Transport of hydrogen peroxide and hydroxyl from a humid atmospheric pressure plasma jet into a liquid for plasma-driven biocatalysis

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Abstract: Plasma-driven biocatalysis requires a controllable source of hydrogen peroxide, which can be provided by atmospheric pressure plasma jets (APPJ). Concentrations of hydrogen peroxide and hydroxyl radicals are measured in a liquid treaded by a humid APPJ. The hydrogen peroxide production is strongly dependent on the humidity and the dissipated plasma power and a production rate of 600 nmol min^{-1} is achieved. The concentration of hydroxyl radicals is fifty times lower. Simulation results support the experimental findings.

Keywords: Humid atmospheric pressure plasma jet, plasma-treated liquid, H_2O_2, OH

1. Introduction

Biological enzymes are suitable for converting a substrate into a valuable product in presence of hydrogen peroxide without producing heavy metal waste, as is often the case in conventional catalysis. Atmospheric pressure plasma jets are able to produce hydrogen peroxide while maintaining a stable environment for the biological enzymes [1]. However, other species can be harmful to the enzymes, e.g. the hydroxyl radical. Thus, a selective production towards hydrogen peroxide is required. Hydrogen peroxide can be produced by plasma jets at atmospheric pressure using humid feed gas, where the hydrogen peroxide is produced within the jet and then transported further [2]. Fundamental knowledge of the generation of reactive species in the plasma and the mechanisms that occur during transport from plasma to a liquid environment is crucial to achieve high selectivity towards hydrogen peroxide. In this work, the delivery of hydrogen peroxide and hydroxyl radicals generated in a humid atmospheric pressure plasma jet into a liquid is investigated and optimisation options are explained.

2. Experiments and simulation

The atmospheric pressure plasma jet used was a capillary plasma jet developed by Winzer et al. [3]. It is comparable to the COST reference jet [4] and was operated in humid helium. The plasma was ignited and maintained with a sinusoidal RF signal at a frequency of 13.56 MHz. To add water vapor to the helium gas flow, an ice-cooled bubbler system was used. Due to the dielectric character of the capillary, the capillary plasma jet can be operated at high plasma powers up to 12 W and at high humidity admixture of up to 6400 ppm.

Liquids were treated for five minutes in a UV cuvette to have optical access to the medium. A volume of 3 mL was treated and the distance between plasma and liquid surface was set to 24 mm, unless otherwise stated.

The concentration of hydrogen peroxide was measured by a spectrophotometric approach using ammonium metavanadate. The reactant of hydrogen peroxide and ammonium metavanadate can be detected by absorption spectroscopy with an absorption maximum at 450 nm. Calibration of the system was performed by calibration solutions from 30 % stock solution of hydrogen peroxide.

The concentration of the hydroxyl radical was measured by the terephthalic acid (TA) dosimeter. TA reacts with OH to 2-hydroxyterephthalic acid (HTA). HTA can be measured by illumination with UV light at 310 nm, resulting in a fluorescence signal of the molecule at 425 nm. The fluorescence was measured using an iCCD camera. This system was calibrated by know HTA solutions.

Furthermore, the distribution of hydroxyl radical in the liquid was visualized by chemiluminescence of luminol. Luminol is excited by highly oxidative species such as hydroxyl or superoxide. Although, superoxide is the dominant exciter of luminol, in plasma-liquid systems luminol can be used to visualize the distribution of the hydroxyl radical [5]. The fluorescence is emitted at 425 nm and was measured using an iCCD camera.

The 0D plasma-chemical kinetics simulation GlobalKin was used to model the plasma chemistry [6]. The gas composition was adapted to the experimental conditions using helium and water species. In total 46 species in about 600 reactions were considered [7,8]. The mass continuity equation for charged and neutral species and electron energy conservation equation were solved in the simulation. The wall temperature of the capillary in the experiment was measured by a thermocouple and was used as an input parameter for the simulation. Transforming the time evolution given by the gas flow, a pseudo 1D plug flow model was obtained. The densities of the different species in the effluent at a distance of 24 mm downstream of the plasma channel were compared to the measurement results.

3. Results

In figure 1 the hydrogen peroxide and hydroxyl concentrations as a function of feed gas humidity for two different plasma powers are shown. For hydrogen peroxide, the concentration increases linearly up to a humidity of 1500 ppm. Thereafter, the increase flattens out significantly. This trend can be seen in the experiment and in the simulation. It should be mentioned that the simulation provides only gas phase density, while in the experiment liquid concentrations are measured. Thus, it is not possible to adequately compare absolute values, but trends can be compared.

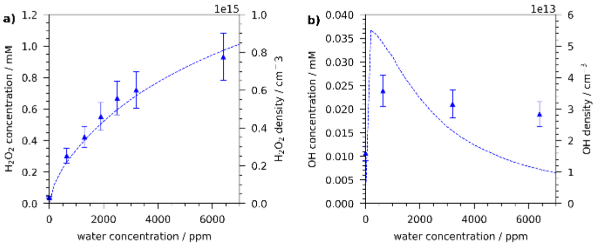

Fig. 1. Concentrations of a) hydrogen peroxide and b) hydroxyl measured in the liquid as a function of feed gas humidity at a plasma power of 6 W. Dashed lines correspond to results of the simulation.

To explain the trend, the production and destruction of hydrogen peroxide must be considered. Hydrogen peroxide is generated via the hydroxyl radical in the following three-body reaction:

$$OH + OH + M \rightarrow H_2O_2 + M. \qquad (1)$$

Hydroxyl is generated by electron dissociation of water in the plasma phase:

$$H_2O + e^- \rightarrow H + OH + e^-. \qquad (2)$$

With increasing humidity, more hydroxyl radicals are generated in the plasma resulting in an enhanced hydrogen peroxide production. Furthermore, the hydroxyl radical is also a consumer of hydrogen peroxide via

$$OH + H_2O_2 \rightarrow H_2O + HO_2. \qquad (3)$$

With higher humidity, the loss of hydrogen peroxide by hydroxyl radicals become more important resulting in the break of the initial linear increase.

The maximum hydrogen peroxide concentration measured in the liquid is about 1 mM. This corresponds to a production rate of 600 nmol min^{-1}, which is higher by a factor of three compared to the COST reference plasma jet [1].

The concentration of hydroxyl measured in the liquid shows an initial steep increase at a low humidity admixture in the feed gas. From a humidity of 1000 ppm, the hydroxyl concentration slightly decreases. The same trend can also be seen in the hydroxyl density obtained from the simulation. There, the hydroxyl density peaks at a slightly lower humidity of less than 500 ppm. As described above, a higher humidity leads to an enhanced production of hydroxyl radicals in the plasma, which also enter the liquid. At higher humidity concentrations, the destruction of hydroxyl in the effluent increases and the concentration in the liquid no longer increase or even decreases slightly.

Compared to the hydrogen peroxide concentration, the hydroxyl concentration measured in the liquid is a factor of fifty lower. This ratio can also be observed in the simulation. As the hydroxyl radical is highly reactive, it is more influenced by reactions in the effluent than the long-lived molecule hydrogen peroxide. This becomes more evident by investigating the influence of an increased transport path from the plasma to the liquid. This is shown in figure 2, where the concentrations and densities are normalised to their respective maximum value.

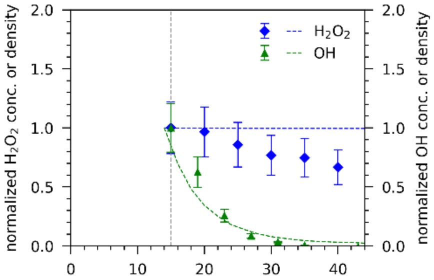

Fig. 2. Normalized concentrations of hydrogen peroxide and hydroxyl measured in the liquid as a function of distance from capillary end to liquid surface. The plasma was operated at 6400 ppm humidity at 6 W. Dashed lines correspond to the normalized results of the simulation.

The hydrogen peroxide concentration slightly decreases with increasing distance between capillary end and liquid. In the simulation, no significant change in the hydrogen peroxide density can be observed. This difference might be due to an enhance diffusion to the side as the gas flow widens with distance. Diffusion is not considered in the simulation but is unavoidable in the experiments. However, at a longer distance of 40 mm, the hydrogen peroxide concentration decreases by only 35 %. On the other hand, the hydroxyl concentration in the liquid shows a strong exponential decay for an increasing distance. This trend is well reproduced by the simulation. At a distance of 35 mm, even no hydroxyl can be measured in the liquid. Thus, a longer transport path from plasma to liquid can be used to achieve a higher selectivity in the liquid towards hydrogen peroxide.

The measured distribution of reactive species in the liquid is shown in figure 3. At the liquid surface, a strong chemiluminescence signal is visible at the centre of the surface in extension where the capillary points to the surface. The strong signal has an expanse of 1 mm, which corresponds to the width of the capillary. It penetrates the liquid to a depth of 3 mm, but already decreases sharply below the liquid surface. At the sides a weaker signal is present, which extends less than 2 mm into the liquid. This can be attributed to hydroxyl radicals carried to the sides by diffusion. Overall, the reactive species mainly hit the surface in the centre of the liquid. The hydroxyl radical reacts directly at the surface of the liquid and the reactive species penetrate only a few millimetres into the liquid.

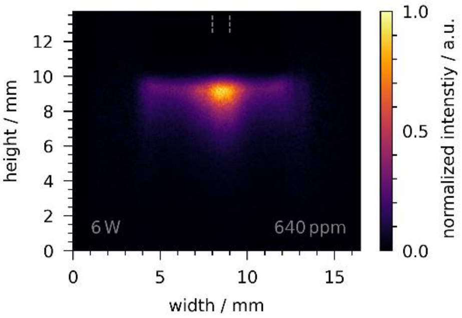

Fig. 3. Normalized chemiluminescence signal of luminol under plasma treatment. The plasma was operated at a humidity of 6400 ppm and a plasma power of 6 W. Dashed lines indicate the direction of the capillary.

4. Conclusion

The concentrations of hydrogen peroxide and hydroxyl radicals were measured in a liquid treated by a humid atmospheric pressure plasma jet. A spectrophotometric approach using ammonium metavanadate was used to measure the hydrogen peroxide concentration. The terephthalic acid dosimeter was used to measure the hydroxyl concentration.

With increasing humidity of the feed gas, the hydrogen peroxide concentration increases. A maximum production rate of 600nmol min^{-1} is achieved for a humidity of 6400 ppm and a plasma power of 6 W. The concentration of hydroxyl is fifty times lower and has a maximum concentration at low humidity. The simulation reproduces the experimental findings well.

With a longer transport path from the plasma to the liquid hydrogen peroxide is less affected and the concentration slightly decreases mainly due to diffusion. The concentration of hydroxyl shows a strong dependence on the length of the transport path. Thus, a longer transport path of the reactive species from plasma to liquid can be used to enhance the selectivity towards long-lived species such as hydrogen peroxide.

The distribution of the hydroxyl radical, visualized by the chemiluminescence of luminol, shows that it interacts mainly at the liquid surface, where the capillary faces the surface.

All the results show that a humid atmospheric pressure plasma jet can be used as a controllable hydrogen peroxide source for applications such as plasma-driven biocatalysis. The concentration in the liquid is easily controllable by adjusting plasma parameters such as humidity or plasma power, and a high selectivity towards hydrogen peroxide can be achieved.

5. Acknowledgement

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