Numerical modeling of the plasma processes taking into account the products of transfer processes from aqueous solution of sodium chloride being used as a cathode

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Abstract. The modeling of the formation processes and further transformations of active particles in atmospheric pressure discharge plasma with a sodium chloride solution used as a cathode is performed. Experimental data on the composition of the gas phase and the physical parameters of plasma were used in the numerical simulation. It is determined that electron collisions with water molecules leads to a change in the form of the electron energy distribution function. As a result, the rates of the processes occurring under the action of the electron impact are altering. In addition, the transfer of water molecules to the gas phase leads to the appearance of new active particles, such as $\text{OH}^·$, $\text{HO}_2^·$, $\text{H}_2\text{O}_2$. It has been established that the products of the transfer of solutes influence on the balance of charged particles thus the electric field strength are reduced. This results in changing of the rate constants of the processes occurring in the plasma.

1. Introduction
Investigation of gas discharge plasma in contact or in liquids is one of the priority areas in plasma physics [1]. Atmospheric pressure discharges with liquid electrolyte electrodes are of interest as sources of active species for a variety of plasma-chemical applications one of which is the purification and disinfection of water and aqueous solutions [2, 3]. Plasma is the source of various active particles; some of them (for example, atoms of O, ozone, OH radicals) are formed in the gas phase followed by penetration into the solution and participation in the destruction of organic and other water pollutants. For estimation of processes mechanism in the liquid phase, it is necessary to know the active species concentrations in a gas phase and their change under alterations of discharge parameters. Such data are very limited with the exception of ozone concentration. Data on the containing of other active particles in the plasma zone of discharges with an electrolyte cathode are practically absent, which is due to the experimental difficulties in measuring the concentrations of active components. The concentration of hydroxyl radicals ($1.3 – 1.8 \times 10^{16} \text{ cm}^{-3}$) by the method of laser-induced fluorescence spectrometry at currents of discharge from 10 to 28 mA was determined in [4]. The concentration of oxygen atoms by the method of two-photon laser-induced fluorescence spectrometry using a nanosecond laser was measured in [5].

The large number of works devoted to plasma chemistry modeling was published in recent years [6–8]. In particular, the modeling of processes in the discharge of atmospheric pressure in air using the distilled water as a cathode was carry out in [6]. The concentrations of a range of active particles were obtained using the experimental values of the electric field strength in the plasma and the gas
temperature. The authors used the value of the mole fraction of water equaled of 0.2%. Taking into account the transfer products in a parametric form, without relying on experimental measurements is a disadvantage of these theoretical calculations.

The aim of the investigation is to determine the composition of the gas phase above the electrolyte surface in discharge - electrolyte cathode system by means of the numerical simulation method using experimental data of physical parameters and transfer processes. The influence of transfer processes on the chemical processes in the plasma and the physical properties of the discharge will be established.

2. Experimental part

The numerical model included 233 reactions which describe the concentrations of the following species: \( \text{O}_2 \), \( \text{O}_3(a^1\Delta_a) \), \( \text{O}_3(b^3\Sigma_g^-) \), \( \text{N}_2 \), \( \text{N}_2(\text{A}^3\Sigma_g^-) \), \( \text{N}_2(\text{A}^3\Pi_g) \), \( \text{N}_2(\text{B}^5\Sigma_g^-) \), \( \text{N}_2(\text{C}^3\Pi_u) \), \( \text{O}(3\Pi) \), \( \text{O}(1D) \), \( \text{O}(1S) \), \( \text{O}_2^+ \), \( \text{O}^- \), \( \text{O}^+ \), \( \text{N}(^4S) \), \( \text{N}(^2P) \), \( \text{N}(^2D) \), \( \text{H}_2\text{O} \), \( \text{H}_2\text{O}(^3\Sigma_g^+) \), \( \text{H}_2 \), \( \text{NO} \), \( \text{NO}(3\Sigma_g^+) \), \( \text{NO}^+ \), \( \text{NO}^- \), \( \text{H}_2\text{O}^+ \), \( \text{H}^- \), \( \text{O}_3^- \), \( \text{Na}(^3P) \), \( \text{Na}(^3S) \), \( \text{Na}^+ \), \( \text{OH} \), \( \text{OH}(^4\Sigma_g^+) \), \( \text{OH}^- \), \( \text{H} \), \( \text{HO}_2 \), \( \text{O}_3 \), \( \text{HNO}_2 \), \( \text{H}_2\text{O}_2 \), \( \text{NO}_3 \), \( \text{N}_2^+ \), \( \text{H}_2\text{O}^+ \), \( \text{N}_2\text{O} \), \( \text{Cl} \), \( \text{Cl}_2 \), \( \text{HCl} \), \( \text{NaO} \), \( \text{NaO}_2 \), \( \text{NaNO} \), \( \text{NaCl} \), \( \text{Cl}^- \), \( \text{Cl}^+ \) and electrons. The system of equations of chemical kinetics was solved in the stationary approximation using the zero–dimensional model. In the calculation, the experimental values of the mol fractions of the electrolyte cathode components were used. The mol fraction of water molecules in the plasma is 1% and mol fractions of atoms of Na and Cl are 0.003 – 0.006% [9]. The temperature dependences for the rate constants of reactions of heavy particles were taken into account. The calculations were carried out for a gas temperature of 1600 K. The rate constants of processes interaction electrons with heavy particles were obtained using the electron energy distribution function founded by a numerical solution of the Boltzmann kinetic equation. The experimental values of the reduced electric field strength \((E/N)\) were used in the calculations: \(E/N = (2.2 – 3.0) \times 10^{16} \text{ V} \cdot \text{cm}^{-3}\) (water used as a electrolyte cathode), \(E/N = (1.5 – 2.3) \times 10^{16} \text{ V} \cdot \text{cm}^{-3}\) (solution of NaCl used as an electrolyte cathode).

3. Results and discussions

The transfer processes alter the composition of the gas phase and it results in the changing cathode voltage drop and electric field strength in plasma [9]. The changes of the reduced electric field strength and the set of electron collisions in the plasma should affect the electron energy distribution function (EEDF). The calculations of EEDF with variation of mole fraction of H2O in the plasma showed that collisions with water molecules lead to a decrease in the average electron energy and, as a consequence, the rate constants of the threshold processes with electrons participation. The electron concentration is \((3 – 6) \times 10^{12} \text{ cm}^{-3}\) at a discharge current of \(10 – 70\) mA and it depends on the mol fraction of water. The change of the rate constants of processes and the concentration of electrons results in a decrease of the rates of processes occurring under the action of an electron impact. Thus, the rates of low-threshold processes reduce at several times, and the rate constants with high thresholds (ionization, dissociation) decrease in order of magnitude.

The numerical calculation of the plasma composition was carried out using the zero–dimensional model in the stationary approximation in order to estimate the concentrations of the main active particles. At the first stage, the concentrations of the main active components: \(\text{O}(3\Pi)\), metastable electronically excited \(\text{O}_3(a^1\Delta_a)\) and \(\text{O}_3(b^3\Sigma_g^-)\), ozone were obtained by modeling processes in a system containing initially only \(\text{N}_2\) and \(\text{O}_2\) molecules. The calculations showed that the concentration of \(\text{O}(3\Pi)\) increases with the discharge current and reaches \(\sim 3 \times 10^{16} \text{ cm}^{-3}\), the concentration of \(\text{O}_3(a^1\Delta_a)\) does not exceed \(2.6 \times 10^{16} \text{ cm}^{-3}\), the ozone concentration is \(\sim (3.2 – 37.5) \times 10^{15} \text{ cm}^{-3}\). The nitrogen oxides are formed in the plasma: \(\text{NO} \sim (0.34 – 1.42) \times 10^{16} \text{ cm}^3\), \(\text{NO}_2 \sim 5 \times 10^{14} \text{ cm}^3\), \(\text{NO}_3 \sim 10^{10} \text{ cm}^3\) and \(\text{N}_2\text{O} \sim 10^{14} \text{ cm}^3\).

Radicals OH, HO2 and hydrogen peroxide are generated in the plasma when water molecules in the gas phase are taken into account. In this case, an additional process for the formation of \(\text{O}(3\Pi)\) atom appears: \(\text{OH} + \text{OH} \rightarrow \text{O}(3\Pi) + \text{H}_2\text{O}\). It should be noted that the channel formation rate is commensurate with the rates of formation of atoms upon dissociation of \(\text{O}_2\) molecules by electron
impact and in collisions with electronically excited nitrogen molecules. The main channels for the 
formation of hydroxyl radicals in the plasma are the processes: \( \text{O}^3P + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \) and the 
dissociative attachment of electrons to \( \text{H}_2\text{O} \) molecules \( (\text{H}_2\text{O} + e \rightarrow \text{H}^+ + \text{OH}) \). Subsequent reactions 
with OH radicals lead to the formation of hydrogen peroxide \( (\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2) \), HO\(_2\) radicals 
\( (\text{NO}_2 + \text{OH} \rightarrow \text{NO} + \text{HO}_2) \) and hydrogen atoms. In addition, the reactions affect the balance of 
nitrogen oxides in the plasma.

The discharge with the solution of sodium chloride used as cathode has low values of the reduced 
electric field strength in the plasma that is caused by the change in the balance of charged particles. 
The calculations showed that the ionization frequency of Na atoms exceeds the ionization frequency of 
the initial plasma components at a molar fraction of Na atoms in the gas phase \( \chi > 2 \times 10^{-6} \). Assuming 
that chlorine is in the form of Cl\(_2\) molecules in the plasma, the frequency of dissociative attachment of 
electrons to chlorine molecules \( (\text{Cl}_2 + e = \text{Cl}^- + \text{Cl}) \) is too small to affect significantly the electron 
balance (fig. 1).

In the discharge with a solution of sodium chloride, used as a cathode, the electric field strength is 
reduced. As a result, the form of the energy distribution function of electrons changes and, as a 
consequence, the rate constants of the threshold processes that 
influence the transfer processes on the properties of the discharge can be 
defined. First, the balance of charged particles in the plasma is varied which leads to reduces the 
electric field strength. Second, the set of electronic collisions is altered, which results in a change in the 
form of the EEDF. Eventually, this leads to a change of the rate constants of processes involving 
electrons. Thirdly, there are new reactions of formation and loss of active particles. As a result, the 
concentrations of all active components of the plasma are changed.

| The initial components | \( \text{O}^3P \), \( 10^{15} \) | \( \text{O}_2(a^3\Delta_g) \), \( 10^{15} \) | \( \text{O}_3 \), \( 10^{13} \) | \( \text{NO} \), \( 10^{15} \) | \( \text{OH} \), \( 10^{14} \) | \( \text{HO}_2 \), \( 10^{11} \) | \( \text{H}_2\text{O}_2 \), \( 10^{12} \) |
|-----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( \text{N}_2 \)::\( \text{O}_2 \) = 0.79:0.21 | 1.4\( \pm \)30.7 | 25.9\( \pm \)2.4 | 37.5\( \pm \)3.2 | 14.2\( \pm \)3.4 | | | |
| \( \text{N}_2 \)::\( \text{O}_2 \)::\( \text{H}_2\text{O} \) = 0.785:0.205:0.01 | 4.5\( \pm \)8.7 | 9.4\( \pm \)0.9 | 20.2\( \pm \)3.4 | 10.3\( \pm \)1.7 | 0.5\( \pm \)5.5 | 5.0\( \pm \)0.5 | 1.5\( \pm \)5.0 |
| \( \text{N}_2 \)::\( \text{O}_2 \)::\( \text{H}_2\text{O} \)::\( \text{Na} \)::\( \text{Cl} \) = 0.785:0.205:0.01:(3-6)\( 10^{-3} \) | 3.4\( \pm \)5.5 | 6.9\( \pm \)0.2 | 2.4\( \pm \)0.3 | 2.7\( \pm \)0.4 | 0.7\( \pm \)1.9 | 4.2\( \pm \)0.5 | 0.8\( \pm \)1.8 |

\( a \) \( E/N = (2.2 - 3.0) \cdot 10^{-16} \). \( b \) \( E/N = (1.5 - 2.3) \cdot 10^{-16} \) \( \text{Vcm}^2 \)
Figure 1. The frequencies of ionization and electron attachment of particles in the plasma:
1 – N$_2$ + e = N$_2^+$ + 2e ($\varepsilon$=15.51 eV)
2 – O$_2$ + e = O$_2^+$+2e ($\varepsilon$=12.08 eV)
3 – Na + e = Na$^+$ + 2e ($\varepsilon$=5.14 eV)
4 – H$_2$O + e = O$^-$ + H$_2$ ($\varepsilon$=4.95 eV)
5 – H$_2$O + e = H$^+$ + OH ($\varepsilon$=5.39 eV)
6 – Cl$^-$ + e = Cl + 2e ($\varepsilon$=3.42 eV)
7 – Cl$_2$ + e = Cl$^-$ + Cl ($\varepsilon$=2.51 eV)

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