Modeling and characterization of field-enhanced corona discharge in ozone-generator diode

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Abstract. Electric field enhanced corona plasma discharge in ozone generator diode of axial symmetry has been investigated and characterized in theory. The cathode K of diode is made of a large number of sharpened nozzles arranged on various radial planes on the axial mast and pervaded in oxygen gas inside the anode cup A, produces high fields over MV/m and aids in the formation of a corona plume of dense ozone cloud over the cathode surface. An r-z finite difference scheme has been devised and employed to numerically determine the potential and electric field distributions inside the diode. The analyses of cathode emissions revealed a field emission domain conformed to modified Child-Langmuir diode-current. Passage of higher currents (over µA) in shorter A-K gaps d gave rise to cathode heated plasma extending from the corona to Saha regimes depending on local temperature. Plasma densities of order $10^2-10^6$ m$^{-3}$ are predicted in these. For larger d however, currents are smaller and heating negligible and a negative corona favoring ozone formation is attained. High ozone yields about 20 per cent of oxygen input is predicted in this domain. The generator so developed will be applied to various important applications such as, purification of ambient air /drinking water, ozone therapy, and so on.

1. Introduction

Ozone is a powerful disinfectant and oxidant for purification [1] of ambient air and potable water, preservation of food etc. Also, ozone is used for many other important applications, such as, fumigation of operation theaters in hospitals, ozone therapy [2], and sterilization of operation tools and personnel. Corona plasma discharge route is found to be most effective [1] method for production of high ozone concentrations in a generator as compared to the ultraviolet (UV) radiation method. In the present study a high voltage (HV) driven corona discharge formed ozone generator is studied and characterized in theory. The generator so developed could be of use in all of above applications. More details of the generator are given in a companion paper [3] and elsewhere [4]. In the plasma diode of generator, a negative corona discharge is formed over the cathode surface which is at a negative potential which is at the system ground while the anode is floating at the raised positive voltage (1 - 60 kV) with respect to cathode. This work theoretically investigates the potential and field distributions inside the plasma diode, formation of corona discharge over the cathode surface, possible joule heating inside diode, and estimation of plasma densities. All SI units are used in present theoretical treatment unless stated otherwise.
2. Ozone-generator diode configuration and details

Figure 1 illustrates the typical geometry of plasma diode. It consists of a cylindrical cathode (K) configuration which is coaxially surrounded by an anode cup (A) and separated by the radial anode-cathode (A-K) gap d where K is held at negative potential connected to the system ground and A is held at the raised high positive potential with respect to K. Cathode in detail is made of a large number (N) of nozzles assembled, for example, in 12 radial planes held on a central tubular mast as in figure 1 with 16 nozzles on each plane totaling N=192 in this example. The nozzles are made extra sharp on their free ends facing anode in order to produce high electric field over the cathode surface. The nozzles also allow entry of oxygen gas inside the A-K gap routed through the tubular mast as required for ozone production. The applied voltage ($\phi_a$) between the two electrodes is varied from 0-60 kV and used as a parameter in the study apart from the gas pressure P (0.01 to 2 bar), gap d (1 to 30 mm), and the number of nozzles N (24 to 192) being other parameters of study. The inner radius $r_A$ of the anode in all above cases is 115 mm while the radius $r_K$ of cathode emission surface is varied from 85 to 114 mm choosing suitable d by adjusting the position of nozzle pinnacles appropriately. High voltage is applied to the anode cup which is insulated from the system ground and supported by a HV Teflon bushing. Both cathode and anode are made of the most ozone resistant metal [2], viz. stainless steel (SS-316). The diode assembly is enclosed inside a suitable vessel also made of SS-316 and other ozone resistant materials [2], and pervaded in oxygen gas.

![Figure 1. Plasma diode geometry with 12 nozzle planes and computed potential map in the axial plane of symmetry.](image)

3. Modeling of corona plasma and ozone-generation

3.1. Corona formation in diode

The free-space potential ($\phi$) distribution and electric field (E) inside A-K gap formed by the applied voltage ($\phi_a$) are described by Laplace equation in r, z co-ordinates as
High $E_r$ around the cathode nozzle tips gives rise to a surge of field emission and heats up the tips and initiate thermionic emission in times of picoseconds. The emission is thereafter sustained by both the field ($E_r$) and the temperature ($T$) as T-F emission [5]:

$$I_{TF} = 2\pi r_c A_F \frac{E_r^2}{\varphi} \exp\left(-\frac{c_F \varphi^{1/2}}{E_r T}\right)$$  \hspace{1cm} (3)$$

where $e$ is electronic charge, $\varphi$ is work function of cathode, $k_B$ is Boltzmann constant, $l$ and $f$ are cathode length and a factor describing effective emitter surface respectively, $A$ is thermionic constant, and $c$ is T-F constant. Whereas for extremely high $E_r$, field emission (FE) is dominant which happens in times of sub-picoseconds and the field emission current [5] given by:

$$I_F = 2\pi r_c l f A_F \frac{E_r^2}{\varphi} \exp\left(-\frac{c_F \varphi^{1/2}}{E_r}\right)$$  \hspace{1cm} (4)$$

where $A_F$ and $c_F$ are FE constants. The electrons from (3) , (4) on energized by the electric field, collide with the gas particles transiently form a corona plasma over the cathode surface in initial phase. This plasma tends to expand towards the anode and attains steady state. This corona plasma does not fill the full A-K gap at any given time and in steady state and hence does not cause any breakdown in the gap.

Electrons in same plasma collide with oxygen molecules ($O_2$) and produce the free-radicals ($O$) which combine with $O_3$ molecules and form ozone ($O_3$) the allotrope. Ozone has a short half life about tens of minutes around the ambient temperature which reduces with temperature rise and causes early reversal of $O_3$ to $O_2$ and $O$ with higher temperatures. Above $O_3$ formation and reversal processes are denoted as:

$$O_2 \leftrightarrow O^- + O^-$$  \hspace{1cm} (5)$$

$$O_2 + O^- \leftrightarrow O_3$$  \hspace{1cm} (6)$$

The energy required to overcome the binding energy 5.13 eV of $O_2$ [6] into O as in (5) having cross section around $1.3 \times 10^{-18}$ cm$^2$ [6, 7] is provided by the plasma electrons. Electrons also get attached to the atomic radicals and make them over reactive. O through contact with cathode also aids the attachment process. O$^-$ thereupon joins with other $O_2$ and forms $O_3$ as in (6) having cross sections of $3.7 \times 10^{-17}$ cm$^2$ [6] and making use of binding energy 1.49 eV from the background corona.

### 3.2. Plasma heating model

Electrons emitted from cathode attributed to (3), (4) as the case may be, being energized by the electric field tend to move towards the anode cup but are inhibited by collisions with background gas on their way. The electron current then reaching anode is substantially small and given by the modified Child-Langmuir law [5]:
\[ I_b = 2.34 \times 10^{-2} a \phi^{3/2} \left( \frac{1}{(d - x)^2 + R \phi^{1/2}} \right) \]  
\[ \text{(7)} \]

where \( a = 2\pi r_a \), \( r_a \) is anode radius, \( x \) is the inhibition factor given by the corona plume depth, \( R = \eta d / a \) is resistance offered by the gas [8] of density \( n_o \), plasma resistivity \( \eta = 7 \times 10^{-3} T_e^{1/2} n_o / n_e \), \( n_e \) and \( T_e \) are plasma density and temperature respectively. As noted above, the corona plasma does not fill the full A-K gap but only fills up to an extent of \( x \) over the cathode surface and so complete neutrality inside the gap at no times is present where the plume depth \( x \) provides a correction in the space charge through its inclusion in \( d \) as in (7). So with the onset of current \( I_b \), Poisson equation describing the potential and field in A-K gap in presence of corona plasma is given as:

\[ \frac{d^2 \phi}{dr^2} + \frac{1}{r} \frac{d \phi}{dr} + \frac{d^2 \phi}{dz^2} = -\frac{\rho}{\varepsilon} \]
\[ \text{(8)} \]

So space charge density \( \rho \) is always present in our model and obtained here as

\[ \rho = \frac{J}{\varepsilon} \]
\[ \text{(9)} \]

\[ J = \frac{I_b}{m_b^2} \]
\[ \text{(10)} \]

\( \varepsilon \) is electron velocity, \( \varepsilon = \varepsilon_r \varepsilon_0 \), \( \varepsilon_r \) is relative permittivity of oxygen gas, and \( \varepsilon_0 \) is permittivity of free space. Onset of current here is accompanied by Joule heating inside A-K gap and written as:

\[ M_K S_K T + M_A S_A T + M_O S_O T + L_o = \phi_0 I_b t \]
\[ \text{(11)} \]

where \( M_K, M_A, \) and \( M_O \) are heat affected masses of cathode, anode, and gas respectively; \( S_K, S_A, \) and \( S_O \) similarly their specific heats, \( L_o \) is heat losses mainly due to convection and conduction [8] here, and \( t \) is time for attaining steady state temperature \( T \). \( L_o \) is negligible at the lower temperatures close to ambient but closely matches the heat taken up by electrodes for temperatures around 1000 K. Applied \( \phi_0 \) does not change here as there is no breakdown and the electron currents drawn are very small. \( T \) here is larger than ambient temperature only for \( I_b \) values over \( \mu A \). The corona plasma density \( n_e \) resulting in a heated gas at elevated temperature \( T \) due to higher \( I_b \) is depicted [9] as:

\[ n_e \approx 1.14025 \times 10^5 n_o \left( \frac{k_B T}{(eV_i)^{3/4}} \right)^{3/4} \exp\left(-\frac{eV_i}{k_B T} \right) \]
\[ \text{(12)} \]

where \( k_B \) is Boltzmann constant and \( V_i \) is ionization potential. For higher \( n_e \) with appropriate \( T \) [9] such that, \( n_e / T^{1/2} > 3 \times 10^{13} V_i^{1/4} \) where \( T \) is in eV units, Saha model is applicable [10] which is written as:
\[ n_e \approx n_0 \left( 2.4 \times 10^{-4} \frac{T^{5/2}}{P} \exp \left( -\frac{eV_i}{k_BT} \right) \right)^{1/2} \]  

(13)

where \( P \) is gas pressure in Torr.

4. Computation procedure

For the present axially symmetric diode geometry, the Poisson’s equation (8) is written in a 5-point matrix \( r-z \) finite difference [8, 11] form as:

\[ \phi_{r,z} = \left[ \phi_{r,z+h} + \phi_{r,z-h} + (1 + h/2r) \phi_{r+h,z} + (1 - h/2r) \phi_{r-h,z} + h^2 \rho / \varepsilon \right] / 4 \]  

(14)

where \( h \) is mesh step. Equation (14) was solved employing MATLAB [12-16] in a matrix having 660 X 340 nodes with a mesh size (\( h \)) of 0.0005 mm, and potential and field distributions inside plasma diode were obtained. A successive over-relaxation method with a relaxation factor (\( \omega \)) of 1.8 was used to iteratively solve the potentials at each node point. The potential relaxations converged to 1 \( \times 10^{-6} \) per cent in about 3000 iteration cycles. From the converged potential map in the A-K gap the electric field at each node was determined as:

\[ E_r = \frac{\phi_{r+h,z} - \phi_{r-h,z}}{2h} \]  

(15)

\[ E_z = \frac{\phi_{r,z+h} - \phi_{r,z-h}}{2h} \]  

(16)

The computer code was applied here to study the plasma diode in various schemes, viz. Scheme-1: cathode having 6 nozzle planes, Scheme-2: cathode with 12 nozzle planes as in figure 1, and Scheme-3: number of cathode nozzle planes same as in figure 1 but also having corona discs on either sides of nozzle planes. Generation of plasma and heating if any in these schemes were also determined using (3)–(13). Results of these studies are presented and discussed in the following.

5. Results and discussions

Potential \( \phi_{r,z} \) distributions and field (\( E \)) variations with distance \( \delta \) inside the A-K gap were determined for different gaps \( d \), pressure \( P \) and applied voltage \( \phi_0 \) in above schemes. Of these, potential distribution for typical \( d=5 \text{mm} \) and arbitrary \( \phi_0 \) in scheme-2 is as illustrated in figure 1. The potentials show bumps around the nozzle pinnacles. Bumps become more pronounced and peaked in smaller \( d \) cases and respective electric field higher but decrease exponentially with radial distance \( \delta \), while a larger \( d \) tends to flatten bumps with presence of lesser fields. \( E_r \) variations with distance \( \delta \) in scheme-2 for \( \phi_0=10 \text{kV} \) are illustrated in figure 2 for various gaps \( d \). As seen electric field over cathode surface is around \( 6.19 \times 10^6 \text{ V/m} \) for \( d=2 \text{ mm} \) gap while it is \( 8.3 \times 10^6 \text{ V/m} \) for \( d=25 \text{ mm} \). Fields compared in schemes 2 and 3 reveal that effect of presence of corona rings on either side of the nozzle planes as in Scheme-3 is to flatten the field bumps over cathode pinnacles and lower the \( E_r \) there. So in similar conditions \( E_r \) in scheme-3 is lower at 6\( \times 10^6 \text{ V/m} \) around the pinnacle for \( d=2 \text{ mm} \) and \( E_r = 6.5 \times 10^5 \text{ V/m} \) for \( d=25 \text{ mm} \) as compared and shown in figure 3, while the fields in scheme-1 for same considerations are the maximum around \( 6.23 \times 10^5 \text{ V/m} \) and \( 1.05 \times 10^6 \text{ V/m} \) respectively as also seen in figure-3.

T-F emissions from cathode given by (3) in above scheme-2 at arbitrary values of temperatures chosen below the melting point of present cathode made of SS-316 (\( \varphi =4.4 \text{ eV} \) [17]) are plotted in figure 4 and reveal that they are extremely low at the lower temperatures and
Figure 2. Electric field $E_r$ variation with radial distance $\delta s$ inside A-K gaps $d$ in scheme 2 having 12 radial nozzle planes separated 10 mm apart.

Figure 3. Comparison of radial electric field close to cathode vs. A-K gap $d$ in the three diode schemes.
fields. For example, corresponding J values are as low as $2.3 \times 10^{-13} \text{ A/m}^2$ at a typical temperature $T = 900 \text{ K}$ and electric field $E_r = \text{kV/m}$ and approach mA/m only at the higher temperatures close to the melting point of present cathode material. Whereas, the field emissions depicted by (4) and plotted also in figure 4 show that they are dominant at the higher fields. For example, field emission densities in present diode are around tens of kA/m$^2$ for electric fields around MV/m. The transition between the two regions here is attributed to space charge crowding surrounding cathode which reduced with higher $E_r$. The present corona formation gets initiated by the T-F emissions and the field emission mechanisms take over from this point onwards into the steady state.

Current drawn by the plasma diode for applied voltage $\phi_0 = 10 \text{ kV}$ depicted by (7) is presented in figure 5 against gap $d$ and show that these values are in the $\mu\text{A}$ region for which cathode emission currents are a few orders higher as noted in section 3.2 and closer to the F-emission currents at the lower temperatures in figure 4. It is thus clear that field emission is driving the current in present plasma diode. So also is the negative plasma in present study which is at a temperature close to the ambient and characterized by field emission mechanisms giving lower currents. The charge density surrounding cathode at such fields and gas pressure of 1 bar and more are as large as $10^{25} \text{m}^{-3}$ and more. In these conditions, oxygen radicals produced as described in section 3.1 could be equally high as observed in some of the experiments with over 20 per cent efficiency reported [1].

Temperature rises estimated from (11) based on the dissipation of diode current in figure 5 reveal that they are in general close to the ambient temperature for A-K gaps of 10 to 30 mm and 1 bar gas pressure. For lower $d$ however the temperatures are higher and exceed 1000K for extremely small $d$ and pressures less than 0.1 bar. So depending on the temperature inside the A-K gap, a hot plasma state is also described here in conditions valid for (12) and (13). Accordingly, corona plasma is attained for temperature below 1150 K and a thermally equilibrated plasma for temperatures above 1400 K as illustrated in figure 6. The transition region between the two
\[ I_b = \frac{2.34 \times 10^{-2} a^2 \phi^{32}}{[(d-x)^2 + R^2]^2} \]
\[ \eta = 7 \times 10^{-4} T_e^{1/2} n/e \]

Figure 5. Diode current \( I_b \) vs. A-K gap distance \( d \).

Figure 6. Plasma density behavior vs. temperature in plasma diode.
temperatures in this figure is brought about by expansion of plasma to a larger distance and volume inside the A-K gap as stated in section 3.1 and turning it into a thermally equilibrated Saha state, thereon. So the plasma densities encountered here are spread in the two respective regimes, viz. Corona and Saha extending from order $10^2$ m$^{-3}$ to over $10^6$ m$^{-3}$. A corona plasma with temperatures close to ambient is only suitable for ozone formation and retention.

6. Conclusions
Corona plasma formation in an electric field driven ozone generator has been investigated. Ozone is formed inside the plasma diode made of a cathode assembly which is coaxially placed inside the anode cup. The cathode assembly is made of a large number of gas nozzles arranged in many radial planes located on the central tubular mast which admits the oxygen gas. An r-z five point finite difference scheme has been implemented to numerically study the potential and electric field distributions in different plasma diode configurations. Sharp endings on the nozzles created peak electric field $\sim 10^6$ V/m over the cathode surface in the form of bumps and aided in formation of an intense oxygen corona plume. The analyses of cathode emissions revealed a field emission dominated regime which conformed to the modified Child-Langmuir diode-current drawn. Here an intense plume with low current resulted in dense O$^-$ radical and O$_3$ production. Enhanced diode currents over µA in shorter A-K gaps heated the oxygen gas and gave rise to a thermal electron induced plasma in corona to Saha region depending on the temperature. Plasma densities extending from $10^2$ to $10^6$ m$^{-3}$ are predicted in these. For larger $d$ however, currents are small and heating negligible and only a negative corona favorable for ozone formation is formed. High ozone yields of 20 per cent in oxygen input of order 1 bar are possible in this regime. The generator so developed will be employed for various important applications, such as, ozone therapy, purification of ambient air and drinking water.

Acknowledgements
The authors thank Dr. K M Vasudevan Pillai, Secretary & CEO, MES and Dr. (Mrs.) Daphne Pillai, Joint Secretary & Rector, MES for the encouragements; Dr. G T Thampi, Principal, PIIT and Dr. A K Das, Head, L&PTD, BARC for discussions. The authors thank Department of Science & Technology (DST) Government of India under whose sponsorship and support this work is carried out.

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