Fundamentals of gas conversion in pulsed DBD plasma.

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Abstract: The results of experimental investigation of pulsed DBD as a tool for gas-phase plasma chemistry are presented. The barrier discharge was initiated by unipolar rectangular high voltage pulses with rise time of tens of nanoseconds. The gas conversion of methane at atmospheric pressure and room temperature was performed. Summary of fundamental DBD investigation and experiments on gas conversion allowed making a conclusion that a thermal stimulation was a dominant mechanism of gas conversion in described conditions.

Keywords: dielectric barrier discharge, pulsed power, atmospheric pressure, methane conversion, diffuse mode formation.

1. Introduction

The non-equilibrium plasma is widely concerned as a tool for plasma chemistry applications in a whole and for gas conversion as a part [1, 2]. Among other sources of non-equilibrium plasma, the gas discharge which development restricted by dielectric (DBD) attracts additional attention, mainly due to the ability to realize it under relatively high pressures and current limitation through an electrical circuit due to the presence of a dielectric barrier. The non-thermal plasma produced by this way is considered as a promising alternative method in gas-phase reactants activation and conversion. In non-thermal plasma high-energy electrons can directly excite, dissociate and ionize molecules to create vibrationally and electronically excited species and radicals at comparatively low temperatures, thereby overcoming the necessity of high operational temperatures contrary to conventional chemical technologies [3, 4].

Depending on the gas composition, pressure, dielectric material and type of supply voltage, you can get a different type of barrier discharge, both as in appearance mode and in electrical parameters (current density, its peak value and duration) [5-8]. Research performed with cross-correlation spectroscopy has showed that the development of a single microchannel can be divided into four stages: the first one is accumulation of space charge near anode surface, the second is cathode-directed streamer propagation, the third is charge transfer through conducting plasma channel onto dielectric surface until full compensation of electric field, the fourth is relaxation of conducting channel by ions recombination with electrons. It seems that the first and the second stages can be transformed depending on electric field rise rate and strength in terms of location of streamer formation and direction of its propagation. So, under some conditions avalanche to streamer transition can be achieved in a volume of the discharge gap and two streamers (cathode directed and anode directed) occur.

Until now, in spite of the considerable attention paid to DBD and a large amount of research on its applications, their impact onto commercially used technologies is weak enough, what is mainly due to the lower efficiency of the process compared to competing well-established technologies. The most widely used industrial technology of plasma chemistry with the use of DBD plasma remains the generation of ozone, particularly for water purification processes.

What is the reason for the low energy efficiency of plasma chemistry based on DBD? To answer this question, it is necessary to have a clear picture of DBD formation and to know both the concentration of electrons and their temperature what is especially important for specifying DBD as a tool. The electron temperature is a direct function of reduced electric field (REF) value if gas pressure is considered as a constant.

Naturally, the efficient usage of reactor volume for gas phase plasma chemistry will be achieved when filling the reactor by the plasma. Moreover, when a discharge appeared in a multichannel mode, one should expect that the electron temperature would be lower in average, since the channel conductivity was higher and, REF inside it was lower consequently.

An experiment with methane conversion for verification of assumption about greater efficiency of the volumetric DBD mode was carried out. It was expected to detect an extremum on the reaction products yield curve in region that corresponds to DBD mode changing from filamentary to diffuse depending on gas flow rate [9]. Such event denotes a significant change in the efficiency of the methane conversion.

2. Setup

The experimental setup shown in Figure 1 consists of a plasma-chemical reactor of coaxial construction, a generator of high-voltage rectangular pulses, a system for recording electrical parameters (current and voltage sensors, an oscilloscope), a gas flow meter (Bronkhorst F-201AV-50K-AAD-33-V), and an analyzer for the chemical composition of the output gas flow (MKS Instruments Cirrus 300 quadrupole mass spectrometer).

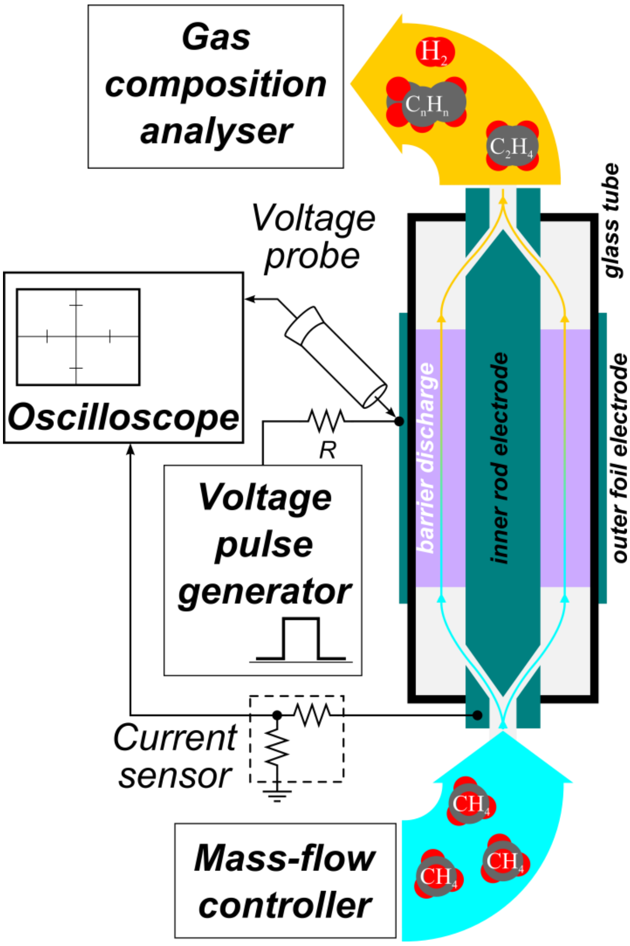

Fig. 1. Experimental setup for methane conversion by pulsed DBD.

The diameter of the inner metal rod electrode is 18 mm. The outer electrode is aluminum foil envelop around borosilicate glass tube with 25 mm outer diameter and 2 mm thickness. So the discharge gap distance was 1.5 mm with length of 115 mm.

The frequency of the supply pulses from tailor-made pulse generator [10, 11] was varied in the range from 1 to 5 kHz. Rectangular-shaped unipolar pulses with rise and fall time less than 100 ns, duration of 60 us, and amplitude of 15 kV were used. The flow rate ranged from 0.4 to 10 l / min. Two modes of DBD were realized in the experiment: diffuse mode at low frequency and high flow rate, and the filamentary (multichannel) mode at high frequency and low flow rate. Methane temperature and pressure in the experiment were close to atmospheric.

To represent the concentration function of the output reaction products, the parameter of the average energy contribution to the reactor was used:

$$E_{dep} = \frac{P_e}{F_g}$$

, where P_e – an electrical power delivered to the plasma reactor, F_g – the gas flow. The E_{dep} can be interpreted in electron-volts per molecule.

3. Results and discussion

The values of energy per volume (Epv) delivered into the discharge for the diffuse mode and for filamentary one are represented in figure 2 to compare. It is seen that E_{pv} for the diffuse mode is greater than in a case of the filamentary mode.

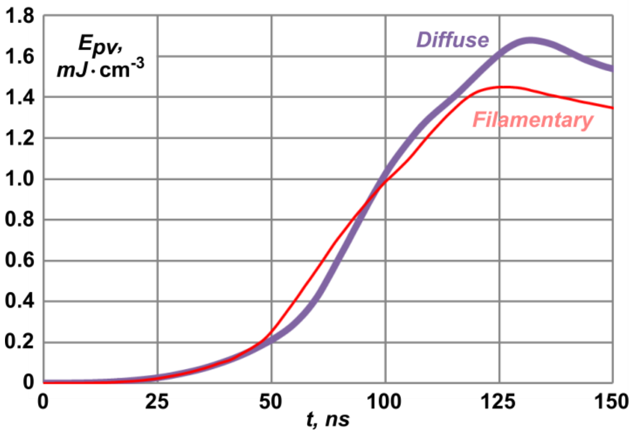

Fig. 2. Temporal evolution of specific discharge energy at rising edge of applied voltage pulse for diffuse and filamentary modes of DBD.

The experimental dependences of the reaction products yield on the deposited energy are presented in figures 3–5. The orange dotted vertical line indicate border between diffuse mode of DBD (D-mode in figures) and filamentary mode (F-mode). At an energy input of 3.25 eV/molecule, the selectivity for the main reaction products was: acetylene – 11.56%, ethylene – 14.76%, ethane – 30.51%, propylene – 16.84%, propane – 15.01%, hydrogen – 7.02%.

The yield of the reaction products is well approximated by a linear dependence on the energy supplied to the plasma reactor, and there is no visible extremum near the mode border. This behavior characterizes the discharge as a heating source or at least indicates a dominant role of the gas media heating process relative to the non-equlibrium excitation. By this reason the discharge mode under the considered shape of supply voltage does not have a discernible effect on the methane conversion efficiency. This result can be interpreted as the predominant contribution of the DBD charge transfer stage into the methane conversion process.

The reduction of the energy percentage contribution into this stage seems to be a promising direction for the progress in plasma methane conversion technology.

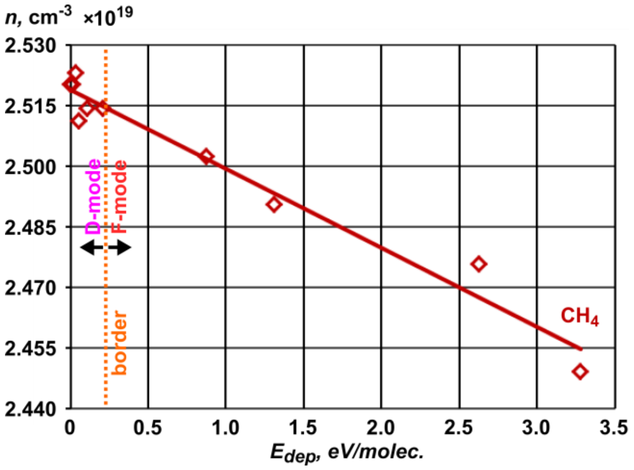

Fig. 3. Methane concentration via deposited energy.

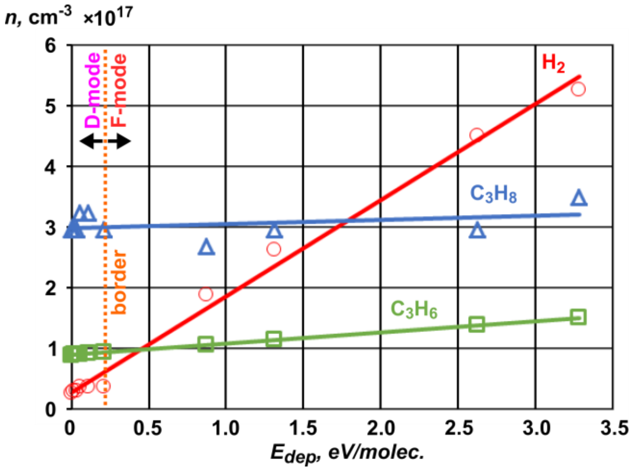

Fig. 4. Yield concentration for hydrogen (red), propane (blue) and propene (green) via deposited energy.

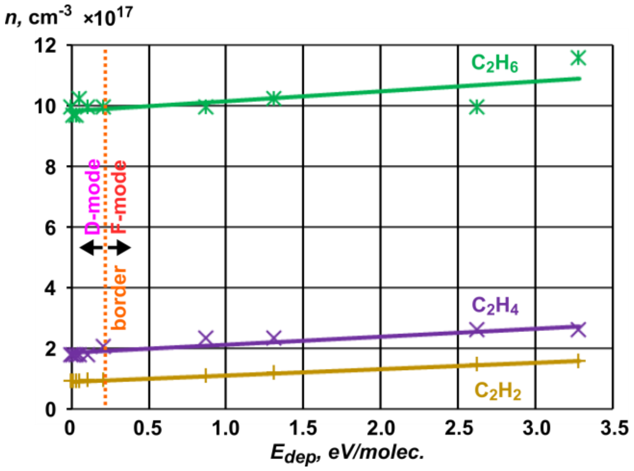

Fig. 5. Yield concentration for ethane (green), ethylene (violet) and acetylene (dark yellow) via deposited energy.

4. Conclusion and outlook

Basing on experimental results together with qualitative model of DBD formation it can be concluded that the methane conversion process in described conditions mainly governed by the thermal mechanism of initiation and continuation of the reaction chain.

Apparently, for more efficient use of expensive electric energy of high-voltage pulses, it is necessary to minimize energy losses for environment heating. The last can be realized by special voltage waveforms using that provide high REF values and their rise rate at the stage of low-temperature plasma formation, and then suppress the reverse discharge development for some time period by rapidly reducing the field in the discharge gap.

5. Acknowledgements

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6. References

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