Ozone Modeling Within Plasmas for Ozone Sensor Applications

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Abstract: *Ozone (O_3) is potentially hazardous to human health and accurate prediction and measurement of this gas is essential in addressing its associated health risks. This paper presents theory to predict the levels of ozone concentration emitted from a dielectric barrier discharge (DBD) plasma for ozone sensing applications. This is done by postulating the kinetic model for ozone generation, with a DBD plasma at atmospheric pressure in air, in the form of a set of rate equations. Rate constants are taken from the literature and previously unconsidered ozone producing hydroxyl reactions are incorporated into the work, yielding more accurate results for the concentration of ozone for sensing applications. An application of this work is that knowing levels of ozone produced within an atmospheric DBD plasma allows for ozone sensors to be more accurately tuned to the particular requirements of the plasma system.*

1. INTRODUCTION

In recent years DBD plasmas have been researched considerably and applications now include surface modification, ozone production, thin-film deposition, etching and sterilization of bacteria. These surface modifications and microorganism sterilization are achieved by active plasma species (oxygen metastables, ozone, etc.) reacting with polymers and microorganisms [1], [2]. These species, in addition to ozone, pose health dangers to those in the immediate vicinity of the plasma and hence it is imperative to predict and detect the quantities of these species present. A schematic of such a plasma system is shown in figure 1.

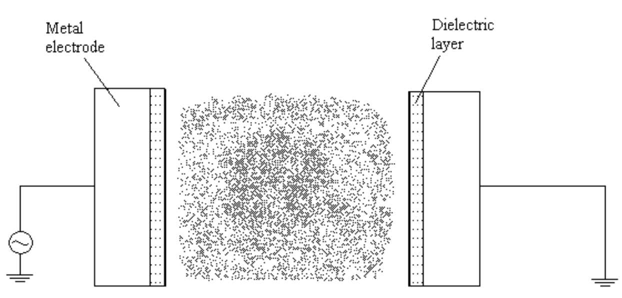

Figure 1: Dielectric barrier discharge plasma system

A correct modelling process of the evolution of the species within a plasma system is essential in determining the concentration of these species at the output of such a system. Quantities such as the rate constants for a specific reaction and the densities of the respective molecular and atomic species characterise the processes in a discharge volume. The interaction between plasma and a dielectric surface is usually insignificant and therefore the surface processes are not taken into account. Scattering mechanisms and molecular dissociation by ultra-violet radiation are additionally not considered due to their relative inconsequential effects on net molecular production within a DBD plasma.

2. KINETIC MODEL

It is proposed to calculate the density of ozone generated by DBD plasmas at atmospheric pressure in air by numerical simulation of rate equations governing the production (dissociation) and loss (recombination) of the main ozone producing reactions. The rate equations (1-5) governing the production and loss of ozone molecules in the DBD plasma are given. Rate constants, $k_1 - k_5$ were taken from [3], k_6 and k_8 were taken from [4], k_7 and k_9 were taken from [5] and k_{10}-k_{12} were taken from [6]. n_e and N represent the electron number density and buffer gas density respectively. The value for n_e, the free electron number density, was taken from previous simulations [7] in which the Boltzmann kinetic equation, the Poisson equation and the continuity equations for electrons and positively charged ions were iterated until convergence was achieved.

$$\frac{d[OH]}{dt} = k_1 n_e [H_2O] + k_2 n_e [OH] - k_2' n_e [OH] - k_4 N [OH] - k_5 n_e [OH] - k_3 [OH] - k_{11} [O][OH] \quad (1)$$

$$\frac{d[H_2O]}{dt} = -k_1 n_e [H_2O] \quad (2)$$

$$\frac{d[O]}{dt} = -k_7 [O][O_2]^2 + k_8 [O_3][O_2] - k_9 [O][O_3] - 2k_6 [O]^2 [O_2] + k_{10} n_e [O_2] - k_{12} N [O][O_3] \quad (3)$$

$$\frac{d[O_3]}{dt} = k_7 [O][O_2]^2 - k_8 [O_3][O_2] + k_9 [O][O_3] + k_{12} N [O][O_3] \quad (4)$$

$$\frac{d[O_2]}{dt} = -k_{10} n_e [O_2] + k_{11} [O][OH] - k_{12} N [O][O_3] \quad (5)$$

3. Results

Figures 2-6 show the results obtained from numerical simulation of the rate equations. Different timescales were used when creating these graphs in order to show the evolution of molecules more precisely. Figure 2 shows the density of singlet oxygen atoms increasing to a maximum after about 20 seconds and subsequently decaying to a constant value. Figure 3 shows that the density of water molecules will have decayed to a very low value after approximately 1.4 hours of operation. This however assumes that no new influx of water molecules is traversing the process volume during the time taken for species generation.

The hydroxyl ions of figure 4 increase to a peak value after about 14 seconds and after a small decay increase to a constant value after about 90 seconds. This can be attributed to the fact that in the decay region, singlet oxygen atom concentration and water molecule concentration is decreasing, but electron number density and buffer gas density are taken to be constant. This will serve to provide the means for hydroxyl atom increase even subsequent to the decrease of the productive species in figures 2 and 3.

Figure 5 shows the evolution of oxygen and how it takes approximately 11.5 days to reach its maximum value. This is due to the fact that the plasma creates different molecular oxygen isotopes in abundance, quantities that give the plasma such strong sterilization and material treatment properties.

Figure 6 depicts the increasing concentration of ozone up to a relatively constant value of approximately 250 ppm. In the first few hours of system operation there is a steady increase in ozone levels, thus demonstrating the fact that DBD plasma systems in air create ozone in abundance [8]. Due to the fact that ozone is very unstable at atmospheric pressure, the molecules created will not survive long after leaving the plasma volume. However, the concentration predicted is such that considerable health risks exist to anyone in close proximity to the system. Therefore, accurate ozone sensing apparatus would be a prerequisite of constructing such a reactor. Due to the fact that ozone concentrations reach a maximum after a period of days and tend to saturate after this maximum has been achieved, a long-life ozone sensor would additionally be desirable for continuous plasma system operation. Studies are currently ongoing regarding ozone sensors operating at room temperature, constructed from ZnO, In_2O_3 and SnO_2. Currently a ratio of 90:3:7 for the In_2O_3:ZnO:SnO_2 concentrations is being investigated and it is hoped that this will result in improved reliability over long periods of time.

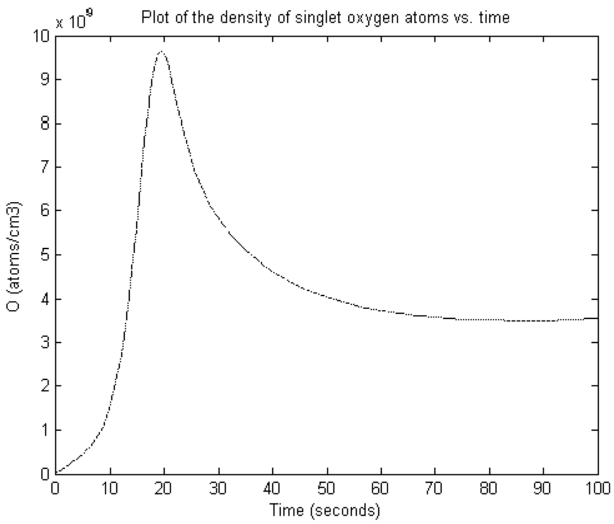

Figure 1: Evolution of the density of singlet oxygen atoms

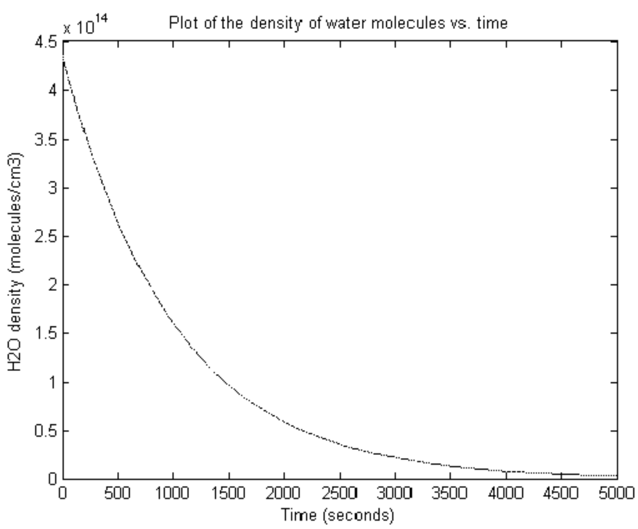

Figure 2: Evolution of the density of water molecules

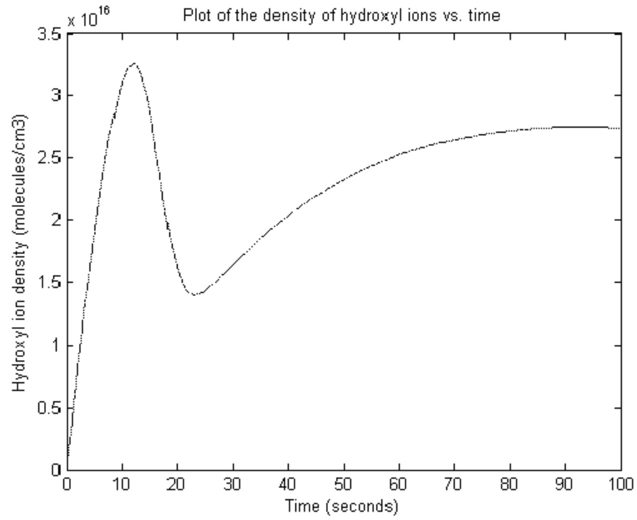

Figure 3: Evolution of the density of hydroxyl ions

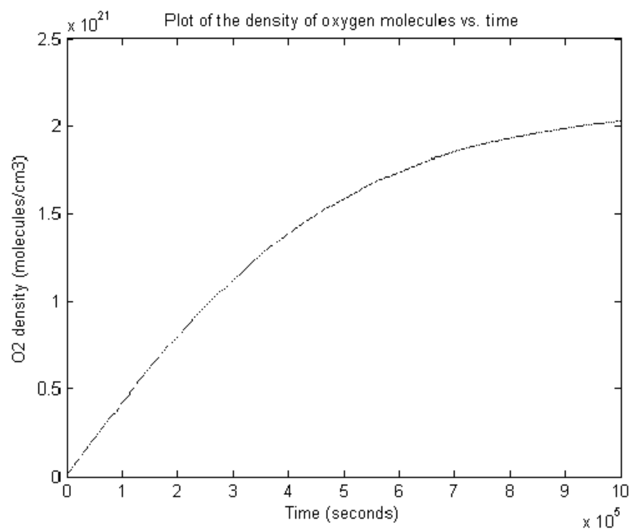

Figure 4: Evolution of the density of oxygen molecules

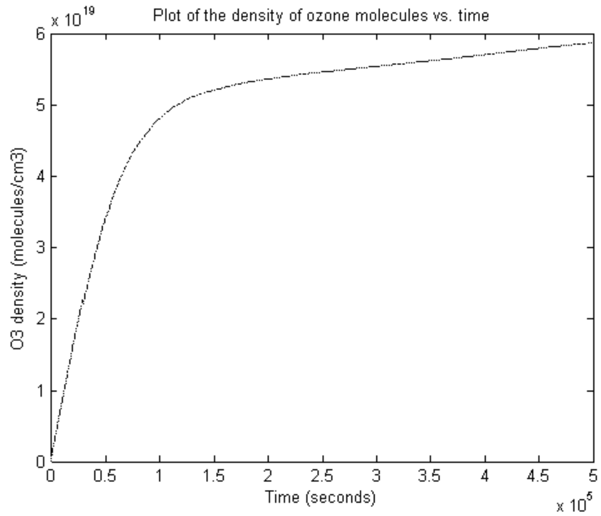

Figure 5: Evolution of the density of ozone molecules

4. CONCLUSIONS

The quantity of ozone produced by a dielectric barrier discharge plasma in atmospheric air has been calculated numerically. Numerous ozone producing atmospheric reactions have been considered to enhance the accuracy of the generation process. Ozone formation is found to be heavily dependent on the respective concentrations and evolution of singlet oxygen and molecular oxygen in particular, while the effects of water molecule density and hydroxyl ion density are found to be less important. Ozone concentration increases sharply at the onset of a plasma system being turned on up to a peak value of approximately 250ppm: far in excess of safe concentrations for humans. Thus, the requirement for accurate sensing apparatus is demonstrated. It is also suggested that for this concentration magnitude, a scrubbing mechanism utilizing a catalyst such as MnO be used. Currently Fe_2O_3:MnO in a 60:40 ratio is being investigated to decompose ozone by the reaction: $2O_3 \rightarrow 3O_2$ with a space velocity of approximately 10,000 hr^{-1}.

ACKNOWLEDGMENTS

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