PLASMOCHEMICAL SYNTHESIS IN CONTINUOUS ELECTRON-BEAM SUSTAINED DISCHARGE

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ABSTRACT

Synthesis of nitrogen hydrides in the plasma of continuous electron-beam sustained discharge is studied to reveal the discharge condition ensuring maximum energy input at the optimum field. Specific power characteristics and the product yield are shown to increase at lower pressure and higher gas velocity with the electron beam density increased accordingly.

1. INTRODUCTION

The continuous electron-beam sustained discharge (CEBSD) has been the subject of numerous studies as a gas laser pumping source. There are practically no reports on the use of the discharge for the initiation of chemical reactions, though there is a number publications on the similar pulse dicharge for the purpose. However, the use of continuous electron-beam sustaned discharge as an activator of chemical reactions compares favorably to that of the pulse discharge as it supports continuous operation of a reactor and high effeciency of the process.

We studied synthesis of nitrogen hydrides in plasma of CEBSD. At the first stage the discharge parameters were correlated to establish conditions of maximum energy input in the electric field optimum for the activation.

2. EXPERIMENTAL

Studies were made on a unit in which the continuity of the discharge is assured by a continuous electron beam (beam density = 1 to 50 mcA/cm^2, electron energy = 100 keV) introduced through a thin aluminium foil into the reaction volume (1 to 3 cm^3). The unit enabled experiments with various gas mixtures (N_2 + H_2 + NH_3) in discharge, different ways of quick mixing of gases beyond the discharge zone, operating pressure of 0.05 to 1.0 atm and gas velocity of 0.5 to 300 m/s. The discharge current density was up to 100 mA/cm^2. Fixed nitrogen in the reaction product was determined by gas chromatographic technique and by back titration.

3. RESULTS

In a chemical process application the discharge variables of importance are electric field and energy input, these being responsible for the vibrational activation of nitrogen gas molecules (1). Plots current vs. voltage obtained at different pressures, gas velocities, and gaseous mixtures enable to reveal conditions leading to higher W, E/p, and unit effeciency. First, presence of hydrogen and, especially, ammonia in the discharge zone leads to a sharp decrease of the discharge energy. Therefore, it is advisable to introduce pure nitrogen into the discharge zone and to add hydrogen or other reagents beyond the zone.

The specific energy input as function of gas (pure nitrogen) velocity is shown in Fig. 1. Within the range of 1 to several dozens of m/s the energy input is almost independent on the gas velocity with E/p constant. The higher E/p the higher energy input. The specific discharge power P is a linear function of the gas velocity. At higher gas velocities (i.e. higher gas flow rate) W decreases due to a lower specific ionisation of gas by electron beam. A more powerful ionisation source (i.e. more dense electron beam, j_e) is required to support high W at high gas velocity.

The specific energy input is one of the variables determining chemical reaction in plasma (1). We fail to exceed 0,15 J/cm^3 atm at the atmospheric pressure, the being not in excess of 6 V/cm.torr (higher E/p lead to discharge strimmering).

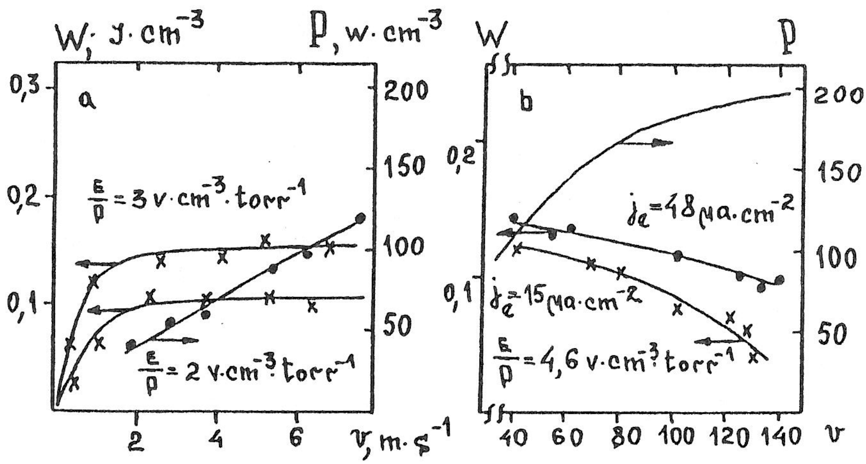

Fig.1. The specific energy input W as function of gas velocity, v.

The energy input increases steeply with lowering pressure due to an increase of the discharge current and the upper limit to E/p value at which uniformly distributed unstrimmered. Thus, at the beam current of 12 mcA/cm^2 the specific energy input increases from 0.05 J/cm^3. atm when the pressure decreases from 1.0 to 0.05 atm. (Fig.2), and the threshold E/p value increases up to abt. 10 V/cm.torr, which is close to the value, optimum for the vibrational activation of nitrogen, and therefore, for the chemical reactions (1).

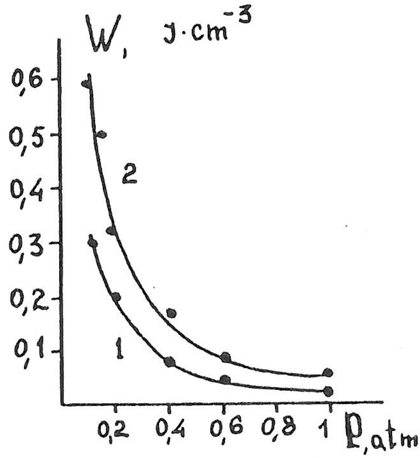

Fig.2. Energy input W as function of pressure, p,
I - mixture $N_2:H_2$ = I:I , 2 - pure N_2.

In studying synthesis of nitrogen hydrides in the CEBSD a stress was made on the correlation between the product yield (i.e. concentration of nitrogen hydrides) and the pressure in the reaction zone. The product yield (calculated as ammonia) in relative units is shown in Fig.3 as function of pressure for the activation of hydrogen-nitrogen gas mixture (curve I) and for activation of pure nitrogen followed by the addition of hydrogen beyond the discharge zone (curves 2 and 3). The plots show the product yield rising steeply with lowering pressure when pure nitrogen is activated. In the experiments with premixed gas the yields were much lower and showed slight pressure dependence.

The product yield as function of the gas velocity is shown in Fig.4. There are the following features of the plots: 1) The maximum yield is produced at the gas velocities about 100 m/s; 2) Maximum conventration of the product and the optimum gas velocity increase as the electron beam density, j_e increases.

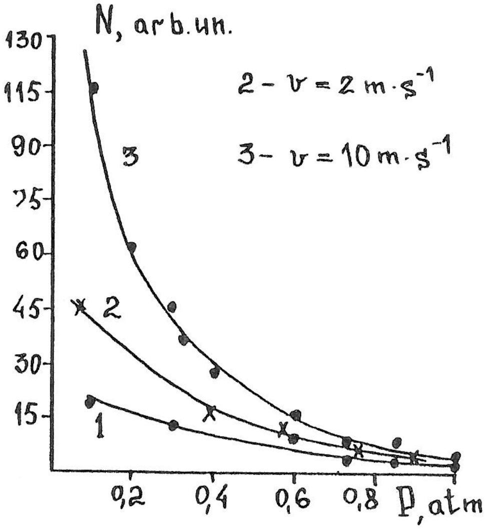

Fig.3. Fixed nitrogen yield, N as function of gas pressure, p, I - premixed gas, N_2:H_2 =I:I; 2,3 - pure nitrogen activation followed by the H_2 addition beyond the discharge zone.

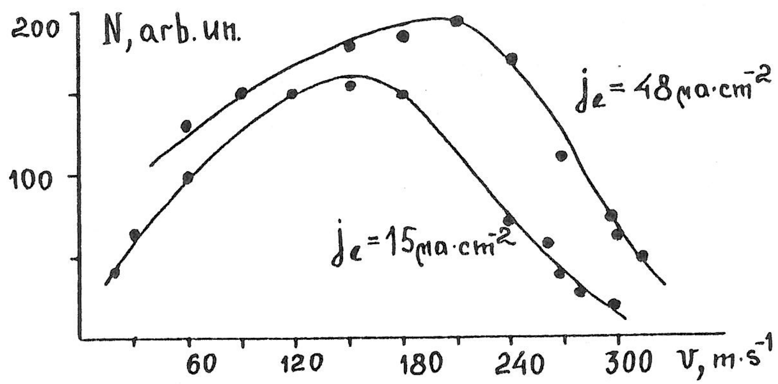

Fig.4. Productyield, N , as function of gas velocity, v .

Furthermore, the yield increasing is occured up to abt. 100 m/s, i.e. in the range with constant, or even decreasing energy input.

This behaviour is explained by a dependance of nitrogen activation in the CEBSD not only on specific energy input, but on the rate of energy input to the gas volume connected with the competition of two processes: vibrational excitation of nitrogen (and its chemical activation therefore) and vibrational-tranlational relaxation is resulted in heating of gas.

The following conclusions can be drawn from the results of the study:

a) CEBSD can produce an efficient activation of nitrogen for the chemical synthesis.

b) Correlations between the energy input, electric field and the gas flow velocity observed point to a predominant role of vibrational activation for plasmochemical synthesis of nitrogen hydrides;

c) Product yield rises as the pressure decreases and as the gas velocity increases, if the electron beam density increases accordingly. The product yield rise spells an appropriate improvement of the unit effeciency.

REFERENCES

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