MECHANISM OF THE BARRIER DISCHARGE AND IT'S CHEMICAL ACTIVITY IN AIR

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1. Introduction

It should be recognized that even nowadays, after more than a hundred years of the research of ozone generation process in the barrier discharge (BD, sometimes also referred to as dielectric-barrier discharge or silent discharge), despite of a great number of scientific publications put forth mostly in the last few decades, our knowledge of the subject appears to be insufficient to provide an adequate quantitative theoretical description for the system under consideration [1-3]. It means that for example, to solve a problem of optimization of the operating conditions of an ozonizer, or to develop a new more efficient type of ozone generator, we are not able to use a computer simulation technique instead of the hard way of empirical search.

The reason for such a state of affairs seems to be not a technical one (e.g. a necessity to use 3-dimensional computer models instead of 2-dimensional ones, or an inevitable need to include several hundreds of elementary reactions into the kinetic scheme). Actually, this reason is our poor understanding of the physics of electrical breakdown, initial and determining stage of the consequent plasma-chemical processes.

A BD in oxygen, air, or mixtures O_2/N_2 consists of a number of microdischarges (MDs, sometimes also referred to as partial discharges [4] or discharge filaments [1]) of nanosecond duration, randomly but uniformly distributed over the dielectric surface. Under the typical conditions of the BD operation (discharge gap width of 1-2mm, dielectric: glass of 1-2 mm thickness and dielectric constant ε = 5-7, gas pressure: 1-3 bar), these MDs can be treated as tiny plasma-chemical reactors that act independent from each other [1,2,5,6]. That is why the study of the dynamics of a single MD is one of the most important research topics in the field of the BD physics and chemistry. It is hard to carry out any experiment with a single MD, since high temporal resolution (in a sub-nanosecond range) and spatial resolution (down to 10^{-1}-10^{-2} mm) is required. Moreover, in the case of a commonly used parallel-plane electrode arrangement, it is usually impossible to predict the location of a MD emergence.

Thus, it is no wonder that a great deal of effort has been devoted to computer simulation of the MD development [7-13]. As regards experimental findings, the following important milestones should be mentioned: 1972 – identification of the separate MDs [4]; 1980 - streak-photography of the single MD [14,15]; 1983 – accurate measurement of the MD current pulses [16]; 1995 – determination of the spectrally resolved spatio-temporal distributions of the MD luminosity by means of the cross-correlation spectroscopy [17,18]. It should be mentioned that the authors [17] also used their experimental data for a qualitative characterization of the spatio-temporal structure of electric field within a MD channel.

A remarkable progress in experimental investigation of the MD evolution has been achieved recently. The authors [19] reported their results of an accomplished procedure of a BD plasma diagnostics by means of the spatially resolved CCS, including the quantitative estimation of the electric field, relative electron density and ozone yield within a MD channel. All the measurements and calculations have been performed for a BD with the symmetrical electrode arrangement, discharge gap width of 1.2 mm, in air at atmospheric pressure, i.e. under the typical conditions of ozone generation technologies. These data have been demonstrated to provide essentially deeper understanding of the MD mechanism as well as a detailed quantitative description of the chemical activity of plasma within the MD channel.

2. Chemical activity of plasma within the MD channel

In order to understand, in what way does the physics of electrical breakdown determine chemical activity of a BD-plasma, it seems reasonable to begin with the analysis of the chemical mechanism of the formation of ozone, usually the dominant product of plasma synthesis. This mechanism was established relatively long ago, and at present the kinetic schemes for ozone generation in oxygen and air may be regarded as sufficiently reliable ones [1,2].

According to the results of the kinetic analysis, under the typical for an ozonizer conditions, there are only two dominant reaction channels as follows.

Ozone formation: $O + O_2 + M \xrightarrow{k_1} O_3 + M \qquad (M = O_2, N_2)$ (1)

Ozone decomposition: $O + O_3 \xrightarrow{k_2(T)} O_2 + O_2$ (2)

This leads to the conclusion that atomic oxygen can be treated as a sole precursor of ozone, and the conversion degree for the gross reaction $O + O_2 \rightarrow O_3$ is determined by the ratio of the rate constants k_1/k_2 as well as by the background (initial) concentration of O_3. Due to comparatively strong temperature dependence of the rate constant k_2, this conversion degree may be considerably decreased by a local temporary gas heating within the MD channel (i.e. it depends upon the power density profile). Obviously, a spatial distribution of the power density is determined by the spatio-temporal structure of a MD, consequently, by it's mechanism. This can be the first possible way to affect chemical yield of ozone by means of influencing the characteristics of electrical breakdown in an ozonizer.

The second way is related to the reactions leading to the formation of atomic oxygen.

$$e + O_2 \xrightarrow{k_3(E/N)} O + O + e \qquad (3),$$

$$e + N_2 \xrightarrow{k_4(E/N)} N_2^* + e; \qquad N_2^* + O_2 \rightarrow N_2 + O + O \qquad (4).$$

Here the asterisk denotes the triplet excited states of molecular nitrogen (A, B, and C, [20]). Within the frame of the concept of local equilibrium (i.e. an equilibrium between electric field and electron energy distribution function), for a given composition of a mixture ($N_2 + O_2$), the rate constants k_3 and k_4 may be treated as the sole functions of the reduced field strength (E/N). It should be noted that in air, the channel (4) seems to provide up to 50-70% of the total yield of atomic oxygen, the second elementary reaction shown in this scheme being a dominant process among the different pathways of N_2^* relaxation [6,11].

In accordance with the simplified scheme (3,4), the maximal possible energetic yield of atomic oxygen can be calculated as a ratio of O-atoms production rate to electric power released by drifting electrons, as follows

$$Y_{O,max}(E/N) = \frac{k_3(E/N)\,[O_2] + k_4(E/N)\,[N_2]}{e\,E\,w_e(E/N)} \qquad (5),$$

where e is the elementary charge, and $w_e(E/N)$ is the drift velocity of electrons. Square parentheses are used to denote the concentrations of the corresponding species.

Actually, equation (5) takes into account the branching of electron energy losses. The explicit dependence of $Y_{O,max}$ upon the parameter E/N reveals the dependence of the energetic yield of ozone upon the spatio-temporal structure of a single MD, the latter being defined as the spatio-temporal distributions of electric field $E(\mathbf{r},t)$ and electron density $n_e(\mathbf{r},t)$.

In order to complete the consideration of energy losses within the channel of a separate MD in an ozonizer, ion drift should be taken into account as well. Obviously, the value of ion losses also depend on the mechanism of electrical breakdown, and it has to be included into the general formula for energetic yield of ozone.

$$Y_{ozone}(E/N) = C\,\frac{\{P_e(\mathbf{r},t)\}}{\{P_e(\mathbf{r},t)+P_i(\mathbf{r},t)\}}\;\;\frac{\{Y_{O,max}(\mathbf{r},t)\,P_e(\mathbf{r},t)\}}{\{P_e(\mathbf{r},t)\}} = C\,\frac{\{Y_{O,max}(\mathbf{r},t)\,P_e(\mathbf{r},t)\}}{\{P_e(\mathbf{r},t)+P_i(\mathbf{r},t)\}} \qquad (6),$$

where C is the conversion degree for the gross reaction $O + O_2 \rightarrow O_3$ ($0<C<1$); the local power densities for electrons and ions are defined as $P_e(\mathbf{r},t) = e\,n_e(\mathbf{r},t)\,E(\mathbf{r},t)\,w_e(\mathbf{r},t)$, and $P_i(\mathbf{r},t) = e\,n_i(\mathbf{r},t)\,E(\mathbf{r},t)\,w_i(\mathbf{r},t)$, respectively; the parentheses {} denote integration over the whole MD volume and over the time of its existence (to be more precise, from the moment of an appearance of the first electrons, and until the vanishing point for positive and negative ions within the MD volume). The central part of the expression (6) consists of three terms, corresponding to the described above three different ways of DBD physics influence on the chemical efficiency of an ozonizer.

3. Review of the MD models

Generally, a complete model of the MD in an ozonizer includes the descriptions for electrical breakdown (time scale: 10^{-8}-10^{-7} s), chemical kinetics (10^{-6}-10^{-4}s), and the consequent diffusion and heat transfer, occurring in a millisecond scale [1,2]. Below, the attention is focused only on the first phase of the MD development, and the term „model“ is related to the process of electrical breakdown of the discharge gap of an ozonizer.

All the proposed physical models of MD mechanism appeared either as a result of interpreting experimental observations and measurements, or by means of the powerful technique of computer simulation. It should be noted, however, that in the latter case a model is implicitly defined by a choice of initial and boundary conditions for the coupled Poisson and continuity equations (i.e. in fact, before the simulation procedure itself).

3.1 Electrical breakdown via avalanche-to streamer transition

The first attempt to provide a full theoretical description for a single MD in an ozonizer by means of 2-dimensional numerical modeling was made by the authors [7]. It is interesting to mention that at the time when this modeling was being carried out, there were no reliable experimental results concerning microscopic structure of the MD. So, it was some kind of an *„ab initio“* computation, and only a few years later it has become clear that its results essentially disagree with experimental data. Initial and boundary conditions used in the model under consideration (initial electric field somewhat higher than the corresponding Paschen value, initial avalanche starts from about 10^6 electrons located near the cathode) account for the mechanism of „avalanche-to-streamer transition“ (fig.1). The authors [8] later assumed this mechanism to control the efficiency of the ozonizer with a 5 mm discharge gap, in order to interpret experimentally obtained dependence of the ozone yield on the working pressure of oxygen.

The origin of this model belongs to the field of the physics of electrical breakdown in the long gaps (characteristic size in the 10^1-10^2 cm range). Under such conditions, any starting from the cathode avalanche may be expected to reach a critical number of electrons in it necessary to cause a transition to the streamer. For the ozonizers (gap width of a few millimeters), this mechanism has been never observed experimentally and it seems to be hardly possible, excepting probably only the case of the devices with pulse feeding voltage (rise time of about 1kV/ns [9]).

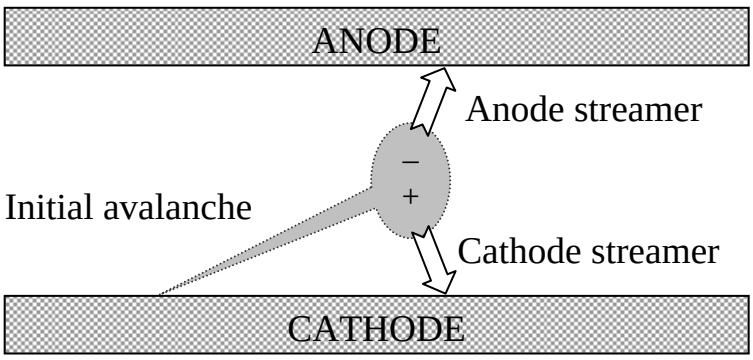
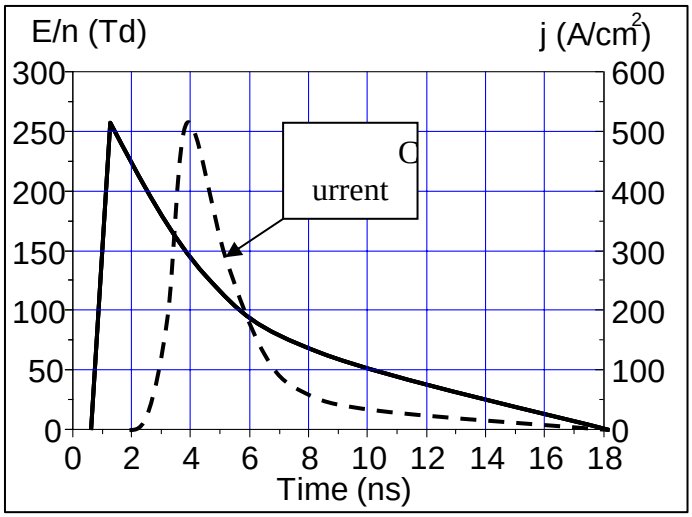


Figure 1. *Schematic illustration for the breakdown mechanism within the frame of the model of “avalanche-to-streamer transition”. Time axis is directed from the left to the right, and for the discharge gap width of 1 mm it has a scale range of a few nanoseconds.*

3.2 The model with a pulsed electric field

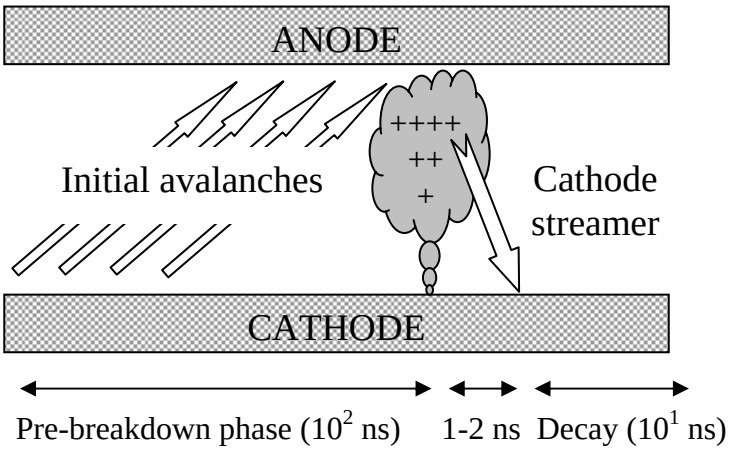


This model may be considered as a semi-empirical one, based on the results of the first measurements of the microdischarge current pulse [16]. In order to simulate the experimentally observed current pulse within the frame of a simplified 0-dimensional (homogeneous) kinetics, the authors [5,16] used a corresponding „pulse“ variation of the reduced field (fig.2). Despite of complying with the current measurements and using of extremely detailed kinetic scheme, the model failed to provide a reasonable estimate for the ozone yield [2].

Figure 2. *Model of the “pulsed electric field” used in the computer simulation of the MD in oxygen [5,16]. Assumed variation of the reduced field (solid line), and calculated current density (dashed line, right Y-axis), fitted to comply with the results of experimental measurements [16].*

3.3 Accumulation of positive space charge followed by the cathode-directed streamer

This model has been widely used in a number of computer simulations of the MD development since 1986 [9]. The first experimental evidence for the existence of a cathode-directed streamer in a BD was obtained by means of the technique of streak-photography. To interpret their results, the authors [15,16] formulated the basic ideas of the breakdown mechanism, schematically presented below in fig.3. All the later investigations of the model under consideration have been carried out by means of computer modeling. The authors [9] demonstrated that if the development of the breakdown begins with a single electron emitted from the cathode, than for a sinusoidal feeding voltage, the development of the MD proceeds according to the presented in fig.3 model, but for the impulse voltage, the mechanism of the „avalanche-to-streamer transition“ can be realized. Such a transformation of the MD mechanism caused by an increase of the voltage pulse steepness has been found to result in considerable growth of the energetic yield of ozone due to the decrease of ion losses. However, the latter conclusion disagrees with the modeling results [6,10-12], according to which the fraction of ion losses appears to be very low even in the case of a sinusoidal feeding voltage.



According to the described model, the development of the cathode-directed streamer is caused by the distortion of electric field due to a positive space charge within the MD channel (fig.3). Accumulation of this charge occurs during the pre-breakdown phase of a MD development, which can take up to 10^{-7} s [9,11]. The final phase of decay is characterized by the deposition of the charge carriers (electrons and ions) onto a dielectric surface resulting in a monotonous decrease of electric field.

Figure 3. *Schematic illustration of the breakdown mechanism for the model of “cathode-directed streamer, caused by a positive space charge”. Time axis is directed from the left to the right. “Initial avalanches” denote here a continuos process including the electron drift, ionization, and the secondary emission from the cathode.*

3.4 Accumulation of negative space charge followed by the cathode-directed streamer

This model appeared as a result of the attempts to give a reasonable interpretation to certain experimental findings of the authors [17,18], in particular, to the existence of a weak but profound pre-breakdown anode glow of a microsecond duration. Some ideas of the MD mechanism including an accumulation of the negative space charge during the pre-breakdown phase have been stated in [17], and more detailed description of the corresponding physical model (fig.4) is presented in [19]. However, this model has not been used in computer simulations as yet.

Contrary to all the described above MD mechanisms, the scheme in fig.4 takes into account surface charge left on the dielectric electrodes after a previous MD. Initial electric field is therefore assumed to be non-homogeneous, the mean value of the field strength being considerably lower than that one corresponding to Paschen law (probably, proportional to the ratio of the burning and ignition voltages of the BD). Under such conditions, ionization may be expected to occur mostly near the charged dielectric surface, and attachment in the center of a gap [3]. An appearance of the negative space charge causes certain rearrangement of initial electric field, the maximum of the field strength being located exactly on the anode surface. Duration of this „pre-breakdown" phase of the MD development is at least a few μs. Cathode-directed streamer starts from the anode surface and propagates through the medium enriched with negative ions, and its velocity depends on electro-negativity of the feeding gas.

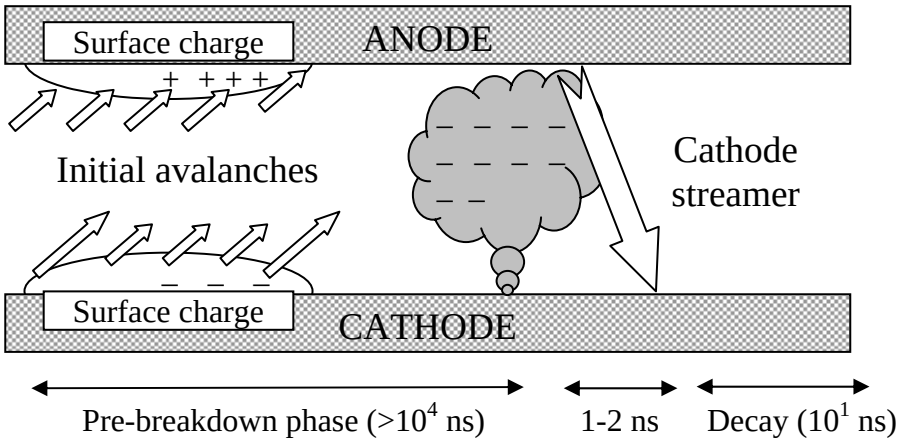


Figure 4*. A scheme for the microdischarge mechanism, based on the assumption of a pre-breakdown accumulation of the negative space charge within the microdischarge channel. Initial avalanches are caused by a local field enhancement due to the surface charges on the dielectric electrodes. It is also assumed to be a continuous process including electron drift, ionization, attachment and secondary emission from the cathode (see text for the details).*

4. Recent advances

As already mentioned, an essential progress in experimental investigation of the MD in an ozonizer in air at atmospheric pressure has been achieved recently by means of the spatially resolved CCS-technique [19]. Quantitative estimates for electric field strength E(x,t) and for relative electron density $n_e(x,t)/n_e^{max}$ were derived from the experimentally determined spatio-temporal distributions of the luminosity for the spectral bands of the 0-0 transitions of the 2^{nd} positive system of N_2 (λ = 337.1 nm) and the 1^{st} negative system of N_2^+ (λ = 391.5 nm). Some of these results are presented in figure 5. A cathode-directed wave of electric field is clearly seen in this figure. High electric field strength is observed mostly near the cathode, and a high electron density, on the contrary, near the anode. The streamer starts directly from the surface of the anode and crosses the gap with an increasing velocity that reach 10^6 m/s. Electric field strength of the streamer grows respectively from 120 Td at the anode to 240 Td at the cathode.

The authors [19] confirmed also that there are three distinct phases of the MD development. The pre-breakdown phase lasts for a period of more than 0.5 μs. It is characterized by a continuous glow on the glass surfaces of both electrodes. During the last 100 ns of the pre-breakdown phase, the maximal light intensity is observed on the anode. The third phase of the MD is a phase of decay of the light and current pulses.

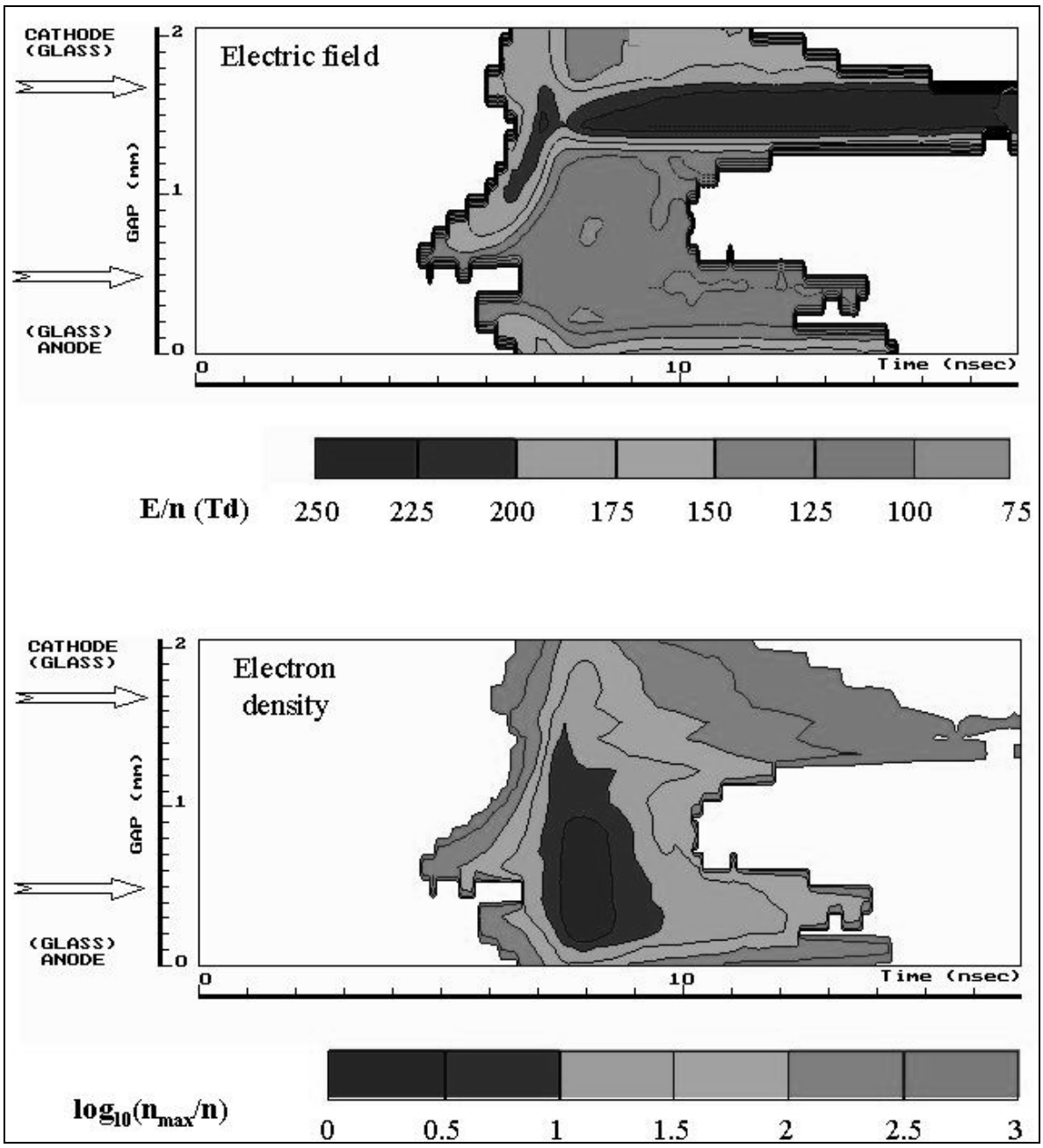


Figure 5. *Results of the authors [19]: calculated distributions of electric field and electron density. Positions of the electrode tips (semi-spherical glass electrodes of the radius of curvature 7.5 mm were used, see [19] for more details) are pointed at the left by the arrows.*

The authors [19] used their experimental data and the results of their processing to test the validity of the considered above physical models of electrical breakdown in a BD, in particular the model of accumulation of positive space charge followed by the cathode-directed streamer (**3.3**), and the model of accumulation of negative space charge **(3.4**). They came to the conclusion that their results provide an unambiguous experimental evidence in favor of the model **3.4**. Taking into account the initial conditions, assumed for the model **3.3**, we may expect this model to describe some special cases of a BD operation. For example, it can account for the first electrical breakdown event in an ozonizer (i.e. at the moment when an ozonizer is just switched on), since only at this moment there are no surface charges on the dielectrics. Also, in some laboratory experiments, the BD was operated in a special single-pulse mode, when the periodical slow voltage pulses were applied to the discharge cell. In order to get rid of a surface charge, a rest time interval of about 30 minutes between the successive single pulses was

provided [15]. Obviously, for an ordinary (continuous) operation mode of a BD, the model **3.4** should be used.

Therefore, it is very important to distinguish between two different modes of a BD operation: single pulse and continuous. To provide a correct theoretical description of the MDs for an ordinary continuous mode, a model should be used, that takes into account an existence of initially non-uniformly charged dielectric surfaces.

In order to propose a qualitative description of the influence of the MD spatio-temporal structure on the kinetics of ozone synthesis, the authors [19] used the following semi-empirical method. From the arrays of electric field strength $E(x,t)$ and relative electron density $n_e(x,t)/n_e^{max}$ the spatially resolved kinetics of the formation of atomic oxygen and triplet nitrogen N_2^* by the reactions (3,4) in a nanosecond time scale was calculated. The rate constants $k_3(E/n)$ and $k_4(E/n)$ were taken from [11]. Since the relative values of electron density were used, the results of these kinetic calculations also contain an unknown constant. However, this constant does not depend on the space-time coordinates. Therefore, thus calculated spatio-temporal distributions of the relative concentrations of considered species may be expected to represent the real kinetics within the MD channel. The latter results lead to the following important conclusions concerning chemical activity of plasma within the MD channel.

There are two distinct regions with essentially different plasma properties of plasma within the MD channel. Electric field near the cathode is higher than near the anode, and electron density, on the contrary, is considerably lower. Furthermore, different physical properties of these regions result in a noticeable difference in chemical kinetics. For example, as it was demonstrated in [19], the properties of the plasma in the region near the anode favor dissociation of molecular oxygen by direct electron impact. In the case of the excitation of triplet nitrogen states, the contributions of both regions to this process appear to be comparable.

5. Concluding remarks

Various physical models, explicitly or implicitly used in a number of computer simulations of coming into being, development, and decay of a separate MD, are distinguished, actually, by the choice of initial and boundary conditions for the coupled Poisson and continuity equations. Assuming essentially different mechanisms of electrical breakdown, they determine different contributions of the terms in eq.(6), corresponding to the conversion degree for ozone formation, fraction of electron losses, and maximal yield of atomic oxygen, respectively. All these models fail to provide a reasonable interpretation for the detailed spatio-temporal structure of a real MD in air [3].

Using of the briefly described above improved physical model of the MD development under the conditions of initially charged dielectric surface [19] in a computer simulation may be expected to avoid the discrepancies between theoretical results and experimental data. It should be noted, however, that this model needs a detailed information concerning the distribution of a surface charge over the dielectric electrode, as well as the values of the secondary emission coefficient (for electrons and ions) for a charged dielectric surface, which have been never measured.

There are also two essential gaps in the understanding of the MD behavior near the cathode surface which should be filled, in order to develop an adequate numerical model for it. In the case of a dielectric cathode, it is a need to simulate a 3-dimensional surface discharge (Lichtenberg figures) which has been proved to occur simultaneously with a volume breakdown within the MD channel. In the case of a metallic cathode, it is an evolution of the cathode sheath. Formation of the normal cathode sheath under atmospheric pressure with the reduced field strength of some thousands Td [12] seems to hardly possible, and the mechanisms leading to a complete or partial destruction of this sheath are not quite clear.

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