Optical diagnostics of a pulsed microwave discharge for better plasma-based CO_2 conversion

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Abstract: A pulsed surfaguide microwave discharge has been characterized by optical spectroscopy methods for further understanding and optimization of the plasma-assisted CO_2 conversion process. Spatially-resolved measurements of the discharge characteristic temperatures (T_{gas}, T_{vibr}, T_e) were performed. It was shown that the discharge losses its non-equilibrium and may be thermalized at few hundred Torr, whereas the CO_2 conversion and energy efficiencies are about to be optimum under these conditions.

Keywords: CO_2 conversion, microwave discharge, optical diagnostics, green energy.

1. Introduction

The idea of using non-equilibrium discharges for greenhouse gas conversion has been proposed about 40 years ago, when chemical selectivity of these discharges has been demonstrated [1]. Such plasma selectivity is a result of the non-equilibrium between the main discharge energetic subsystems, such as discharge electrons, vibrational and translational excitation of molecules. In the case of CO_2 the role of excitation of the *asymmetric* stretch mode for CO_2 decomposition has been underlined. It is known now that the most efficient channeling of the electron energy toward CO_2 vibration takes place when $T_e = 1\text{-}2$ eV [1,2], as the direct electron impact decomposition of CO_2 is rather improbable requiring > 8 eV [3]. The corresponding reduced electric field value is typically about 30 Td in this case [2].

The detailed characterization of a plasma discharge used for gas conversion is critical in order to understand all the particularities of CO_2 conversion process, as well as to optimize the process itself. In order to increase our knowledge on CO_2 conversion, in this work the methods based on optical emission spectroscopy (OES) and laser-induced fluorescence (LIF) were utilized for detailed characterization of the pulsed microwave surfaguide discharge working under different conditions.

2. Diagnostic methods

This work is focused on determination of the discharge characteristic temperatures, such as the gas temperature, vibrational temperature (of N_2 molecules) and electron temperature along the discharge volume (quartz tube), as well as on determination of the overall CO_2 conversion and energy efficiency, based on the discharge energetic parameters [4]. In our case gas temperature (T_{gas}) has been determined based on the rotational temperature (T_{rot}) of the CO (B,0) excites state. The vibrational temperature (T_v) was calculated using nitrogen admixtures, based on the N_2 (C,v-4 – B,v) ro-vibrational band from the Second Positive System of N_2. The electron temperature (T_e) has been estimated using the Ar emission line ratio, following the recent work of Silva et al. [5].

LIF technique has been applied for determination of the CO molecular density in the discharge afterglow, following by calculation of the CO_2 conversion (χ) and energy efficiency (η) based on the mean applied power and total gas flow, as described in [4].

3. Selected results

3.1. Diagnostics results. The schematics of the studied microwave discharge, its actual appearance, as well as the measured characteristic temperatures in the discharge are shown in Fig. 1. The discharge appears symmetric, as clear from Fig. 1(b), even though the working gas flow has resulted in the gas velocity in the tube up to 100 m/s under our conditions. In the case of CO_2-N_2 gas mixture, the discharge looks more pinkish on the left side, where gas is introduced, and bluish on the right side, i.e. after passing the excitation point, where CO_2 molecules undergo decomposition. This is the result of the emission from N_2 ro-vibrational bands (mainly First Positive System) on the left, and from the CO Angstrom ro-vibrational emission band on the right, as explained in [6].

The obtained electron temperature is about 2 eV at low pressure in our case (Fig. 1(c)), which is in a good agreement with the typical values in low-pressure MW discharges. As pressure increases, however, T_e drops significantly down to about 0.5 eV (at 12 Torr). The spatial profile of T_e remains rather flat during this process. The results correspond to 0.7 kW of power.

At the same time, the spatial profiles for vibrational (Fig. 1(d)) and rotational (Fig. 1(e)) temperatures along the discharge tube both reveal a maximum in the center, where the waveguide is located. This is likely related to the maximum energy transfer from the plasma electrons to rotational and vibrational excitations at this point.

The maximum energy coupling with the plasma electron at the discharge center is also confirmed by the CO_2 conversion efficiency data obtained in [6] at close discharge conditions (0.4 kW, 2 Torr). The restored curve of the power absorbed along the discharge tube points out on the maximum power consumption by plasma electron at the discharge center, as shown in Fig. 1(f).

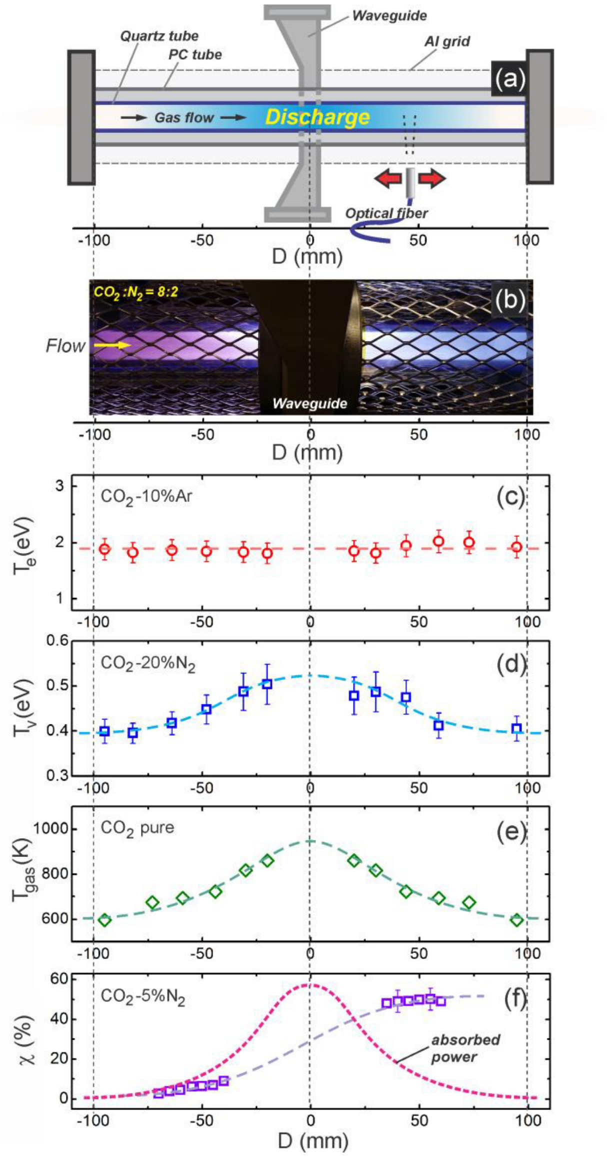

Fig. 1. Schematics of active zone of the MW discharge with optical fiber used for spectroscopic diagnostics (a); a photograph of the discharge active zone (b); spatial profile of electron (c), $N_2(C)$ vibrational (d), and gas (e) temperatures measured by OES; CO_2 conversion efficiency along the gas tube (symbols) along with the calculated curve for relative power absorption by plasma (dashed line) (f).

The gradual loss of the discharge non-equilibrium, as the total pressure in the system increases, has been confirmed in our work. During this process the electron temperature drops from about 2 eV (at 1 Torr) to about 0.5 eV (> 10 Torr) in the discharge center. At the same time the gas temperature increases from about 800 K to 1200 K in the same point. The corresponding degree of non-equilibrium, normally expressed as T_e/T_{gas}, changes from about 30 to 3 in our case, as pressure increases. The pressure at which the discharge may become thermal was estimated to be ~ 100-200 Torr in our case.

3.2. CO_2 conversion results. During the pressure increase, on the other hand, a clear increase in the energy efficiency (η) of the CO_2 decomposition has been observed. At high pressure the energy efficiency approaches the value of about 0.1 (see black symbols in Fig. 2). The conversion efficiency drops naturally, since the specific energy drops at higher pressure.

This observation somewhat contradicts to the previous studies where much higher (about 0.4) energy efficiency value in a thermal discharge case had been estimated for MW discharge [1]. The question about the role of vibrational excitation in the conversion process under the variation of the working pressure in the studied range also remains open, requiring more advanced diagnostics approaches in this future.

In general, the CO_2 conversion efficiency is supposed to be further optimized by adjusting the plasma pulse parameters in order to minimize the V-T transfer in the discharge, by synchronization of power delivery with the gas residence time in the active zone [4], as well as by using the gas cooling in the discharge, e.g. using the gas expansion technique, as studied in [7].

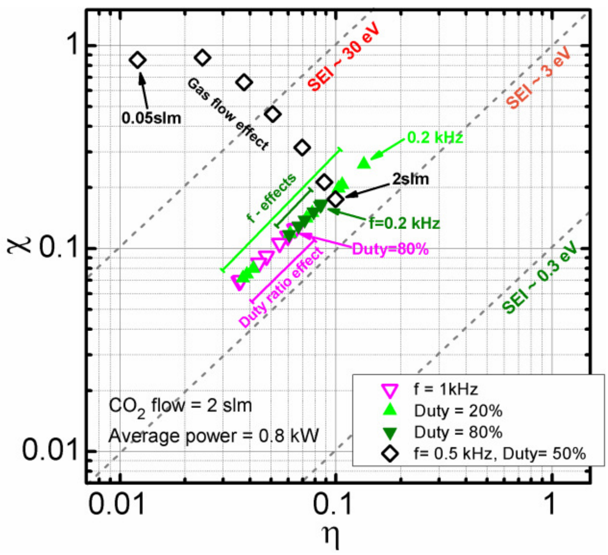

Fig. 2. CO_2 conversion (χ) - energy efficiency (η) diagram, showing the effects of the plasma pulse repetition rate, pulse duty ratio, as well as the gas flow effect.

4. References

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