LOW TEMPERATURE PLASMA AND PLASMA TECHNOLOGIES

https://doi.org/10.46813/2022-142-079

GLOW DISCHARGE WITH A HOLLOW CATHODE IN CARBON DIOXIDE

V.A. Lisovskiy, S.V. Dudin, P.P. Platonov, R.O. Osmayev, V.D. Yegorenkov

V.N. Karazin Kharkiv National University, Kharkiv, Ukraine

E-mail: lisovskiy@yahoo.com

This paper is devoted to an experimental study of the dc discharge with a hollow cathode within the carbon dioxide pressure range of 0.06...2 Torr. The registered CVCs in the pressure range below 0.5 Torr possess a hysteretic pattern with transitions between glow and hollow modes. We have demonstrated that the value of the product of gas pressure and distance between cathode plates $p \cdot d_h = 0.32$ Torr·cm is optimum for the application of the discharge with hollow cathode for plasma conversion of the carbon dioxide when the maximum discharge current is observed. Then the cathode cavity is filled with a high density discharge. Treating the optical emission spectrum has revealed that in the negative glow there have to be present the electron flows with the energy above 18 eV, what must provide the high rate of the CO_2 molecules conversion via direct electron impact. Slow electrons produced inside the negative glow itself have to supply an additional contribution to the conversion process and to make an efficient excitation of oscillatory levels of CO_2 molecules.

PACS: 52.80.Hc

INTRODUCTION

Discharges with a hollow cathode are widely applied in analytical spectroscopy [1, 2], gas discharge lasers [3, 4], plasma technology processes of surface modification [5-7], ion thrusters [8, 9]. Therefore a large number of papers are devoted to experimental and theoretical studies of the discharge with a hollow cathode (see e.g. [10-16]).

The cathodes are called hollow when they possess a negative curvature. They may be cylindrical, rectangular, their walls may be of a solid metal or a grid. One also regards as hollow the cathodes consisting of two parallel plates connected electrically. The shape of a hollow cathode is chosen such that it may be optimally applied in a given plasma technology. In the common glow discharge with flat cathode electrons that escape the sheath can lose their energy along the full length of the negative glow which can measure in tenths of centimeters [14, 17, 18] in low pressures. In a hollow cathode that is filled with negative glow (in the so-called hollow mode) almost all the energy gathered by electrons is dissipated within the cavity itself, which allows the high density plasma to stay there [12, 15, 16]. Meanwhile in the negative glow itself there are not only fast electrons (with energy of tenths eV) which were accelerated in the cathode sheath, but also cold electrons (with energy of about 1 eV) that were produced in the negative glow or near its borders with the cathode sheath.

This presence of electrons with different energies allows application of hollow cathode discharge for CO_2 plasma conversion optimization. The active utilization of fossil fuels led to the heightened CO_2 emissions to the atmosphere and, as a consequence, to the strengthening of the greenhouse effect. Therefore great effort is put not only into limiting the CO_2 emissions but also in the search for methods of CO_2 conversion into the CO/O mixture, syngas and other types of raw materials and fuel. Plasma methods of CO_2 conversion turned out to be among the most effective [19-23].

Earlier we studied the process of CO_2 conversion in a number of low pressure gas discharges – in the inductively plasma (ICP) discharge [22], the magnetron and ion beam discharge [23], in the glow discharge with a flat cathode [24, 25]. In the paper [14] the optimum range of the hollow cathode discharge in nitrogen was found. Therefore there is an interest in finding the optimum range for the hollow gas discharge in CO_2 with a goal to further increase the CO_2 plasma conversion process efficiency.

1. EXPERIMENTAL SETUP AND DIAGNOSTICS

Hollow cathode dc discharge was ignited in a chamber schematically shown in Fig. 1. Fused silica tube had an inner diameter of 56 mm. The hollow cathode consisted of two aluminum plates 2 mm thick and 37 mm long. The distance between them was fixed at 8 mm. These plates were placed on the metal disc 55 mm in diameter. The moving anode was 63 mm away from the edges of the hollow cathode plates, therefore the maximum distance from the flat parts of anode and cathode was 100 mm.

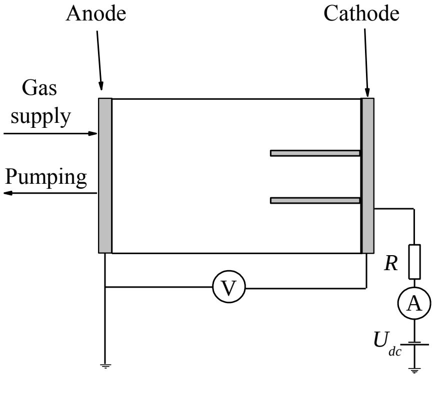

Fig. 1. The scheme of the experimental setup

CO_2 was fed into the discharge chamber by the gas supply system. The gas pressure was measured by Baratron 627 capacitance manometer (MKS Instruments) with the maximum value measured of 10 Torr in the range of 0.06...2 Torr.

Optical emission spectrum of the discharge plasma in the cavity of the cathode was recorded with the Horiba iHR 320 spectrometer in the wavelength range of 280...1000 nm. Oxygen atom emission line table was taken from the NIST Atomic Spectra Database Lines Data (https://physics.nist.gov). The reference book [26] was used to identify the emission lines of molecules (CO, CO_2, CO_2^+).

2. EXPERIMENTAL RESULTS

The hollow cathode discharge can exist in different modes. In the pressure range that we were studying there are glow and hollow modes [14, 27] (see the corresponding photos in Fig. 2). In the glow mode the negative glow is outside the cavity on the outer parts of the cathode. When gas pressure is low the electric field lines geometry is such that secondary electrons that were produced by positive ions striking the cathode surfaces are driven from the cavity along its axis. If the gas pressure is high enough when the discharge current is rising the boundary of the negative glow has the shape of a funnel. Its tip is pointed into the cavity. When its tip is pushed inside the cavity the so-called “pendulum effect” occurs. Fast electrons that got their energy in the sheath near one of the cathode plates are penetrating into this conical plasma area and cause there ionizing collisions with the gas molecules and go through it completely. Then they again enter the sheath near the opposite cathode plate and after decelerating due to the opposing field return into the plasma again. Such a pendulum-like motion of electrons between the opposing cathode surfaces lets them use the energy they got in the cathode sheath effectively to ionize the gas molecules.

Electrons oscillating in the cathode cavity form a remarkable negative space-charge which compensates the positive space-charge of the cathode drop and brings the plasma boundary closer to the cathode surface. Cathode sheath thickness near every surface becomes smaller and the conical boundary of the negative glow propagates deeper into the cavity. This leads to the plasma rushing into the hollow cathode, the current increases and the voltage between the electrodes lowers. There occurs the hollow cathode effect caused by the oscillation of a significant number of fast electrons inside the cathode cavity. The discharge transits into a hollow mode.

The voltage between electrodes in the hollow cathode discharge is lower than in the common glow discharge with flat electrodes. Fast electrons accelerated in the cathode sheath cause unlocalized ionization in the negative glow (where the electric field is low) and even in the opposite cathode sheath of the cavity where the electric field is decelerating electrons. In the discharge between the flat electrodes, fast electrons leave the cathode sheath, lose their energy in collisions with gas molecules and then escape to the anode and the walls of the tube due to diffusion. Thus fast electron losses in the flat electrode discharge are much higher than in the hollow cathode discharge where fast electrons are held within the cavity, losing their energy to ionize and excite the gas molecules.

Moreover, due to the hollow cathode effect the current under set voltage will be higher than in the case where a flat cathode is used and will increase rapidly when the negative glow areas near opposite cathodes overlap and the dark Faraday space disappears.

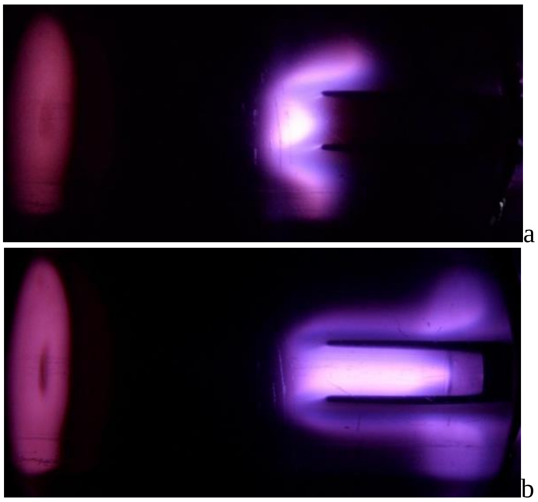

Fig. 2. Hollow cathode discharge photo $p(CO_2)$ = 0.15 Torr: a – glow mode; b – hollow mode. Flat anode on the left, hollow cathode on the right

Below, we will find out under which CO_2 pressure the discharge current in the hollow mode will reach its maximum. In order to do so let us look at the discharge I-V curves measured for different CO_2 pressure values (Fig. 3). In the range of low pressure values (below 0.1 Torr) the discharge is burning only in the glow mode (at least while the voltage across the electrodes is less than 2000 V), never penetrating the cathode cavity. The discharge touches the outer surfaces of the cathode plates (outside the cavity) and also when currents are higher with the flat surface of the electrode to which the hollow cathode is fixed. Under these conditions the I-V curve of the discharge is increasing uniformly.

With the increase of current and/or gas pressure the tip of the conical negative glow moves closer to the cathode cavity. When some threshold value of current is reached, which is getting lower with the increase of gas pressure, the negative glow jumps to fill the cathode cavity. This leads to a rapid decrease of voltage across the electrodes and an increase of discharge current although the hollow mode can be sustained under lower current values than needed to transit from the glow mode. When gas pressure values are small, lowering the voltage leads to a uniform lowering of current not only in the glow mode but in the hollow mode as well. As was mentioned before, the hollow mode is sustained under lower voltage values than the glow mode. Therefore there is a hysteresis on the I-V curve of the discharge. Its width is decreasing with the increase of gas pressure. When the lowest threshold value of current is reached the discharge jumps back from the hollow mode to the glow mode, leaving the cathode cavity. Hysteresis is observed until

CO_2 pressure reaches 0.5 Torr, but at that pressure it is so weakly expressed that in Fig. 3 it becomes smaller than the size of dots and may be studied only after magnifying the corresponding area of the I-V curve.

When the gas pressure is increased further, and current values are at their lowest, the discharge is occurring between the edges of cathode plates and the flat anode. Then with the current increasing it penetrates the cathode cavity and gradually occupies the outer surfaces of those plates and spreads to the flat surface of the cathode (which is parallel to the anode). In fact, with a cathode of complex form the discharge glows in a normal mode until all its surfaces are covered with the discharge after which it transits into an abnormal mode.

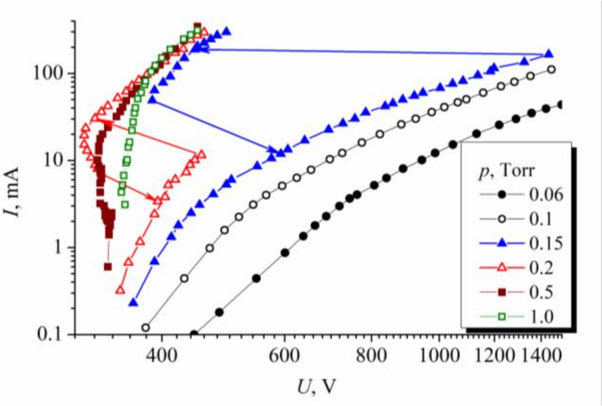

Fig. 3. Gas discharge current-voltage characteristics under different gas pressure values

Moreover, at low pressure the negative glow penetrating the cathode cavity is narrow and almost all volume of the cavity is filled with two cathode sheaths, pressing into cathode plates. With gas pressure increase the thickness of cathode sheaths decreases and the negative glow widens. At pressure values higher than 1 Torr the discharge structure in the cavity changes. Due to frequent collisions with gas molecules, fast electrons that left one cathode sheath manage to lose their energy due to inelastic collisions with gas molecules before reaching the cavity's central area. Therefore two cathode sheaths are observed (one near each of the cathode plates) corresponding to negative glows and in the center of the cavity one can see a dark sheath that consists of two overlapping dark Faraday spaces.

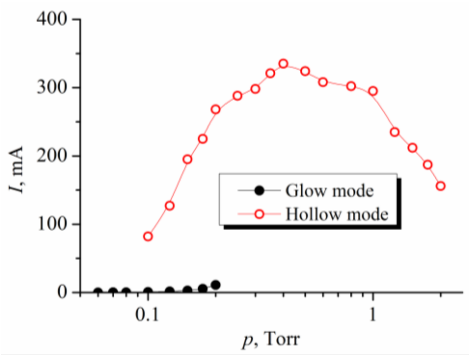

Fig. 4. Discharge current vs. gas pressure
U = 450 V

As with the increase in pressure the structure of the discharge in the hollow changes, this leads to a strong dependence of discharge current on the gas pressure. Fig. 4 shows that when the voltage between the electrodes is held constant, increasing gas pressure is followed by a uniform increase of current in a glow mode. The current value in a glow mode is small though and at the scale of the plot experimental points are almost lying on the x axis. The discharge transition into a hollow mode leads to a considerable increase in current up to tens-hundreds of milliamperes. With the increase of gas pressure the discharge current first rises, at a CO_2 pressure of 0.4 Torr reaches maximum and then decreases. At an optimum pressure that corresponds to the current maximum the sum of two cathode sheath widths is approximately equal to the width of the negative glow in the cavity. Let us remark that the distance between cathode plates of the hollow was $d_h = 0.8$ cm. Therefore the optimum conditions for sustaining the hollow mode are observed at the value of product $p \cdot d_h = 0.32$ Torr·cm. As under these conditions the discharge current reaches maximum the values of conversion coefficient and CO_2 conversion energy efficiency in a chamber with a hollow cathode should be maximum. This will be considered in our further studies of the CO_2 conversion process in a glow discharge.

Let us also note that $p \cdot d_h = 0.32$ Torr·cm considerably diverges with the value of gas pressure and distance between flat electrodes $p \cdot d = 0.44$ Torr·cm, under which the minimum on the dc discharge breakdown curve is observed [28]. This divergence is not surprising because the gas breakdown evolves in an almost uniform electric field with only a small number of charged particles taking part. In a hollow cathode electric field is approximately linearly decreasing in a sheath from the first cathode plate to the negative glow, it is very small in the negative glow itself and then it increases again in the sheath near the second cathode plate.

Using the Horiba iHR 320 spectrometer we measured the optical emission spectrum of the radiation from the cathode cavity within the wavelength range of 280...1000 nm (look in Fig. 5). This spectrum consists of three different bands. In the UV range the lines of CO_2^+ ions are dominating. The bands with the main lines of 288.3 and 289.6 nm (often called UV CO_2^+ doublet system) are particularly well defined and correspond to the $B^2\Sigma_u \rightarrow X^2\Pi_g$ transition. The presence and high intensity of these lines in the negative glow of the cathode cavity points to the presence of a large quantity of electrons with the energy higher than 18 eV. In the near UV and in the visible range (from 300 to 700 nm) the Angstrom system of CO ($B^1\Sigma^+ \rightarrow A^1\Pi$) band is predominantly observed, inside which much weaker lines of other bands of CO, O_2 and Fox-Duffendack-Barker CO_2^+ system (300...440 nm, $A^2\Pi_u \rightarrow X^2\Pi_g$) bands are spread. Let us note that in order to excite the Angstrom system of CO ($B^1\Sigma^+ \rightarrow A^1\Pi$) band it is necessary to either in one electron collision simultaneously perform CO_2 molecule dissociation with the excited reaction product CO (for this the electrons with at least 17 eV of energy are needed), or with the first electron hit (with energy no less than 7 eV dissociate the CO_2 molecule to CO and O, and then the CO molecule needs to be excited by another electron hit with the energy greater than 11 eV.

Another mechanism of dissociation, that in the presence of cold electrons with energy about 1 eV becomes the main one, consists of an excitation of molecular oscillations of CO_2 and subsequent exchange of oscillation energy [20, 21].

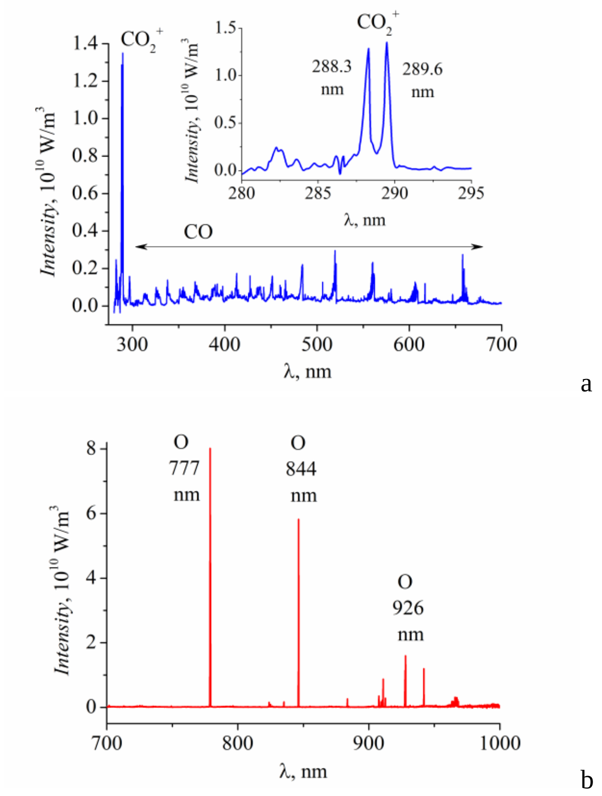

Fig. 5. Optical emission spectrum of the radiation from the cathode cavity

In IR band the spikes of atomic oxygen for $3p^5P \rightarrow 3s^5S$ (with the wavelength of 777 nm), $3p^3P \rightarrow 3s^3S$ (844 nm) and $3p^5D \rightarrow 3s^5P$ (926 nm) transitions are dominating. As in the case of CO molecules the glow of oxygen atoms we pointed out can be caused by either the dissociative excitation of CO_2 (with exciting $3s^5P$, $3p^3P$ and $3p^5D$ levels O, that needs electrons with energy no less than 17 eV), or the excitation of previously produced oxygen atoms by electrons with energy greater than 11 eV.

All that points to the fact that in a cathode cavity in the negative glow there is a large quantity of fast electrons capable of efficiently dissociating CO_2 molecules. On the other hand, slow electrons present in the negative glow may give a considerable contribution into the process of CO_2 molecules dissociation through oscillation levels of excitation. This makes the hollow cathode glow discharge attractive for conducting an effective CO_2 conversion.

CONCLUSIONS

In this paper the modes of hollow cathode DC discharge in CO_2 for a wide range of pressures are studied. Current-voltage characteristics of glow and hollow modes of discharges are measured. The hysteretic character of transition between modes in the CO_2 pressure range of less than 0.5 Torr is shown. In a hollow mode, when the cathode cavity is filled with the discharge the maximum discharge current is observed at the value of gas pressure and cathode plates distance product $p \cdot d_h = 0.32$ Torr·cm. These conditions are optimum for utilizing a hollow cathode discharge in CO_2 plasma conversion. The optical emission spectrum measured has allowed us to come to the conclusion that in the cathode cavity there is a large quantity of electrons with the energy greater than 18 eV. Therefore in a hollow cathode discharge the process of CO_2 conversion by direct electron impact should be conducted with high efficiency. Additionally, the presence of slow electrons may introduce a considerable contribution to the conversion due to oscillatory levels excitation of CO_2 molecules.

REFERENCES

1. R.K. Marcus. *Glow Discharge Spectroscopies*. New York: "Springer US", 1993, 514 p.
2. N. Baguer, A. Bogaerts, R. Gijbels. Hybrid model for a cylindrical hollow cathode glow discharge and comparison with experiments // *Spectrochimica Acta, Part B*. 2002, v. 57, p. 311.
3. M. Ivkovic, N. Konjević. Glow-to-arc transitions in a hollow cathode CO_2 laser // *Japanese Journal of Applied Physics*. 1995, v. 34, p. 5610.
4. A. Bogaerts, M. Grozeva. Axial non-uniformity of longitudinal hollow-cathode discharges for laser applications: numerical modeling and comparison with experiments // *Appl. Phys. B*. 2002, v. 75, p. 731.
5. S. Muhl, A. Perez. The use of hollow cathodes in deposition processes: a critical review // *Thin Solid Films*. 2015, v. 579, p. 174.
6. H. Baránková, L. Bardos. Hollow cathode and hybrid plasma processing // *Vacuum*. 2006, v. 80, p. 688.
7. T.S. Matlock, D.M. Goebel, R. Conversano, R.E. Wirz. High flux plasma source for plasma-materials interactions experiments // *Plasma Sources Sci. Technol*. 2014, v. 23, p. 025014.
8. A. Jorns, S.E. Cusson, Z. Brown, and E. Dale. Non-classical electron transport in the cathode plume of a Hall effect thruster // *Phys. Plasmas*. 2020, v. 27, p. 022311.
9. D.M. Goebel, G. Becatti, I.G. Mikellides, A. Lopez Ortega. Plasma hollow cathodes // *Journal of Applied Physics*. 2021, v. 130, p. 050902.
10. N. Baguera, A. Bogaerts, Z. Donko, R. Gijbels, and N. Sadeghi. Study of the Ar metastable atom population in a hollow cathode discharge by means of a hybrid model and spectrometric measurements // *J. Appl. Phys*. 2005, v. 97, p. 123305.
11. G. Bano, Z. Donko. On the high argon metastable atom density measured near the cathode surface of a hollow cathode discharge // *Plasma Sources Sci. Technol*. 2012, v. 21, p. 035011.
12. V.A. Lisovskiy, I.A. Bogodielnyi, V.D. Yegorenkov. Axial structure of hollow cathode DC glow discharge in different burning modes// *Problems of Atomic Science and Technology. Series "Plasma Electronics and New Methods of Acceleration" (86)*. 2013, № 4, p. 144.
13. V.A. Lisovskiy, R.O. Osmayev, D.I. Khilko, V.D. Yegorenkov. Structure and modes of dc glow discharge in nitrogen with hollow cathode or anode // *Problems of Atomic Science and Technology. Series "Plasma Physics" (118)*. 2018, № 6, p. 210-213.

14. V.A. Lisovskiy, D.I. Khilko, R.O. Osmayev, V.D. Yegorenkov. Comparing properties of dc discharges in tubes possessing a hollow cathode or anode in an undergraduate laboratory // *Eur. J. Phys*. 2019, v. 40, p. 045203.

15. G. Sary, L. Garrigues, J.P. Boeuf. Hollow cathode modeling: I. A coupled plasma thermal two-dimensional model // *Plasma Sources Sci. Technol*. 2017, v. 26, p. 055007.

16. Y. Fu, J.P. Verboncoeur, A.J. Christlieb, X. Wang. Transition characteristics of low-pressure discharges in a hollow cathode // *Phys. Plasmas*. 2017, v. 24, p. 083516.

17. V.A. Lisovskiy, K.P. Artushenko, V.D. Yegorenkov. Influence of the inter-electrode gap on the cathode sheath characteristics (voltage drop across it and its thickness) // *Physics of Plasmas*. 2017, v. 24, p. 053501.

18. V.A. Lisovskiy, V.A. Koval, E.P. Artushenko, V.D. Yegorenkov. Validating the Goldstein-Wehner law for the stratified positive column of dc discharge in an undergraduate laboratory // *Eur. J. Phys*. 2012, v. 33, p. 1537.

19. G. Chen, R. Snyders, N. Britun. CO_2 conversion using catalyst-free and catalyst-assisted plasma-processes // *Journal of CO_2 Utilization*. 2021, v. 49, p. 101557.

20. R. Snoeckx and A. Bogaerts. Plasma technology – a novel solution for CO2 conversion? // *Chem. Soc. Rev*. 2017, v. 46, p. 5805.

21. A. Bogaerts, G. Centi. Plasma Technology for CO_2 Conversion: A Personal Perspective on Prospects and Gaps // *Frontiers in Energy Research*. 2020, v. 8, p. 111.

22. S.V. Dudin and A.N. Dakhov. Conversion of carbon dioxide in low-pressure plasma // *Problems of Atomic Science and Technology*. *Series "Plasma Physics" (118)*. 2018, № 6, p. 194-197.

23. S.V. Dudin, A.V. Zykov, S.D. Yakovin. Plasma assisted conversion of carbon dioxide in low-pressure gas discharges // *Problems of Atomic Science and Technology*. *Series "Plasma Electrons and New Methods Acceleration" (122)*. 2019, № 4, p. 141-146.

24. V.A. Lisovskiy, S.V. Dudin, P.P. Platonov, V.D. Yegorenkov. Studying CO_2 conversion in dc glow discharge // *Problems of Atomic Science and Technology*. *Series "Plasma Physics" (130)*. 2020, № 6, p. 179-184.

25. P.P. Platonov, S.V. Dudin, V.A. Lisovskiy. Simulation of gas dynamics in plasma reactor for carbon dioxide conversion// *Problems of Atomic Science and Technology*. *Series: "Plasma Physics" (131)*. 2021, № 1, p. 131-134.

26. R.W.B. Pearse, A.G. Gaydon. *The identification of molecular spectra*. London: «Chapman», 1950, 369 p.

27. V.A. Lisovskiy, R.O. Osmayev, D.I. Khilko, and V.D. Yegorenkov. Structure and properties of glow discharge in argon with hollow cathode// *Problems of Atomic Science and Technology. Series "Plasma Electrons and New Methods Acceleration" (122)*. 2019, № 4, p. 159-164.

28. V.A. Lisovskiy, S.V. Dudin, P.P. Platonov, V.D. Yegorenkov. Dc gas breakdown and Townsend discharge in CO_2 // *Problems of Atomic Science and Technology*. *Series "Plasma Physics" (130)*. 2020, № 6, p. 154-158.

Article received 05.10.2022

ЖЕВРІЙНИЙ РОЗРЯД З ПОРОЖНИСТИМ КАТОДОМ У ВУГЛЕКИСЛОМУ ГАЗІ

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

Представлено експериментальне дослідження жеврійного (тліючого) розряду з порожнистим катодом у діапазоні тиску вуглекислого газу 0,06...2 Торр. Виміряні вольт-амперні характеристики в діапазоні тиску менше 0,5 Торр мають гістерезисний характер з переходами від тліючого до порожнистого режимів. Показано, що оптимальними для використання розряду з порожнистим катодом для плазмової конверсії вуглекислого газу є величина добутку тиску газу і відстані між катодними пластинами $p\,d_h = 0{,}32$ Торр·см, коли спостерігається максимальний розрядний струм. При цьому катодна порожнина заповнена розрядом із високою густиною. Аналіз виміряного оптичного емісійного спектра показав, що в негативному світінні в катодній порожнині мають бути потоки електронів з енергією вище 18 еВ, що повинно забезпечувати високу швидкість процесу конверсії молекул CO_2 прямим електронним ударом. Додатковий внесок у процес конверсії мають давати повільні електрони, народжені в негативному світінні, які ефективно збуджують коливальні рівні молекул CO_2.