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INFLUENCE OF CARBON DIOXIDE CONVERSION ON THE ELECTRON TRANSPORT PARAMETERS IN THE RF ELECTRIC FIELD

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In this research, the average electron energy, mobility, diffusion coefficient, full attachment and ionization frequencies in a radio-frequency electric field in the reduced field range of $E/N = 1…10^4$ Td were calculated using the BOLSIG+ code. Calculations were made for carbon dioxide and $CO_2/CO/O_2$ mixtures arising after the plasma conversion of CO_2. The influence of the conversion coefficient χ on the electron transport parameters has been revealed. The values of E/N have been determined at which the mixture composition change has a weak effect on the above transport parameters. The conversion coefficient's most pronounced effect on each of the transport parameters is observed in the range of weak combined electric field $E/N < 20$ Td. In this range, the main process of negative ions formation is the 3-particle attachment of low-energy electrons to oxygen molecules. In the strong electric field $E/N > 2000$ Td, negative ions are born mainly due to the dissociative attachment of electrons to CO and O_2 molecules.

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INTRODUCTION

Accumulation of carbon dioxide in the Earth's atmosphere has increased the significance of the tasks of both reducing CO_2 emissions during the burning of fossil fuels and converting existing CO_2 into raw materials for the chemical industry. Plasma methods of CO_2 conversion are among the most effective [1, 2], especially in catalyst-assisted plasma processes [3]. To increase the conversion efficiency, discharges of different types in CO_2 are widely studied: at atmospheric pressure [4–7] and at a pressure of hundreds of Torr [4, 8, 9], as well as discharges of lower pressure of the order of 1 Torr and below – pulsed [10, 11], DC glow discharge with flat electrodes [12, 13] and hollow cathode [14], capacitive [15, 16] and inductive [17–19] RF discharges, and others [20]. These discharges in CO_2 are intensively studied experimentally, and numerical models of gas dynamics in the discharge chamber [21], kinetic processes in plasma [4, 18], etc. are developed.

Carbon dioxide, fed to the discharge plasma, is converted to some extent into carbon monoxide CO and oxygen O_2, which means that to use hydrodynamic models it is necessary to know the electron transport parameters in this complex gas mixture. Therefore, in this research, such electron transfer parameters as the average energy, diffusion coefficient, mobility, total ionization and attachment rates in gas mixtures corresponding to different degrees of carbon dioxide conversion were calculated in a wide range of the reduced electric field $E/N = 1…10^4$ Td.

1. CALCULATION PROCEDURE

The process of plasma conversion of CO_2 molecules by electron impact goes through the following reactions:

$$CO_2 + e^- \rightarrow CO + O, \quad (1)$$

$$CO_2 + O \rightarrow CO + O_2. \quad (2)$$

Briefly, this can be written as follows:

$$CO_2 + e^- \rightarrow CO + 0.5O_2 + e^-. \quad (3)$$

Let us introduce the conversion coefficient $\chi = (Q_{in} - Q_{out})/Q_{in}$, where Q_{in} and Q_{out} are the CO_2 flows entering and leaving the discharge chamber, respectively. The composition of the gas mixture will be determined as follows. For a given value of χ, the CO_2 concentration will be a fraction of $(1 - \chi)$ of the total gas concentration in the mixture, then the fraction of CO will be $2/3\ \chi$, and the fraction of O_2 is $1/3\ \chi$ (see (1)–(3)). For example, with a conversion coefficient $\chi = 0.5$, the gas mixture will consist of 50% CO_2, 33% CO, and 17% O_2.

Calculations of the electron transport parameters were performed using the BOLSIG+ code [22]. This code numerically solves the Boltzmann equation for pure gases and their mixtures. For this purpose, tables of cross-sections for elastic and inelastic collisions of electrons with gas molecules are included into the input file. We used the cross sections given on the Web-Based Platform LXCat [23]. Note that the calculations were performed for an alternating electric field with a frequency of 13.56 MHz.

2. RESULTS OF MODELING

Now let us consider the results of calculations using the BOLSIG+ code. Fig. 1 shows the dependence of the average electron energy ε on the reduced electric field E/N (N is the density of gas molecules) for different values of the carbon dioxide conversion coefficient χ. The average energy is established as a result of the balance between the energy gain by electrons in the electric field and the losses during their elastic and inelastic collisions with gas molecules. It is evident from the figure that in weak electric fields at $E/N < 27$ Td, an increase in the degree of carbon dioxide conversion leads to an increase in the average electron energy. At $E/N \approx 27$ Td, the curves for different values of χ are very close (the average electron energy in the range is 0.6…0.7 eV), i.e. a change in the composition of the gas

mixture has little effect on the average electron energy. In the range $E/N \approx 27\ldots460$ Td, the average electron energy decreases with χ increase. This can lead to a change in the mechanism of carbon dioxide conversion, since at high electron energies the process of direct dissociation of CO_2 molecules is observed, while at low electron energies the dissociation process occurs due to the exchange of vibrational energy between CO_2 molecules. Finally, at $E/N > 460$ Td an increase in the conversion coefficient χ again leads to the rise of average electron energy.

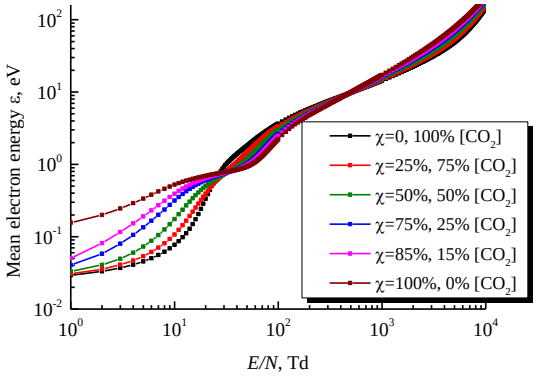

Fig. 1. Dependences of the average electron energy on the reduced electric field for different values of the conversion coefficient χ

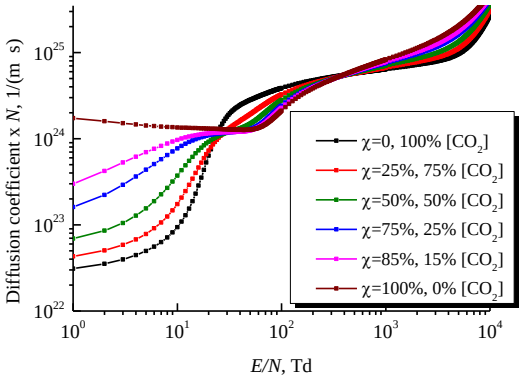

Fig. 2. Dependences of the product of the electron diffusion coefficient and the density of gas molecules N on the reduced electric field for different values of the conversion coefficient χ

Now let us consider the effect of the degree of conversion on electron diffusion in the gas mixture formed during the conversion of carbon dioxide. Fig. 2 shows the dependence of the product $D_e \cdot N$ (D_e is the electron diffusion coefficient) on the reduced electric field E/N for different conversion coefficients χ. Here, two values of $E/N = 25$ and 390 Td are also observed, for which the diffusion spreading of electrons occurs at almost the same rate for any composition of the gas mixture formed during the conversion of carbon dioxide. При $E/N < 25$, an increase in the degree of CO_2 conversion significantly increases the value of the electron diffusion coefficient. In the range $E/N \approx 25\ldots390$ Td, the diffusion spreading of electrons occurs faster in pure carbon dioxide, but at a stronger electric field the situation again changes to the opposite.

Electron mobility μ_e is the proportionality coefficient between the electric field strength and the drift velocity $V_{dr} = \mu_e \cdot E$. At $E/N \approx 180$ Td, the curves for different χ values practically converge (Fig. 3), i.e. a change in the conversion degree has little effect on their drift velocity in the discharge plasma. At $E/N < 180$ Td, a complex dependence of electron mobility on E/N is observed. At weak fields $E/N < 10$ Td, the highest electron mobility will be at high values of the conversion coefficient χ. At $E/N > 10$ Td, the mobility in pure CO_2 reaches a maximum, and at high χ, minima can be observed. Finally, at $E/N < 180$ Td, the fastest drift motion of electrons will be in a mixture with a high χ.

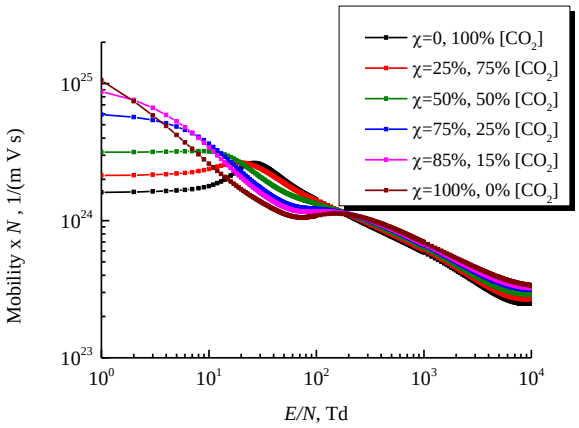

Fig. 3. Dependences of the product of electron mobility and gas molecule density N on the reduced electric field for different values of the conversion coefficient χ

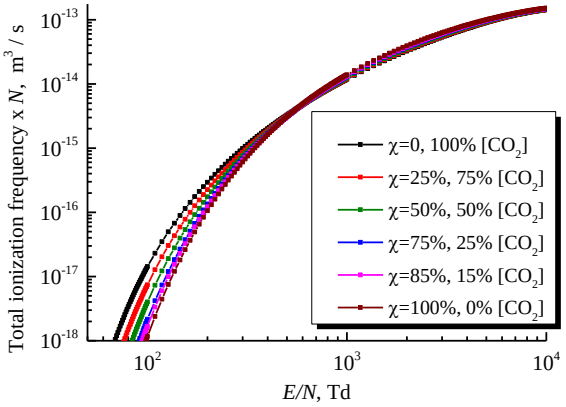

Fig. 4. Dependences of the product of the total ionization frequency and the density of gas molecules N on the reduced electric field for different values of the conversion coefficient χ

The ionization frequency in a gas mixture is determined by their concentrations, ionization thresholds, cross-sections for each type of gas, and the electron energy distribution function. In Fig. 4, we show the total ionization frequency, i.e. the sum of the ionization frequencies for each component of the mixture. It is evident from the figure that at $E/N < 560$ Td, the ionization process will be most intense in pure carbon dioxide, and an increase in the conversion coefficient χ leads to a monotonic decrease in the ionization rate. In the range of $E/N > 560$ Td, the situation changes, and ionization occurs faster in mixtures with a low carbon dioxide content.

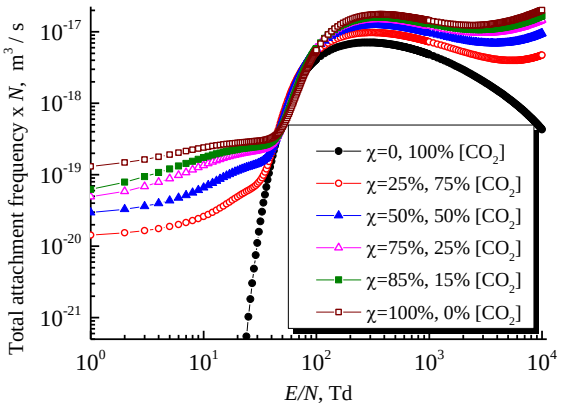

Fig. 5. Dependences of the product of the total attachment frequency and the density of gas molecules N on the reduced electric field for different values of the conversion coefficient χ

Fig. 5 deserves special attention, as it shows the dependence of the total attachment frequency on the reduced electric field *E/N* for different χ values. The attachment frequency in pure carbon dioxide increases monotonically, reaches a maximum at $E/N \approx 280$ Td, and then decreases monotonically. The threshold energy for dissociative attachment of electrons in CO_2 is 3.85 eV [21], so this process is practically absent in weak electric fields $E/N < 20$ Td. However, even at a small value of the conversion coefficient χ, noticeable attachment is observed even at $E/N = 1$ Td, when the average electron energy does not exceed 0.1 eV. Dissociative attachment of electrons to CO molecules begins at a threshold energy of 9.2 eV, so it is obvious that this process does not occur in a weak electric field. The threshold energy of dissociative attachment to O_2 molecules is 4.4 eV, which also makes it unlikely at low *E/N*.

At the same time, three-body attachment is also possible in oxygen, when first a low-energy electron attaches to an oxygen molecule, transforming it into a vibrationally superexcited negative ion O_2^{-**} [24]. Then two processes are possible. Autoionization of the O_2^{-**} ion can occur, that is, an electron is torn away from this negative ion, and this process is the most probable [24] and leads to the loss of the negative ion. However, O_2^{-**} can collide with another molecule and transfer some of its vibrational energy to it. Then a stable negative ion with a moderate level of vibrational excitation O_2^{-*} will be formed. Recall that this process occurs at a low electron energy, which is insufficient for dissociative attachment. Then the behavior of the total attachment frequency at $E/N < 20$ Td (see Fig. 5) becomes clear. The more molecular oxygen is present in the gas mixture, the higher the frequency of attachment to its molecules.

At $E/N > 20$ Td, the total attachment frequencies first increase with *E/N* and reach maxima at $(E/N)_{max}$, which increase linearly with χ. Thus, in pure carbon dioxide ($\chi = 0$) $(E/N)_{max} = 290$ Td, and at $\chi = 1$ $(E/N)_{max} = 364$ Td. After passing the maxima, the total attachment frequencies for $\chi > 0$ first decrease, reach minima, and then increase with a further increase in the reduced electric field ($E/N > 2000$ Td). This increase in the attachment frequency is absent in pure CO_2, since for it the dissociative attachment cross section rapidly decreases with an increase in the average electron energy and *E/N*. However, in CO and O_2 the dissociative attachment cross sections of electrons are higher [21]. Moreover, as we have already mentioned in the analysis of Fig. 3, at high *E/N* the electron mobility (and drift velocity) is higher in mixtures with a high conversion coefficient, which promotes the process of electron attachment in them.

CONCLUSIONS

In this paper, the BOLSIG+ code is used to study the electron motion in $CO_2/CO/O_2$ gas mixtures that arise during plasma conversion of carbon dioxide. The composition of these mixtures is determined by the conversion coefficient χ. The following electron transport parameters are calculated in a wide range of the reduced electric field *E/N* and at $\chi = 0…100\%$: average energy, mobility, diffusion coefficient, total ionization and attachment frequencies of electrons. It is shown that at certain *E/N* values, these electron transport parameters may weakly depend on the degree of carbon dioxide conversion. The mechanisms influencing the behavior of each of the transport parameters in different *E/N* ranges are explained. The results obtained are necessary for analytical and hydrodynamic models of processes in radio-frequency discharges in carbon dioxide.

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ЧИСЕЛЬНЕ МОДЕЛЮВАННЯ ВПЛИВУ СТУПЕНЮ КОНВЕРСІЇ ВУГЛЕКИСЛОГО ГАЗУ У ВЧ-ЕЛЕКТРИЧНОМУ ПОЛІ НА ПАРАМЕТРИ ПЕРЕНОСУ ЕЛЕКТРОНІВ

В. Лісовський, С. Дудін, П. Платонов, В. Єгоренков

За допомогою BOLSIG+ code розраховано середню енергію електронів, рухливість, коефіцієнт дифузії, повні частоти прилипання та іонізації у ВЧ-електричному полі у діапазоні зведеного поля $E/N = 1…10^4$ Td. Розрахунки проведено для вуглекислого газу та сумішей $CO_2/CO/O_2$, які виникають при плазмовій конверсії CO_2. З'ясовано вплив коефіцієнта конверсії χ на параметри переносу електронів. Визначено величини E/N, при яких зміна складу газової суміші під час конверсії CO_2 слабко впливає на наведені параметри переносу. Показано, що найбільш яскравий вплив коефіцієнта конверсії на кожен з параметрів переносу спостерігається в діапазоні слабкого зведеного електричного поля $E/N < 20$ Td. У цьому діапазоні основним процесом формування негативних іонів є 3-частинкове прилипання електронів низької енергії до молекул кисню. У сильному електричному полі $E/N > 2000$ Td негативні іони народжуються переважно при дисоціативному прилипанні електронів до молекул CO та O_2.