Hydrogen generation in self-sustained normal DC atmospheric pressure glow discharge in helium-ammonia mixture

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Abstract: The possibility of ammonia dissociation in the atmospheric pressure glow discharges in both the ammonia-helium and ammonia-argon mixtures and hydrogen generation is demonstrated. Influence of the initial ammonia concentration and mixture flow rate through the cathode region on the hydrogen production is investigated. The ammonia conversion efficiency more than 60% was obtained.

Keywords: atmospheric pressure glow discharge, non-equilibrium plasma, hydrogen.

1. Introduction

The main advantages of non-equilibrium plasma technology include moderate operating conditions (atmospheric pressure and temperature exceeding not strongly a room one), rapid start-up, compact system, and so on. Lately, an increasing interest is paid to the development of small-sized portable devices for hydrogen production in which hydrogen is generated in a non-thermal plasma. Hydrogen generation in a microhollow cathode discharge in atmospheric pressure ammonia-argon gas mixture was investigated in [1, 2]. It was shown that about 20% ammonia is dissociated in 6% NH$_3$/Ar gas mixture. According to [2], dissociation of the ammonia molecules in about 95% cases occur due to collisions with electrons and only in 5% cases due to thermal processes.

In this paper, the use of the cathode region non-thermal plasma of atmospheric pressure glow discharge (APGD) [3] is suggested for ammonia conversion. The volume of plasma generated in APGD cathode region is essentially larger than in microdischarge. Therefore we expect ammonia to hydrogen conversion to be more productive in case of the APGD. Therewith, ammonia is the one of main components of the gas vent of packing plants and poultry factories. Deodorization and decontamination of these ventilation gases is actual task. The study of ammonia dissociation in different gases APGDs we consider as first step in the solution of this problem.

2. Experimental setup

The reactor consists of the sealed chamber with two electrodes (Fig. 1). Weakly rounded tungsten anode was 6 mm in diameter and flat copper cathode was 36 mm in dia. The working gas mixture flow of about 1 liter per minute was organized through the discharge chamber. To provide the transit of working gas through the APGD cathode region the exhaust was organized through the three hole (1 mm in diameter) drilled in the cathode centre. The external power supply PS with an output voltage up to 600 V was connected to the APGD via a 100 Ω ballast resistor (R) (Fig. 1). The discharge current could be set in the range of 0.5-1.5 A. DC APGD was ignited by contacting cathode and anode and then separating them. The interelectrode gap was about 2-3 mm. The discharge current of about 0.8 A provided the full cover of the cathode surface area where the holes were located. The discharge current was measured using amperemeter A and the discharge sustaining voltage was determined by a voltmeter V.

The gas flow rates of helium (or argon) and ammonia were controlled by mass flow controllers MFC and the mixing ratio of the two gases is determined by the ratio of the respective flow rates. We could also prepare a gas mixture in gas cylinder beforehand. Typical ammonia concentrations ranged from 1 to 20 %. A vacuum pump was connected to the system to evacuate the APGD chamber before backfilling it with the gas mixture under study. The gas composition at the exit of the APGD reactor
was collected in a previously evacuated cylinder C or monitored by a special spectroscopic analyzer (Fig. 3).

3. Results and discussion
3.1. Spectroscopic investigations

Atomic hydrogen is produced due to plasma decomposition of ammonia. The formation of molecular hydrogen occurs in reactor due to atomic hydrogen recombination. To detect the availability of hydrogen in effluent gas mixture we used an emission spectroscopic method. In the experiment, the mixture of ammonia with helium in the ratio of 1:99 was used. The gas mixture exhaust from reactor was directed into other discharge chamber (Fig. 2) named analyzer. The design of the analyzer chamber was like the reactor. A few differences take place. Analyzer cathode was without holes. At the same time, effluent gas mixture from reactor flowed through analyzer chamber and free gas outlet was provided in a ventilation network. The self-sustained normal APGD in this gas mixture burned in analyzer chamber was used as a source for emission spectra excitation.

A scanning 0.5m high resolution monochromator (two gratings with 1800 grooves/mm) was used for the spectral decomposition of the APGD emission. The inverse linear dispersion was $\sim 0.5$ nm mm$^{-1}$, and the halfwidth of the Gaussian instrumental profile was equal to $\Delta \lambda_0 \approx 0.011$ nm. A photomultiplier FEU-171 was used as a converter of light intensity to electric signal. The two times enlarged discharge image was focused onto the entrance slit of a monochromator using an lens. The electrodes were oriented so that the optical axis and the entrance slit of the monochromator were parallel to the cathode surface.

![Fig. 2. Schematic of the analyzer for spectroscopic measurements. PS – power supply, R – ballast resistance.](image)

![Fig. 3. Schematic of the analyzer for spectroscopic measurements. PS – power supply, R – ballast resistance.](image)

![Fig. 3. Band spectrum of the Fulcher system of molecular hydrogen in the negative glow. Mixture is 99%/He+1%/NH$_3$, discharge current is 1A.](image)

![Fig. 4. Temporal behavior of the H$_2$ (603.2 nm), He (587.6 nm) and H (656.3 nm) line intensities.](image)

In experiment, the discharge in reactor was alternately switched on/off. Simultaneously, the temporal behaviors

![Fig. 4. Temporal behavior of the H$_2$ (603.2 nm), He (587.6 nm) and H (656.3 nm) line intensities.](image)
of the intensities of the following spectral lines were registered: the Q3 (603.2 nm) line of the (0,0) band of the Fulcher H2 system, the helium (587.6 nm) line and atomic hydrogen Hα (656.3 nm) line (Fig. 4). It is seen, that the intensity of molecular hydrogen line increases when the discharge in reactor operates. On the contrary, the intensities of mentioned atomic lines simultaneously decrease. This fact denotes the increase of the molecular hydrogen concentration in the mixture.

### 3.2 Hydrogen generation in the NH3/He mixture

The estimation of the efficiency of the APGD reactor for H2 generation from NH3 was performed by the comparison of pressure increase rates at the hydrogen inleakage through the palladium membrane into evacuated volume for both the exhaust gas mixture and etalon mixture with known hydrogen concentration. Schematic diagram of setup is shown in Fig. 5. It consists of two volumes V1 and V2 devided by the palladium membrane. These volumes were previously evacuated by forepump. Using the heater H, the heating of the palladium membrane was provided. Then, the volume V1 was filled by reactor gas mixture collected in gas outlet of reactor (see Fig. 1). Hydrogen penetrates membrane in volume V2. At the same time, the pressure growth rate was registered by recorder RG. The same operations of the evacuation, filling and leakage through palladium membrane were performed for one-two helium-hydrogen mixtures with known percentage of hydrogen in helium. Comparing the leakage rates through palladium membrane for both the reactor mixture and etalon one we can determine a quantity of hydrogen in mixture after reactor.

In Fig. 6, the dependence of the hydrogen concentration in reactor exaust against the ammonia concentration in the reactor inlet is shown. One can see, this dependence is close to the linear one represented by the dasched line. Conversion efficiency can be defined as a ratio of the hydrogen quantity obtained at the reactor exit with the plasma on to the hydrogen quantity, which can be obtained at the complete dissociation of ammonia containing in the inlet mixture. We know the mole concentration of ammonia {NH3}in in mixture before the APGD treatment and we determine the mole concentration of hydrogen {H2}out in mixture into reactor exhaust. In this case, conversion efficiency can be expressed by these parameters as follows

$$k = \frac{2\{H_2\}_{out}}{3\{NH_3\}_{in} \cdot (1 - \{H_2\}_{out}/1.5)}.$$  \hspace{1cm} (1)

Conversion efficiency depends on the mixture flow. This dependance for the ammonia-helium mixture (10% of ammonia) is shown in Fig. 7. As it is seen, conversion efficiency is maximal at the flow of about 0.5 litre/min. At smaller mixture flows, conversion efficiency practically does not change. At flows greater than 0.5 litre/min, it decreases in two times.
3.3 Hydrogen generation in the NH$_3$/Ar mixture

In this experiment, ammonia was diluted in argon as the carrier gas. Argon properties differ from helium one. It will allow establishing the influence of carrier gas on the ammonia dissociation in the APGD. Of course, the discharge stability in argon is worse in comparison with helium APGD. We used different ammonia-argon mixture containing from 1% up to 20% of ammonia.

Dependences of the hydrogen concentration in reactor exhaust against the ammonia concentration in the reactor inlet for gas flows 0.5 litre/min and 1 litre/min are shown in Fig. 8. A few differences are observed in these dependences in comparison with a case of helium APGD, the results of which are shown by dashed line. Hydrogen yield is not a linear function of the NH$_3$ concentration in ammonia-argon mixture at its concentration less than 20% and hydrogen production is two-three times less than in ammonia-helium APGD. At the ammonia concentration of about 20% in both the ammonia-argon and ammonia-helium mixtures, hydrogen productions are practically the same. Probably, in this case, the quantity of ammonia in gas mixture is sufficient to determine the parameters of both discharges.

The other difference is in an influence of gas mixture flow on the hydrogen production. For the ammonia-helium APGD, hydrogen production decreases about two times at the flow increase from 0.5 litre/min up to 1 litre/min. Hydrogen production in the ammonia-argon mixture practically does not depend on mixture flow in the same flow range. Therefore, the dependence of hydrogen production efficiency on the sort of the carrier gas takes place.

References