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Modelling of plasma chemical processes in pulsed corona discharges

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Abstract. By a two-dimensional numerical simulation of positive streamers in atmospheric air in sphere–plane gaps, the *G*-values (numbers of radicals per 100 eV of input energy) for the production of oxygen and nitrogen atoms are obtained. Calculated *G*-values weakly depend on the applied voltage and parameters of the gap and are about 3–4 and 0.3–0.4 respectively.

In the frame of the qualitative theory of streamer propagation in nonuniform electric fields, approximate formulae for *G*-values in streamer corona discharges are derived. The *G*-values are determined by the magnitudes of the reaction rate coefficients at electron energies corresponding to the maximum of the electric field in the streamer head. The formulae obtained describe well the relations between the *G*-values for different plasma chemical reactions and can be used for estimations of the absolute *G*-values with an accuracy up to a factor of two.

1. Introduction

Pulsed corona discharges are actively studied in connection with their possible use for various plasma chemical applications such as ozone generation from air and oxygen, removal of toxic agents from flue gases and polluted air, etc [1]. Chemically active particles (radicals) are produced in streamers—thin plasma channels propagating in a discharge gap. Streamer plasma is highly nonequilibrium and nonuniform. The main part in the production of radicals is played by hot electrons in the region of a strong electric field (in the streamer head). For an accurate prediction of the efficiency of plasma chemical processes in pulsed corona discharges, detailed knowledge of the spatial–temporal distributions of streamer plasma parameters obtained by numerical methods is needed. But for estimations it is desirable to have simple analytical expressions analogous to that obtained earlier [2] for the stable glow corona regimes. Simple estimates are useful especially as the rate constants of reactions of radical production by electron impact are not often known with high accuracy. Several works on 2D simulation of streamers in nonuniform electric fields revealing the streamer structure and the main characteristics of its propagation have appeared recently [3–7]. It has been shown [7] that the results of simulation are in reasonable agreement with simple relations obtained in the frame of qualitative theory of streamer propagation in nonuniform fields [8]. This agreement makes it possible to use the approach [8] for calculation of the plasma chemical efficiency of streamer corona discharges.

In this work, by a two-dimensional (2D) simulation of positive streamers in atmospheric air in sphere–plane gaps, the *G*-values (defined as numbers of radicals produced per 100 eV of input electrical energy) for oxygen and nitrogen atom generation are calculated. In the frame of the theory [8] simple analytical expressions for the *G*-values in a streamer corona are obtained. The estimations of the *G*-values for oxygen and nitrogen atom production by positive streamers in atmospheric air are compared with the results of the 2D simulation and with available experimental data.

2. Results of numerical simulation

Calculations of radical production by positive streamers in atmospheric air in a sphere–plane electrode configuration were made with the use of the 2D model described in [7]. The model includes the balance equations for concentrations of charged particles and the equation for the potential of the electric field. The generation of nitrogen atoms in the dissociation reaction

$$\mathrm{N_2 + e \rightarrow N + N + e} \qquad (1)$$

and oxygen atoms in two reactions: dissociation

$$\mathrm{O_2 + e \rightarrow O + O + e} \qquad (2)$$

and excitation of N_2 molecules

$$\mathrm{N_2 + e \rightarrow N_2(A^3\Sigma) + e} \qquad (3)$$

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with the subsequent reaction

$$N_2(A^3\Sigma) + O_2 \to N_2 + O + O \qquad (4)$$

was considered. The values of the reaction rate constants depending on the electron energy distribution function (EEDF) were taken as functions of the local value of the electric field. For the rate constant of reaction (1) the data obtained in [9] for pure nitrogen were used (note that in strong fields needed for radical production the values of the EEDF in air and nitrogen do not differ significantly). The rate constant of oxygen atom production including processes (2), (3) and (4) was taken in accordance with [2].

The results of calculations show that N and O atoms are produced mainly in the region of strong electric field E (in the streamer head). The dependencies of the maximal value of electric field in the head E_h on the streamer length L obtained for various values of the sphere (anode) radius R_{sph}, the gap length d and the applied voltage U (assumed to be constant during the streamer propagation) are given in figure 1. It is seen that after the streamer has passed the region of high applied (Laplacian) electric field near the sphere and is moving in the weak field (at $L > R_{sph}$) the value of E_h does not change appreciably with L and is nearly the same for different parameters of the gap and applied voltages. The weak dependence of E_h on L leads to the rate of radical production being almost independent of L. An example of the resulting distributions of the radical concentrations along the streamer channel is given in figure 2 where the axial profiles of the linear number densities (integrals of the concentrations in the radial direction—normal to the direction of streamer propagation z) of nitrogen and oxygen atoms for two time instants are shown. The values of E in the streamer channel (∼5–8 kV cm^{-1}) are more than an order of magnitude lower than E_h and radical production in the channel is negligibly small, excluding the region near the anode where the field is about 20–30 kV cm^{-1}. Comparison of curves 1 and 2, 3 and 4 at $z < 0.1$ cm shows that the concentrations of atoms close to the anode continue to grow for the whole duration of streamer propagation. The growth in concentration of oxygen atoms is especially remarkable, because reactions (2) and (3) leading to O atom production have a lower energy threshold than process (1). Even for the generation of O atoms the contribution of the region near the anode is several times less than that of the streamer head.

Calculated spatial–temporal distributions of the concentrations of O and N atoms in the streamer channel were used for obtaining corresponding G-values (depending on time t or on the streamer length L)

$$G_j(t) = \frac{N_j(t)}{\int_0^t UI(t')\,dt'} \qquad (5)$$

where $N_j(t) = \int n_j(\boldsymbol{r}, t)d\boldsymbol{r}$ where n_j are the concentrations of radicals of sort j in the streamer channel (the number densities integrated over the streamer volume) and I is the discharge current. In figures 3 and 4 the G-values calculated for different discharge conditions are presented. It is seen that for streamers with $L \gg R_{sph}$ the values of G weakly depend both on L and on the discharge conditions (the applied voltage and gap parameters).

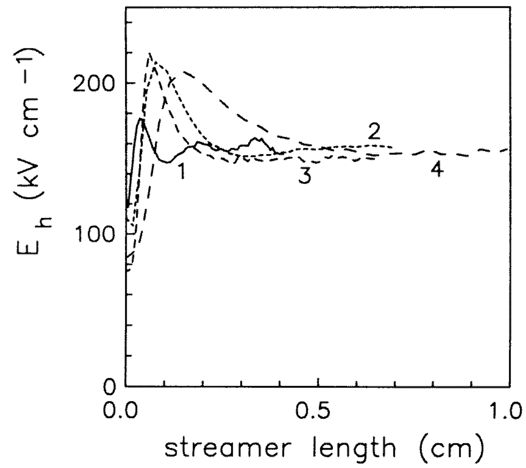

Figure 1. The dependence of the electric field in the streamer head E_h on the streamer length for R_{sph} = 0.05 (1), 0.2 (2,3) and 0.5 (4) cm, d = 0.5 (1), 1 (2,3) and 4 (4) cm, U = 6 (1), 20 (2), 14 (3) and 40 (4) kV.

It is interesting to compare the obtained G-values with available experimental data. In [9] streamers in nitrogen in a wire–cylinder configuration generated N atoms with $G_N = 0.42$. If streamer parameters in air and nitrogen are assumed to be identical, then recalculation of this G-value to air gives $G_{N\,air} \approx 0.8\ G_{N\,nitrogen} = 0.34$. In [10] the value $G_{NO} = 0.26$ for nitrogen oxides production by positive streamers in air in point–plane gaps has been obtained. Nitrogen oxides NO, NO_2, NO_3 are formed in a chain of reactions, the first link of which is reaction (1). Almost all N atoms convert to nitrogen oxide molecules, so $G_{NO} \approx G_N$. Note that in discharges in air another process of N atom and nitrogen oxide generation may take place: the reaction of O atoms with vibrationally excited N_2 molecules. The role of this process and the corresponding value of G_{NO} grow with an increase of relative concentrations of radicals and excited molecules (with increase of the energy input) [10]. The measured values of G_{NO} [10], as G_N [9], do not depend on the energy input (on the applied voltage). The lack of such dependence and the closeness of the values G_{NO} [10] and G_N [9] confirm the assumption that reaction (1) is the main source of generation of N atoms (with the following transformation to nitrogen oxides) in streamers in air.

Typical values of G_O obtained in the streamer regime of positive DC coronas (supplied with a constant voltage) in atmospheric air are 1.4–2.4 [10, 11] (the G-values for ozone production have been measured in the cited works; these values are close to G_O because almost all O atoms transform into ozone molecules in three-body reactions of association with O_2 molecules). Note that in these conditions the discharge current may have a constant component which does not give a noticeable input to ozone production. The use of a pulsed positive corona increases the value of G_O up to 4.4 [12]. Thus both G_N and G_O calculated values are in reasonable agreement with the experimental data.

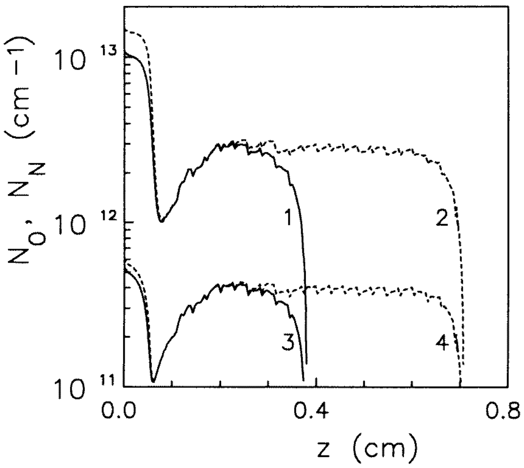

Figure 2. Profiles of oxygen (1,2) and nitrogen (3,4) linear number densities for R_{sph} = 0.2 cm, d = 1 cm, U = 14 kV at time instants t = 4.2 (1,3) and 7.1 (2,4) ns.

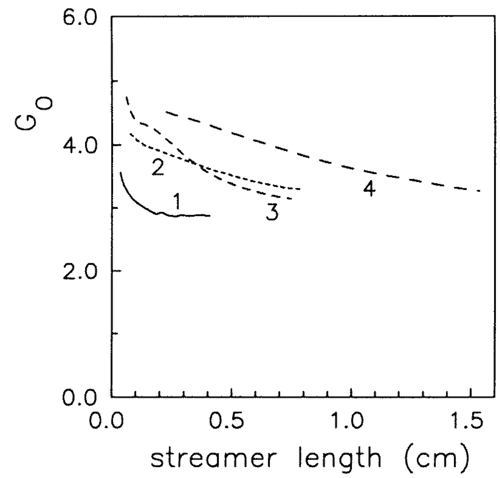

Figure 3. The dependence of G-value for oxygen atom production on the streamer length. Curves 1–4 correspond to the conditions of figure 1.

Note that calculated values of G_O for positive streamers are about an order of magnitude greater than obtained in [2] for the glow regime of a positive corona discharge. This conclusion agrees with the observation [11] of a sharp increase of G_O in a positive DC corona discharge with the transition from glow to streamer regime.

3. Analytical treatment

The generation of active particles in reactions with rather high energy thresholds is examined, when the main deposit is made by the region of streamer head. Positive streamer propagation in the positive direction of the z axis is considered (the results for negative streamers are analogous to those obtained for positive streamers, see below). The streamer head is characterized by a very steep decrease of E along z behind the maximum. The width of this region (transient from head to channel) is much less than the streamer radius. So the parameters of this region may be calculated in a 1D approximation [8]. In a reference system moving with the streamer head, the balance equations for the electron number density n_e, radical number density n_r and the difference n_s between the densities of positive and negative charged particles have the form

$$-V\frac{\mathrm{d}n_e}{\mathrm{d}z} - \frac{\mathrm{d}(n_e v_e)}{\mathrm{d}z} = \nu_i n_e \tag{6}$$

$$-V\frac{\mathrm{d}n_r}{\mathrm{d}z} = \nu_r n_e \tag{7}$$

$$-V\frac{\mathrm{d}n_s}{\mathrm{d}z} + \frac{d(n_e v_e)}{\mathrm{d}z} = 0 \tag{8}$$

where V is the streamer velocity, v_e is the drift velocity of electrons and ν_i and ν_r are the rates of ionization and radical production (drift velocities of ions are several orders of magnitude less than v_e, so the drift terms in the balance equations for ions can be neglected). For the electric field the equation

$$\frac{\mathrm{d}E}{\mathrm{d}z} = 4\pi e n_s \tag{9}$$

is valid. The relation

$$n_e v_e = n_s V \tag{10}$$

is achieved by using (8) with account of the boundary condition in front of the head. If the streamer velocity V is much greater than v_e the second term on the left-hand side of (6) can be omitted. From (6), (7), (9) and (10) the equations

$$-\frac{\mathrm{d}n_{e,r}}{\mathrm{d}E} = \frac{\alpha_{i,r}}{4\pi e} \tag{11}$$

can be obtained, where $\alpha_i = \nu_i/v_e$, $\alpha_r = \nu_r/v_e$ are the ionization and reaction rate coefficients respectively. Integration of (11) gives the number densities of electrons n_{ec} and radicals n_{rc} in the streamer channel as

$$n_{ec,rc} = \frac{1}{4\pi e}\int_{E_c}^{E_h} \alpha_{i,r}\,\mathrm{d}E \tag{12}$$

where E_c is the value of E in the channel (behind the transient region). Both the concentrations of electrons and radicals in the channel are determined by the dependencies of the reaction rate coefficients on E in the region of high electric field near the maximum E_h. If the standard approximation for the rate coefficients is used

$$\alpha_j = A_j \exp(-B_j/E) \tag{13}$$

then (12) gives

$$n_{jc} \approx \frac{1}{4\pi e}\frac{\alpha_j(E_h)E_h^2}{E_h + B_j}. \tag{14}$$

From (14) the relation between G-values for production of any two sorts of radicals can be obtained

$$\frac{G_j}{G_k} = \frac{\alpha_j(E_h)}{\alpha_k(E_h)}\frac{E_h + B_k}{E_h + B_j}. \tag{15}$$

For estimation of the absolute G-values several simplifying assumptions are made. The streamer length

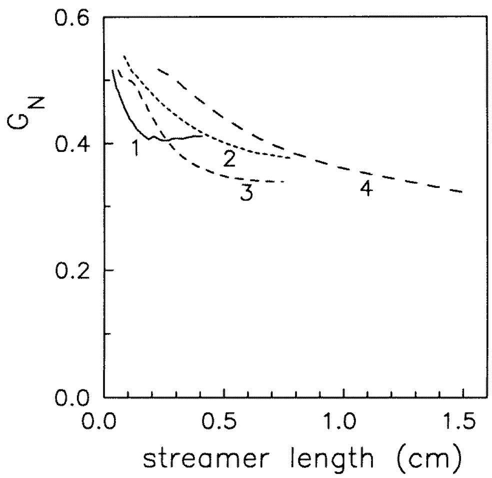

Figure 4. The dependence of G-value for nitrogen atom production on the streamer length. Curves 1–4 correspond to the conditions of figure 1.

L is assumed to be in the interval $R_{sph} \ll L < U/E_c$; the duration of streamer propagation is taken to be short enough so that the decrease of streamer channel conductivity due to electron–ion recombination and the attachment of electrons to molecules is not essential (in atmospheric air this condition corresponds to times less than several tens of nanoseconds). Calculations [7] show, in accordance with theoretical consideration [8], that in such conditions the streamer propagates with almost constant velocity and current. In this case it follows from (5) that

$$G_j \approx \frac{n_{jc}SL}{IUL/V} = \frac{n_{jc}V}{j_e U} \tag{16}$$

where S is the cross section of the channel and $j_e = I/S$ is the mean current density. The latter is related to the character transverse size R (streamer radius) by the approximate equation (see [7])

$$j_e \approx \frac{VE_h}{4\pi R}. \tag{17}$$

The substitution in (17) of the approximate relation [8] (see also [7])

$$R \approx \frac{U}{E_h \ln(L/R)} \tag{18}$$

and the use of (14) gives for the G-value (16) the following simple estimate

$$G_j = \frac{C\alpha_j(E_h)}{e(E_h + B_j)\ln(L/R)} \tag{19}$$

(the numerical factor C of the order of 1 is introduced in (19) to emphasize the approximate character of the estimate). The values of G (19) do not depend on discharge conditions, in accordance with the results of the numerical simulation presented above, and are determined by the values of the rate coefficients. Note that for most reactions the dependence of the rate coefficients on E at values near E_h is weak (close to saturation) and the estimations (15) and (19) can be used even if the exact value of E_h is not known.

Consideration of negative streamers is completely analogous, except for the possible difference between E_h values in negative and positive streamers.

For comparison of the obtained estimations with the results of the numerical simulation, the approximations (13) of the rate coefficients for production of N and O atoms in air are used with $A_O = 5.6 \times 10^{-16} n_m$, $A_N = 1.8 \times 10^{-16} n_m$ (cm^{-1}), $B_O = 2.1 \times 10^{-18} n_m$, $B_N = 5.2 \times 10^{-18} n_m$ (kV cm^{-1}), where n_m is the concentration of molecules, in cm^{-3}. Equation (15) gives the relation between G-values for O and N atom production $G_O/G_N = 7.2$ (the value $E_h = 150$ kV cm^{-1} for atmospheric air is used, see figure 1). The estimate for the ratio G_O/G_N is in agreement with the results of the numerical simulation.

The absolute values of G_O and G_N given by equation (19) with use of the typical value $\ln(L/R) = 3$ agree with numerical results if the factor C in (19) is taken equal to 1.6–2.0.

4. Conclusions

The G-values for oxygen and nitrogen atom production by positive streamers in atmospheric air in sphere–plane gaps obtained by a 2D numerical simulation are shown to weakly depend on the discharge conditions. The calculated values of G_O and G_N agree with experimental data.

Simple analytical formulae have been obtained for absolute and relative G-values in streamer corona discharges. These formulae can be used for estimations of the efficiencies of different plasma chemical processes.

Acknowledgments

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