

Role of solution conductivity in the electron impact dissociation of H₂O induced by plasma processes in the pulsed corona discharge in water

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Abstract: Effect of solution conductivity on production of H₂O₂, H₂ and O₂ generated by the pulsed corona discharge in water has been investigated. Hydrogen was dominant product of plasmachemical activity of the discharge when its formation significantly increased with increasing solution conductivity. Compared to H₂O₂ its production rose from ratio of 2:1 at 100 μS/cm up to 5:1 at 500 μS/cm. Possible routes of electron impact dissociation of water induced by plasma in water in dependence on the solution conductivity was proposed.

Keywords: corona discharge in water, dissociation, hydrogen peroxide, hydrogen, oxygen.

1. Introduction

Non-thermal plasma produced by electrical discharges in water initiates a variety of chemical and physical processes. These processes include a high electric field, intense ultraviolet radiation, overpressure shock waves and, of particular importance, formation of various reactive chemical species such as radicals (OH, H, O) and molecular species (H₂O₂, H₂, O₂, O₃). It is expected that primary chemical activity of electrical discharges in water is associated largely with the initial production of OH and H radicals formed by electron collisions with water molecules in the plasma discharge zone. General mechanism of their formation is assumed to be similar to that in radiolysis of water, i.e. by electron impact dissociation of water to form H and OH radicals with threshold electron energy of 5.1 eV (eq. 1).



Formed OH and H radicals may in dependence of energy distribution of electrons in the streamer head either react with each other to form product molecules H₂ and H₂O₂ or reform water or diffuse away from each other and to be available to react with solutes [1].

Generation of OH and H radicals by the electrical discharge in water has been proven by emission optical spectroscopy. The production of H₂O₂ and H₂ was confirmed by chemical methods [1]. However, the experimentally determined yields of H₂O₂ and H₂ showed that the production rate of hydrogen is double that of the rate of H₂O₂ production, which is in contrast with the scheme presented above proposing H₂O₂ and H₂ production in the ratio 1:1 [2]. Consequently, emission spectroscopy measurements revealed in addition to OH and H radicals also presence of atomic oxygen lines followed with evidence of production of gaseous molecular oxygen. It has been also observed that chemical activity of the pulsed electrical discharge in water significantly depends on the solution conductivity, e.g. production of H₂O₂ was found to de-

crease with increasing solution conductivity. This effect can be partly related to increasing UV radiation from the discharge with higher solution conductivity that leads to the increasing photolytic decomposition of H₂O₂ [3]. However, overall it is apparent that electron impact dissociation of water just to H and OH radicals (eq. 1) cannot explain observed experimental results. It should be noted that there are also other models proposing electric field-assisted dissociation of water [1] and high temperature (~ 3 500 K) induced dissociation of water in the discharge channel [4]. However, these models also do not consider the effect of solution conductivity on plasmachemical activity of the discharge. Therefore, exact mechanism of plasma induced dissociation of water by the discharge is still unknown.

In the present study the role of solution conductivity in the electron impact dissociation of H₂O induced by the pulsed corona discharge in water is investigated in more detail. Chemical activity of the discharge is evaluated with regard to the production of H₂O₂, H₂ and O₂ in dependence on the solution conductivity in the range of 100 - 500 μS/cm and compared with the results from the emission spectroscopy measurements of the discharge emission in water. Consequently, possible mechanism of electron impact dissociation of H₂O by the discharge in water is proposed.

2. Experimental

The reactor used for generating of the pulsed corona discharge in water was described earlier in detail in [5]. Briefly, electrode system of the needle-plate geometry immersed in a cylindrical glass vessel was used with the needle-plate distance of 52 mm. Needle electrode was made from conically shaped tungsten rod (ø 2 mm), which was almost totally insulated from surrounding water by Teflon insulator. A pulsed high voltage applied to the needle was provided by a pulse power supply. It consists of a variable voltage 0 - 30 kV DC source, a low inductance

storage capacitor ($C = 7 \text{ nF}$) and a rotating double spark gap giving the pulse repetitive frequency up to 100 Hz. In this work applied voltage of the positive polarity ($U=17 - 27 \text{ kV}$) was used with the repetition rate regulated in the range of 35-89 Hz to keep constant power input P of 90 W in all experiments. The power input was calculated from the applied voltage U , charging capacity C and pulse repetition frequency f as $P=fE_p$, where pulse energy E_p was evaluated as storage energy of the charged capacitor $E_p=\frac{1}{2}CU^2$. The reactor was operated typically in a batch mode with the solution volume of 1250 ml. The liquid in the reactor vessel was cooled by a water circulation system ($\sim 3^\circ\text{C}$) to maintain an isothermal condition ($\sim 16^\circ\text{C}$). A magnetic stirring bar at the bottom of the reactor provided sufficient mixing of the solution. Flow reactor was used for measurements of dissolved hydrogen and oxygen with the solution volume of 1800 ml. The water was circulated through the reactor using a membrane pump with the rate of 1 l/min.

The concentration of H_2O_2 produced by the discharge was determined colorimetrically using the reaction of H_2O_2 with titanil ions. Hydrogen generated by the discharge was measured either directly in water as dissolved hydrogen (H_2)_{diss} or in the gas stream exiting the discharge reactor. Concentration of dissolved hydrogen was determined using H-meter developed at the Institute of Chemical Technology, Prague, Czech Republic. The same device was used for measurement of dissolved oxygen. Measurement of gaseous hydrogen was accomplished by purging the liquid in the discharge reactor with argon through a sparger at flow rate was 1 l/min. Sparger was placed at the bottom of the reactor so that no bubbles of argon in water came into contact with the plasma discharge. The H_2 present in purged gas mixture was sampled into 1 l Tedlar bags (Supelco) at various times. Concentration of hydrogen in purged gas was measured using a gas chromatograph CE Instruments GC 8000 with thermal conductivity detector HWD 800. Column 2 m \times 3 mm i.d. packed with molecular sieve 5A and argon as the carrier gas was used in chromatographic analysis. Emission spectrometry measurements were performed using ISA JobinYvon HR-320 and Chromex-500i spectrometric systems and laser line and bandpass filters (Thorlabs).

3. Results and discussion

Fig. 1 shows a typical example of the production of H_2O_2 by the corona discharge in water with the solution conductivity of 100-500 $\mu\text{S/cm}$. The same applied voltage (21 kV) and the power input (90 W) was used in each case. The conductivity of aqueous solutions was varied by the addition of dilute sulfuric acid to deionized water as an electrolyte. The pH of the solutions was in the range of 2.8-3.0. Sulfuric acid was used because sulfate ions are relative unreactive towards $\text{OH}\cdot$ and $\text{H}\cdot$ radicals. In addition, due to high molar conductivity and ion mobility

of protons the concentration of H_2SO_4 required to adjust a conductivity of the solution in the range of 100-500 $\mu\text{S/cm}$ was as low as $1-6 \times 10^{-4} \text{ mol/l}$. Hence the formation of H_2O_2 was independent of the electrolyte composition.

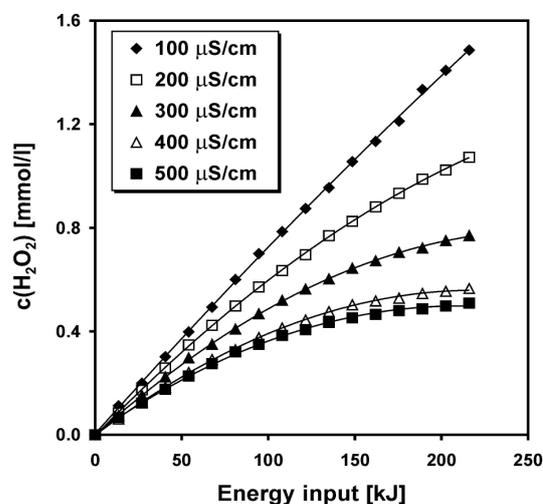


Fig. 1 Effect of solution conductivity on kinetics of H_2O_2 production by pulsed corona discharge in water (21 kV, 90 W).

As seen in Fig. 1, the concentration of H_2O_2 initially increased with increasing discharge treatment time (applied energy input) and became saturated at later times. Consequently, both the production rate and the saturation level decreased with increasing solution conductivity.

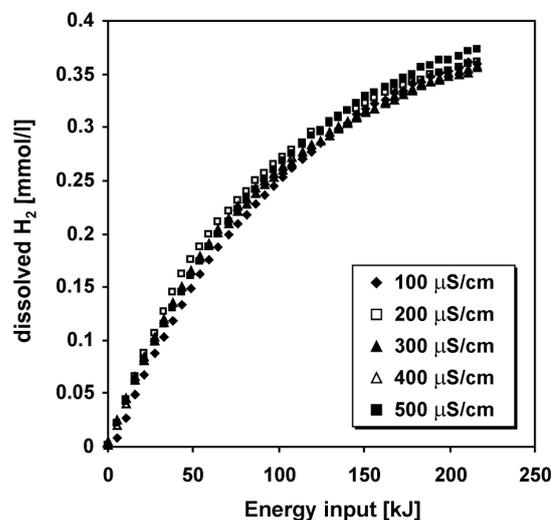


Fig. 2 Effect of solution conductivity on kinetics of H_2 dissolution in water produced by underwater discharge (27 kV, 90 W).

Different results were observed for production of H_2 generated by the discharge in water. Fig. 2 shows kinetics of dissolution of H_2 produced by the discharge in dependence on the solution conductivity. The same applied voltage (27 kV) and the power input (90 W) was used in each case. The concentration of H_2 in water increased with increasing discharge treatment time (applied energy input)

and became saturated at later times reaching about a half value of the maximum solubility of H₂ in water (0.84 mM). Fig. 2 shows very similar concentration of dissolved H₂ in the range of 100-500 μS/cm. It is apparent that solution conductivity had no effect on the hydrogen formation in water compared to the strong dependence of H₂O₂ production on the solution conductivity. These results were further confirmed by the measurements of production of gaseous hydrogen generated by the discharge that were performed under the same experimental conditions by purging H₂ the solution in the reactor by argon (Fig. 3). Data for H₂ production obtained by both methods were in good correlation and about one third of hydrogen totally produced by discharge was dissolved in water (Table 1).

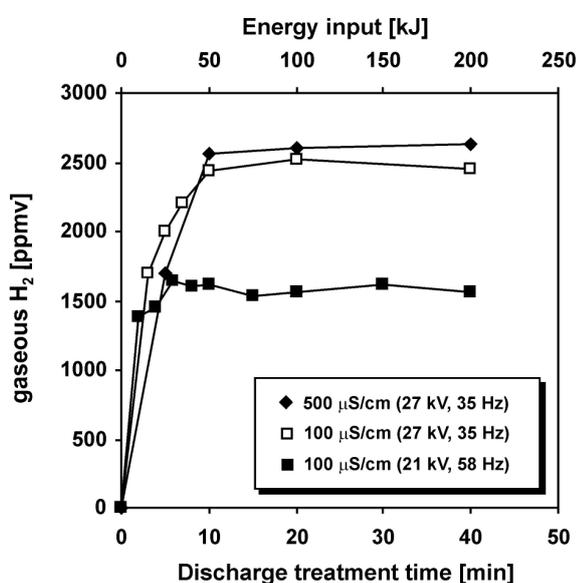


Fig. 3 Effect of applied voltage and solution conductivity on kinetics of H₂ production by underwater discharge (90 W).

Fig. 3 shows another important result. For the same power input (90 W) the production of H₂ increased with higher voltage (i.e., see difference in H₂ production for 100 μS/cm at 21 and 27 kV). This is different result compared to what was observed for H₂O₂ formation (Fig. 4). In that case the same production of H₂O₂ was determined at 21 and 27 kV. It is also interesting to note that the ratio of H₂O₂ and H₂ production was changing with increasing solution conductivity with respect to the higher yields of H₂ compared to H₂O₂.

Table 1. Energy yields of H₂ and H₂O₂ produced by discharge in water

σ [μS/cm]	U [kV]	f [Hz]	G [$\times 10^{-8}$ mol/J]			H ₂ :H ₂ O ₂
			(H ₂) _{gas}	(H ₂) _{diss}	H ₂ O ₂	
100	21	58	1.30	0.50	0.93	1.4:1
100	27	35	1.98	0.67	0.93	2.1:1
500	27	35	2.15	0.70	0.40	5.4:1

Table 1 summarizes the energy yields of H₂O₂, (H₂)_{diss} and (H₂)_{gas} produced by the discharge that were determined under different conditions based on data shown in Figs. 1-4. From Table 1 follows H₂:H₂O₂ ratio 2:1 at conductivity of 100 μS/cm. This is in agreement with [2], however, with increasing conductivity this ratio increased up to 5:1 at 500 μS/cm.

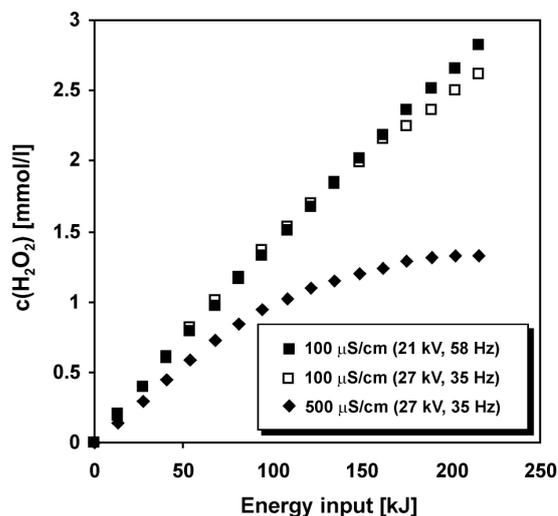


Fig. 4 Effect of applied voltage and solution conductivity on kinetics of H₂O₂ production by underwater discharge (90 W).

Concerning different effect of solution conductivity on H₂O₂ and H₂ production by the discharge, it has been determined previously that electron and power density in the discharge increases significantly with higher solution conductivity [6]. Electron density above 10¹⁸ cm⁻³ in the streamer discharge has been determined from the H_α spectral line profile. With increasing water conductivity stronger radiation and higher electron density in the discharge have been determined (above 10¹⁹ cm⁻³) [5-8].

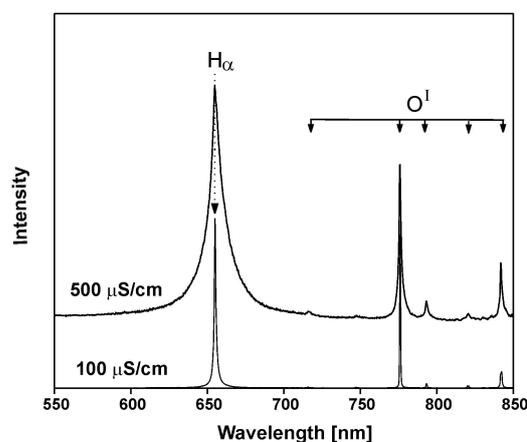


Fig. 5 NIR emission spectra of corona discharge in water with solution conductivity of 100 and 500 μS/cm.

Fig. 5 shows spatially and temporally integrated NIR spectra of corona discharge in water with the conductivity of 100 and 500 $\mu\text{S}/\text{cm}$. The emission spectrum is dominated by atomic H_α and O^I (e.g., 777, 822, 844 nm) lines. It is apparent, that H and O line profiles are significantly broader at higher conductivities. Thus, apparently denser plasma is generated at higher water solution conductivities. This suggests that more energetic processes might be more feasible with higher solution conductivity. Taking into account higher yields of H_2 than H_2O_2 and evidence of atomic oxygen lines in the emission spectrum of the corona discharge in water additional electron impact dissociation channels of H_2O next to route via eq. 1 might be involved as source of H_2 and O.



The former route (eq. 2) produces excited oxygen atom with transition emission at 844 nm ($\text{O } 3p^3P - 3s^3S^0$), while the latter route (eq. 3) produces oxygen atom with emission at 777 nm ($\text{O } 3p^5P - 3s^5S^0$) [9]. These routes require higher electron energies (~ 17 eV) than H_2O dissociation to H and OH radicals (eq. 1), however, significant emissions lines at 777 and 844 nm registered in the emission spectra of the discharge (Fig. 5) indicate that both routes (eqs. 2,3) are likely taking place in the plasmachemical dissociation of water. Unfortunately, since both processes require very similar electron energy they are hardly applicable for evaluation of the role of solution conductivity in the more energetic pathways of electron impact dissociation water induced by the underwater discharge. Therefore, other routes of formation of excited oxygen atoms by the discharges are investigated.

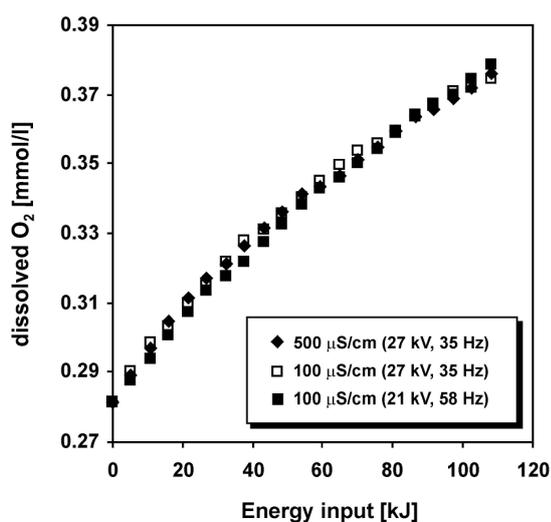


Fig. 6 Effect of applied voltage and solution conductivity on kinetics of O_2 dissolution in water treated by discharge (90 W).

Nevertheless, it is evident that once oxygen atoms are formed by the discharge they will more likely recombine to form oxygen. Fig. 6 shows kinetics of production of O_2 dissolved in water that is produced by the discharge in dependence on the solution conductivity. The same power input (90 W) was used in each case. The concentration of O_2 in water increased with increasing discharge treatment time (applied energy input), however the saturation level last significantly longer times compared to H_2 saturation (Fig. 2). Moreover, no difference was observed in the concentration of O_2 dissolved in water with change of solution conductivity and applied voltage (constant power input of 90 W). The reason for these observations might be a lower molar solubility of oxygen in water (0.28 mM under air atmosphere) than of hydrogen. Therefore, further measurements of oxygen production performed using gas chromatography are needed to evaluate production of oxygen by the underwater discharge in more detail.

4. Conclusions

Hydrogen was determined as a dominant product of plasmachemical activity of the discharge in water when its formation significantly increased with increasing solution conductivity. Compared to the yield of H_2O_2 its production rose from ratio of 2:1 at 100 $\mu\text{S}/\text{cm}$ up to 5:1 at 500 $\mu\text{S}/\text{cm}$. The observed results indicates that more energetic pathways of electron impact dissociation of water induced by the discharge are taking place with higher solution conductivity in addition to H_2O dissociation to OH and H radicals (e.g., via formation of atomic oxygen and H_2).

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