Numerical modelling of plasmachemistry induced by cold atmospheric plasma jet near surface

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Abstract. Recently the cold plasma jets are widely used for the development of anticancer therapy. The main mechanism of atmospheric plasma jet action on cells is related to the production of nitrogen and oxygen radicals in plasma-stimulated chemical reactions, followed by the diffusion of radicals into the media with cells. The increase of the plasma jet treatment efficiency depends on a detailed study of the plasma-chemical processes that occur when the plasma jet interacts with the target. In this work, a numerical study of the plasma-chemical processes for dry air is carried out, the main ways of production and loss of RONS are detected and mixture composition near the surface during plasma jet processing is estimated.

1. Introduction
Nowadays cold atmospheric plasma jets (CAPJs) are on the stage of in vitro and in vivo tests [1-3] as a perspective instrument for anti-cancer treatment. During the contact of CAPJ with ambient air large amount of various reactive oxygen and nitrogen species (RONS) are being produced near the bio target. Negative ions, atomic oxygen and nitrogen, excited states and ozone (O₃) are also important for medical applications.

The typical cold atmospheric plasma jet devices operate at 10-50 kHz-driven AC voltage of 2.5-6.5 kV amplitude and with the cylindrical and plane designs. The inert gas (helium or argon) is pumped through the plasma device with the rate of 1-5 l/min. A sequence of streamers generated with the frequency of applied voltage propagates along the flow of noble gas to the target. Intensive generation of RONS occurs in the head of the streamer due to the presence of the strong electric field and energetic electrons.

For the efficient applications of CAPJs the detailed study of plasma enhanced chemical processes is required. With appropriate plasma chemical model it is possible to detect the main trends in chemical processes, define optimal parameters of the experiment for the most intense generation of certain group of radicals, estimate their concentrations and obtain the main ways of their production and loss.

Two- or one- dimensional models of plasma chemistry require the solution of the system of 2D or 1D mass-balance equations for every species together with the solution of the balance equation of ions and electrons, the energy equation and Poisson’s equation (see, for example [4]). This type of models requires an enormous computational resources so large amount of chemical reactions cannot be included into the plasma chemistry model. In this work, for the first step, we use the 0D model. In this approach all spatial derivatives in mass-balance equations are assumed to be zero and only time evolution is considered. Obviously, 0D model is not able to fully describe the plasma-chemical
processes in plasma jets since the latter are an extremely heterogeneous phenomenon both in time and space. Typically, 0D models are used to describe plasma chemistry in more simple configurations, for example, for a dielectric barrier discharge (DBD) between two flat electrodes. Nevertheless, 0D model allows us to obtain qualitative and quantitative conclusions about the chemical processes that occur in the plasma and for more complex geometries. Using 0D model, it is possible to take into account a larger number of chemical reactions in order to describe the main trends in the plasma enhanced chemistry.

In this work, we study plasma chemistry near the surface with a periodical change of electron temperature that corresponds to the AC voltage behavior. In this study relative humidity of the air is assumed to be zero. Our purpose is to obtain the main ways of production and loss of RONS and estimate their concentrations near the target surface.

2. Numerical simulation

For plasma treatment only the composition of the mixture near the surface is the most important. Therefore, in this work plasma chemical processes are studied over the target surface where the gas flow rate is assumed to be zero and it is possible to neglect convection transfer of mass. For the calculation the point where the streamer touches the surface was chosen. As shown in [6], the streamer has a toroidal shape. In the point of plasma-surface contact, the generation of RONS is the most intense because of the high density of electrons \((10^{12} - 10^{13} \text{ cm}^{-3})\) and their high temperature \((3.7 \text{ eV})\). The initial electron density was taken from 2D fluid model simulations [6] and assumed to be \(2 \cdot 10^{12} \text{ cm}^{-3}\). Initial concentrations of \(He, N_2, O_2\) were obtained from the solution of Navier-Stokes equations \(He/N_2/O_2 = 0.977/0.018/0.005\).

A 2D calculation of the dynamics of streamer breakdown [6] shows that the value of the electron temperature at the surface is approximately constant for \(3-5 \mu s\) after the arrival of the streamer which corresponds to a part of positive half-cycle of the voltage. Then there is a sharp drop in the intensity of ionization and excitation and during the next \(~ 70 \mu s\) ionization is absent. This indicates that electron temperature at this time is very low as well as their concentration. The plasma device periodically generates streamers on the positive half-wave of alternating voltage so when the next streamer arrives, the process repeats again.

To simulate the process of streamer coming to the surface, the electron temperature is set in the form of a periodic function of time. Each period of this function is divided into 4 parts: 1) a constant maximum value of electron temperature \(T_e = T_{e,\text{max}} = 3 \text{ eV}\), 2) lowering \(T_e\) to gas temperature \(T_{\text{gas}} = 300 \text{ K}\), 3) a constant value of the electron temperature \(T_e = T_{\text{gas}}\), 4) increasing of electron temperature \(T_e\) to maximum. Function of \(T_e\) and calculated evolution of electron concentration are shown in figure 1.

The evolution of concentration of species is described with the following equations

\[
\frac{\partial n_\alpha}{\partial t} = \sum_{\lambda=1}^{N_\sigma} (\nu^R_\lambda - \nu^L_\lambda)k_\lambda \prod_{i=1}^{M} n_\xi^i, 
\]

where \(n_\sigma\) is number density of \(\alpha\)th component, \(\nu^R_\lambda\) and \(\nu^L_\lambda\) are right- and left-handed stochastic coefficients of \(\lambda\)th reaction, \(N_\sigma\) is the total number of reactions where \(\alpha\)th component participated, \(k_\lambda\) is the rate coefficient of \(\lambda\)th reaction.

The kinetic scheme includes 627 chemical reactions and 38 related components. There are reactions of ionization processes (including Penning ionization), excitation and quenching of electronic states, dissociation, recombination, charge exchange, etc.

59 of all chemical reactions involve electrons. They include reactions of ionization, dissociation, attachment and excitation. The rate coefficients of these reactions were calculated from the electron energy distribution function obtained from a numerical solution of the Boltzmann equation. The Boltzmann equation was periodically solved using the scattering cross sections of the corresponding processes and the current mixture composition, using the BOLSIG+ [7] program. The reaction rate
coefficients were formed in the form of tables and linearly interpolated for the current value of the electron energy.

![Graph](image)

**Figure 1.** Function of electron temperature and calculated evolution of electrons.

### 3. Results

When the temperature of electrons is maximal their concentration reaches the value of $2.5 \times 10^{13}$ cm$^{-3}$. An analysis of relative contributions of the reactions showed that Penning ionization plays important role in electron production (about 55%). That are reactions of ionization of $N_2$, $O_2$ and $O$ by excited helium:

$$
He^* + N_2 \rightarrow He + N_2^+ + e, \quad k = 7 \times 10^{-11} \text{ cm}^3/\text{s}, \quad (~30\%)
$$

$$
He^* + O_2 \rightarrow He + O_2^+ + e, \quad k = 2.6 \times 10^{-10} \text{ cm}^3/\text{s}, \quad (~12\%)
$$

$$
He^* + O \rightarrow He + O^+ + e, \quad k = 3.96 \times 10^{-10} \frac{T_{gas}}{300}^{0.17} \text{ cm}^3/\text{s}, \quad (~12\%)
$$

Reaction of ionization of molecular nitrogen by electrons ($e + N_2 \rightarrow 2e + N_2^+$) contributes about one fifth in total electron production. Ionization of molecular and atomic oxygen contributes only 11% due to smaller amount of oxygen. Reaction of ionization of atomic nitrogen ($e + N \rightarrow 2e + N^+$) does not play significant role because of relatively high threshold energies of dissociation of $N_2$ and ionization of $N$ (~10 eV and ~14.5 eV, respectively).

Negative ions of $O$ and $O_2$ are formed during the part with maximum electron temperature by the reactions of electron attachment. As soon as the electron temperature drops to the gas temperature negative ions intensively recombine with positive ions. Concentrations of $O^-$ and $O_2^-$ reach the values of $3.5 \times 10^{11}$ cm$^{-3}$ and $2.4 \times 10^{11}$ cm$^{-3}$, respectively.

Due to high energy of electrons dissociation processes also occur. Every time streamer comes to the surface, concentration of atomic nitrogen increases to the value of $6 \times 10^{14}$ cm$^{-3}$ due to reactions of dissociation of $NO$ and $N_2$:

$$
e + N_2 \rightarrow e + 2N, \quad f(e)
$$

$$
e + NO \rightarrow e + N + O, \quad k = 7.4 \times 10^{-9}\exp\left(-\frac{6.5}{T_e}\right) \text{ cm}^3/s
$$

$$
e + NO \rightarrow N + O^-, \quad f(e)
$$

$$
N_2(a^1\Sigma_u^+) + NO \rightarrow N_2 + N + O, \quad k = 3.6 \times 10^{-10} \text{ cm}^3/s
$$
Concentration of atomic oxygen reaches the value of $3 \cdot 10^{16}$ cm$^{-3}$ due to dissociation of $O_2$ by electrons.

As soon as the electron temperature drops to the gas temperature $O$ and $N$ are being converted into molecules $O_2$ and $N_2$, respectively, through chain reactions:

\[
e + O_2 \rightarrow O + O + e, \quad k = 7.1 \cdot 10^{-9} \exp\left(-\frac{8.6}{T_e}\right) \text{cm}^3/\text{s}
\]
\[
e + O_2 \rightarrow O\left(^1D\right) + O + e, \quad f(e)
\]
\[
O\left(^1D\right) + M \rightarrow O + M, \quad k = 5 \cdot 10^{-12} \text{cm}^3/\text{s}
\]
\[
N + NO \rightarrow N_2 + O, \quad k = 8.2 \cdot 10^{-11} \exp\left(-\frac{410}{T_{gas}}\right) \text{cm}^3/\text{s}
\]
\[
N + O_2\left(\alpha^1\Delta_g\right) \rightarrow NO + O, \quad k = 2.5 \cdot 10^{-10} \text{cm}^3/\text{s}.
\]

So the concentrations of $O$ and $N$ decrease by several orders of magnitude till the next streamer comes to the surface. Evolution of concentrations of atomic and molecular oxygen and nitrogen are illustrated in figure 2.

**Figure 2.** Calculated evolution of concentration of atomic and molecular oxygen and nitrogen, $NO$ and electrons.

Because of high concentration of $O$ and $N$ in the discharge, such components as $NO$, $O_3$, $NO_3$, $N_2O_3$ and $N_2O_4$ are being generated through reactions of attachment of $O$ and $N$ with $O_2$, $N_2$ and each other. $NO$ is very important for medical applications because of its extremely high reactivity [8]. $O_3$ on the other hand can cause cell’s death via oxidative stress [9]. Calculated evolution of these species can be seen in figure 3.

It should be noted that concentrations of species averaged over the period vary greatly during the first ~5000 periods. As it is seen from figure 4 they gradually reach their equilibrium states.

### 4. Conclusion

In this work plasmachemical processes that occur during interaction of cold atmospheric plasma jets with dry air were studied. In order to simulate a sequence of streamer coming to the surface electron temperature was set as a periodical function of time. Using 0D modelling concentrations of RONS and ions near the surface were calculated. The calculation revealed that $O$, $N$, $NO$, $O_3$, $NO_3$, $N_2O_3$ and $N_2O_4$ are being actively generated in plasma jets. The main ways of their production and loss were determined. An analysis of relative contributions of various reactions also showed that Penning ionization reactions play crucial role in such systems.
Figure 3. Calculated evolution of species concentrations.

Figure 4. Evolution of species concentrations averaged by the period of applied voltage.

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References
[1] Gjika E, Pal-Ghosh S, Tang A, Kirschner M, Tadvalkar G, Canady J, Stepp M A and Keidar M 2018 ACS Appl. Mater. Interfaces 10 9269–79
[2] Chen Z, Zhang S, Levchenko I, Beilis I I and Keidar M 2017 Sci. Rep. 7 12163
[3] Chen Z, Simonyan H, Cheng X, Gjika E, Lin L, Canady J, Sherman J H, Young C and Keidar M 2017 Cancers 9 61
[4] Schweigert I V, Vagapov S, Lin L and Keidar M 2018 J. Phys. Conf. Ser. 1112 012004
[5] Breden D, Miki K and Raja L L 2012 Plasma Sources Sci. Technol. 21 034011
[6] Schweigert I V, Vagapov S, Lin L and Keidar M 2019 J. Phys. D. 52 29
[7] Hagelaar G J M and Pitchford L C 2005 Plasma Sources Sci. Technol. 14 722–33
[8] Fridman G, Friedman G, Gutsol A, Shekhter A, Vasilyev S and Fridman A 2008 Plasma Process. Polym. 5 503–533
[9] Laroussi M 2009 IEEE Trans. Plasma Sci. 37 714–25
[10] Ariskin D A, Schweigert I V, Alexandrov A L, Bogaerts A and Peeters F M 2009 J. Appl. Phys. 105 063305