A Global Model for He - H₂O Chemistry

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Abstract

Global warming is one of the critical contemporary problems for mankind. Transformation of CO₂ into fuels, like CH₄, that are transportable with the current infrastructure is a promising idea to solve this threatening issue. The final aim of this research is to produce CH₄ by using a microwave plasma in CO₂-H₂O mixture and subsequent catalytic processes. In this contribution we present a global model for He-H₂O chemistry. This verified and validated model for H₂O should be added to CO₂ chemistry later to fulfill the final aim of the project.

Keywords: He, H₂O, Global Model, Microwave, RF discharge

1 Introduction

Achieving CO₂ neutrality can be defined as a proper step to deal with global warming problem. In this contribution, conversion of CO₂ to CH₄ by the help of microwave plasma and catalytic processes is a promising idea. The first step of this idea is using microwave plasma to achieve two main products in CO₂ and H₂O mixture: either CO accompanied by feed gases, CO₂ and H₂O, or H₂ with CO₂.

In order to simulate a microwave discharge of CO₂-H₂O, one of the key elements is the governing chemistry. A lot of researches have been carried out to understand the governing chemistry of CO₂ in both microwave and direct barrier discharges [1] [2] [3] [4], but based on our knowledge, there are less plasma modeling researches on H₂O discharges. As a first step to achieve a verified and validated H₂O model in microwave plasma, we found three papers that mainly focus on modeling chemistry of H₂O by studying the He-H₂O atmospheric discharges. Liu et al. [5] investigated the He-H₂O discharge in atmospheric pressure by investigating the effect of H₂O concentration on He discharge with a global model that contains 46 species and 577 reactions. Vasko et al. [6] compared their global model and 1D fluid model of H₂O-He with experimental results and global model of [5]. They used the presented chemistry in [5] and improved it by adding some vibrational states of H₂O. Ding et al. [7] focused on atmospheric He-H₂O discharge by a hybrid two-temperature global model.

In addition to the mentioned papers, the work of Van Gaens et al. [8] studied the kinetic of an argon plasma jet in atmospheric pressure humid air, so they considered a subset of water chemistry that is provided in [5] and adding some of the vibrational states of H₂O molecule to their species list.

In all of the introduced paper, the chemistry was first derived from [5] and after that it was improved or modified. Therefore, to start to have a verified and validated model, we made a similar decision and made a model based on [5]. We can validate our model qualitatively with the works of [5] and [6]. Due to some discrepancies between models and unclear assumptions, quantitatively validation is impossible.

In the following sections, the global model that is used in this research is described in section 2. Then, some results from our model will be presented in section 3. In addition, some possible reasons for discrepancies between models are explained in more detailed. Finally, a brief conclusion and possible future works to understand more deeply the important mechanism of H₂O discharges will be covered in section 4.

2 Global Model

The PLASIMO modeling software is used in this research. The species density balance together with the electron energy balance are solved iteratively as a function of time in our global model.

The species balances are given by:

\[
\frac{dn_i}{dt} = S^V + \frac{A}{V} S^s - \frac{A}{V} \alpha \Gamma - S_{conv} - S_{diff} \quad (1)
\]

where \( n_i \) presents the density of each species; \( A \) is the total area of electrodes; and \( V \) is the volume of plasma.

The first term on right-hand side of equation [1] is the net of volumetric production and consumption of species. The second term presents production of species due to surface reactions. The third term is loss of species in surface reactions where \( \alpha \) is the probability of occurrence of the reaction, and \( \Gamma \) is the flux of species toward the electrodes. The fourth and fifth terms are loss due to transport, convection and diffusion from the plasma volume, respectively.
Because we made our model based on [5], we used the same assumptions as well. In their work, they simulated a radio frequency (RF) atmospheric discharge with H$_2$O and He as feed gases. Feed gases come into the reactor, then plasma is formed between two circular electrodes, and species can leave the plasma region. The made assumptions for this model are:

- The species balance (equation [1]) is solved for each species except H$_2$O and He. They are considered as background species, and their densities are assumed to be constant during simulation.

- The flux ($\Gamma$) of negative ions toward electrodes are considered to be zero.

- The species balance is not solved in our model for electrons. In order to satisfy quasi-neutrality, the density of the electrons is put equal to the net densities of positive and negative ions.

- For electron impact reactions, BOLSIG+ is used to calculate the rate coefficients of reactions based on the computed electron energy distribution function (EEDF). For these reactions, cross sections are gathered from literature.

- The flux of ions is $nu_B$, where $u_B$ is the Bohm velocity.

- The diffusion loss from the plasma side is calculated as $\frac{1}{4}n \langle v \rangle A_s V$, where $A_s$ is the side area of the plasma. This term is considered just for neutral species.

In our model the electron energy balance is solved coupled with the density balances. The energy balance is given by:

$$\frac{dE_e}{dt} = P_{in} - P_{elastic} + P_{inelastic} - P_{ion \ surface} - P_{e \ surface}$$ 

$E_e$ represents the mean electron energy density. This variable is calculated at each iteration and is connected to the electron temperature by $E_e = \frac{3}{2} k_B T_e$, where $k_B$ stands for Boltzmann constant. The first term on the righthand side of equation [2] is the input power density. It is assumed to be constant in our model. The second term is the power loss of electrons due to elastic collisions. The third term is power loss or gain of electrons due to inelastic collisions. The fourth term is the power loss due to flux of ions to the electrode, which is assumed to be 100 eV in our model; this power loss is due to the ion shield passing. The last term is power loss due to the electron flux toward electrodes, which is assumed to be $2k_B T_e$.

3 Results

In this section, we present the result of our model for constant power input of 20 W based on the simplified chemistry set "M"s of [5]. Figure 1 depicts the comparison of our model with [5] for variation of electron temperature and electron density at different H$_2$O concentration. It should be mentioned that our model shows the same trend as what is presented in [5], but quantitatively our results are not the same, especially for electron temperature.

These discrepancies can be due to:

- Different data for cross sections and consideration of different resolution for BOLSIG+ calculation
- Implementation of different calculations for flux, diffusion and convection term of species balance equation.
- Having a different system of ODEs, for example, not considering the electron energy balance

In addition to above comparison, we compared our model with presented results in [6] based on the global model of [5]. For this case the operational conditions and dimensions of the RF discharge are a bit different; the H$_2$O
concentration, gas temperature, and flow rate are 0.47%, 348 K, and 2 slm, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GM [5]</th>
<th>presented GM</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_e (m^{-3}))</td>
<td>6.9 (\times) 16</td>
<td>1.4 (\times) 16</td>
</tr>
<tr>
<td>(T_e (eV))</td>
<td>3.96</td>
<td>3.51</td>
</tr>
<tr>
<td>(n_{H_2O_2} (m^{-3}))</td>
<td>1.1 (\times) 21</td>
<td>1.296 (\times) 21</td>
</tr>
<tr>
<td>(n_{OH} (m^{-3}))</td>
<td>2.24 (\times) 20</td>
<td>2.64 (\times) 20</td>
</tr>
</tbody>
</table>

Table 1: comparison between presented model with results of [6].

It should be noted that the main important parameters in the densities of \(H_2O_2\) and OH are gas temperature and diffusion to the side of the plasma in the condition of [6]. The densities of these species can vary 6 orders of magnitude due to the diffusion term. However, in our model, the diffusion term is not considered for neutral species.

4 Outlook

Validation and verification of \(H_2O\) chemistry is not straightforward due to the lack of both well-documented models in literature and reliable data for chemistry. In order to fill this gap as much as possible, we present a model based on the work of Liu et al. [5] and compare and improve it with previous researches. In the future, sensitivity and uncertainty analysis will be done in our model to have a better understanding of important parameters and reactions in \(H_2O\) discharges. By adding the final model to a \(CO_2\) chemistry model, we will be able to achieve one of the key goals in simulation of microwave discharge of \(H_2O-CO_2\) mixture.

References


