2D model of CCRF discharge with liquid electrode

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Abstract. A mathematical model of RF discharge between metal rod and liquid electrodes in argon media at decreasing pressure in range of $10^3$–$10^5$ Pa at a local approach is constructed. Electrons, atomic and dimer ions, excited atoms and dimers of Ar as well as effect of vorticity electromagnetic field and processes on plasma-liquid interphase boundary are considered.

1. Introduction
Plasma technologies is widely used for ecologies and environment defenses. Plasma is used for waste water purification from both organic and heavy metals impurities. For example, a possibility of DC glow discharge application for an industrial effluent purification from heavy metal ions is showed in [1]. Methods of impoverishments of harmful organic impurities in water by strong non-equilibrium discharges is showed in paper [2]. These methods are most effectively at high percentage of impurities in water. In this case the plasma gives rise to stimulated combustion of organics which results in energy cost reduction. Furthermore, at percentage more than 20% these wastes can be a source of low-quality fuel for heating up of an engineering and utility services room. A technique for controlling of the water plant species of Cyanobacteria Microcystis Aeruginosa on water and wastewater treatment facility is presented in [3].

A specific feature of plasma technologies applications is a possibility of decontaminating of objects which is remoted on some tens or more distances from the used technical equipment. For example, authors of [4] presents experimental results of planktonic microorganisms and their consortiums by a plasma jet. A flood lamp system based on pulsed high pressure short-arc xenon lamp is proposed in paper [5] for using as a generator of peaky directional emission of the biocidal band. Likewise, a great interest to another plasma with liquid electrode application is taken worldwide [6-12].

The most studied kinds of discharges with liquid electrodes now are the DC discharges. The rf discharge between solid and liquid electrodes is studied not long ago. There is no a theory of such discharges. Results of experimental studies of discharges with liquid electrodes can be found in [13-16].

In this regard the work objectives is a construction of approximate 2d-model of RF discharge when one of electrode is liquid and the other is solid.
2. System of equation

A mathematical model of RF discharge between metal rod and circular metal plate dipping into a weak electrolyte. The rod is connected to RF current source and the plate is tied to ground. The discharge is burned in Ar media at pressure in range from $10^3$ to $10^5$ Pa. The discharge chamber is a dielectrically cylinder by $g$ in radius.

Let us introduce the cylindrical coordinate system $rOz$ where axis Oz is perpendicularly to the plate and origin of coordinates is placed in the center of the rod end (see figure 1).

![Figure 1](image)

The scheme of discharge chamber for burning of the discharge between the metallic rod and liquid.

The mathematical model includes the following equations:

- An equation of diffusion-drift for the atomic ions:

$$\frac{\partial n_k}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left( r \left( D_n \frac{\partial n_k}{\partial r} \right) \right) - \frac{\partial}{\partial z} \left( D_n \frac{\partial n_k}{\partial z} + \mu_k n_k E_z \right) = R_1 n_e N + R_2 n_m + R_3 n_m n_e - R_4 n_e n_k - R_5 n_k^2 n_e + R_{12} n_e n_k - R_1 n_k N^2 + R_{20} N n_{k_2}.$$

Here $n_e$, $n_m$, $n_k$, $n_{k_2}$ is densities of electrons, metastable, atomic and dimeric ions, $N$ – is the density of neutral atoms in the ground state, $\mu_k$ and $D_n$ are the mobility and diffusion coefficient of atomic ions, $E_z$, $E_i$ are components of the potential electrical tense vector $E = E_i \hat{i} + E_\theta \hat{j}$, where $\hat{i}$, $\hat{j}$ are basis vectors, $R_{\alpha}, i=1...20$ are coefficients of rates of plasma chemical reactions (see table 1):

**Table 1.** Kinetic processes taken into account in model of RF discharge with liquid electrodes in Ar media [17].

| Designation | Reaction | Designation | Reaction |
|-------------|----------|-------------|----------|
| $R_1$       | Ar$^+$+e→Ar$^++2$e;  | $R_2$       | Ar$^++$Ar$^→$Ar$^++$Ar$^+e$;  |
| $R_3$       | Ar$^+$e→Ar$^++2$e;  | $R_4$       | Ar$^++$e→Ar$^++h$;  |
| $R_5$       | Ar$^++2$e→Ar$^++e$;  | $R_6$       | Ar$^++e→Ar^++;e$;  |
| $R_7$       | Ar$^++Ar^++h$;  | $R_8$       | Ar$^++Ar^++2$Ar;  |
| $R_9$       | Ar$^++2$Ar$^+e$;  | $R_{10}$    | 2Ar$^++2$Ar$^+→2$Ar$^++;e$;  |
| $R_{11}$    | Ar$^++Ar^++e$;  | $R_{12}$    | Ar$^++e→Ar^++2$Ar$^+e$;  |
| $R_{13}$    | Ar$^++e→Ar^++Ar$;  | $R_{14}$    | Ar$^++→2$Ar$^++;e$;  |
| $R_{15}$    | Ar$^++2$Ar$^+→Ar^++Ar$;  | $R_{16}$    | Ar$^++2$Ar$^++→e+2$Ar$^++Ar^+e$;  |
| $R_{17}$    | Ar$^++Ar^++e+Ar^++Ar^+$;  | $R_{18}$    | e$+Ar^++→2$Ar$^++e$;  |
| $R_{19}$    | Ar$^++2$Ar$^+→3$Ar$^++h$;  | $R_{20}$    | Ar$^++2$Ar$^+→2$Ar$^++2$Ar$^+e$;  |

- An equation of diffusion-drift for the molecular ions:
\[
\frac{\partial n_{2+}}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left[ r \left( D_{2+} \frac{\partial n_{2+}}{\partial r} \right) \right] - \frac{\partial}{\partial z} \left( D_{2+} \frac{\partial n_{2+}}{\partial z} + \mu_{2+} n_{2+} E_{z} \right) = \\
= R_{14} n_{m}^{2} + R_{17} n_{e} N^{2} - R_{12} n_{e} n_{2+} - R_{13} n_{e} n_{2+} + R_{16} n_{2+}^{2} + R_{17} n_{m} n_{2+} - R_{20} N n_{2+}.
\]

Here \( D_{2+} \) is the diffusion coefficient of molecular ions, \( \mu_{2+} \) is the mobility of molecular ions;

- An equation of diffusion-drift for the electrons:
\[
\frac{\partial n_{e}}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left[ r \left( D_{e} \frac{\partial n_{e}}{\partial r} \right) \right] - \frac{\partial}{\partial z} \left( D_{e} \frac{\partial n_{e}}{\partial z} - \mu_{e} e E_{z} \right) =
\]
\[
= R_{1} n_{e} N + R_{2} n_{m}^{2} + R_{3} n_{m} n_{e} - R_{4} n_{e} n_{4} - R_{5} n_{e}^{2} n_{4} + R_{10} n_{m}^{2} - R_{13} n_{e} n_{2+} + R_{16} n_{2+}^{2} + R_{17} n_{m} n_{2+}.
\]

Here \( D_{e} \) is the diffusion coefficient of electrons, \( \mu_{e} \) is the mobility of electrons, \( n_{2+} \) is the Ar dimer density;

- The Poisson equation for electric potential \( \phi \):
\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi}{\partial r} \right) - \frac{\partial^{2} \phi}{\partial z^{2}} = \frac{e}{\varepsilon_{0}} (n_{+} + n_{2+} - n_{e}).
\]

- The Maxwell equation for electromagnetic curl field:
\[
\frac{\partial \vec{H}_{\phi}}{\partial z} = i \varepsilon_{0} \varepsilon \omega \vec{E}_{r},
\]
\[
- \frac{1}{r} \frac{\partial}{\partial r} \left( r \vec{H}_{\phi} \right) = j + i \varepsilon_{0} \varepsilon \omega \vec{E}_{r},
\]
\[
\frac{\partial \vec{E}_{r}}{\partial z} - \frac{\partial \vec{E}_{z}}{\partial r} = i \mu_{0} \omega \vec{H}_{\phi}.
\]

Here \( \vec{H}_{\phi}, \vec{E}_{r}, \vec{E}_{z} \) are complex amplitudes of the electromagnetic curl field, \( i \) is the imaginary unit, \( \varepsilon_{0} \) is the electrical constant, \( \varepsilon \) is the relative permittivity, \( \omega = 2\pi f \) is the cyclic frequency, \( f \) is the generator frequency, \( j \) is the axial component of the RF current in a rod as well as in the discharge. We suppose that radial component of conduction current in discharge is negligibly small.

- An equation of diffusion for excited atoms, taken into account a fast mixing of electronically excited levels due to electron impact:
\[
\frac{\partial n_{m}}{\partial t} - \frac{1}{r} \frac{\partial}{\partial r} \left[ r \left( D_{m} \frac{\partial n_{m}}{\partial r} \right) \right] - \frac{\partial}{\partial z} \left( D_{m} \frac{\partial n_{m}}{\partial z} \right) =
\]
\[
= R_{6} N n_{e} + R_{15} n_{m}^{2} - R_{7} n_{e}^{2} n_{m} - R_{7} n_{e} n_{m}^{2} - R_{8} n_{m}^{2} n_{e} - R_{9} N n_{m} -
R_{7} n_{m} n_{e}^{2} - R_{15} N^{2} n_{e} - R_{14} n_{m} n_{e} - R_{19} n_{m} N^{2}.
\]

Here \( D_{e} \) is the diffusion coefficient of excited atoms;

- A kinetic equation for excited dimers of:
\[
\frac{\partial n_{2+}}{\partial t} = R_{14} n_{m}^{2} + R_{15} N^{2} n_{m} - R_{14} n_{2+}^{2} - R_{16} n_{2+}^{2} - R_{17} n_{m} n_{2+} - R_{18} n_{e} n_{2+} + R_{19} n_{m} N^{2}.
\]

- A kinetic equation for ground-state atoms
\[
\frac{\partial n}{\partial t} = -R_{1} n_{e} N + R_{2} n_{m}^{2} + R_{4} n_{e} n_{4} + R_{5} n_{e}^{2} n_{4} - R_{6} N n_{e} + R_{7} n_{m} + R_{8} N n_{m} + R_{9} n_{m} n_{e} -
R_{11} n_{m} N^{2} + 2R_{12} n_{e} n_{2+} + 2R_{13} n_{e} n_{2+} + 2R_{14} n_{2+} - R_{15} N^{2} n_{m} + 2R_{16} n_{2+} +
R_{17} n_{m} n_{2+} + R_{19} n_{m} N^{2}.
\]
3. Boundary conditions
Here the following notations are used: \( d \) is the rod length, \( c \) is the radius of the rod, \( m_+ \), \( m_- \), \( m_c \), \( m_r \) are masses of corresponding particles, \( T_+, T_{2+}, T_+, T_r \) are their temperature (let us suppose that difference between rotational, vibrational, and translational temperatures is negligible), \( V_a \) is the magnitude of electrode voltage, \( G_{+r}, G_{2+}, G_{e+r}, G_{m+r} \) are particle fluxes in the radial axis, \( G_{+x}, G_{2+x}, G_{e+x}, G_{m+x} \) are particle fluxes in the Oz direction. Hereinafter, we suppose that there is no tangential particle flux.

3.1. On the surface of the load electrode

- at \( z=d \) and \( 0 \leq r \leq c \) the following conditions are formulated:

\[
G_{+z} = \begin{cases} -\sqrt{8kT_+/(\pi m_+)}n_+/4 + \mu_+n_4E_z, & \text{if } E_z < 0, \\ -\sqrt{8kT_+/(\pi m_+)}n_+/4, & \text{if } E_z \geq 0. \end{cases}
\]

\[
G_{2z} = \begin{cases} -\sqrt{8kT_{2+}/(\pi m_{2+})}n_{2+}/4 + \mu_-n_{2+}E_z, & \text{if } E_z < 0, \\ -\sqrt{8kT_{2+}/(\pi m_{2+})}n_{2+}/4, & \text{if } E_z \geq 0, \end{cases}
\]

\[
G_{e,z} = \begin{cases} -\sqrt{8kT_e/(\pi m_e)}n_e/4 + c(G_{+z} + G_{+z}), & \text{if } E_z < 0, \\ -\sqrt{8kT_e/(\pi m_e)}n_e/4 - \mu_en_eE_z, & \text{if } E_z \geq 0, \end{cases}
\]

\[
G_{m,z} = -\sqrt{8kT_a/(\pi m_a)n_m/4},
\]

\[
V_a = \cos(\omega t),
\]

\[
\dot{E}_r = 0, \dot{E}_z = 0, \dot{H}_\phi = i\exp(i\omega t).
\]

- at \( r=c \neq 0 \leq z \leq d \) the following conditions are formulated:

\[
G_{+r} = -\sqrt{8kT_+/(\pi m_+)}n_+/4,
\]

\[
G_{e,r} = -\sqrt{8kT_e/(\pi m_e)}n_e/4,
\]

\[
G_{m,r} = -\sqrt{8kT_a/(\pi m_a)n_m/4},
\]

\[
V_a = \cos(\omega t),
\]

\[
\dot{E}_r = 0, \dot{E}_z = 0, \dot{H}_\phi = i\exp(i\omega t).
\]

3.1 On dielectrically surfaces

On dielectrically surfaces the normal to a particle flow is set equal to flux of Brownian particle and

\[
-\partial \phi / \partial r = q/\varepsilon_0, \partial q / \partial t = e(G_{+\perp} + G_{2+\perp} - G_{e\perp}),
\]

where \( q \) is surface-charge density defined by equation of charge collection.

3.2. On the interphase surface water-gas the following conditions are formulated.

Let us allow that specific conductance of weak electrolytes tends to water specific conductance and water does not have time to polarize. Then Ohm’s law \( j = \sigma \dot{E} \) is valid, where \( \sigma \) is water specific conductance. Along the interface with electrolyte, the flow of particles is Brownian.

Plasma chemical processes depending on electrical field direction are considered on the interphase surface too. If the field is directed back to rod electrode, then water dissociation processes are prevailed \( y_1 \rightarrow y_3 \) (see table 2). Dissociation product is reacted with each to other in processes denoted as \( Rw11-Rw15 \). At this phase the negative charge \( O^- \) is accumulated than it is incompletely neutralized at changing of field direction in reactions \( Rw16-Rw18 \). As a result, \( atE_z < 0 \) the following conditions are formulated

\[
G_{+x} = \sqrt{8kT_+/(\pi m_+)}n_+/4,
\]

\[
G_{2+x} = \sqrt{8kT_{2+}/(\pi m_{2+})}n_{2+}/4,
\]

\[
G_{e,x} = \sqrt{8kT_e/(\pi m_e)}n_e/4 - \mu_en_eE_z,
\]

\[
G_{m,x} = \sqrt{8kT_a/(\pi m_a)n_m/4},
\]
Table 2. Kinetic processes taken into account on the interphase surface.

| Designation | Reaction | Designation | Reaction |
|-------------|----------|-------------|----------|
| \( \gamma_1 \): | \( e + H_2O \rightarrow H + OH^+ \); | \( Rw_{14} \): | \( H^+ + e \rightarrow 2e + H \); |
| \( \gamma_2 \): | \( e + H_2O \rightarrow H_2 + O^+ \); | \( Rw_{15} \): | \( 2OH + H_2 \rightarrow 2e + 2H_2O \); |
| \( \gamma_3 \): | \( e + H_2O \rightarrow OH + H^+ \); | \( Rw_{16} \): | \( O^+ + O \rightarrow O_2 + e \); |
| \( Rw_{11} \): | \( OH^+ + O \rightarrow e + H_2O \); | \( Rw_{17} \): | \( O^+ + Ar^+ \rightarrow O + Ar^* \); |
| \( Rw_{12} \): | \( OH + H \rightarrow e + H_2O \); | \( Rw_{18} \): | \( O^+ + Ar^+ + Ar \rightarrow O + 2Ar \); |
| \( Rw_{13} \): | \( H^+ + H \rightarrow e + H_2 \); |

At \( E_z > 0 \) the following conditions are formulated:

\[
\begin{align*}
G_{e,x} &= \sqrt{8kT_e/(\pi m_e)}n_e/4 + \mu_e n_e E_z, \\
G_{2+,x} &= \sqrt{8kT_{2+}/(\pi m_{2+})}n_{2+}/4 + \mu_{2+} n_{2+} + E_z, \\
G_{e,x} &= \sqrt{8kT_e/(\pi m_e)}n_e/4 - \gamma(G_e + G_{2+}), \\
G_m &= \sqrt{8kT_a/(\pi n_a)}n_m/4.
\end{align*}
\]

The interphase surface is exposed to ion bombardment during the discharge burning what leads to water dissociation and ionization. As a result, radicals of hydrogenium, oxygenium, and hydroxyl appear in the discharge zone. For this reason, the following system of a kinetic equations at zero initial conditions is considered:

\[
\begin{align*}
\frac{\partial n_{OH^-}}{\partial t} &= \gamma_1 G_e - Rw_{11} n_0 n_{OH^-} - Rw_{12} n_H n_{OH^-}, \\
\frac{\partial n_{H^+}}{\partial t} &= \gamma_2 G_e + Rw_{13} n_H n_{H^+} - Rw_{15} n_{OH^+} n_{H^+}, \\
\frac{\partial n_{OH}}{\partial t} &= \gamma_3 G_e - Rw_{15} n_{OH^+} n_{H^+}, \\
\frac{\partial n_{O^-}}{\partial t} &= \gamma_4 G_e - Rw_{16} n_0 n_{O^-} - Rw_{17} n_4 n_{O^-} - Rw_{18} n_{O^+} n_{O^-}, \\
\frac{\partial n_{H^-}}{\partial t} &= \gamma_5 G_e - Rw_{13} n_H n_{H^-} - Rw_{14} n_{e} n_{H^-}, \\
\frac{\partial n_{H}}{\partial t} &= \gamma_1 G_e - Rw_{12} n_H n_{OH^-} - Rw_{13} n_H n_{H^-} + Rw_{14} n_{e} n_{H^-}, \\
\frac{\partial n_{O}}{\partial t} &= -Rw_{11} n_0 n_{OH^-} - Rw_{16} n_0 n_{O^-} + Rw_{17} n_4 n_{O^-} + Rw_{18} n_{O^+} n_{O^-}.
\end{align*}
\]

The model is hybrid because charged particle distribution functions of both electron and ions, their integral characteristics such as transport coefficients and rate coefficients, as well as water radical pervasion into discharge should be modelling by Monte-Carlo method [18-20].

4. Conclusion

A mathematical model of RA discharge between rod metallic and liquid electrodes in argon media at decreased pressure in range of \( 10^3 - 10^5 \) Pa is constructed. Electrons, atomic and molecular ions, excited atoms and dimers, plasma chemical processes on the interphase surface between water and gas, as well as electromagnetic curl field is considered.
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