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STUDYING CO_2 CONVERSION IN DC GLOW DISCHARGE

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We have registered the mass-spectra of the gas mixture leaving the chamber and the discharge current-voltage characteristics and determined the specific energy input (SEI), the absolute conversion coefficient χ and the conversion energy efficiency η in the CO_2 pressure range of 0.05...5 Torr. Converting CO_2 molecules was performed in the glow discharge in a chamber with distributed same-side gas supply and pumping. As a result the conversion coefficient χ equaling 70% was achieved, but the conversion energy efficiency η did not exceed 1...3 % because of considerable power loss due to acceleration of positive ions, gas and electrode heating as well as to inelastic collisions between electrons and gas molecules not leading to CO_2 conversion.

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1INTRODUCTION

The growing footprints of carbon dioxide and other gases lead to the greenhouse effect enhancement and climate changes. It is important not only to limit the emission of greenhouse gases but to develop the means of their utilization. The plasma conversion of carbon dioxide CO_2 molecules into carbon monoxide CO and oxygen O_2 molecules is one of the most efficient methods. A large number of papers is devoted to this problem (see, e.g. papers [1-6]). The reviews [1, 2] have performed the analysis of the contemporary state of research into the plasma conversion in gas discharges of different types. Two extreme cases are usually observed. In the first case the conversion coefficient (ratio of the number of decomposed molecules to the initial number of CO_2 molecules) may be large (some tens of percent) but at the same time the conversion energy efficiency (the portion of power introduced into conversion of CO_2 molecules) may amount some parts or units of percents. In the second case one increases the power contribution into the conversion process but at the same time the number of converted molecules is small.

Therefore it is imminent to find such type of the discharge and chamber design with which one can manage to get the maximally large values for both the conversion coefficient and conversion energy efficiency. This circumstance has induced a large number of papers devoted to studying the processes in gas discharges in carbon dioxide and its mixtures with other gases (see, e.g. [7-10]). Contemporary papers present the results of research into carbon dioxide conversion in discharges of ambient pressure or lowered one (hundreds Torr). However, studying the applicability of low pressure discharges to solve this problem is also of interest, and here we continue the line of research presented in papers [5, 6].

This paper presents the study of the plasma conversion of carbon dioxide in DC glow discharge of low pressure. Through the employment of the mass-spectrometer and optical spectrometer we have determined the conversion coefficient and conversion energy efficiency values in the wide range of power deposited into the discharge.

1. EXPERIMENTAL

Experiments have been performed in the device possessing the distributed same-side gas supply and pumping. We have employed a shower nozzle electrode (photo in Fig. 1), where the orifices for gas supply and pumping are uniformly distributed over its surface (265 orifices in total). The necessity of combining in a single electrode all orifices for gas supply and pumping was due to the circumstance that the second electrode was a high-voltage one and connecting gas pipes to it might produce undesirable discharges outside the chamber limits. In order to exclude parasitic discharge in orifices or gas supply and pumping systems, this shower nozzle electrode was always above and was grounded. The second electrode was solid, placed below, and a DC supply unit was connected to it. A negative or positive potential was fed to it. Correspondingly, the upper electrode may be either an anode (below this case will be named as 'Top anode') or a cathode ('Top cathode'). Both electrodes were of stainless steel.

Fig. 1. The photo of the shower nozzle (top) electrode

Between the electrodes a piece of fused silica tube was located of 93 mm inner diameter and vacuum sealed, with the inter-electrode distance of 60 mm. The vacuum chamber was evacuated with preliminary vacuum and turbo-molecular pumps.

Experiments have been performed in the carbon dioxide pressure range from 0.05 to 5 Torr. The gas

pressure was measured with the capacitive-type Baratron 627 probe (MKS Instruments) with the maximum registered value of 10 Torr. The carbon dioxide gas flow in all experiments was 2 sccm.

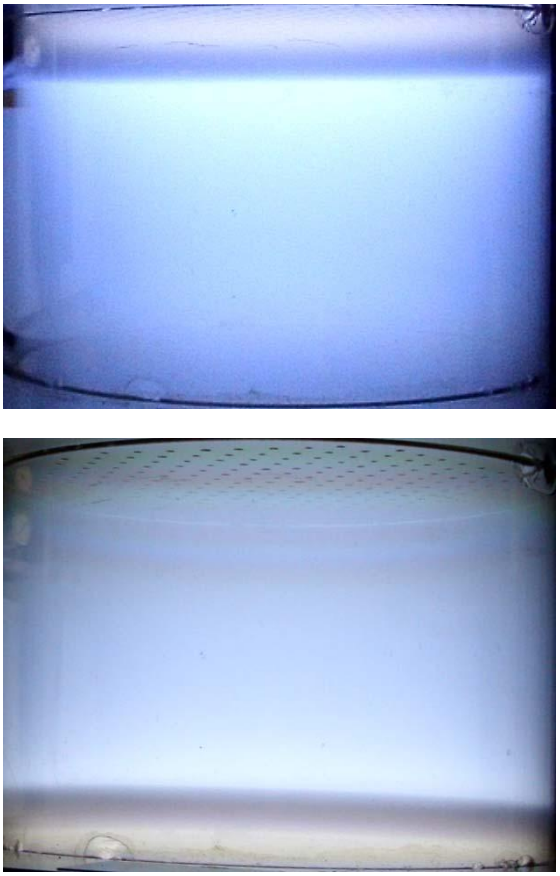

Fig. 2. Photos of dc discharge in CO_2 gas at the pressure of 0.1 Torr for 'Top cathode' and 'Top anode' cases with the current value of 120 mA

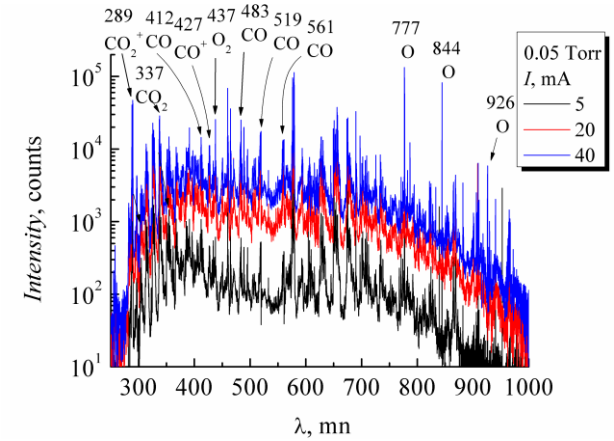

Fig. 3. Emission spectra of dc discharge at the CO_2 pressure of 0.05 Torr for different current values. 'Top cathode' case

The gas mixture leaving the discharge chamber was measured with ROMS-4 mass-spectrometer. We used the optical spectrometer Horiba iHR-320 to study the discharge emission which contained a diffraction grating with 1800 lines/mm and permitting to measure the spectrum in the 200...1000 nm range with the accuracy not less than 1 Å. The optical fiber was positioned at the distance of 5 mm from the upper electrode and it was not moved in the process of measurements.

Carbon dioxide conversion is characterized by three parameters: specific energy input (SEI), absolute conversion coefficient χ and the conversion energy efficiency η. Specific energy input is the ratio of the power contributed to the discharge to the gas flow:

$$SEI\left[J\cdot cm^{-3}\right]=\frac{P\left[kW\right]}{\frac{dm}{dt}\left[L\cdot\min^{-1}\right]}\cdot 60\left[s\cdot\min^{-1}\right]\times$$
$$\times\frac{6.24\cdot 10^{21}\left[eV\cdot kJ^{-1}\right]\cdot 24.5\left[L\cdot mol^{-1}\right]}{6.022\cdot 10^{23}\left[mol^{-1}\right]},$$

where P is the power, dm/dt is the magnitude of the gas flow. The absolute conversion coefficient χ is the portion of CO_2 molecules converted under gas passage through the plasma volume:

$$\chi=\frac{N_{in}-N_{out}}{N_{in}},$$

where N_{in} and N_{out} are the flows of the reagent (CO_2), which are fed into the chamber and removed out of it, respectively. Energy efficiency compares between the energy expenses in a standard case with the standard enthalpy of the process:

$$\eta=\chi\cdot\frac{\Delta H}{SEI},$$

where ΔH =2.93 eV per molecule.

Thus when one registers with a mass-spectrometer the concentrations of CO_2 molecules without plasma and in the burning discharge and knows the power deposited into plasma and the gas flow, one may determine both χ and η against SEI. This technique has been described in more detail in papers [5, 6].

2. EXPERIMENTAL RESULTS

The 'Top cathode' and 'Top anode' cases mean that the CO_2 feeding and the removal of conversion products were made through the upper electrode serving correspondingly as a cathode or an anode. The discharge photos for these two cases are presented in Fig. 2. A cathode sheath with the thickness depending on the gas pressure and the discharge current adheres to the cathode. At the lowest CO_2 pressure (0.05 Torr) the optical fiber collected the discharge emission out of the cathode sheath. Fig. 3 presents the spectra for different current values for the 'Top cathode' case. For the 'Top anode' case the spectra differ only quantitatively, because the flows of fast electrons responsible for inelastic collisions in plasma are available both in the cathode sheath as well as in the negative glow [11-17]. It is clear from Fig. 3 that the discharge emission is dominated by oxygen atoms (lines with the wavelength values of 777 and 844 nm usually dominate), along with the CO molecules (Angstrom system, transition $B\ ^1\Sigma \rightarrow A\ ^1\Pi$ from the second to the first state of the electronic excitation, with Fig. 3 showing the most intensive lines) and O_2 (Schumann-Runge system, $B\ ^3\Sigma \rightarrow X\ ^3\Sigma$437 nm). One also observes the CO_2 line (337 nm) and two lines of positive CO_2^+ions (288 and

289 nm) closely located. The wavelength values of molecular lines are presented in paper [18]. Domination of atomic oxygen and CO molecule lines indicates the intense conversion of CO_2 molecules in the plasma volume. However, the registered intensities of emission lines demonstrate the summary radiation from different discharge regions which exhibit different conversion degrees. Therefore in order to calculate the conversion coefficient we will further pay the main attention to the results obtained with the mass-spectrometer connected to the output tube, because they show the efficiency of the discharge as a whole for performing the conversion process.

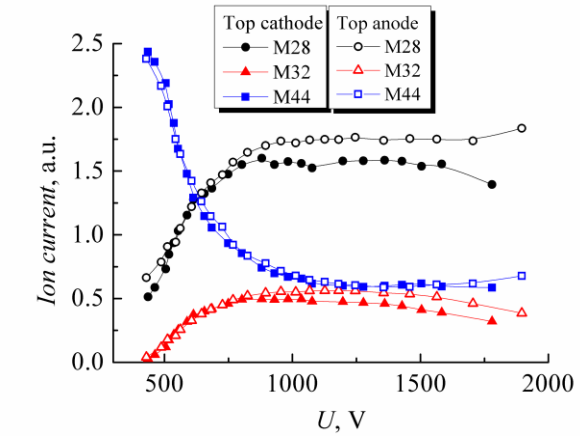

Fig. 4. Peak intensities of the mass-spectra corresponding to 28 (CO), 32 (O_2), and 44 (CO_2) masses against applied voltage for CO_2 pressure of 0.1 Torr and the gas flow of 2 sccm 'Top cathode' and 'Top anode' cases

Fig. 4 presents the peak intensities on the mass-spectra corresponding to CO, O_2, and CO_2 against the voltage applied across the electrodes. The figure shows that the dependences for the 'Top cathode' and 'Top anode' cases happened to be close to each other. With the voltage growing the CO_2 peak intensity experiences a fast (approximately 5 times) decrease and then saturates with a weak tendency of growth. CO and O_2 concentrations grow with voltage uniformly and then experience saturation. It is not expedient to consider the behavior of the peak corresponding to the atomic oxygen (mass number 16) as it describes only the occurrence of the O atoms in the ionization chamber of the mass-spectrometer, and O atoms formed in the discharge volume have time to recombine into O_2 and CO_2 molecules on the walls of the vacuum system and of a capillary furnishing the gas to be analyzed into the mass-spectrometer.

We have employed the data presented in Fig.4 and obtained the dependences of the conversion coefficient χ and the conversion energy efficiency η against the applied voltage (Fig. 5) and against SEI (Fig. 6). These figures make clear that the maximum conversion energy η is observed at the smallest voltage values of the discharge burning and it amounts to 1...2 %. Conversion coefficient χ uniformly grows and then approaches saturation approaching 65...70 %. Increasing the applied voltage leads to the fast η lowering due to the increase of the conversion product concentration in the discharge volume in which the energy is deposited but this energy contribution is useless. The results for the 'Top cathode' and 'Top anode' cases happened to be close to each other.

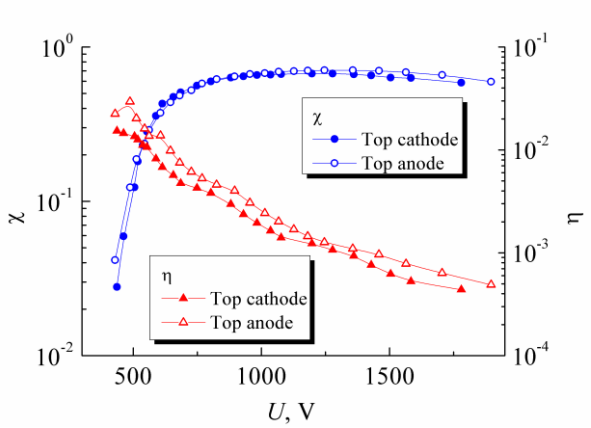

Fig. 5. Conversion coefficient χ and conversion energy efficiency η against applied voltage for CO_2 pressure of 0.1 Torr, gas flow of 2 sccm for 'Top cathode' and 'Top anode' cases

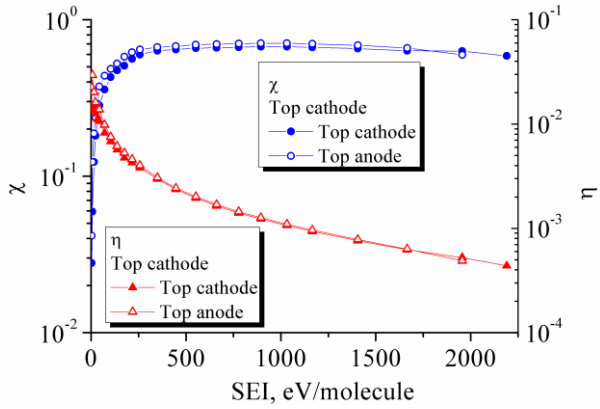

Fig. 6. Conversion coefficient χ and conversion energy efficiency η against SEI for CO_2 of 0.1 Torr, the gas flow of 2 sccm and 'Top cathode' and 'Top anode' cases

Similar results have also been obtained on the dependences of χ and η against SEI (see Fig. 6). This figure demonstrates that energy expenses for converting one CO_2 molecule are sufficiently high. The matter is that the electrons having gained their energy from the electric field spend it further not only for a direct dissociation of CO_2 molecules and for oscillatory excitation of these molecules but also for the electronic excitation and ionization. At the same time, the positive ions accelerated in the cathode sheath may heat the cathode to high temperatures spending a considerable energy for that.

The conversion energy efficiency η against the conversion coefficient χ for the considered CO_2 pressure value of 0.1 Torr is shown in Fig. 7. The $\eta(\chi)$ curve possess a characteristic patter, the qualitatively similar curves may be constructed for all types of plasma conversion [1, 2, 5, 6]. For the cases of 'Top cathode' and 'Top anode' the results are similar qualitatively but the case of 'Top anode' demonstrates superiority in energy efficiency (up to doubling) and in the conversion coefficient.

Now consider the results obtained for different CO_2 pressure values. Consider now only one 'Top cathode' case, because the results for both cases are close to each other.

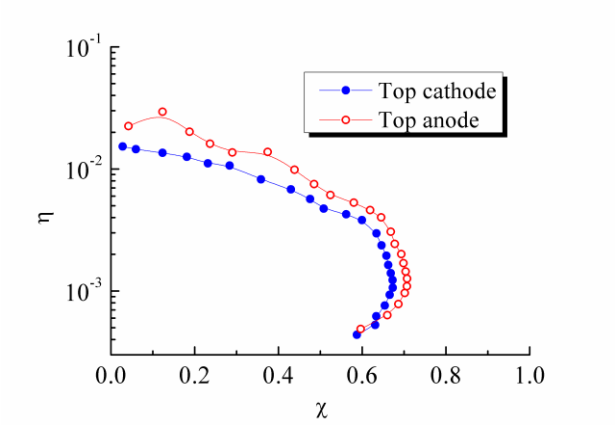

Fig. 7. Conversion energy efficiency η against conversion coefficient χ for CO_2 pressure of 0.1 Torr, gas flow of 2 sccm and 'Top cathode' and 'Top anode' cases

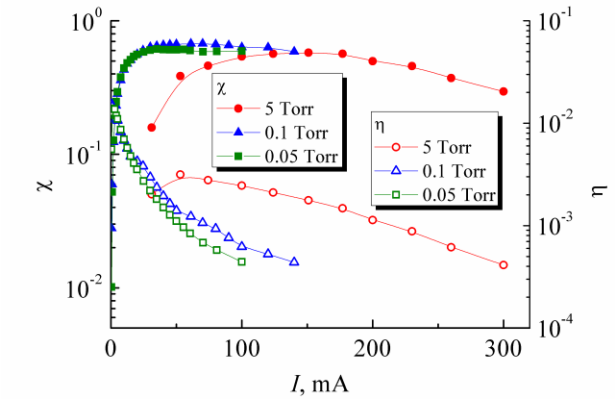

Fig. 8. Conversion coefficient χ and conversion energy efficiency η against discharge current for different CO_2 pressure values. 'Top cathode' case

In Fig. 8 we demonstrate the dependences of the conversion coefficient χ and conversion energy efficiency η against the discharge current for the CO_2 pressure values of 0.05, 0.1, and 5 Torr. If we construct the dependences against voltage as it was done in Fig. 5, then in the scale of this figure the curves for 5 Torr would be two short segments. This is due to the fact that at a sufficiently high gas pressure a normal mode of discharge burning is observed [12, 14, 19-25], when the discharge on the cathode (and on the anode) occupies only a portion of the surface (photo in Fig. 9), the current may vary in the wide range whereas the applied voltage remains almost unchanged. Therefore it is more expedient to show the dependence of the conversion coefficient χ and the conversion energy efficiency η on the discharge current and not on voltage. Note that the discharge in the normal mode of burning is not suitable for the efficient conversion because a portion of the gas may enter the chamber and leave it not passing through the plasma region.

Fig. 8 clearly shows that at the pressure of 5 Torr and low current values (below 100 mA) the conversion coefficient χ is substantially lower than at low pressure values (0.1 and 0.05 Torr), but with the current increase the χ values for different CO_2 values become comparable in value. The conversion energy efficiency η at the pressure value of 5 Torr and the current values above 50 mA some times larger than for low pressure values but it does not exceed 0.3 %. However at the pressure of 5 Torr the discharge cannot burn if the current is below 20 mA and it is extinguished. At the same time, at low pressure the discharge can be supported with the current values of 1 mA and lower, and the conversion energy efficiency η becomes approximately 1 % and higher.

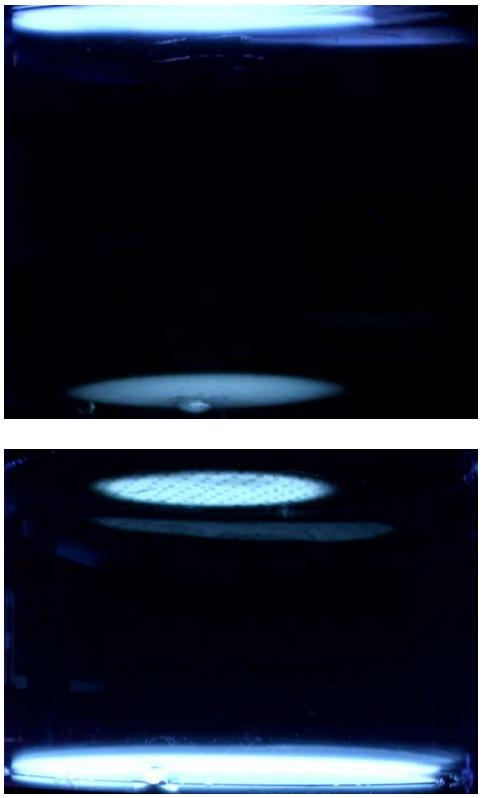

Fig. 9. Discharge photos at the pressure of 5 Torr for 'Top cathode' (above) and 'Top anode' (below) cases

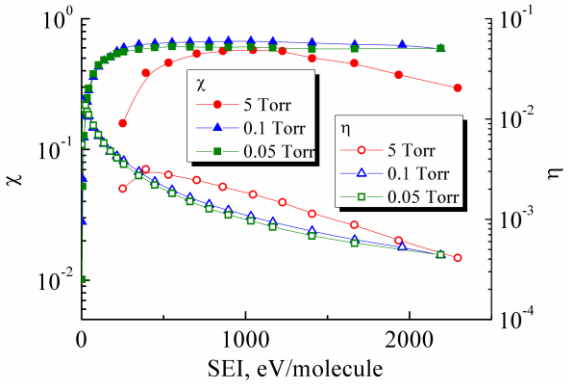

Fig. 10. Conversion coefficient χ and conversion energy efficiency η against SEI for different CO_2 pressure values. 'Top cathode' case

The dependences of the conversion coefficient χ and the conversion energy efficiency η against SEI for different CO_2 pressure values are shown in Fig. 10, from which it follows that in the total pressure range we

have studied one requires considerable expenses for the CO_2 conversion, the SEI may approach 2000 eV/molecule. This is due to the fact that our studies encompassed the wide range of the input power including knowingly excessive power for converting the employed flow of carbon dioxide. However, even in the best case one spends for the conversion itself not more than 1...2 % of the power contributed into the discharge. Therefore it is expedient to perform further studies with other types of the gas discharge (RF, pulsed) and in discharge chambers of other designs.

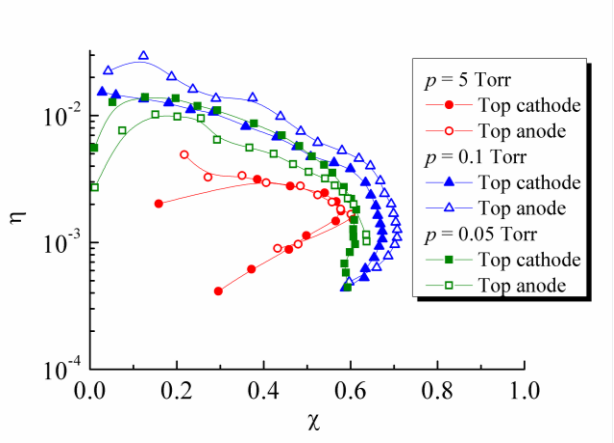

Fig. 11. Conversion energy efficiency η against conversion coefficient χ for different CO_2 pressure values

At last let us consider Fig. 11, in which we compare the dependences of the conversion energy efficiency η on the conversion coefficient χ for different CO_2 pressure values. The best results have been obtained at the pressure of 0.1 Torr for the 'Top anode' case: the maximum conversion coefficient amounts approximately to 70 %, but the conversion energy efficiency may exceed 2 %. Under these conditions the plasma filled the whole discharge chamber, and near the anode (in the negative glow) there was a large number of fast electrons capable to produce a direct dissociation colliding with CO_2 molecules as well as slow electrons with the energy 1...2 eV, causing the excitation of molecular oscillatory levels. It is known that mutual collisions of such excited molecules may lead to even larger dissociation than the direct dissociation via electron impact [1, 2]. In the cathode sheath the electron concentration is small excluding its portion located near the negative glow. CO_2 molecules penetrated into the chamber for a short time and moving in the cathode sheath may have no time to experience dissociation before their escape to the evacuating system. At large pressure (5 Torr) the cathode sheath is narrow and a bright anode glow is pressed to the anode. That is, the there must be many charged particles near both electrodes. But the conversion efficiency then becomes lower because the effect of the normal current density resulting in the plasma occupying only a portion of the discharge chamber volume. Therefore the conversion coefficient χ and the conversion energy efficiency η become lower at large gas pressure.

CONCLUSIONS

We have performed the research into conversion of CO_2 molecules in the dc discharge in a chamber with distributed same-side gas supply and pumping. We have measured the mass-spectra of the gas mixture leaving the chamber as well as optical emission spectra in the 200...1000 nm range. We have determined from mass-spectra such important parameters as the conversion coefficient χ and the conversion energy efficiency η in the broad range of gas pressure, applied voltage and discharge current values. We dealt separately with the cases when feeding and pumping were performed through a cathode or an anode. We have demonstrated that the conversion coefficient χ may attain 70 % (at low gas pressure values) with the conversion energy efficiency η not exceeding 1...3 %.

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ИССЛЕДОВАНИЕ ПРОЦЕССА КОНВЕРСИИ CO_2 В ТЛЕЮЩЕМ РАЗРЯДЕ

В.А. Лисовский, С.В. Дудин, П.П. Платонов, В.Д. Егоренков

С помощью измеренных масс-спектров газовой смеси, выходящей из камеры, а также вольт-амперных характеристик разряда определены удельный энергетический вклад (SEI), абсолютный коэффициент конверсии χ и энергетическая эффективность конверсии η в диапазоне давлений CO_2 0,05...5 Торр. Процесс плазменной конверсии молекул CO_2 проводился в тлеющем разряде в камере с распределенными напуском и откачкой газа с одной стороны. В результате достигнута величина коэффициента конверсии $\chi \sim 70$ %, однако энергетическая эффективность конверсии η не превышала 1...3 % из-за значительных потерь мощности на ускорение положительных ионов, нагрев электродов и газа, а также при неупругих столкновениях электронов с молекулами газа, которые не приводят к конверсии CO_2.

ДОСЛІДЖЕННЯ ПРОЦЕСУ КОНВЕРСІЇ CO_2 У ТЛІЮЧОМУ РОЗРЯДІ

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

За допомогою виміряних мас-спектрів газової суміші, що виходить з камери, а також вольт-амперних характеристик розряду визначені питомий енергетичний внесок (SEI), абсолютний коефіцієнт конверсії χ та енергетична ефективність конверсії η в діапазоні тиску CO_2 0,05...5 Торр. Процес плазмової конверсії молекул CO_2 проводився у тліючому розряді в камері з розподіленими напусканням та відкачуванням газу з одного боку. У результаті досягнута величина коефіцієнта конверсії $\chi \sim 70$ %, проте енергетична ефективність конверсії η не перевищувала 1...3 % через значні втрати потужності на прискорення позитивних іонів, нагрівання електродів і газу, а також при непружних зіткненнях електронів з молекулами газу, які не призводять до конверсії CO_2.