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PLASMA CONVERSION OF CO_2 IN RF CAPACITIVE DISCHARGE WITH DISTRIBUTED GAS INJECTION AND EXTRACTION

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In this paper, the process of plasma conversion of carbon dioxide in a discharge chamber with gas inlet and outlet distributed over the electrode surface is investigated. The experiments were carried out in a radio frequency capacitive discharge (13.56 MHz) in the carbon dioxide pressure range of 0.015…5 Torr. Mass spectrometry and optical emission spectroscopy were used to analyze the process of plasma conversion of CO_2. With the proper correction of readings, both methods give close results. It is shown that the conversion coefficient can reach 70% and decreases with increasing gas pressure. The energy efficiency of conversion is 1…2% at low RF discharge voltages, but with a further increase in RF voltage, it decreases. The reason for this is the elevated losses of the power dissipated in the discharge due to the acceleration of positive ions in the near-electrode sheaths, heating the gas and electrodes, as well as power losses for excitation and ionization of the conversion products (CO and O), which worsens the energy efficiency of conversion.

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INTRODUCTION

Due to the intensive combustion of fossil fuels, an increased concentration of carbon dioxide CO_2 accumulates in the Earth's atmosphere [1]. In turn, this leads to an increase in the greenhouse effect and climate change. Therefore, the current tasks are to reduce CO_2 emissions into the atmosphere and search for various methods of its utilization [2]. Plasma-based CO_2 conversion methods are among the most effective, which has generated great interest among researchers in this topic (see, for example, [3-5]). Dielectric barrier discharges [6], gliding arc [7], microwave discharge [8, 9], DC glow [10,11], radio frequency (RF) capacitively coupled plasmas (CCP) [12], corona [13], nanosecond pulse [14], RF inductively coupled plasmas (ICP) and other types of discharges [15-18] are widely used for plasma CO_2 conversion.

It should be noted that such parameters as the conversion coefficient (the ratio of the number of converted molecules to the initial number of CO_2 molecules entering the plasma volume) and the energy efficiency of conversion (the portion of the discharge power spent on the process of converting CO_2 molecules) differ significantly in discharge plasmas of different types. Thus, in nanosecond pulse plasmas, corona and pulsed corona [19], the energy efficiency of conversion does not exceed 10%, while the values of the conversion coefficient are also low (less than 30%). In gliding arcs, the energy efficiency of conversion can be 50% or higher, but the conversion coefficient reaches approximately 10%. In radiofrequency CCP and ICP, glow, microwave dielectric barrier discharges high values of conversion coefficient (more than 50%) can be achieved, but the energy efficiency of conversion is low (1…10% and lower).

It is obvious that for an economically efficient CO_2 conversion, high values of both energy efficiency and conversion coefficient are simultaneously required. Therefore, additional studies in various types of gas discharges are essential to determine the optimal conditions for plasma conversion of CO_2.

The present work is devoted to the experimental study of the process of plasma conversion of carbon dioxide in low-pressure RF CCP in the discharge chamber with gas injection and extraction distributed over the electrode surface. The conversion and the energy efficiency were measured in a wide range of input power using a mass spectrometer and optical emission spectroscopy.

1. CHARACTERIZATION OF THE CONVERSION PROCESS OF CO_2

Three parameters are used to describe the conversion process allowing comparison of the efficiency of different gas discharges, experimental conditions, etc. The first is the specific energy input (SEI), which is the ratio of the power dissipated in the gas discharge to the gas flow rate:

$$SEI\left(eV/molecule\right)=\frac{P\left(kW\right)}{\frac{dm}{dt}\left(L\cdot\min^{-1}\right)}\cdot 60\left(s\cdot\min^{-1}\right)\times$$

$$\times\frac{6.24\cdot10^{21}\left(eV\cdot kJ^{-1}\right)\cdot 24.5\left(L\cdot mol^{-1}\right)}{6.022\cdot10^{23}\left(molecule\ mol^{-1}\right)},$$

where P is the power (in the case of RF CCP, this is the active power), dm/dt is the gas flow rate.

The second parameter is the conversion coefficient showing the part of the CO_2 molecules converted after the gas passed through the gas discharge plasma:

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

Here N_{in} and N_{out} are the CO_2 input and output flows, respectively. Since the following reaction occurs during the conversion process

$$CO_2 + e^- \rightarrow CO + (1/2)O_2 + e^-,$$

in which one CO_2 molecule produces just one CO molecule, then in the formula for χ, the numerator may be the CO flow at the chamber outlet instead of the difference between input and output CO_2 flows.

And the third important parameter is the energy efficiency of the conversion process η. A minimum energy of ΔH =2.93 eV is needed for the above conversion reaction, which is called the standard enthalpy of the process.

Energy efficiency η allows us to say how many times the energy costs in a specific discharge for CO_2 conversion will be greater than the standard process enthalpy (1):

$$\eta = \chi \cdot \frac{\Delta H}{SEI} \cdot \quad (1)$$

Ideally, $\chi = 1$ and $\eta = 1$ could be expected, but in real plasma, energy is spent on other processes necessary to maintain the discharge or occurring simultaneously with its burning, rather than only on the conversion reaction.

2. EXPERIMENTAL SETUP AND METHODS

2.1. SETUP DESCRIPTION

We studied the carbon dioxide conversion process in an experimental discharge chamber with RF CCP (Fig. 1). Voltage from an RF generator with a frequency of 13.56 MHz was applied to the lower solid electrode. The upper shower-like electrode had 256 holes for the gas inlet and outlet, which were uniformly distributed over its surface. The upper electrode was kept at the Earth potential to suppress the ignition of parasitic hollow cathode discharges in the holes. This has allowed us to conduct studies in a wide range of RF voltage amplitudes.

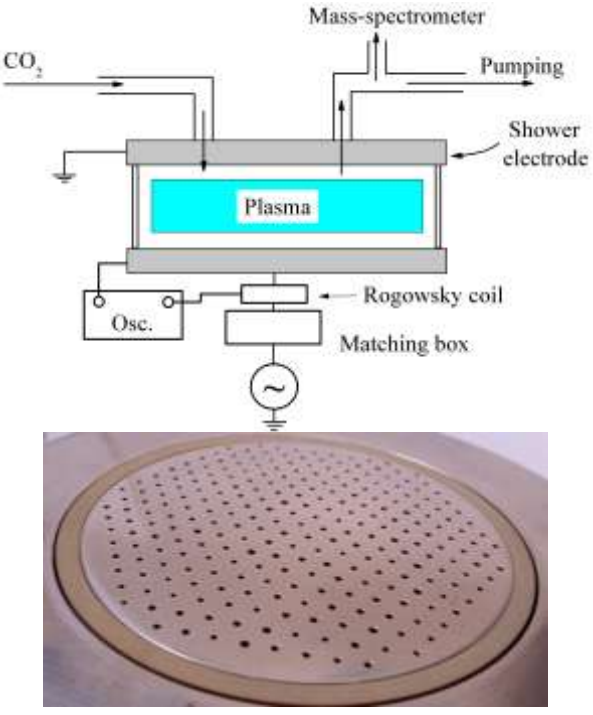

Fig. 1. Schematic of the experimental setup and the photo of the shower-like (top) electrode

A section of quartz tube was vacuum-sealed between the electrodes, with the electrodes completely covering its cross section. The inner diameter of the tube was 93 mm, and the distance between the stainless-steel electrodes was 60 mm. The experiments were conducted with RF power input into the discharge of up to 100 W.

The discharge chamber was evacuated by roughing and turbomolecular pumps. The process of carbon dioxide conversion was studied in the pressure range from 0.015 to 5 Torr. A Baratron 627 capacitive type sensor (MKS Instruments) with a maximum measurable value of 10 Torr was used to measure the gas pressure. The carbon dioxide flow to the discharge chamber was maintained at a fixed rate of 2 sccm in all experiments.

2.2. MASS SPECTROMETRIC STUDY OF CARBON DIOXIDE CONVERSION

To determine the conversion coefficient of CO_2, a ROMS-4 quadrupole mass spectrometer pumped by an ion pump was used. A sample of the gas mixture that left the discharge chamber for the pumping system was fed into it. Particular attention was paid to the intensity of the mass peaks 28 (CO), 32 (O_2), and 44 (CO_2), the dependences of which on the amplitude of the RF voltage are shown in Fig. 2.

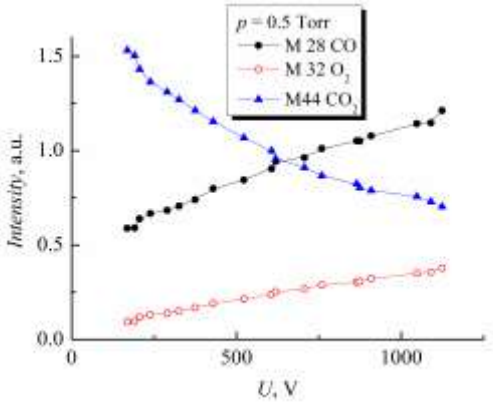

Fig. 2. Peak intensities of the mass-spectra corresponding to 28 (CO), 32 (O_2), and 44 (CO_2) masses against the applied RF voltage for CO_2 pressure of 0.5 Torr and CO_2 flow rate of 2 sccm

Since the sensitivity of the mass spectrometer sensor depends on the type of gas, calibration experiments were carried out before the CO_2 conversion study. Based on the results of these experiments and using the cross-sections [20], it was found that for CO_2 the sensor readings should be divided by 1.45, while to determine the partial pressure of oxygen in the chamber relative to CO_2, the line of mass 32 should be multiplied by 1.3.

It was shown that the most accurate method for determining the conversion coefficient is to consider only the M44 line with subtraction of its intensity without discharge. However, since the pumping speed of the ion pump can be unstable over time and, in addition, changes for a given gas with a change in the pump load with other gases, to compensate for this instability, it is proposed to determine the conversion coefficient not by the absolute value of line M44, but by the ratio M32/M44. In this case, it is possible to use the fact that the pumping speed for all gases changes synchronously and move on to relative calculations. Finally, we used the following formula (2):

$$\chi = \frac{k_{32} M_{32}}{\left(k_{32} M_{32} + M_{44}\right)}, \quad (2)$$

where $k_{32} = 2 \times 1.3$.

2.3. OPTICAL STUDY OF CO_2 CONVERSION

To study the optical emission of the discharge, the Horiba iHR-320 spectrometer was used, which has a diffraction grating of 1800 lines/mm and allows measuring the spectrum in the range of 200…1000 nm with an accuracy of no worse than 1 Å. The optical fiber receiving the plasma emission was installed at a distance of 5 mm from the upper electrode and did not move during the experiments. Thus, the fiber collected the discharge radiation near the boundary of the near-electrode sheath. An example of such a measured radiation spectrum is shown in Fig. 3 for two different voltages, which, as is known, correspond to a low-current α-mode (225 V) and high-current γ-mode (800 V) of the capacitive discharge [21–24]. It shows emission lines of CO_2^+ (288 and 289 nm), CO_2 (337 nm), O_2 (437 nm), a large number of CO bands (460, 483, 519, 561 nm), as well as atomic oxygen lines O (777, 844, 926 nm).

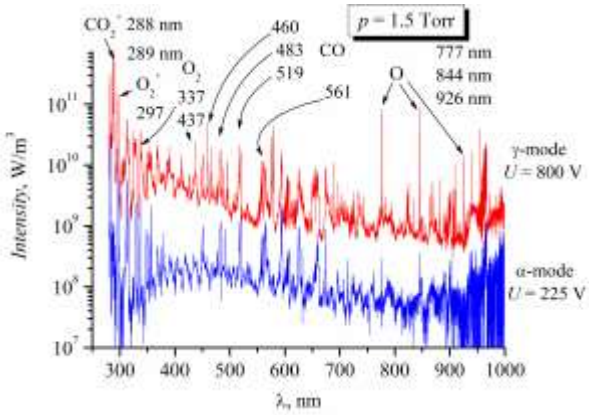

Fig. 3. Emission spectrum of CCP at CO_2 pressure of 1.5 Torr and RF voltages of 225 and 800 V

The optical measurement data processing technique was as follows. The intensities of 337 nm (CO_2), 777 nm (O), and 519 nm (CO) emission lines were determined at different values of RF power. These intensities were normalized to the integral luminosity of the discharge over the entire spectrum. The result of such processing is shown in Fig. 4. It shows the dependences of the emission line intensities on the RF voltage amplitude, the integral intensity, and the intensities of the CO_2 (337 nm), CO (519 nm), and O (777 nm) lines normalized to it. The figure shows that with increasing RF voltage, the emission line intensities increase due to an increase in the discharge current and electron concentration. It is difficult to draw a conclusion about the conversion process from such a dependence. However, the use of line intensities normalized to the integral intensity shows a decrease in the concentration of carbon dioxide molecules and an increase in the concentrations of their dissociation products, CO and O. The conversion coefficient was determined by the normalized CO_2 line attenuation due to the conversion in plasma (3)

$$\chi = \frac{I_{337}^0 - I_{337}}{I_{337}^0}. \quad (3)$$

Fig. 5 compares the carbon dioxide conversion coefficients derived from the mass spectra and optical emission spectra. Except for single outliers, good agreement is observed between the two methods. Therefore, below we will mainly focus on the mass spectrometry results. We will determine the concentrations of CO_2 molecules without plasma and with a burning discharge. Since the gas flow rate and the value of the RF active power input into the discharge are known parameters, they can be used to determine the values of χ and η depending on the SEI. This technique is described in more detail in [15, 16].

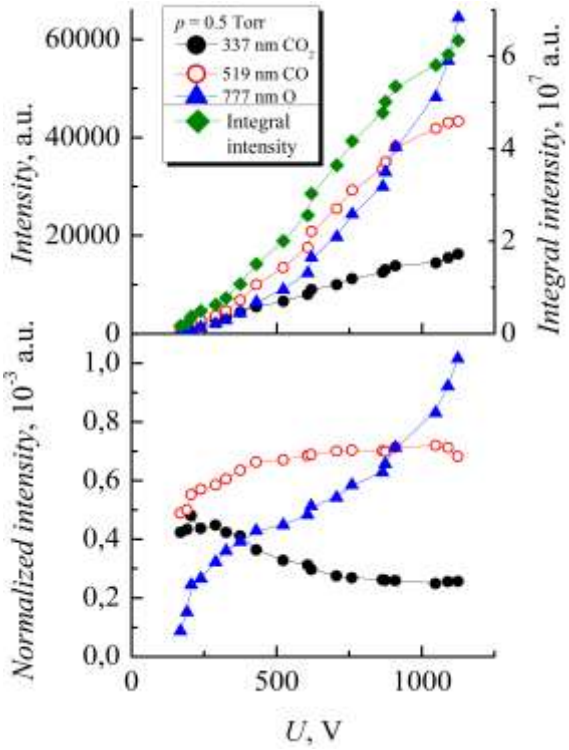

Fig. 4. Line intensities of the optical spectra corresponding to 519 nm (CO), 777 nm (O), and 337 nm (CO_2) against applied voltage for CO_2 pressure of 0.5 Torr and the gas flow rate of 2 sccm

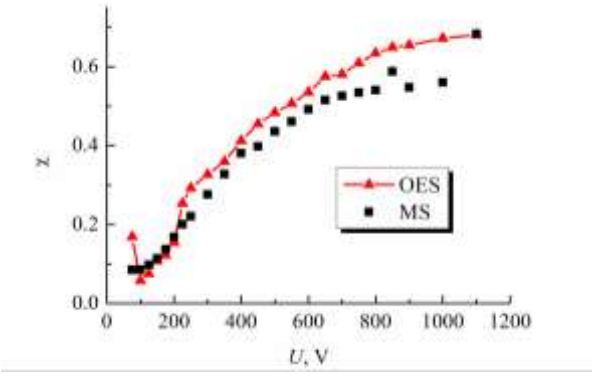

Fig. 5. Comparison of conversion coefficients χ determined from mass spectrometry and optical emission spectroscopy for carbon dioxide pressure of 0.5 Torr

3. EXPERIMENTAL RESULTS

Above we mentioned that the RF capacitive discharge can exist in a low-current α-mode and a high-current γ-mode [21–24] (Fig. 6). These modes differ by the location of predominant heating of electrons and the processes that facilitate this.

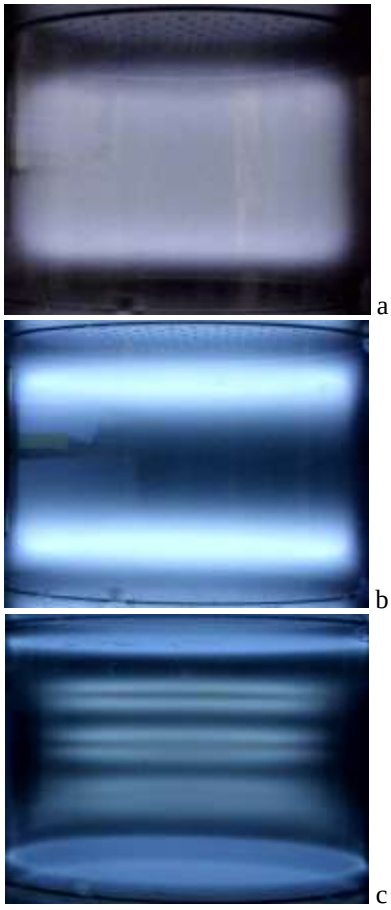

Fig. 6. Photos of CCP discharge in CO_2 at the pressures of 0.05 Torr (photo (a) is for 200 V, α-mode and (b) is for 750 V, γ-mode) and 5 Torr (photo (c) is for 600 V, γ-mode)

In the α-mode, electrons, which in the anodic phase filled the sheath near the temporary anode, after the change in the sign of the electrode potential are expelled from the sheath during its cathodic phase, and in this case, they acquire energy. Additionally, electrons can be heated in the plasma volume by the RF electric field, but in many cases this mechanism of electron heating is auxiliary. Positive ions exit the plasma, accelerate in the time-averaged electric field in the sheaths, and bombard the surface of the electrodes. Electrons released from the electrodes due to ion-induced electron emission are accelerated from the electrode surface toward the sheath boundary. In the α-mode, these electrons pass through the near-electrode sheath without gaining enough energy for ionization.

However, with an increase in the potential difference between the electrodes, the energy of the electrons increases, electron avalanches can develop in the sheaths, and the sheaths themselves will be broken down. The RF discharge goes into γ-mode, in which predominant ionization occurs in the vicinity of the boundaries of the near-electrode sheaths. In gases whose molecular fragments (radicals) have an ionization potential lower than the initial molecules, a dissociative δ-mode can also appear [23–25], however, it is not observed in CO_2.

Typical photographs of discharge glow in carbon dioxide are shown in Fig. 6. In the first photograph (for 0.05 Torr, see Fig. 6,a) we see a low-current α-mode with dark near-electrode sheaths and quasi-neutral plasma between them. When switching to γ-mode, a bright glow is observed near the boundaries of the near-electrode sheaths (see Fig. 6,b), and the region located between them is an analog of Faraday's dark space of DC glow discharge. Fig. 6,c shows the γ-mode for a pressure of 5 Torr, in which we additionally see a positive column with double striations.

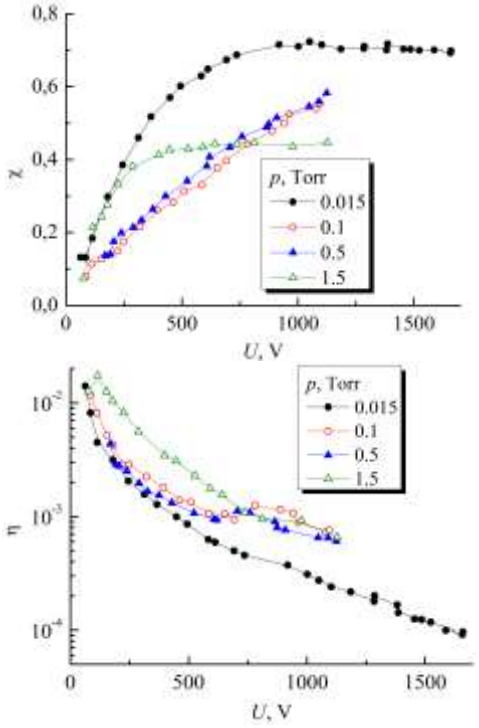

Fig. 7. Conversion coefficient χ and conversion energy efficiency η against applied voltage for different CO_2 pressures and gas flow rate of 2 sccm

Now let us consider the results for CO_2 conversion. Fig. 7 shows the measured dependences of the conversion coefficient χ and the energy efficiency η on the RF voltage amplitude for different carbon dioxide pressures. The figure shows the characteristic behavior of the conversion coefficient χ, which first increases with increasing RF voltage, then saturates at high voltages (approximately 70% at a carbon dioxide pressure of 0.015 Torr and 40% at 1.5 Torr). At the same time, the energy efficiency of conversion η reaches 1…2% at low RF voltages but then decreases monotonically. The rather large spread in Fig. 7 in the dependences of χ and η on the RF voltage amplitude for different CO_2 pressures is noteworthy. However, when plotting these parameters versus the specific energy input (SEI), the discrepancy between the curves is significantly reduced (Fig. 8). Additionally, we present Fig. 9, which shows the dependence of the energy efficiency on the conversion coefficient $\eta(\chi)$.

If we take into account that SEI is proportional to power, and the energy efficiency is inversely proportional to SEI, then we can conclude that it is advisable to reduce the power input into the discharge and especially its losses in processes that do not lead to the dissociation of CO_2 molecules (by electron impact or during energy exchange between vibrationally excited molecules).

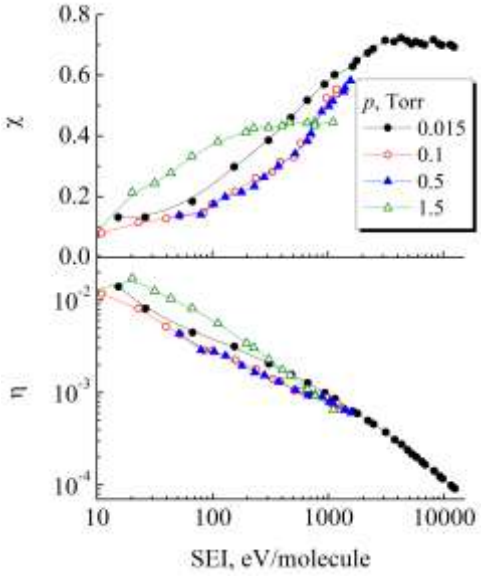

Fig. 8. Conversion coefficient χ and energy efficiency η versus SEI for different CO_2 pressures for the gas flow rate of 2 sccm

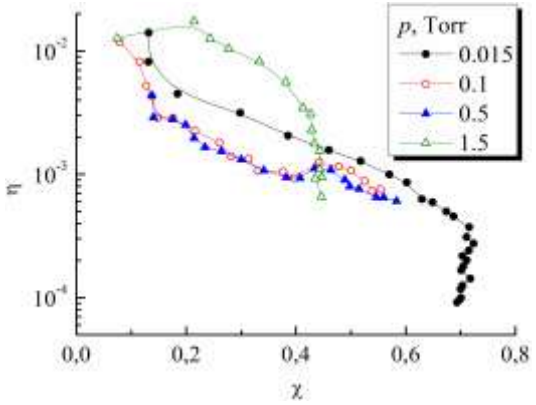

Fig. 9. Energy efficiency η versus conversion coefficient χ for different CO_2 pressures for the gas flow rate of 2 sccm

It should be noted that in the RF capacitive discharge with the gas inlet and outlet distributed over the electrode area (and, accordingly, large electrodes) it is possible to obtain high conversion coefficient values but the energy efficiency is too low for commercial application. Let us briefly analyze the possible reasons for this.

We have indicated above that positive ions move from the plasma volume to the electrodes, accelerating in the near-electrode sheaths. The typical amplitude of the applied RF voltage in our experiments was in the range of hundreds of Volts. The time-averaged voltage drop on the near-electrode sheath (which accelerates positive ions toward the electrode) is of the same order. This leads to large losses of RF power for ion acceleration. Ions, moving through the sheaths, transfer part of the acquired energy to the gas molecules, and then additionally collide with the electrode surface. As a result, both the gas and the electrodes heat up (the electrode temperature could exceed 100 °C). One can see in Fig. 7 that the highest energy efficiency appears just at the lowest RF voltage values. With the voltage increase, the elevated power losses for ion acceleration inevitably lead to a significant decrease in energy efficiency.

In addition, in paper [26] for the given electrode geometry, numerical modeling showed that the CO_2 molecules entering the chamber spend too long in the plasma volume, due to which the electrons not only have time to decompose them into CO and O fragments, but also lose additional energy on excitation, ionization, and heating of these conversion reaction products. All these losses of RF power lead to a significant decrease in the energy efficiency of conversion.

CONCLUSIONS

This work is devoted to the study of the process of plasma conversion of carbon dioxide in a radio frequency capacitive discharge. A discharge chamber with the gas inlet and outlet distributed over the electrode surface was used. The process of plasma conversion of CO_2 was studied by mass spectrometry and optical emission spectroscopy methods, which, with the necessary correction, give close results. In the experiments, high values of the conversion coefficient (up to 70%) were obtained, but the energy efficiency of conversion did not exceed 1…2%. It was shown that the energy efficiency of conversion is worsened by the power loss for the acceleration of positive ions in the near-electrode sheaths, as well as by RF power losses on the excitation and ionization of the conversion products (CO and O).

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ПЛАЗМОВА КОНВЕРСІЯ CO_2 У ВЧ ЄМНІСНОМУ РОЗРЯДІ ІЗ РОЗПОДІЛЕНИМИ НАПУСКОМ ТА ВІДКАЧКОЮ ГАЗУ

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

Досліджено процес плазмової конверсії вуглекислого газу в розрядній камері з розподіленими по поверхні електродів напуском і відкачуванням. Експерименти проведені у високочастотному ємнісному розряді (13,56 МГц) у діапазоні тиску вуглекислого газу 0,015…5 Торр. Для аналізу процесу плазмової конверсії CO_2 використовувалися методи мас-спектрометрії та оптичної емісійної спектроскопії. За виконання корекції показань обидва методи дають близькі результати. Показано, що коефіцієнт конверсії може досягати 70% і знижується у разі підвищення тиску газу. Енергетична ефективність конверсії становить 1…2% при низьких значеннях ВЧ-напруги, але при подальшому підвищенні ВЧ-напруги вона знижується. Причиною цього є підвищені втрати дисипованої в розряді потужності на прискорення у приелектродних шарах позитивних іонів, нагрівання газу і електродів, а також на збудження та іонізацію продуктів конверсії CO і O, що погіршує енергетичну ефективність конверсії.