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The dominant role of impurities in the composition of high pressure noble gas plasmas

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We present in this letter how a molecular gas such as nitrogen at different levels of impurity dominates the ionic composition of an atmospheric pressure noble gas plasma such as in helium. The positive charge in the discharge is only determined by helium ions if the discharge gas contains less than 1 ppm of impurity. Above this impurity level, the positive charge is completely determined by the impurity nitrogen. The higher the relative nitrogen concentration, the more $N^+$ dominates over $N_2^+$. If the impurity level is between 1 and about 20 ppm, $N_2^+$ is clearly the most abundant positive ion but for higher levels of impurity, $N_2^+$ almost completely determines the positive charge. © 2008 American Institute of Physics. [DOI: 10.1063/1.2839613]

The influence of different levels of impurity in gas discharges is important in both experimental and simulation research efforts. In experimental research, one automatically encounters different levels of (im)purity since two experimental setups are seldom completely the same because of the different reactor designs and because not always the same quality grade gas is being used. In simulations, this purity level is sometimes derived from estimations or sometimes used as a fitting parameter to match a fundamental parameter such as gas voltage to the experimental value. Therefore, it is important to investigate the influence of different levels of impurity in order to obtain a more general insight on this matter.

The investigation is carried out using a 2D fluid model, included in the Plasimo modeling framework for an atmospheric pressure glow (APG) discharge in a dielectric barrier discharge (DBD) setup. In this study, we considered either pure helium or helium gas with a certain amount of nitrogen present. The modeled species are the background gases He and $N_2$, the electrons, the ions He$^+$, He$^{2+}$, $N_2^+$, and the metastable helium atoms He$^{m+}$, and the helium excimers He$^+_2$. The ions $N^+$ and $N_2^+$ and the chemically related atomic N were not taken into account for matters of simplicity. These particles are of minor importance in the ionic composition of the atmospheric plasma because $N^+$ is very quickly converted into $N_2^+$ through $N^+ + N \rightarrow N_2^+ + e^-$ and the degradation of $N_2^+$ by $N_2^+ + N \rightarrow N_2^+ + N_2$ is about 6.5 times faster than the equivalent degradation reaction of $N_2^+$, i.e., $N_2^+ + N \rightarrow N^+ + 2N_2$. Inclusion of these particles would only lead to a possible amplification of the impurity effects. The energy dependent transport data and reaction coefficients of the electrons were calculated using BOLSIG (Ref. 6) and the transport data for the other species were obtained from literature. The chemical reaction set used in the model is composed from publications on discharge modeling found in literature and consists of 18 chemical reactions which are shown in Table I and an extra electron energy loss term for the production of radiative species.

The experimental setup under consideration is very similar to the setup used by Massines et al. and Mangolini et al. for the sake of comparison with experiment. The configuration consists of two parallel electrodes both covered with alumina dielectrics ($\varepsilon_r = 9$) of 1 mm thickness. The distance between the dielectric surfaces is 5 mm. One electrode is kept at ground potential and at the other a sinusoidal voltage is applied with a frequency of 10 kHz and an amplitude of 2.6 kV. These conditions have been chosen as such because they allow us to obtain discharge breakdown for every purity level under study. It is worth to mention that a discharge configuration with the above-mentioned electrode

### Table I. Reactions included in the model with their reaction coefficients.

<table>
<thead>
<tr>
<th>Number of reaction</th>
<th>Rate coeff</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e^+ + He \rightarrow e^+ + He^+$</td>
</tr>
<tr>
<td>2</td>
<td>$e^+ + He \rightarrow 2e^+ + He^+$</td>
</tr>
<tr>
<td>3</td>
<td>$e^+ + He^{m+} \rightarrow 2e^+ + He^+$</td>
</tr>
<tr>
<td>4</td>
<td>$e^+ + He^{m+} \rightarrow He^+ + He$</td>
</tr>
<tr>
<td>5</td>
<td>$e^+ + N_2^+ \rightarrow N + N \rightarrow N_2$</td>
</tr>
<tr>
<td>6</td>
<td>$e^+ + N_2^+ \rightarrow N_2 + N_2$</td>
</tr>
<tr>
<td>7</td>
<td>$He^+ + 2He \rightarrow He^{m+} + He$</td>
</tr>
<tr>
<td>8</td>
<td>$He^{m+} + N_2 \rightarrow He^+ + N_2^+$</td>
</tr>
<tr>
<td>9</td>
<td>$N_2^+ + 2N_2 \rightarrow N_2^+ + N_2$</td>
</tr>
<tr>
<td>10</td>
<td>$N_2^+ + N_2 + He \rightarrow N_2 + N_2$</td>
</tr>
<tr>
<td>11</td>
<td>$N_2^+ + N_2 + 2N_2$</td>
</tr>
<tr>
<td>12</td>
<td>$N_2^+ + N_2 + 2N_2 + He$</td>
</tr>
<tr>
<td>13</td>
<td>$He^+ + 2He \rightarrow He^+ + He^+$</td>
</tr>
<tr>
<td>14</td>
<td>$He^{m+} + He^{m+} \rightarrow He^+ + e^-$</td>
</tr>
<tr>
<td>15</td>
<td>$He^+ + N_2 \rightarrow He^+ + N_2^+ + e^-$</td>
</tr>
<tr>
<td>16</td>
<td>$He^+ + M \rightarrow 2He + M$</td>
</tr>
<tr>
<td>17</td>
<td>$He^+_2 + He^+_2 \rightarrow He^+_2 + 2He + e^-$</td>
</tr>
<tr>
<td>18</td>
<td>$He^+_2 + N_2 \rightarrow 2He + N_2^+ + e^-$</td>
</tr>
</tbody>
</table>
properties, a frequency of 10 kHz, an applied voltage amplitude of 2 kV, and an impurity level of 100 ppm of nitrogen is exactly the same as used by Mangolini et al. 1 In this case, a periodic discharge is obtained in which every half period, when the gap voltage reaches 1.5 kV, a narrow current peak occurs with an amplitude of about 2.5 mA/cm². Such current profile is in very good agreement with the experimental current profiles measured by Mangolini et al. 1 In their experiments, the current peaks occur at the same gap voltage of about 1.5 kV, with a somewhat higher current density amplitude of 3.5 mA/cm². For this configuration, however, it was not possible in the model to reach breakdown when no nitrogen impurities were present. Periodic discharge behavior was successfully obtained in pure helium when an applied voltage amplitude of 2.6 kV or higher is used. This result confirms that the presence of nitrogen impurities in helium gas has a decreasing effect on the breakdown voltage. 14

The range of impurity levels under consideration is based on literature. The reported range in literature is quite large with a bottom value of 0.5 ppm (Ref. 3) and an upper value of 0.5%. To our knowledge, all reported values of nitrogen impurities in atmospheric helium are always situated in this range. A very important effect of these impurity levels such as the influence on the breakdown voltage is more or less understood 14 but concerning the influence on the plasma composition, some questions remain unanswered.

In order to illustrate the significant influence of even small amounts of impurity on the composition, the time and spatial average of the charged particle densities in the discharge are presented in Fig. 1 for impurity levels ranging from 0 to 5 ppm. First of all, note that the total positive ion density is about 10%–20% higher than the electron density. As is well known, this can be attributed to the spatial structure of the glow discharge since the plasma sheath is positively charged and the plasma bulk is quasineutral, which cause the spatially averaged charge to be slightly positive. Moreover, both the total ion density and the electron density gradually rise with increasing N2 impurity level for the range shown in Fig. 1. The densities of He⁺ are omitted because these do not achieve values higher than $5 \times 10^{13}$ m⁻³. It is also worth to mention that at the instant of maximum current, the electron and total ion densities in the plasma bulk and presheath are for every nitrogen level to be always in the range from $10^{16}$ m⁻³ to $6 \times 10^{17}$ m⁻³. This maximum value lies much higher than the values shown in Fig. 1 because the values in Fig. 1 are averaged in time and the APG DBD is a pulsed discharge. This range is in good agreement with the results of similar numerical studies reported in literature 11,12,13 which range from $10^{16}$ m⁻³ to $5 \times 10^{17}$ m⁻³.

It is clear that only for discharges with less than 1 ppm of nitrogen impurity, the positive charge is determined by the He⁺ ions. Already at 1 ppm of nitrogen, the time and spatially averaged densities of He⁺ and N2⁺ ions are the same. At about 3.5 ppm of nitrogen, the N2⁺ ion density also attains a value of the same magnitude as the He⁺ ion densities. This proves that even small impurity levels have a great effect on the composition of the plasma, since already in the limited range of 0 to 5 ppm of nitrogen impurity, the He⁺ densities drop from most important ion in the discharge to third-rate ion.

To investigate the effect of impurity levels higher than 5 ppm, the time and spatially averaged values of the charged particle densities are plotted in Fig. 2 for the entire simulated range. Since the largest variations occur with the smallest impurity levels, we use a logarithmic scale for the nitrogen levels, ranging from the lowest nonzero value of 0.5 ppm to the highest simulated value of 0.5%. Figure 2 shows that the He⁺ density drops over the entire range when the relative level of nitrogen in helium gas increases. The He⁺ ions become negligible in comparison with the nitrogen ions for impurity levels of about 17 ppm or higher. As indicated using Roman numerals and vertical dotted lines in Fig. 2, we divide the impurity dependent profile into four separate regions based on which ions are responsible for the positive charge.

The first region (indicated by I, shown fully in Fig. 1) ranges from zero to 1 ppm. In this region, He⁺ is dominating the positive charge, while N2⁺ has an important role but it is still secondary.

The second region (indicated by II) ranges from 1 to about 17 ppm and shows two important features. First, the ionization degree of the discharge gas reaches a time and spatially averaged maximum of about $3 \times 10^{-9}$ at an impurity level of about 1.7 ppm. Second, the total positive ion density is most sensitive to impurity levels in this range, with a slight increase in the nitrogen density.

The third region (indicated by III) starts at about 17 ppm and continues up to the highest simulated value of 0.5%. In this region, He⁺ ions are still present, but their density decreases as the nitrogen concentration increases, while N2⁺ ions become the dominant positive ion species.

The fourth region (indicated by IV) begins at the highest simulated value of 0.5% and extends to the maximum impurity level. In this range, N2⁺ ions are the only positive ion species present, indicating that the discharge has transitioned into a nitrogen-dominated regime.

In summary, the effect of nitrogen impurities on the composition of an atmospheric pressure helium DBD is significant, with the presence of even small amounts of nitrogen causing a decrease in the breakdown voltage and altering the spatial and temporal distribution of charged particles. The influence of these impurities on the plasma composition is complex and depends on the specific impurity level, with different regions characterized by different dominant ion species.
degree of 8 ppm. Second, in this range, the N$_2^+$ ion determines the positive charge in the discharge, while He$_2^+$ decreases in this region from a secondary role to almost negligible and N$_4^+$ rises from an unimportant position to a secondary role in the discharge.

The third region (indicated by III) ranges from about 17 to about 600 ppm. The positive charge is now completely governed by the nitrogen ions and N$_4^+$ has become the most important positive ion in the discharge. The He$_2^+$ ion densities do not attain values higher than $10^{11}$ m$^{-3}$ anymore. We have chosen to designate the boundary of the third region to 600 ppm because for impurity levels higher than this value (i.e., region IV), the N$_2^+$ densities also have become negligible and the positive charge is completely governed by the N$_4^+$ ions.

To provide more insights in the underlying mechanisms, we plot in Fig. 3 the time and spatially averaged total production and destruction rates of the He$_2^+$, N$_2^+$, and N$_4^+$ ions. Figure 3 shows that the reason for the decrease in He$_2^+$ densities in the second region lies in the decrease of the production rate. Our calculations predict that the most important He$_2^+$ production process at low N$_2$ levels, namely, the self-Penning ionization of He$_2^*$ (reaction 17, Table I), becomes unimportant through the loss of He$_2^*$ by its Penning ionization of N$_2$ (reaction 18, Table I) since the time and spatially averaged density of N$_2$ is at 5 ppm already about 150 times bigger than the He$_2^*$ density and the ratio keeps increasing with increasing N$_2$ levels. This causes the drop in the He$_2^+$ production from 0 to 50 ppm, as shown in Fig. 3, and explains the decrease of the He$_2^+$ density in region II in Fig. 2.

In region II in Fig. 2, N$_4^+$ determines the positive charge because the He$_2^+$ density has already dropped significantly, for the reasons mentioned above, and the N$_2$ level is still relatively low. The production of N$_4^+$ in the second region is for more than 80% determined by three reactions which are directly depending on the nitrogen partial pressure, namely, the Penning ionizations of N$_2$ by He$_m^+$ and He$_s^*$ and the charge exchange reaction of He$_2^+$ with N$_2$ (reactions 8, 15, and 18 in Table I). Also, the destruction of N$_4^+$ is directly influenced by the nitrogen partial pressure since it is increasingly determined by the association of N$_2^+$ with N$_2$ and He as a third collision partner (reaction 10, Table I), which is responsible for about 50% of the N$_4^+$ destruction at 1 ppm of nitrogen impurity and already for 87% at 17 ppm of N$_2$.

Consequently, both the production and destruction rise significantly with increasing nitrogen content. However, since the above-mentioned associative reaction is very fast ($k = 1.9 \times 10^{-20}$ cm$^6$ s$^{-1}$) and depends directly on both background gases, the conversion of N$_2^+$ to N$_4^+$ is increasingly promoted, which causes the N$_2^+$ fraction in the discharge to decrease again. It must be noted that this reaction rate coefficient has been experimentally determined for pressures not higher than 2 mbar, which can lead to a possible overestimation when used at atmospheric pressure and cause the results to change somewhat quantitatively.

Our calculations show that the production of N$_4^+$ is almost completely determined by the associative collision of N$_4^+$ with N$_2$ with He as a third partner (reaction 10, Table I) for every impurity level. This reaction is directly related to the partial pressure of nitrogen. The destruction of N$_4^+$ is completely governed by the dissociative electron recombination reaction (reaction 6, Table I) and the dissociative collision with He (reaction 12, Table I), which are not directly related to the partial pressure of nitrogen. Since the above-mentioned N$_2^+$ production reaction is directly related to the nitrogen content and the two destruction reactions are not directly related to the nitrogen content, the N$_4^+$ fraction in the discharge always increases with rising nitrogen levels.

We have shown in this letter that the influence of common molecular impurities, such as nitrogen in helium gas, is very important even at impurity levels of about 1 ppm. Under the assumption that the rate coefficient of the associative conversion of N$_2^+$ (reaction 10, Table I) may be used as such, it can be concluded from our calculations that the molecular N$_2^+$ ion, which is often neglected in this kind of studies, becomes even the most important ion in the discharge, if the impurity level is higher than approximately 17 ppm. Finally, we have addressed how the chemical balances shift, which create the different regions in Fig. 2, characterized by different dominating ions and explain how the N$_4^+$ fraction in the discharge increases when the nitrogen level rises.

We would like to acknowledge the assistance of the Calcula computer facility of the University of Antwerp in the realization of the performed calculations.