# CRITERIA FOR THE GENERATION OF HOMOGENEOUS OXYGEN PLASMAS SUITABLE FOR OZONE SYNTHESIS

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## 1. ABSTRACT

Calculated values are presented for the necessary voltage rise times and preionization electron densities that are required for the initiation of homogeneous discharge plasmas in pure oxygen and dry air. These values are dependent on the electrochemical properties of the gas and the gas pressure. These calculated results are in agreement with earlier experimental observations.

## 2. INTRODUCTION

Recently there has been considerable interest in generating homogeneous atmospheric pressure discharges in oxygen and air because of the predicted and demonstrated improved efficiency for the production of ozone.[1-5] The use of spatially uniform discharges is also expected to allow a substantial increase in the volume of the chemically reactive plasma.

Recent work in the field of pulsed rare gas-halide lasers has provided criteria for the generation of spatially homogeneous avalanches in electronegative gases.[6,7] These criteria involve a sufficiently short rise time for the applied voltage in conjunction with a sufficiently numerous and uniform distribution of preionization electrons. The basic objective is to insure that individual electron avalanches will overlap due to electron diffusion; this will thereby maintain a uniform electric field distribution within the gap during the development of the discharge process and hence reduce discharge instabilities.

We have adapted this earlier work to those gases that are interesting from the point of view of ozone synthesis, namely oxygen and air, and we will show how the homogeneity criteria apply to these gases in particular.

## 3. DISCHARGE MODEL

We are concerned here with discharges in gases at pressures in the atmospheric range and electrode spacings on the order of millimeters; this type of discharge is described by the well-known streamer model.[8] Streamer breakdown takes place when the space-charge electric field near an individual electron avalanche head approaches the magnitude of the applied electric field. The propagation of the streamer is sustained by secondary avalanches which arise from electrons supplied by photoionization of the gas between the discharge electrodes.

For pulsed discharges in the range 1-100 ns, the electrons are the prevalent charge carriers due to their high mobility. The less mobile positive ions are effectively frozen in space behind the diffusively expanding electron avalanche head.

The work reported here essentially follows the reasoning and notation of Levatter and Lin[7]; we will only present the main points of the model here. For all the details of the method employed, the reader is referred to the paper of the above authors.

The main assumptions of the model are: (1) Electron multiplication in an individual avalanche is described by Townsend's differential equation; (2) The electron diffusion process is spherically symmetric with the charge distribution in the avalanche heads being described by a Gaussian profile; (3) Streamer breakdown results when the maximum value of the radial electric field due to the avalanche head space-charge is equal to the applied field; (4) The applied field is a linear function of the time.

Taking these assumptions into account, one can then put in the appropriate values of the physical and electrochemical quantities and integrate the Townsend avalanche equation under the assumptions that the space-charge field is equal to the applied field and that the electrode gap spacing is equal to the avalanche track length; the following criteria are then obtained:

$$\alpha' d = 18.8 + \ell n(d) \qquad \text{(for pure } O_2\text{)}, \qquad \text{Eq.1a}$$

$$\alpha' d = 18.5 + \ell n(d) \qquad \text{(for dry air)}, \qquad \text{Eq.1b}$$

where $\alpha'$ is the effective first Townsend coefficient, including electron attachment, in $cm^{-1}$ and d is the electrode gap spacing in cm.

The avalanche head radius at the critical field can also be derived; this is given as:

$$r_c = 0.082 \left( \frac{\bar{D}/\mu}{E/N} x_c \right)^{\frac{1}{2}} (p/p_o)^{-\frac{1}{2}} , \qquad \text{Eq.2}$$

where $r_c$ is the critical radius in cm, $x_c$ is the critical avalanche track length in cm, $\bar{D}/\mu$ is the characteristic electron energy in volts expressed as the ratio of some field-averaged value of the diffusion coefficient $\bar{D}$ to the electron mobility $\mu$, E/N is the reduced electric field in Td, p is the gas pressure, and $p_o$ is a reference gas pressure.

Equations 1a and 1b apply when the applied field is assumed to be turned on instantaneously; the influence of a finite voltage rise time on the critical avalanche track length, the avalanche head radius, and the electron deficient-layer thickness (the distance the primary electrons drift during the pre-avalanche period) is described by the following relation:

$$A\Psi + 2/3 \left[ (1+\Psi)^{3/2} - 1 \right] + B\Psi^2 = \frac{1}{\phi} \ell n(C\phi\Psi) , \qquad \text{Eq.3}$$

where the nondimensional variables $\Psi$ and $\phi$ and the constants A, B, and C are defined as:

$$\Psi = x_c/x_o \ , \quad \phi = b_1(E/N)_o\, x_o = \tfrac{1}{2} b_1 (E/N)_o\, v_o t_o \ ,$$

$$A = \left[b_o + b_2(E/N)_o^2\right]/b_1(E/N)_o \ ,$$

$$B = (b_2/2b_1)(E/N)_o \ ,$$

$$C = (58.8\ \varepsilon_o/eb_1)\ \frac{\overline{D}/\mu}{(E/N)_o} \ , \ \varepsilon_o = 0.09\mathrm{pF/cm},\ e = 1.6 \times 10^{-19}\mathrm{C},$$

where $v_o$ is the electron drift velocity at the threshold field $(E/N)_o$, $x_o$ is the electron-deficient layer thickness, $t_o$ is the voltage rise time, the other variables are defined as before, and $b_o$, $b_1$, and $b_2$ are constants used in the following polynomial fit for the effective first Townsend coefficient:

$$\alpha' = b_o + b_1(E/N) + b_2(E/N)^2 .$$

The transport coefficient data which we have used are taken from Masek, et al.[9] for $O_2$ and from Fournier, et al.[10] for air. A summary of values of the appropriate physical and electrochemical quantities and constants required for numerical fits are listed in the table at the end of this paper.

Equation 3 can be solved numerically for $\Psi$ as a function of $\phi$ for the particular conditions of concern. From the definition of $\Psi$ and $\phi$ and Eq. 2, we can determine the critical head radius $r_c$ and the electron-deficient layer thickness $x_o$. Figure 3 shows our calculated results for $O_2$; the results for air are not significantly different from those for $O_2$.

## 4. SUMMARY OF HOMOGENEITY CRITERIA

As proposed by Palmer[6], and extended by Levatter and Lin[7], the generation of spatially uniform plasmas requires both a certain preionization electron density and a certain voltage rise time. The criteria are summarized below for two specific conditions.

(1) Preionization is supplied at the time of avalanche initiation: when the initial preionization electron density is large enough, the individual avalanche heads will coalesce to form a homogeneous discharge plasma, that is the mean distance between neighboring avalanche heads must be less than the critical radius. This is expressed as

$$(1/\overline{n}_{eo})^{1/3} < r_c \ , \ \text{or}\ \overline{n}_{eo} > r_c^{-3} , \qquad \text{Eq.4}$$

where $r_c$ is the critical radius and $\overline{n}_{eo}$ is the mean electron density within the pre-avalanche drift space $x_o$. Figure 4 shows our calculated values of $\overline{n}_{eo}$ that satisfy the above criterion as well as the values of the electron multiplication ratio $n_e(x_c)/n_e(0)$ plotted as functions of the voltage rise time.

(2) Preionization is not supplied at the time of avalanche initiation: when there is no source of seed electrons or if the preionization source is turned off before the external field is applied, the applied field rise time must be short enough to ensure that the avalanche heads overlap along the direction of propagation. The electron depletion region thickness must be small enough such that avalanches originating from "stray" electrons

located in various regions of $x_o$ can overlap, that is the electron depletion layer thickness must be smaller than the critical head radius. This is expressed as

$$x_o < r_c \quad . \qquad \text{Eq.5}$$

## 5. CONCLUSIONS

These calculations are in agreement with earlier experimental observations by the present authors and others. In the experiments of Salge, et al.[5], an improved discharge homogeneity was achieved by applying voltage pulses of slope 2 kV/ns to an ozonizer containing oxygen at atmospheric pressure and having an electrode spacing in the range 2-6 mm. This voltage slope gives a rise time to breakdown threshold (E/N = 116 Td or 38 V/cm Torr) of about 20 ns. Examination of Figure 3 shows that a critical radius of about 0.07 mm corresponds to this rise time; application of Eq. 4 to this case yields a value for $n_{eo}$ of about $3 \times 10^6$ $cm^{-3}$. This is a moderate preionization value and can be considered reasonable since the ozonizer was pulsed repetitively at 50 Hz, which probably left residual ionization in the gas. These workers also noticed further homogeneity improvements when textured electrodes were used; this is most likely due to sharp points on these electrodes being able to supply seed electrons by field emission that effectively preionize the discharge.

In the experiments of the present authors[2,3], improved discharge uniformity was achieved with highly polished electrodes, and therefore negligible preionization, by applying single voltage pulses of slope 5 kV/ns and larger to an ozonizer containing oxygen at about 1 atm pressure and having a gap spacing of about 5 mm. The time to reach the breakdown threshold of $(E/N)_o$ was less than 1 ns in this case. Examination of Figure 3 shows that the homogeneity condition with no preionization, i.e., $x_o < r_c$ requires that $t_o$ be near this value.

In our calculations no account is taken of the influence of the dielectric barrier on the discharge development or the homogeneity characteristics; taking this into account may yield new information or criteria which depend on the properties of the dielectric.

Even though it has been shown experimentally[11,12] that the classical ozonizer which has longer voltage rise times operates by the same avalanche streamer mechanism as the pulsed discharge, the classical ozonizer discharge is different in that it is discrete in character since a finite section of the dielectric capacity is charged and discharged by each microchannel.[13,14] One cannot influence this discharge process except in the special case in which the ozonizer time constant is small enough to permit the application of voltage rise times that meet the homogeneity requirements.

The transition from the discrete to the homogeneous discharge character may produce improvements in the electrical efficiency of ozonizers because the observed surface discharges which may be wasteful in the classical device could be eliminated since the dielectric surface is more nearly an equipotential in the homogeneous case. Also, the inductance of the homogeneous discharge is lower; hence the discharge voltage can terminate faster. Quicker voltage turn-off time is known to reduce discharge instabilities in pulsed high pressure lasers.[15] Further work in these areas needs to be done to apply these results to commercial ozonizers to obtain efficiency improvements or a scale-up in active volume.

## 6. REFERENCES


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## 7. NUMERICAL VALUES TABLE

| Quantity | Oxygen value | Air value | Units |
|---|---|---|---|
| $(E/N)_o$ | 116 | 111 | Td |
| $(E/N)_{typical}$ | 152 | 150 | Td |
| $v_o$ | $1.9 \times 10^7$ | $1.5 \times 10^7$ | cm/sec |
| $(\bar{D}/\mu)_{typical}$ | 4.4 | 3.2 | Volts |
| $b_o$ | 2.391 | 86.347 | $cm^{-1}$ |
| $b_1$ | -2.268 | -2.779 | $cm^{-1}$ $Td^{-1}$ |
| $b_2$ | $1.889 \times 10^2$ | $1.808 \times 10^2$ | $cm^{-1}$ $Td^{-2}$ |
| A | -0.975 | -1.002 | ----- |
| B | -0.483 | -0.361 | ----- |
| C | $-4.941 \times 10^5$ | $-3.371 \times 10^5$ | ----- |

Note: gas pressure is 1 atm at 20°C.

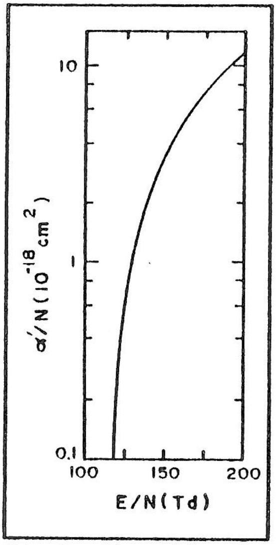


Fig.1: The effective first Townsend coefficient for pure $O_2$ plotted vs the reduced electric field strength E/N.

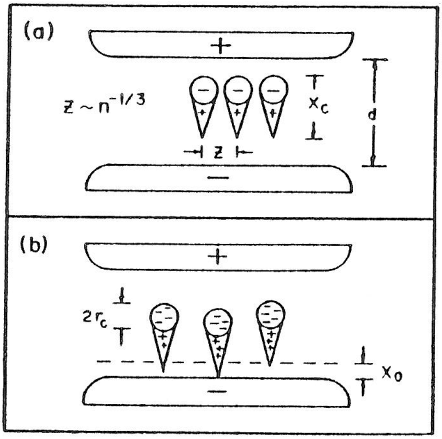


Fig.2: Pictorial diagrams showing the diffusive overlap of avalanche heads due to (a) sufficient preionization and (b) proper points of origin within the electron-depletion region. Homogeneous discharge formation requires that both the preionization and rise time criteria be met: $\bar{n}_{eo} > r_c^{-3}$ and $x_o < r_c$.

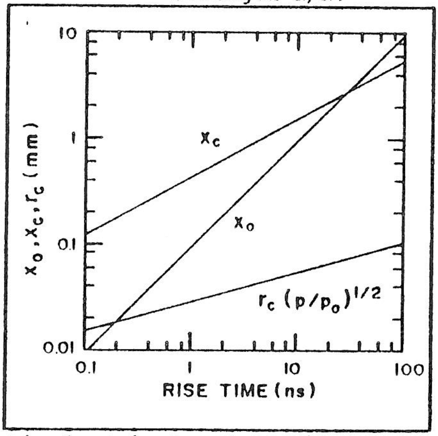


Fig.3: Calculated results showing the effect of a finite voltage rise time on the critical avalanche track length $x_c$, the critical radius $r_c$, and the electron-depletion region thickness $x_o$ for pure $O_2$ at 1 atm pressure. The results for air are not significantly different from those for pure $O_2$.

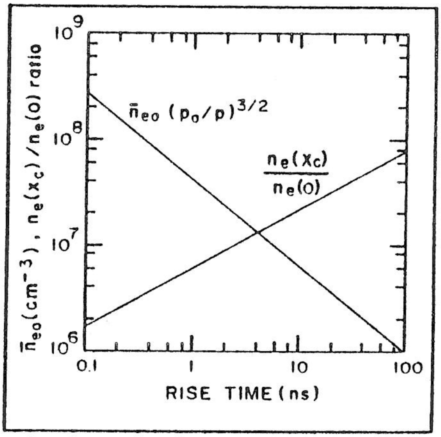


Fig.4: Calculated results showing the effect of a finite voltage rise time on the preionization electron density $\bar{n}_{eo}$ required for homogeneous discharge formation. Also shown is the electron multiplication ratio $n_e(x_c)/n_e(0)$. These results are for pure $O_2$ at 1 atm pressure.