

FB100 Plasma Chemical Processes

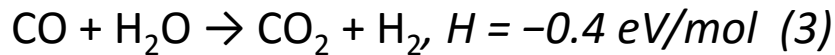
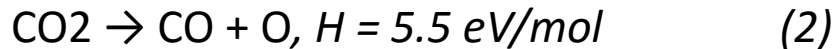
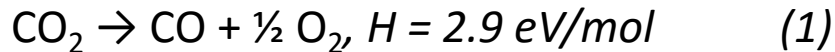
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Outline

- CO₂ decomposition
- Fullerenes, Diamond, Carbon nanotubes
- Graphene
- Nanoparticle formation

CO₂ dissociation



$$\eta = H/E_{\text{CO}} \quad (4)$$

CO₂ dissociation is an important process in CO₂ lasers and can be stimulated with high efficiency with vibration excitation. It is model case for similar “oxides” molecules and their reduction. And its related to CO₂ mitigation in exhaust gases, industrial synthesis of fuel related applications and possible future hydrogen production on Mars.

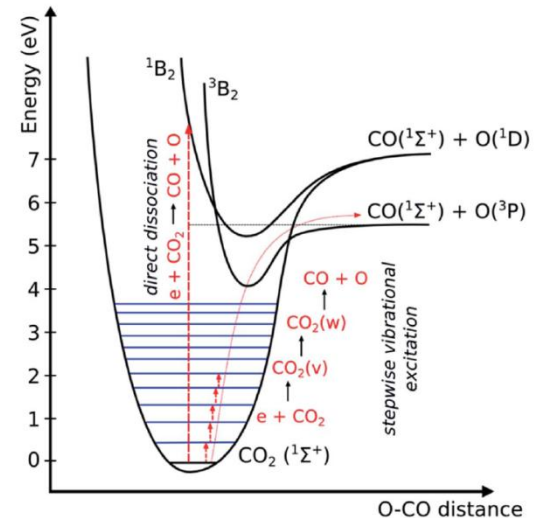


Fig. 7 Schematic diagram of some CO₂ electronic and vibrational levels, illustrating that much more energy is needed for direct electronic excitation–dissociation than for stepwise vibrational excitation, *i.e.*, the so-called ladder climbing process.

CO₂ dissociation

Thermal plasma systems such as electric arcs or high-pressure RF discharges provide CO₂ dissociation by a high-temperature shift of thermodynamic equilibrium in the direction of product formation. It can be seen from Fig. 5–3 that significant CO₂ dissociation requires plasma temperatures of about 2500–3000 K in conditions of thermodynamic quasi equilibrium. Plasma in this case is only a heater – a provider of the required high temperature. a) The products of decomposition (1) generated at high temperature (Fig. 5–3), CO and oxygen, can be protected from reverse reactions only by quenching, that is, by fast non-adiabatic cooling. If the products escape from the hot plasma zone too slowly, the thermodynamic quasi equilibrium is continuously sustained during the temperature decrease and products can be converted back to CO₂. Quenching (cooling rate) 10⁷–10⁸ K/s. b) Absolute quenching of the CO₂ dissociation requires a cooling process sufficient to save all CO formed in the quasi-equilibrium high-temperature zone. As a result the maximum energy efficiency value of CO₂ dissociation in quasi-equilibrium thermal plasmas is only 43%.

→ Higher efficiency can only be reached in non-equilibrium plasma systems

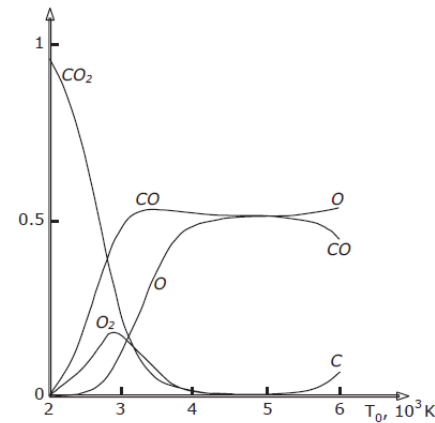


Figure 5–3. Equilibrium molar fraction of products of CO₂ decomposition in thermal plasma as function of temperature in hot discharge zone at fixed gas pressure $p = 0.16$ atm.

CO₂ dissociation

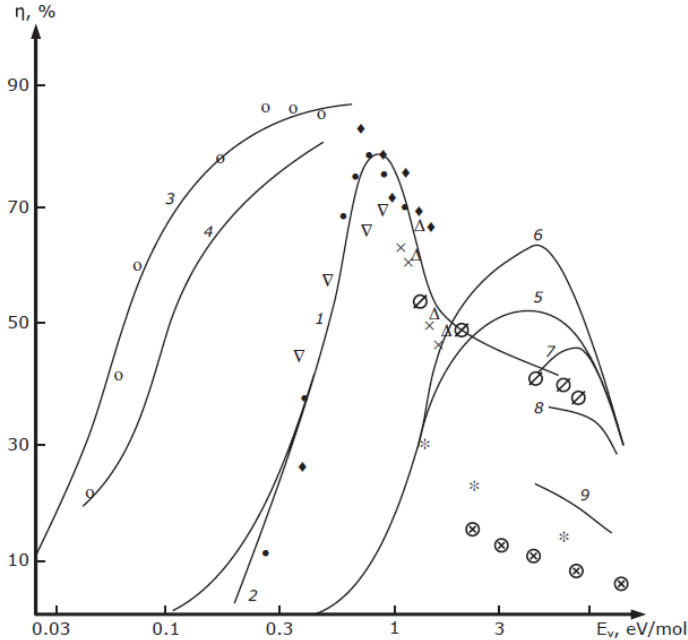


Figure 5-2. Energy efficiency of CO₂ dissociation as a function of specific energy input. (1, 2), non-equilibrium calculations in one- and two-approximations; non-equilibrium calculations for supersonic flows: (3) $M = 5$; (4) $M = 3.5$; calculations of thermal dissociation with (5) ideal and (6) super-ideal quenching; (7) thermal dissociation with quenching rates 10^9 K/s, (8) 10^8 K/s, (9) 10^7 K/s. Different experiments in microwave discharges: o, ♦, Δ, ×. Experiments in supersonic microwave discharges: ●. Experiments in different RF-CCP discharges: ○, ∇. Experiments in RF-ICP discharges: ⊗. Experiments in different arc discharges: ⊗, *.

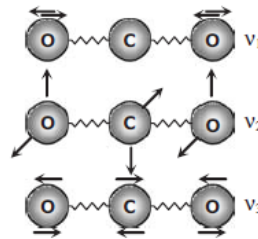
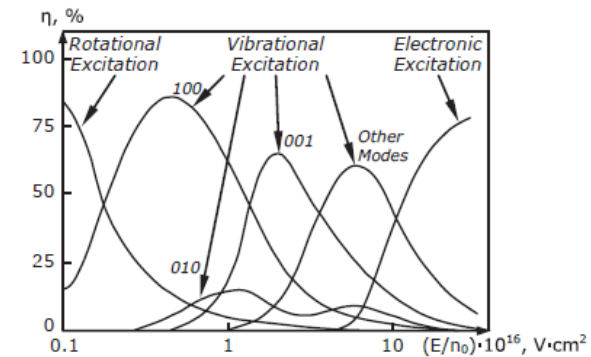


Figure 5-11. Vibrational modes of CO₂ molecules: ν_1 , symmetric valence vibrations; ν_2 , double degenerate symmetric deformation vibrations; ν_3 , asymmetric valence vibrations.

Figure 5-5. Fractions of non-thermal CO₂ discharge energy transferred from plasma electrons to different channels of excitation of the molecule.

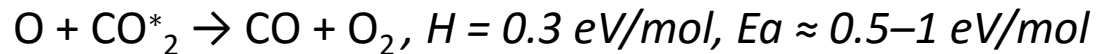


CO₂ dissociation

CO₂ Dissociation in Plasma, Stimulated by Vibrational Excitation of Molecules

The major portion of the discharge energy is transferred from plasma electrons to CO₂ vibration at electron temperature typical for non-thermal discharges ($T_e \approx 1$ eV). Excitation rate $k_{ev} = 1-3 \times 10^{-8}$ cm³/s and vibrational - translational losses are $k_{VT} \sim 10^{-10} \exp(-72/T_0^{1/3})$ cm³/s.

Non adiabatic CO₂ dissociation is favored (5,5 eV against 7 eV) and is stimulated by step by step vibrational excitation. Oxygen atoms can then participate in further reactions



This reaction is faster than the three-body recombination of atomic oxygen ($O + O + M \rightarrow O_2 + M$) and permits one to produce a second CO molecule per dissociation event, when the vibrational temperature is not too low ($T_v \geq 0.1$ eV).

No less than 95% of the total non-thermal discharge energy at electron temperature $T_e = 1-2$ eV can be transferred from plasma electrons to vibrational excitation of CO₂ molecules.

The CO₂ dissociation through electronic excitation can be a dominant mechanism of dissociation in non-thermal plasma with high values of reduced electric fields E/p (usually low-pressure discharges) or when plasma is generated by degradation of very energetic particles. CO₂ dissociation in plasma by means of dissociative attachment of electrons has small cross section 10^{-18} cm² and energy high penalty in loss of electron, similar results are achieved with other CO₂ dissociation mechanisms related to losses of charged particles, like dissociative recombination or ion-molecular reactions.

CO₂ dissociation

Asymmetric and Symmetric CO₂ Vibrational Modes

At $T_e = 1\text{--}2$ eV, plasma electrons mostly provide excitation of low vibrational levels CO₂^{*}(¹Σ⁺).

Then VV relaxation processes lead to population of highly excited vibrational states with non-adiabatic transition ¹Σ⁺ → ³B₂ and dissociation.

There are three main vibrational modes: asymmetric valence vibration ν_3 (energy quantum $h\omega_3 = 0.30$ eV), symmetric valence vibration ν_1 (energy quantum $h\omega_1 = 0.17$ eV), and a double degenerate symmetric deformation vibration ν_2 (energy quantum $h\omega_2 = 0.085$ eV).

The VV-exchange process proceeds at low levels of vibrational excitation independently along symmetric and asymmetric CO₂ vibrational modes.

The symmetric and asymmetric CO₂ vibrational modes can be characterized by individual vibrational temperatures T_{va} and T_{vs} , as well as by individual vibrational energy distribution functions. A major contribution to the population of highly vibrationally excited states of CO₂ and, hence, to dissociation is related to the excitation of the asymmetric vibrational modes.

a) The asymmetric vibrational mode of CO₂ is 1, which can be predominantly excited by plasma electrons at electron temperatures $T_e = 1\text{--}3$ eV. Discharge energy localization within that vibrational mode becomes stronger when CO₂ is mixed with CO, which is a product of its dissociation.

b) The VT-relaxation rate from the asymmetric vibrational mode is much slower than that of symmetric vibrations.

c) VV exchange along the asymmetric mode is several orders of magnitude faster than that along symmetric modes.

CO₂ dissociation

As the level of excitation increases, the vibrations of different types are collisionlessly mixed and the situation results in in the vibrational quasi continuum of the highly excited states of CO₂ molecules.

This situation can be then characterized by one-temperature approximation and two-temperature approximation. If one mode (usually the asymmetric one) is predominantly excited, then the asymmetric vibrational temperature significantly exceeds the symmetric one ($T_{va} \gg T_{vs}$) and two-temperature approximation is used. If $T_{va} \approx T_{vs} \equiv T_v$ one-temperature approximation is valid and in kinetic approximation the situation is called quasi equilibrium of vibrational modes.

Note: The CO₂ dissociation rate is limited not by elementary dissociation itself, but via energy transfer from a low to high vibrational excitation level of the molecule in the VV-relaxation processes and referred as the fast reaction limit.

From kinetics point of view The one- and two-temperature dissociation rate coefficients are not much different numerically at typical values of non-thermal discharge parameters.

CO₂ dissociation

CO₂ dissociation in thermal plasma includes two phases: heating to temperatures necessary to shift chemical equilibrium in the direction of products and fast cooling (quenching) of the dissociation products to stabilize them from reverse reactions.

The maximum energy efficiency of quasi-equilibrium plasma-chemical systems corresponds to the ideal quenching mode, when the CO₂ conversion degree achieved in the high-temperature (heating) phase is saved during the cooling. Ideal quenching means not only saving all main dissociation products (in this case CO) generated at high temperature, but also conversion during fast cooling of all relevant atoms and radicals such as C, C₂, or C₂O into CO. Conversion rate can also be maintained using energy accumulated in internal degrees of freedom, mainly in molecular vibrations. It can take place when cooling is faster than VT relaxation, and the VT non-equilibrium ($T_v > T_0$) is achieved during quenching this process is known as super-ideal quenching.

During slow cooling rate the products can be converted back to initial composition, if cooling is very fast the products are stable and there are two main competing reactions recombination of the oxygen atoms, doesn't change conversion rate, and recombination of the oxygen atoms with the dissociation products (CO), which decreases the conversion. But reaction rate coefficients for reaction of oxygen atoms is 100x higher than oxygen and CO and final change is small.

The maximum value of the CO₂ dissociation energy efficiency in non-thermal plasma (90%) is significantly higher than that in thermal plasma (60%) even in the case of super-ideal quenching. Optimal values of specific energy input are also different: in thermal plasma they are 5–10 times higher than in non-thermal plasma and are about 3–5 eV/mol. Non equilibrium plasma also doesn't require quenching.

CO₂ dissociation

The most common types of plasma used for CO₂ conversion are dielectric barrier discharges (DBDs), microwave (MW) plasmas and gliding arc (GA) discharges. The highest energy efficiency was reported for a MW plasma, i.e., up to 90% but this was under very specific conditions, i.e., supersonic gas flow and reduced pressure (100–200 Torr), and a pressure increase to atmospheric pressure, which would be desirable for industrial applications, yields a dramatic drop in energy efficiency. Indeed, at normal flow conditions and atmospheric pressure, an energy efficiency up to 40% was reported. A GA plasma also exhibits a rather high energy efficiency, even at atmospheric pressure, i.e., around 43% for a conversion of 18% in the case of CO₂ splitting.

The energy efficiency of a DBD is more limited, i.e., in the order of 2–10%, but as demonstrated already for other applications, it should be possible to improve this energy efficiency by inserting a (dielectric) packing into the reactor, i.e., a so-called packed bed DBD reactor.

Adding catalytic functionality should enable further improvement in conversion efficiency and selectivity of final products.

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G. Chena, V. Georgieva, T. Godfroid, R. Snyders, M.-P. Delplancke-Ogletree, Plasma assisted catalytic decomposition of CO₂, *Applied Catalysis B: Environmental* 190 (2016) 115–124.

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CO₂ dissociation

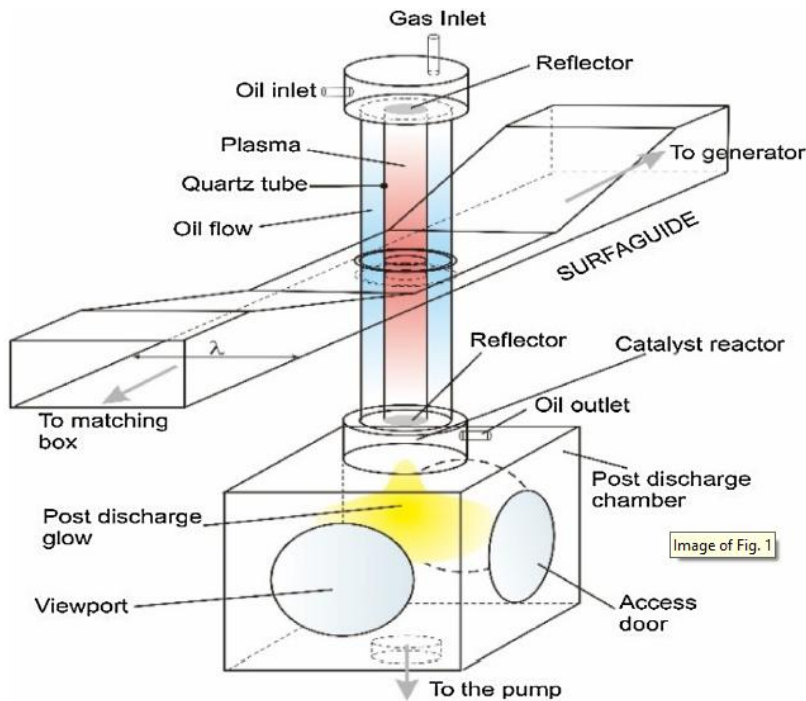


Fig. 1. Schematic representation of surface-wave microwave set-up.

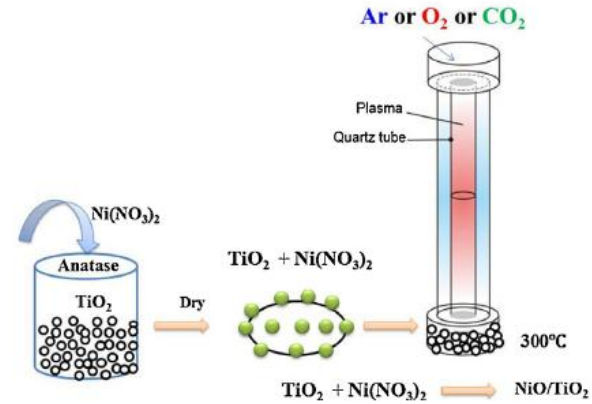


Fig. 2. Schematic representation of catalyst preparation by impregnation and plasma treatment methods.

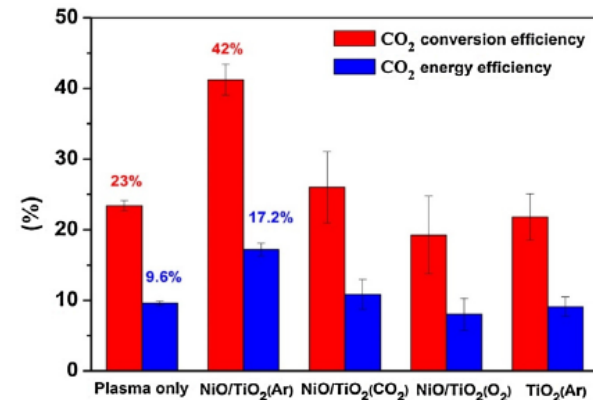


Fig. 7. CO₂ conversion and energy efficiencies, measured during the plasma-catalysis CO₂ dissociation, are shown for the NiO/TiO₂ catalysts prepared by plasma treatment with different gases (O₂, Ar, CO₂).

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CO₂ dissociation

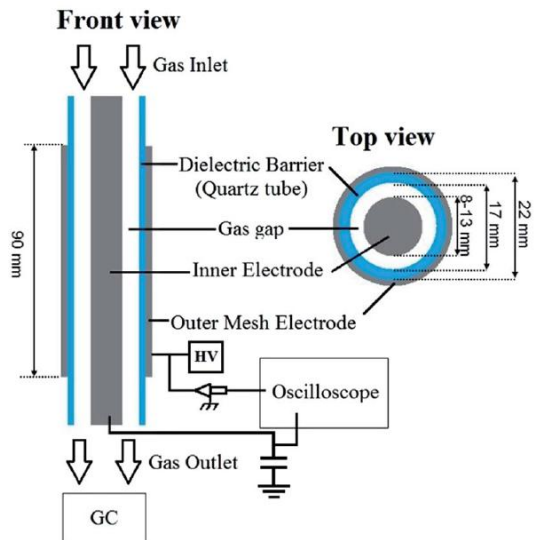


Fig. 1 Schematic diagram of the experimental setup, in front view and top view.

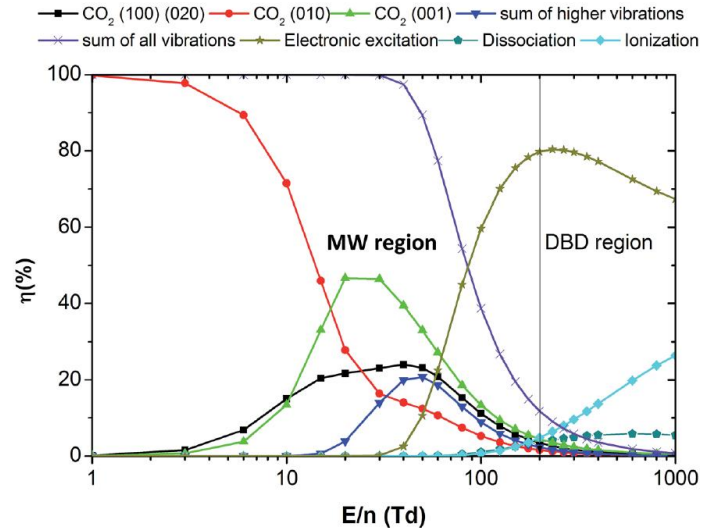


Fig. 4 The fraction of electron energy transferred to different channels of excitation as well as ionization and dissociation of CO₂, as a function of the reduced electric field (E/n), as calculated from the corresponding cross sections of the electron impact reactions. The E/n region characteristic for MW plasma and DBD plasma are indicated.

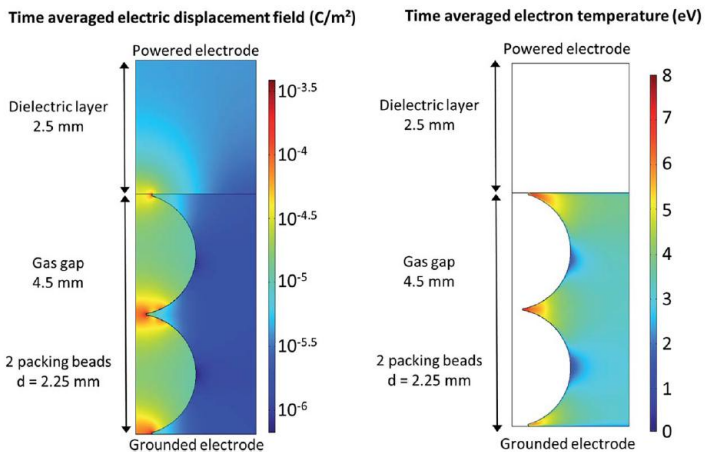


Fig. 9 Calculated time averaged electric displacement field and electron temperature over one period of the applied potential.

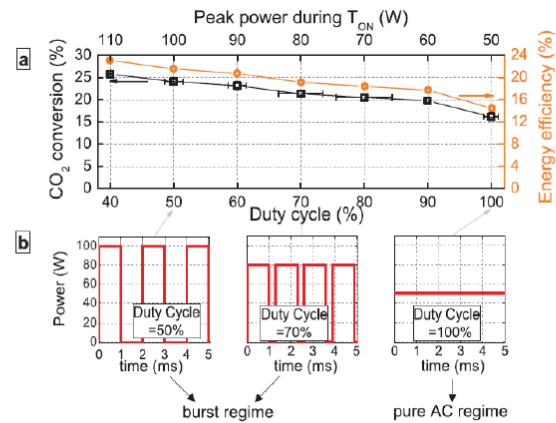


Figure 4. (a) CO₂ conversion and energy efficiency as a function of the duty cycle — Applied = 50 W, $f_{\text{signal}} = 28.6$ kHz, $f_{\text{repetition}} = 400\text{--}900$ Hz and $\Phi(\text{CO}_2) = 200$ mL · min⁻¹; (b) power versus time for $D_{\text{cycle}} = 50, 70$ and 100%.