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Photoelectrochemical reactor to convert Mars CO_2 into space propellant (CH_4) using astronauts greywater

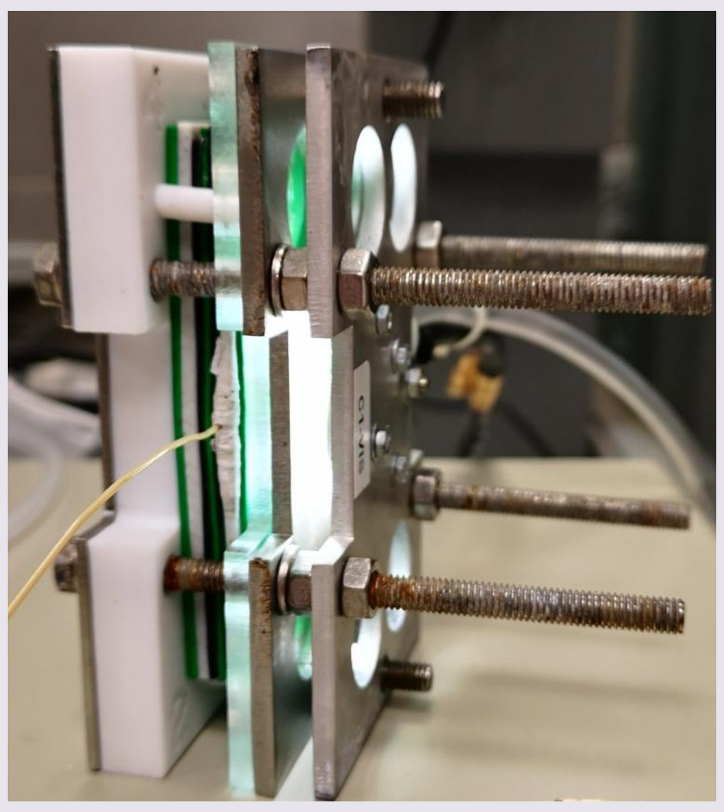
Borja Pozo[1], Jonathan Albo[2], Jean Christophe Berton[3], Antia Villamayor[1], Itziar Azpitarte[1], Ivan Merino[2], Amaia Martinez[1]

C/ Iñaki Goenaga, 5
20600, Eibar (Spain)
borja.pozo@tekniker.es

1-Tekniker, Iñaki Goenanga 5, Eibar, 20600, Gipuzkoa, Spain.
2-Universidad de Cantabria, Chemical & Biomolecular Engineering Department, E.T.S. Ingenieros Industriales y Telecomunicación, Avda. de los Castros 46, 39005, Santander, Spain
3- European Space Agency/European Space Operations Centre, ESA/ESOC, Robert-Bosch-Str. 5, 64293 Darmstadt, Germany

Introduction

The main objective of this work is to develop an efficient and robust photoelectrochemical system (PEC) for CO_2 reduction to produce space propellants based on CH_4 using grey water as the electrolyte to strengthen ISRU activities of future Martian habitats and its operational properties under Mars solar conditions, where the subtracted electrons from this process would reduce CO_2 in the cathode producing space propellant by direct conversion using solar light as energy source.



Objectives

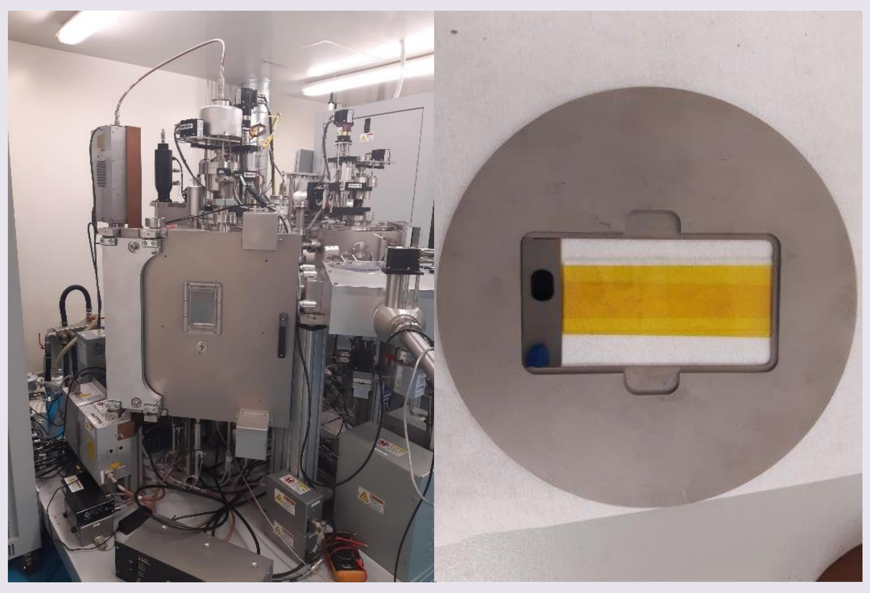
Summarizing, in this work is being developed:

- An operative and efficient (at least 5 %) photoelectrochemical system breadboard
- Electrode area of 100 cm^2
- Integrate a PV for the photoanode
- Achieve 1000 hours of lifetime,
- Use grey water as electrolyte with a flow rate of 100-500 mL/min
- Production CH_4 from CO_2 for future use as space propellant.

Thus, promoting the ISRU concept for future Mars habitats.

Photoanode & Cathode

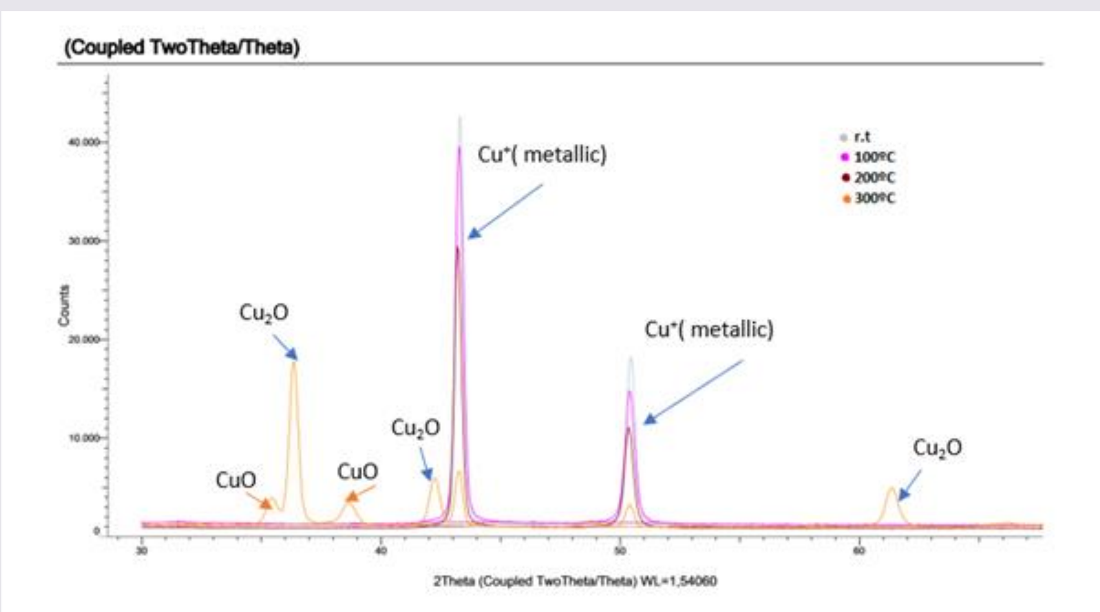
The main objective is to develop a $BiVO_4$ coating with a monoclinic crystal structure and adequate optical properties for visible light absorption for the photoanode



- $BiVO_4$ layers have been deposited in a Kurt J. Lesker sputtering chamber, over glass slides and Si wafers for surface and structure characterisations and over carbon paper and TiO_2/carbon paper substrates
- 5 different deposition process with the $BiVO_4$ have been done, using carbon paper, TiO2+carbon paper, glass slides and Si wafer as substrates
- In the near future, introduce $BiVO_4/WO_3$ photoanodes and experiments at the same conditions

On the cathode side, Cu is the most selective metal for CO_2 reduction to CH_4. Nanoparticle size can be also a factor that influences selectivity, for example, 25 nm nanoparticles favoured C_2H_4 production while ≥60 nm nanoparticles enhanced CH_4 synthesis

- Copper oxide nanoparticles have been synthesized by following a sol-gel route using copper sulfate, ($CuSO_4\ 5H_2O$) or copper chloride, ($CuCl_2\ 2H_2O$) as a copper precursor. Different surfactants have been selected as the main template (dodecylamine, PEO-based block copolymers such as the Pluronics and PVP-10) and co-surfactants (CTAB, SDS)) to achieve nanoparticles with high specific surface area.



Greywater

Greywater is the electrolyte which is located between the photoanode and the cathode and allows the photoelectrochemical reactions, i.e., the H_2O necessary to obtain the CH_4 from CO_2

- The greywater has been generated in an analog mission at Lunares research station. It was from sinks (tooth, hands, and face cleaning) and shower. Avoiding any presence of yellow water.
- The grey water has been tested in 3 different ways: Pure, filtered, and filtered + UV treatment.

Cu cathode	Before using			After 1 use		
Parameters	Greywater	Light	Darkness	Greywater	Light	Darkness
pH	7.1	7.3	7.6	7.1	7.18	7.07
Conductivity (µS/cm)	493	580	590	493	690	728
BOD (mg/l O_2)	608	683	759	608	< 21	< 21
COD (mg/l O_2)	205	195	205	205	501	517
Suspended solids (mg/l)	37.1	49.7	134	37.1	75	84
Dissolved solids (mg/l)	434	494	454	434	493	520
Total nitrogen (mg/l)	20.6	20.5	17	20.6	19.6	19.5
Ammonium-N (mg/l)	13.6	13,1	14	13.6	13.8	13.9
Total phosphorus (mg/l)	0.34	0.52	0.46	0.34	0.15	0.16

- The presence of species in the grey water can also act as a hole scavenger as well, supplying extra electrons to the cathode for an improved current density and thus CO_2 reduction to CH_4, which may also help to achieve a bias-free PEC system (without external energy inputs apart from light illumination).
- The conductivity as well as the pH of the grey water will be taken into account, since these parameters strongly affects the stability of the visible-light active photocatalysts (e.g., $BiVO_4$ and WO_3).
- Thus, after analysing the achieved results, it has been thought that pure greywater or filtered water + UV 10 s could be the best solutions (conductivity/pH/suspended solids).
- It is being analysed that the greywater can be used several times to produce space propellant (recircuit) and then used for Mars gardening when will be not useful to produce electrochemical reactions.

Solar power

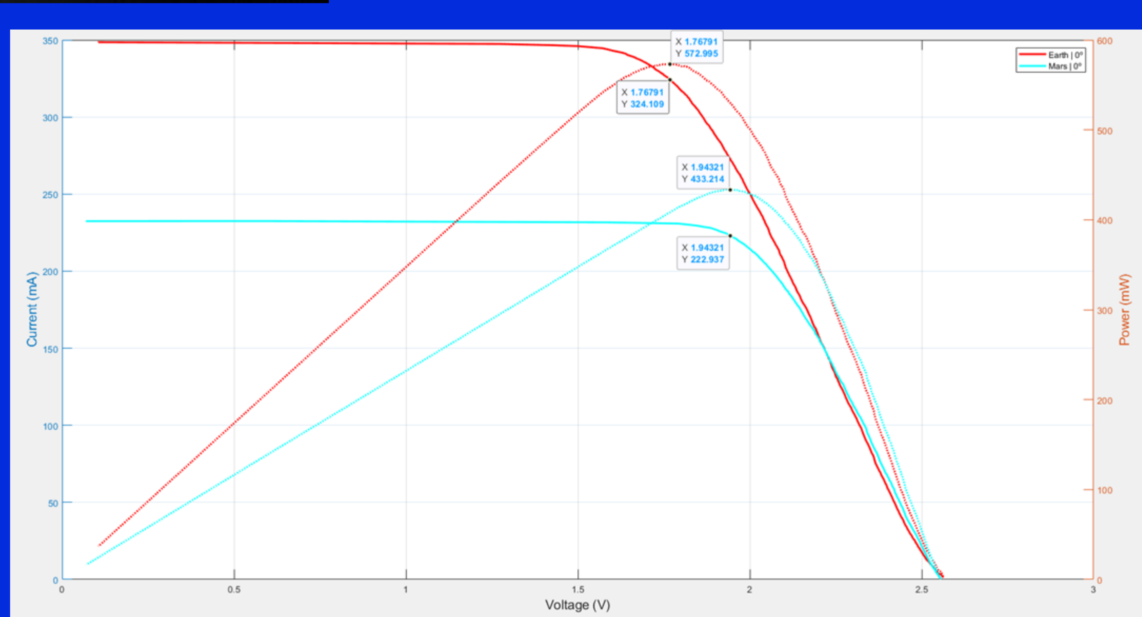
Triple Junction Solar Cells InGaP/GaAs/Ge for Space Applications work in visible range around 500 nm. The solar cell will allow the photoanode concept carrying out the photocatalysis of the PEC cell.

Based in ECSS-E-ST-20-08C standard the test campaign sequence is:

- Visual inspection of solar cells (IV).
- Characterisation of irradiance stability, angles, and wavelength of light.
- Electrical performance (EP) test prior to the start of the test.
- Electrical Performance Acceptance Test (EPA) according to agency criteria.

3 different approaches with 4 different position angles (0, 15, 30, and 45) are being carried out:

1. Earth environment irradiance
2. Mars environment irradiance
3. Mars environment irradiance with dust (different quantity of Mars regolith simulants)

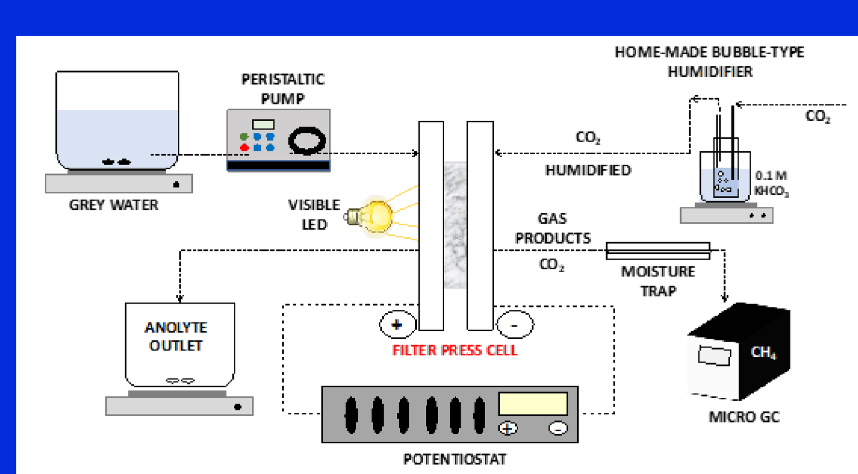


Trade-off test

Continuous PEC conversion of CO_2 to CH_4 at metallic Cu prepared by sol-gel, including a comparison with previous results reached in a gas-phase-based electrochemical system.

Metallic Cu	Light / Dark	H_2	CH_4	CO	C_2H_4	E cathode/ j ($mA \cdot cm^{-2}$)	Cell potential (V)
r ($\mu mol \cdot m^{-2} \cdot s^{-1}$)	Visible	26.2 ± 2.6	94.8 ± 10.1	6.6 ± 2.7	66.6 ± 8.9	-1.8 V vs. Ag/AgCl	2.25
FE (%)		3.2	46.7	0.8	49.2		
STF (%)		0.4	5.2	0.1	5.9	-51.4	
r ($\mu mol \cdot m^{-2} \cdot s^{-1}$)	Dark	44.9 ± 4.2	13.9 ± 3.4	7.6 ± 3.1	90.0 ± 5.6	-1.8 V vs. Ag/AgCl	2.6
FE (%)		6.9	8.6	1.2	83.3		
STF (%)		-	-	-	-	-28.9	
r* ($\mu mol \cdot m^{-2} \cdot s^{-1}$)	Dark*	366.6 ± 20	37.6 ± 5.2	4.5 ± 1.3	1148 ± 136	-1.7 V vs. Ag/AgCl	-
FE (%)*		4.9	2.0	< 0.1	92.8	-7.5	

- Reactor configuration: Cu-GDE cathode / MEA photoanode (Sustainion AEM + $BiVO_4$-GDE)
- GDE cathode: Metallic Cu hexa/octo or CuO. Loading: 1 mg/cm^2
- GDE photoanode: commercial $BiVO_4$. Loading: 2 mg/cm^2
- Catholyte: CO_2 humidified with 0.1 M $KHCO_3$. Q_G: 180 ml/min. pH solution = 6.8
- Anolyte: Real grey waters (without treatment). Q_L: 10 ml/min
- Applied cathode potential: -1.8 V vs. Ag/AgCl.
- Visible light intensity over the photoanode: 59 mW/cm^2



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