Processes of electron attachment and detachment in near breakdown conditions in air plasma

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Abstract. Results of theoretical research on ionization of dry air at different low and moderate values of constant electric field are described. Special attention to the processes of electron attachment to oxygen molecules and electron detachment from negative ions has been paid. New data on the detachment of electrons from oxygen molecular negative ions are taken into account.

1. Introduction
Ionization processes in air, resulting in formation of plasma, are of practical interest, related to the numerous use of gas discharges [1], to understanding of low and moderate values of electric fields in discharge devices and plasma at a surface and inside aircrafts in thunderstorm conditions [2,3]. For analysis of issues related to processes in dry air plasma, in this paper we model the discharge plasma at low and moderate (relative to the threshold) electric fields. The study is based on detailed plasma chemical model for the discharge between large electrodes at constant over the volume electric field. We model the situation close to those of [4,5] for which there are measurements for subthreshold and nearthreshold values of reduced electric field; they correspond to self-maintained glow discharge.

2. Plasma chemical model
As in our paper [1], at numerical simulation of plasma chemistry of dry air we use a system of plasma-chemical and chemical reactions corresponding to works [1,5-7]. This model includes 25 component (neutrals, positive and negative ions, electrons and excited particles) and more than 180 plasma-chemical reactions with their participation. Relatively complete description of plasma-chemical model is presented in [1].
Rate constants of electron-molecule reactions correspond to the works [1,4], where they were calculated on a basis of the Boltzmann equation. The function of electron energy distribution was considered corresponding to glow discharge in air. Costs of excitation, dissociation and ionization of molecules by fast particles are taken from [8]. Attachment and detachment rate constants were taken from [1,9-11].

Into the equation for the gas temperature we have included terms corresponding to heating as a result of relaxation of vibrational and electronic degrees of freedom of molecules, the heating and cooling of the gas in chemical and plasma-chemical reactions, heating of electrons in collisions – the Joule heating. In the simulation were considered reactions with plasma and fast electrons e, e'; positive ions O', O_2^+, O_3^+, O_6^+, O_8^+, N^+, NO^+, N_2^+, O_2^+N_2; negative ions O', O_2^-, O_3^-, atoms N, O, molecules O_2, O_3, N_2, N_3O, NO; nitrogen excited vibrational states N_2(v), excited electronic states of nitrogen N_2(B^3Π_g), N_2(X^1Σ_g^-), oxygen excited vibrational states O_2(v), excited electronic states of oxygen and nitrogen. For ion-molecule reactions we used experimental and theoretical dependences via E/N, gas and ion temperatures, all of them are presented in [1]. They were mainly taken from [5-7] and references from them.

3. Basic elementary processes involving negative ions in air plasma

We single out reliable reactions [1,5-6,9-11] taking place at ionization and attachment-detachment processes in the analysis of simple situations in dry air in pressure range of 100-760 Torr. They are:

- Atmospheric background ionization by fast electrons
  \[ e^+O_2 \rightarrow O_2^+e^-e, \quad e^+N_2 \rightarrow N_2^+e^-e. \quad (1) \]
- 2. Direct ionization of molecules of O_2 and N_2 by slow electrons e
  \[ e+O_2 \rightarrow O_2^+2e, \quad (2a) \]
  \[ e+N_2 \rightarrow N_2^+2e, \quad (2b) \]
accompanyed by the rapid charge-exchange of ions N_2^+ with oxygen molecules.
- Dissociative attachment of electrons to molecules O_2, with the creation of the negative ion O' and oxygen atom O: \[ e+O_2 \rightarrow O^-+O \]. \quad (3) \]
Processes (2) and (3) depend on electrical field value, have thresholds, and play a crucial role at the values of E/N > 30-60 Td [1,2].
- Three-body attachment of slow electrons to molecules plays an important role in the balance of ions in air [12]: \[ e+O_2+O_2 \rightarrow O_2^2+O_2 \]. \quad (4) \]
- We take into account the process of electron detachment from molecular oxygen ion in collisions with neutral molecules in air mixture \[ O_2^-+M \rightarrow e+O_2+M \], \quad (5) \]
and processes detachment of electrons from O' and O^- ions in air \[ O^-+M \rightarrow e+O+M, \quad (6) \]
\[ O^-+N_2 \rightarrow e+N_2O, \quad (7) \]
- Plasma ions O^- and O^+ are produced in reactions \[ O^-+O_2 \rightarrow O_2^-+O, \quad (8) \]
\[ O^-+O_2+O_2 \rightarrow O_4^-+O_2 \]. \quad (9) \]
- Balance of positively charged particles at initial stage of the background plasma is determined by reactions of recombination:
  \[ e+M_2^+ \rightarrow M+M, \quad (10) \]
  \[ O_2^-+M_2^+ \rightarrow O_2+M_2 \]. \quad (11) \]
where $M_{2}^{+}$ is a positive ion.

Reactions (6) - (10) are effective when dissociative attachment of electrons to the oxygen molecules with production of $O$ has already occurred, i.e. at the stage close to the avalanche ionization in the cold gas. But namely reaction (5) is a source of background electrons at the stage when the electron temperature is close to room temperature.

In [5] it was shown using numerical analysis of experiments that there could be an effective process $O_{3} + M \rightarrow e + \text{Products}$, (12)

which was not accounted for in [9]. The rate constant of this process in the range 50-150 Td (13.5-40.5 kV/cm) ranges $(2.2 - 6.5) \times 10^{-14}$ cm$^{3}$/s [5] and it improved an agreement between the theory and the experiment [5]. Estimates made on the basis of [9] show that the rate constant of (12) is smaller than $10^{-15}$ cm$^{3}$/s below $E/N=50$ Td and we do not consider it there. In Fig.1 we present results of charged particles balance calculations at $E/N=50$ Td.

Consider a role of the process (5) at the background and pre-threshold stages. First consider a simplified balance of charged particles at low external electric fields, when a background ionization of molecules occurs. For this, we write the balance equations for electrons, positively and negatively charged ions in the processes (1)-(2), (4)-(5), (10)-(11):

$$\frac{dN_{e}}{dt} = Q - v_{e} \cdot N_{e} + k_{det} \cdot N_{O_{2}} \cdot N_{e} - \alpha_{ei} \cdot N_{e} \cdot N_{O_{2}}$$, (13)

$$\frac{dN_{o_{2}}}{dt} = v_{o_{2}} \cdot N_{o_{2}} - \alpha_{ii} \cdot N_{o_{2}} \cdot N_{o_{2}} - k_{det} \cdot N_{o_{2}} \cdot N_{o_{2}}$$, (14)

$$\frac{dN_{M_{2}^{+}}}{dt} = Q - \alpha_{ei} \cdot N_{e} \cdot N_{M_{2}^{+}} - \alpha_{ii} \cdot N_{o_{2}} \cdot N_{M_{2}^{+}}$$, (15)

here $v_{w} = k_{w} \cdot N_{o_{2}}$ is a frequency of the process (4), $\alpha_{ei}, \alpha_{ii}$ - coefficients of electron-ion and ion-ion recombination (11)-(12), at that $\alpha_{ii}/\alpha_{ei} > 1$ [7], $k_{det}$ - rate constant of the process (5), $N_{o_{2}}$ is the concentration oxygen molecules, $N_{o_{2}}$ is the concentration of $O_{2}^{-}$ ions, and $N_{M_{2}^{+}}$ - is the concentration of ions $M_{2}^{+}$ (at initial stage we consider that a concentration of positive
molecular ions is close to those of the positive molecular ions of oxygen \( N_{M^2 O^+} \approx N_{O_2^+} \). Usually at atmospheric pressure at low ion concentration \( \nu_i \gg \alpha_i \cdot N_{O_2^+} \). For a system of equations (13)-(15) is valid [1] a relation

\[ Q = \alpha_i \cdot N_{O_2^+} \cdot N_{M^2 O^+}, \]

in stationary background conditions or accounting the plasma quasi-neutrality \( N_{O_2^+} \approx N_{O_2^+} \) one has

\[ N_{O_2^+} = \sqrt{Q / \alpha_i}. \]  

(16)

At atmospheric pressure \( Q = 4 \text{ cm}^3 \cdot \text{s}^{-1} \) [1,7], and \( \alpha_i \approx 2 \cdot 10^{-6}, \text{cm}^3/\text{s} \) [6,7], the concentration of ions is about experimentally observed \( N_{O_2^+} \approx 1.4 \cdot 10^5, \text{cm}^3 \).

Electron concentration in this case is defined by the equation

\[ N_e = (Q + k_{det} \cdot N_{O_2^+} \cdot N_{O_2}) / \nu_i, \]  

(17)

For example in the reference [9] at low electric field in semi-empirical calculation was obtained a value \( k_{det} \approx 3.7 \cdot 10^{-19} \text{ cm}^3/\text{s} \), and in the work [11] in modeling by Monte-Carlo of attachment of electrons to oxygen molecules was shown that at the same conditions this value is \( k_{det} \approx 10^{-15} \text{ cm}^3/\text{c} \). Using (17), the rate constant from [9] \( k_{det} \approx 10^{-30} \text{ cm}^6/\text{c} \) [10] one has \( N_e \approx 1.0 \cdot 10^4 \text{ cm}^3 \) and from [11] \( N_e \approx 0.2 \text{ cm}^3 \). So the data from [11] demonstrate better conditions for the background ionization.

Let us consider the simplified balance of electrons at near threshold electric fields, when the ionization frequency (2) by electrons in external electric field \( \nu_i \) is close to the frequency of dissociative attachment \( \nu_a \approx \nu_i \), and atomic negative ions are not yet generated then

\[ \frac{dN_e}{dt} = Q - \nu_i \cdot N_e + k_{det} \cdot N_{O_2^+} \cdot N, \]

and the electron concentration in near threshold conditions is

\[ N_e = \frac{Q + k_{det} \cdot N_{O_2^+} \cdot N_{O_2} - (Q - \nu_i \cdot N_{e0} + k_{det} \cdot N_{O_2^+} \cdot N_{O_2}) \exp(-\nu_i t)}{\nu_i}, \]

at small time, \( \nu_i t \ll 1 \), it transforms to

\[ N_e = N_{e0} + k_{det} \cdot N_{O_2^+} \cdot N_{O_2} \cdot t = N_{e0} + g t. \]

Let us estimate a value of \( g \) which shows a velocity of electron concentration rise at the threshold. The corresponding \( E/N \) threshold value was estimated in [1,5] as \( E/N \approx 110 \text{ Td} \) (the computed breakdown value [1,5]). Inserting \( k_{det} = 3 \cdot 10^{-12} \text{ cm}^3/\text{s} \) [11] at this value one has \( g = 2.5 \cdot 10^{10} \text{ cm}^3/\text{s} \) what is much greater than the background ionization (1). We see that the process (5) plays essential role in near threshold field since it facilitates the start of the ionization.

5. Conclusions

We have conducted a quantitative analysis of ionization phenomena at low and subthreshold electric fields in air at atmospheric pressure. The detailed analysis revealed the necessary features of the complex processes leading to the breakdown phenomena in air. The important
source of background electrons is a reaction of \( \text{O}_2 + \text{M} \rightarrow \text{e} + \text{O}_2 + \text{M} \) which rate constant, is large enough to explain the initial prebreakdown stage in different discharges. At the near-threshold electric field all the considered processes of detachment play an important role. At higher fields, a main role is played by processes of ionization of molecules and dissociative attachment of electrons to oxygen molecules. At accounting for the processes (12) at long time can be realized a sharp rise of plasma concentration and development of thermal instability. Avalanche ionization in discharges near aircrafts [4] most likely takes place in the cathode region of the device at electric field higher than indicated in this work. Air discharge at \( E/N = 40 \text{Td} \) theoretically proposed in [3] using a simple plasma model does not occur.

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