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Modeling the CO_2 dissociation in pulsed atmospheric-pressure discharge

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Abstract. CO_2 dissociation and its subsequent conversion into added-value chemicals is a promising strategy for recycling CO_2 gas into reusable products. One of the possible methods is direct plasma-induced dissociation. In this work we study the efficiency of CO_2 dissociation in pulsed atmospheric-pressure gas discharge between two conducting electrodes by a 0-D numerical plasma model. The purpose of the study is to provide results on the optimal conditions of CO_2 conversion with respect to the energy efficiency and dissociation by varying the maximum power density value and the pulse length. The power density is directly related to the discharge current and the reduced electric field in the discharge. We consider pulse lengths in the range from hundreds of nanosecond up to milliseconds. The results obtained show that the dissociation degree and energy efficiency are sensitive to the pulse length (duration) and the power density, so that a considerable improvement of the discharge performance can be achieved by fine-tuning these parameters. The study is intended to provide guidance in designing an experimental set-up and a power supply with the characteristics necessary to achieve optimal conversion.

1. Introduction

The dissociation of CO_2 into CO and O_2 and their conversion in other substances has attracted considerable research efforts in the last decades, as this is one win-win strategy for dealing with the excessive amounts of CO_2.

In this work, we focus on a pulsed gas discharge between two conducting electrodes. The purpose of the study is to evaluate the energy efficiency and the dissociation degree of the discharge under various conditions and to find the optimal combination with respect to these two parameters. The pulsed discharge provides some unique properties, which makes it very interesting from optimization point of view. It allows a precise control over critical discharge parameters related mainly with the energy deposition. By a proper design of the power supply, the power density deposited into the plasma could be controlled over time by controlling the voltage and the current pulse shapes. In general, during the discharge operation, the voltage and current undergo large variations. If needed, they could be modified in a controllable manner even during the pulse, although this is not easy from a technical point of view. In this work we consider the simplest case of pulse shape – a rectangular pulse

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of the power density. The power density at a certain point in the discharge is determined by the current density and the electric field rather than directly by the total discharge current and voltage. Therefore, in order to achieve a proper control of the power density in a real world experiment, the voltage and current control should be combined with proper control of the gas flow, gas pressure, and electrode shape, which determine the arc contraction or the lack of it, as well as the gas temperature, which can strongly influence the reduced electric field and the CO_2 dissociation efficiency.

The advantages of pulsed discharges have already been recognized; a number of studies have appeared discussing CO_2 dissociation in pulsed discharges with conducting electrodes. In several studies [1-6], nanosecond discharges with pulses shorter than 50 ns were studied at various pressures, including atmospheric pressure and higher. In [7-10], a pulsed glow discharge with the pulse length exceeding few milliseconds at low pressure (few Torr) was studied both experimentally and theoretically.

2. Model description and simulation conditions

The discharge considered here as a basis of our modeling is a simple two flat electrodes discharge with a certain distance between them, normally a few mm, and gas flowing through the electrode gap. The model is 0D and thus ignores the particle and energy fluxes, as well as any electric field; i.e. it is assumed that the energy and particle fluxes do not determine the plasma behavior at a certain point of the discharge. Instead of the electric field, the discharge is sustained by a power-deposition term in the electron energy balance equation. The plasma chemistry in the model is based on previously developed models [11-13]. The species considered are the neutral ground species (CO_2, CO, C, O_2, O), the charged species (CO_2^+, O_2^+, CO_3^-, O^-, e^-) and the neutral excited species ($CO2(v_a)$, $CO_2(v_b)$, $CO_2(v_c)$, $CO_2(v_d)$, $CO_2(v_1\text{-}v_7)$, $CO_2(v_8\text{-}v_{14})$, $CO_2(v_{15}\text{-}v_{21})$, $CO_2(e)$). All symmetric mode vibrational levels $CO_2(v_a, v_b, v_c, v_d)$ are considered separately, while the asymmetric mode vibrational levels $CO2(v_1\text{-}v_{21})$, are lumped in three groups ($v_1\text{-}v_7$, $v_8\text{-}v_{14}$, and $v_{15}\text{-}v_{21}$), following [11]. The model solves the balance equations for all above-mentioned species except one, which is derived from the quasi-neutrality condition. Moreover, the model solves the electron energy balance equation and the gas thermal balance.

The continuous gas flow in a real discharge is represented here by assuming that a single discharge pulse treats a certain amount of gas, which then leaves the treatment chamber. After that, new untreated gas enters the chamber, i.e. a given discharge pulse always treats pure CO_2, so that the pulses are thus completely independent. The gas cooling is considered as an effective process, represented by a loss term in the gas thermal balance expressed as: $\rho_{\text{gas}} C_{\text{p,gas}} (T_{\text{gas}} - T_{\text{room}}) \nu_{\text{cooling}}$, where ρ_{gas} is the gas density, $C_{\text{p,gas}}$ is the gas heat capacity at constant pressure, T_{gas} is the gas temperature, T_{room} is room temperature and ν_{cooling} is a cooling frequency, representing in an effective way the intensity of the gas cooling, which is normally determined by the temperature gradient, the electrode distance and temperature, the gas thermal conductivity, the gas velocity and the intensity of turbulent heat and mass transfer. All these effects cannot be described properly in a 0D model and therefore they are represented here in an effective manner by ν_{cooling}.

The plasma is sustained by a power density term in the electron energy balance equation with pulse shape. The maximum power density P_{max} is varied, while the rise (t_r) and fall (t_f) times of the power density pulse are equal to 5% of the pulse length. The gas pressure is atmospheric and $\nu_{\text{cooling}} = 10^4\ \text{s}^{-1}$ is constant. This value of ν_{cooling} is a rough estimation, corresponding to a gas flow with velocity at least 40 – 50 m/s and intense turbulent heat and mass transport in a domain with a distance between the walls in the order of several millimeters, i.e. the value of ν_{cooling} is realistic and can be achieved easily in experiment.

The major output parameters of the simulation are the degree of dissociation (X_{CO2}) and the energy efficiency (η). They are defined as follows: $X_{\text{CO2}}(\%) = \left(1 - \frac{n_{\text{CO2}}}{n_{\text{CO2, init}}}\right) \times 100(\%)$, where n_{CO2} is the

density of the obtained CO_2 gas, where $n_{CO2,\,init}$ is the initial CO_2 density; $\eta(\%) = \frac{e\Delta H}{\frac{E_{tot}}{n_{CO}}} \times 100(\%)$, where e is the elementary charge, $\Delta H = 2.9$ eV/molecule is the enthalpy of the CO_2 dissociation reaction, E_{tot} is the total energy (in eV/m^3) deposited into the discharge and n_{CO} is the CO density. The simulations were run until the gas was completely cooled up to few degrees above T_{room}, which is sufficient to ensure that no further conversion takes place in the gas mixture. Usually this time is in the order of millisecond and more.

3. Results and discussions

Figure 1 illustrates the energy efficiency and dissociation degree as a function of the pulse length, for various values of the maximum power density.

We selected only limited ranges of power density pulse lengths because outside the plotted ranges either X_{CO2} or $\boldsymbol{\eta}$ become very small. Values of X_{CO2} below 1% are omitted, because we consider these results as being subject to considerable uncertainty.

The results show that the dissociation degree remains small in the order of 10% and below. It is higher at higher power densities during the pulse, but apparently this is at the expense of the energy efficiency, which is reduced. These results do not provide categorical evidence as to which case is the optimal. If we consider a more complete system for conversion of CO_2 into CO, as it was done in [14], we should account for the capital cost of the system as a whole. It was shown [14] that the separation of CO from CO_2 and O_2 adds considerable cost, comparable to the conversion. The sensitivity analysis in [14] roughly shows almost a twice as low system cost if either the conversion or the energy efficiency is improved twofold. If we assume that the same relation holds true under our conditions and discharge (although certainly not accurate) for illustrative purposes, we may construct a new variable, which is equal to the product ($\boldsymbol{X}_{CO2} * \boldsymbol{\eta}$). This variable is presented in figure 2; it is evident that the variation of the peak values for the different power density cases is within 10 %, i.e. the different values of P_{max} could achieve similar performance. The above interpretation is very rough and ignores the different types of equipment and conditions considered in [14], as well as the probable nonlinearities in the trends.

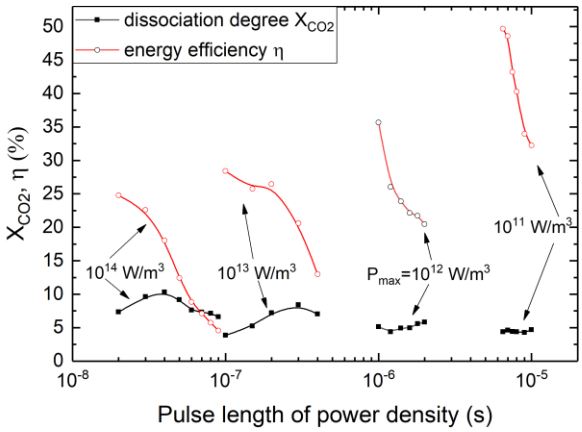

Figure 1. Dissociation degree and energy efficiency of CO_2 dissociation as a function of the pulse length for several different values of P_{max}.

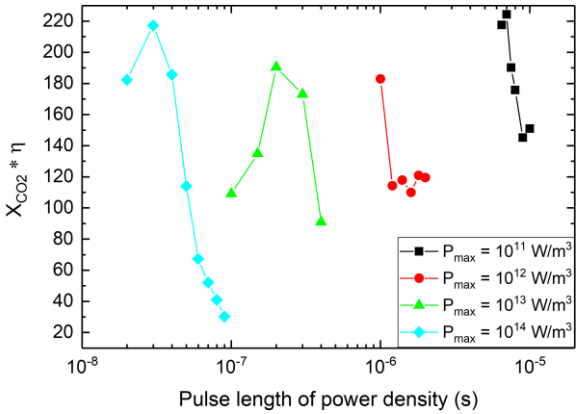

Figure 2. The product of the dissociation degree and the energy efficiency of CO_2 dissociation as a function of the pulse length for several different values of P_{max}.

In order to better understand the behavior observed in the above figures, we look also at the temporal behavior of both the conversion and the energy efficiency, as well as the gas temperature, at a given P_{max}. Figure 3 presents the evolution of the discharge for $P_{max} = 10^{13}$ W/m^3 and two values of the pulse length – 100 ns and 400 ns.

Based on figure 3, at a fixed peak power density and a varying pulse length, we can conclude that the higher energy efficiency (figure 3(a)) is related to a shorter time during which the gas is at a higher gas temperature. As noted earlier, the gas is subjected to continuous cooling; thus, keeping the gas at a higher temperature for a longer period of time will lead to higher energy losses, the energy being dissipated through cooling, while the final dissociation degree (conversion) is almost the same for both cases shown in figure 3. Therefore, the energy efficiency in the first case is considerably higher than in the 400-ns case (figure 3(b)). It is also important to note that (figure 3(b)) at 400 ns CO_2 becomes practically completely converted for a long period of time due to the higher temperature, but later with the time and during the gas cooling, the dissociation degree drops to about 7%. The analysis of the individual processes responsible for the CO balance during the pulse shows that the dissociation of CO_2 by heavy particles (O and any neutral particles) dominates over the electron impact dissociation.

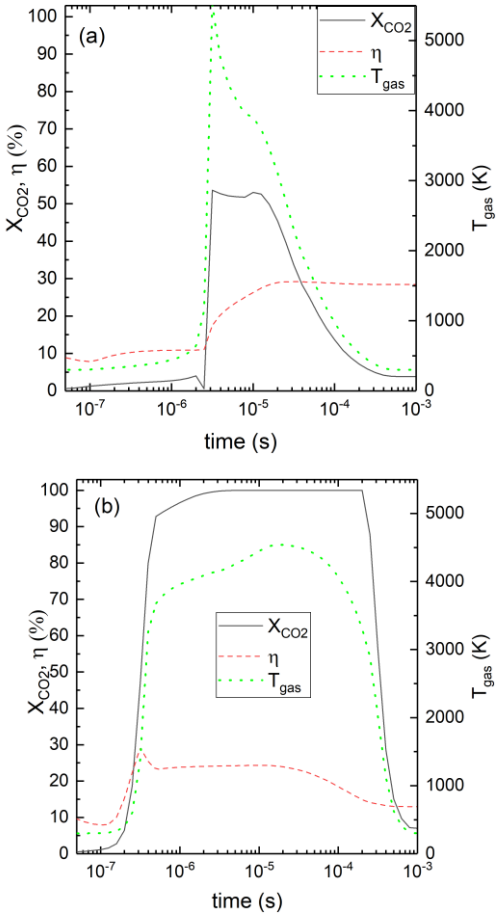

Figure 3. Temporal behavior of the dissociation degree X_{CO2}, the energy efficiency $\boldsymbol{\eta}$ and gas temperature T_{gas} for $P_{max} = 10^{13}$ W/m^3 and two values of the pulse length: (a) 100 ns and (b) 400 ns.

4. Conclusions

We developed a 0D model of a CO_2 discharge in a pulsed mode. The results show that a considerable variation of the energy efficiency may occur depending on the power density and the pulse length. Generally, the lower values of the power density seem to be preferable if a higher efficiency is required but this is accompanied by a low dissociation degree in the order of 5%. A higher power density and shorter pulses increase the dissociation degree, but the energy efficiency is reduced. This work will be extended towards a 2D model of the discharge, including the effects of gas expansion during the discharge ignition as a result of intense fast heating.

Acknowledgments

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