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Gas phase hydrogen peroxide production in atmospheric pressure glow discharges operating in He-H₂O

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The gas phase production of hydrogen peroxide (H₂O₂) 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 H₂O₂ 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 H₂O₂ 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 H₂O₂ [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 (H₂O₂) 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 H₂O₂ 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 H₂O₂ is being applied.

A recent review on H₂O₂ 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 H₂O₂ 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 H₂O₂ production in a He + H₂O (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 H₂O₂ production in the order of tens of g/kWh.

The experimental setup and applied methods are presented first, followed presenting the H₂O₂ production as a function of the gas flow rate and the discussion of the main production and destruction reactions of H₂O₂ 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 H₂O₂ 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 (NH₄VO₃), the resulting oxidation of V⁷⁺ to V⁵⁺ by H₂O₂ induces a colour change from which the concentration of H₂O₂ can be obtained. This method is highly selective on and sensitive to H₂O₂ in presence of other reactive species as described in detail in [13].

From the absorption signal, the concentration (c) of H₂O₂ 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 \( \varepsilon \) the molar extinction coefficient of NH₄VO₃ [13]. For every measurement run, the first obtained spectrum is used as a reference signal. Solving the equation for \( c \), the H₂O₂ concentration in mol.1⁻¹ 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 H₂O₂ yield in mol.1⁻¹.min⁻¹ in the detection volume. The density of H₂O₂ in the plasma volume, \( n_{H_2O_2} \), 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 H₂O₂. 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 H₂O₂ is lost due to insufficient mixing, two recipients were connected in series and \( c_{H_2O_2} \) 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.

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

4. Hydrogen Peroxide production as a function of flow

In figure 2, trends for H₂O₂ efficiency and densities are shown as a function gas flow at a constant plasma power of 5 W and 1% water content. Both \( n_{H_2O_2} \) and \( \eta \) increase with flow, but while \( \eta \) steadily increases, \( n_{H_2O_2} \) seems to reach a maximum at 2 slm. An important consideration of the calculation of the density should be made here: the calculation of \( n_{H_2O_2} \) 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 H₂O₂ 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 H₂O₂ 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 H₂O₂ (discussed in the following). The calculated values of \( n_{H_2O_2} \) can thus be considered to accurately reflect the H₂O₂ density in the reactor.

Figure 1: H₂O₂ concentration as a function of time obtained using a colorimetric method in the detection vessel.

Figure 2: H₂O₂ gas phase density and energy efficiencies for He + 1% H₂O at \( p_{plasma} = 5W \) as a function of varying the total flow.
To explain this result, the balance of production and destruction processes of H$_2$O$_2$ in the plasma at different flows has to be considered. This balance in the stationary state can be written as

\[ (n_{\text{OH}} n_{\text{H}_2\text{O}_2} k_i + \Phi + \Gamma_s) n = n_{\text{OH}} n_{\text{H}_2\text{O}_2} k_i, \]

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

The main source for forming H$_2$O$_2$ 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]

\[ \text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}. \]

As the OH density is larger than the O and H density and the rates are smaller [8] their contribution in H$_2$O$_2$ 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$_2$O 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.

Molecules in the discharge can also be lost at the metal surfaces of the electrodes. An estimate of the net flux $\Gamma_s$ of H$_2$O$_2$ 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 $n_{\text{OH}}$ for the two cases of 2 and 4 slm results in a good balance with $n_{\text{OH}} = 1.5\times10^{14}$ cm$^{-3}$ (figure 2). Reducing $n_e$ does not yield a good balance with a realistic $n_{\text{OH}}$. The obtained $n_{\text{OH}}$ seems to be in line with densities reported in [19], where the reported value is only 3% 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 $n_{\text{OH}}$ 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$_2$O$_2$ losses, which are not accounted for in the model.

From figure 3 it shows that the dominant loss mechanisms for H$_2$O$_2$ are OH induced losses in the bulk and losses of H$_2$O$_2$ to the surfaces of the reactor.

5. Conclusions

In this work a colorimetric method is used to determine the H$_2$O$_2$ 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$_2$O$_2$ allow estimating the OH density. This yields a density of $1.5\times10^{14}$ cm$^{-3}$ similar to measured densities previously reported in literature. The main loss mechanism of H$_2$O$_2$ is the recombination with OH radicals in the bulk of the plasma.

6. Acknowledgments

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5. References