DYNAMICS OF OZONE GENERATION IN A SILENT OXYGEN DISCHARGE

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Abstract

Assuming a constant molecular oxygen ($O_2$) flow velocity, the expressions describing the dynamics of ozone generation in a silent discharge, for gas pressures higher than 100 torr, are obtained. Expressions for both atomic oxygen ($O$) and ozone ($O_3$) are reduced to a compact form through the use of Green’s functions. The latter are of great aid for studying the generation of ozone for pulsed and continuous operation regimes depending explicitly on initial and boundary conditions. It is shown that the behavior of $O$ and $O_3$ densities is strongly dependent on time. Results here reported confirm the fact that, close to the electrodes, further production of high-concentration ozone can be obtained taking into account the time evolution.

1. Introduction

The importance of ozone generation in the corona discharge, most frequently used in several electrostatic precipitators, remains as an actual problem due to the fact that ozone is one of the most powerful oxidants that can be used in a great number of technological applications [1,2,3]. It has been established [3] that the silent discharge occurring in a high-pressure gas consists of multiple current filaments of short duration. A previous experimental and theoretical study on ozone generation [4] considers the dissociation rate produced by electronic impact as strongly dependent on the electric field. Assuming a constant velocity of the molecular oxygen flux introduced into the reaction chamber, the solution to the system of equations which describes the temporal evolution of the atomic oxygen and ozone densities both along the radial direction and along the streamer channel were obtained in [5]. The steady-state ozone production from oxygen in a pulsed discharge considering the radial dependence of the molecular oxygen flow velocity of the Poiseuille type was studied in [6]. The aim of this work is to study the dynamics of ozone generation in a silent discharge. Assuming a constant molecular oxygen flow velocity, more general solutions for the atomic oxygen and ozone densities, in the high pressure limit, are obtained.

2. Basic equations

The system of equations for ozone generation is obtained following the procedure proposed in [7]: the law of particle mass conservation (for species $\sigma$), the Fick’s law for the diffusion flux of particles and the conservation of total number of particles. It will be adopted a cylindrical geometry with the streamer channel along the $Oz$ axis [8]. It will be assumed an axial gas flow
(the velocity \( \overline{w} \) has only a \( O_2 \) component) as was considered in the analysis carried out in [2], which involved the influence of the axial and normal flows. Assuming symmetry with respect to \( \varphi \), it follows the system of two coupled equations for the atomic oxygen \( (n_1) \) and ozone \( (n_3) \) densities in which the molecular oxygen \( (n_2) \) is constant,

\[
\frac{\partial N_1}{\partial \tau} + \frac{\partial N_1}{\partial \zeta} = d_1 \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial N_1}{\partial \rho} \right) + \left( \frac{R}{T} \right)^2 \frac{\partial^2 N_1}{\partial \zeta^2} \right] + \alpha N_3 - \beta N_1 N_3 - \gamma N_1, \tag{1}
\]

\[
\frac{\partial N_3}{\partial \tau} + \frac{\partial N_3}{\partial \zeta} = d_3 \left[ \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial N_3}{\partial \rho} \right) + \left( \frac{R}{T} \right)^2 \frac{\partial^2 N_3}{\partial \zeta^2} \right] - \alpha N_3 - \beta N_1 N_3 + \gamma N_1, \tag{2}
\]

where the following dimensionless quantities [8], have been introduced

\[
\begin{align*}
\zeta &= z/l, \\
\rho &= r/R, \\
\tau &= u_0 t/l, \\
N_1 &= n_1/n_2, \\
N_3 &= n_3/n_2, \\
K_3 &= k_3 n_3^2, \\
K_4 &= k_4 n_2, \\
K_5 &= k_5 n_2,
\end{align*}
\]

where \( \overline{w}_0 \) is the average molecular oxygen flow velocity, \( n_\sigma = n C_\sigma, n \) is the total density and \( C_\sigma \) is the concentration of species \( \sigma \), \( D_\sigma \) is the diffusion coefficient and \( R_\sigma \) is the kinetic term. In deriving equation (1) it has been assumed a laminar fluid \((\nabla \cdot \overline{w}_0 = 0)\). Here, \( k_3, k_4 \) and \( k_5 \) are the reaction coefficients [7], \( R \) is the limit radius of the reaction volume, \( l \) is the gap discharge length and \( D_1 \) and \( D_3 \) are the diffusion coefficients for atomic oxygen and ozone respectively.

3. Ozone generation

If we assume that the atomic oxygen generated in the reaction equation [7] \( e + O_2 \xrightarrow{k_6} e + O + O \) is a function of the radius and axis and considering that the ozone is recombined in such a way that the ozone on the surface of the reaction volume becomes equal to zero, the initial and boundary conditions have the form

\[
\begin{align*}
N_1^{(0)}(\rho, \zeta, 0) &= f_1(\rho, \zeta), \\
N_1^{(0)}(1, \zeta, \tau) &= 0, \\
N_3^{(0)}(\rho, \zeta, 0) &= 0, \\
N_3^{(0)}(1, \zeta, \tau) &= 0.
\end{align*}
\tag{4}
\]

Using the variable separation method for the parabolic type equations [9] we obtain from (1) for the zeroth order, in respecting to the small parameter \( \alpha \), atomic oxygen density \( N_1^{(0)}(\rho, \zeta, \tau) \) the following expression

\[
N_1^{(0)}(\rho, \zeta, \tau) = \int_{-\infty}^{\infty} d\zeta \int_{0}^{1} f_1(\rho', \eta) G_1(\rho, \zeta, \rho', \eta) \rho' d\rho',
\tag{5}
\]

where the Green’s function \( G_1(\rho, \zeta, \rho', \eta) \) has the form

\[
G_1(\rho, \zeta, \rho', \eta) = \frac{l}{R \sqrt{2d_1 \tau}} \exp \left[ -\gamma \tau - \frac{\eta - \zeta + \tau}{R} \right] \frac{J_0(\mu^{(0)} \rho)}{J^2_1(\mu^{(0)} \rho)} \exp \left[ -\frac{(\mu^{(0)})^2}{4d_1 \tau} \right],
\tag{6}
\]

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and \( J_0(x), J_1(x) \) are the Bessel functions of zeroth and first order respectively. \( \mu_m^{(0)} \) is the \( m \)-th root of the equation \( J_0(\mu_m^{(0)}) = 0 \). In a similar way, using the variable separation method, formulas (5) and (6), we have for the case of high pressures (> 100 torr), for the ozone density

\[
N_3^{(0)}(\rho, \zeta, \tau) = \int_{-\infty}^{\infty} d\eta \int_0^1 f_1(\rho', \eta) G_3(\rho, \zeta, \rho', \eta, \rho') d\rho',
\]

where

\[
G_3(\rho, \zeta, \rho', \eta) = \sum_{m=1}^{\infty} \frac{I_0(\mu_m^{(0)} \rho)}{\sqrt{\pi} R J_1^2(\mu_m^{(0)})} \left[ 1 - \frac{1}{\gamma} \left( \mu_m^{(0)} \right)^2 (d_1 - d_3) \right] \\
\times \left\{ \frac{1}{\sqrt{d_3 \tau}} \exp \left[ -\left( \mu_m^{(0)} \right)^2 d_3 \tau - \left( \frac{1}{R} \right)^2 \frac{(\eta - \zeta + \tau)^2}{4d_3 \tau} \right] \\
- \frac{1}{\sqrt{d_1 \tau}} \exp \left[ -\gamma \tau - \left( \mu_m^{(0)} \right)^2 d_1 \tau - \left( \frac{1}{R} \right)^2 \frac{(\eta - \zeta + \tau)^2}{4d_1 \tau} \right] \right\},
\]

(8)

The explicit initial condition for the atomic oxygen density is obtained from equations

\[
\frac{dN_1^{(0)}}{d\zeta} = -\gamma N_1^{(0)},
\]

(9)

\[
\int_0^1 N_1^{(0)}(\rho, \zeta, 0) d\zeta = N_0.
\]

(10)

Equation (9) arises from the zeroth order stationary equation (1) (for fixed radius) and represents the reaction \( e + O_2 \rightarrow e + O + O \). Equation (10) is a normalization condition along the axis. From (9) and (10)

\[
f_1(\rho, \zeta) = \frac{N_0}{1 - \exp(-\gamma)} h(\zeta) \exp(-\gamma \zeta),
\]

(11)

where the step function \( h(\zeta) \) has been introduced. Substituting (11) into (5) and (7), from Figs. 1A and 1B it can be seen that the dynamics of atomic oxygen and ozone densities along the axis are strongly dependent on time. Here, the diffusion time is considered to be longer than the current pulse \( \Delta t \approx 1.6 \times 10^{-10} \) s [1] and in particular, the case of ozone generation at atmospheric pressure is considered as it is the most important pressure for practical applications although this analysis can be extended to any other pressure higher than 100 torr. The values of the variables were chosen in order to show the strong time dependence [8]. It is observed from the time evolution of ozone generation, shown in Fig. 1A, that ozone density, for a fixed radius \( r = 0.0 \) cm and in dependence of the value of \( z \), has a maximum value and then decreases. Fig. 2B shows that the generation of ozone occurs in time close to the beginning of the axis e.g. near to the electrodes in dependence of the discharge polarity.

As has been established in [5], the generation of ozone is a direct consequence of the atomic oxygen production. Considering a continuous operation regime it is necessary to assume that at the boundary of the reaction volume some amount of atomic oxygen different from zero remains, as is shown from

\[
\left\{ \begin{array}{ll}
N_1^{(0)}(\rho, \zeta, 0) &= f_1(\rho, \zeta), \\
N_3^{(0)}(\rho, \zeta, 0) &= 0,
\end{array} \right.
\]

\[
\left. \begin{array}{l}
\frac{\partial N_1^{(0)}}{\partial \rho} \bigg|_{\rho=1} = 0, \\
\frac{\partial N_3^{(0)}}{\partial \rho} \bigg|_{\rho=1} = 0.
\end{array} \right.
\]

(12)
Fig. 1: A) Time evolution of the ozone density for several points along the axis: \( z = 0.0 \) cm (solid), \( z = 0.01 \) cm (dashed), \( z = 0.02 \) cm (dotted), and B) Axial distribution of the ozone density for several times: \( t = 1 \times 10^{-5} \) s (solid), \( t = 2 \times 10^{-5} \) s (dashed), \( t = 3 \times 10^{-5} \) s (dotted), \( t = 4 \times 10^{-5} \) s (\ldots\ldots), \( t = 5 \times 10^{-5} \) s (\ldots\ldots\ldots\ldots\ldots\ldots), at \( r = 0.0 \) cm. \( P = 760 \) torr, \( T = 300 \) K and \( u_0 = 400 \) cm/s. \( R = 0.05 \) cm, \( l = 0.05 \) cm.

4. Conclusions

General solutions (5)-(8) obtained through the Green’s functions can be used in an easy way to study the ozone generation in both pulsed and continuous operation regimes as determined by the initial and boundary conditions. The generation of ozone mainly occurs close to the electrodes as Fig. 2B illustrates. It is shown, in the frame of the proposed diffusive model, that reaction \( O + O_2 + O_2 \rightarrow k_3 \rightarrow O_2 + O_3 \) is decisive for the ozone generation process in an oxygen discharge, as may be noticed from the analysis regarding the initial and boundary conditions (12). In considering a continuous operation regime, the adequate initial and boundary conditions (12) are adopted.

References