

## FULL PAPER

Plasma-driven dissociation of CO<sub>2</sub> for fuel synthesis

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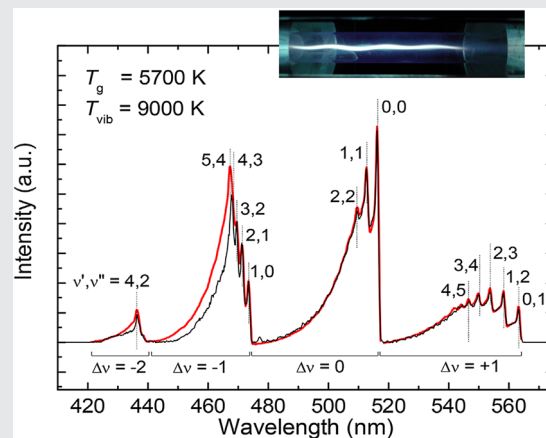
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Power-to-gas is a storage technology aiming to convert surplus electricity from renewable energy sources like wind and solar power into gaseous fuels compatible with the current network infrastructure. Results of CO<sub>2</sub> dissociation in a vortex-stabilized microwave plasma reactor are presented. The microwave field, residence time, quenching, and vortex configuration were varied to investigate their influence on energy- and conversion efficiency of CO<sub>2</sub> dissociation. Significant deterioration of the energy efficiency is observed at forward vortex plasmas upon increasing pressure in the range of 100 mbar towards atmospheric pressure, which is mitigated by using a reverse vortex flow configuration of the plasma reactor. Data from optical emission shows that under all conditions covered by the experiments the gas temperature is in excess of 4000 K, suggesting a predominant thermal dissociation. Different strategies are proposed to enhance energy and conversion efficiencies of plasma-driven dissociation of CO<sub>2</sub>.



## KEYWORDS

CO<sub>2</sub>-dissociation, efficiency, plasma, power-to-gas, solid-oxide-electrolyser

## 1 | INTRODUCTION

Sustainable energy sources will form a significant part of the global energy mix in 2025.<sup>[1]</sup> The intermittency and regional spread of renewable energy sources require efficient and large-scale storage and transport of energy in the form of synthetic chemical fuels, compatible to the present infrastructure. Such a Power-to-Gas (P2G) technology is based on

electrically driven dissociation of CO<sub>2</sub> and H<sub>2</sub>O to produce synthetic fuels such as syngas or methane. Methane can be formed either by direct internal reforming or via Fischer-Tropsch or Sabatier synthesis routes. Among the dissociation technologies of feedstock CO<sub>2</sub> and H<sub>2</sub>O, solid oxide electrolysis and plasmolysis are considered as the most promising technologies.<sup>[1]</sup> Plasmolysis offers significant advantages over competitive technologies in that it can

quickly adapt to a fluctuating supply of renewable sources, no scarce materials are employed, and overall energy efficiency is high, whilst operation is in principle possible near ambient temperature and pressure.<sup>[2]</sup> In this paper, dissociation of CO<sub>2</sub> is studied using plasmolysis setups at DIFFER (Eindhoven, The Netherlands) and IGVP (Stuttgart, Germany).<sup>[3]</sup> The focus of the experiments is on optimization of the energy efficiency.

## 2 | PLASMA DISSOCIATION OF CO<sub>2</sub>

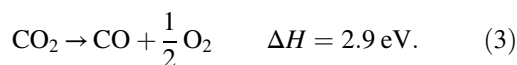
The electron-induced dissociation of CO<sub>2</sub> is characterized by a high reaction enthalpy.<sup>[2]</sup>



The formed atomic oxygen is able to react with another CO<sub>2</sub> molecule, according to reaction



The overall reaction can thus be represented by



Dissociation of CO<sub>2</sub> in the plasma can take place via two possible mechanisms. The first is by thermal dissociation, which relies on a reversible shift in the chemical equilibrium towards the products induced by thermal heating. The dissociation fraction is governed by the gas temperature  $T_g$  and becomes significant at temperatures typically above 2000 K. Retention of the dissociation products is only achieved by a fast non-equilibrium cooling trajectory to prevent the reverse reaction. At a temperature of 3000 K, an optimal energy efficiency of 50% can be achieved under ideal quenching conditions.<sup>[4]</sup> This, however, does not take into account the possibility of heat recirculation, which can potentially lead to a higher overall energy efficiency. The quenching performance is determined by the instantaneous gas cooling rate, which is optimal between  $10^7$  and  $10^9 \text{ K s}^{-1}$  for full preservation of reaction species.<sup>[5]</sup> A super-ideal quenching mode has also been described.<sup>[2]</sup> Here, radicals and other short-lived activated species contribute to additional conversion in the quenching phase, leading to energy efficiencies up to 60%.<sup>[2]</sup>

The second mechanism of dissociation is initiated via electron-induced vibrational excitation. The vibrational dissociation is driven by non-equilibrium plasma conditions, which are characterized by a high vibrational temperature  $T_{\text{vib}}$ , and a low translational or gas temperature  $T_g$  of the CO<sub>2</sub> molecules. In the non-equilibrium

regime, the plasma energy is efficiently deposited in the vibrational dissociation channel, while gas heating via other excitation channels of the CO<sub>2</sub> molecule is minimized. High efficiencies up to 90% have been reported,<sup>[6]</sup> but have not been reproduced until now.

The energy efficiency  $\eta$  of CO<sub>2</sub> dissociation is

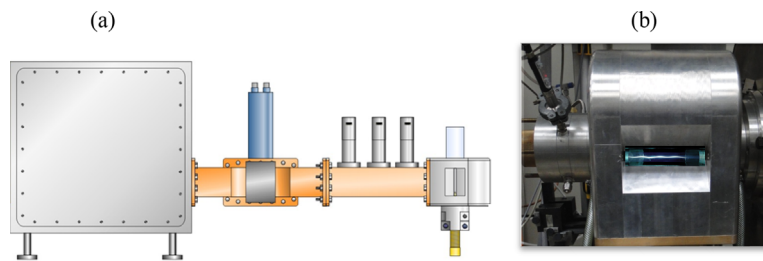
$$\eta = \alpha \cdot \Delta H / SEI \quad (4)$$

where  $\alpha$  is the fractional CO<sub>2</sub> conversion, defined as the ratio of the loss of CO<sub>2</sub> by dissociation to its feed into the reactor,  $\Delta H$  the dissociation enthalpy for a CO<sub>2</sub> molecule (2.9 eV/molecule) and  $SEI$  the specific energy input (eV/molecule). Three main factors contribute to  $\eta$ <sup>[2]</sup>

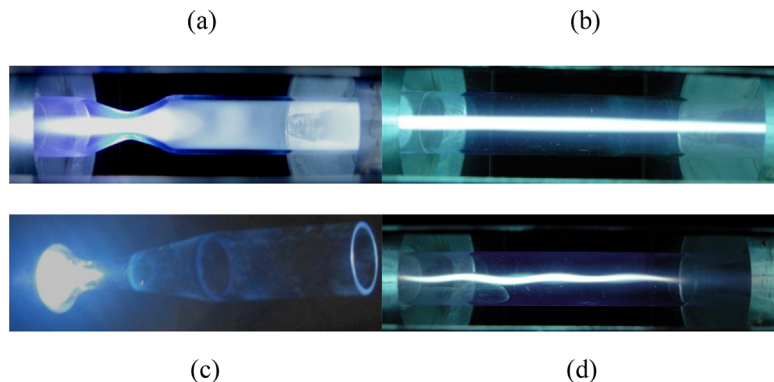
$$\eta = \eta_{\text{ex}} \cdot \eta_{\text{rel}} \cdot \eta_{\text{chem}}. \quad (5)$$

The excitation factor  $\eta_{\text{ex}}$  is the fraction of discharge energy directed toward the relevant excitation channel. The coupling of electron energy to the asymmetric vibrational modes of CO<sub>2</sub> can be as high as 95% for an optimal electron energy distribution function (EEDF), which is achieved upon applying a reduced electric field ( $E/n$ ) in a narrow range of typically 20–50 Td.<sup>[2,7]</sup>

The relaxation factor  $\eta_{\text{rel}}$  indicates the extent in which the principle active species are conserved for the reaction rather than being quenched via, for example, relaxation or recombination. Vibrational relaxation is primarily determined by the vibrational-to-translational (VT) relaxation process, which has a strong positive dependence on  $T_g$ .<sup>[2,8]</sup> Specifically at moderate to low  $T_g$  and large values of  $\eta_{\text{ex}}$ , a strong VT decoupling ( $T_{\text{vib}}/T_g > 30$ ) occurs and a VT non-equilibrium plasma can be sustained.<sup>[6]</sup> Additionally, the particle residence time in the plasma in relation to the characteristic VT relaxation time is found to play an important role in determining the value of  $\eta_{\text{rel}}$ .<sup>[7]</sup> It is reasoned that as long as the characteristic excitation time – approximated by the particle residence time – is much shorter than the characteristic relaxation time, the active (vibrational) species should be well conserved.



**FIGURE 1** (a) Schematics of the 915 MHz 3–30 kW plasma setup at IGVP. The system is equipped with (from left to right) a magnetron, circulator, straight waveguide, 3-stub tuner (all WR-975), and the plasma source, consisting of a quartz tube placed inside the TM<sub>010</sub> cylinder mode cavity with tangential gas injection. (b) Photograph of the plasma source



**FIGURE 2** Photographs of the plasma obtained using the 915 MHz plasma reactor: (a) supersonic expansion of the plasma in the MW cavity at 1 mbar gas pressure; (b) plasma in the MW cavity (MW power 5.0 kW; flow rate 11 slm; pressure 200 mbar); (c) subsequent quenching of the plasma after the nozzle into the vacuum vessel (1 mbar), and (d) plasma in the MW cavity (MW power 3.1 kW; flow rate 75 slm; pressure 200 mbar). Note the supersonic shockwaves after the nozzle in (a)

Lastly, the chemical factor  $\eta_{\text{chem}}$  indicates the efficiency of the principle active discharge species in driving the chemical reaction of interest. In general, any surplus of the vibrational energy above the reaction enthalpy involved in the dissociation process is lost and decreases the  $\eta_{\text{chem}}$ . Vibrational  $\text{CO}_2$  dissociation is relatively efficient since the process involves a so-called “ladder-climbing” process with small vibrational quanta, in contrast to for instance electron-impact excitation dissociation, where a large surplus of electron energy from the tail of the EEDF can be converted to heat.<sup>[9]</sup> An additional contribution that limits  $\eta_{\text{chem}}$  relates to the oxygen radical chemistry.<sup>[7]</sup> Depending on the pressure, the atomic oxygen produced in reaction (1) may recombine at the wall to form  $\text{O}_2$  or take part in reaction (2). Only in the latter case, an average minimum energy for dissociation of  $\text{CO}_2$  of  $\sim 2.9$  eV/molecule is required. The rates of reactions (1) and (2) should be similar to meet this requirement.

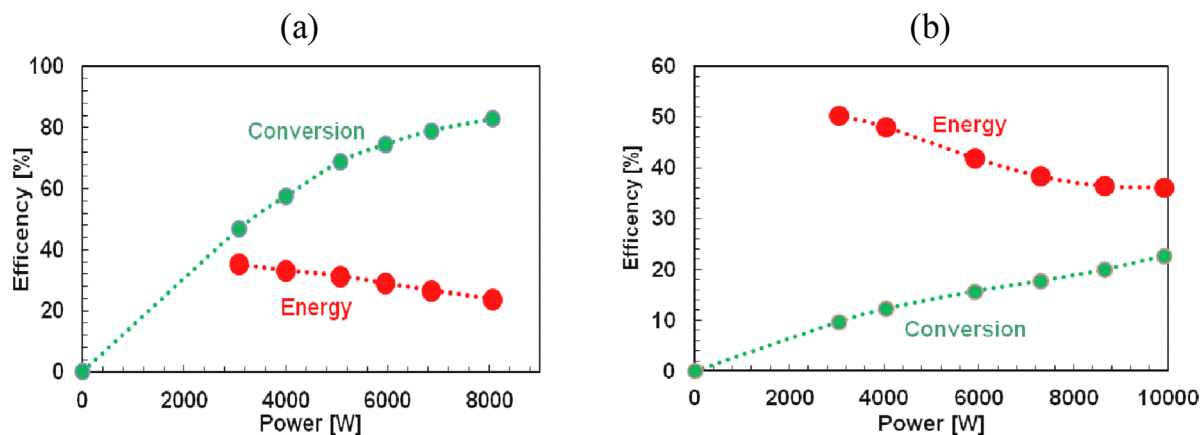
In summary,  $E/n$ ,  $T_g$ , residence time and the oxygen radical chemistry are important parameters for optimisation

of the vibrational dissociation of  $\text{CO}_2$ . High vibrational activation and low VT relaxation can be achieved by applying a narrow range of  $E/n$ , keeping a low value of  $T_g$ , and using a short residence time in comparison to the characteristic VT-relaxation time.

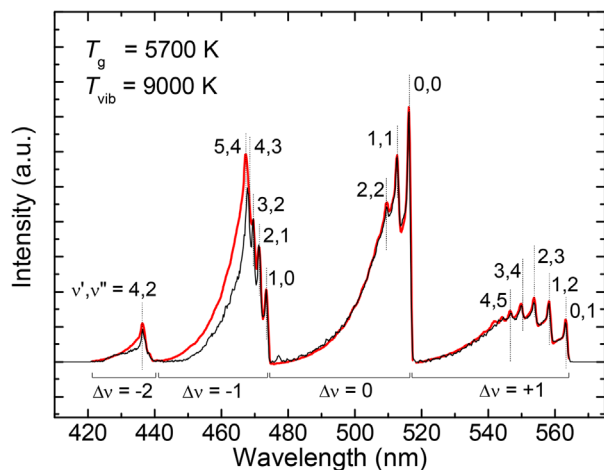
### 3 | EXPERIMENTAL SECTION

In this study, the influence of microwave (MW) field, residence time in the plasma reactor, quenching, and vortex plasma configurations on energy efficiency of  $\text{CO}_2$  dissociation was investigated. Plasma experiments were carried with two different setups.

At IGVP, the experiments were conducted using a 915 MHz plasma system using WR-975 waveguide components with dimensions  $24.8 \times 12.4$  mm<sup>2</sup>. The plasma source of this system is based on a transverse magnetic cylinder mode cavity ( $\text{TM}_{010}$ , with internal diameter of 225 mm) through which a quartz tube (with internal/external diameter of 30 mm/34 mm) is inserted.<sup>[10]</sup> The schematics and a photograph of the plasma source are shown in Figure 1. At DIFFER, a 2.45 GHz 1 kW plasma system (InitSF) with WR-340 waveguide components with dimensions  $86.4 \times 43.2$  mm<sup>2</sup> was used. Distinct from the setup shown in Figure 1, a quartz tube (with internal/external diameter of 27 mm/30 mm) was placed inside the transverse electric rectangular waveguide cavity to form a  $\text{TE}_{101}$  mode. To enhance the field at the gas injection location, a central resonator pin was used to form a circular transverse electromagnetic mode coaxial cavity coupled to the rectangular waveguide mode cavity. The 3-stub tuner was used to minimize the reflected power and to measure the actual



**FIGURE 3** Energy and conversion efficiencies in quenching experiments, using the 915 MHz plasma reactor. Data were obtained at a  $\text{CO}_2$  gas flow rate of (a) 11 slm, and (b) 75 slm, both at a plasma pressure of 200 mbar



**FIGURE 4** Experimental (black) and simulated (red)  $C_2$  ( $d \ ^3\Pi_g \rightarrow a \ ^3\Pi_u$ ) Swan bands. Experimental data were obtained at 0.9 eV/molecule (MW power 5 kW;  $CO_2$  gas flow rate 75 slm) and at a plasma pressure of 200 mbar. The measured spectrum is baseline-corrected, that is, contributions from broadband continuum radiation were subtracted. The  $C_2$  ( $d \ ^3\Pi_g, v' \rightarrow a \ ^3\Pi_u, v''$ ) transitions are indicated

plasma impedance. The MW electrical field was calculated from the plasma impedance using the ANSYS HFSS electromagnetic software package.<sup>[11]</sup>

The vortex in both setups was created by tangential gas injection nozzles. In case of 915 MHz plasma source, a single nozzle (4 mm internal diameter) was used, whereas a double nozzle (1 mm internal diameter) was used for the 2.45 GHz InitSF plasma system. The product formation in both setups was measured downstream using a mass spectrometer (MS) (Hiden HAL RC 201QIC with a capillary inlet) relative to calibrated reference gas mixtures. Optical emission spectroscopy (OES) (HR2000 and HR4000, Ocean Optics) was used to identify the constituents of the plasma and to determine their rotational temperature  $T_{rot}$  and vibrational temperature  $T_{vib}$ . Spectra were collected via an optical fibre pointing at the brightest point of the plasma in the centre of the quartz tube. A relative calibration was carried out to correct for variations in fibre transmittance and spectrometer sensitivity as a function

of wavelength. Simulation of the  $C_2$  Swan bands and emission intensities for electronic transitions in emitting diatomic molecules was carried out using SpecAir,<sup>[12]</sup> which enabled evaluation of the  $T_{rot}$  and  $T_{vib}$  of the  $C_2$  molecules, which are assumed to be in thermal equilibrium with heavier molecular species in the plasma. The shape of  $C_2$  Swan bands is determined only by these temperatures, and is independent of the absolute intensity of the emission so that a relative calibration of the experimental spectra suffices.

## 4 | RESULTS AND DISCUSSION

### 4.1 | $CO_2$ dissociation experiments using the 915 MHz MW reactor at IGVP

Several forward vortex (FV) plasma configurations were investigated using the 915 MHz reactor at IGVP with a MW power up to 10 kW.<sup>[2]</sup> In supersonic plasma expansion experiments, a constriction (nozzle) in the quartz tube expanded the plasma into the cavity.<sup>[13]</sup> The experiments were conducted at  $\sim 1$  mbar gas pressure. In quenching experiments, in which the gas pressure was  $\sim 200$  mbar, the nozzle was positioned after the cavity, such that the exhaust gas expanded supersonically. The latter configuration was intended to quench the plasma gas and to freeze the conditions of  $CO_2$  dissociation. Figure 2 presents photographs of the obtained plasmas in both configurations.

The supersonic expansion experiments using the 915 MHz MW plasma reactor showed a maximum  $\eta$  of 15% in the range of MW power 3–10 kW. Following Fridman,<sup>[2]</sup> such a low value of  $\eta$  can be explained by a low plasma pressure. Both energy and conversion efficiencies were found to be much higher in quenching experiments as described below.

In quenching experiments, the energy and conversion efficiencies varied from  $\eta = 24\%$  and  $\alpha = 83\%$  at a SEI of 10.3 eV/molecule (MW power 8.1 kW) to  $\eta = 35\%$  and  $\alpha = 47\%$  at a SEI of 3.9 eV/molecule (MW power 3.1 kW),

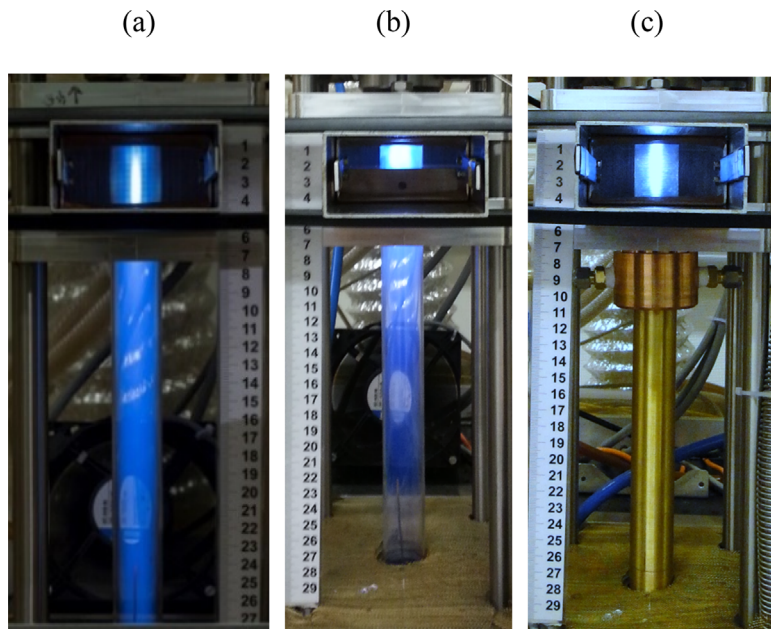
**TABLE 1** Operating conditions and configurations maintained during different experiments using the 2.45 GHz plasma source (InitSF) at DIFFER

Experiment	Configuration	Flow-type	Field enhancement	Quenching	SEI [eV/molecule]
(1)	A	FV	No <sup>a</sup>	–	0.9
(2)	B	FV	Half-height WG	–	0.9
(3)	C	FV	No <sup>a</sup>	Conductive	0.9
(4)	C	FV	Resonator pin <sup>a</sup>	Conductive	0.9
(5)	C	RV	No <sup>a</sup>	Convective	0.9
(6)	A	FV	No <sup>a</sup>	–	1.7
(7)	C	RV	No <sup>a</sup>	Convective	0.8
(8)	C	RV	No <sup>a</sup>	Convective	1.7

Photographs of the different configurations are given in Figure 5.

<sup>a</sup>Full-height waveguide (WG) configuration.





**FIGURE 5** Different configurations of the 1 kW 2.45 GHz plasma source at DIFFER, denoted as (a) A, (b) B, and (c) C in Table 1. In all cases the plasma is seen through a metal grid, which acts as a short-circuit of the TE<sub>10</sub> mode in the waveguide cavity. The CO<sub>2</sub> gas is tangentially injected from the top just above the waveguide cavity to create a vortex gas flow separating the visible part of the plasma from the quartz tube. Photographs were recorded using gas pressures (a) 130 mbar, (b) 150 mbar, and (c) 130 mbar

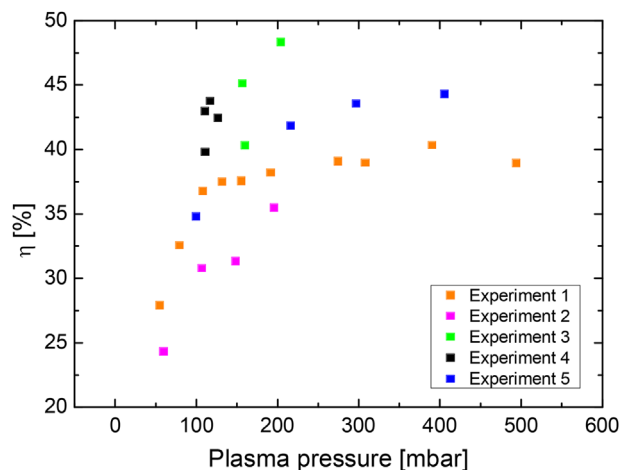
as shown in Figure 3a.  $\eta$  and  $\alpha$  increases and decreases, respectively, if the *SEI* is reduced, as expected from literature.<sup>[2]</sup> To lower the *SEI* range, the CO<sub>2</sub> gas flow rate was increased from 11 to 75 slm. Figure 3b confirms that  $\eta$  increased from 40 to 51%, and  $\alpha$  decreased from 23 to 11%, upon decreasing the *SEI* from 1.9 eV/molecule (MW power 10 kW) to 0.6 eV/molecule (MW power 3.1 kW). A photograph of the plasma obtained at an input gas flow rate of 75 slm and a *SEI* of 0.6 eV/molecule (MW power 3.1 kW) is shown in Figure 2d. Below a MW power of 3.1 kW, the plasma could not be sustained.

Optical emission data of the C<sub>2</sub> ( $d^3\Pi_g, v' \rightarrow a^3\Pi_u, v''$ ) Swan bands are shown in Figure 4. These data were obtained using the plasma configuration shown in Figure 2d. At the moderate pressures used in this work, the C<sub>2</sub> molecules are assumed to be in thermal equilibrium with heavier molecular species in the plasma. Hence, the shape of the Swan bands is determined by the values of  $T_{rot}$  and  $T_{vib}$  of these constituents.<sup>[14]</sup> The value of  $T_{rot}$  is assumed to be equal to the translational gas temperature  $T_g$ . The latter is supported by the good agreement between the simulated data of  $T_{rot}$  and those of  $T_g$  measured previously in our laboratory using Rayleigh scattering on MW plasmas created under conditions similar to those used in the present study.<sup>[4]</sup> The value of  $T_{vib}$  serves as an indicator for the VT non-equilibrium at given  $T_g$ . For the bands  $\Delta\nu = 0$  and  $+1$ , the observed spectra match well with the simulated spectra for  $T_g = 5700$  K and  $T_{vib} = 9000$  K. For the bands with  $\Delta\nu = -1$  and  $-2$ , the simulated spectra depart significantly from the measured ones. A similar departure was

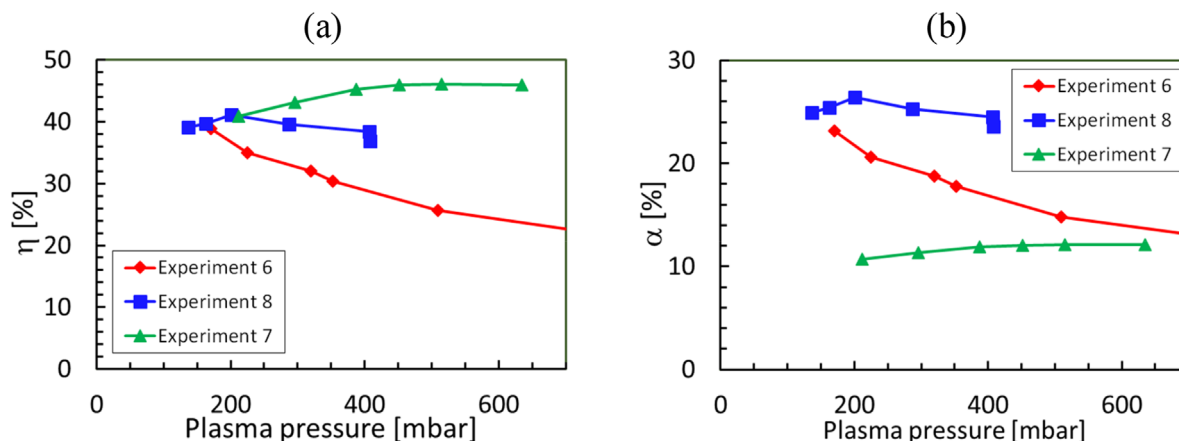
observed in a MW plasma study using CO<sub>2</sub>-Ar mixtures by Spencer and Gallimore.<sup>[15,16]</sup> The discrepancy is attributed to the fact that only a single value of  $T_{vib}$  is used in simulation for the fitting. The clear difference between  $T_g$  and  $T_{vib}$  at  $v' < 4$  points to a significant VT non-equilibrium in the plasma. Whether this holds for the vibrational distribution of all heavy species in the plasma is uncertain. Due to a high VT relaxation rate at  $T_g = 5700$  K thermal dissociation of CO<sub>2</sub> is predominant at this temperature.<sup>[2,4,9]</sup>

## 4.2 | CO<sub>2</sub> dissociation experiments using the 2.45 GHz MW Reactor at DIFFER

Several experiments were performed using different reactor configurations (flow type, field enhancement, and quenching) of the 2.45 GHz plasma source (InitSF) at DIFFER. Experiments and configurations are listed in Table 1. Experiments (1) and (2) were conducted using the reactor in the FV flow configuration,<sup>[17]</sup> with the gas inlet before and the exhaust after the MW cavity, both at full- and half-height waveguide configurations, and at a *SEI* of 0.9 eV/molecule (MW power 1 kW; CO<sub>2</sub> gas flow rate 14 slm), in order to investigate the influence of electric field and residence time on  $\eta$ . Corresponding photographs of the plasmas obtained for both configurations, denoted as A and B in Table 1, are shown in Figure 5a and b, respectively. In Experiment (3), conductive quenching of the outlet gas was applied to prevent backward reactions. Quenching was achieved by



**FIGURE 6** Energy efficiency  $\eta$  as a function of plasma pressure during different tests using the InitSF plasma reactor. Experimental conditions and configurations maintained during these tests are listed in Table 1. Standard errors (95% confidence interval of the mean) are within 3%

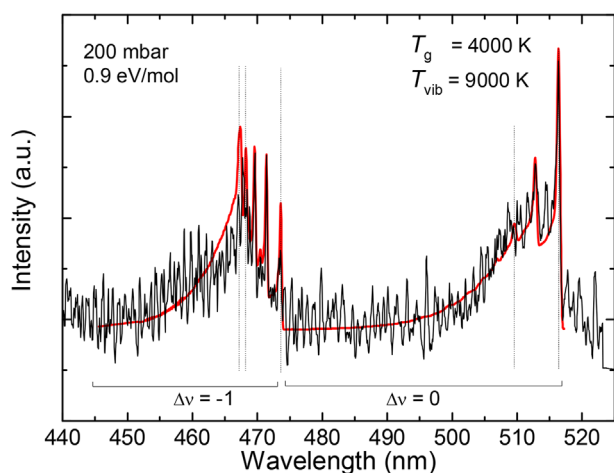


**FIGURE 7** (a) Energy and (b) conversion efficiency as a function of plasma pressure obtained from measurements using the InitSF plasma reactor. Experimental conditions and configurations maintained during these tests are listed in Table 1. Standard errors (95% confidence interval of the mean) are within 3%

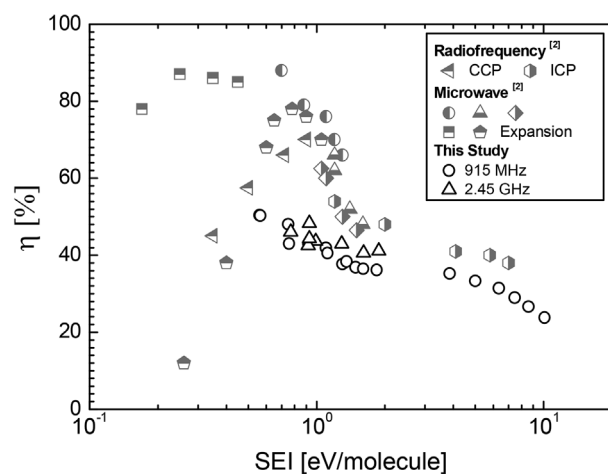
placing a water-cooled brass quencher with a nozzle ( $\sim 5$  mm constriction) in the exhaust of the reactor operated at full-height waveguide. A photograph of the plasma obtained for this configuration, denoted as C in Table 1, is shown in Figure 5c. In Experiment (4), a resonator pin was installed inside the gas inlet system to enable transverse electromagnetic mode coaxial cavity at the gas inlet to increase the field at equal waveguide height. In Experiment (5), the InitSF plasma reactor was operated in the reverse vortex (RV) flow with the bottom exhaust/quencher closed in order to have both gas input (tangential) and output (central) at the top. A copper quenching tube as short as  $\sim 2$  cm was placed inside the coaxial cavity to optimize heat exchange between input and output gas.

Values of  $\eta$  as a function of plasma pressure obtained during different tests recorded at a *SEI* of 0.9 eV/molecule are shown in Figure 6. In the basic FV configuration (Experiment

(1)), that is, without additional quenching,  $\eta$  reaches up to  $\sim 40\%$  at a plasma pressure of 400 mbar.  $E/n$  is in the range 70–80 Td for the reactor in the full-height waveguide configuration, corresponding to an average electron energy  $> 2$  eV.<sup>[18]</sup> According to Fridman,<sup>[2]</sup> a value for  $E/n$  of  $\sim 20$  Td is required to obtain the appropriate electron energy distribution function (EEDF) for exciting the asymmetric vibrational mode of the  $\text{CO}_2$  molecule. As can be seen from Figure 6, the value of  $\eta$  drops upon halving the height of the waveguide (Experiment (2)), that is, upon enhancing the electric field. In Experiment (3), having the reactor in the full-height waveguide configuration and with additional quenching,  $\eta$  increases to a maximum value of  $\sim 47\%$  at a plasma pressure of 200 mbar. However, in this mode of operation the plasma could not be sustained at pressures higher than 200 mbar. In Experiment (4), the electric field within the plasma is enhanced by application of a resonator pin. As can



**FIGURE 8** Measured (black) and simulated (red)  $\text{C}_2(d^3\Pi_g \rightarrow a^3\Pi_u)$  Swan bands. Measured data were obtained at a *SEI* of 0.9 eV/molecule (MW power 1 kW;  $\text{CO}_2$  gas flow rate 14 slm), and at a plasma pressure of 200 mbar. The measured spectrum is baseline-corrected, that is, contributions from broadband continuum radiation were subtracted



**FIGURE 9** Energy efficiency  $\eta$  as a function of *SEI*. Comparison of results from this study with data reported by Fridman.<sup>[2]</sup> Results from Fridman are presented for radiofrequency (3–30 MHz) and microwave (915–2.45 GHz) discharges with and without expansions

be seen from Figure 6,  $\eta$  is found in the range 40–43% at gas pressures  $\sim 100$  mbar. Quenching leads to unstable plasma operation in the FV configuration. Operating the reactor in the RV flow configuration (Experiment (5)), shifts operation again to higher plasma pressures, achieving the highest value of  $\eta = 46\%$  at 500 mbar.

Values of  $\eta$  and  $\alpha$  as a function of plasma pressure from Experiments (6), (7) and (8) listed in Table 1 are plotted in Figure 7a and b, respectively. The main purpose of these tests was to show the effect of flow pattern and *SEI* on both efficiencies with the reactor in FV and RV flow configurations. As seen from Figure 7, both  $\eta$  and  $\alpha$  decrease with increasing plasma pressure when using a FV flow (Experiment (6)). The results further show that at similar value of *SEI* an improved performance is obtained when the reactor is configured to have a RV flow. This might be explained by two factors: firstly, the radial pressure gradient in the RV flow maintains more excited particles within the plasma volume compared to when using a FV flow, and secondly, the output gas in the RV flow configuration is quenched by the input gas.

The optical emission from  $C_2(d^3\Pi_g, \nu' \rightarrow a^3\Pi_u, \nu'')$  Swan bands was measured during Experiment (1) in the core of the plasma. Corresponding data are shown in Figure 8. Simulation of the Swan bands gave  $T_g = 4000$  K and  $T_{vib} = 9000$  K at a *SEI* of 0.9 eV/molecule. The values again point to a significant VT non-equilibrium in the plasma. The high value of  $T_g$  indicates a minor contribution of vibrational excitation to the rate of  $CO_2$  dissociation due to a high VT relaxation rate. The high  $T_g$  gives rise to a relatively high  $E/n$  since the plasma gas density drops with increasing temperature.

## 5 | CONCLUDING REMARKS

The experiments using the plasmolysis setups at IGVP and DIFFER, operating at 915 and 2.45 GHz, respectively, show that for plasma dissociation of  $CO_2$  values of  $\eta$  as high as  $\sim 50\%$  can be achieved. Figure 9 shows a comparison of  $\eta$  as a function of *SEI* from this study with corresponding survey of data reported by Fridman.<sup>[2]</sup> In general, lower values of  $\eta$  are obtained at higher *SEI* values. Clear discrepancies between the results from this study and those reported by Fridman occur below a *SEI* of 1 eV/molecule. Fridman's data are claimed to be characterized by a strong VT non-equilibrium in the plasma.<sup>[2]</sup>

The results from this study are obtained near the maximal thermal equilibrium dissociation limit, which indicates that the thermal dissociation mechanism is predominant. The latter is in agreement with the observations made by optical emission spectroscopy, which indicate that the values of  $T_g$  in the plasmas of both setups under chosen experimental conditions are too high to achieve VT non-equilibrium conditions. Similar observations have been reported previ-

ously.<sup>[4,9,19]</sup> Quenching of the plasma has a beneficial effect on  $\eta$ . In this study, quenching could enhance  $\eta$  to a maximum value of  $\sim 47\%$  at a plasma pressure of 200 mbar. This observation is predicted by Fridman for plasmas in the thermal regime.<sup>[2]</sup>

A number of possible explanations for the observed thermal behavior of plasma dissociation of  $CO_2$  can be given. The observed decrease of  $\eta$  upon enhancing the electrical field as well as the electromagnetic simulations of the cavity electric field distribution in the plasma indicate that values of 70–80 Td for  $E/n$  are too high, where values of 20–50 Td are optimal for high-temperature plasmas.<sup>[2,7]</sup> It should be noted that the value of  $T_g$  has a significant influence on  $E/n$  since the plasma density is inversely proportional to  $T_g$ . High temperatures in the plasmas core may account for the observed high values of  $E/n$ . Furthermore, the VT relaxation rate has a strong dependence on  $T_g$ . Hence, the temperature during discharge should be as low as possible to reduce vibrational energy losses via VT relaxation.<sup>[2,7]</sup> Future experiments will be directed towards reducing  $E/n$ , by increasing the cavity dimensions, and reduction of  $T_g$  by lowering the temperature of the injected gas.<sup>[20–24]</sup>

A known issue with plasma dissociation of  $CO_2$  at high  $\eta$  is that there is an upper limit in the conversion.<sup>[2]</sup> Recently, researchers from the Tokyo Institute of Technology explored a hybrid reactor, integrating a dielectric barrier discharge (DBD) plasma reactor and a solid oxide electrolysis cells (SOEC's).<sup>[25]</sup>  $CO_2$  conversion was significantly enhanced in the hybrid reactor. Complete  $CO_2$  conversion was found at a temperature as low as 600 °C.<sup>[26]</sup> These results were obtained using a simple DBD, which is known to have a low  $\eta$  ( $< 5\%$ ). The value of  $\eta$  of a MW plasma reactor is known to be one order of magnitude higher.<sup>[2,6]</sup> It can be expected that the synergistic integration of high-temperature SOECs into a MW plasma reactor holds promise for dissociation of  $CO_2$ .

## 6 | LIST OF SYMBOLS AND ABBREVIATIONS

$\alpha$	fractional $CO_2$ conversion/conversion efficiency (–)
$\Delta H$	reaction enthalpy or dissociation enthalpy for a $CO_2$ molecule (eV)
$\eta$	energy efficiency (–)
$\eta_{chem}$	chemical factor (–)
$\eta_{ex}$	excitation factor (–)
$\eta_{rel}$	relaxation factor (–)
DBD	dielectric barrier discharge
$E/n$	reduced electrical field (Td)
EEDF	electron energy distribution function
FV	forward vortex
InitSF	Initial solar fuel plasma reactor at DIFFER

MS	mass spectrometer
MW	microwave
OES	optical emission spectroscopy
RV	reverse vortex
SEI	specific energy input (eV/molecule)
SOEC	solid oxide electrolysis cell
TEM	transverse electromagnetic
$T_g$	gas temperature (K)
$T_{rot}$	rotational temperature (K)
$T_{vib}$	vibrational temperature (K)
$\nu$	vibrational quantum number
VT	vibrational-to-translational
WG	waveguide

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## REFERENCES

- [1] C. Graves, S. D. Ebbesen, M. Mogensen, K. S. Lackner, *Renew. Sustain. Energy Rev.* **2011**, *15*, 1.
- [2] A. Fridman, *Plasma Chemistry*, Cambridge University Press, New York **2008**.
- [3] A. P. H. Goede, W. A. Bongers, M. F. Graswinckel, M. Leins, J. Kopecki, A. Schulz, M. Walker, *EPJ Web Conf.* **2014**, *79*, 01005.
- [4] N. den Harder, D. C. M. van den Bekerom, M. F. Graswinckel, J. M. Palomares, F. J. J. Peeters, S. Ponduri, T. Minea, W. A. Bongers, M. C. M. van de Sanden, G. J. van Rooij, *Plasma Process. Polym.* **2016**, this issue.
- [5] L. Chiappetta, M. B. Colket, *J. Heat Transf.* **1984**, *106*, 460.
- [6] V. D. Rusanov, A. Fridman, G. V. Sholin, *Usp. Fiz. Nauk.* **1981**, *134*, 185.
- [7] T. Kozák, A. Bogaerts, *Plasma Sources Sci. Technol.* **2014**, *23*, 045004.
- [8] J. A. Bauer, H. R. Nickerson, A Survey of Vibrational Relaxation Rate Data for Processes Important to CO<sub>2</sub>-N<sub>2</sub>-H<sub>2</sub>O Infrared Plume Radiation, Technical report AFRPL-TR-73-57, Ultra-systems, Inc., Irvine, California, USA **1973**.
- [9] G. J. van Rooij, D. C. M. van den Bekerom, N. den Harder, T. Minea, G. Berden, W. A. Bongers, R. Engeln, M. F. Graswinckel, E. Zoethout, M. C. M. van de Sanden, *Faraday Discuss.* **2015**, *183*, 233.
- [10] M. Leins, L. Alberts, M. Kaiser, M. Walker, A. Schulz, U. Schumacher, U. Stroth, *Plasma Process. Polym.* **2009**, *6*, 227.
- [11] Available at: <http://www.ansys.com/Products/Electronics/ANSYS-HFSS>.
- [12] Available at: <http://www.specair-radiation.net/>.
- [13] R. I. Azizov, A. K. Vakar, V. K. Zhivotov, M. F. Krotov, O. A. Zinov'ev, B. V. Potapkin, V. D. Rusanov, A. A. Rusanov, A. A. Fridman, *Sov. Phys. Dokl.* **1983**, *28*, 567.
- [14] G. Lombardi, B. Benedic, F. Mohasseb, K. Hassouni, A. Gicquel, *Plasma Sources Sci. T.* **2004**, *13*, 375.
- [15] L. Spencer, “The Study of CO<sub>2</sub> Conversion in a Microwave/Catalyst System,” PhD Thesis, University of Michigan, Michigan, USA **2012**.
- [16] L. Spencer, A. D. Gallimore, *Plasma Chem. Plasma P.* **2011**, *31.1*, 79.
- [17] Yu. P. Butylkin, V. K. Givotov, E. G. Krashennnikov, V. D. Rusanov, A. Fridman, *Sov. Phys. J. Tech. Phys.* **1981**, *51*, 925.
- [18] A. Fridman, L. A. Kennedy, *Plasma Physics and Engineering*, Taylor & Francis, New York, London **2004**.
- [19] A. Essiptchouk, High pressure plasma reactor for thermal dissociation of carbon dioxide, *ESCAMPIG XX* **2012**.
- [20] T. Verreycken, P.M.J. Koelman, D.C.M. van den Bekerom, J.M. Palomares-Linares, S. Ponduri, J. van Dijk, G.J. van Rooij, M.C.M. van de Sanden, W.A. Bongers, Investigation of the effect of on- and off time on the dissociation of CO<sub>2</sub> in a pulsed microwave discharge, submitted to *EPJ AP*, 15th High pressure low temperature plasma chemistry symposium, September 11–16, Brno, Czech Republic **2016**.
- [21] N. A. Zyrichev, S. M. Kulish, V. D. Rusanov, *CO<sub>2</sub> Dissociation in Supersonic Plasma-Chemical Reactor*, Kurchatov Institute of Atomic Energy, Moscow **1984**, vol. 4045, p. 6.
- [22] A. K. Vakar, V. K. Givotov, E. G. Krashennnikov, A. Fridman, *Sov. Phys. J. Techn. Phys. Lett.* **1981**, *7*, 996.
- [23] T. Nunnally, K. Gutsol, A. Rabinovich, A. Fridman, A. Gutsol, A. Kemoun, *J. Phys. D: Appl. Phys.* **2011**, *44*, 274009.
- [24] V. K. Givotov, E. G. Krashennnikov, M. F. Krotov, V. D. Rusanov, A. Fridman, *3rd World Hydrogen Energy Conference, Tokyo* **1980**, 92.
- [25] Y. Tagawa, et al., *Kagaku Kogak Ronbunshu* **2011**, *37*, 114.
- [26] L. L. Tun, N. Matsuura, S. Mori, *22nd International Symposium on Plasma Chemistry*, **2015**, O-15-3.