Numerical modeling of positive streamer in air in nonuniform fields: Efficiency of radicals production

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1 Introduction

Positive streamer is a bright plasma filament, which rapidly bridges the overvolted electrodes. One of the electrodes can be sharpened; the high Laplacian field is then concentrated near that electrode. Streamer is originated in a high field and moves towards the other electrode, where the field is low.

Such a geometry (e.g. wire anode and coaxial tube cathode) is usually used in pulsed streamer corona devices [1, 2, 3]. It allows to produce multiple streamers in a large discharge gap applying voltage pulses of relatively low amplitude (10–100 kV). The variants include dielectric barrier discharge, when a thin dielectric covers one of the electrodes or a discharge in a space filled with dielectric pellets [4].

In all these cases the chemical reactions in a gas are induced by species, generated in the streamer head, where a high polarization field exists. The high field facilitates production of electrons, which destroy and excite molecules. The products of electron–molecure reactions (radicals) then initiate multiple chemical reactions in a gas leading to removal of harmful components.

Recent experiments on gas cleaning by means of pulsed streamer discharge showed, however, low efficiency of streamer corona. According to [5] in pure N_2 the energy cost of one N atom production by means of streamer corona is about 300 eV. Currently this technology is more expensive than the electron beam processing, when radicals are generated in a gas by electron beam. Under the action of beam the cost of N atom in pure N_2 is about 80 eV [5].

The efficiency of streamer corona, however, depends on a number of factors such as geometry of electrodes, voltage pulse parameters, gas pressure etc.. In a past 5 years a two–dimensional models of streamer in nonuniform fields in air [6, 7, 8, 9, 10] have been developed. These models allow to simulate streamer dynamics and generation of species and to investigate the influence of external parameters on species production. In this work the influence of Laplacian field on efficiency of radicals generation is investigated.

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2 The model of streamer in air

Streamer dynamics in air is described by the following system of equations:

$$\frac{\partial n_e}{\partial t} + \frac{1}{r}\frac{\partial (r j_{er})}{\partial r} + \frac{\partial j_{ez}}{\partial z} = S_{ph} + S_i - S_{att} - L_{ep} \tag{1}$$

$$\frac{\partial n_p}{\partial t} = S_{ph} + S_i - L_{ep} - L_{pn} \tag{2}$$

$$\frac{\partial n_n}{\partial t} = S_{att} - L_{pn} \tag{3}$$

$$\Delta V = -\frac{e}{\varepsilon_0}(n_p - n_e - n_n), \tag{4}$$

where

$$\mathbf{j}_e = -D_e \nabla n_e - \mu_e \mathbf{E} n_e \tag{5}$$

is electron flux, $\mathbf{E}$ electric field strength: $\mathbf{E} = -\nabla V$, V potential, n number density, D and μ diffusion coefficient and mobility respectively. Subscripts "e", "p" and "n" refer to electrons, positive and negative ions respectively, "e" in (4) is absolute value of electron charge.

Right hand sides of (1)–(3) describe the rates of charged particles production and loss. The S_i is the rate of molecules ionization in collision with electrons, S_{ph} the rate of photoionization in a gas, S_{att} the rate of electrons attachment to oxygen molecules, L_{ep} the rate of electron–positive ion recombination, L_{pn} the rate of positive–negative ions recombination.

The expressions for S_i, S_{att}, L_{ep} and L_{pn} are given in [11, 7]. The calculation of the rate of photoionization is based on the model [12] and is described in [13]. Boundary conditions and details of numerical solution of system (1)–(4) can be found in [7, 14].

3 Generation of radicals

The system (1)–(4) defines the evolution of electron density and electric field in the course of streamer prop-

agation. Knowing these values one may calculate the number of radicals, generated by the streamer in air.

The number density n_a of radicals of a sort a obeys the equation

$$\frac{\partial n_a}{\partial t} = s_a k_a \, \xi_{par} n \, n_e \qquad (6)$$

where ξ_{par} is fraction of parent molecules (O_2 or N_2) in the air, s_a stoichiometric coefficient, $k_a(E/n)$ the rate constant. Following [15], the reactions listed in Table 1 were taken into account.

The rate constant of nitrogen dissociation

$$\mathrm{e} + \mathrm{N_2} \rightarrow \mathrm{e} + \mathrm{N} + \mathrm{N} \qquad (7)$$

was taken from [16]. Lowke and Morrow [16] calculated EEDF and rate of nitrogen dissociation for the flue gas. The energy of N_2 dissociation is rather high and the rate constant of that process is defined by high–energetic tail of electron energy distribution function, where no vibrational excitation of molecules occurs. For that reason ionization coefficients in air and flue gases are close to each other. One may therefore expect, that this is true for nitrogen dissociation rate constant. We interpolated data [16] with a following expression:

$$k_7 = 4 \times 10^{-8} \sqrt{\frac{E/n}{2800}} \exp\left(-\frac{680}{E/n}\right) \quad \mathrm{cm^3 s^{-1}}\,, \qquad (8)$$

where E/n is in Td (1 Td $\equiv 10^{-17}$ V cm^2). Note that this fit agrees well with those presented in [17].

The rate constants of reactions, listed in Table 1 have the form

$$k_a = A_a \exp\left(-c\,\frac{B_a}{E/n}\right) \quad \mathrm{cm^3 s^{-1}} \qquad (9)$$

where E/n is in Td, $c \equiv \ln(10)$. The parameters A_a and B_a are listed in Table 1.

4 Results and discussion

The streamers are simulated for atmospheric pressure air ($p = 760$ Torr, $T = 300$ K) in 2–cm gap between the curved anode and a plane cathode. Cylindrical coordinates with the origin at the cathode surface opposite to the anode tip are used. The z–axis is directed towards the anode tip.

The two anodes were considered: dull (Anode 1) and sharp (Anode 2) (Figure 1). Both have a form of hyperboloid of revolution:

$$\left(\frac{z}{b}\right)^2 - \left(\frac{r}{a}\right)^2 = 1 \qquad (10)$$

with the radius of tip curvature $r_{tip} = a^2/b$. For both anodes $b = 2$ cm. For Anode 1 $a = 0.32$, $r_{tip} = 0.0512$ cm and for Anode 2 $a = 0.15$ cm, $r_{tip} = 0.0113$ cm. The radius of tip curvature of the Anode 1 is almost 5 times higher, than that of Anode 2. Under the same applied voltage (10 kV) it gives 3 times lower Laplacian field near the tip.

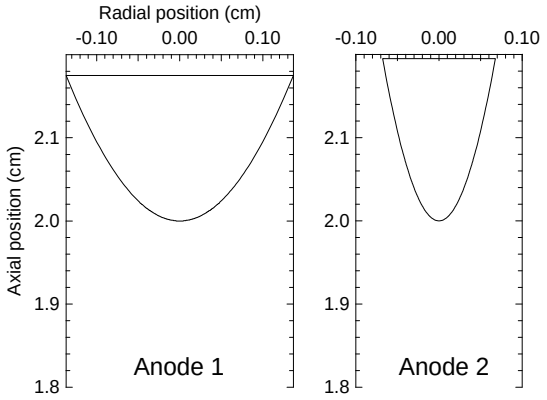

Figure 1: The two anodes, used in simulations.

In both cases the applied voltage is 10 kV. To initiate streamer a small spot of a seed plasma is placed near the anode tip. It should be emphasized, that the only difference between two variants is the shape of the anode. All other parameters, including initial and boundary conditions remain the same. This allows to elucidate the role of Laplacian field in production of radicals.

The streamers for both variants at the moment 5 ns are shown in Figure 2. It is seen, that near the dull anode the streamer is narrower and shorter, than near the sharp one. In case of sharp anode the high field region occupies much larger volume and hence radicals are produced much faster.

Figure 3a shows that the streamer near the sharp anode produces radicals almost 10 times faster, than streamer near dull anode. Figure 3b demonstrates that in 1.5 ns the streamer near sharp anode becomes more effective than near the dull one. The mean energy cost of one specie near sharp anode is about 10 eV.

The cost of O atom is twice lower, than the cost of each dissociation event. The number of O atoms directly produced in the reactions, listed in Table 1 is shown in Figure 3. The energy cost of each O atom at the moment 10 ns is about 55 eV for Anode 1 and 39 eV for Anode 2. However, in both cases most part of generated active species are excited nitrogen molecules (Figure 3a). These molecules are rapidly converted to oxygen atoms in the reaction

$$\mathrm{N_2^*} + \mathrm{O_2} \rightarrow \mathrm{N_2} + \mathrm{O} + \mathrm{O} \qquad (11)$$

and hence from practical point of view the energy cost shown in Figure 3b is the cost of oxygen atom.

The results presented show, that the sharp anode has evident advantages over the dull one. Due to higher Laplacian field the streamer near sharp anode is created with higher head radius, it produces species faster and on time scale 10 ns the mean cost of each specie is lower.

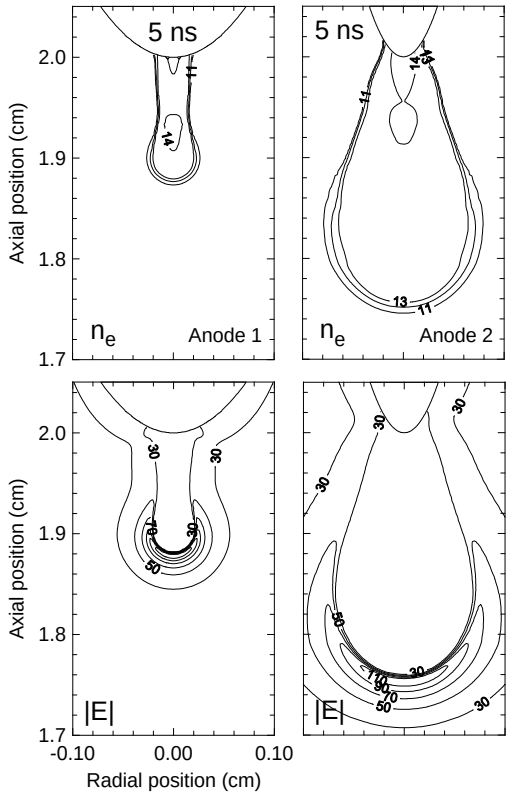

Figure 2: Contour lines of electron density and absolute value of electric field for the moment 5 ns for the two anodes. Left pair of maps: Anode 1, right pair: Anode 2. Top maps: electron density, bottom maps: absolute value of electric field strength. Electron density contours are labeled with the power of 10: 10^{11} to 10^{14} cm^{-3}. The outermost contour is 10^{11} cm^{-3}. Electric field contours are 30, 50, 70 ... kV/cm.

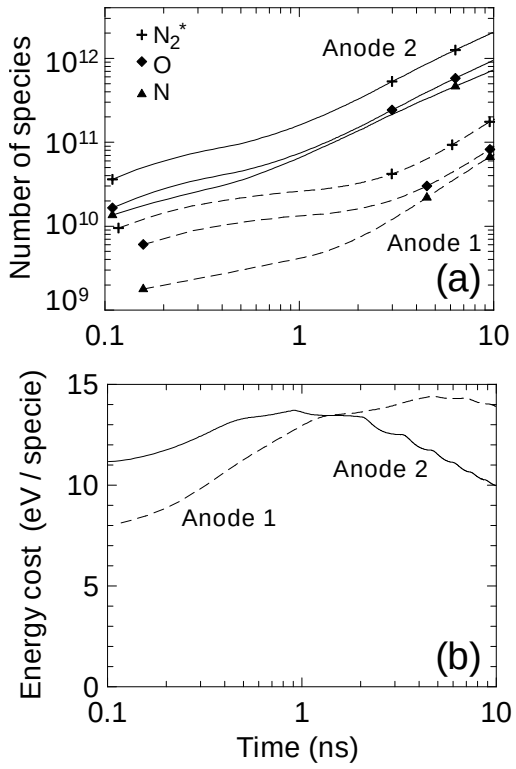

Figure 3: (a): Total number of species, produced by the two streamers. Dashed curves: streamer near dull anode (Anode 1), solid curves: streamer near sharp anode (Anode 2). (b): Mean energy cost of each specie for the two streamers. Dashed curve: Anode 1, solid curve: Anode 2.

In [7, 9] we have reported the values 35 and 30 eV/specie respectively, resulted from numerical simulation of streamers in similar conditions. However, in [7, 9] among possible channels of nitrogen excitation, only production of $N_2(A^3\sigma)$ was taken into account. The set of reactions used here (Table 1) takes into account all the channels of nitrogen excitation recommended in [15] which lead to lower energy cost.

A streamer near sharp anode cannot proliferate far into the low field region: it is then transformed into a streamer with smaller radius of head [13]. The effect of energy cost reduction, therefore, is caused by the high field near the anode. This is in line with the prediction [13] that in low field only the standard streamer can exist, whose properties depend only on gas pressure. The streamer shown in Figure 2 (Anode 2) is non–standard in that sense and this is the reason for its better performance.

It was assumed, that the voltage is applied to the anode instantly. In practice, however, high voltage circuit provides pulses with finite rise time τ and formation of streamers depends also on τ.

Consider a long wire anode. If τ is large, most of the streamers will start before the voltage reaches peak value. These streamers grow and propagate initially in the low field, they have small radius and poor efficiency of radicals production. If voltage rise time is small, the voltage grows faster than streamer moves and one may expect formation of non–standard streamers near the anode. To ensure high performance of species production it is beneficial to create high field near the anode as fast as possible and to interrupt voltage pulse before streamers will loose efficiency. Today the generation of short pulses in large–scale setups is hardly possible. However, such pulses can be generated in a small gaps ($\simeq$ 1 cm). Besides, the high voltage technology progresses and one may expect that soon this problem will be solved.

In large–scale setups for streamer corona cleaning the coaxial geometry is used and τ is usually hundreds nanoseconds to microseconds [3]. The diameter of the inner cylinder (anode) is 1.5 mm or more. The peak Laplacian field at the surface of inner cylinder is $V/(r\ln(R/r))$, where R and r are radii of outer and inner cylindrical electrodes. The voltage pulses are about 20–40 kV, therefore the peak field near the anode is about 100 kV/cm. This corresponds to the conditions near dull anode described above. Under voltage pulses

with such a large τ streamers form in low Laplacian field and this may explain their low efficiency.

Comparison showed, that the better efficiency provides Siemens reactor, where the anode "was structured to obtain a homogeneous distribution of microdischarges..." [3]. This stricture can enhance local Laplacian field. In spite of very low voltage rise time (1 μs) some streamers are born when the field is high and this could be an explanation of better reactor efficiency.

In the present sumulations the cost of nitrogen atom at the moment 10 ns is 70 eV for Anode 1 and 50 eV for Anode 2. The experiments with streamer corona in pure N_2 [4, 5] gave the values 240 to 300 eV per N atom under the voltage rise time $\simeq$ 100 ns. It is not clear, what is the efficiency of streamer in pure nitrogen, since parameters of such a streamer can differ significantly from that of in air [13]. The electron beam in pure nitrogen and in air gives N atom at a cost $\simeq$ 80 eV per atom [3, 5]. The results presented show that in air the pulsed streamer corona technology with short pulses and sharp anodes may give even better performance, than electron beam technique.

Reaction	A(cm^3/s)	B (Td)
e + O_2 $\rightarrow$e + O(^{3}P)+O(^{3}P)	$10^{-7.9}$	134
e + O_2 $\rightarrow$e + O(^{3}P)+O(^{1}D)	10^{-8}	169
e + O_2 $\rightarrow$e + O(^{3}P)+O(^{1}S)	$10^{-8.8}$	119
e + N_2 $\rightarrow$e + N_2(A)	$10^{-8.4}$	140
e + N_2 $\rightarrow$e + N_2(B)	$10^{-8.2}$	148
e + N_2 $\rightarrow$e + N_2(W^3,B')	$10^{-8.3}$	154
e + N_2 $\rightarrow$e + N_2(B')	$10^{-8.7}$	168
e + N_2 $\rightarrow$e + N_2(a')	$10^{-8.8}$	167
e + N_2 $\rightarrow$e + N_2(a,w^1)	$10^{-8.5}$	174
e + N_2 $\rightarrow$e + N_2(a')	$10^{-8.7}$	175
e + N_2 $\rightarrow$e + N_2(C)	$10^{-8.2}$	211
e + N_2 $\rightarrow$e + N_2(E,a")	$10^{-10.1}$	254
e + N_2 $\rightarrow$e + N_2(E)	$10^{-9.2}$	262

Table 1: List of ractions and parameters of their rate constants (9) (data of [15]).

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