CARBON DIOXIDE DISSOCIATION IN NON-EQUILIBRIUM PLASMA

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ABSTRACT

The search of discharge regimes permit to obtain the highest energy efficiency of the chemical process is one of the most fundamental task of the modern plasma chemistry. Theoretical and experimental studies of this question for carbon dioxide dissociation: $CO_2 \rightarrow CO + 1/2\ O_2$ $\Delta H = 2.9 \frac{eV}{mol}$ (1)

have been conducted in this report. In addition the peculiarities of the non-equilibrium discharge organization in supersonic gas flow have been discussed here. The results of the experimental stadies of the CO_2 dissociation process in the moderate pressure (100 - 200 Torr), non-equilibrium microwave and R.F. discharge have been presented too.

1. CARBON DIOXIDE DISSOCIATION MECHANISMS IN PLASMA. Carbon dioxide dissociation mechanisms in plasma are exceptional variously. The dissociation process may be carried out by principle different way with various energy efficiency in depends on ionization degree, electron and translational temperature, pressure and power density in discharge.
The role of discharge in traditional plasma chemical systems with quasi - equilibrium plasma is reduced to the gas heating. In this case energy efficiency is restricted by tempering opportunities and achieves the value 20 p.c. in theoretical limit. More higher energy efficiency can be attained in non-equilibrium plasma chemical systems. However the value of energy efficiency in this case strongly depends on the concrete dissociation mechanisms [1].
For example, the dissociation through electron excited states ($^1B_2$, ^3B) is the main carbon dioxide dissociation mechanism in glow and in other low pressure discharges. Theoretical calculations show that maximum efficiency in this case is 30pc. but maximum experimental value so far obtained is 10 p.c. [2]. Theoretical analysis shows that the highest energy efficiency can be obtained if the process (1) is stimulated by vibrational excitation of the ground electron state of CO_2 molecule in non-equilibrium plasma.
Intensive vibrational excitation of CO_2 molecules by electron impact and small V-T relaxation rate under low translational temperature provide energy efficiency up to 80 p.c., in the optimum regime. The results of the calculation [3] of the energy efficiency dependence on specific energy input and ionization degree are represented in fig. 1.

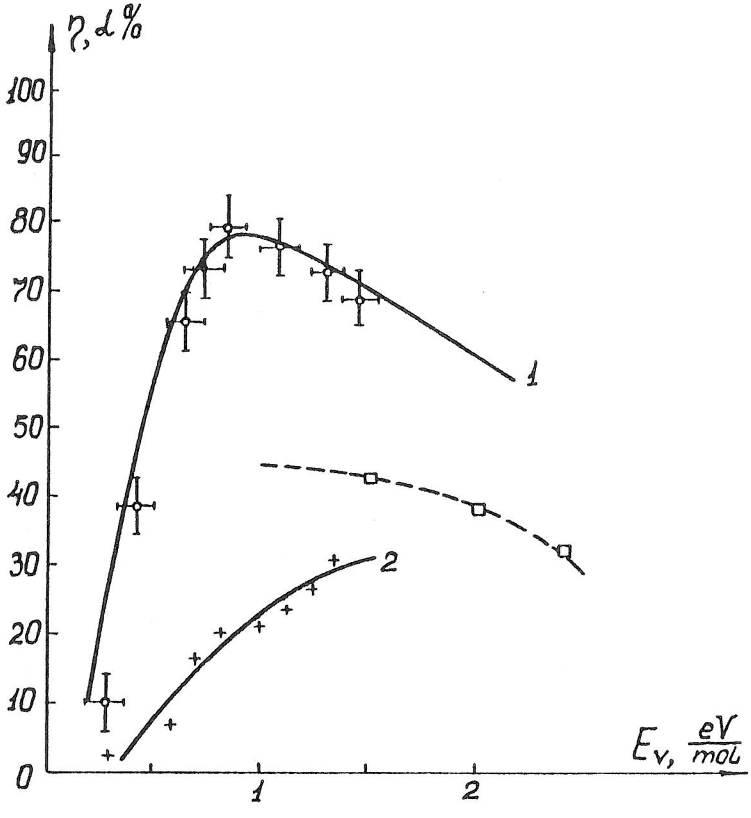

fig.1
Efficiency dependence on the specific energy input :
1 - theoretical calculation ,
⟊ , ◻ - experiments in microvave and radio frequency discharges respectively.
2 - dissociation degree dependence on energy input for micro-wave discharge.

The maximum value of the energy is achieved for the electron

temperature T_e = 1 eV, ionization degree $n_e/n_o > 10^{-6}$ and at the specific energy input E = 1 eV/mol.
It will be shown in the third paragraph that in the moderate pressure systems higher energy efficiency value can be achieved for T_o < 300 K in particular for the discharge organization in supersonic flow.
Let us consider the experiments with discharge refimes close to theoretical optimum ones.

2. EXPERIMENTAL INVESTIGATION OF CO_2 DISSOCIATION.

a) microwave discharge. Experiments with microwave (2400MHz) discharge have been carried out at power level of 2 KW and at pressure of 50-200 Torr. The gas outlay was between $1.5 \cdot 10^2$ and $2 \cdot 10^3$ cm3atm/s that allowed to realize specific energy input between 0.6 and 6 J/cm^3 ; experimental investigations permited to fix the next discharge parameters : degree $n_e/n_o \simeq 3\ 10^{-6}$, electron temperature T_e = 1,5 eV, vibrational temperature of the non-symmetric mode 3-4 10^3 K, symmetric modes - 2 10^3 K, translational temperature 10^3 K. Experimental dependence of the energy efficiency on specific energy input is shown in fig.1. One can see that maximum value of energy efficiency is 80 p.c. This fact may be explain only if the mechanism of dissociation involving vibrationally excited molecules makes a dominant to the CO_2 dissociation. The other confirmation of this mechanism is the availability of the threshold in energy input . The value of the threshold did not depend eithe on the setting way of E_v or on the pressure and coincided with theoretically predicted one in framework of dissociation mechanism though the vibrational excitation of the CO_2 ground state by the plasma electrons.
b) Radiofrequency discharge. Radiofrequency discharge experiments have been carried out at the frequency of 5, 20, 60 MHz at power levels of order of 1 - 10 KW, at pressures 50 - 250 Torr, and at gas outline between 1.5 10^2 - 3 10^2 cm^3/s. The plasma parameters were close to one's of the microwave discharge. Energy efficiency dependence on specific energy input obtained in this discharge shown in fig.1 .
One can see that maximum energy efficiency is 50 p.c. Experiments produced in the same discharge at power level up to 100 KW gave dissociation energy efficiency of 40-45 p.c.

3. CARBON DIOXIDE DISSOCIATION IN NON-EQUILIBRIUM DISCHARGES. PRODUCED IN SUPERSONIC GAS FLOW .

As it was mentioned above high energy efficiency CO_2 dissociation is achived when specific energy input 1 eV/mol. This fact leads to the conclusion that increase of the discharge power requires proportional increase of the volume rate of the gas flow. The nesessity of keeping the discharge non-equilibrium and gomogeneous restrics the possibility of pressure and reactor cross section increase. Owing to this fact the increase of the gas outlay should lead to the necessity of increase of the translational velosity of gas and when the discharge power is more than 0.5 mW the translatioal velocity should be supersonic.

Plasma chemical process of CO_2 dissociation in the supersonic flow has a number of advanteges. The first: low value of the translational gas temperature before the translational gas temperature before the discharge zone significantly decreases relaxation losses-"freezes" vibrational modes and hence increase energy efficiency of CO_2 dissociation. The calculation of the energy balance for this conditiones showed that the maximum energy efficiency can achived 95 p.c. [4] This energy efficiency could be determined only by losses due to unharmonicity of the VV-exchange and due to the heat production in the exothemal stages of the chemical reaction (1), but not due to V-T relaxation losses.

The second important pecuciarity of the supersonic discharge is that in spite of necessity of moderate pressure (100- 200 Torr) keeping in discharge zone the pressure at the discharge output may be higher (2 atm) than atmospheric one. This permits us to provide the optimum operating conditiones of the gas transport system.

The motion of gas flow in the discharge zone and behind it is essentially determined by characteristics of the heat production. It is important to underline here that in supersonic flow due to low value of the translational tempertature the V-T- relaxation rate is so small that the region of the main heat is situated far from the discharge zone. The linearization of the energy balance equation and gas motion on equation leads to V-T- relaxation length:

$$L = \frac{C_s M}{\nu_{VT}} \cdot \frac{M^2-1}{2+(kM^2-1)\frac{\partial \ln k_{VT}}{\partial \ln T}} \qquad (2)$$

If $M \gtrsim 2$ this length exceed the characteristic system dimension (10 cm) [4] . Here C_s - sonic velocity, ν_{VT}, k_{VT} — relaxation friquency and rate constant, k - adiabatic number, M- Mach number.

Nevertheless insignificant heat production take place in the discharge zone due to VV exchange uncharmonicity and exothermal stages of the reaction (1). The total value of this heat production is $q \lesssim$ 0.05 eV/mol. Maintaining heat leads to the encrease of the total gas temperature $T_* = q/C_p$ (C_p - heat capacity) and reduces flow rate:

$$\sqrt{T_0^*} \Big/ \frac{M\sqrt{1+\frac{k-1}{2}M^2}}{1+kM^2} = const \qquad (3)$$

Critical heat production value (ΔT_0 = 100°C) reduced flow to M=1 can be obtained from this equation. Further heat production can lead to the formation of unstationary gas flow disturbances propogated against to the gas flow direction with the speeds exceeded the absolute value of the gas motion velocity. These disturbances lead to the frustration of the non-equilibrium plasma state and to the sharp energy efficiency lowering of the plasma chemical process. Supperession of the heat production effect is possible by means of choosing of the profile of the nozzle system and by intermission of noble gas. One should note, that the role of the dilutor may be partly performed by CO_2, passing by active discharge zone. Experiments have been carried out in microwave discharge at power level up to 100 KW and at gas outline up to 5 10^4 sm^3/s. The gas pressure at the entrance of the nozzle was

was between 3 and 6 atm. In critical cross section the pressure was twice lower. Behind critical cross section in the discharge zone the gas flow accelerated up to M 2, and the pressure fells to 70 - 150 Torr. For the same pressure at the entrance of the nozzle flow rate achieved to M = 3-3.5 and pressure feel to 20-50 Torr. The approximate value of translational temperature was 100 K. Carbon dioxide vibrational temperature have been measured by the spectroscopy methods and was between 3000 - 5000 K. The electron concentration n_e measured by interferometer was 10^{12} sm^{-3}. Energy efficiency dependence obtained in this experiments is shown at the fig.2.

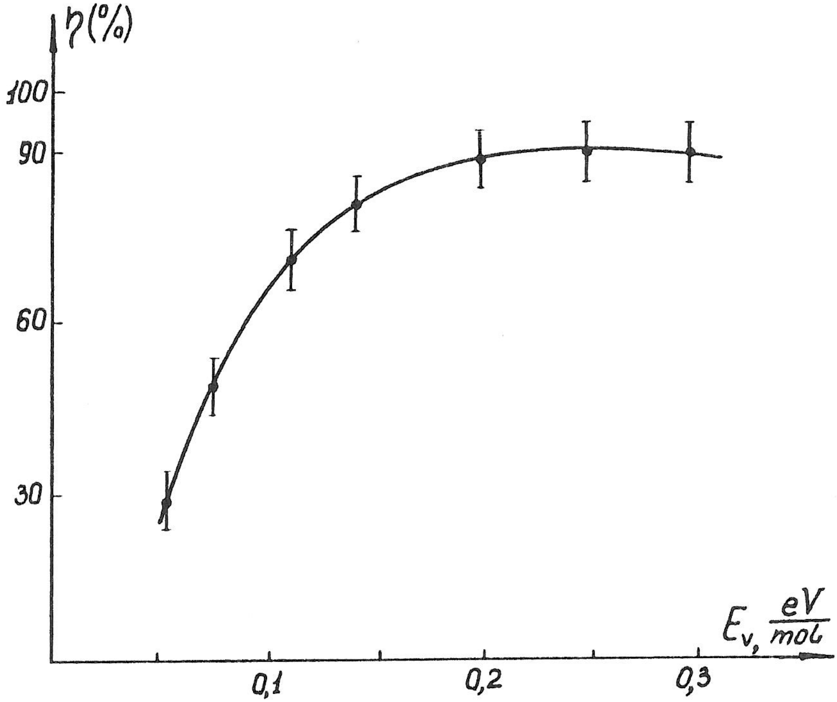

fig.2

Efficiency dependence on the specific energy input in the supersonic microwave discharge.

The maximum value of energy efficiency (90 ± 5 p.c.) is in a good agreement with the theoretical colculation and was achieved at power level of 20 KW. A portian of the gas passed by active discharge zone (being some-kind of the diluter) and due to this fact the mean specific energy input is lower than calculated one and besides the degree of convertional was relatively small (5-10 p.c.).

CONCLUSIONS

It is shown that the energy efficiency of CO_2 dissociation in the non-equilibrium plasma can be extremely when produced throgh the vibrational excitation of the ground electron state. In the R.F. and M.W. discharge with subsonic gas flow results in low temperature and relaxation rate and extremly high CO_2 dissociation efficiency 90 ± 5 p.c.

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