INVESTIGATION OF OZON ELEKTROSYNTHESIS.

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ABSTRACT

The process of ozone electrosynthesis in ozonirer, in oxygen, was investigated by the method of numerical experiment. The spatial-temporal distributions of concentrations, electric field intensity and electron energy into the discharge channel so that the the ozcne electrosynthesis kinetic curves were obtained.

1. INTRODUCTION

The mathematical model of ozonizer was set up for the purposes of the investigation of the mechanism and kinetics of the ozone electrosynthesis. This model reflects the following ideas connected with this last one:
the discharge into the ozonizer consist of a number of separate sparks-microdischardges between the dielectric electrodes in the gas gap. The charge transfered from cathode to anode takes place in the microdischarge channel. The value of the transfered charge defines the concentration of microdischarge channel ingredients. Chemical reactions occuring in the microdischarge cause the ozone concentration increase and after the discharge is stoped, ozone will diffuse frome the microdischarge channel to the surrounding gas. Physical and chemical kinetics of ozone electrosynthesis in ozonizer was satisfactorily described the following microdischarge channel ingredients: O_2; O_2^+; O_2^-; O; O^-; O('D); O_3; O_3^-; O_2 and electrons. The 29 reactions connecting these ingredients were considered (1).

Taking into consideration all these moments the plasma dynamics and kinetics (with the assumption of the axissymmetry of the microdischarge channel) were described by the system of differential equations

$$\frac{\partial n_i}{\partial t} + div(\bar{v}_i; n_i) = \sum_i K^i_{m,k}(T,E)\, n_m\, n_L$$

$$n_{i,m,k} = \{O_2, O_2^+, O_2^-; O_3; O_3^-, O, O^-, O('D); O_2^*; e\} \quad \bar{v}_i = b[E] \qquad /1/$$

$$\partial^2\varphi/\partial z^2 + \frac{1}{z}\frac{\partial}{\partial z}\left(z\frac{\partial \varphi}{\partial z}\right) = -\frac{e}{\varepsilon_0}\left([O_2]^+ - [O^-] - [O_2^-] - [O_3^-] - [e]\right) \qquad E = -grad\,\varphi$$

where $K^i_{m,L}$ - rate constant of "i" reaction; bi - mobility of "i" ion; V_i - volosity of ion; φ - electric field potential.
Boundary and initial conditions were following:

$$n_i(0) = 0 \quad i = \{O_2^+; O_2^-, O_2^*; O; O^-; O('D); O_3^-\} \quad [O_2](0) = O_2; [e](0) = e(0)\ [O_3](0) = O_3 \qquad /2/$$

$$\varphi(z, Z, 0) = \varphi_0\frac{Z}{d} \qquad \varphi(z_{max}; Z; t) = \varphi_0\frac{Z}{d} \quad \varphi(z, 0, t) = 0$$

$$\varphi(z,d) = \varphi_0 - \frac{\varepsilon \cdot d}{\varepsilon_0} \int_0^t \bar{v}_e \cdot n_e \cdot dt$$

where φ_0 - initial anode potential; d - value of the discharge gap; z, r - longitudinal and radial variables.

All calculations were made for the dry pure oxygene under atmospheric pressure, discharge gap was equal to 1 mm.

The system /1/ with initial and bondary conditions was solved by the method of finite elements with usual procedure of fractional steps of time. The chemical kinetics was computed by Kunge-Kutta method; the Pousson equation was solved by Buneman method (4).

The conformity of the designed mathematical model with the real process of ozone electrosynthesis was verified and tested in the preliminary calculations in which the electron energy dependence from the local intensity of electric field were defined (5). Besides the Towensend coefficients were calculated. For this purpose experiments in which the initial electrons produced with help of γ -radiation or α -particles were modeled (6). Morover the average molecular temperature in microdischarge channel was difined in the preliminary numerical experiments (7). As it was showen the latter one was equal to electrodes temperature. Detail analysis of the data obtained and literature results allowed us to explain such low value of temperature. The role of volume photoionisation and its influence on the electron avalanche kinetics is negligible (7).

Thus, all numerical experiments on the investigation of the electron avalanche kinetics and dynamics took place under conditions of room temperature, neglecting the volume photoionisation but taking into considaration the volume charge and modification of the anode potential induced by the electron current.

Different variants of numerical experiments distingwished by the initial electron number in the microdischarge channel (10^6 ÷ 10^7) and discharge gap overvoltage value (5-12%). This variations of initial conditions were caused by the absence of the experimental data for these parameters.

2. SPATIAL-TEMPORAL DISTRIBUTIONS OF MICRODISCHARGE PARAMETERS

Experiments which were carried out showed that volume charge defines the development of electron avalanche in our investigation. It cause the the fast stop of average intensity of the electric field into the microdischarge channel when the electron avalanche is approaching to the anode (fig. 1, curve 6,7). Radial intensity is observed in this case. This last fenomenon caused the displacement of maximum of electron concentration from the channel axis.

The appearence of the electron current on the anode at the moment of the electrons avalancho is approching to the anode ($\tau \sim 5$ n sec.) and anode potential reduction (2) sharply breaks gas ioniation in channel. From this moment electron concentrations in the channel diminished also (fig.2).

As the result of the calculation of the spatial-temporal distribution of the concentration of channel ingredients and cloc-

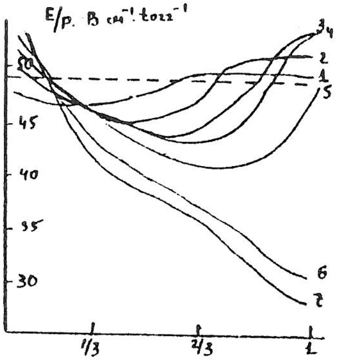

fig.1

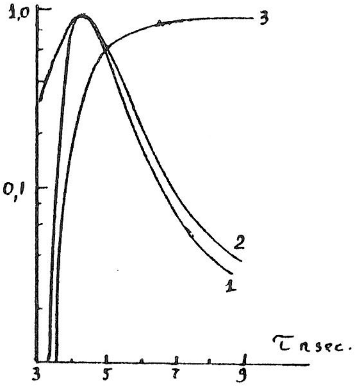

fig.2

Fig.1. The change of electric field intensity on channel axix time of processing 1 - 2,2; 2 - 3,0; 3 - 3,5; 4 - 3,7; 5 - 4,0; 6 - 4,7; 7 - 5,4 ns. $ne(o) = 6 \cdot 10^8$; overvoltage - 8%. Dotted line-initial uniform electric field.

Fig.2. Anode current change and the total number of electrons in microdischarge channel. 1 - $I(t)/I_{max}$. 2 - $Ne(t)/Ne_{max}$ 3 - $q(t)/q_{max}$; ($I_{max} = 5,73$ mA; $q_{max} = 9,74 \cdot 10^{-11}$ Ql; $Ne_{max} = 1,62 \cdot 10^8$) . Initial conditions are the same as on fig.1.

tric potential were obtained (1). It is possible to understand the channel chemical kimetics from the tho analisys of the time reduction of the full number of the channel ingredients. From fig.3 on can see that the electron reactions stop to 10 nsec; ion-molecular and exited states reactions exist up to 100 nsec and the finish reaction in channel as those the neutral particles.

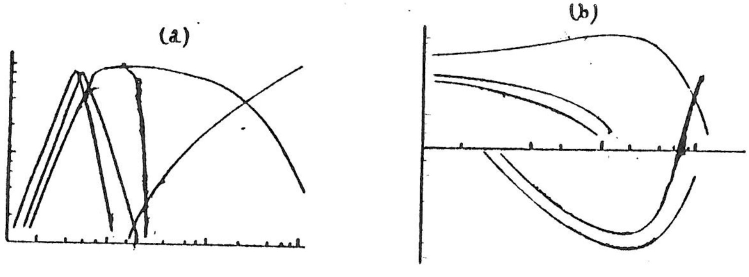

fig.3

Fig.3: The change of total number of channel ingradients

a) $[O_3]_{(0)} = 0$; 1 – $[e]/[e]_m$; 2 – $[O^-]/[O^-]_m$; 3 – $[O_3^-]/[O_3^-]_m$; 4 – $[O]/[O]_m$; 5 – $[O_3]/[O_3]_m$.
$[O_3]_m : [O]_m : [O^-]_m : [e]_m$ = 103:100:0,33:0,22; $[O_3]_m = 1{,}06.10^{11}$

b) $[O_3]_{(0)} > 0$ 1 – $[O]$; 2 – $[O_2]$; 3 – $[O(^1D)]\cdot 100$; 4 – $[O_3]$ when $[O_3]_{(0)}$ = 1%. 5 – $[O_3]$ when $[O_3]_{(0)}$ = 10%. Initial conditions are the same as on fig.1.

The main part of ozone produced through the reaction of the atomic oxygen with molecular oxygen (fig.3) and atomic oxygen concentration dropps in two order up to 2 mksec. It'snecessary to note that ozone formation by the ion-molecular reactions /1. Table 1, react. 11, 12, 20/ is less that 3%, but it is these reactions and electron reaction that define the spatial volume charge configuration and finally define rhe channel chemical kinetics.

The fact of the existance of the limited (stationary) ozone concentration into the ozonizer is well known for a long time. And it was established that this level (10-12%) is defined by the exited states reactions ($O(^1D)$ and O_2), which effectively dissiciate ozone /1, table 1, react. 25-29/. The appearence of those exited particles from the ozone reactions causes the ozone concentration change. Each microdischarge is strongly dependent from the initial concentration od of the last one (fog.3,b b). And in approaching the ozone concentration to the stationary level this ozone concentration change approaches zero. Computional result of the ozone concentration changes by the sole microdischarge is less than 10^{-4}%.

But it is necessary to note that the alternative mechanism of stationary ozone concentration production is possible - the electron energy drop caused by the ozone concentration rises. The latter fenomenon may cause a fast drop of the power of the molecular oxygen dissociation. Existation of low electron levels of ozon is well known (8), but the absence of the quantitative data about this phenomenon made the investigation of this alternative mechanism in range of our model impossible.

Thus, all chemical reactions in the microdischarge channell ended up to 1-2 mKsec that is much less then diffusion time № (5 m sec). This time separation of chemical and diffusial kinetics in the ozone synthesis allowed us to consider the process of the ozone electrosynthesis in ozonizer as an additive accumulation of ozone by each microdischarge.

3. THE KINETICS CHARACTERISTICS OF OZONIZER

The calculations of the kinetics characteristics of the whole ozonizer demanded the correllation between the specific electric power (9), number of microdischarges at the unit of surface? electric and kinetics characteristics of the sole microdischarge. Analysis of the numerical experiment results showed that all spatial-temporal distibutions of avalanche parametrs were termined simply ba the transfered charge i.e. the value of the charge which reached the anode. The transfered charge is an experimentaly known parameter but divergence into the value this parameter exists up to date.

Thus the transfered was the single parameter which connected the change of ozone concentration by the sole microdischarge with the initial ozone concentration in the region near the microdischarge. Defined analytical expession

/3/

between the electric power (u); volume gas velosity (v); breakdown potential (v), transfered charge (q) and the number of microdischarge in time unit (N) allowed us to carry out the calculation of ozone electrosynthesis in whole ozonizer.

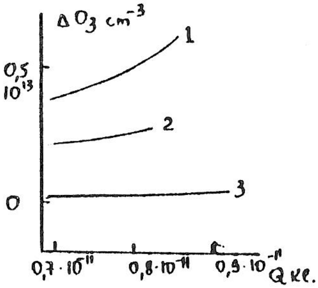

Fig.4. The dependence between the ozone concentration change, transfered change and initial zozone concentration in microdischarge
1 - $[O_3]_{(0)} = 0\%$
2 - $[O_3]_{(0)} = 6\%$
3 - $[O_3]_{(0)} = 10\%$

Diffusion ozone coefficient was equal to laminar value ($0{,}23\,\frac{sm^2}{sec}$) The kinetics curves of ozone electrosynthesis and experimental data (11) are presented in fig.5 in the same place. As on can see these results are in good agreement.

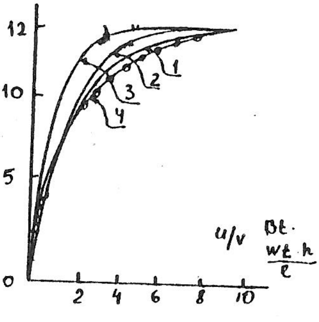

fig.5

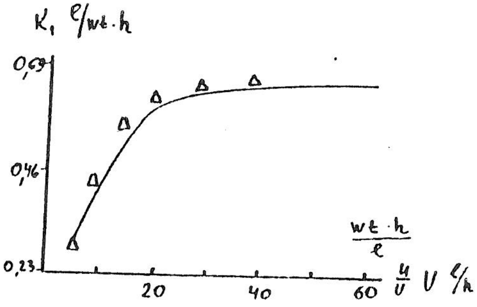

fig.6

Fig.5. Kinetics curves of ozone electrosynthesis. Gas velosity: (1 - 1,5; 2 - 2; 3 - 15 ℓ/h; 4 - data from (9)).

Fig.6. Dependence of ozone decomposition coefficient from gas velosity in ozonizer. (1 - data from (9)).

Such well known empirical parameters of ozonizer as kinetics coefficients of ozone decomposition and production computed with the help of curves (fig.5) are in good agreement with experimental ones (9).

The dependence of ozone decomposition coefficient from gas velosity was established in numerical experimental results (fig. 6) and this dependence was in good agreement with the experiment data too (9).

As the result of our numerical experiments the following facts were discovery and folling data were obtained: electrosynthesis takes place at room temperature; the spatial-temporal distributions of microdischarge parameters were established, the role of volume photoionization, diffusion and individual chemical reactions were cleaved up: the parameter, which defines the power of ozone concentration reduction by the single microdischarge-transfered charge was found and calculated. Kinetics curved were in good agreement with experimental results.

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