# EFFECTS OF ELECTRON DETACHMENT FROM NEGATIVE IONS ON THE CURRENT-FLOW MECHANISM IN A MEDIUM-PRESSURE GLOW DISCHARGE

V. V. Breev, S. V. Dvurechenskii, and S. V. Pashkin UDC 537.525

Medium-pressure glow discharges are widely used in pumping fast-flow molecular lasers. Electron detechment from negative ions is important in relation to the current-flow mechanism and to the description of the energy balance and the discharge instabilities. Although there is some experimental evidence for an important role for detachment in the mechanism [1], it is still largely an open question how such processes can influence the discharge characteristics.

There are three groups of electron-detachment processes from negative ions in a medium-pressure glow discharge:

1) electron detachment in the collision of negative ions with molecules [2]:

$$O^- + H_2 \rightarrow H_2O + e,\ k_d = 6\cdot10^{-10}\ \mathrm{cm^3/sec}; \tag{1}$$

2) detachment in the collision of negative ions with metastable particles, with the concentration of these increasing with the energy deposition in the discharge [2]:

$$O_2^- + O \rightarrow O_3 + e,\ k_d = 3\cdot10^{-10}\ \mathrm{cm^3/sec}; \tag{2}$$

$$O_2^- + O_2(^1\Delta_g) \rightarrow 2O_2 + e,\ k_d = 2\cdot10^{-10}\ \mathrm{cm^3/sec} \tag{3}$$

3) detachment when negative ions collide with molecules due to the high kinetic energy of the ions taken up from the electric field in the discharge [2]:

$$O_2^- + O_2 + 0.43\,\mathrm{eV} \rightarrow 2O_2 - e,\ k_d = 2.2\cdot10^{-18}\ \mathrm{cm^3/sec} \tag{4}$$
$$T = 300\ \mathrm{K}\ \text{and}\ k_d = 3\cdot10^{-14}\ \text{at}\ T = 600\ \mathrm{K}.$$

The rate constants for these types of elementary processes are dependent very substantially on the type of negative ion, which remains somewhat undetermined because of the abundance of fast ion-molecule reactions and the presence of uncontrolled impurities under real conditions. Therefore, in a numerical study it is reasonable to vary the detachment rate constant within fairly wide limits.

The effects of a type (1) process have been examined when the detachment frequency $\nu_d$ is independent of time as regards the parameters of a positive column (PC) [3]: the voltage-current characteristic (VCC), the distribution of the electron concentration $q_e$, and the same for the positive and negative ions $q_+$ and $q_-$. In an inhomogeneous PC, detachment usually produces a voltage increase across the PC. A study has been made [4] of the effects of processes such as (2) on a PC when $\nu_d$ increases with the energy deposition, where it was shown that the accumulation of detachment particles alters the electric-field distribution in the discharge and produces a nonmonotone distribution of the ion currents in the PC, which contain striations moving towards the anode.

No previous detailed studies have been made of the effects of detachment of the type of (1) on the anode region (AR) in the discharge, or of the effects of processes of the type of (4) on the PC and AR. The present study fills this gap.

A difference from [3] is that the current-flow mechanism is considered without assuming that the plasma is quasineutral, which thus incorporates the anode region.

A numerical solution was obtained to a system of equations describing a three-component glow-discharge plasma in the one-dimensional approximation (the plasma contains positive and

---

Troitsk. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 6, pp. 25-31, November-December, 1983. Original article submitted October 14, 1982.

0021-8944/83/2406-0786$07.50

negative ions together with electrons); see [5] for a detailed analysis of this system of equations:

$$\partial q_+/\partial t + \partial(\mu_+ q_+ E)/\partial x = \nu_i q_e - k_e q_e q_+ - k_r q_- q_+; \tag{5}$$

$$\partial q_-/\partial t - \partial(\mu_- q_- E)/\partial x = \nu_a q_e - k_r q_- q_+ - \nu_d q_-; \tag{6}$$

$$j = \sigma E,\ \partial j/\partial x = 0,\ \sigma \equiv \mu_+ q_+ + \mu_- q_- + \mu_e q_e; \tag{7}$$

$$\partial E/\partial x = 4\pi q,\ q \equiv q_+ - q_- - q_e; \tag{8}$$

$$U = j\left(R_\text{b} + \int_0^L \frac{dx}{\sigma}\right), \tag{9}$$

where $\nu_i$, $\nu_a$, $\nu_d$ are the frequencies of ionization, attachment, and detachment; $k_e$ and $k_r$, rate constants for electron—ion and ion—ion recombination; $\mu_e$, $\mu_+$, $\mu_-$, mobilities of the electrons and of the positive and negative ions; j, current density; $\sigma$, conductivity; q, space-charge density; U, voltage from the power supply; and $R_b$, ballast resistor.

We denote by $\sigma + \mu_e q \equiv S$ the quasineutral conductivity, with $S \equiv \sigma$ if $q = 0$. We substitute $E = j/\sigma$ from (7) into (8) and determine j from (9) to get

$$q = \frac{1}{4\pi}\,\frac{U}{R_\text{б} + \int \frac{dx}{S - \mu_e q}}\,\frac{\partial}{\partial x}\left(\frac{1}{S - \mu_e q}\right) \tag{10}$$

as an integrodifferential equation of q, which will be used instead of (8).

The boundary conditions for (5) and (6) are formulated as follows: $q_+|_A = 0$, $q_-|_C = 0$, with A and C denoting the anode and cathode, correspondingly, here and in the figures. The boundary condition for (10) is put as a zero space charge at the cathode boundary, i.e., we specify quasineutrality: $q|_C = 0$.

Therefore, the cathode boundary in this case denotes the actual boundary of the cathode region — positive column (subsequently called the cathode), and we eliminate the cathode region from consideration. Then we subtract the cathode potential drop $U_C = 400$ V from the source voltage.

We solve (5) and (6) for $q_+$ and $q_-$ by means of standard difference schemes, i.e., we perform a step in time and determine $S = aq_+ + bq_-$, $a = \mu_+ + \mu_e$, $b = \mu_- - \mu_e$ in the new time layer. It is then necessary to solve (10) for S with respect to q(x). We describe a successive-approximation procedure for (10) on a difference net in $x{:}x_i = ih$, $i = 0, 1, \ldots, N$, with h the space step. As the zeroth approximation, we take $q^0$ from the previous time layer: we put $\dfrac{U}{R_\text{b} + \int_0^L \frac{dx}{S - \mu_e q}} = j^0$. We substitute $j^0$ in (10) and integrate the left part by means of the trapezium formula $\dfrac{q_i^1 + q_{i+1}^1}{2}h = \dfrac{j^0}{4\pi}\left(\dfrac{1}{S_{i+1} - \mu_e q_{i+1}^1} - \dfrac{1}{S_i - \mu_e q_i^1}\right)$ to get an algebraic equation for $q_{i+1}^1$. As we know that $q|_C = 0$ at the cathode, we calculate the distribution $q^1(x)$ successively up to the anode. The result $q^1$ will be used as the new approximation and the procedure is repeated. The convergence is checked and the calculations are continued until good accuracy is attained. Then we determine j from (9), $\sigma = S - \mu_e q$, and also E from (7). We perform a new time step, and so on.

The values of the coefficients in (5) and (6) were taken from [6], apart from $\nu_d$. We took the detachment frequency in processes of the type of (1) as constant: $\nu_d = 3 \cdot 10^4$ sec$^{-1}$, while the rate constant for detachment of the type of (1) was taken in the form

$$k_d = A_0 \mu_- E \exp(-Bp/E); \tag{11}$$

$$k_d = A_0 \mu_- E \exp(Bp^2/E^2), \tag{11a}$$

where one usually has $A_0 = 5.6 \cdot 10^{-16}$ cm$^2$, $B_1 = 113$ m•Pa/V, $B_2 = 2430$ m$^2$•Pa$^2$/V$^2$; then $k_d = 1.1 \cdot 10^{-14}$ cm$^3$/sec for E/p = 27 V/m•Pa.

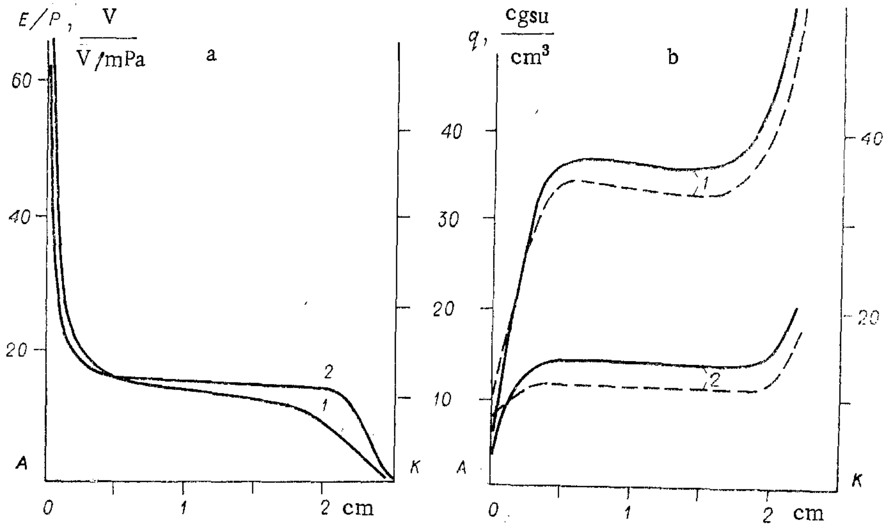

Fig. 1

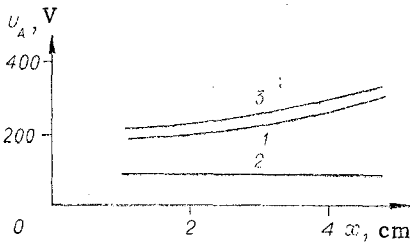

Fig. 2

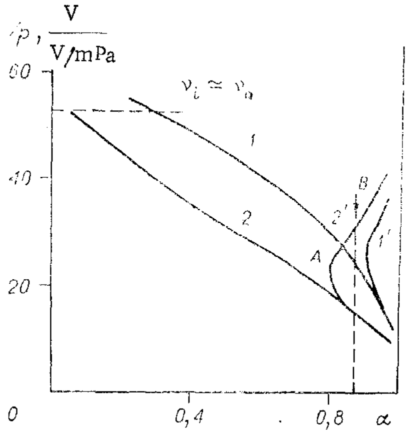

Fig. 3

During the solution of the nonstationary problem, we found stationary distributions for $q_+$, $q_-$, $q_e$, and E for all the given values of the detachment coefficients of the type of (1) or (4).

We now consider the results for detachment of the type of (1) on the AR and also on the VCC. We assume that detachment that reduces the charge density in the AR increases the size of the anode layer, and therefore the anode potential drop $U_A$ should increase. Our results, however, show that such arguments are incorrect, because it must be borne in mind that detachment alters also the characteristics of the PC, and therefore affects the boundary conditions for the AR at the boundary of the AR and PC. Figure 1a shows distributions of E/p, while Fig. 1b shows the concentrations of positive ions (solid lines) and negative ones (broken lines) in the gap between the electrodes, with curves 1 and 2 corresponding to the following detachment frequencies: 1) $\nu_d = 0$; 2) $\nu_d = 3 \cdot 10^4$ sec$^{-1}$. The pressure was taken as 8 kPa and the current density as $j = 5$ mA/cm$^2$. Figure 1 shows that in the presence of detachment (case 2) the ion concentration is reduced by a substantial factor, while there is a slight rise in the electric field strength (a) in the PC [3] and a reduction in the field in the AR by comparison with the case $\nu_d = 0$.

Figure 2 shows the dependence of the anode potential drop on the distance between the electrodes for the same j and p as in Fig. 1. The increase in $U_A$ with h agrees with experiment [7]. Figure 2 implies that the anode potential drop in the case of constant-frequency detachment (curve 2) is lower than in the absence of detachment (curve 1), while the dependence of $U_A$ on h is weaker.

The behavior of $U_A$(h) indicates only a small role for detachment under the conditions of [7] and that the PC was inhomogeneous along the discharge current.

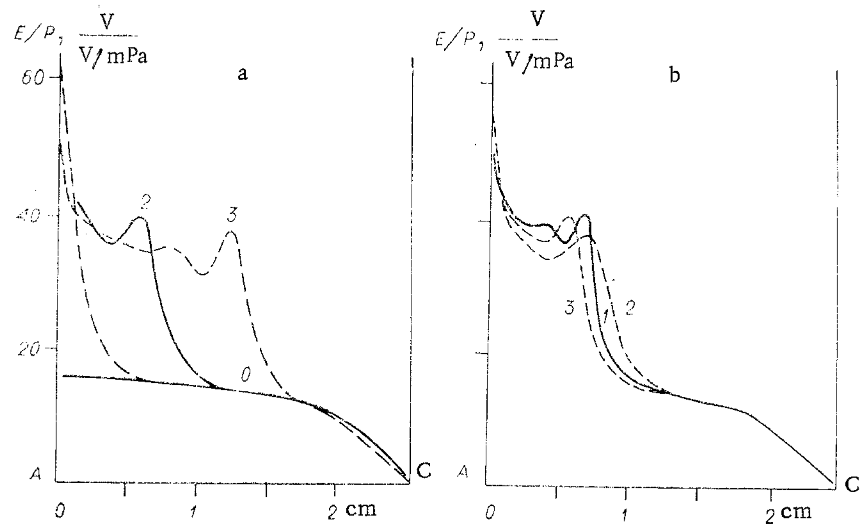

Fig. 4

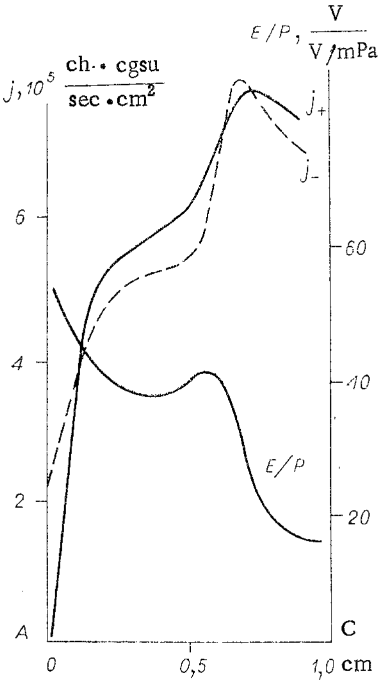

Fig. 5

The case of detachment of the type of (4) is more complicated, as the detachment frequency is a function of the electric field. We consider this in more detail. We assume that the plasma is stationary and write the condition for quasineutrality for the weakly inhomogeneous glow discharge [3]:

$$(\nu_i + \nu_a)q_e = 2k_r q_+ q_- + k_e q_e q_+ + \nu_d q_- . \qquad (12)$$

It can be shown that in $\alpha = j_e/j$, E/p coordinates (7) is represented by curves that differ substantially for $\nu_d = 0$ (curves 1 and 2 in Fig. 3) and $\nu_d = \nu_d(E)$ (curves 1' and 2'), with the relationship taken from (11). The numbers 1' and 2' correspond to different values of the current density, with the value of j corresponding to 1' less than that of j corresponding to 2'.

In the case $\nu_d$ = const there is a single-valued relation between α and E/p. In the case $\nu_d = \nu_d(E/p)$, a given ratio of the ion and electron currents may correspond to two values of the electric field, one value, or none at all. The minimum in α(E/p) for a quasineutral plasma is readily found if we differentiate (12) with respect to E and equate dα/dE to zero (point A in Fig. 3):

$$\nu_a\hat{\nu}_a \simeq \nu_d\hat{\nu}_d \frac{1-\alpha}{2\alpha} \frac{\mu_e}{\mu_-}, \text{ where } \hat{\nu} \equiv \frac{\partial \ln \nu}{\partial \ln E}.$$

Near the cathode, $\alpha \simeq 1$, with a fall to the anode in accordance with the law defined by

$$j\frac{d\alpha}{dx} = \frac{dj_e}{dx} \simeq (\nu_i - \nu_a)\, q_e - k_e q_e q_+ + \nu_d q_- \tag{13}$$

($j_e$ is the electron current density), which follows from (5) and (6). The value of E/p increases monotonically near the anode (point B in Fig. 3). In the case $\nu_d = 0$, the homogeneous state in the PC is attained with real values for the coefficients at $\nu_i \simeq \nu_\alpha$ [3], while in the case $\nu_\alpha = 0$ it is attained at $\nu_i\mu_e E \simeq k_e j$, and in the case $\nu_\alpha$, $\nu_d \neq 0$ at $\nu_a, \nu_d \neq 0$, where $\nu_a \simeq \nu_d \frac{1-\alpha}{2\alpha}\frac{\mu_e}{\mu_-}$.

We have $\hat{\nu}_d > \hat{\nu}_\alpha$ for these values for the coefficients, so point B should lie at values of $\alpha$ larger than the minimum in $\alpha(E/p)$, and states of the PC plasma lying to the left of point B in Fig. 3 are not realized in practice.

Therefore, if we consider the behavior of the PC plasma parameters from cathode to anode, in the case $\nu_d = \nu_d(E/p)$ there can be a marked discontinuity in the electric field (with deviation from quasineutrality) without discontinuity in the ion currents at sufficiently large distances between the electrodes.

On the cathode side of this step, the charged-particle balance and the electric field are determined as usual [3] by the balance between the rates of attachment (for $\partial q/\partial x$) and recombination (for $\partial q_+/\partial x$), and the ion currents increase from the cathode to the step, as (5), (6), and (12) show. On the anode side of the step, there is a region where the electric field strengths are high, and here the charged-particle balance and E/p are determined by detachment ($\partial q_-/\partial x$) and ionization ($\partial q_+/\partial x$), with the ion currents falling from the step towards the anode [5, 6].

The values of $B_1$ in (11) or $B_2$ in (11a) characterize the rate at which $\nu_d$ increases with the electric field. Calculations show that change in $B_1$ or $B_2$ with the corresponding choice of $A_0$ does not have a substantial effect on the field distribution in the PC and AR.

Figure 4 shows calculated E/p distributions as affected by (a) the amplitude $A_0$ of the detachment as specified by (11) (B = 150) or (b) by the slope $B_1$ or $B_2$ in (11) and (11a). If the value of $A_0$ is small (curve 1 in Fig. 4a, $A_0 = 2.8\cdot10^{-16}$), the distribution of the PC and AR parameters is analogous to that in the case $\nu_d = 0$ (curve 1 in Fig. 1a, which corresponds to the stationary distribution of E/p in the PC obtained by the method of [3], which is shown by curve 0 in Fig. 4a).

As A increases, an elevated-field region EFR arises at the anode, which is separated by a sharp step in the field from the rest of the PC, in accordance with the above current-flow mechanism. Above a certain value of $A_0$, the coordinate dependence of the electric field becomes nonmonotone, and in the EFR adjoining the anode there may be one or more local minima (curves 2 - $A_0 = 2.8\cdot10^{-16}$, 3 - $A_0 = 8.4\cdot10^{-6}$ in Fig. 4a). Figure 5 shows the distribution of the ion currents in the PC for these cases, which agrees with the above current-flow mechanism.

The calculations also show that at a given current density the potential difference across the discharge increases with $A_0$ in (11) and (11a). The size of the EFR, including the AR, is the larger the higher the pressure and the lower j (this dependence on j and p is also characteristic for the AR in the absence of detachment [8]). These laws apply also to the potential difference on this region: The field strength falls as the current density increases and the pressure falls. If the value of this potential difference is comparable with the potential difference across the PC, and the $U_{efr}(j)$ dependence is strong, then the potential difference across the entire gap may decrease as the current density rises. A negative VCC for the discharge was in fact obtained in the calculations ($A_0 = 5.6\cdot10^{-16}$, $B_1 = 150$), for example in the region of $j \simeq 2$-10 mA/cm$^2$ at p = 8 kPa, when $U_{pc}(j)$ increases slightly but $U_{efr}(j)$ falls rapidly. On further increase in the current density, $U_{pc}$ increases more rapidly, while $U_{efr}$ is small and on the whole the VCC for the discharge at $j > 10$ mA/cm$^2$ is a rising one. The VCC has a minimum at $j \simeq 10$ mA/cm$^2$. As the pressure falls, the minimum on the VCC is attained at smaller j and vice versa.

The presence of an EFR with a falling VCC should affect the stability of the discharge with respect to the formation of spots and filaments near the anode. This is a familiar phenomenon in experiment, and one of the mechanisms for it may be that described above.

We now consider the effects of detachment of this type on $U_A$. Detachment of small amplitude $A_0 \sim 2.8 \cdot 10^{-16}$ is expressed in (6) as an increase in the size of the AR without effect on the processes in the PC, and, correspondingly, in an increase in $U_A$ (curve 3 in Fig. 2). Any further increase in A results in a region of quasineutral plasma with elevated values of E/p near the anode, which it is undesirable to consider as the AR, while the value of $\int E dx$ over this region should not be taken as the anode potential drop. Then the value $\int E dx$ taken over this region near the anode, where there is a considerable deviation from quasineutrality, is much smaller than in the absence of detachment on account of the EFR.

## LITERATURE CITED

1. A. A. Besshaposhnikov, V. I. Blokhin, et al., "A study of the formation of ozone in an elevated-pressure glow discharge in a flow of air and technical nitrogen," Khim. Vys. Energ., 15, No. 2 (1982).
2. B. M. Smirnov, Negative Ions [in Russian], Atomizdat, Moscow (1978).
3. V. V. Breev and S. V. Pashkin, A Numerical Study of the Stationary States of the Positive Column in a High-Voltage Diffuse Discharge at Medium Pressures [in Russian], Preprint No. 2956, IAE, Moscow (1978).
4. A. A. Besshaposhnikov, V. I. Blokhin, et al., "Stratification of a glow discharge in a gas flow with elevated energy deposition," Dokl. Akad. Nauk SSSR, 262, No. 1 (1982).
5. V. V. Breev, S. V. Dvurechenskii, and S. V. Pashkin, "A numerical study of nonstationary processes in the positive column of a high-voltage diffuse discharge: analysis of the system of equations," Teplofiz. Vys. Temp., 17, No. 1 (1979).
6. Yu. S. Akishev, S. V. Dvurechenskii, et al., "A study of elementary processes in a low-temperature plasma," Fiz. Plazmy, 7, No. 6 (1981).
7. V. I. Blokhin and S. V. Pashkin, "A study of the anode potential drop in a high-voltage diffuse discharge in a transverse flow of air," Teplofiz. Vys. Temp., 14, No. 2 (1976).
8. V. I. Blokhin, V. V. Breev, et al., "A study of the anode region in a gas discharge controlled by bulk processes," Teplofiz. Vys. Temp., 19, No. 5 (1981).