Innovative reactor for surface plasma-based water treatment

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Abstract: Significant research has been carried out on the chemistry of water-based liquids treated with atmospheric pressure plasmas. Multiple reactor designs have been described, differing in the efficiency and chemical composition of the final solution. Here we propose a flow-through type reactor with transient pulsed discharges. The discharges are produced in air, and are in contact with the liquid surface only. We investigated the reactor performance in terms of chemical composition of the treated distilled water.

Keywords: plasma activated water, surface discharge, water treatment.

1. Introduction

Electric discharges and atmospheric plasmas staying in contact with water or water-based liquids affect their chemical composition, which reflects composition of the plasma itself. In some applications the treated liquid may be more desired than the plasma, for instance, if the site to be treated is not accessible to the plasma device. Several areas of application emerge for plasma activated water (PAW) or media (PAM), including disinfection, cancer cells killing and other medical treatment. Plasma treated water has also been tested in agriculture and food preservation area. Plasma activated liquids may improve plant growth.

Plasma-water interactions embrace tens of chemical species and hundreds of reactions in the gas and liquid phases. Nevertheless, there are some common products and methods of their quantification that are helpful when trying to characterize the changes in the water treated [1]. For example, plasma in contact with the air always results in nitrogen oxides which generate NO_2^- in water. It can be further oxidized to NO_3^- [2] by hydrogen peroxide formed in the gas phase from water vapor and transferred to the liquid phase [3]. As pH is low enough (under 3) peroxynitrite can arise efficiently from NO_2^- and H_2O_2 [4]. Its toxicity to bacteria has been known for a long time [5], and lately it was identified as the key bactericidal agent in PAW [6]. Another common, highly reactive product of plasma is ozone.

In order to meet the growing demand for plasma activated liquids, many different reactors were built, exploiting most of known types of plasma sources [7]. This article describes a compact plasma reactor utilizing pulsed corona discharge on water surface, where plasma of the discharge is in contact with water surface only. Electric properties and measurements of H_2O_2 and NO_2^- energy yield are presented.

2. Reactor design and experimental setup

Fig. 1 depicts the experimental setup used for measurements on the plasma reactor. The reactor consists of a plastic vessel. There are three brass electrodes in the vessel, which are separated by insulating partitions with blades. The liquid flows from the left side in Fig. 1 to the right. The liquid output is separated from the rest of the vessel by an overflow covered by an absorbent glass felt. This sets height of the liquid surface in the vessel approximately 1 mm above edges of the blades. The liquid flow rate was approximately 23 mL·min^{-1}.

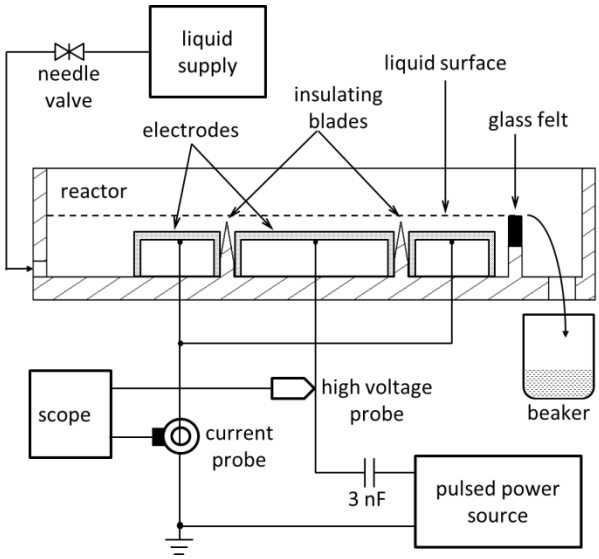

Fig. 1 Setup used for experiments on the designed plasma reactor.

The top of the reactor was flat, and could be covered with a glass lid if exchange of gas and liquid vapor with the surroundings had to be reduced. The reactor was connected to 28 kV pulsed power supply (Suematsu Electronics MPC3010S-50PL). Experiments were conducted at three different repetition rates: 20, 40, and 80 pulses per second. Voltage and current waveforms were measured by an oscilloscope (Tektronix TDS 3054C) using a high-voltage divider (North Star PVM-1, 1:2000) and a current probe (Pearson Electronics m. 2877).

The principle of the discharge generation is as follows. The 1 mm thin layer of water above the insulating blades represents high-resistance area with large potential drop of several kV·mm^{-1}. This potential drop appears also in the gas at the liquid surface as the result of boundary conditions for electric field $\nabla \times \vec{E} = 0$. Therefore, breakdown at the surface is initiated, since dielectric strength of the gas is much smaller than that of the liquid. The early plasma produces streamers propagating into areas remote from the place of the initiation due to high

conductivity of plasma channels [8]. The streamers stay held on the liquid surface only. Thus, the liquid surface is the only material next to the surrounding air which is in contact with the produced plasma.

Concentrations of hydrogen peroxide were measured according to [9], i.e. using the common titanium sulfate method. Briefly, H_2O_2 reacts with titanyl ions in acidic conditions (supplied by Sigma-Aldrich), resulting in a yellow complex with the molar extinction coefficient of 6.89×10^2 $l\cdot mol^{-1}\cdot cm^{-1}$. Sodium azide was used to prevent hydrogen peroxide consumption by the nitrites [2].

Measurements of nitrites concentrations were based on the Griess method. 0.5 ml of the sample was mixed with 0.25 ml of the Griess reagent. Standard curve was prepared using the sodium nitrite solutions of known concentrations and the quantification was done on the Varioskan® Flash microplate reader.

3. Results and Discussion

Experiments were performed with distilled water (1.2 $\mu S\cdot cm^{-1}$). For high yield of chemical products in the liquid it is important to generate plasma covering large surface area of the liquid [10]. Fig. 2 depicts photos of plasma discharges at water surface during the reactor operation.

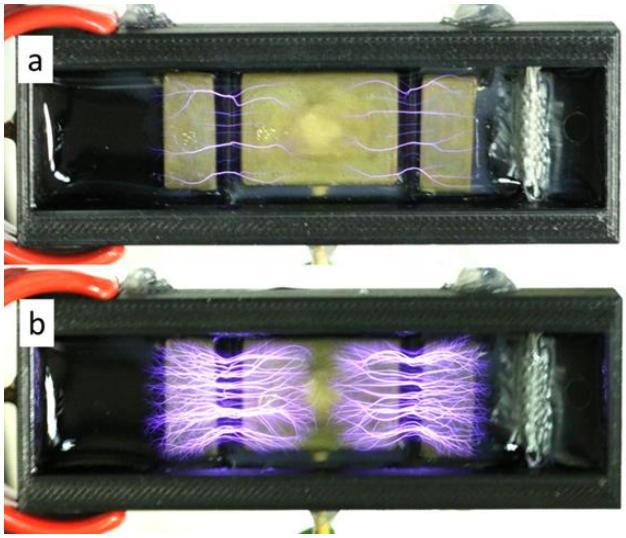

Fig. 2 Surface discharges in the reactor. (a) Single voltage pulse; (b) 8 voltage pulses at the repetition rate of 80 pulses per second.

The liquid conductivity was not constant, but increased over time due to its contamination with generated chemical products (Fig. 3) [11]. As the liquid conductivity increased, average energy per single voltage pulse dissipated in the reactor also increased, although the initial conditions were otherwise identical (Fig. 3). This effect was most significant when the reactor top was covered with a glass lid. Fig. 4 depicts measured voltage and current waveforms.

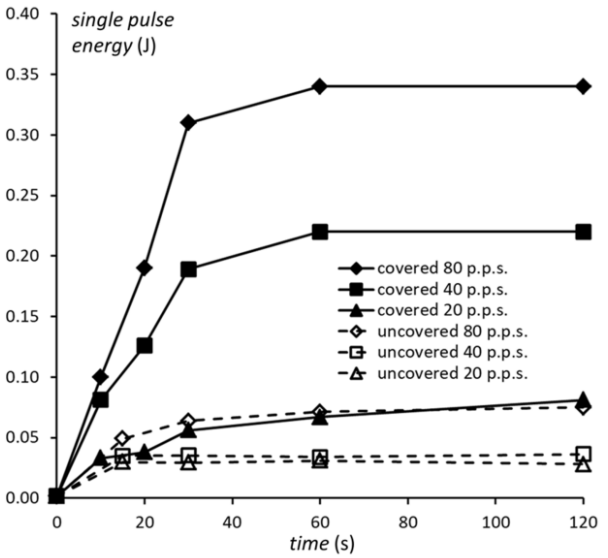

Fig. 3 Dependence of energy delivered into the reactor in single voltage pulse as a function of time delay from the experiment beginning. The reactor was filled with distilled water (initial conductivity 1.2 $\mu S\cdot cm^{-1}$), and it was either opened or covered as indicated.

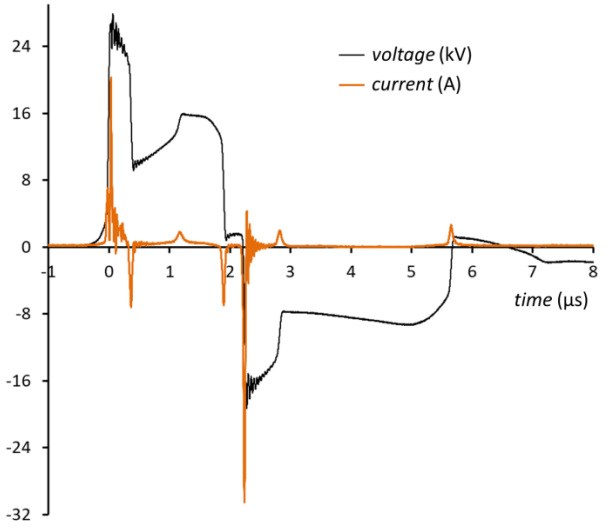

Fig. 4 Measured voltage and current waveforms of a single pulse on uncovered reactor.

The concentrations of products were plotted against the total delivered energy, which was calculated using the values in Fig. 3, and the total volume of liquid passed through the reactor. Although the character of our discharge system does not exclude the formation of reactive nitrogen and oxygen species directly in the liquid phase, it seems that the most important reactive processes occur in the gas phase [4]. Plasma-produced nitrogen oxides undergo reactive dissolution in water, above all

$NO_2(aq) + NO_2(aq) + H_2O(l) \rightarrow NO_2^- + NO_3^- + 2H^+$
$NO(aq) + NO_2(aq) + H_2O(l) \rightarrow 2NO_2^- + 2H^+$

Hydrogen peroxide is formed by the recombination of OH radicals produced by plasma at the gas/liquid interface [3]

$OH + OH \rightarrow H_2O_2$.

Fig. 5 plots concentrations of NO_2^- and H_2O_2 measured in produced liquid after 120 s of continuous operation. Both species exhibit approximately linear dependence on the delivered energy.

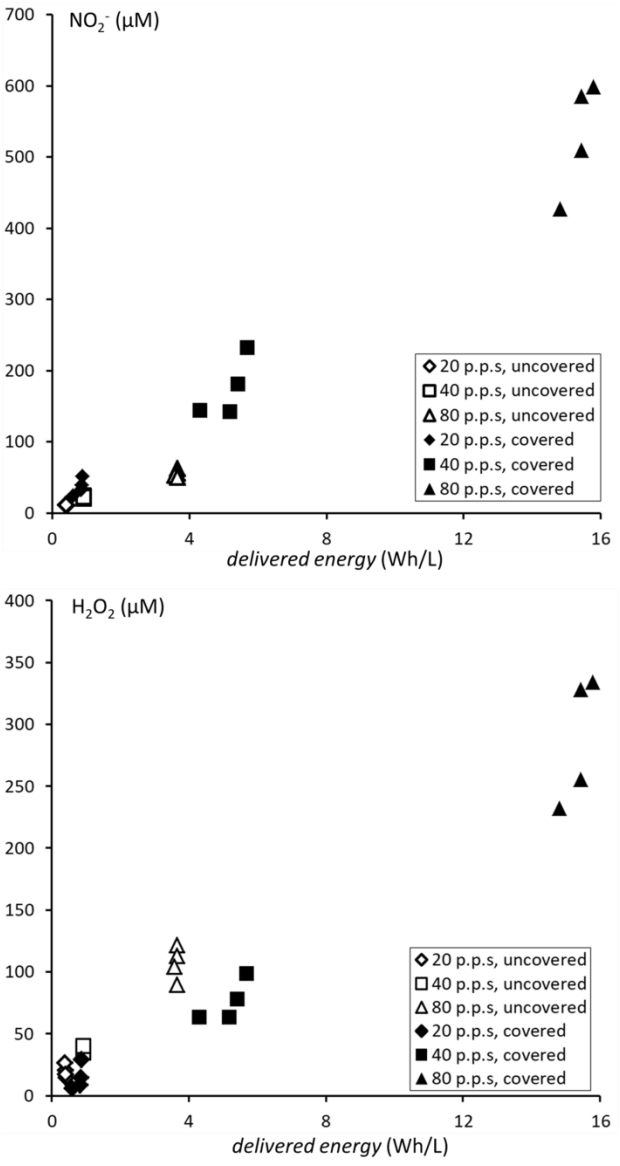

Fig. 5 NO_2^- and H_2O_2 concentrations as functions of input energy. Measurements were performed at different repetition rates, and with the reactor uncovered or covered with a sealed glass lid.

It was found that covering the reactor had much higher, positive effect on the NO_2^- production than on the H_2O_2 production, which may be explained as follows. For the flowing system (in our case flowing water) without perpendicular convective mixing, the dissolution equilibrium of gaseous species is important. When the reactor is uncovered, poorly soluble gases will rather escape than dissolve. This is the case of NO and NO_2, whose dimensionless Henry's law constants are [12] 0.044 and 0.28, respectively. On the other hand, the constant for H_2O_2 is very large, 1.92×10^6, which may explain why the production of H_2O_2 is much less affected by covering the reactor.

Compared to the published results on other reactors, we achieved very high yields of NO_2^- (~34 mmol·kWh^{-1}). The yield of H_2O_2 was modest (~30 mmol·kWh^{-1}), but similar to that of NO_2^-. The pH reached value of 3-3.5, enabling the formation of peroxynitrite and post-discharge activity of the treated water.

4. Conclusions

Simple and easily manufacturable reactor for generation of plasma discharges over water surface without contact of plasma with other materials than air and the liquid was developed. This property should have positive impact on the reactor lifespan. Analysis of chemical production showed superior yields of NO_2^- in comparison to published results on most other reactors. The yield of H_2O_2 was modest. It was also found that gas ventilation above water surface influenced significantly the chemical yields: covering the reactor had much higher, positive effect on the NO_2^- production than on the H_2O_2 production. The reactor is capable to produce plasma activated water.

5. References

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