# CONVERSION OF CARBON DIOXIDE IN LOW-PRESSURE PLASMA

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The paper reports the results of experimental study of efficiency of carbon dioxide conversion to CO and $O_2$ in gas-discharge plasma at low gas pressure. The inductively coupled plasma source operates at 13.56 MHz in the RF power range 5…500 W. Pure $CO_2$ at pressure of 1…100 mTorr is fed into the plasma while the internal composition of atomic and molecular species is estimated using optical emission spectroscopy. Using the mass spectrometry method, the dependencies of the conversion rate and the energy efficiency of carbon dioxide conversion on the gas pressure and the power deposited in the discharge was measured. The maximum achieved conversion rate is 82 %, while the energy conversion efficiency is up to 50 %.

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## INTRODUCTION

One of the most serious problems facing humanity is climate change due to excessive levels of greenhouse gases, particularly $CO_2$, so its conversion into fuel and valuable chemical raw materials is one of the most effective ways of simultaneously solving the environmental and energy problems. Different methods of thermal, electrochemical and photochemical conversion of $CO_2$ into fuel and other useful substances are known, as well as their advantages and disadvantages [1]. Con-version of $CO_2$ allows receiving not only CO, but also (with the addition of hydrogen, methane) HCOOH, HCHO, $CH_3OH$, hydrocarbons and polymers.

It was emphasized in [2], that it is the plasma methods that are most effective for the conversion of $CO_2$. One of the most popular discharges for the $CO_2$ conversion is dielectric barrier discharge at atmospheric pressure [3]. However, other types of gas discharges can be no less effective, but the creation of efficient industrial technologies is impossible without additional fundamental research to better understand the basic mechanisms of complex plasma-chemical processes occurring in discharges in $CO_2$.

The present paper reports the results of experimental study of efficiency of carbon dioxide conversion to CO and $O_2$ in gas-discharge plasma at low gas pressure. The inductively coupled plasma source operates at 13.56 MHz in the RF power range 5…500 W. Pure $CO_2$ is fed into the plasma while the internal composition of atomic and molecular species is estimated using optical emission spectroscopy, and the output gas composition is measured by a mass spectrometer. $CO_2$ pressure was changed in the range of 1…100 mTorr. Using the mass spectrometry method, the dependencies of the conversion rate and the energy efficiency of carbon dioxide conversion in plasma on the gas pressure and the power deposited in the discharge was measured. Using a Langmuir probe, the dependencies of plasma density and electron temperature on the gas pressure and input power has been measured.

## 1. EXPERIMENTAL SETUP

A schematic diagram of the experimental setup used in our investigation is shown in Fig. 1. The cylindrical discharge vessel has a radius $R$ = 7 cm and height $L$ = 6 cm. The sidewall of the vessel is made of metal. The glass top cover and the inductive coil are cooled by air flow created by a fan. The vessel is evacuated by a turbo molecular pump down to a base pressure of about $10^{-6}$ Torr. The experiments are performed in the gas pressure range 1…100 mTorr. The RF field is induced by a three-turn spiral copper coil with variable radius. RF power in the range 1…500 W at 13.56 MHz is coupled to the coil via a matchbox.

The measuring of the main plasma parameters have been led by means of the Langmuir cylindrical probe of diameter $D_p$ = 0.1 mm and length of $L_p$ = 5 mm. The probe data processing was done using the “Plasma Meter” [4] device. Optical emission spectra were measured using Q-Mini (RGB Lasersystems) spectrometer. Mass-spectrometric research of the sampled from the discharge chamber was performed using the ROMS-4 mass-spectrometer pumped by an ion pump with 100 l/s throughput.

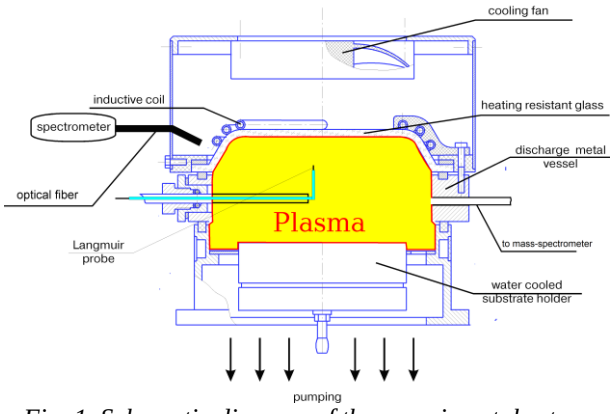


*Fig. 1. Schematic diagram of the experimental set-up*

## 2. EXPERIMENTAL RESULTS

### 2.1. PRINCIPLES OF CONVERSION RATIO MEASUREMENT

Conversion of carbon dioxide to CO an $O_2$ gases occurs in inductively coupled plasma. Pure $CO_2$ is fed to the plasma chamber, while exhaust gas mixture going to pump contains CO, $O_2$, and non-converted $CO_2$. The main instrument allowing measurement of percentage of carbon dioxide being converted in the presented experiments was the mass-spectrometer connected to the plasma chamber at side wall. An example of mass-

spectrum of the products of plasma conversion is shown in Fig. 2.

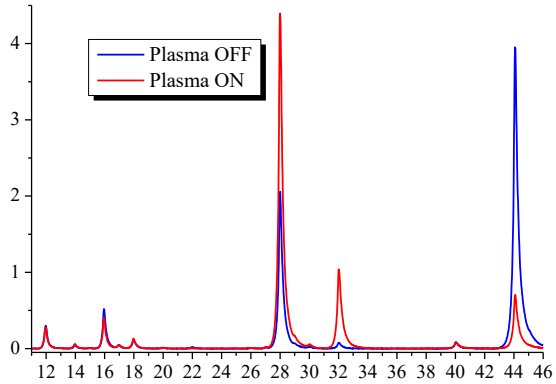


*Fig. 2. Typical mass-spectrums before and after plasma ignition (pure $CO_2$ is fed to the chamber)*

In order to determine the conversion efficiency of carbon dioxide quantitatively a series of calibration experiments was done preliminary, that allowed tabulating a series of empirical factors (which are unique for our mass-spectrometer). For pure $CO_2$ (without plasma) we have obtained:

M44/M28 = 2.15;
M44/M32 = 120 (may be neglected);
M44/M16 = 7.8;
M44/M12 = 14.

Next the M44/M32 ratio vas determined as 1.3 for pure $CO_2$ and pure $O_2$ cases. Thus, the algorithm of calculation of partial pressures of the reaction products may be expressed in the following formulae:

$P_{CO2}$ = M44 ,
$P_O$ = M32 * 1.3 * 2 ,
$P_{CO}$ = (M28 – M14 * 16.2 – M44 *2.15) * 0.75.

If we normalize these values to M44 without plasma, letting $P_{CO2}(0)$ = 100 %, the percent distribution of the reaction products will be obtained. An example of such distribution depending on the discharge power is shown in Fig. 3. The upper curve, which is the sum of all the products, allows to estimate the accuracy of our measurements.

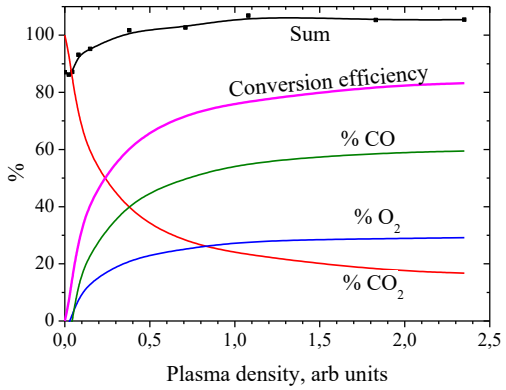


*Fig. 3. An example of distribution of $CO_2$ conversion reaction products depending on the discharge power*

## 2.2. CONVERSION EFFICIENCY

As it was mentioned above, the $CO_2$ conversion efficiency grows with the applied power increase. Another important factor influencing the conversion efficiency is the gas pressure and flow. The gas pressure defines electron temperature [5] which is of crucial importance for the carbon dioxide dissociation due to strong bond of $CO_2$ molecule. The input gas flow rate is in direct connection to the energy required for dissociation, so at constant input power the conversion efficiency is expected to be dependent not only on pressure but also on the gas flow rate. We have possibility to realize two different pumping speed: with turbomolecular pump (700 l/s), or with a rotary vane pump (16 l/s). Fig. 4 shows measured $CO_2$ conversion efficiency versus discharge power at different gas pressures and with the two different pumping speeds. On can see that the efficiency with turbo pump is always lower, that looks natural taking into account that the gas flow rate is much higher in this case. The pressure dependence is non-monotonous with minimum at about 15 mTorr. The physical reason for this will be discussed below. Note that the pressure variation was performed changing the pumping speed, with constant gas flow rate.

Taking into account the enthalpy $\Delta H$ = +283 kJ/mol of $CO_2$ splitting reaction taken from [2], the energy efficiency of $CO_2$ conversion was calculated (Fig. 5). It is maximal at lower powers and drops with the power growth. The maximum values of the energy efficiency (up to 50 %) are reached at the highest researched pressure.

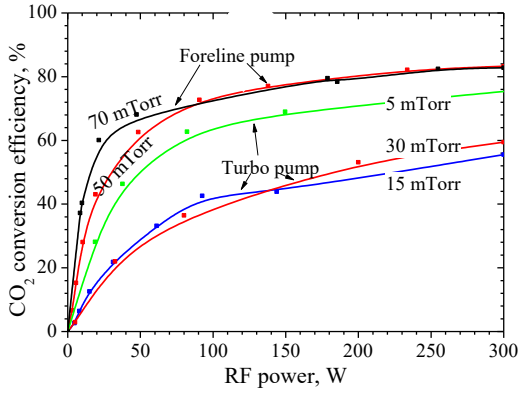


*Fig. 4. $CO_2$ conversion efficiency versus discharge power at different gas pressures*

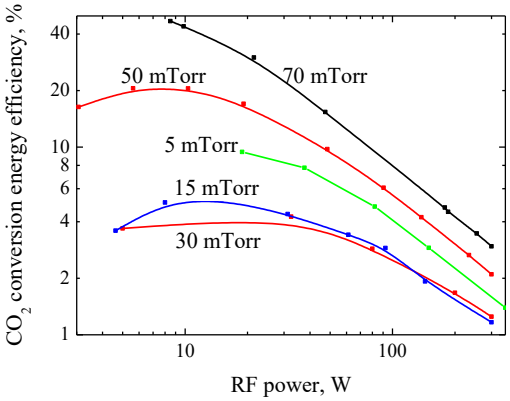


*Fig. 5. $CO_2$ conversion energy efficiency versus discharge power at different gas pressures*

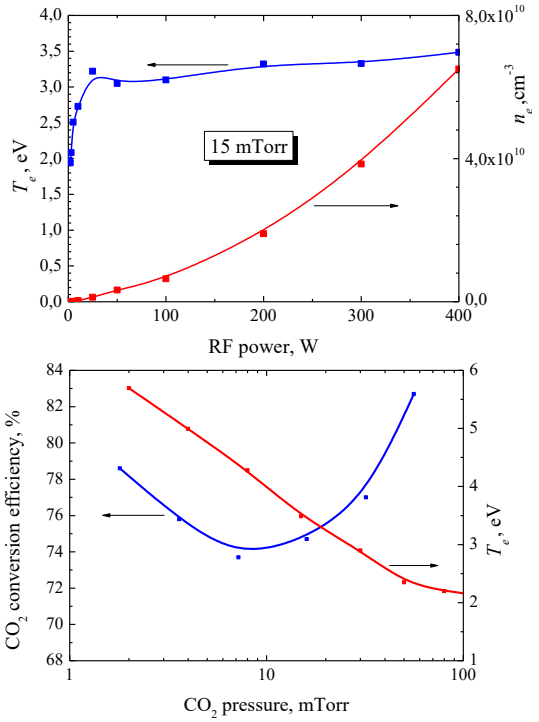


*Fig. 6. Electron temperature and density in dependence on RF power and gas pressure in comparison with $CO_2$ conversion efficiency*

### 2.3. LANGMUIR PROBE MEASUREMENTS

In order to know electron temperature $T_e$ and electron density $n_e$ and their dependences on the system parameters systematic measurements was done using Langmuir probe technique. The measured dependence on the RF power and the gas pressure is shown in Fig. 6. It is seen that $T_e$ shows week dependence on the RF power, while the plasma density is growing faster then proportional. This behavior is different from usual from ICP plasma in Argon atmosphere where the electron temperature is independent on the power and the plasma density is directly proportional to the absorbed power. This may be attributed to changes in the gas mixture inside the chamber taking place due to $CO_2$ dissociation. The electron temperature decreases monotonously with the pressure, while the conversion efficiency has a minimum at intermediate pressure.

This could be explained by assumption that at the low pressure when the electron temperature is more then 5 eV, the carbon dioxide molecule dissociation occurs after electron impact, while at low pressure when the electron temperature is about 2 eV, cascade excitation of molecular vibrational levels plays the main role.

### 2.4. OPTICAL EMISSION SPECTROSCOPY

Optical emission spectra at different RF powers are shown in Fig. 7. One can see that at low RF power the spectrum contains mainly molecular lines of $CO_2$ molecules emission, while at high RF power two intense lines of atomic oxygen rise with wavelengths of 777.4 and 844.6 nm. This is the evidence of appearance of significant amount of oxygen due to the carbon dioxide conversion.

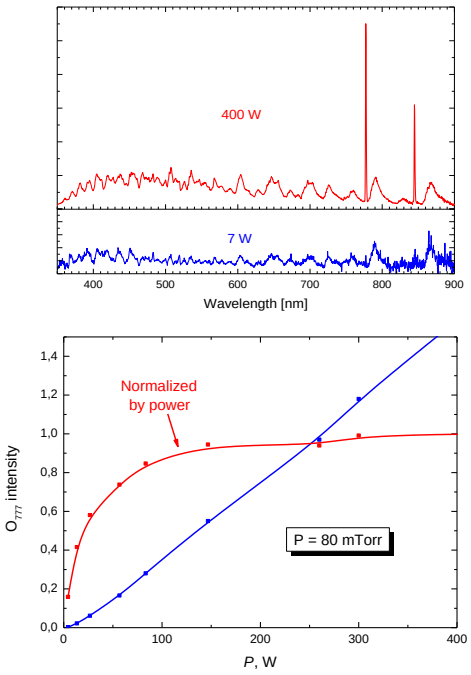


*Fig. 7. Optical emission spectra at different RF powers and dependence of intensity of line $O_{777}$ on RF power*

In order to characterize this process quantitatively, the dependence of intensity of line $O_{777}$ on RF power was measured. It is shown in the Fig. 6. The line intensity looks proportional to the applied RF power, however, if we normalize the intensity value by the power, we can see, that the relative intensity grows significantly with the power having saturation after 100 W. This demonstrates the increase of atomic Oxygen density due to increased $CO_2$ conversion at higher powers. It should be noted that the shape of this dependence is similar to the dependence of the conversion efficiency on RF power shown in Fig. 4.

## CONCLUSIONS

Thus, in the present research, the dependencies of the conversion rate and the energy efficiency of carbon dioxide conversion in plasma on the gas pressure and the power deposited in the discharge was measured using the mass spectrometry method. The maximum achieved conversion rate is 82 %, the energy conversion efficiency is up to 50 %. It is shown that the maximum conversion rate is achieved at the lowest pressures (down to 1 mTorr) and at the highest pressures of the researched range (up to 100 mTorr) while at intermediate pressures the conversion rate has a minimum.

This could be explained by assumption that at the low pressure when the electron temperature is more then 5 eV, the carbon dioxide molecule dissociation occurs after electron impact. Fig. 8 shows estimated $CO_2$ dissociation length in dependence on electron temperature and on plasma density. It is clear that high $T_e$ and $n_e$ simultaneously are required to achieve the lowest possible dissociation length. At the same time, at low pressure when the electron temperature is about 2 eV, cascade excitation of molecular vibrational levels presumably plays the main role [3].

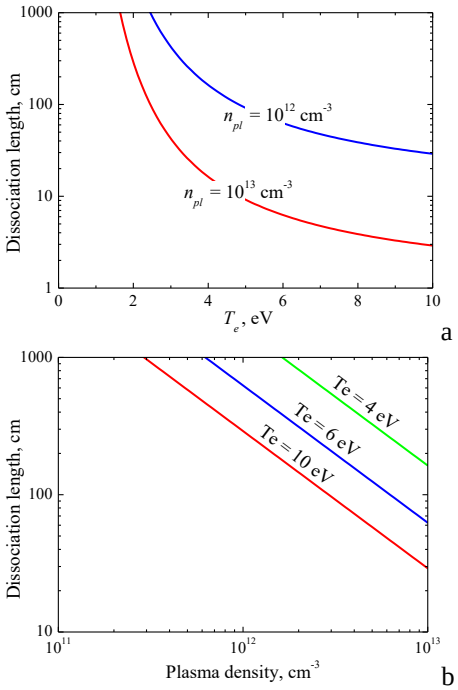


*Fig. 8. Estimated $CO_2$ dissociation length in dependence on electron temperature (a) and on plasma density (b)*

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## КОНВЕРСИЯ ДИОКСИДА УГЛЕРОДА В ПЛАЗМЕ НИЗКОГО ДАВЛЕНИЯ

***С.В. Дудин, А.Н. Дахов***

Представлены результаты экспериментальных исследований эффективности конверсии двуокиси углерода в CO и $O_2$ в газоразрядной плазме при низком давлении газа. Источник индуктивно связанной плазмы работал на частоте 13,56 МГц в диапазоне мощности 5…500 Вт. Чистый $CO_2$ подавался в плазму при давлении 1…100 мТорр, а состав атомных и молекулярных частиц оценивался с использованием спектроскопии оптического излучения. Используя метод масс-спектрометрии, были измерены зависимости скорости конверсии и энергоэффективности конверсии двуокиси углерода от давления газа и мощности, вводимой в разряд. Максимально достигнутый коэффициент конверсии составляет 82%, а энергетическая эффективность преобразования энергии ~ до 50 %.

## КОНВЕРСІЯ ДИОКСИДУ ВУГЛЕЦЮ В ПЛАЗМІ НИЗЬКОГО ТИСКУ

***С.В. Дудін, О.М. Дахов***

Представлено результати експериментальних досліджень ефективності конверсії двоокису вуглецю в CO і $O_2$ у газорозрядній плазмі за низького тиску газу. Джерело індуктивно зв'язаної плазми працювало на частоті 13,56 МГц у діапазоні потужності 5…500 Вт. Чистий $CO_2$ подавався в плазму при тиску 1…100 мТорр, а склад атомних і молекулярних частинок оцінювався з використанням спектроскопії оптичного випромінювання. Використовуючи метод мас-спектрометрії, були виміряні залежності скорості конверсії та енергетичної ефективності конверсії двоокису вуглецю від тиску газу і потужності, що вводиться в розряд. Максимально досягнутий коефіцієнт конверсії становить 82%, а енергетична ефективність ~ до 50 %.