THE ROLE OF THE HETEROGENEOUS ATOM RECOMBINATION ON THE PARTICLE BALANCE IN AN OXYGEN DC GLOW DISCHARGE

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ABSTRACT

Numerical analysis of the discharge characteristics was performed considering different values of atom recombination and metastables deactivation coefficients on the wall and the results were compared with experiments.

1. INTRODUCTION

The active particles responsible for an enhanced chemical reactivity in homogeneous or heterogeneous reactions, respectively, are produced either directly in plasma phase or they can originate indirectly through some surface processes. In the steady state, in which the dc discharge is sustained by an external electric field, the concentrations of particles in the plasma result from balancing between their total production and the total losses. The particles are produced and destroyed in mutual collisions, by the diffusion and recombination as well as the deactivation on the wall of experimental tube or vessel.

2. THEORETICAL APPROACH

The concentrations of the most important particles in the positive column of dc glow discharge in oxygen were analysed for the model involving O^- and O_2^+ ions, electrons, atoms and molecules in the ground and metastable ($a^1\Delta_g$) states. The particle balance equations can be schematically written in the form

$$(1) \qquad P_i = \frac{N_i}{\tau_{D_i}} + L_i$$

which are completed by the conservation low of the number of particles

$$(2) \qquad N = \frac{1}{2} N_1 + N_2 + N_M$$

where P_i and L_i represent the volume production and loss terms of the above mentioned particles, N_i/τ_{D_i} their diffusion decay to the walls and N is the initial concentration of neutral gas molecules (in (2) indices 1,2,M indicate atoms, neutral and metastable molecules). The exact form of these equations is presented in a preceeding paper[1]; the term $1/\tau_{D_i} = K_{D_i} = D_i \lambda^2/R^2$ was used for metastable molecules and charged particles with an effective diffusion coefficients in the latter case (D_i- diffusion coefficient, R - tube radius, $\lambda = 2{,}405$ is the first root of Bessel function) and the term $1/\tau_W = K_W = k_R \bar{v}/2R$ for atoms (k_R - - recombination coefficient of atoms on the wall, $\bar{v}$ - mean kinetic energy).

The system of equation was solved numerically for the reduced discharge currents I/R from 0,1 to 100 mA/cm in the region of neutral gas concentrations corresponding to NR 3×10^{15} to 3×10^{17} cm^{-2}. The calculations showed that the solution depends strongly on the recombination coefficient k_R, which can vary in a wide range in dependence on the wall material, surface quality and its temperature. Greaves and Linnett[2] report values approximately from 10^{-2} to 1 for metals and 10^{-5} - 10^{-2} for non-metals, oxides and glass. They measured[3] also in temperature region from 20°C to 600°C; k_R changed from $1{,}6 \times 10^{-4}$ to $1{,}4 \times 10^{-2}$. The later experiments of other authors confirmed these results, in principle[4].

Taking into account both the diffusion and effect of heterogeneous reactions on the wall the loss of species can be treated as an effective first order reaction with a total rate coefficient[5] given by

$$(3) \qquad K_{DW} = \frac{1}{\tau_{DW}} = \frac{1}{\tau_D + \tau_W} = \frac{K_D \cdot K_W}{K_D + K_W}$$

According to the ratio of K_D/K_W in (3) the decay process is limited by the diffusion or by the surface processes and as a consequence either a radial density distribution of atoms or the constant dissociation degree across the tube is established. The diffusion limitation, $K_W/K_D > 10$, is practically reached for $NR > 1.4 \times 10^{16}/k_R$ ($ND_1 = 7.89 \times 10^{18}$ cm^{-1}s^{-1}, $\bar{v} = 6.5 \times 10^4$ cms^{-1} for $T_g = 320$K). It means that k_R would have to be higher than 1×10^{-1} for the values of NR considered in our calculations. On the other hand the ratio $K_D/K_W > 10$ indicates the surface processes limitation for $NR < 1.4 \times 10^{14}/k_R$ if k_R does not exceed the value of 1×10^{-3} in considered region.

3. RESULTS AND DISCUSSION

Calculated voltage - current characteristics are presented in Figs 1,2 for different values of k_R (1×10^{-5} - 1×10^{-3}

and 1 as a limiting case) together with the experimental points of Sabadil[6] and Günterschulze[7]. The dashed area represents the region where the curves for $k_R=1 \times 10^{-3} - 1$ lie and both processes of diffusion and recombination on the wall must be considered simultaneously. The similar set of the curves but for different currents and one fixed value of k_R was obtained in[1]; this shows the tight connection of discharge current with k_R due to a great influence of the dissociation degree on the discharge characteristics.

The voltage-current characteristics are not the only criterion for a suitable choice of value of k_R; the dissociation degree is more sensitive to this coefficient, as it is seen from Figs 3,4 (full lines). The measured values of dissociation degree in oxygen dc glow discharge by different authors range from several up to 10% (compared in[8]). This justifies our choice of $k_R=1 \times 10^{-3}$ in[1] even if it may seem relatively high. The explanation for this higher value is that in real situation the surface of metal electrodes must be taken into account and that the internal surface of glass discharge tube is perhaps contamined by metal particles due to the sputtering of electrodes (e.g. k_R for nickel[2] is 2.8×10^{-2}) and has a higher temperature than it is supposed.

A similar analysis can be performed for metastable deactivation on the wall. In calculations the deactivation coefficient k_D is usually put equal to 1, while Zipf[9] refer the values of $2 \times 10^{-3} - 1 \times 10^{-2}$ and McNeal[10] even only 1.5×10^{-5}. Preliminary calculations for $k_D=2 \times 10^{-3}$ proved the lowering of voltage-current characteristics while the dissociation degree remains practically unchanged in the considered region (dashed lines in Figs 3-5).

It can be concluded, that the heterogeneous reactions on the wall influence the discharge processes in an essential way. The knowledge of exact values of recombination and deactivation coefficients of atoms and molecules on the wall and the wall temperature would be necessary for quantitative comparison of the theory with respective experimental results concerning e.g. the observation of two gradient forms and/or the plasma chemical reactions.

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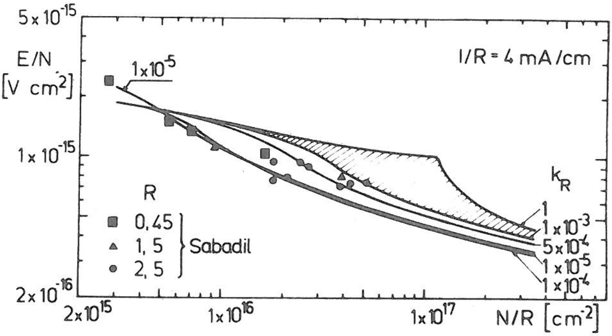

Fig. 1.

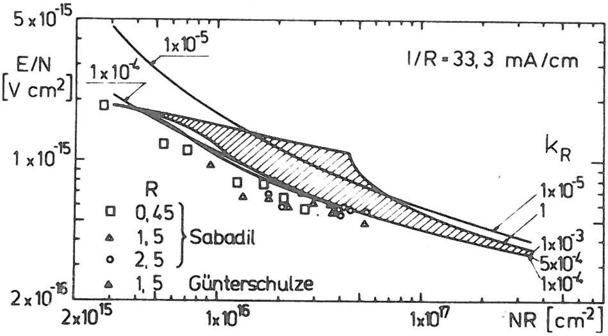

Fig. 2.

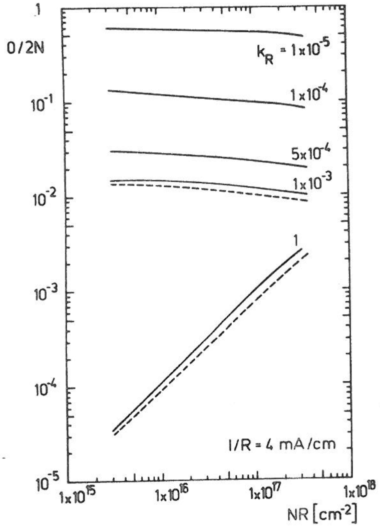

Fig. 3.

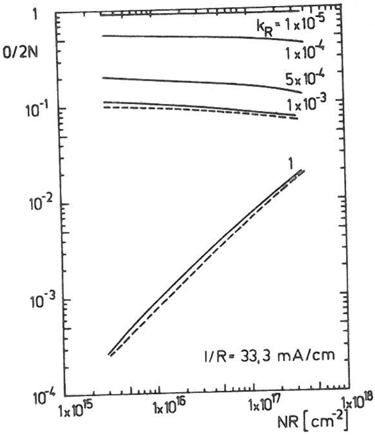

Fig. 4.

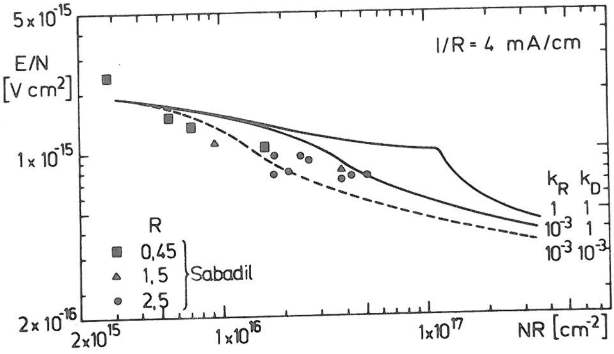

Fig. 5.