One-Dimensional Modeling on the Chemically Reactive Species in a Helium-Oxygen Radio-Frequency Atmospheric Glow Discharge

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Abstract: A one-dimensional (1-D), unsteady fluid model is employed to simulate the helium-oxygen radio-frequency atmospheric-pressure glow discharge with different oxygen-helium ratios ($\eta$). The variations of the discharge structures at different values of $\eta$ are discussed with the analysis of the chemical reactions.

Keywords: Helium-oxygen mixture, Radio frequency, Glow discharge

1. Introduction

Radio-frequency atmospheric-pressure glow discharge (RF APGD) plasmas provide a critical advantage over widely used low-pressure plasmas (LPPs) due to the removal of the expensive and complicated vacuum systems. They show bright prospects to potentially replace the LPP devices in some applications, or to create new application fields, such as plasma-based sterilization/disinfecting, microbe evolution breeding, decontamination of chemical/biological warfare agents, gas purification, surface treatment, etching, etc. In actual applications of LPPs, small amount of oxygen is often added into the helium working gas to provide the chemically reactive species (e.g., oxygen atom). Recently, studies on the helium-oxygen RF APGDs, including the experimental studies and the numerical modeling concerning the chemical reaction processes using a global model, are reported (e.g., [1]).

In order to investigate the variations of the oxygen atom concentrations and the discharge structures in different helium-oxygen gas mixture discharges, which cannot be revealed by the global model completely, a one-dimensional (1-D), unsteady fluid model is employed to simulate the helium-oxygen RF APGDs with different oxygen-helium ratios ($\eta$) in this paper.

2. Descriptions on the numerical model

![Schematic diagram of the calculation domain.](image-url)
As shown in Figure 1, the distance between the two bare metallic electrodes \((L)\) is 2.4 mm. The assumptions employed in this modeling are as follows: (i) the plasma working gas is in static state and no surrounding air exists; (ii) the gas pressure and temperature are constant throughout the discharge processes; (iii) all metastable species and ions are assumed to quench or neutralize at the electrode surfaces and return back to the inter-electrode space as stable neutral species; (iv) the drift-diffusion approximation is employed for calculating the number fluxes of all charged species.

Based on the preceding assumptions, the governing equations for 1-D case are as follows:

**Species continuity equation:**

\[
\frac{\partial n_i}{\partial t} + \frac{\partial \bar{\Gamma}_i}{\partial x} = S_i \tag{1}
\]

where \(n_i\), \(\bar{\Gamma}_i\) and \(S_i\) represent the number density, number flux and the homogeneous production/destruction rate of species \(i\), while \(t\) and \(x\) are the time and inter-electrode axial distance, respectively.

**Poisson equation:**

\[-\varepsilon_0 \nabla^2 \phi = \varepsilon_0 \nabla \cdot \bar{E} = e \sum_i q_i n_i \tag{2}\]

where \(\phi\) is the electric potential, \(\varepsilon_0\) is the vacuum permittivity, \(e\) is the elementary charge, \(q_i\) is the charge number of species \(i\).

**Electron energy conservation equation:**

\[
\frac{\partial (n_e e\bar{E})}{\partial t} + \frac{\partial \bar{Q}_e}{\partial x} = -e\bar{\varepsilon} \frac{\partial \phi}{\partial x} - \sum_j \Delta E^j_k e K_j - \frac{m_e}{m_{He}} K_{Ba}(T_e - T_g) \tag{3}
\]

where the subscript “e” stands for electrons, \(\Delta E^j\) and \(K_j\) are the energy loss during the inelastic collision process \(j\) and the corresponding reaction rate, \(m_e\) and \(m_{He}\) are the masses of electrons and helium atoms or ions, \(K_{Ba}\) is the momentum transfer rate between electrons and the background helium, while \(k_B\), \(T_e\) and \(T_g\) (393 K) are the Boltzmann constant, electron temperature and the background helium gas temperature, respectively. The three terms on the right hand side of Equation (3) represent the Joule heating, energy transfer due to inelastic collisions and elastic collisions, respectively.

**Auxiliary equations:**

In the foregoing equations, the electron thermal flux is given by the Fourier’s law as

\[
\bar{Q}_e = \frac{5}{3} \bar{x} \varepsilon_0 - \frac{5}{3} D_e n_e \frac{\partial \varepsilon}{\partial x} \tag{4}
\]

And the drift-diffusion approximation for the species number flux is expressed as

\[
\bar{\Gamma}_i = \text{sgn}(q_i)n_i \mu_i \frac{\partial \phi}{\partial x} - D_i \frac{\partial n_i}{\partial x} \tag{5}
\]

where \(\mu_i\) and \(D_i\) are the mobility and diffusion coefficient of species \(i\), respectively, \(e\) is the electron energy, while ‘sgn’ is the signum function.

The flux boundary conditions are imposed for all species number densities at the electrode surfaces. For electrons, the flux at the electrode surface is determined as a sum of the kinetically limited Maxwellian flux and the secondary electron emission flux. For ions, they are assumed to be mobility limited at the boundaries [2]. According to the third assumption, the number fluxes for the metastable species are determined as the kinetically limited Maxwellian flux; and the number fluxes for the stable neutral species are the sum of the corresponding ion/metastable fluxes with reverse direction. For electric potential, the constant values of zero and sinusoidal function with a frequency of 13.56 MHz are specified on the electrode surfaces. The electron energy flux at the boundary is given as a sum of the kinetically limited energy flux and the energy of secondary electrons.

The mobility, diffusion coefficient, mass and sec-
ondary electron emission coefficient of species are compiled from literatures [2-5], and are evaluated assuming that the species transport in a helium background gas at the gas temperature of 393K under atmospheric pressure (\( p = 760 \) torr). The chemical reaction mechanism (Table 1) is compiled from the literatures [4, 5] where the corresponding reaction rates can be found.

<table>
<thead>
<tr>
<th>( G_i )</th>
<th>Reaction (pure He)</th>
<th>( G_i )</th>
<th>Reaction (O₂-He)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_1 )</td>
<td>( e + He \rightarrow He^+ + e )</td>
<td>( G_{10} )</td>
<td>( O_2 + e \rightarrow O_2^+ + 2e )</td>
</tr>
<tr>
<td>( G_2 )</td>
<td>( e + He^+ \rightarrow He + e )</td>
<td>( G_{11} )</td>
<td>( O_1 + O \rightarrow O_2 + O_2 )</td>
</tr>
<tr>
<td>( G_3 )</td>
<td>( e + He \rightarrow He^+ + 2e )</td>
<td>( G_{12} )</td>
<td>( O_2^+ + e \rightarrow O + O )</td>
</tr>
<tr>
<td>( G_4 )</td>
<td>( e + He^+ \rightarrow He^+ + 2e )</td>
<td>( G_{13} )</td>
<td>( O_2 + O^+ \rightarrow O_2^+ + O )</td>
</tr>
<tr>
<td>( G_5 )</td>
<td>( He^+ + He^+ \rightarrow )</td>
<td>( G_{14} )</td>
<td>( He^+ + O_2 \rightarrow )</td>
</tr>
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<td></td>
<td>( He^+ + He + e )</td>
<td></td>
<td>( He + O_2^+ + e )</td>
</tr>
<tr>
<td>( G_6 )</td>
<td>( e + He^+_2 \rightarrow )</td>
<td>( G_{15} )</td>
<td>( He^+ + O \rightarrow )</td>
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<td></td>
<td>( He^+ + He )</td>
<td></td>
<td>( He + O^+ + e )</td>
</tr>
<tr>
<td>( G_7 )</td>
<td>( e + He^+_2 \rightarrow )</td>
<td>( G_{16} )</td>
<td>( He + O + O \rightarrow )</td>
</tr>
<tr>
<td></td>
<td>( He^+_2 + 2e )</td>
<td></td>
<td>( He + O_2 )</td>
</tr>
<tr>
<td>( G_8 )</td>
<td>( He^+ + 2He \rightarrow )</td>
<td>( G_{17} )</td>
<td>( He + O_2 + O \rightarrow He + O_3 )</td>
</tr>
<tr>
<td>( G_9 )</td>
<td>( He^+ + 2He \rightarrow )</td>
<td>( G_{18} )</td>
<td>( He + O_3 \rightarrow )</td>
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<tr>
<td></td>
<td>( He_2^+ + He )</td>
<td></td>
<td>( He + O_2 + O )</td>
</tr>
<tr>
<td>( G_{19} )</td>
<td>( O_2 + e \rightarrow O_2^+ )</td>
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</table>

**Figure 2.** Simulated voltage and current density waveforms for a 0.01% oxygen-helium ratio with a 2.4-mm inter-electrode spacing and a power density of 1.2 W/cm².

Figure 2 shows a smooth and near-sinusoidal current density waveform with an applied sinusoidal voltage which is consistent with the experimental measurements. The calculated current waveform leads the voltage waveform by 38.0°, which is smaller than the measured phase difference for a \( \alpha \)-mode discharge, but is close to the He-N₂ modeling result (35.7°) in Ref. [5].

![Figure 3](image)

**Figure 3.** Time-averaged spatial profiles of (a) oxygen atom and (b) ozone number densities with different oxygen-helium ratios.

![Figure 4](image)

**Figure 4.** Time-averaged spatial profiles of (a) the main reaction rates of oxygen atom productions/destinations and (b) the net charge number densities.

Figure 3 shows the time-averaged spatial profiles of the oxygen atom and ozone number densities with different oxygen-helium ratios ranging from 0.01% (100 ppm) to 4% (40000 ppm). To provide a clear view of the variation trends, the data is draw in a three-dimensional Cartesian coordinates with projections on every coordinate plane. It can be seen that, with the increase of \( \eta \), there exist a peak value for the oxygen atom number density ([O]) at \( \eta = 0.1\% \), while the ozone number density ([O₃]) increases monotonically. Although the variation trends of [O] and [O₃] are consistent with the experimental measurements qualitatively, the calculated values of them are lower than those of the measured data. This may...
be due to the fact that the time interval in this modeling (0.1 ms) is not long enough to reach the equilibrium state for the neutral species (e.g., O and O₃) in system physically. So, it is necessary to develop a novel model to improve the calculation efficiency.

In order to explain the different variation trends of [O] and [O₃], the spatial profiles of the time-averaged reaction rates contributed to the productions/destorutions of oxygen atoms and ozone (G₁₂, G₁₇) are presented in Figure 4(a). It can be seen that the reactions G₁₂ and G₁₇ contribute to the production and destruction of the oxygen atoms, respectively, and the corresponding reaction rates increase with increasing η.

For lower oxygen ratio in the helium-oxygen mixture (e.g., η < 0.1%), the reaction rate of G₁₂ is larger than that of G₁₇, which leads to the increase of [O] with the increase of η, while for higher values of η (e.g., η > 0.1%), the value of [O] decreases with the increase of η because the reaction rate of G₁₂ becomes smaller than that of G₁₇. On the other hand, the value of [O₃] increases monotonically with increasing η due to the monotonous increase of the reaction rate of G₁₇. Figure 4(b) shows the spatial profiles of the time-averaged net charge number densities with different oxygen-helium ratios, in which the sheath edge can be identified obviously. It can be seen that the sheath thickness is reduced greatly when oxygen is added into helium which is related with the changes of the number densities of the charged particles (e.g., [e⁻], [He⁺], [O₂⁺]) in the discharge space.

The modeling results also show that, with the increase of η in the helium-oxygen gas mixture glow discharges, the number densities of the chemically reactive species in pure helium plasmas (e.g., He⁺, He₂⁺ and He₂⁺), as well as the electron temperature (Tₑ), are reduced greatly; while at the same time, the number densities of electrons ([e⁻]) and O₂⁺ ([O₂⁺]) increase significantly. These results indicate that in a helium-oxygen RF APGD, the primary source of the chemically reactive species is not helium but oxygen when η is greater than 0.1%.

4. Conclusions

In this paper, a 1-D unsteady fluid model is employed to simulate the discharge characteristics and structures for the helium-oxygen RF APGDs. The main conclusions are as follows: (i) the calculated waveforms of the discharge current are smooth and near-sinusoidal with an applied sinusoidal voltage waveform; (ii) the oxygen number density reaches a peak value at η = 0.1%, while the value of [O₃] increases monotonically with the increase of the oxygen-helium ratio; (iii) the dominating chemically reactive species in a helium-oxygen RF APGD plasma is oxygen when the oxygen-helium ratio is larger than 0.1%.

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References