STUDY OF N₂/CH₄ ACTIVE DISCHARGE BY COMPUTER EXPERIMENT

Miroslav Vicher¹, Rudolf Hrach¹, Jean-Claude Legrand², Anne-Marie Diamy² and Vira Hrachová¹

¹ Faculty of Mathematics and Physics, Charles University
V Holešovičkách 2, 180 00 Prague 8, Czech Republic
² Laboratoire de Chimie des Surfaces, CNRS ESA 7069, Université Pierre-et-Marie-Curie
4 Place Jussieu, case 196, 75252 Paris Cedex 05, France

Abstract

A computer experiment designed for the analysis of methane plasma chemistry in various types of active discharges was prepared. The model consists of nearly 300 reactions between 70 kinds of neutral, charged and excited species resulting from decomposition of methane in nitrogen discharge.

1. Introduction

Basic understanding and modelling of reactive plasmas is very important both in fundamental and applied research. One of the most important fields is the methane plasma chemistry as it has direct application in plasma polymersisation, in deposition of hydrogenated amorphous carbon thin films and crystal diamond films as well as in preparation of higher hydrocarbons from natural gas, detoxification of gases generated by combustion, etc. Typical experimental technique is a radio-frequency glow discharge, though another types of plasmas induced by microwaves, ECR or dc discharges are sometimes used, too. Moreover, besides processing in active discharges, the flowing afterglow conditions are better suited for some of these tasks, giving rise to slightly different methane chemistry due to lower energies of interacting particles in plasma.

The key to the successful application of methane plasma in plasma-chemical technologies is a detailed knowledge of physical and chemical processes taking part during methane decomposition and following reactions in the bulk plasma or on the substrate. For this task the combined approach - real experiment followed by computer experiment - seems to be very convenient tool.

The kinetics of methane decomposition in N₂/CH₄, H₂/CH₄, Ar/CH₄, and etc. plasmas has been studied since at least forties. During last ten years many models of methane conversion and carbon containing thin films deposition were suggested, some of them detailed enough - e.g. [1] and [2] for radio-frequency discharge in pure methane, [3] for dc glow discharge in nitrogen-methane mixture or [4] for microwave discharge in hydrogen-methane gas mixture. Some of these models concentrate on the surface processes taking part during thin film growth - e.g. [5] or [6], while others study the gas-phase physics and chemistry only - e.g. [7]. The typical simulation technique for the modelling of methane decomposition is the macroscopic kinetic approach, sometimes connected with the Boltzmann
equation solver or with fluid model of discharge physics. However, for the simulation of surface processes besides plasma chemical models the approaches typical in thin film physics, as kinetic Monte Carlo method, are can be used too [8]. This variety of simulation techniques together with variety of experimental conditions under which the input data for modelling were derived, leads to results of simulations that is often difficult to compare and to use for the discussion of another experimental results.

In our laboratories the main goal of the study of methane decomposition was the conversion of methane into higher hydrocarbons in afterglow conditions and for this purpose several models were prepared - e.g. [9] and [10]. In order to compare processes taking part in these conditions with processes in active discharges an attempt to prepare a detailed model of gas-phase chemistry in the N\textsubscript{2}/CH\textsubscript{4} plasmas was made. The first results of this simulation are presented in another contribution in the Proceedings of ISFC 15.

2. Experimental

In our laboratories both the N\textsubscript{2}/CH\textsubscript{4} plasma and pure nitrogen plasma was studied. In UPMC the processes in N\textsubscript{2}/CH\textsubscript{4} microwave plasma were analysed and most of measurements were made in the flowing afterglow conditions. A 2.45 GHz microwave generator produced the plasma in a silica discharge tube filled with nitrogen. Methane was introduced in the reactor either upstream or downstream the dinitrogen plasma, the distance of entrance ports being one of the parameters of experiment. Other parameters were the concentration of methane, nitrogen flow rate and the incident microwave power. The experimental set-up enabled to measure:

- vacuum conditions - pressure and gas flows,
- gas temperature - by means of Pt-Pt/10 \% Rh thermocouple
- electron temperature and density - by Langmuir probe diagnostics
- chemical analysis of stable products - by gas chromatography
- optical characteristics of discharge - by optical emission spectroscopy
- concentrations of some species - by mass spectrometry.

Although most of measurements were performed downstream of the cavity in the flowing afterglow, an active discharge was a starting point of the afterglow time axis, so these data were available too. The measurements in de glow discharge in nitrogen were performed at CU. The main methods for the plasma characterisation were Langmuir probe diagnostics and optical emission spectroscopy.

The main task of our study was to analyse the methane conversion into higher hydrocarbons. In this case the concentration of methane was high - typically several tens percents [9]-[10] for the total pressure of order 10\textsuperscript{3} Pa. However, when the physical and chemical processes between active species in discharge were analysed, the experiments were carried out with smaller ratio of methane - less than 5 \% [11] or even less than 0.1 \% [13] for the gas pressure 10\textsuperscript{2} - 10\textsuperscript{3} Pa. The typical microwave power absorbed in plasma was 150 - 700 Watts.

In the active part of the microwave discharge was observed that the emission intensity of the first negative system of N\textsubscript{2}\textsuperscript{+} decreased and the CN violet band increased with methane concentration increase in the N\textsubscript{2}/CH\textsubscript{4} mixture [11].

The electron concentrations and temperatures were about 1\texttimes10\textsuperscript{10} cm\textsuperscript{-3} and 20,000 K resp., exact values depended on microwave power - the introduction of methane into mixture decreased these values [11].

Further results concerned densities of excited molecular and atomic species in pure nitrogen discharge [12] and in N\textsubscript{2}/CH\textsubscript{4} mixture [13]. From the combined measurement of optical and
mass spectrometry the dependencies of some active species in the discharge – N, N₂(A), N₂(a'), N₂⁺(B,0), etc. – on methane concentration were obtained.

Similar characteristics were derived in the dc glow discharge conditions both in our laboratory and elsewhere – e.g. [14]. All these data as well as other results found in the literature are used as input data for the preparation of the model of chemical processes in the N₂/CH₄ active plasma.

3. Model

In order to discuss both our experimental results and other data, the model of gas phase kinetics of methane decomposition in N₂/CH₄ plasma is being constructed. The main task of our computer experiment is to find the common features of methane plasma chemistry in various types of active discharges, contrary to our previous models of the flowing afterglow conditions [9] and [10].

3.1. Computational technique

The technique used for the modelling of methane conversion was based on a macroscopic kinetic approach. First, it is necessary collect the chemical reactions describing the studied problem, in our case the methane dissociation followed by further conversions. For local densities of individual species in plasma the partial differential equations derived from the balance equation can be written. If the diffusion in the gas flow direction can be neglected and the diffusion to the wall of discharge tube is included into the set of chemical reactions, the resulting set of ordinary differential equations will be derived

\[
dn_i/dt = Q/V + A_i(n_1,\ldots,n_m) - B_i(n_1,\ldots,n_m), \quad i=1,\ldots,m
\]

where \(n_i\) is the concentration of the \(i\)-th species, \(m\) the total number of species in the kinetic mechanism and \(A_i\) and \(B_i\) represent the creation and loss processes, respectively. Term \(Q/V\) differs from zero only for the basic input species, N₂ and CH₄, and represents the number of molecules externally introduced into the unit volume of reactor chamber per unit time. The terms describing the creation processes or the loss processes consist of the expressions \(\pm k_p\times n_i\); \(\pm k_p\times n_i\times n_j\) or \(\pm k_p\times n_i\times n_j\times n_k\) for reaction steps of the first, second or third order. The rate constants \(k_p\) may depend on gas temperature \(T_g\) or electron temperature \(T_e\). The resulting set of stiff ordinary differential equations was solved on the PC computer in FORTRAN programming language with the help of a semi-implicit extrapolation method. The adjustment of the model on concrete experimental configurations is made by introducing the experimentally derived dependencies of temperatures \(T_g, T_e\) into rate constants \(k\) either directly or through the numerical integration of corresponding cross-sections.

3.2. Reduction of reaction mechanism

However, sometimes the kinetic scheme is so complex, that before the final calculations it is necessary to reduce it and to preserve more important reactions only. There are several techniques of simplification of the set of gas phase reactions, between them the approach based on the speed of each reaction at each time of the kinetic calculation [15]. In order to reduce the stiffness of the set of differential equations, the number of chemical reactions in the model must be decreased. First it is necessary to reorder the list of reactions according to their importance in the chemical mechanism. For this purpose, two new quantities must be introduced:
Differential weight factor of the \(i\)-th reaction \(w_i(t)\), i.e. the sum of the absolute values of all terms \(k_i \times n_{i1} \times n_{i2} \times \ldots \times n_{in}\) (and \(k_i' \times n_{i1} \times n_{i2} \times \ldots \times n_{in}\)) with the same rate constant \(k_i\) of \(i\)-th reaction, where \(n_{i1}, n_{i2}, \ldots, n_{in}\) are concentrations of reacting species.

Integral weight factor \(W_i(t)\) of the \(i\)-th reaction, i.e. the integral of \(w_i(t)\) for \(t \leq \langle 0, t \rangle\).

While the differential weight factors serve for the detailed discussion of reaction mechanisms, the integral weight factors \(W_i(\approx)\) can be used for the simplification of kinetic scheme. The list of chemical reactions must be rearranged according to their weights and only the top part of this list can be used. The threshold value in the list depends on the requested accuracy of simulation. However, this approach reduces not only the number of reactions but also the number of species in the model. Therefore, this reduction method is not the absolute one. If it is necessary to take into consideration some species with small absolute concentrations but important for the whole kinetic scheme, corresponding chemical reactions must be preserved and several more reactions must be added to the reduced system of reactions. This last task was not automated yet.

3.3. \(\text{N}_2\) model

In order to prepare the realistic detailed model of the reactions in \(\text{N}_2/\text{CH}_4\) plasma, where typically the methane creates only several per cent (or less) of the whole gas volume, the information about the exact composition of nitrogen plasma must be derived first. The complete model must consist of three types of chemical reactions – reactions between the nitrogen species (neutral, excited and ionised atomic and molecular nitrogen plus electrons), reactions between hydrocarbon gases, radicals and ions and crossed reactions between species containing \(\text{C}/\text{H}\) atoms and \(\text{N}\) atoms. For the solving of the first task there are two possible approaches:

- either to obtain the concentrations of important species in nitrogen discharge under given experimental conditions from independent measurements,
- or to prepare the detailed model of the \(\text{N}_2\) plasma first, simplify it by the above mentioned reduction technique and introduce the most important reactions into the model of whole mixture.

In our computer experiment we used the second approach. Although the preparation of the realistic model of nitrogen plasma is a complicated task – see e.g. [14], [16], [17], the detailed information about processes in \(\text{N}_2\) plasma will be necessary for further study of processes in the nitrogen-methane mixture.

In the present moment our model of processes in \(\text{N}_2\) plasma consists of more than 40 reactions between 17 species. The first results of simulation correspond approximately to experimentally derived concentrations of important species [14]:

\[
\begin{align*}
\text{N}_2(\text{X} \, ^3\text{O}_2^+) &= 1 \times 10^{17}\, \text{cm}^{-3}, \\
\text{N}_2(\text{A} \, ^3\text{O}_2^+) &= 1 \times 10^{12}\, \text{cm}^{-3}, \\
\text{N}_2(\text{B} \, ^3\text{D}_2) &= 1 \times 10^{11}\, \text{cm}^{-3}, \\
\text{N}(^2\text{S}) &= 1 \times 10^{15}\, \text{cm}^{-3}, \\
\text{N}(^2\text{D}) &= 1 \times 10^{13}\, \text{cm}^{-3}, \\
\text{N}(^2\text{P}) &= 1 \times 10^{12}\, \text{cm}^{-3}, \\
\text{N}_2^+ &= 1 \times 10^{10}\, \text{cm}^{-3}, \\
\text{N}_4^+ &= 1 \times 10^{7}\, \text{cm}^{-3},
\end{align*}
\]

With the help of the reduction technique the number of species can be reduced to about 7 - 10, the exact value depending on a requested accuracy of simulation. However, in the model there exist some fitting parameters that must be adjusted according to given experimental conditions, so this model is not self-consistent yet.

3.4. \(\text{N}_2/\text{CH}_4\) model
The complete model of chemical reactions in the N\textsubscript{2}/CH\textsubscript{4} discharge consists in the present moment of 285 reactions between 70 species, between them 7 species coming from the N\textsubscript{2} model, 47 species C/H (neutral, excited and ionised C, C\textsubscript{2}, C\textsubscript{3} and C\textsubscript{4} hydrocarbons) and 16 mixed C/H/N species. Numbers of chemical reactions of three basic types — reactions between the nitrogen species, reactions between hydrocarbon species and crossed reactions correspond approximately to number of species in following groups.

The resulting model was analysed by a macroscopic kinetic approach. However, the derived set of ordinary differential equations for concentrations of individual species was so stiff, that it was not possible to solve it directly. Therefore, the technique of reduction of kinetic scheme had to be applied. The first derived results are presented in our second contribution in the Proceedings of ISPC 15.

References


Acknowledgements

The research was sponsored by EC through the INCO-COPERNICUS Grant ERB IC15 CT98 0805. The support of Ministry of Education of Czech Republic, Grant OK-409, and Grant Agency of Czech Republic, Grant 202/98/P246, is gratefully acknowledged.