Carbon dioxide splitting with a plane parallel dielectric barrier discharge arrangements – Effects on chemistry

M. Schiorlin[1] , V. Brueser[1] and R. Brandenburg[1,2]

[1] *Leibniz Institute for Plasma Science and Technology, Greifswald, Germany*
[2] *Institute of Physics, University of Rostock, Rostock, Germany*

Abstract: A planar volume dielectric barrier discharge is investigated in pure carbon dioxide. The formation of carbon monoxide (CO) as main product and its energy yield as well as the formation of other by-products are investigated. The type of electrode, the barrier material, the discharge gap and the barrier thickness are varied and their influences are analyzed systematically. No correlation with the geometric parameters of the barrier discharge arrangement are observed.

Keywords: Carbon dioxide conversion, carbon monoxide formation, dielectric barrier discharge, power-to-X.

1. Introduction

Carbon dioxide (CO_2) causes global warming and in recent decades many research facilities and companies around the world have been investigating methods to remove this compound from the atmosphere. Instead of just trapping it and disposing of it e.g. underground, the goal of many researchers is to convert it into a useful chemical. The latter method offers the possibility of converting a surplus of electricity, produced from non-continuos sources (like solar or wind power), into chemical energy. This process is called Power-to-X and it is very important for the energy transition from fossil to renewable energy sources. This technology must be able to be started and stopped in a short period of time and must go to capacity almost instantenously. What better solution than nonthermal plasma to achieve this goal? From all the possible types of nonthermal plasma sources, we used a dielectric barrier discharge (DBD), in particular a plane parallel arrangement. The choice was made because they can be constructed easily and upscaling is relatively simple by stacking of electrodes and dielectric plates [1]. To keep the geometry of the reactor as simple as possible gave us the possibility to vary different parameters to evaluate which of them influences the chemical performance most. The type of electrodes (plate or grid), the dielectric material (ceramic or phlogopite), the discharge gap *g* as well as the dielectric plate thickness *b* were varied and we quantified how much carbon monoxide (CO) as the main product of the conversion of CO_2 can be formed. In order to make a better contribution to the evaluation of the system´s efficiency, oxygen (O_2) and ozone (O_3) were also quantified. After running this whole series of experiments, it was found that the only parameter that affects CO production and thus, efficiency is the amount of energy supplied to the system.

2. Experimental Set-up and Procedures

The reactor used in this study consists of two plane parallel electrodes separated by an insulting plate in between. The discharge gap *g* at both sides is obtained using 2 or 3 spacers made of insulating material.

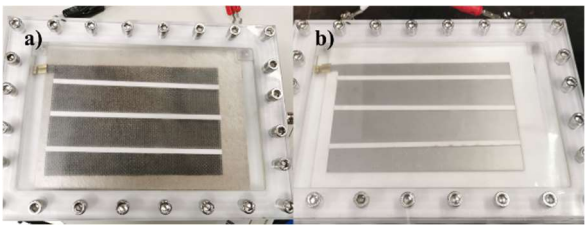

Fig. 1. a) grid electrodes with phlogopite. b) plate electrodes with ceramic dielectric.

The electrodes are mounted in a housing made of Teflon with a cover plate made of polycarbonate to enable visible inspection (see Fig. 1). The in- and outlet of the gas are centered with an inner diameter of 4 mm. All experiments were conducted at 1 slm (or 1 L_n/min) using pure carbon dioxide or synthetic air (the latter just for comparison of the electrical parameters). The reactor is powered with sinusoidal high voltage generated with a function generator (Chroma, Model 61603) and a high voltage transformer (Bremer Transformatoren GmbH). The high voltage is measured using a 1,000:1 probe (Tektronik, P6015A). charge is measurd via a polypropylene film capacitor (WIMA FKP1, 220 nF) and a voltage probe (Rigol, RP2200). Both signals were recorded with an oscilloscope (Rohde&Schwarz, HMO3004 with 4 GSa/s and 500 MHz bandwitdht). The discharge power is determined from the voltage-charge plots and the frequency measured in this way. The applied voltage is changed to vary the plasma power while the frequency is kept constant at 400 Hz. To determine the amount of CO and O_2 produced by the reactor the gas oultlet is analysed with a Micro Gas Chromatograph (MicroGC) (Inficon, 3000 MicroGC). O_3 is measured with an ozone monitor (BMT Messtechnik, BMT 963) for some of the configurations. The overall performance of the reactor is evaluated using two parameters: the specific input energy (*SIE*) and the energy yield (*EY*). These are determined as follows:

$$SIE = \frac{P}{F} \tag{1}$$

$$EY = \frac{[CO] \cdot M_{CO}}{SIE \cdot V_m} \times \frac{1}{(1-0.5\,[CO])} \tag{2}$$

F is the gas flow, in standard liters (L_n) per time unit, [CO] is the carbon monoxide molar fraction, M_{CO} the molar mass of CO and V_m is the molar volume. We prefer to use the *EY* in (g/kWh) since it gives the amount of product per energy coupled into the plasma. The second term in equation (2) considers the increase of the molecular amounts due to the dominant gross reaction:

$$CO_2 \rightarrow CO + ½\ O_2$$

3. Experimental results

The CO fraction is measured with the MicroGC, calibrated with cylinder gases. Fig. 2 shows the CO fraction as a function of *SIE*. All investigated configurations are represented by symbols as given in the legend. The blue dotted line in the diagram corresponds to an *EY* of 30 g/kWh. As can be seen from the data, the various configurations do not lead to different CO fractions and only depend on *SIE*. Higher CO fractions are obtained with ceramics as dielectric, only because a higher discharge power and thus, *SIE* is coupled to the plasma. A similar result was found by Bremer et al. in a plane parallel DBD with only one discharge gap [2].

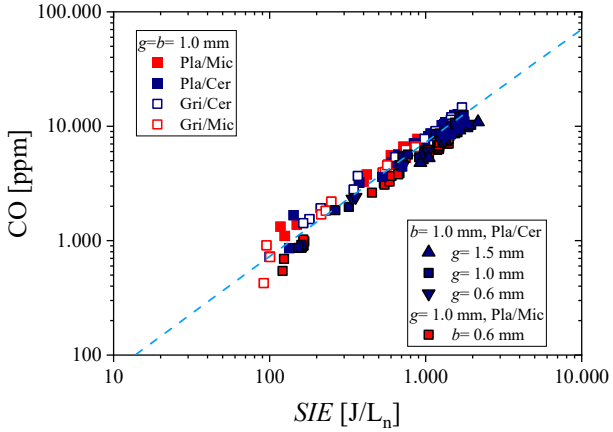

Fig. 2. CO fraction as a function of *SIE* in the different reactor configurations. The colors represent the dielectric, full symbols are for plate electrodes, open symbols are for grid electrodes.

In order to compare the performance in the different configurations, we also calculated the energy output as specified in equation (2). As shown in Fig. 3 the *EY* values are in the range from 20 to 45 g/kWh, but most of the values are concentrated around (30±8) g/kWh. We compare the EY with some literature values [2-6]. We obtain higher values of *EY*, but together with the literature values a decrease with the *SIE* can be supposed. Since [CO] increases with *SIE*, this is also called "the trade-off" between effectiveness and efficacy in the literature. However, even at higher *SIE* than in our study values close to 30 g/kWh and contrary, at similar *SIE* a lower *EY* is obtained, there might be experimental conditions which enable an increase of the *EY*. However, the parameters studied here do not show a clear influence on the *EY*.

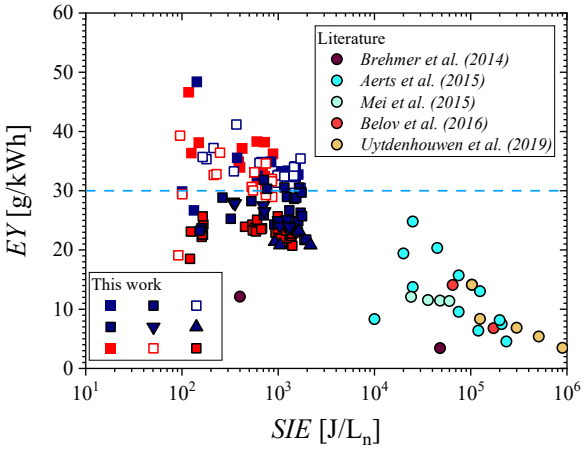

Fig. 3. Energy yield of CO formation as a function of SIE for the different DBD reactors.

The splitting of the CO_2 molecules by electron collisons leads to the formation of CO and an oxygen atom. The latter forms oxygen or ozone in three-body collisions (M= 3rd partner) or by electron detachment.

$$e^- + CO_2 \rightarrow CO + O + e^-$$
$$e^- + CO_2 \rightarrow CO + O^-$$

$$O + O + M \rightarrow M + O_2$$
$$O + O_2 + M \rightarrow M + O_3$$
$$O^- + O_2 \rightarrow O_3 + e^-$$
$$O^- + O_3 \rightarrow 2\ O_2 + e^-$$
$$O + O_3 \rightarrow 2\ O_2$$
$$O_3 + M \rightarrow M + O + O_2$$

The highest fraction of O_3 is measured at about 1000 ppm, and only O_2 is measured at *SIE* below 200 J/L_n. The formation of oxygen and ozone can also be studied with the stoichiometric ratio between CO and O_2 as shown in Fig. 4. When the ozone contribution is added (in particular at higher *SIEs*), the stoichiometric ratio is almost correct (unfortunately, not visible in Fig. 4).

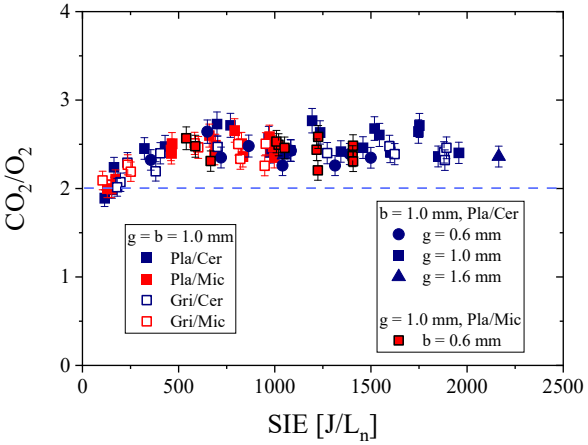

Fig. 4. Stoichiometric ratio considering only molecular oxygen for the balance in the different DBD reactors.

Chromatographic analysis did not detect any other carbon-containing compounds. The reactor operated for several hours and several days, but no carbon deposits were found on the dielectrics, electrodes or inner walls of the reactor vessel. The fact that the stoichiometric ratio is not exactly 2 (as it should be), but slightly larger (even taking into account the contribution of Ozone) can be attributed to the fact that, after a certain period of use, the surfaces of the steel electrodes exposed to the plasma zone become oxidized. This explains where a fraction of the oxygen produced, is “lost”.

4. Conclusion

The systematic variation of different geometric parameters in the plane plate arrangement resulted in finding that the only parameter that matters is the specific input energy. This is a sole scaling parameter for the conditions of our experiments. Carbon monoxide as well as O_2 and O_3 are produced in the pure carbon dioxide plasma. Both of the latter species must be taken into account in order to perform a matter balance. No other carbon-containing products have been found; even no amorphous carbon deposits on the surface of the dielectric or inner walls of the reactor housing.

For future studies, we will use more electrodes and dielectrics to explore the effect of gas retention time on the efficiency. Lower gas flows will be used to achieve higher *SIE*. Different electrode materials will be used to demonstrate a possible catalytic effect.

5. References

[1] S. Müller, R.-J. Zahn, Contribution Plasma Physics, **47**, 520 (2007)

[2] F. Brehmer, S. Welzel, M.C.M. van de Sanden, R. Engeln, Journal of Applied Physics, **116**, 123303 (2014).

[3] R. Aerts, W. Somers, A. Bogaerts, ChemSusChem, **8**, 702-716 (2015)

[4] D. Mei, PhD-Thesis University of Liverpool (2015)

[5] I. Belov, S. Paulussen, A. Bogaerts, Plasma Sources Science Technology, **25**, 015023 (2016)

[6] Y. Uytdenhouwen, K.M. Bal, I. Michielsen, E.C. Neyts, V. Meynen, P. Cool, A. Bogaerts, Chemical Engineering Journal, **372**, 1253-1264 (2019)