheme (left) and photograph (right) of plasma streamers creation in the diaphragm discharge in water – negative plasma channels on the left side of the diaphragm.

Static V-A characteristics of the diaphragm discharge ignition were measured in NaCl solutions of conductivity varying from 50 to 1400 $\mu\text{S}\cdot\text{cm}^{-1}$. Obtained results are demonstrated in Fig. 3 for selected values of solution conductivity. The moment of the discharge ignition (the breaking point) was represented by the breakage in the slope of current dependence on applied voltage, which means that the slow increase of current with the increasing voltage changes into the rapid current enhancement with further voltage increase. Values of current and voltage corresponding to this point represented breakdown characteristics of the diaphragm discharge in electrolyte solution. It is obvious that the moment of ignition was highly dependent on solution conductivity with inversely proportional tendency. The breaking point was shifted to the lower breakdown voltage with the increasing solution conductivity. This fact resulted from the decreasing resistance of the system due to the enhanced amount of charge carriers coming from the dissolved electrolyte.

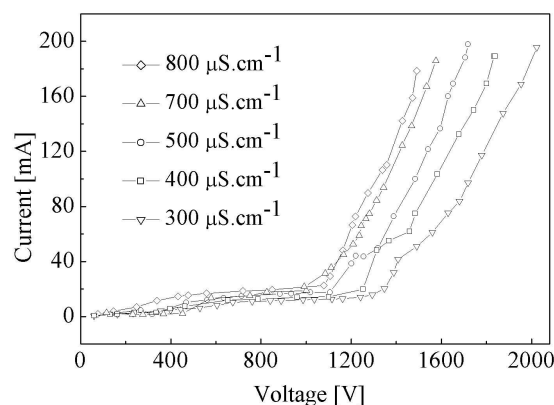


Fig. 3: Selected V-A characteristics of the DC diaphragm discharge in the NaCl solution as a function of solution conductivity.

Application in water treatment

Generation of electrical discharge in water initiates production of reactive species such as radicals (hydroxyl, hydrogen, oxygen), ions and oxidizing molecules (hydrogen peroxide) [3]. These species are responsible for subsequent chemical reactions leading to decomposition of especially organic compounds dissolved in water. Thus this plasma kind can be used as a method in water treatment. In this field, degradation of phenol and its derivatives has been widely studied [2, 4] as well as some other organic compounds harmful for the environment. Recently, research focused on the removal of organic dyes from wastewater produced by textile industry rapidly started [7, 9, 10]. However,

this topic has still a lot of questions. Therefore our work has investigated the possibility of the dye decomposition by the diaphragm discharge.

Water solution containing selected organic dye (DR 79) and supported electrolyte (5 mM NaCl) were treated in the discharge reactor for 80 minutes. Absorption spectra of treated solution from both parts of the reactor (on each side of the diaphragm) were recorded each 20 minutes. Obtained results are demonstrated in Fig. 4. It is obvious that the dye concentration (represented by the intensity peak at approximately 506 nm) decreased during the treatment in both parts. However, dye decomposition caused by negative streamers went much rapidly than in the other part and moreover, the decreasing intensity maximum revealed a remarkable shift to the shorter wavelength. This shift was probably caused by the creation of various degradation by-products and resulted from different energy dissipation on both sides of the diaphragm [5].

Comparing to other methods used for the dye removal, ozonation seemed to be of more or less similar efficiency as the discharge treatment [10], however, use of hydrogen peroxide did not show so good results and moreover, its application required proper pH adjustment [10].

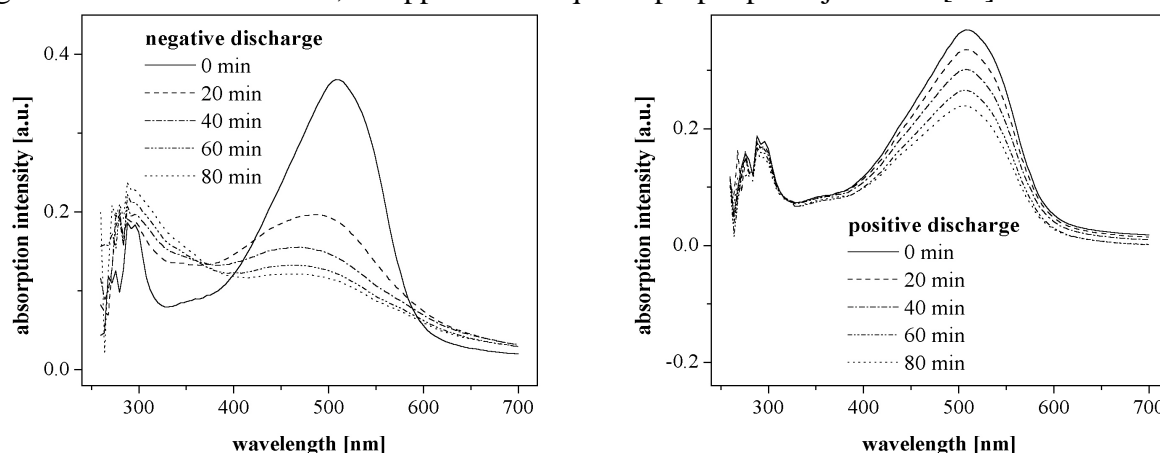


Fig. 4: Absorption spectra of water solutions containing organic dye DR 79 and NaCl supported electrolyte (5 mM) during the discharge treatment at input power of 120 W.

Conclusions

Generation of two kinds of plasma streamers in the DC diaphragm discharge in water solutions of electrolytes was confirmed by records taken by the fast digital camera. Influence of solution conductivity on the discharge ignition was determined by static V-A characteristics. Application of the discharge for removal of organic dyes from water was assumed as sufficient method and a big difference in discharge polarity effect on the dye decomposition was observed.

Acknowledgements

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