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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_4^+ 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_4^+ 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 gas (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.^{1,2} In simulations, this purity level is sometimes derived from estimations¹ or sometimes used as a fitting parameter to match a fundamental parameter such as gas voltage to the experimental value.³ 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 framework⁴ 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 N_4^+ , the metastable helium atoms He_m^* , and the helium excimers He_2^* . The ions N^+ and N_3^+ 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 $N^+ + N + He \rightarrow N_2^+ + He$ and the degradation of N_3^+ by $N_3^+ + N \rightarrow N_2^+ + N_2$ is about 6.5 times faster⁵ than the equivalent degradation reaction of N_4^+ , i.e., $N_4^+ + N \rightarrow N^+ + 2N_2$. 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.^{7,8} The chemical reaction set used in the model is composed from publications on discharge modeling found in literature^{1,9–11} 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.¹²

The experimental setup under consideration is very similar to the setup used by Massines *et al.*¹³ and Mangolini *et al.*¹ for the sake of comparison with experiment. The configuration consists of two parallel electrodes both covered with alumina dielectrics ($\epsilon_r=9$) 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. The first three reaction coefficients are calculated using BOLSIG. In reaction 16, M denotes a heavy collision partner and the destruction frequency is taken from Golubovskii *et al.*¹¹

Number of reaction	Rate coeff
1 $e^- + He \rightarrow e^- + He_m^*$	$f(\sigma)$
2 $e^- + He \rightarrow 2e^- + He^+$	$f(\sigma)$
3 $e^- + He_m^* \rightarrow 2e^- + He^+$	$f(\sigma)$
4 $e^- + He_2^+ \rightarrow He_m^* + He$	$8.9 \times 10^{-9} \left(\frac{T_g}{T_e}\right)^{1.5} \text{ cm}^3 \text{ s}^{-1}$
5 $e^- + N_2^+ \rightarrow N + N \rightarrow N_2$	$4.8 \times 10^{-7} \left(\frac{T_g}{T_e}\right)^{0.5} \text{ cm}^3 \text{ s}^{-1}$
6 $e^- + N_4^+ \rightarrow N_2 + N_2$	$2 \times 10^{-6} \left(\frac{T_g}{T_e}\right)^{0.5} \text{ cm}^3 \text{ s}^{-1}$
7 $He^+ + 2He \rightarrow He_2^+ + He$	$1.1 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$
8 $He_2^+ + N_2 \rightarrow He_m^* + N_2^+$	$1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$
9 $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$	$1.9 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$
10 $N_2^+ + N_2 + He \rightarrow N_4^+ + He$	$1.9 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$
11 $N_4^+ + N_2 \rightarrow N_3^+ + 2N_2$	$2.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$
12 $N_4^+ + He \rightarrow N_2^+ + N_2 + He$	$2.5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$
13 $He_m^* + 2He \rightarrow He_2^* + He$	$2 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$
14 $He_m^* + He_m^* \rightarrow He_2^* + e^-$	$1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$
15 $He_m^* + N_2 \rightarrow He + N_2^+ + e^-$	$5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
16 $He_2^* + M \rightarrow 2He + M$	10^{-4} s^{-1}
17 $He_2^* + He_2^* \rightarrow He_2^+ + 2He + e^-$	$1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$
18 $He_2^* + N_2 \rightarrow 2He + N_2^+ + e^-$	$3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

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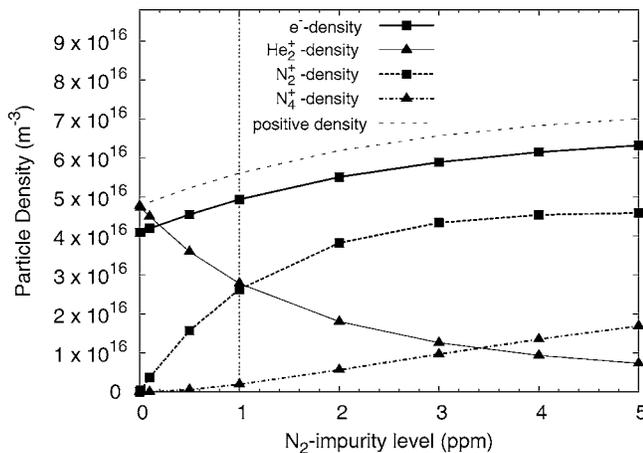


FIG. 1. Calculated time and spatially averaged densities of the important charged particles in an atmospheric DBD in helium with different levels of N_2 impurity. The vertical dotted line indicates the boundary between the He_2^+ governed part and the N_2^+ governed part. The upper dotted curve indicates the sum of the positive ion densities.

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 understood¹⁴ 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 N_2 impurity level for the range shown in Fig. 1. The densities of He^+ are omitted because these do not achieve values higher than $5 \times 10^{13} \text{ m}^{-3}$. It is also worth to mention that at the instant of maximum current, the electron and total ion densities in the plasma bulk and

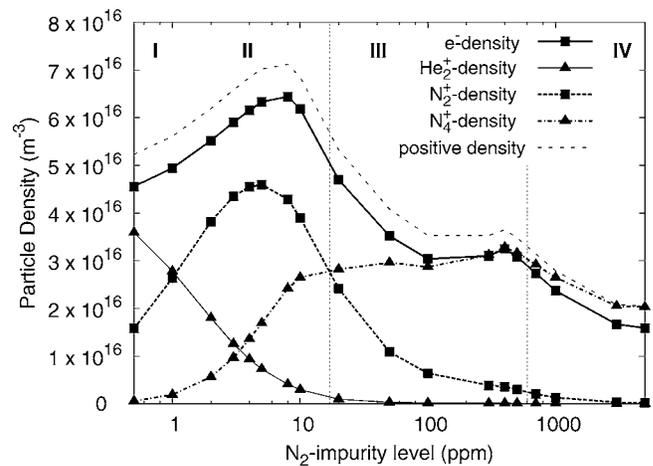


FIG. 2. Calculated time and spatially averaged densities of the important charged particles in an atmospheric pressure helium DBD with nitrogen impurity levels ranging from 0.5 ppm to 0.5%. Region I denotes the He_2^+ governed part, region II the N_2^+ governed part, region III the N_4^+ governed part with significant N_2^+ contribution, and region IV is completely governed by N_4^+ ions.

presheath are for every nitrogen level to be always in the range from 10^{16} m^{-3} to $6 \times 10^{17} \text{ m}^{-3}$. 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^{1,11,13} which range from 10^{16} m^{-3} to $5 \times 10^{17} \text{ m}^{-3}$.

It is clear that only for discharges with less than 1 ppm of nitrogen impurity, the positive charge is determined by the He_2^+ ions. Already at 1 ppm of nitrogen, the time and spatially averaged densities of He_2^+ and N_2^+ ions are the same. At about 3.5 ppm of nitrogen, the N_4^+ ion density also attains a value of the same magnitude as the He_2^+ 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_2^+ 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_2^+ density drops over the entire range when the relative level of nitrogen in helium gas increases. The He_2^+ 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_2^+ is dominating the positive charge, while N_2^+ 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 3×10^{-9} at an impurity

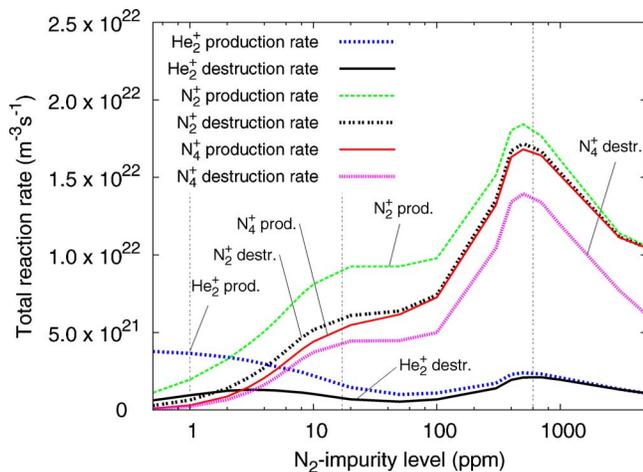


FIG. 3. (Color online) Calculated sums of total production and destruction rates for He_2^+ , N_2^+ , and N_4^+ .

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^{15} 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_2^+ 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_2^+ 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_2^* and the charge exchange reaction of He_2^+ with N_2 (reactions 8, 15, and 18 in Table I). Also, the destruction of N_2^+ 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_2^+ 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 ($k = 1.9 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$) 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,¹⁰ 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_2^+ 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_4^+ 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_4^+ 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.

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