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# INFLUENCE OF HIGH-FIELD EFFECTS ON THE CHARACTERISTICS OF THE NEAR-CATHODE LAYER IN A MOLECULAR GAS PLASMA

M. S. Benilov, G. A. Lyubimov,
A. Kh. Mnatsakanyan, and G. V. Haidis

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It is well known that for quite high values of the electric field intensity E the kinetic and transport coefficients of a weakly ionized plasma depend on E. This paper is concerned with estimating the influence of this effect on the characteristics of the charged layer near the cold cathode in the plasma formed by combustion products with a potassium additive under conditions realized in the channels of open-cycle MHD generators.

The distribution of ion and electron densities $n_i$ and $n_e$ and of the electric field intensity E in the near-wall layer of a volume discharge (Debye layer) at the cathode is described by the following nonlinear boundary-value problems [1]:

$$J_i' = f, \quad j' = 0, \quad J_i = \mu_i n_i E, \quad J_e = -\mu_e n_e E,$$
$$j = e(J_i - J_e), \quad E' = 4\pi e(n_i - n_e);$$
$$y = 0, \ J_e = 0; \ y = y_D, \ E = 0, \ \frac{J_i}{D_{iD}} + \frac{J_e}{D_{eD}} = -2n_D x_D'. \tag{1}$$

Here $J_i$, $J_e$, $\mu_i$, $\mu_e$, $D_i$, $D_e$ are the diffusion fluxes, mobilities, and coefficients of diffusion of ions and electrons; j is the electric current density (fixed quantity); the terms on the right sides of the first equation and the last boundary condition take into account, respectively, the increase in the number of charged particles due to volume ionization and transport out of the quasineutral region due to concentration diffusion; the y axis is oriented along the normal away from the electrode surface; $y_D$ is the coordinate of the external boundary of the Debye layer; the prime indicates differentiation with respect to y; and the index D indicates the value of the corresponding quantity at $y = y_D$.

In writing down the boundary condition on the cathode surface, it was assumed that there was no emission current.

To solve the problem formulated it is necessary to know the ionization function f and the transport coefficients $\mu_i$, $\mu_e$, $D_{iD}$, $D_{eD}$.

The ionization function f can be represented as the sum

$$f = f_1 + f_2, \tag{2}$$

where $f_1$ corresponds to stepped ionization of the atoms of the additive with the participation of heavy particles (primarily water molecules) and electrons; $f_2$ describes direct ionization of heavy particles by electron bombardment.

The quantity $f_1$ in the limit of a weak field (at an electron temperature $T_e$ equal to the gas temperature T) can be represented, with acceptable accuracy, as a sum [2]

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$$f_1 = n_p \left(K_{H_2O} n_{H_2O} + K_e n_e\right), \tag{3}$$

where $n_p$, $n_{H_2O}$ are the concentrations of potassium atoms and water molecules; $K_{H_2O}$ and $K_e$ are the rate constants of stepped ionization of potassium in collisions with water molecules and electrons. Here, in typical regimes of operation of the MHD channel, the second term in (3) can be neglected. For $T_e \neq T$ the additive representation of the rate of stepped ionization becomes inapplicable. The calculation of $f_1$ under these conditions, proposed according to the scheme in [2, 3] and taking into account the transitions between excited levels of the potassium atom in collisions with electrons as well as with water and nitrogen molecules, showed the following. For a large excess of $T_e$ above T, the quantity $f_1$ can greatly exceed the isothermal value (3), if the relative electron density is not too small. Under such conditions, however, direct ionization of atoms from the ground state makes an even greater contribution to (2). In the same region of parameters, where stepped ionization is the main source of charged particles, expression (3), with only the first term retained (i.e., inclusion of the contribution of molecules), can be used.

To determine the rate of direct ionization $f_2$, we use Maxwell's distribution for the electron energies. The electron temperature was determined from the energy balance equation

$$e(E/n)^2 \mu_e n = \sum_i x_i \sum_j I_{ij} \langle v\sigma_{ij} \rangle [1 - \varphi_{ij}(T)/\varphi_{ij}(T_e)], \tag{4}$$

where

$$\mu_e n = \frac{e}{3T_e} \sum_i \frac{1}{x_i} \left\langle \frac{v}{\sigma_i} \right\rangle, \tag{5}$$

from the local values of the parameter E/n (ratio of the field intensity to the density of molecules) and of the gas temperature. Here, v is the velocity of electrons; $x_i$ is the molar fraction of the i-th component; $\sigma_i$ is the corresponding scattering cross section of an electron with transfer of momentum; the index j enumerates the inelastic scattering processes with cross sections $\sigma_{ij}$ and energy transfers $I_{ij}$; the angular brackets indicate averaging over the energy distribution of electrons. The functions $\varphi_{ij}$ characterize the role of collisions of the second kind – with energy transfer from heavy particles to electrons. Thus, to excite rotations $\varphi(T) = T$, to excite vibrations of $CO_2$ molecules $CO_2$ $\varphi(T) = [\exp(\omega/T) - 1]^{-1}$, where $\omega$ is the vibrational quantum, and so on (see [4]).

The balance of energy (4) includes losses to the excitation of rotational levels of $H_2O$, the vibrational and electronic levels of $N_2$, the vibrational levels of $CO_2$ as well as the resonance level of the potassium atom (the contribution of other processes is not significant). The cross section for excitation of rotations of $H_2O$ from the ground state was calculated in the dipole approximation [5]; the fact that the rate of loss of energy with excitation of rotations does not depend on the gas temperature was used [6]. Energy losses accompanying excitation of vibrations of $N_2$ were taken into account according to [4], and the data in [7] were used for $CO_2$. The vibrational and rotational temperatures of molecules were assumed to equal T, which is justified due to the smallness of the corresponding relaxation times. The values of the constants for excitation of electronic states of $N_2$ in [8] were used and the excitation of potassium was calculated using the cross sections in [9]. The mobility of electrons was calculated by averaging the transport cross section [10] with a Maxwellian distribution.

The rate of direct ionization $f_2$ was calculated using the expression $f_2 = n_e n \sum_i x_i \langle v\sigma_i^u \rangle \equiv$ $n_e n K_u$ with cross sections from [11]. Figure 1 shows the dependence of $K_u$ (in $cm^3 \cdot sec^{-1}$) on E/n (in $10^{-15}$ $V \cdot cm^2$) in the products of combustion of natural gas in air with the molar fraction of potassium equal to 1%. The continuous curve corresponds to a gas temperature of T = 2000°K and the dashed curve corresponds to a gas temperature of T = 1000°K. The dot–dash curve corresponds to ionization of only potassium atoms. It is evident that in quite strong fields ionization of the main components of the combustion products becomes significant.

We note that the replacement of the true electron energy distribution by a Maxwellian distribution can lead to incorrect values of the ionization constants $K_u$ at low electron temperatures, $T_e \lesssim 1$ eV [$E/n \lesssim (6\text{-}8) \cdot 10^{-16}$ $V \cdot cm^2$]. For small $T_e$, however, the rate of direct ionization is small compared to stepped ionization, and the error in determining $K_u$ does not affect the results of the calculations.

The determination of the ion mobility $\mu_i$, generally speaking, requires a calculation of the ionic composition of the plasma. In a strong field, primarily $N_2^+$ and $H_2O^+$ ions form

near the cathode. Later, charge exchange between molecular ions and potassium atoms occurs with the formation of excited states of molecules and their subsequent de-excitation:

$$M^+ + \mathrm{K} \rightleftarrows M^* + \mathrm{K}^+, \quad M^* + M \to M + M$$

(M, M*, $M^+$ are the molecule in the ground and the electronically excited state and the molecular ion). Since de-excitation occurs quite rapidly and its inverse process, due to the low temperature of the gas compared with the excitation energy (a quantity of the order of the difference of the ionization potentials of the molecule M and of the potassium atom) is inefficient, charge exchange in the opposite direction is insignificant. An estimate using the charge exchange cross sections in [12, 13] shows that the time for charge exchange of molecular ions is small compared with the times of flight of ions through the Debye layer, i.e., potassium ions are the main type of ion. Their mobility was determined following [14], and the weak dependence of $\mu_i$ on E was neglected. The quantity $\mu_e$ was calculated using Eq. (5). The quantities $D_{iD}$, $D_{eD}$ were determined from the Einstein relations ($y = y_D E = 0$ and $T_e = T$).

The quantity $n_D x_D'$ was determined just as in [1], and it was thereby assumed that under conditions when the contribution of this term is significant (i.e., for not very large values of $|j|$ [1]), the isothermality does not affect the solution in the quasineutral region.

The particle density n was determined from the equation of state, the pressure was assumed to be given and constant in the Debye layer, and the distribution of the gas temperature in the region near the wall was also assumed to be given (estimates show that under the conditions examined the liberation of Joule heat in the Debye layer per unit surface area of the cathode $j\psi_w$, where $\psi_w$ is the voltage drop in the layer, is small compared to the convective heat flux density, and for this reason the distribution of the plasma temperature in the first approximation does not depend on the electric field and can be found by solving the corresponding gasdynamic problem).

In the limit of an isothermal plasma (i.e., in the limit of a weak field), when the dependence on E in the expression for $\mu_e$ can be neglected, and the second term in the expression for f can be neglected, the problem formulated has an exact analytic solution [1]. In the general case, such a solution does not exist and this problem must be solved numerically. We shall first introduce the new independent variable $z = E^2$ and we shall express $n_i$, $n_e$, $J_i$, E, j in terms of $J_e$, z:

$$n_i = -\frac{J_i}{\mu_i \sqrt{z}}, \quad n_e = \frac{J_e}{\mu_e \sqrt{z}}, \quad J_i = \frac{\mu_i z'}{8\pi e} - \frac{\mu_i}{\mu_e} J_e,$$
$$E = -\sqrt{z}, \quad j = e\left[\frac{\mu_i z'}{8\pi e} - \left(1 + \frac{\mu_i}{\mu_e}\right) J_e\right]. \tag{6}$$

For the functions $J_e$ and z, we obtain the problem

$$J_e' = f; \tag{7}$$

$$z' = -8\pi e \frac{J_{eD}(1 + D_{iD}/D_{eD}) - J_e(1 + \mu_i/\mu_e) + 2D_{iD} n_D x_D'}{\mu_i}; \tag{8}$$

$$y = 0, \; J_e = 0; \; y = y_D, \; z = 0. \tag{9}$$

We note that for $y = y_D$ the functions $n_i$, $n_e$, determined by Eqs. (6), have singularities. This is related to the fact that near the outer boundary of the Debye layer there is a transitional layer [15], in which the degenerate system of equations (1) is inapplicable. For this reason, generally speaking, there arises the question of the method for calculating the second term in the expression for f in the vicinity of the point $y = y_D$. However, since in this neighborhood, the first term in expression (2) is the main term, this question is not significant. In this paper, the quantity $n_e$ in the term $f_2$ was determined as the smaller of the quantities $J_e/(\mu_e\sqrt{z})$, $n_{er}$ ($n_{er}$ is the local, chemically equilibrium density of charged particles). We note that the introduction here of the factor 0.1 in front of the quantity $n_{er}$ does not affect the results of the solution, which confirms the assumed smallness of the second term in the expression for f near the point $y = y_D$.

The problem formulated was solved for fixed $y_D$. After its solution, the corresponding value of the current density at the electrode j and the voltage drop in the Debye layer $\psi_w$

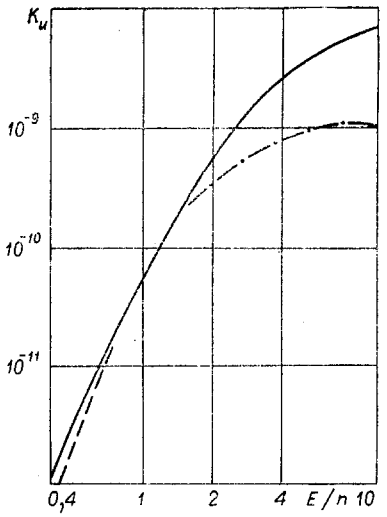

Fig. 1

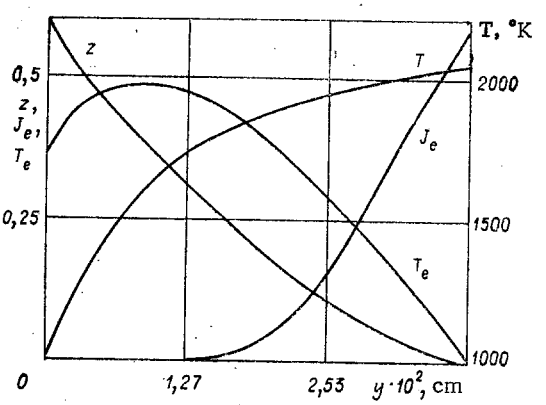

Fig. 2

were determined. By repeating this process for different $y_D$ it is possible to obtain a complete parametric description of the current–voltage characteristics of the Debye layer.

This approach is applicable if the function $y_D(j)$ is a monotonically increasing function; this is precisely the case under the conditions examined in this work. On the other hand, for a nonmonotonic dependence the problem can be solved by an analogous method with a given value of j.

To solve the problem formulated we used an iterative process, at each step of which Eq. (7) was investigated with the help of the boundary condition (9) [the Runge–Kutta method was used; Eq. (4) at each node of the difference grid was solved by Newton's method] and Eq. (8) was integrated with the second boundary condition (9) (using Simpson's rule).

The analytic solution obtained in the approximation of an isothermal plasma [1] was used as the initial approximation.

We present below the results of the calculations performed for the following conditions: the pressure equaled $10^5$ Pa, the molar concentration of potassium atoms in the Debye layer was constant and equal to 1%, and the temperature of the surface of the electrode was 1000°K. For the temperature distribution in the plasma, we choose the two typical working profiles shown in Figs. 2 and 3 and referring, respectively, to conditions at the beginning and end of the channel of a large-scale MHD generator [16].

Figures 2 and 3 show the distributions of the functions z (in $10^9$ $V^2 \cdot cm^{-2}$), $J_e$ (in $10^{17}$ $cm^2 \cdot sec^{-1}$), and $T_e$ (in $2 \cdot 10^5$°K) for the indicated profiles of the plasma temperature with $j = -13$ mA/cm$^2$ ($\psi_w = -516$ V), $j = -6.9$ mA/cm$^2$ ($\psi_w = -534$ V), respectively. The distribution in Figs. 2 and 3 are qualitatively similar, although the corresponding numerical values in Fig. 2 are somewhat higher. It is interesting that for the monotonic profile of the electric field, the profile of the electron temperature is nonmonotonic, which is related to the strong change in the density of the gas in the Debye layer (the function E/n nonmonotonic).

The outer part of the Debye layer makes the main contribution to the generation of charged particles. This is related to the fact that in the inner (next to the cathode) part of the Debye layer, due to the decrease in the gas temperature, ionization of potassium atoms with collisions with water molecules proceeds very weakly. Ionization in collisions with electrons, due to the smallness of the number of primary electrons, likewise proceeds very weakly (we note that if the first term in the expression for f is dropped, then the problem under examination has the solution $n_e = J_e = 0$).

Figure 4 shows the current–voltage characteristics (the curves 1, 3 correspond to the temperature profiles presented in Figs. 2 and 3). The curves 2 and 4 represent the current–voltage characteristics calculated in the approximation of an isothermal plasma using the analytic formulas in [1]. It is easy to see that for $|\psi_w| \lesssim 200$ V, isothermality has no effect at all, and for 200 V $\lesssim |\psi_w| \lesssim$ 400 V it does not exceed ~20%. Such a weak effect is apparently related to the smallness of the number of electrons in the inner part of the Debye layer, as discussed above.

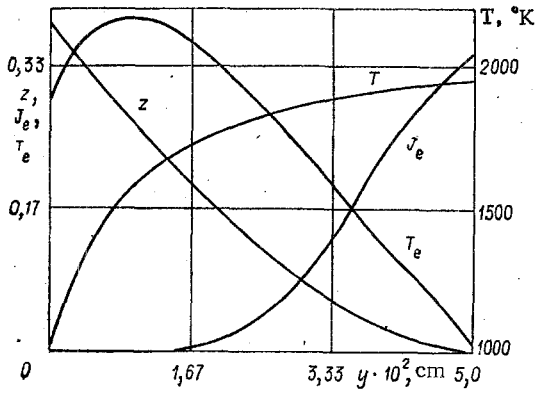


Fig. 3

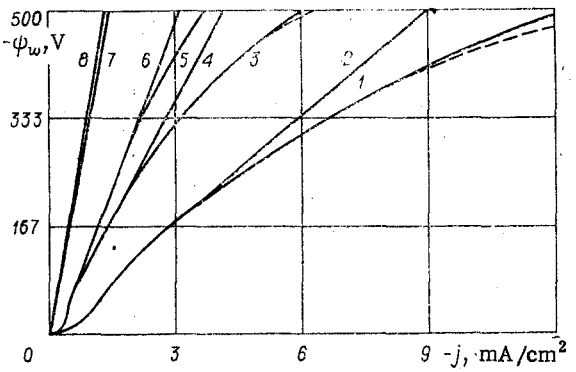


Fig. 4

To estimate the effect of nonisothermality for small concentrations of potassium atoms, the calculation was performed with a molar fraction an order of magnitude lower of potassium ions (0.1%). The current–voltage characteristics are presented in curves 5 and 7 in Fig. 4; curves 6 and 8 show the results of the calculation using the analytic formulas in the weak field limit (with $T_e = T$). It is evident that the effect in this case is even weaker.

All results presented above were obtained under the assumption that emission from the cathode is completely absent. However, in the presence of a strong field near the cathode, even a small, compared with the total current, emission current due to the avalanche-like growth in the process of ionization can strongly affect the parameters of the plasma in the Debye layer. The role of the emission current can be estimated using the relation

$$\tilde{j}_e(y) = j_e(0) \exp\left\{\int_0^y \frac{nK_u}{\mu_e E}\, dy\right\},$$

where $\tilde{j}_e$ is the correction to the current density of electrons, related to the presence of the emission current $j_e(0)$. Thus, under the conditions of Fig. 2 this correction is small, i.e., the emission is not significant, if $j_e(0) \lesssim 2 \cdot 10^{-3}$ mA/cm$^2$. Using the Richardson–Dashman–Schottky formula, we find that the thermoemission current with a cathode temperature of 1000°K is less than the indicated magnitude, if the electronic work function on the cathode surface $\varphi > 2.8$ eV. The ion-electron emission current satisfies the inequality presented, if the corresponding emission coefficient $\gamma_i \lesssim 2 \cdot 10^{-4}$. Since, as already noted above, potassium ions, which cannot knock out an electron from the cathodes with a work function exceeding one half the ionization potential of the potassium ion, $\varphi > 2.2$ eV, make the main contribution to the ionic current, it may be expected that the quantity $\gamma_i$ is quite small and the ion-electron emission current is insignificant. For this reason, under the conditions examined the main source of electron emission is the photoeffect, arising due to the radiation of highly excited electronic states of molecules, primarily nitrogen molecules. To estimate the influence of this effect we performed a calculation in which the boundary condition for $j_e$ was taken as the emission current $j_e(0)$, determined from the formula

$$j_e(0) = \frac{1}{2}\gamma_p \theta \int_0^{y_D} n_{N_2} n_e \langle v\sigma_{exc} \rangle\, dy.$$

Here $\gamma_p$ is the photoemission coefficient; $\sigma_{exc}$ is the cross section for excitation of radiation; the factor $\theta$ takes into account the de-excitation of the emitting states in collisions with molecules, as well as the correction to the emission current related to the presence of the reverse current. The quantity $\gamma_p$ for most metals increases sharply with increasing photon energy $\varepsilon_p$ for $\varepsilon_p \lesssim 10$ eV and remains approximately constant at the level of 0.03–0.1 for $\varepsilon_p \gtrsim 10$ eV [17]. In the calculation, we used the value $\gamma_p = 0.1$ and the cross section of excitation of radiation of nitrogen molecules with $\varepsilon_p \gtrsim 10$ eV from [18]. The de-excitation constant of the emitting states was assumed to be the same as in air [19]. Absorption of radiation in the Debye layer was neglected, which gives an upper limit estimate for $j_e(0)$. The result of the calculation of the current-voltage characteristics taking into account the photoeffect is shown in Fig. 4 by the dashed lines. It is evident that in the range of parameters examined, the influence of the photoeffect is small.

In all cases examined in this work, the current–voltage characteristic of the Debye layer is monotonic (there are no descending sections). On the other hand, it is known from experiments that when some critical value of the current density is reached, the diffusion form of the discharge transforms into the arc form (breakdown of the near-electrode layer occurs). Evidently, this breakdown is a result of the development of some instability. To describe this instability the model examined in this paper can probably be used. In this connection, we note that although the nonisothermality of the plasma in accordance with the above discussion has virtually no effect on the current–voltage characteristics in the near-breakdown region, this nonisothermality can be determining in the mechanism responsible for breakdown.

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