Effect of electronegative additives on physical properties and chemical activity of gas discharge plasma

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Abstract. Effect of electronegative additives (oxygen O$_2$, sulfur dioxide SO$_2$, carbon disulfide CS$_2$, and carbon tetrachloride CCl$_4$) on physical properties and chemical activity of plasma formed by pulsed corona discharge and by non-self-sustained discharge supported by pulsed electron beam in atmospheric pressure gas mixtures was investigated. It is shown that a decrease in discharge current depends on a sort of the additive and on its concentration. The reason is the difference in rate constants of electron attachment processes for the above molecules. In experiments on volatile organic compounds (VOCs) conversion in air by streamer corona it is obtained that an addition of CCl$_4$ both decreases the discharge current amplitude and increases the VOCs conversion degree. An installation for investigation of electron attachment processes and for study of toxic impurities conversion in plasma formed by non-self-sustained discharge initiated by pulsed nanosecond electron beam is created.

1. Introduction
Electronegative additives have a significant impact on processes in plasma formed by electron beams and discharges in gas mixtures. As a result physical properties and chemical activity of the plasma may change. The reason is that electron attachment processes to electronegative molecules decrease a concentration of plasma electrons and increase a concentration of negative ions. Such processes play an important role in oxygen discharge plasma [1] and in argon-oxygen rf gas-discharge dusty plasma [2].

It was shown that processes involving negative ions allow to increase the efficiency of sulfur dioxide conversion significantly during pulsed electron beam and non-self-sustained discharge processing of flue gases [3]. Effect of electron attachment processes in air and oxygen on energy inputs into the gas in various types of discharges, including pulsed corona discharge, is presented in [4].

It is known that dissociative attachment processes may lead to the formation of negative ions of various types from an electronegative molecule of one type. For example, the formation of various negative ions in dissociative attachment reactions to carbon disulfide under the action of pulsed electron beam was investigated in [5].

Since chlorine- and fluorine-containing molecules have maximum values of electron affinity, an addition of such molecules to gas mixtures leads to a most significant changes in the discharge and plasma properties. For this reason low energy electron attachment processes to CCl$_4$ and
Figure 1. Calculated temporal dependencies of ion concentrations in atmospheric pressure mixture of nitrogen (90%) and oxygen (10%) irradiated by pulsed electron beam which starts at $t = 0$ for electron beam current density $j_{eb} = 4 \times 10^{-3}$ (a) and $1 \times 10^{-3}$ A/cm$^2$ (b): 1—$N_2^+$; 2—$O_2^-$. 

SF$_6$ molecules were investigated [6]. Mass spectra of various negative ions formed under action of electrons 0–12 eV on tetrachloroethylene were obtained [7].

In this paper, we investigate an effect of electronegative additives (oxygen O$_2$, sulfur dioxide SO$_2$, carbon disulfide CS$_2$, and carbon tetrachloride CCl$_4$) on physical properties and chemical activity of plasma formed by pulsed corona discharge and by non-self-sustained discharge supported by pulsed electron beam in atmospheric pressure gas mixtures.

2. Electron attachment processes to O$_2$ and SO$_2$ molecules
During experiments presented in [3] we also studied temporal characteristics of electron attachment processes. It is evident that under atmospheric pressure the major contribution to the formation of negative oxygen ions make three-body attachment processes. Within the framework of a simplified model we calculated temporal dependencies of plasma electron concentration and $N_2^+$ and $O_2^-$ ions concentration under action of electron beam on atmospheric pressure nitrogen-oxygen mixtures. We took into account ionization, electron–ion recombination and ion–ion recombination processes. Results of the calculation are presented in figure 1.

It is seen that the time to establish steady-state concentrations of $N_2^+$ and $O_2^-$ ranges from 4 to 10 $\mu$s, depending on the electron beam current density. Besides, close $N_2^+$ and $O_2^-$ concentration values indicate that the plasma electrons concentration is significantly lower than ions one in mixtures containing no less than 10% of oxygen.

In experiments on sulfur dioxide removal from air in pulsed non-self-sustained discharges we investigated the role of electron attachment processes to O$_2$ and SO$_2$ molecules in atmospheric pressure plasma and their influence on parameters of the discharge [8]. Numerical simulation of concentrations of charged particles was executed, taking into account the processes of gas ionization, recombination of charged particles and attachment of electrons to O$_2$ and SO$_2$ molecules and without taking into account further processes of recharge. The simplified model does not give the possibility to evaluate the process of SO$_2$ conversion quantitatively, but makes it possible to calculate amplitudes and waveforms of current of the non-self-sustained
Figure 2. Experimental waveforms of non-self-sustained discharge current $I_d$, supported by pulsed electron beam, in atmospheric pressure gas mixtures for various oxygen (a) and sulfur dioxide (b) concentrations. Beam current density amplitude $j_{eb}=1\times10^{-3}$ A/cm$^2$. Beam current pulse duration $\tau_{eb}=50\ \mu$s. Average electric field strength in the discharge gap $E=100$ V/cm. Mixtures composition: (a) N$_2$ (main component), H$_2$O (5%), SO$_2$ (0.1%), O$_2$ (1—1%; 2—10%; 3—20%); (b) N$_2$ (main component), H$_2$O (5%), O$_2$ (10%), SO$_2$ (1—0.02%; 2—0.3%; 3—1.6%).

discharge supported by electron beam, and to compare the obtained values with parameters of the discharge measured during the experiments. Experimental waveforms of non-self-sustained discharge current, supported by pulsed electron beam, in atmospheric pressure gas mixtures for various oxygen and sulfur dioxide concentrations are shown in figure 2.

As it seen, an increase in O$_2$ concentration from 1 to 20% reduces the discharge current twice. However, an insignificant increase in SO$_2$ concentration (from 0.02 to 1.6%) leads to a considerable decrease in the discharge current (three times). To explain this result it is necessary to compare electron attachment rate constants to O$_2$ and SO$_2$ molecules. Three-body electron attachment rate constant to O$_2$ $k_{ox}^{3a}=10^{-33}$–$10^{-30}$ cm$^6$/s, depending on sort of the third particle (N$_2$, O$_2$, or H$_2$O) [9]. There are various three-body electron attachment processes to SO$_2$, and no precise data exist about each of which. So, according to [10], a two-body attachment process with a rate constant $k_{2a}^{so}$ $=10^{-11}$ cm$^3$/s is considered as an averaging of various three-body processes. For comparison with the two-body attachment rate constant, the three-body one should be multiplied by a concentration of the third particle. Such a two-body electron attachment suppositive process rate constant to O$_2$ $k_{2a}^{ox}=10^{-14}$–$10^{-12}$ cm$^3$/s, i.e. attachment rate constant to SO$_2$ exceeds corresponding two-body one to O$_2$ by an order of magnitude or more. That is the reason why the discharge current decreases significantly with small additions of SO$_2$. It should be noted that a difference in the parameters of the calculated and measured waveforms does not exceed 15%.

For research of electron attachment processes in a nanosecond range of times a pulsed corona discharge of nanosecond duration was formed in atmospheric pressure gas mixtures. Experimental setup, configuration and parameters of which were similar to [11], was used. Experimental waveforms of an output voltage and pulsed corona discharge current are presented in figure 3.

It is seen that pulsed corona discharge current $I_d$ (curves 3 in figure 3) amplitudes have only little difference in nitrogen and in air, i.e. an addition of 10–20% of O$_2$ to an atmospheric
pressure nitrogen leads to a decrease in pulsed corona discharge current less than 30%. In comparison with figure 2, the oxygen addition has a weaker impact on the discharge parameters in a nanosecond range of times than in a microsecond one. The reason of the difference is as follows. As it was mentioned above, the time to establish steady-state concentrations of \( \text{N}_2^+ \) and \( \text{O}_2^- \) ions ranges from 4 to 10 µs. When the beam current with a pulse duration \( \tau_{\text{eb}} = 50 \) µs is used, a steady-state \( \text{O}_2^- \) concentration is achieved during the beam pulse duration time, and substantial part of plasma electrons attach to \( \text{O}_2 \) molecules with the formation of \( \text{O}_2^- \) ions. A contribution of the electrons to the total discharge current decreases significantly. Despite high ions concentration, the ion current is substantially lower than the electron one because of lower ion mobility. As a result we observe a substantial decrease in discharge current with an addition of oxygen. When corona discharge with a pulse duration \( \tau_d = 20–30 \) ns is used, a steady-state \( \text{O}_2^- \) concentration cannot be achieved during the discharge pulse duration time. Only a small portion of the plasma electrons have time to attach to \( \text{O}_2 \) molecules. A contribution of the electrons to the total discharge current decreases slightly. So only a slight decrease in corona discharge current is observed with an addition of oxygen.

3. Electron attachment processes to \( \text{CS}_2 \) and \( \text{CCl}_4 \) molecules

In experiments on carbon disulfide conversion by pulsed corona discharge [12] we also investigate electron attachment processes to carbon disulfide and carbon tetrachloride. Experimental waveforms of an output voltage and pulsed corona discharge current are presented in figure 4.

Figure 4 shows that an addition of 1% of \( \text{CS}_2 \) leads to a decrease in the corona discharge current amplitude by 3 times. Moreover, an addition of 1% of \( \text{CCl}_4 \) gives a decrease in the discharge current amplitude by about 10 times. For explanation of this result we should compare electron attachment rate constants to \( \text{O}_2 \), \( \text{SO}_2 \), \( \text{CS}_2 \) and \( \text{CCl}_4 \) molecules. A two-body electron attachment suppositive process rate constant to \( \text{CS}_2 \) \( k_{2n}^{\text{CS}_2} = 10^{-10}–10^{-9} \) cm\(^3\)/s, i.e. attachment rate constant to \( \text{CS}_2 \) exceeds corresponding two-body one to \( \text{SO}_2 \) by 1–2 orders
Figure 4. Experimental waveforms of an output voltage $U_{\text{out}}$ (curves 1) and an output current $I_{\text{out}}$ (curves 2) of the SM-4N generator, and calculated waveforms of a pulsed corona discharge current $I_d$ (curves 3) at a pulse repetition rate $F = 10$ Hz. Mixtures composition: atmospheric pressure air with 1% of CS$_2$ (a); atmospheric pressure air with 1% of CCl$_4$ (b). Vertical scale: 75 kV/cell (curves 1); 270 A/cell (curves 2, 3). Horizontal scale: 10 ns/cell.

of magnitude [13]. A two-body electron attachment suppository process rate constant to CCl$_4$ $k_{\text{ctc2}} = 2.4 \times 10^{-7}$ cm$^3$/s, so this rate constant exceeds corresponding two-body one to CS$_2$ by 2–3 orders of magnitude [14]. That is why a small addition of CCl$_4$ leads to attachment of almost all plasma electrons to CCl$_4$ molecules within a few nanoseconds, and corona discharge current is completely determined by the ion current.

4. Influence of electron attachment processes to CCl$_4$ molecules on the VOCs conversion in air by pulsed corona discharge

We are currently conducting research on the development of the method of standard mixtures which should be a criterion of efficiency of air cleaning from VOCs impurities by pulsed discharges. One of the problems of the investigations is an influence of electron attachment processes on the VOCs conversion efficiency. Various mixtures containing nitrogen, air, VOCs and electronegative additives are processed by pulsed corona discharge. Experiments are conducted on an installation similar to [11]. Discharge parameters and VOCs conversion efficiency are controlled in the experiments. Dependencies of relative concentrations of tetrachloroethylene C$_2$Cl$_4$ in gas mixtures processed by pulsed corona discharge on the number of discharge pulses are presented in figure 5.

It is seen that the processes of C$_2$Cl$_4$ conversion are more effective in air than in nitrogen. Besides, an addition of a small amount of CCl$_4$ leads to an increase in tetrachloroethylene conversion efficiency. As it was mentioned above, carbon tetrachloride has a very large value of electron attachment rate constant, and with its addition almost all plasma electrons attach to these molecules. Because tetrachloroethylene molecules are electronegative too, the processes of electron attachment to C$_2$Cl$_4$ take place. In addition, oxygen of the air is electronegative gas too, and processes of electron attachment to O$_2$ take place too. As a result, almost all negative charge of the plasma focused in negative ions. We can assume that plasma-chemical processes leading to C$_2$Cl$_4$ conversion are more effective when various negative ions involved therein, not plasma electrons. Accordingly, the most effective C$_2$Cl$_4$ conversion takes place in
Figure 5. Dependencies of relative concentrations $C/C_0$ of tetrachloroethylene $\text{C}_2\text{Cl}_4$ in gas mixtures processed by pulsed corona discharge on the number of discharge pulses $N$. Initial gas mixture compositions: 1—atmospheric pressure nitrogen with 0.1% of $\text{C}_2\text{Cl}_4$; 2—atmospheric pressure nitrogen with 0.1% of $\text{C}_2\text{Cl}_4$ and 0.1% of carbon tetrachloride $\text{CCl}_4$; 3—atmospheric pressure air with 0.1% of $\text{C}_2\text{Cl}_4$; 4—atmospheric pressure air with 0.1% of $\text{C}_2\text{Cl}_4$ and 0.1% of $\text{CCl}_4$.

the mixture containing all three electronegative components (oxygen, tetrachloroethylene, and carbon tetrachloride). It should be noted that carbon tetrachloride $\text{CCl}_4$ concentration does not change substantially during pulsed corona discharge processing, and this substance acts as a catalyst. We noted above that $\text{CCl}_4$ addition leads to a substantial decrease in discharge current. This fact results in a substantial decrease in energy input into the gas mixture when $\text{CCl}_4$ adds (from 0.27 to 0.19 J/pulse). Thus, simultaneous conversion efficiency increase and energy input decrease leads to a very large increase in energy efficiency of the $\text{C}_2\text{Cl}_4$ conversion in pulsed corona discharge plasma with an addition of $\text{CCl}_4$.

5. Electron attachment processes in $\text{CS}_2$-containing mixtures processed by a non-self-sustained discharge initiated by a nanosecond electron beam

At the time we carry out research on optimization of electrophysical influence on gas mixtures with the aim of conversion of sulfur-containing impurities in electron-beam and electric-discharge plasma. It is evident that electron attachment processes will play an important role in the processes of sulfur-containing impurities conversion. But the results presented above do not allow to make quantitative estimates of electron attachment and other plasma-chemical processes when the plasma is formed by a nanosecond electron beam or by a non-self-sustained discharge initiated by a nanosecond electron beam. Exactly like this electrophysical influence will be used in our research. So the first step in these investigations is study of the role of electron attachment processes. For this purpose a special installation has designed and built. Design of the installation is shown in figure 6.

The installation allows to measure waveforms of an output voltage of the SM-4N generator, electron beam current pulses and non-self-sustained discharge current pulses initiated by electron beam. Measured parameters of the electron beam and of the discharge are: energy of electrons up to 200 keV; adjustable electron beam current amplitude in a vacuum diode 50–100 A; adjustable electron beam current amplitude in the discharge gap 0–50 A; electron beam current
Figure 6. Design of the installation for study of carbon disulfide conversion processes in a non-self-sustained discharge initiated by a nanosecond electron beam: 1—to vacuum pump; 2—support grid; 3—protective net; 4—output foil; 5—high-voltage nanosecond generator SM-4N; 6—measuring connector for the output voltage $U_{out}$; 7—measuring connector for the output current $I_{out}$; 8—gas mixing path; 9—anode of the discharge; 10—reaction chamber; 11—electron beam; 12—explosive emission cathode; 13—vacuum diode; 14—shunt $R_1$; 15—capacitor $C_1$; 16—measuring connector for the electron beam current $I_{eb}$ and the discharge current $I_d$; 17—gas mixture inlet; 18—charging resistor $R_2$; 19—charging voltage $U_0$; 20—fan.

pulse duration 5–10 ns; electron beam cross-section 30 per 5 cm; electron beam current density amplitude in the discharge gap 0–0.3 A/cm²; electron beam current pulse repetition rate up to 100 Hz; voltage at the discharge gap up to 20 kV; non-self-sustained discharge current amplitude up to 1 kA. Thus, the installation will allow to investigate both electron attachment processes and carbon disulfide conversion ones in the future experiments.

6. Conclusions
Effect of electronegative additives on physical properties and chemical activity of plasma formed by pulsed corona discharge and by non-self-sustained discharge supported by pulsed electron beam in atmospheric pressure gas mixtures was investigated. It is shown that addition of 0.02–1.6% of SO₂ to an atmospheric pressure air leads to a substantial decrease in amplitude of non-self-sustained discharge current supported by an electron beam of 50 µs duration because of intense attachment of electrons to sulfur dioxide.

With the use of pulsed corona discharge of 20 ns duration an addition of 10–20% of O₂ to an atmospheric pressure nitrogen did not lead to a significant decrease in discharge current amplitude. However, an addition of 1% of CS₂ led to a decrease in the discharge current amplitude by 3 times. Moreover, an addition of 1% of CCl₄ gave a decrease in the discharge current amplitude by about 10 times. The reason is the difference in rate constants of electron attachment processes for the above molecules.

In experiments on C₂Cl₄ conversion by pulsed corona discharge it is obtained that an addition of CCl₄ both decreases the discharge current amplitude and increases the C₂Cl₄ conversion degree. The result is a significant increase in energy efficiency of C₂Cl₄ removal.
An installation for investigation of electron attachment processes and for study of sulfur-containing impurities conversion in plasma formed by non-self-sustained discharge initiated by pulsed nanosecond electron beam is created.

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