LIVING ON MARS:

HOW TO PRODUCE OXYGEN AND FUEL TO GET HOME

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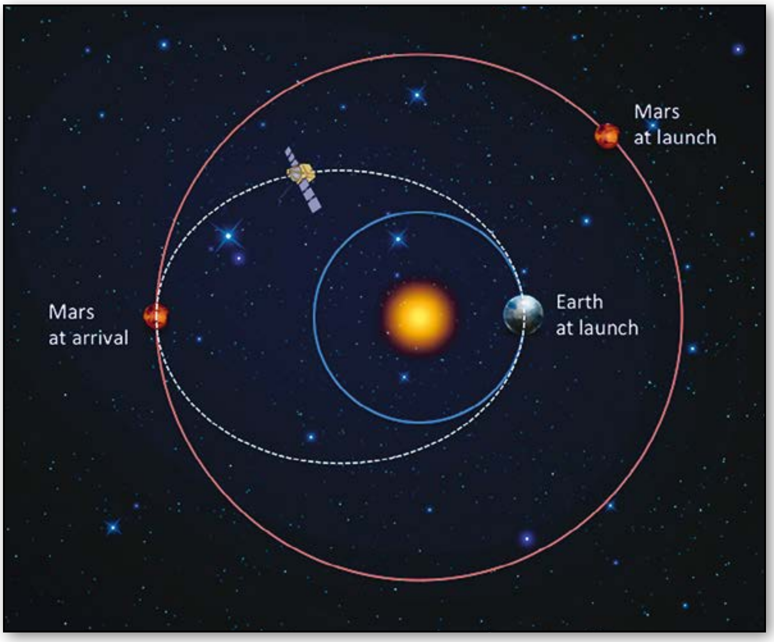
Sending a manned mission to Mars is one of the next major steps in space exploration. Creating a breathable environment, however, is a substantial challenge. A sustainable oxygen supply on the red planet can be achieved by converting carbon dioxide directly from the Martian atmosphere. A new solution to do so is on the way: plasma technology.

Space exploration is on the verge of an exciting new era, with Mars on the agenda. Ambitious programmes on Mars exploration, Mars Sample Return (MSR) missions and the prospect of future manned missions have been recently presented by the main space agencies – ESA (European Space Agency), NASA (National Aeronautics and Space Administration), Roscosmos (Roscosmos State Corporation for Space Activities, Russian Federation) and JAXA (Japan Aerospace Exploration Agency) – often in partnership with private companies.

Travelling to Mars is an extraordinary endeavour. The distance between Earth and Mars varies between 55 and 400 millions of kms, depending on the position of the planets on their orbits. The correct conjugation of trajectories implies that there is an optimal window for launching approximately every two years, corresponding to a launch along the Hohmann transfer orbit represented in figure 1, for a trip of around six months, and that in a manned mission astronauts would have to stay on Mars for about one year. Clearly, any local resources that can be used will reduce the logistics and costs of the mission, increase self-sufficiency and reduce risks to the crew. Hence the interest devoted nowadays to *in-situ resource utilisation* (ISRU), the harnessing of resources in the exploration site that would have to be brought from Earth otherwise.

The main component of the Martian atmosphere is CO_2, accounting for about 96% (with approximately 2% Ar and 2% N_2). This is the resource of interest here. Indeed, carbon dioxide can be used as a raw material to locally produce oxygen, which can be collected and made available for breathing. The process relies on the decomposition of carbon dioxide

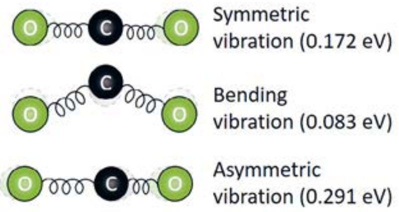


▲ **FIG. 1:** Spacecraft trajectory along the Hohmann transfer orbit, the trajectory that uses the least energy. Launch windows are periodic according to the synodic period, 780 days in the case of Mars.

into carbon monoxide and oxygen and would constitute a major breakthrough towards the establishment of an outpost on the red planet. The decomposition procedure comes with a bonus: not only would it provide a stable, reliable supply of oxygen, but a source of fuel as well, as carbon monoxide and oxygen have been proposed as to be used in a propellant mixture in rocket vehicles. In the long run the decomposition can even be sought to go all the way down to carbon, that can be used as a building block for different carbon structures and organic molecules.

A major challenge is that CO_2 is a very stable molecule, hence very hard to decompose. In other words, CO_2 dissociation is a strongly endothermic process, requiring the supply of a considerable amount of energy, at least 5.5 eV. Current technology for CO_2 dissociation on Earth is based on Solid Oxygen Electrolysis Cells (SOEC), which has the advantage of being a very robust technology. However, it has very low energy efficiency and often uses scarce and expensive rare-earth metals. Moreover, it operates at high pressure and high temperature, which will further decrease its efficiency in Martian conditions. Despite these drawbacks, NASA's exciting MOXIE programme for oxygen production on Mars is an electrolysis experiment based on SOEC, to be included in its Mars 2020 mission [1]. Biological solutions, based in algae or bacteria, seem to remain purely speculative to date. A radically different and new approach to the question, proposed very recently, would be to use low-temperature plasmas [2].

▸ **FIG. 2:** Vibration modes of the CO_2 molecule.



Why plasma?

Low-temperature plasmas or non-equilibrium plasmas are ionized gases where only a fraction of the gas is ionised. The different particles – electrons, positive ions, neutrals and photons – have very different properties and energies.

Electrons are light and are easily accelerated by applied electric fields. They become very energetic and create different chemically reactive species, while keeping the background gas temperature low enough to limit the losses into gas heating. Low-temperature plasmas are thus formidable convertors of electrical energy into chemical energy.

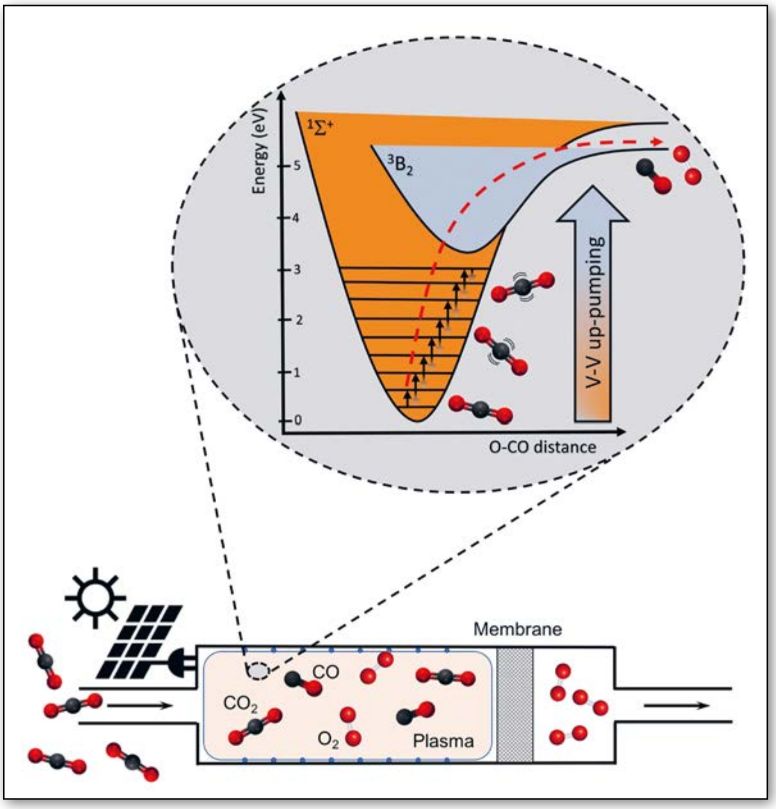
The required power for discharge operation is typically ~100 W but can be as low as ~25 W, depending on the operating conditions. These power requirements are perfectly feasible on Mars. For instance, the Mars Exploration Rover solar arrays generate, when fully illuminated, about 140 W of power for up to four hours per sol (a Martian day, 24h40'). Another merit of the plasma technology is the possibility of instant start and stop of operation, perfectly adapted to the cycles of supply of power to an ISRU unit on Mars.

The technology can take advantage of the non-equilibrium nature and energy efficiency of low-temperature plasmas and use optimal conditions to selectively use the electron energy to drive the chemistry towards the desired products, O_2 and CO. High energetic electrons can break the CO_2 molecule upon direct impact. It is a good step, but it might be not good enough. On the one hand, the process goes via the excitation of electronic states with energies of 7 eV or more, well above the dissociation energy of CO_2; on the other hand, only a small fraction of the electrons has enough energy to decompose the molecule. To make it unbeatable there is one magic ingredient missing: "making the molecules sing."

The song of the molecules

In a molecule like CO_2 the bonds between the carbon and the oxygen atoms can be bent or elongated and, as such, the molecule starts vibrating (see figure 2). These vibrations store energy. A plasma created on Martian conditions can easily produce electrons that transfer more than 90% of their energy into vibrational excitation of the CO_2 molecules. This feature, which could be thought as a drawback at first sight, since the energy is not being used to decompose CO_2, turns out to be a major asset. First, to put the molecules to vibrate requires about 10 times less energy than to directly dissociate the molecule by electron impact. Second, it is possible to favour energy transfers between vibrating molecules along the asymmetric stretching mode, in such a way that some of them gradually increase their amplitude of vibration. It is not the same phenomenon as breaking a crystal glass by singing, but this simplistic image is good enough for a first impression: if the molecules are vibrating significantly, they become easier to break!

The "song of the molecules" is known as the *vibration-vibration* (V-V) *up-pumping* mechanism [3]. When two vibrating molecules with about the same vibrational excitation collide, there is a relatively high chance that they will exchange vibrational quanta, since this is a nearly resonant mechanism. The word "nearly" is essential. The energy spacing between two consecutive vibration levels decreases as we move up on the vibrational ladder. Thus, the exothermic sense of the exchange of quanta is the one where the molecule with a higher degree of vibrational excitation becomes even more excited, increasing further its amplitude of vibration, at the expense of the vibration of the less excited molecule. Vibrational quanta are "up-pumped" and several molecules may reach large vibration amplitudes and participate in dissociation. A schematic representation outlining how the low-temperature plasma / V-V up-pumping mechanism results in O_2 is given in figure 3.



▲ **FIG. 3:** Schematic representation of the O_2 production mechanism.

Mars: the perfect environment for plasma!

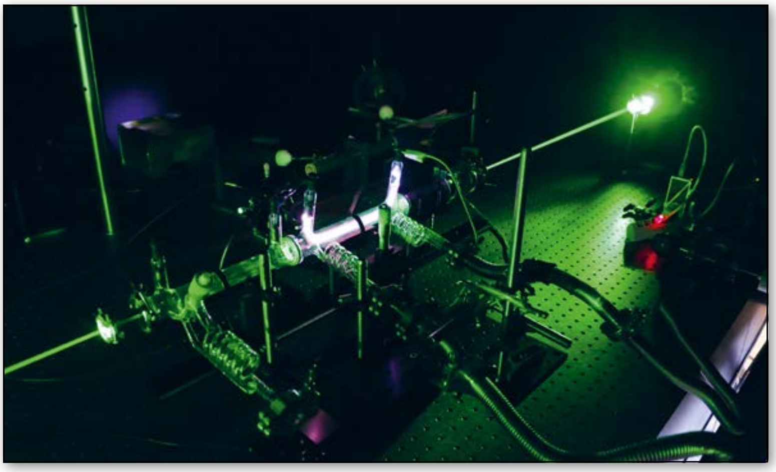
The general ideas to use plasmas to decompose CO_2 are being pursued on Earth, prompted by the problems of climate change and production of solar fuels. An overview of this research effort is available as a 2016 *Feature* at Europhysics News [4]. The challenge here is to understand if and how the results on Earth can somehow be adapted to Mars. The interesting discovery recently reported in [2] is precisely that Mars has excellent conditions for In-Situ Resource Utilisation (ISRU) by plasma. In fact, one can take advantage of the conditions on Mars, to the point that it almost looks like Mars has been designed for it.

The atmosphere is mainly CO_2, so there is no need to capture it and plasma can be ignited in ambient Martian atmosphere. The traces of Ar and N2 present can only help: argon aids shaping the electron energy distribution to higher energies, contributing to an increased efficiency of the process [5]; nitrogen favours the transfer of energy into the vibration of the asymmetric stretching mode of carbon dioxide, as in a CO_2 laser [6], further promoting the V-V up-pumping.

The pressure on Mars – of 600 Pa (4.5 Torr), about 150 times lower than on Earth – is close to the ideal for advantageous plasma operation, so there is no need to use vacuum pumps or compressors on the first steps of the process. A too high pressure means the electrons collide too often and, accordingly, are difficult to accelerate to the required energies. In turn, at too low pressure electrons are easily accelerated but collisions are rare, so that the transfer of energy to the heavy-particles is ineffective.

Finally, the low temperature of the Martian atmosphere – ranging from -150 °C to 20 °C, with an average value of -60 °C – slows down the back reactions (that would convert CO and O back to CO_2), giving more time for product separation. And, very important, the low-temperature also promotes the V-V up-pumping mechanism, both by favouring the exchange of vibrational quanta (V-V) due to an enhanced role of long-range attractive forces and by limiting the losses of vibrational energy to gas heating as a result of collisional deactivation.

The new results were obtained by simulations made at the N-PRIME team of IPFN (Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Portugal) [2,7] and are supported by experiments made at LPP (Laboratoire de Physique des Plasmas, Ecole Polytechnique, Palaiseau, France) and TU/e (Technische Universiteit Eindhoven, The Netherlands) in pulsed DC plasmas [8]. This early research focuses on the characterization and control of the degree of vibrational excitation, crucial to achieve an efficient plasma decomposition of CO_2. Figure 4 shows the experimental apparatus at LPP, while figure 5 depicts two critical parameters, calculated for conditions on Mars and on Earth: the ratios T_3/T_g and

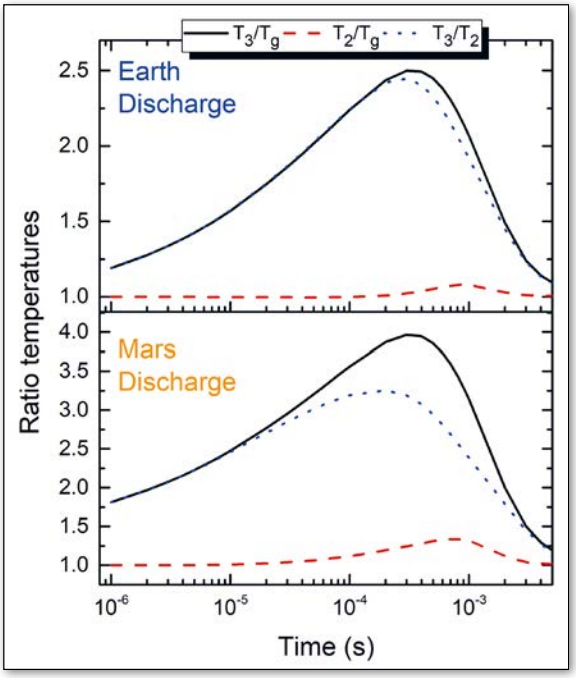


▼ **FIG. 4:** CO_2 plasma created by DC discharge at LPP, for a pressure of 600 Pa and a discharge current of 50 mA (© guaitella 2017).

T_3/T_2, where T_3 is the characteristic temperature of the asymmetric stretching mode, T_2 is the characteristic temperature of the bending mode (typically very similar to the characteristic temperature of the symmetric stretching mode) and T_g is the gas temperature [2]. These ratios characterize the degree of non-equilibrium of the plasma [9]. The higher they are, the larger amount of energy is stored in the vibrational mode leading to decomposition of CO_2. Figure 5 hence confirms the advantageous conditions of the Martian atmosphere to ISRU by plasma.

The emerging plasma technology is therefore very promising. Its efficiency on Mars will increase compared to that on Earth, as demonstrated in the foundational work [2]. On the contrary, the efficiency of solid oxide electrolysis is likely to decrease, because extra energy is necessary to heat the gas up to 1100 K and to compress it up to 1 atm. Current studies indicate that MOXIE's target of about 10 g per hour for a power of ~300 W [1] is perfectly within the reach of an optimized plasma device. A subsequent upscale may reach a production equivalent to the on-board oxygen consumption of the International Space Station (ISS), presently in the range of 2-5 Kg/day. The use of plasma activated catalysts and membranes for product separation will further enhance the efficiency of the plasma process, positioning plasmas as a viable and very interesting alternative to SOEC for oxygen production on Mars on the long run.

The installation of an In-Situ Resource Utilization (ISRU) technology on the red planet will provide a continuous production of consumable oxygen and propellants from the Martian atmosphere. A giant leap for mankind and a significant contribution towards the viability of manned missions to Mars and to the sustainability of a future colony. ■



▸ **FIG. 5:** Time evolution of the ratio of different characteristic temperatures on a DC pulsed discharge at pressure p=5 Torr, discharge current I=50 mA, pulse length Δt=5 ms, for conditions on Earth and on Mars. The higher values of T_3/T_2 and T_3/T_g on Martian conditions confirm the interest of the plasma technology. Adapted from [2].

About the Authors

Vasco Guerra is Associate Professor with the Physics Department at IST and researcher at IPFN. He received the PhD in Physics from IST in 1998. His research focuses on the modeling of non-equilibrium kinetics of low-temperature molecular plasmas. In 2016 he was awarded the EPS/PSST William Crookes Prize.

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Olivier Guaitella is a researcher at the plasma physics laboratory of the Ecole Polytechnique in France, where he also obtained his PhD in physics in 2006. His experimental work is mainly devoted to plasma/surface interaction and has applications in fields as varied as indoor air treatment, CO_2 recycling or biomedical applications.

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