Mathematical model of an initial stage of capacitive coupled RF discharge between solid and liquid electrodes

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Mathematical model of capacitive coupled RF discharge between solid and liquid electrodes is presented. The model describes the distribution of charged particles, neutral atoms in the ground and excited states, the electric field in the electrode gap with the processes of dissociation of water molecules in the gas-liquid boundary.

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1. Introduction

Plasma of reduced pressure RF capacitive discharges (RFCDs) operating between solid electrodes is widely used to modify surfaces of organic and inorganic materials. RFCDs make it possible to purify and polish the surface; deposit thin film coatings; strengthen the surface layer; and increase the fatigue endurance, wear resistance, and lifetime of materials and products [1].

In recent years, there appeared a series of works dedicated to studying the characteristics of electric discharges in liquids and gases with liquid electrodes [2-5]. It follows from a few experimental works that studies of RFCDs with liquid electrodes can lead to interesting scientific results and open new technological possibilities [5].

The nonequilibrium plasma of an RFCD with liquid electrodes is more complicated than the plasma of DC electric discharges. The fundamentals of its physics still remain poorly understood. The main reason for this is the limited number of methods suitable for the diagnostics of such discharges.

This work is aimed at studying specific features of an RFCD operating between a dropletjet electrolytic electrode and an electrolytic cell in a wide pressure range, as well as of an RFCD burning between a copper rod and the surface of non_flow electrolyte at atmospheric pressure.

2. Formulation of the problem

The distance between the electrodes in mathematical model is set equal to the depth of the electrolyte. Accordingly, the coordinate *x*=0 corresponds to a grounded electrode *x*=*l* corresponds to a loading electrode, *x*=*a* corresponds to the boundary between liquid and gas.

The model includes the following equation for argon plasma:

1. Diffusion-convection equation for the electron density ∂n_e:

$$\frac{\partial n_e}{\partial t} - \frac{\partial}{\partial x}\left(D_e \frac{\partial n_e}{\partial x} + \mu_e E n_e \right) = \nu_i n_e - \beta n_e n_+ + \\ + R_1 n_e n_m + R_2 n_m^2, \qquad (1)$$

with boundary conditions $\Gamma_e = \gamma \Gamma_+$, when electrical field is directed into an electrode, $\partial \Gamma_e / \partial x = 0,$ when electrical field is directed from an electrode;

2. Diffusion-convection equation for ions

$$\frac{\partial n_+}{\partial t} - \frac{\partial}{\partial x}\left(D_+ \frac{\partial n_+}{\partial x} + \mu_+ E n_+ \right) = \nu_i n_e - \beta n_e n_+ + \\ + R_1 n_e n_m + R_2 n_m^2, \qquad (2)$$

with boundary conditions $\partial \Gamma_+ / \partial x = 0,$ when an electrical field is directed into an electrode, $\Gamma_+ = 0$ when electrical field is directed from an electrode.

Here D_e, D_+ is coefficients of electrons and ions diffusion, μ_e, μ_+ is the mobility of electrons and ions, β is effective coefficient of recombination, ν_i – ionization rate defined by Townsend dependence, n_m is metastable density, R_1, R_2 are rate of step-wise and penning ionization, respectively, γ is the secondary emission coefficient,

$$\Gamma_e = -D_e \frac{\partial n_e}{\partial x} - \mu_e E n_e, \; \Gamma_+ = -D_+ \frac{\partial n_+}{\partial x} + \mu_+ E n_+,$$

are electrons and ions flow densities.

3. The metastable atoms balance equation:

$$\frac{\partial n_m}{\partial t}-\frac{\partial}{\partial x}\left(D_m\frac{\partial n_m}{\partial x}\right)=-R_1 n_e n_m-R_2 n_m^2+ \qquad (3)$$
$$+R_3 N n_e-R_4 N n_m-R_5 N^2 n_m-R_6 n_m,$$

with boundary condition n_m=0 at $x=l$.

Here D_m is coefficient of metastable diffusion, N is concentration of atoms in the ground state, R_i, i=1,…,6 are rate constants for the reactions of excitation (in parentheses hereinafter designated process number) $\mathrm{Ar}+e\rightarrow\mathrm{Ar}^*+e$ (3) and extinction processes: $\mathrm{Ar}^*+\mathrm{Ar}\rightarrow 2\mathrm{Ar}$ (4), $\mathrm{Ar}^*+2\mathrm{Ar}\rightarrow\mathrm{Ar}_2+\mathrm{Ar}$ (5), $\mathrm{Ar}^*\rightarrow\mathrm{Ar}+h\nu$ (6).

4. The neutral atoms balance equation:

$$\frac{\partial n_n}{\partial t}-\frac{\partial}{\partial x}\left(D_n\frac{\partial n_n}{\partial x}\right)=\beta n_e n_+-R_3 N n_e+ \qquad (4)$$
$$+R_4 N n_m-R_5 N^2 n_m+R_6 n_m,$$

with boundary condition $n_n=p/kT_{el}$ at $x=l$. Here D_n is diffusion coefficient of neutral atoms, k – Boltzmann constant, T_{el} – electrode temperature, p – gas pressure.

At the water-gas ($x=a$) boundary the following plasma-chemical processes is considered. If the field directed from the electrode, water molecule dissociation processes prevail on the surface of the water: $e+\mathrm{H_2O}+(3{,}2\text{эВ})\rightarrow\mathrm{H}+\mathrm{OH}^-$ (8), $e+\mathrm{H_2O}+(3{,}6\text{эВ})\rightarrow\mathrm{H_2}+\mathrm{O}^-$(9), $e+\mathrm{H_2O}+(4{,}25\text{эВ})\rightarrow\mathrm{OH}+\mathrm{H}^-$(10). Dissociation products come in the next reaction: $\mathrm{OH}^-+\mathrm{O}\rightarrow\mathrm{H_2O}+e$ (11), $\mathrm{OH}^-+\mathrm{H}\rightarrow\mathrm{H_2O}+e$ (12), $\mathrm{H}^-+\mathrm{H}\rightarrow\mathrm{H_2}+e$ (13), $\mathrm{H}^-+\mathrm{e}\rightarrow\mathrm{H}+2e$ (14), $2\mathrm{OH}+\mathrm{H_2}\rightarrow 2\mathrm{H_2O}+2e$ (15). In this phase, there is an accumulation of negative charge O^-, which is partially extincted in the following processes when the field directs from the electrode: $\mathrm{O}^-+\mathrm{Ar}^+\rightarrow\mathrm{O}+\mathrm{Ar}^*$, $\mathrm{O}^-+\mathrm{Ar}^++\mathrm{Ar}\rightarrow\mathrm{O}+2\mathrm{Ar}$ и $\mathrm{O}^-+\mathrm{O}\leftrightarrow\mathrm{O_2}+\mathrm{e}$ (16).

In this regard, the boundary conditions for equation (3) and (4) at $x=a$ are follows:

$$-D_m\frac{\partial n_m}{\partial x}=\gamma_1\Gamma_+ n_{\mathrm{O}^-},\ E>0, \qquad \frac{\partial n_m}{\partial x}=0,\ E<0,$$
$$-D_n\frac{\partial n_n}{\partial x}=\gamma_2\Gamma_+ n_{\mathrm{O}^-},\ E>0, \qquad \frac{\partial n_n}{\partial x}=0,\ E<0,$$

5. Poisson's equation for electric potencial

$$-\frac{\partial^2\varphi}{\partial x^2}=\frac{e}{\varepsilon_0}\left(n_+-n_e\right) \qquad (5)$$

with boundary conditions $i=-\sigma\,\partial\varphi/\partial x$ at $x=a$ and $\varphi=V_a\sin(\omega t)$ at $x=l$.

Here σ is electrical conductivity of water, i is a current density on the grounded electrode, e – the elementary charge, ε_0 – the electrical constant, ω – circular frequency of an electrtic field, V_a – the voltage amplitude.

For calculations of plasma-chemical reactions on the water-gas boundary the Cauchy problem with zero initial conditions is considered:

$$\frac{\partial n_{\mathrm{OH}^-}}{\partial x}=R_8 n_e-R_{12} n_{\mathrm{OH}^-} n_{\mathrm{H}}-R_{11} n_{\mathrm{OH}^-} n_{\mathrm{O}},$$
$$\frac{\partial n_{\mathrm{H_2}}}{\partial x}=R_9 n_e+R_{13} n_{\mathrm{H}^-} n_{\mathrm{H}}-R_{15} n_{\mathrm{OH}^-}^2 n_{\mathrm{H_2}},$$
$$\frac{\partial n_{\mathrm{OH}}}{\partial x}=R_{10} n_e-R_{15} n_{\mathrm{OH}^-}^2 n_{\mathrm{H_2}},$$
$$\frac{\partial n_{\mathrm{O}^-}}{\partial x}=R_9 n_e-\gamma_1\Gamma_+ n_{\mathrm{O}^-}-\gamma_2\Gamma_+ n_{\mathrm{O}^-}-R_{16} n_{\mathrm{O}^-}^2 n_{\mathrm{O}},$$
$$\frac{\partial n_{\mathrm{H}^-}}{\partial x}=R_{10} n_e-R_{13} n_{\mathrm{H}^-}^2 n_{\mathrm{H}}-R_{14} n_{\mathrm{H}^-}^2 n_e,$$
$$\frac{\partial n_{\mathrm{H}}}{\partial x}=R_8 n_e-R_{12} n_{\mathrm{OH}^-} n_{\mathrm{H}}-R_{13} n_{\mathrm{H}^-}^2 n_{\mathrm{H}}+R_{14} n_{\mathrm{H}^-}^2 n_e,$$
$$\frac{\partial n_{\mathrm{O}}}{\partial x}=\gamma_1\Gamma_+ n_{\mathrm{O}^-}+\gamma_2\Gamma_+ n_{\mathrm{O}^-}-R_{16} n_{\mathrm{O}^-}^2 n_{\mathrm{O}}-R_{11} n_{\mathrm{OH}^-} n_{\mathrm{O}},$$

Rate constants characterizing these processes, are taken from [6, 7] and experimental data.

The constructed mathematical models allows to evaluate the main characteristics of initial stage of of capacitive coupled RF discharge with liquid electrode.

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