STUDIES ON NITROGEN FIXATION IN GLOW DISCHARGES

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ABSTRACT

Nitric oxide synthesis from nitrogen and oxygen has been studied. On the ground of a discussion concerning the rate of the process a semiemprical model equation is proposed. Unknown coefficients have been found from the experimental data. Some properties of the model have been shown and commented.

1. INTRODUCTION

The nitric oxide synthesis in a low pressure arc is known since the beginning of the 20-th century /1,2/ and it has been the subject of numerous discussions and research which focussed mainly on non-equilibric and non-isothermic properties of plasma under these conditions. From the chemical point of view it is manifested in obtaining very high NO concentrations from air and nitrogen-oxygen mixtures. Many interesting publications have been devoted to the subject /3,4/. Much attention has been paid to the process at the Moscow University, Gas Electrochemistry Laboratory /5....12/. The synthesis has been examined in circulation and flow systems. The results have been commented on with regard to the so called power catalysis theory formulated by Kobozew, Wasiliew and Eremin /13/. The theory adopted as its starting point kinetic considerations and the assumption of the linear dependence of the process rate on the power of plasma generating discharges. It leads to the exponential functions including the "energy density" as an important variable. The functions may constitute mathematical models of synthesis processes in the glow discharges plasma.

In our research works dealing with the NO synthesis under analogical conditions, we base consistently on kinetic considerations and in this way we have obtained several variants of equations describing the process both in the circulation system and in the flow system /14,15,16/. In the presently reported work we have undertaken the elaboration of the results obtained in our experiments, adopting the rate equation as the starting point but assuming the power dependence of the rate of the reaction on some chosen factors. As a result we have also obtained the power function as the process model but in a more general form. In spite of introducing some simplifying assumptions the model seems to be an interesting way of recording the results obtained in the strong, non-equilibric glow discharge plasma.

2. DETERMINATION OF THE MODEL EQUATION

Leaving aside the detailed, probable mechanism of NO synthesis in non-isothermic plasma, the basic equation of reversible reaction is adopted as the starting point:

$$1/2\ N_2 + 1/2\ O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO \qquad /1/$$

The rate of the reaction is determined as:

$$r_r = \frac{d\ x_{NO}}{d\ \frac{1}{\dot{V}}} \qquad /2/$$

where: x_{NO} – NO fraction; $\dot{V}$ – the rate of flow of the substrate gas through the reactor. The further procedure aims at finding a function approximating real x_{NO} dependence on variables characterizing the glow discharge plasma.

It may be assumed that rate of the examined reaction can be generally described by the function:

$$r_r = f\ /x_{O_2},\ x_{N_2},\ x_{NO},\ I,\ U,\ p,\ V,\ T,\ geom.\ .../ \qquad /3/$$

where: x – concentration of substances defined by indices; I – current intensity; U – voltage; p – pressure; T – temperature; geom... – geometrical properties of the reactor. The following form of the r_r function has been adopted:

$$r_r = k_1 \cdot x_{N_2}^m \cdot x_{O_2}^n - k_2 \cdot x_{NO} \cdot F \qquad /4/$$

and

$$F = I^{a1} \cdot U^{a2} \cdot p^{a3} \cdot \dot{V}^{a4} \cdot T^{a5} \cdot const \qquad /5/$$

It means that the rate of the process is assumed as dependent on the reactants concentration analogically to the processes taking place outside the plasma region, and the effect of the remaining factors is presented in the form of the power function of unknown exponents. Geometrical properties of a given type of the reactor are included as a constant and in further considerations the discharge temperature is assumed to be dependend on other factors, particularly on

$I, U, p, \dot{V}$. Having done all the above simplifications and integrating equation /5/ the following relation is obtained:

$$x_{NO} = A \cdot x_{N_2}^{m} \cdot x_{O_2}^{n} \left[1 - \exp\left(- B \cdot I^{a1} \cdot U^{a2} \cdot p^{a3} \cdot \dot{V}^{a4}\right)\right] \quad /6/$$

The dependence /6/ may be confronted with the experimental data.

3. EXPERIMENTAL

The experiments have been carried out in a flow reactor with a capillary contraction in the positive column /Fig.1/. Glow discharges were generated by alternating current of 50 Hz frequency. The design of the apparatus in explained in Fig.1.

The experiments have been carried out under different conditions with pressure ranging from 6.7 kPa to 80.4 kPa /50-600mmHg/, the current intensity from 50-300 mA, and the gas flow from $0.83 \cdot 10^{-6}$ to $8.3 \cdot 10^{-6}$ m^3/s /3-30 dm^3/h/.

Various nitrogen-oxygen mixtures have been applied. Typical courses of the dependence of NO concentration in the post-reaction gas on the pressure and on the current intensity have been obtained. An exemplary dependence $x_{NO} = f/I/$ is presented in Fig.2. "Rising" curves for pressures up to 26.8 kPa and "falling" curves for higher pressures are plotted in the diagram.

4. DISCUSSION ON THE RESULTS

Both types of dependences "rising" and "falling" indicated above may be described by means of the equation /7/. The introduction of the discharge power P in the place of I and U proved to be justified. Moreover, it has been observed that for the rising and falling curves the following identical coefficients are obtained: $A = 0.6$: $m = 0.8$: $n = 1$: $a_4 = 0.5$. Further, for the rising curves: $a_1 = a_2 = +1$: $a_3 = +1$: For the falling curves: $a_1 = a_2 = a_3 = -1$. It can be also calculated : for the first case $k_1 = 9.0 \cdot 10^{-7}$, $k_2 = 15 \cdot 10^{-7}$: for the second: $k_1 = 3.24 \cdot 10^5$: $k_2 = 5.4 \cdot 10^5$. Coming back to the initial rate equation and considering the calculated coefficients the following equation is obtained:

$$r_r = k_1 \cdot x_{N_2}^{0.8} \cdot x_{O_2} - k_2 \cdot x_{NO} \cdot P^{\pm 1} \cdot p^{\pm 1} \cdot \dot{V}^{0.5} \quad /7/$$

The peculiar symmetry of the coefficients obtained for the rising curves under lower pressures and for the falling curves under rising pressures is conspicuous. It is worth mentioning that in the optimal case 16% of NO content in the post-reaction gas has been obtained.

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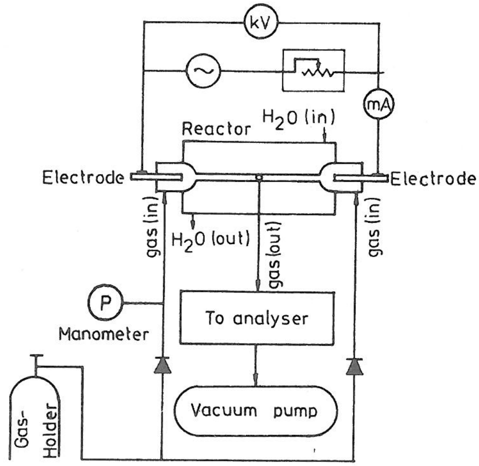

Fig. 1 Experimental set-up

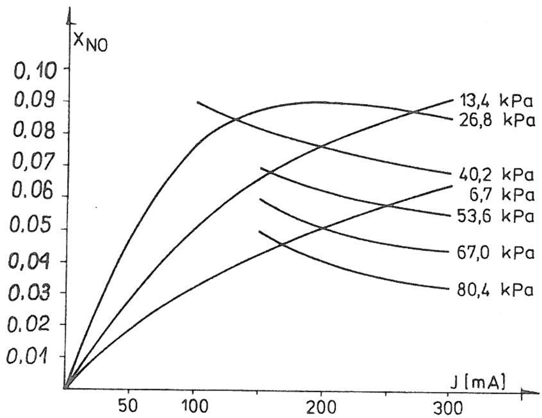

Fig. 2 Effect of current on NO-fraction in gas-products