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Gas phase hydrogen peroxide production in atmospheric pressure glow discharges operating in He-H_2O

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The gas phase production of hydrogen peroxide (H_2O_2) in a RF atmospheric pressure glow discharge with helium and water vapour has been investigated as a function of the gas flow. It is shown that the production of H_2O_2 is through the recombination of two OH radicals in a three body collision and the main destruction is through radical reactions involving OH or surface losses at the electrodes. Balancing these production and losses of H_2O_2 allows estimating OH densities which correspond with reported densities in literature for this type of discharge.

1. Introduction

Non-equilibrium atmospheric pressure plasmas can produce a great amount of reactive species, including O, OH and H_2O_2 [1].

A clear understanding of the mechanisms underlying the production of these reactive species may be of benefit to many different areas, such as biomedical, chemical and environmental applications. Among these reactive species, hydrogen peroxide (H_2O_2) has recently become a focus of interest. It is an important oxidant, only second to molecular oxygen [2], and as the by-product of oxidizing reactions involving H_2O_2 in controlled environments is only water, can be considered as a green alternative for many applications [1,3,4]. Industrial/communal waste water treatment [3-5], detergents [5], as oxidant in catalytic reactions, disinfection, bleaching and wound healing [6] are further examples where H_2O_2 is being applied.

A recent review on H_2O_2 production [7] revealed that a number of very different gas discharges have been investigated in the past and have reported a range of energy efficiencies η covering more than two orders of magnitude (0.1 – 80 g/kWh). As the dependencies of H_2O_2 production and destruction in plasmas are not well understood, directly comparing fundamentally different discharges becomes a challenging task.

In this work we present results on H_2O_2 production in a He + H_2O (1%) RF driven diffuse atmospheric pressure glow discharge (APGD) reactor for various gas flow rates. APGDs offer certain advantages for this investigation, such as low gas temperatures, a well defined residence time and a homogenous discharge. Results of modelling such an APGD [8] report efficiencies for H_2O_2 production in the order of tens of g/kWh.

The experimental setup and applied methods are presented first, followed presenting the H_2O_2 production as a function of the gas flow rate and the discussion of the main production and destruction reactions of H_2O_2 in the plasma.

2. Experimental Methods

The plasma is a capacitively coupled RF driven APGD operating at ambient pressure and temperature as investigated in [9-11]. The reactor consists of two parallel stainless steel electrodes with approximately 1 mm gap and is operated with helium containing 1 % water vapour. To power the plasma, a RF signal is amplified using a power amplifier and coupled into the reactor using a matching network. A bidirectional coupler with thermal probes monitoring forward/reflected powers is placed between amplifier and the matching network, which consists of a coil and a resistor to ground. A current- and a voltage probe are used to monitor current and voltage signals. The APGD is operated around 9.5 MHz, with power operated at approximately 5 W, measured similar to the work in [12].

3. Hydrogen peroxide detection

The detection of H_2O_2 produced in the APGD is based on Optical Absorption Spectroscopy (OAS). The effluent gas from the reactor is exposed to a solution of ammonium metavanadate (NH_4VO_3), the resulting oxidation of V^{VII} to V^{V} by H_2O_2 induces a colour change from which the concentration of H_2O_2 can be obtained. This method is highly selective on and sensitive to H_2O_2 in presence of other reactive species as described in detail in [13].

From the absorption signal, the concentration (c) of H_2O_2 can be determined using the Beer-Lambert Law

$$I = I_0 e^{-\varepsilon c d}$$

with I/I_0 being the ratio of measured to reference intensity, d the optical absorption path length and ε the molar extinction coefficient of NH_4VO_3 [13]. For every measurement run, the first obtained spectrum is used as a reference signal. Solving the equation for c, the H_2O_2 concentration in mol.l^{-1} per sample can be obtained. Performing a measurement every minute results in a graph like in figure 1, where the slope of these points represent the H_2O_2 yield in mol.l^{-1}.min^{-1} in the detection volume. The density of H_2O_2 in the plasma volume, n_{H2O2}, can be estimated from the total gas flow and the obtained concentrations. All measurements in this work have been performed using this method.

A LED with a maximum light intensity around 450 nm was chosen as light source. This is close to the highest reported sensitivity of the peroxovanadium solution to H_2O_2. The LED has a high stability in time and a good signal to noise ratio. This allows for short integration times and a high reproducibility.

Gas mixing in the detection vessel was also considered, as gas enters the vessel through a fairly large gas sieve forming bubbles in the volume above, where they interact with the liquid. The efficiency of this exchange depends on surface to volume ratio of the gas bubbles and the time these spend rising through the liquid column. In order to establish if any H_2O_2 is lost due to insufficient mixing, two recipients were connected in series and c_{H2O2} was measured in simultaneously both vessels with the same method. No absorption signal was detected in the second vessel, even after a measurement time 4-5 times longer than the usual measurement times. The reproducibility of the measurements is within 10 % and clearly of key importance. Systematic errors cannot be fully excluded at this point. However, the errors in this work are mostly determined by the discharge conditions and not by the detection method.

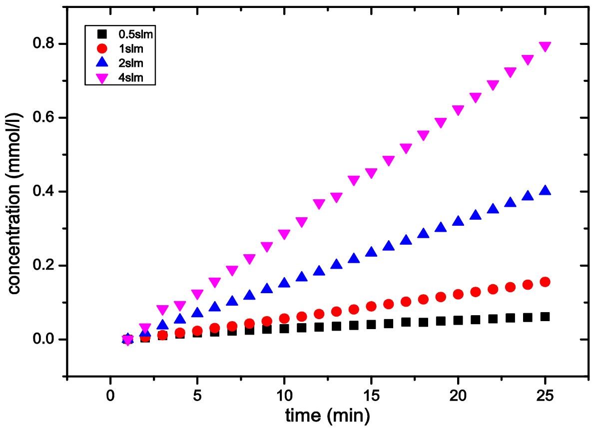

Figure 1: H_2O_2 concentration as a function of time obtained using a colorimetric method in the detection vessel.

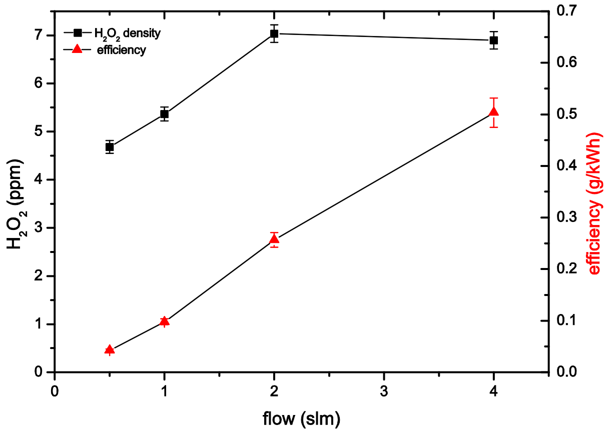

Figure 2: H_2O_2 gas phase density and energy efficiencies for He + 1% H_2O at P^{plasma} = 5W as a function of varying the total flow.

Combining the power dissipated in the plasma with the concentration of H_2O_2 in the liquid volume, the energy efficiency η of the reactor can be calculated. Gas phase densities of H_2O_2 n_{H2O2} can be calculated knowing the total flow through the reactor.

4. Hydrogen Peroxide production as a function of flow

In figure 2, trends for H_2O_2 efficiency and densities are shown as a function gas flow at a constant plasma power of 5 W and 1% water content. Both n_{H2O2} and η increase with flow, but while η steadily increases, n_{H2O2} seems to reach a maximum at 2 slm. An important consideration of the calculation of the density should be made here: the calculation of n_{H2O2} in the plasma implicitly includes the assumption that no molecules are lost between production in the plasma and detection in the liquid phase. However, the dissociation of H_2O_2 on surfaces is a known issue in surface chemistry and has been studied on various surfaces [14,15]. Losses for initial densities of 40000 ppm H_2O_2 on Pyrex of 488 K have been reported to be below 0.1 % in [15]. Rescaled to the densities (order of 10 ppm) here, considering the surface area of parts exposed to the effluent gas before detection and their low temperature, this loss is negligible compared to other losses and the production rate of H_2O_2 (discussed in the following). The calculated values of n_{H2O2} can thus be considered to accurately reflect the H_2O_2 density in the reactor.

To explain this result, the balance of production and destruction processes of H_2O_2 in the plasma at different flows has to be considered. This balance in the stationary state can be written as

$$(n_{OH})^2 n_M k_1 = n_i n_{H2O2} k_i + \Phi + \Gamma_s,$$

where the production equals bulk chemical losses with reactions induced by OH, H, O and electrons, losses due to gas flow Φ and surface reactions yielding a flux Γ_s. The individual contributions will be discussed in the following.

The main source for forming H_2O_2 in non-equilibrium cold (300 – 400 K) atmospheric pressure plasmas containing water is via the three body recombination of the hydroxyl radical to form hydrogen peroxide [7,8]

$$OH + OH + M \rightarrow H_2O_2 + M.$$

As the OH density is larger than the O and H density and the rates are smaller [8] their contribution in H_2O_2 destruction can be neglected compared to the OH Recent results for a RF plasma jet investigating atomic oxygen formation [16] reported an electron density $n_e = 10^{11}$ cm^{-3}, for a power density comparable to our case. As a similar value can be expected for the He - H_2O case, this can be applied to find an approximation for the electron induced losses. Using the rate for both electron attachment and dissociative attachment (calculated based on [17] with $T_e = 3$ eV) and $n_e = 10^{11}$ cm^{-3}, these losses are less important compared to OH induced losses.

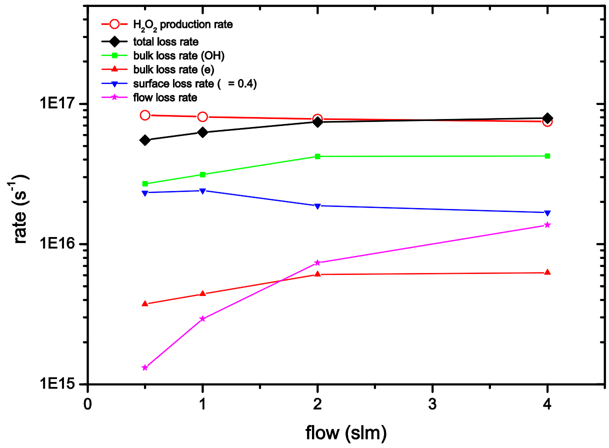

Figure 3: Balancing production and losses of H_2O_2 for a fitted OH density.

Molecules in the discharge can also be lost at the metal surfaces of the electrodes. An estimate of the net flux Γ_s of H_2O_2 molecules to a surface can be made based on considerations in [15].

Using the reaction rates available in literature [8,18] with assuming $n_e = 10^{11}$ cm^{-3} and fitting n_{OH} for the two cases of 2 and 4 slm results in a good balance with $n_{OH} = 1.5 \cdot 10^{14} cm^{-3}$ (figure 2). Reducing n_e does not yield a good balance with a realistic n_{OH}. The obtained n_{OH} seems to be in line with densities reported in [19], where the reported value is only 35% lower when the same power density is considered. As the discharge gap is half of that in reference [19], surface losses will be more important in the present case which could explain the slightly lower n_{OH} obtained in the fit. The observed discrepancy at lower flows in figure 3 could be attributed to higher impurities at low gas flow rates. These lead to higher OH losses and thus to higher H_2O_2 losses, which are not accounted for in the model.

From figure 3 it shows that the dominant loss mechanisms for H_2O_2 are OH induced losses in the bulk and losses of H_2O_2 to the surfaces of the reactor.

5. Conclusions

In this work a colorimetric method is used to determine the H_2O_2 density in an APGD. Its maximum value is 7 ppm and depends on the gas flow. Balancing the main production and loss mechanisms for H_2O_2 allow estimating the OH density. This yields a density of 1.5 10^{14} cm^{-3} similar to measured densities previously reported in literature. The main loss mechanism of H_2O_2 is the recombination with OH radicals in the bulk of the plasma.

6. Acknowledgments

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