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Plasma reforming for oxygen production on Mars

Polina Ogloblina⋆†, *Vasco Guerra*† *Ana Sofia Morillo Candas*‡, *Olivier Guaitella*‡
†*Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal*
‡*LPP, CNRS, Ecole Polytechnique, Université Paris Sud-11, Palaiseau, France*
polina.ogloblina@tecnico.ulisboa.pt · vguerra@tecnico.ulisboa.pt
ana-sofia.morillo-candas@lpp.polytechnique.fr · olivier.guaitella@lpp.polytechnique.fr
⋆Corresponding author

Abstract

In this work we undertake an experimental investigation of plasmas in DC glow discharge, in CO_2/Ar/N_2 mixture, for pressures in range 1-6 Torr and currents from 10 to 50 mA, with gas at room and Mars-like temperatures. The vibrational temperatures, the conversion factor and the reduced electric field are measured. The study shows that Martian conditions can effectively pump the asymmetric stretching vibration mode and achieve a stronger non-equilibrium, believed to have a positive influence in dissociation. The results establish experimental evidence of the feasibility of plasma conversion of CO_2 from the Martian atmosphere.

1. Introduction

Mars exploration draws more and more attention nowadays, with new plans from space agencies and private companies announced frequently. With the high speed of the technologies being developed it is likely that in the next couple of decades we will witness people landing on Mars. One of the ways to secure a safe return is to use resources in-situ to produce needed products instead of bringing them from Earth. The red planet has resources that can be used to build a sustainable settlement. In particular, the local production of oxygen on Mars will help solving the problems of manufacturing fuel for coming back on Earth and of creating a breathable environment for a future outpost. In fact, the main component of the Martian atmosphere is carbon dioxide (95.9%), with smaller percentages of Ar (1.9%), N_2 (1.9%) and other gases. CO_2 can be converted into oxygen (O_2) and carbon monoxide (CO). In this *In Situ Resource Utilisation* (ISRU), O_2 can then be collected and made available for breathing, while both CO and O_2 can be used in a propellant mixture in rocket vehicles.[4]

Gaseous CO_2 can be converted into O_2 and CO using different methods. It is believed that plasma-based processes can provide the most efficient way to do so.[1,8] Even though CO_2 reforming is a widely discussed topic and a vast research is devoted to it in terms of reduction of greenhouse emission, production of solar fuels and chemical materials on Earth, very few studies are available regarding the conditions in the Martian atmosphere. In a recent study, the idea of oxygen plasma production on Mars directly from its atmosphere was proposed.[2,3] In particular, it was advocated that the cold Martian atmosphere may enhance vibration-vibration (V-V) up-pumping and hinder vibration-translation (V-T) deactivation, thus leading to a higher degree of non-equilibrium, and that the pressure on Mars (∼4.5 Torr) is very suitable for plasma operation. Furthermore, small additions of the trace gases Ar and N_2 act as energy savers and can only increase efficiency. O_2 can then be collected and made available for breathing, while both CO and O_2 can be used in a propellant mixture in rocket vehicles.

The CO_2 molecule is not easy to brake. It has 3 vibrational modes - symmetric stretch, bending and asymmetric stretch. The latter is believed to have an important role in the dissociation process, since most of the energy absorbed by electrons is transmitted to the excitation of the vibrational levels of the CO_2 asymmetric mode, which could be up-pumped in V-V energy exchanges along this vibration mode.[1] However, other V-V and V-T processes can depopulate the higher vibrational levels of the asymmetric mode and populate other modes of CO_2 or the internal modes of other species. One of the ways to prevent the loss of CO_2 asymmetric vibration and the quenching process of back reaction is by fast adiabatic cooling, when the composition achieved at higher temperature remains initially the same after quenching.

Recent simulations show very promising results,[2,3] but no experimental confirmation was attempted to date. The aim of this work is to experimentally demonstrate the relevance of plasma vibrational up-pumping of the CO_2 molecule and the contribution of Ar and N_2 in Mars' atmosphere conditions as compared with Earth. To achieve this goal this we

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experimentally investigate the influence of the gas temperature and atmospheric composition on the vibrational kinetics of CO_2 molecule, the conversion factor and the reduced electric field, in simple continuous DC glow discharge.

2. Methods

In situ Fourier transform infrared (FTIR) spectroscopy is used in order to detect and accurately determine the vibrational state densities in the plasma. The plasma reactor under study is a cylindrically shaped Pyrex tube, with a 2 cm inner diameter and a length of 23 cm. The electrodes are positioned 17 cm apart, opposite to the gas in- and outlet. This configuration ensures that IR absorption measurements (line-of sight-integrated) are taken only through the positive column of the glow discharge. The reactor is connected in series with a 40 kΩ resistor to a DC power supply.

There were two gas composition tested - pure CO_2 gas and the mixture of CO_2 with 2% of Ar and 2% of N_2. In order to control the power deposited per molecule, the residence time of the gas inside the plasma volume should be the same for all conditions. Thus, the total gas flow is controlled at 19.25 sccm using a mass flow controller (Bronkhorst). The pressure is varied between 1 and 6 Torr, using a scroll pump (Edwards), and a pressure gauge (Pfeiffer) with feedback to an automated pressure regulating valve (Pfeiffer).

The reactor is positioned in the sample compartment of a FTIR spectrometer (V70 Bruker). The absorption spectrum is corrected and the emission spectrum is subtracted.[5] The detected IR spectrum contains several lines of CO and CO_2 vibrational transitions and was fitted according the procedure described by Klarenaar *et al*.[5] Only insignificant amounts of O_3 were detected in the spectra.

For simulation of Mars-like temperature conditions the reactor was immersed into a mixture of dry ice and ethanol. The mixture temperature was controlled with a temperature probe (Mouser). The probe was calibrated in the cooling thermostat (Huber Ministat 230) with controlled temperature from 243 to 303 K. The calibration curve was approximated for lower temperatures up to 200 K. For comparison with Earth atmosphere temperatures, the same conditions were tested for the reactor without the surrounding of dry ice and ethanol.

The rotational temperature of CO_2 (T_{rot}) was obtained by fitting the FTIR absorption spectra.[5] It is assumed that the rotational and vibrational temperatures are uniform along the length of the reactor and reach a steady state on relatively short distances from the entrance of the reactor. The temperature of the gas before experiencing the plasma was controlled by the FTIR measurements and by the temperature probe and was approximately 220 - 230 K. Both techniques agree within a 5% error for "plasma off“ gas temperature measurements. As the temperature probe sensor is a an intrusive diagnostics, it was not used for the "plasma on“ measurements and only results of the FTIR absorption spectra fitting were considered.

The reduced electric field in the reactor is measured with two metal pins radially pointing inside the positive column of the reactor. The radial gradient of the electric field was not taken into account.

3. Results and discussion

The axial electric field was obtained from the voltage drop across the positive column of the glow discharge between the two tungsten probes. The measured values and the corresponding reduced electric field versus pressure are shown in figure 1. For both temperature conditions the reduced electric field decreases with pressure and at a given pressure the reduced field increases with current due to gas heating. Measurements performed at Mars temperature exhibit similar trends, with 5 - 10 Td smaller reduced field values due to the increased gas density at a lower gas temperatures. Addition of Ar and N_2 increases the reduced electric field for the same operating conditions as compared with the pure CO_2 case.

Dissociation or the conversion factor of CO_2, *alpha*, is determined from the measurement of the CO and CO_2 densities with following formula:

$$\alpha = \frac{[CO]}{[CO] + [CO_2]}, \tag{1}$$

where [CO_2] and [CO] are the molecular concentrations of CO_2 and CO, respectively. Figure 2 shows the results of the conversion factor versus pressure, measured for different currents, for temperatures close to Mars and Earth atmospheric conditions. For a given current the conversion factor is slightly increasing with pressure, while for given pressure a higher electric current gives higher dissociation. The slightly lower dissociation for Mars-type of discharge in figure 2.(a) is perfectly correlated with the lower reduced electric field shown on figure 1. Addition of argon and nitrogen increases the reduced field and, as a consequence, the dissociation of CO_2 molecule by direct electron impact.

At the conditions investigated, the Martian conditions lead to an interesting dissociation of CO_2, but do not lead to a significantly higher production of CO and oxygen. This is related to the discharge type used in this study, which corresponds to a low excitation regime,[7] where the vibrational up-pumping processes do not play significant role in

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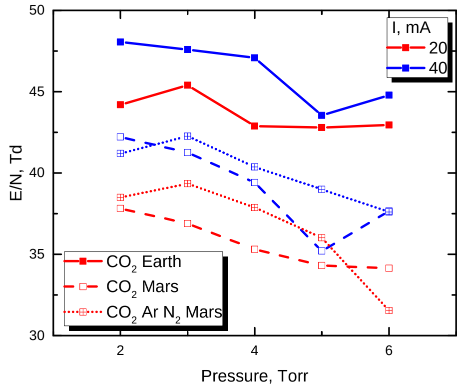

Figure 1: Measured variation of the reduced electric field as a function of the pressure at discharge currents 20 and 40 mA as a function of pressure for Earth-like temperature in pure CO_2 and Mars-like temperature in pure CO_2 and in mixture with argon and nitrogen.

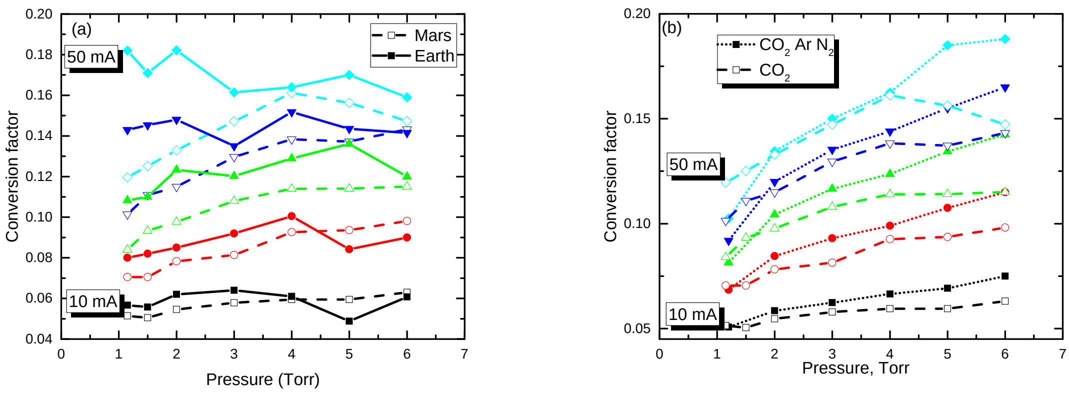

Figure 2: Measured conversion factor as function of pressure for different discharge currents, (—) 10 mA, (—) 20 mA, (—) 30 mA, (—) 40 mA, and (—) 50 mA: (a) for pure CO_2 plasmas at Martian and Terrestrial temperature conditions; and (b) for pure CO_2 and CO_2/Ar/N_2 mixture at Martian temperature.

dissociation. Although vibrational dissociation is most likely not efficient in the present conditions, these DC discharge systems are perfect to trace the power input into the vibrational modes as a result of the electron kinetics. Thus, vibrational temperatures can be a relevant measure of the initial redistribution of energy on the first vibrational levels. Figure 3 shows the results of the measurements of the gas temperature (T_g), the common characteristic temperature of the symmetric stgretching and bending modes (T_{12}, and of the characteristic vibrational temperature of the asymmetric stretching mode (T_3), where the ratios T_3/T_g and T_{12}/T_g are obtained in continuous DC discharges as a function of pressure for 20 and 40 mA discharge current, when the gas temperature is initially 300 K (Earth) and 220 K (Mars).

It can be immediately verified that a discharge on Martian atmospheric conditions is very suitable to induce vibrational non-equilibrium, with a larger difference between T_3 and both T_g and T_2 as it was recently predicted theoretically.[3] At lower pressures the degree of non-equilibrium is significantly higher, due to the lower gas density and the slower thermalisation between the asymmetric mode and the gas temperatures. At the average Mars pressure, the T_3/T_g ratio on Mars is 1.3 and 1.2 times higher that on Earth, for discharge currents of 20 and 40 mA, respectively.

4. Conclusions

It was shown that the lower gas temperature on Mars (~220 K) induces a stronger vibrational up-pumping than what can be achieved on Earth. Traces of Ar and N_2 help conversion by increasing the reduced electric field. The average atmospheric pressure on Mars, of about 4.5 torr, is on the good range for plasma reforming, allowing the operation of a

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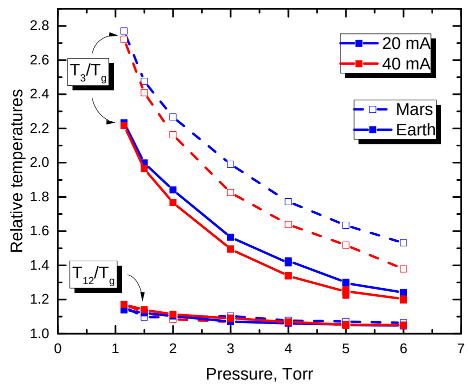

Figure 3: Relative temperatures measured as a function of a pressure at discharge current 20 and 40 mA at Mars and Earth temperature conditions.

discharge without the need to use vacuum pumps or compressors to tune the discharge pressure, simplifying the design and operation of a plasma oxygen production system.

The present investigation does not give a high CO_2 conversion or energy efficiency, but demonstrates the possibility of implementing plasma technologies for oxygen production from the Martian atmosphere. Plasma technologies for CO_2 reforming on Earth are already competitive nowadays with solid oxide electroliser cells (SOEC). Therefore, our investigation evinces that a non-equilibrium plasma process can probably perform better than SOEC for O_2 production on Mars, the technology proposed by the exciting MOXIE programme.[6] Together with the numerical simulations previously performed,[3] this work gives a firm step of fundamental investigation towards bilding plasma assisted CO_2 conversion on Mars.

5. Acknowledgments

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