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"Relaxing Phenomena" in Negative Corona Discharge in Air: New Aspects.

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Introduction

There are two, besides the others, conspicuous differences between the positive and the negative discharges in air observed in small discharge gaps:
1. The mean discharge current I of the negative corona discharge (NCD) is substantially higher than the positive one at the same voltage and air parameters. Therefore from the current voltage characteristics calculated mean mobility of charged particles drifting through the drift region of NCD is evidently higher (2-10 times) as these, corresponding to the mobility of ions which were detected in drift region of NCD by masspectrometric measurements. On the contrary to this, the accordance between calculated mobilities and known mobilities of positive ions can be concluded.
2. The mean current I is strongly influenced by the addition of gaseous electronegative impurities in air. An addition of some halogencarbons or other gases can cause a remarkable decrease current even if concentration of the impurity is very low (10 ppm) [1].

The third, but only rarely discussed phenomena, is the time dependence of current I, called by Gagarin like "relaxing of CV-characteristics" [2]. At the same conditions the mean current I is stable. This phenomena can be easily observed only if NCD is initiated between electrodes situated in closed discharge reactor (no-flowing regime). When the suitable step-like voltage is applied on electrodes, the main current I continuously decreases from initial value I_0, to the saturated value I_s, which is 30 - 50 % below the initial value. The saturated value and the rate of decay depends on the volume of the discharge reactor as it was conclude by Schwab and Zentner, who first described such phenomena [3].

The observed phenomena was explained by two theoretical models [4], [5] considering the ion-molecule and chemical reactions in the NCD in air., especially the ozone production. The aim of presented paper is to discuss the discrepancies of above mentioned models, to re-examine the earlier experimental data and presumptions used in models in a light of the latest experimentally confirmed facts

Experimental Apparatus

The experiments have been carried out in ambient air at pressures 40 - 80 kPa and at temperature 20 ^{0} C. All details concerning to apparatus are described in our earlier paper [4].

Experimental results and discussion

One set of selected time dependencies of mean current I and ozone concentration measured by absorption of UV light in discharge reactor C are shown in Fig. 1a and 1b.

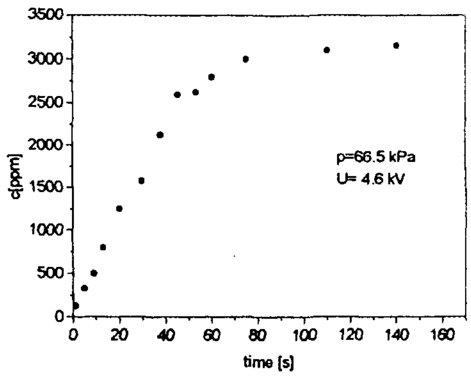

Fig 1a

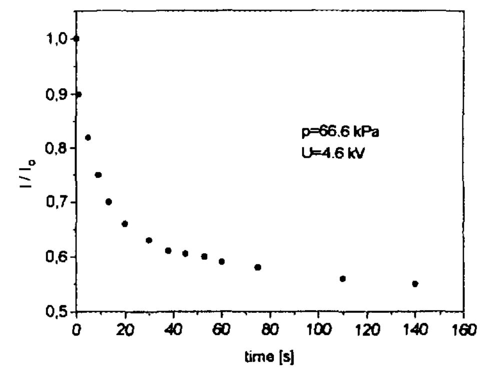

Fig 1b

The similarity of both curves as well as the time T_S needed for saturation of I and C suggests, that the decay of mean current is caused by the increase of the ozone concentration in the discharge gap. This is a basic presumption of both models, confirmed later by measurements in flowing air mixtures with ozone [6]. The principal difference between above mentioned models is the mechanism of ozone effect. Gagarin [4] presumed only the charge transfer ion-molecule reactions in which the primary negative ion O^-, created via dissociative attachment

$$e + O_2 \rightarrow O^- + O \qquad (1)$$

are changed to ions having smaller mobility like previous ion

$$O^- + O_2 \rightarrow e + O_3 \qquad (2)$$
$$O^- + O_3 \rightarrow O_3^- + O \qquad (3)$$
$$O_3^- + NO \rightarrow NO_3^- + O. \qquad (4)$$

He did not take into account the most important reaction

$$O^- + CO_2 + M \rightarrow CO_3^- \qquad (5)$$

in which the important ion CO_3^- is created. These ions or their hydrated forms was experimentally confirmed to be the dominant ions in NCD in air [7], [8], [9].
The first weakness of discussed model is the reaction (2) producing free electrons. These should cause the increase of the mean mobility of charged particles and thus the increase of mean current. The second disagreement with experimental facts is contained in the presumption used for calculation of time for saturation of current T_S. He presupposed that the equilibrium of process influencing the current decay is reached if the concentration of ozone in discharge gap C is of range 10^{19} cm^{-3}, i.e. comparable with the concentration of oxygen in air. As it follows from theoretical

calculations [10] and experimental measurements [11], the saturated concentration of ozone produced by NCD in air can not be higher like $10^{16} cm^{-3}$. Thus the calculated values of T_S should be 10^3 times shorter as measured data. It must be noted that Gagarin did not take into account the volume of the discharge reactor. The role of this was confirmed experimentally earlier [3].

On the contrary to the model [4], in our calculations the free electrons are taken into account. We presumed that a part of nonattached electrons via reaction (1), very effective only near a high stressed electrode, is attached by three-body process

$$e + O_2 + M \rightarrow O_2^- + M \quad (6)$$

or by ozone molecules

$$e + O_3 + O_2 \rightarrow O_3^- + O_2 \quad (7)$$

Ozone is generated in separated kinetic structure, the base of which are two processes

$$e + O_2 \rightarrow O + O + e \quad (8)$$
$$O + O_2 + M \rightarrow O_3 + M \quad (9)$$

Similarly, like in Gagarin`s model, the reaction (5) was not considered. Later performed experiments shown that the increase of ozone density in discharge gap causes the apparent increase abundance of CO_3^- and $CO_3^-.(H_2O)_n$ ions in the spectrum of ions extracted from the drift region of NCD, whereas only a small increase of ozone negative ions or theirs hydrated forms was observed. The retarding potential method, used in experiments also shown the decrease of free electrons component, especially these having low energies (estimated 2 eV). On a base of these new experimental facts the doubtful process (7) was replaced by dissociative attachment [6]

$$e + O_3 \rightarrow O^- + O_2 \quad (10)$$

Taking into account processes (1) and (10) the ratio of the rate attachment coefficients of mentioned two reactions was calculated. The calculated values k_{10}/k_1 were of the range (180 - 270). Our last cross beam experiments confirmed that reaction (10) has its maximum of attachment cross section at energy of electrons 1.5 eV [13].

The revised model was used for calculation of attachment coefficient k_{10} by simple formula presented earlier [6] from the old experimental data [5]. The mean value $k_{10}=2.5 \times 10^{-9} cm^3.s^{-1}$ is very close to the values calculated from attachment cross section [13] and practically in agreement with data Gibalov et.all [14]. Due to the fact that in model the influence of space charge distribution on electric field distribution was not considered and the mean values of electron velocity in the drift region of NCD as well as the mean value of k_1 were used, we can not make no claim for the great accuracy of the calculated values k_{10}. Despite of it a rather good agreement of calculated data with known is surprising.

Conclusions

1. The current of free electrons trough drift region of NCD in air free of electronegative impurities is an important part of the total current if the discharge gap is small.
2. The decay in time of the discharge current of NCD in air is caused by dissociative attachment of free electrons by ozone molecules, generated in the discharge.
3. In all NCD experiments performed in non-flowing or very slowly flowing air, the existence of ozone impurity must by taken into account[15].

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