

CO₂ dissociation studies in dielectric barrier discharges

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An atmospheric pressure plasma process for efficient CO₂ to CO conversion is presented. A dielectric barrier discharge in pure CO₂ is used for the dissociation. The setup is designed in a parallel plate configuration to optimize the optical access for *in-situ* diagnostics. Careful electrical characterization along with infrared absorption spectroscopy are carried out to analyse the gas composition and establish energy efficiencies.

Recent concerns about expected fossil fuel depletion and growing green house gas emissions have stimulated research in novel fuel processing, cleaner combustion as well as CO₂ capturing and conversion. In any scenario for converting CO₂ to value-added chemicals, the dissociation of CO₂ is known as the process limiting step. This is especially true for an approach that considers storing renewable energy through fuel processing from CO₂ using a closed global carbon cycle: firstly, CO₂ is split to CO and, secondly, hydrogen or water are added to the CO to form a fuel which may also serve as chemical energy storage.

Non-equilibrium plasma processing of CO₂ is considered as alternative approach to surpass the efficiencies observed for conventional (photo-)catalytic production routes of value-added hydrocarbons. A non-equilibrium (atmospheric pressure) plasma can be used to selectively excite vibrational levels of CO₂. This vibrational pumping is known to result in high dissociation efficiencies [1]. In this way, the highly endothermic dissociation of CO₂ is separated from the hydrogenation step, that may be carried out afterwards. Our plasma process for the CO₂ conversion uses a dielectric barrier discharge (DBD), which has a large potential for up scaling, as it is shown by applications such as ozone production and foil treatment [2].

The DBD is designed as flow-tube (figure 1a). The active discharge zone of 1 mm is enclosed by quartz plates serving as barrier. Metal electrodes are mounted on the outside of the dielectric material. Figure 1b shows a N₂ plasma inside the reactor which is usually much brighter than CO₂ in the visible range. The parallel plate design allows direct access to the active plasma zone to carry out high-speed imaging and optical emission spectroscopy parallel and perpendicular to the tube axis. It also provides a convenient basis for electronic modifications of the matching circuit.

To achieve maximum efficiency in running costs of the final process, the experiments were carried out in pure CO₂ at atmospheric pressure, i.e. noble gases and vacuum equipment were not essentially required. Furthermore gas flow rates in the range of 0.1 to 3 slm were investigated to set a link to high throughput situations. For determination of the reaction products infrared absorption spectroscopy was applied in a sampling cell downstream of the reactor under flowing conditions.

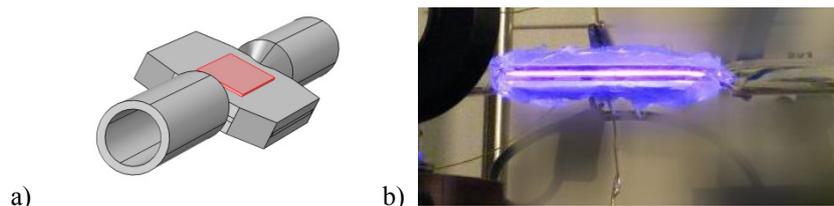


Fig. 1: a) Sketch of the parallel plate flow reactor. The red surface in the sketch represents the electrode attached to grey quartz plate. b) A N₂ plasma in the flow tube.

To specify the energy efficiency a thorough electrical characterisation was essential: The injected power was recorded directly via voltage and current measurements as well as using Lissajous figures. Both methods were in good agreement. Figure 2a shows the typical voltage and current characteristics of an atmospheric pressure DBD in CO₂. It should be mentioned that the current distribution function showed clearly different behaviour compared to other molecular gases (e.g. N₂, air) under similar experimental conditions.

The conversion of CO₂ to CO and by-products was studied downstream of the flow reactor using Fourier-Transform infrared (FT-IR) absorption spectroscopy. In first experiments, only CO and significant amounts of O₃ could be measured. The produced CO scaled weakly with the injected power, expressed as specific energy in figure 2b. The analysis of both absorption features, ν_1 and $2\nu_1$, yield the same trend. However, the fundamental CO band (ν_1) was close to saturation while the lines of the overtone band of CO ($2\nu_1$) were of low signal-to-noise ratio.

In optical emission spectra of the CO₂ plasma mainly ultraviolet radiation was observed, which can be assigned to CO₂⁺ ions. The intensity of the observed bands scaled with the injected power, and served therefore as sensitive marker for the mismatch in the electronic circuitry.

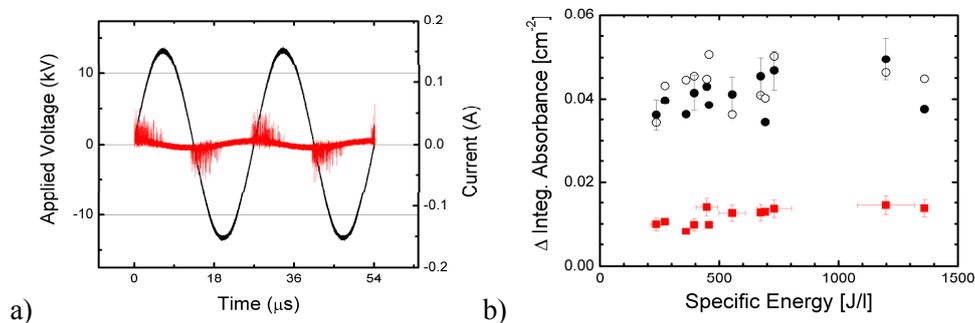


Fig. 2: a) Voltage and current characteristics of a CO₂ plasma at a pressure of 1 bar and an applied frequency of 37 kHz. The current signal consists of the capacitive displacement current and fast current peaks in the discharge. b) Species measured downstream of the flow reactor with FT-IR: full circle = CO ν_1 , open circle = CO $2\nu_1$ (x10), squares = O₃.

References

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- [2] U. Kogelschatz, *Plasma Chem. Plasma Process.* **23** (2003) 1–46.