Oxygen and propellant production on Mars

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LPP

Travelling to Mars

Mars exploration

- NASA Mars 2020 Preserverance rover - prepare future human expeditions
- ESA ExoMars - study Martian atmospheric conditions
- SpaceX - first landing 2022

Challenging endeavor: *in situ* resource utilization (ISRU)

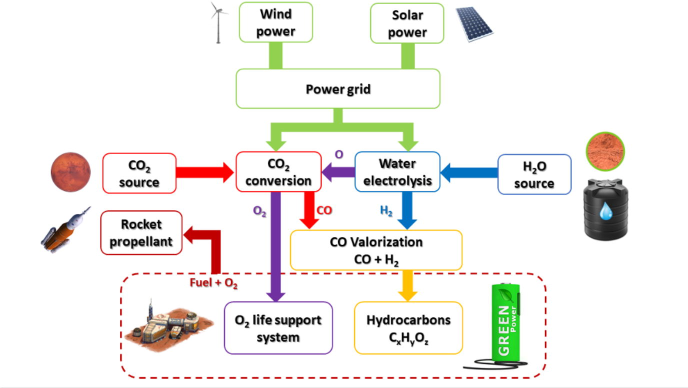
- Create a breathable environment (O_2)
- Production of propellants ($CO+O_2$)

Taking advantage of Martian conditions

- Atmosphere: $CO_2/N_2/Ar$
- Decompose CO_2
- Plasmas

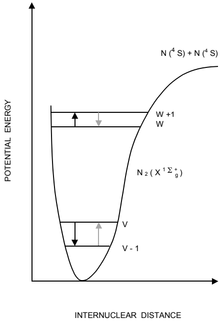
Power-to-liquid scheme for ISRU on Mars

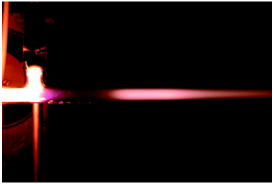
- CO_2 neutral fuels on Earth
- Critical steps: decomposing CO_2 & separation

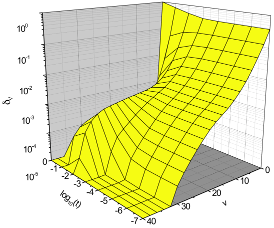


Thanks to Gonçalo Raposo (MSc thesis, January 2021)

- It has been claimed that CO_2 dissociation can be strongly enhanced "using" vibrational excitation
- V-V up-pumping: nitrogen pink afterglow



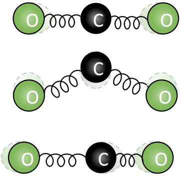




[P. A. Sá *et al* *J. Phys. D: Appl. Phys.* **37** (2004) 221-231]

The CO_2 molecule: vibration modes

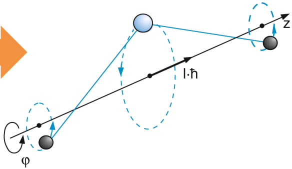
Three vibrational modes: $CO_2(\nu_1, \nu_2^l, \nu_3)$



Symmetric vibration (0.172 eV)

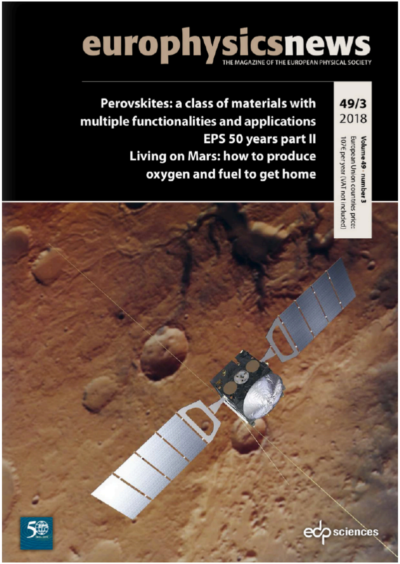
Bending vibration (0.083 eV)

Asymmetric vibration (0.291 eV)



- Electron impact (e-V) mechanisms
$$e + CO_2(v) \rightleftharpoons e + CO_2(v')$$
- Vibration-to-Translation (V-T) energy exchanges
$$CO_2(v) + CO_2 \rightleftharpoons CO_2(v') + CO_2$$
- Vibration-to-Vibration (V-V) energy exchanges
$$CO_2(v) + CO_2(w) \rightleftharpoons CO_2(v') + CO_2(w')$$

ISRU on Mars



Mars has excellent conditions for *In Situ Resource Utilisation* by plasma!

- $\sim$ 96% CO_2 atmosphere
- Traces of N_2 and Ar
- Lower pressures
- Lower temperatures

[V. Guerra *et al*, *PSST* **26** (2017) 11LT01]

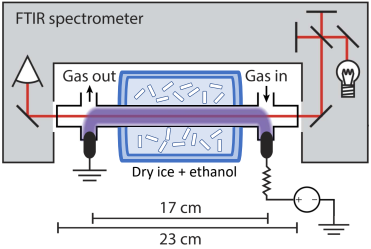
[V. Guerra *et al*, *EPN* **49** (2018) 15-18]

Aim of this work:

- prove these ideas!
- joint experimental / modelling investigation

[P Ogloblina *et al* *PSST* **30** (2021) 065005]

DC discharge
$I = 10 - 50$ mA
$p = 1 - 5$ Torr
Mixture of ethanol and dry ice ~ 200 K
Temperature of the gas $\sim 220 - 230$ K



Fourier Transform Infra Red spectroscopy

Self-consistent model for CO_2 plasmas

The LoKI (LisbOn KInetics) code:

- Electron kinetics in the $CO_2/CO/O_2/O$ mixture

  [M. Grofulović *et al*, *J. Phys. D: Appl. Phys.* **49** (2016) 395207]

  [P. Ogloblina *et al*, *Plasma Sources Sci. Technol.* **29** (2020) 015002]
- Vibrational kinetics

  e-V, V-T, V-V processes ($\sim$ 70 individual vibration levels)

  [T. Silva *et al*, *Plasma Sources Sci. Technol.* **27** (2018) 015019]
- Chemical kinetics

  CO_2, $CO(X, a)$, $O_2(X, a, b)$, $O(^3P, ^1D)$, O_3, O_3^*, C, C_2O

  ${CO_2}^+$,CO^+, ${O_2}^+$, O^+, O^-

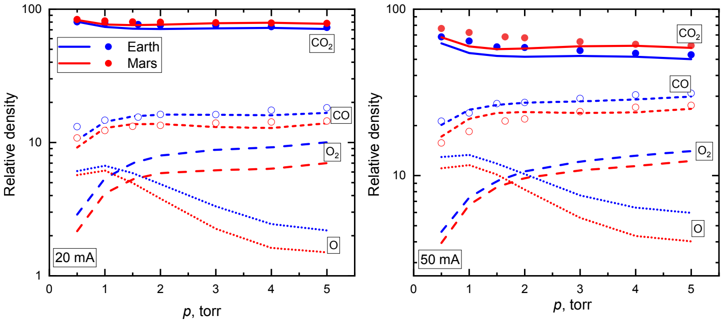
  [A. Annušová *et al*, *Plasma Sources Sci. Technol.* **27** (2018) 045006]

  [A. Silva *et al*, *Plasma Sources Sci. Technol.* **29** (2021) 125020]
- Electron and ion transport + q.n. (self-consistent E/N)

  [V. Guerra and J. Loureiro, *Plasma Sources Sci. Technol.* **8** (1999) 110]

  [P. Coche *et al*, *J. Phys. D: Appl. Phys.* **49** (2016) 235207]

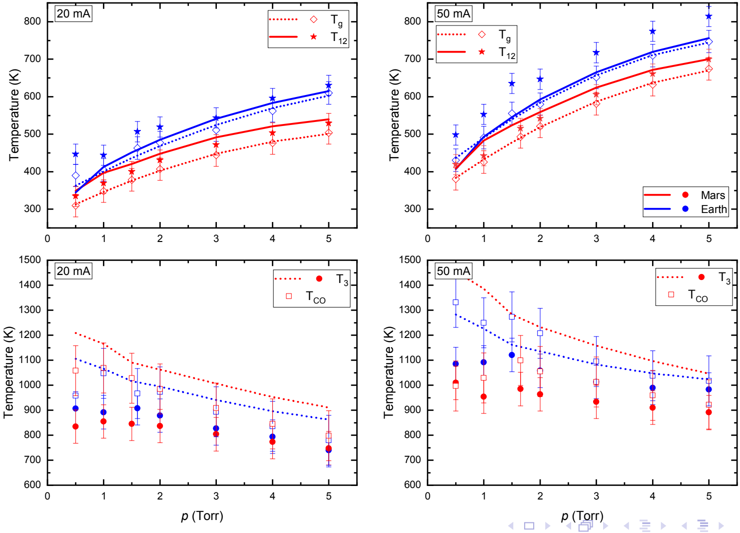
CO_2 decomposition: Earth *vs.* Mars



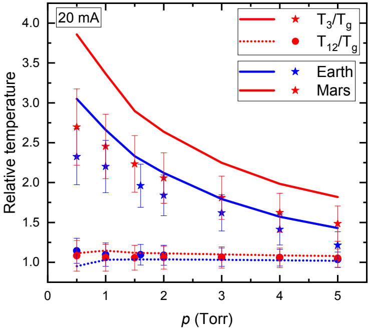
(○, •) experiment (—) simulation

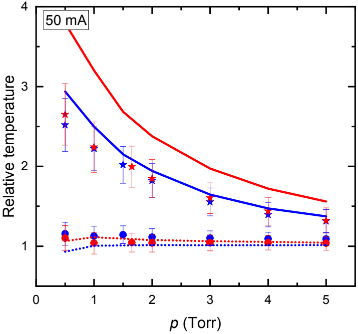
Electron impact dissociation from (00^00), (01^10), (02^20) and $(10^00 + 02^00)$

Vibrational temperatures

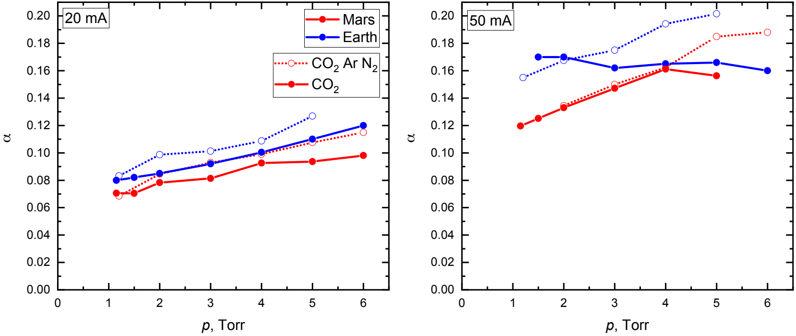


Relative temperatures





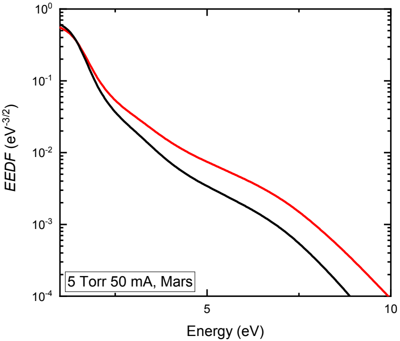
Martian atmosphere (room temperature)



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

(—) pure CO_2 (···) CO_2:Ar:N_2 96:2:2

Influence of trace gases



(—) pure CO_2 (—) CO_2:Ar:N_2 96:2:2

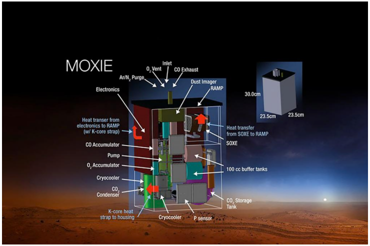
Plasmolysis *vs* electrolysis

MOXIE: Mars OXygen In situ resource utilization Experiment

- 5.5g of O_2 per hour for $P = 300$ W
- 17 kg ; $24 \times 24 \times 31$ cm
- High temperature and high pressure

+ Robust and ready technology
− Very low energy efficiency of $\sim 15\%$
− Scarce and expensive rare-earth metals

- 0.32 g O_2 per hour per kg



Plasma technologies

- Recently achieved energy efficiencies of $\sim 50\%$ for CO_2 decomposition [G. van Rooij *et al*, *Faraday Discuss.* **183** (2015) 233]
- 14g of O_2 per hour for $P = 250$ W
- 5 kg ; $25 \times 20 \times 5$ cm

+ Scalability and adequate for intermittent operation
− Product separation is still challenging

- 3.5 g O_2 per hour per kg

Conclusions

- Confirmed that Mars has excellent conditions for ISRU by plasmas. . .

  . . . favouring both non-equilibrium *and* electron impact dissociation
- CO_2 dissociation and vibrational temperatures measured for the first time in Martian conditions
- Dissociation fractions up to 30% were observed
- Positive effect of the atmospheric composition
- The plasma chemistry is strongly influenced by the kinetics of *electronically* excited states [$O_2(a)$, $O_2(b)$, $O(^1D)$, $CO(a)$]
- Knowledge on Earth can be transposed to Mars
- Light and compact reactor, competitive with SOEC

Next steps

- MIT-Portugal project IMPACT
  - Carmen Guerra-Garcia (PI)
  - Benjamin Martell
  - Ahmed Ghoniem
  - Jeffrey Hoffman
  - Tiago Silva
  - Vasco Guerra
- ESA project PERMORMER
  - Vasco Guerra (PI)
  - Tiago Silva
  - Nuno Pinhão
  - Floran Peeters
  - Olivier Guaitella
  - Richard van de Sanden
- FCT project ROADMARS
  - Tiago Silva (PI)

Special issue on vibrational kinetics in plasmas

- Plasma Sources Science and Technology
- Guest editors

  Annemie Bogaerts, University of Antwerp, Belgium
  Elena Kustova, Saint Petersburg State University, Russia
  Lucia Daniela Pietanza, Consiglio Nazionale dele Ricerce, Bari, Italy
  Vasco Guerra, Instituto Superior Técnico, Universidade de Lisboa
- Scope
  - Basic data
  - Diagnostics of vibrational states
  - Kinetic modelling
  - Vibrationally-stimulated plasma chemistry
  - Plasma-surface interactions and plasma-assisted catalysis
- Submission deadline: 31 March 2022

https://iopscience.iop.org/journal/0963-0252/page/Special-Issue-on-Vibrational-Kinetics-in-Plasmas