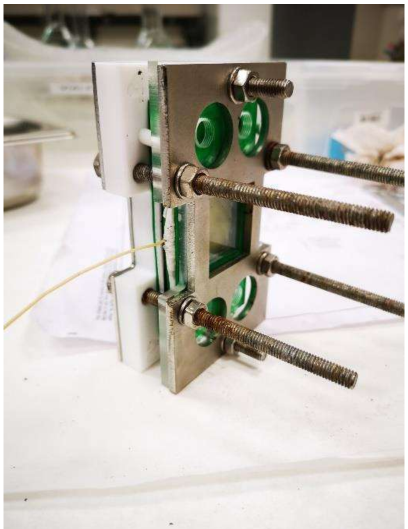

Photoelectrochemical system for CO2 reduction to produce fuels and sewage treatment (HISRU)

Executive summary

Early technology development

Campaign: Towards a Sustainable Hydrogen Production Technology

Affiliation(s): Fundación Tekniker (TEK), Universidad de Cantabria (UC)

Activity summary:
Development of an innovative system for the generation of methane from the photoelectrochemical reduction of CO2 coupled to astronauts' greywater oxidation in an ISRU approach for future Martian habitats. The results obtained comprise the synthesis of copper metallic nanoparticles for the cathode, the analysis and optimization of the photoanode with a multi-layered BiVO4/WO3 surface, the verification of the feasibility of using greywater as electrolyte, the improvement of data in terms of production rate (114.7 µmol m^{-2} s^{-1}), Faradaic Efficiency (65.2 %) and Energy-to-Fuel (7.7 %) and the integration of the photoelectrochemical cell into the designed and manufactured autonomous system.

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1. Introduction

In space missions, in which the materials can be scarce, CO2 appears as a valuable resource to yield chemicals and fuels. This technological approach is of particular interest in future missions to Mars, where CO2 is 95 % of the atmosphere composition.

The main objective of this project is to develop an efficient and robust photoelectrochemical system for CO2 reduction to produce space propellants based on CH4 using greywater as electrolyte to strengthen ISRU activities of future Martian habitats and its operational properties under Mars solar conditions, carry out with its implementation, from preliminary design to a verification test campaign on a representative breadboard, demonstrating that the selected materials, configuration, technologies and solution are feasible and ready for Mars application, concluding with a roadmap to bring the technology to future industrialization.

The sub-objectives of this project are the next ones:

- Consolidate the technical requirements for the development of the photoelectrochemical system for Mars taking into account the needs of the future space missions.
- Investigate photoanode, cathode, PEC membrane materials, composition, architecture and perform a trade-off, with a particular focus on operativity, efficiency, robustness, simplicity, scalability, easy mechanical integration, minimisation of cost, and compatibility to present and future space developments. In addition, investigate greywater composition and define and perform a trade-off for adequate operation as cell electrolyte.
- Analyse commercial photovoltaic cells for photoanode construction oriented to Mars ground solar and atmospheric conditions, making a mechanical integration with the cell and allowing the photoelectrochemical reactions.
- Design, develop, manufacture, and mount photoelectrochemical system breadboard (under technical discussion and approval from the Agency), detailing the selected system design, with focus on efficiency, optimizing the performance, maximizing the lifetime, low cost, scalability and the requirements set in the first phase.
- Verification and validation of the photoelectrochemical breadboard operation in a lab environment, testing them with Mars solar level, controlled greywater and reduction of CO2 to produce CH4, accomplishing all the technical requirements set in the definition of the test campaign.
- Define and stablish an industrialization roadmap for the photoelectrochemical cell commercial development, including its qualification, improvements and limitations (independently of the underlying source of scheme and funding).
- Stablish the scalability parameters of the system for future developments, i.e., lifetime, efficiency, size, etc.

2. Project Background

The activity has been focused on the development of advanced coatings, compounds, architectures, controls that have a combination of excellent electrochemical, mechanical integration, automation, monitoring and operation efficiency together in a complex system.

The efficiency of the photoelectrochemical CO2 reduction systems is limited by many factors such as electrodes band gap configuration, system's charge and mass transfer resistance, catalyst selectivity or cell design. Stability is restricted by cell potentials and harsh reaction environment which is not suitable for many chemical elements. Density currents for the whole system are usually lower than 10 mA cm^{-2} and regarding solar to fuel efficiencies there is almost no information of CO2 reduction towards methane due to the novelty of the system.

Regarding literature's state of the art, the most effective PEC cell approximation is a two chamber cell photoanode-dark cathode configuration due to several factors as the use of n-type semiconductors for the photoanode, which are earth abundant, stable and cheap materials, the use of photoactive materials that can reduce voltage input compared to electrochemical processes or photocathode-dark anode configuration and also improve CO2 reduction by supplying extra negative potential to the cathode. For this type of PEC CO2 reduction coupled with greywaters treatment system there are no literature reports found. We took as bibliographic example greywaters treatment coupled to a PEC hydrogen production system in order to assess materials for photoanode. One major problem of coupling wastewater treatment with PEC CO2 is that the oxidation of the organic matter and compounds produce CO2 at the photoanode chamber poisoning the electrode and diminishing its catalytic activity.

PEC reactors consist of a three electrodes arrangement with a working electrode, a reference electrode, and a counter electrode. Usually the reference electrode is Ag/AgCl. For the photoelectrochemical CO2 reduction reactors exist three types of configurations: photoanode-dark cathode, photocathode-dark anode and photocathode-photoanode. These last two are not suitable for CO2 reduction due to low electron supply to the anode for the former and very low efficiency for the latter. The counter electrode would be the dark cathode, and both the photoanode and the dark cathode are in different compartments separated by a membrane.

Usually, for the photoanode n-type semiconductors such as TiO2, Fe2O3, ZnO, BiVO4 or WO3 are used due to their band energies, their ability to absorb photons and stability for H2O oxidation reaction. Some of these oxides like TiO2 or ZnO have a relatively big band gap which limits the maximum current density. On the other hand, BiVO4 or WO3 have a smaller band gap, allowing them to reach higher current densities but they tend to have crystallographic disorder which leads to high levels of recombination, low charge carrier mobility and poor stability. There are several options that could solve these problems like doping, forming heterojunctions, nanostructuration, using co-catalysts or a PV cell coupled photoanode.

On the cathode side, Cu is the most selective metal for CO2 reduction to methane. In general, for photoanode-cathode system it has been more intensely researched that the cathode, usually they use Cu wire. The crystal structure of Cu affects its selectivity towards CH4, Cu (111) is more CH4 selective while C2H4 is enhanced over Cu (100), but pH and cell potential can influence this selectivity as well. Nanoparticle size can be also a factor that influences selectivity.

In recent years, various techniques have been developed for preparation of thin films in order to be used for photoelectrochemical water splitting. Generally, they may be categorized into three major groups based on the nature of the reactions utilized, namely, physical vapor deposition, chemical deposition such as hydro/solvothermal or sol gel and electrochemical deposition.

It is noted that in a complex thin film, which may include multiple layers, each layer may be prepared by a different method. However, in all processes there are parameters that are important to be controlled to achieve the maximum efficiency of the process:

- film thickness and its morphology are essential in order to maximize light absorption. A suitable thickness improves light absorption but can also shorten the excited charge lifetime.
- crystallinity of the film due to the energy band gap of each material is fully linked with the light absorption and therefore with the photoactivity of the electrode.

- crystallite size and the connectivity between particles because they directly impact in electrochemical properties of the final film.

The use of sewage water (greywater) as electrolyte in photoelectrochemical cell is one of the ways for recycling and reusing of the water in the habitat contributing to the sustainability of available water resources. Before the use of the sewage water as electrolyte, it is necessary to treat this water using mainly physical and biological processes to remove solid and organic residue to avoid the contamination of electrolytes in the cell. Another important parameter is the pH of the wastewater as it determines the efficiency in working electrode.

Methane is one of the promising space propellants for future missions to Mars and/or return to Earth. Methane is more stable than liquid hydrogen, which is one of the common rocket propellants. In addition, it can also be stored easily and is more manageable at different temperatures.

Taking all this background into account, the idea has been to make signs of progress for a photoelectrochemical (PEC) system, related to reactor design, process control, and developing innovative photoelectrodes with high efficiency catalytic materials towards the production of space propellants based on methane. The catalyst is a fundamental component of a PEC cell because is responsible for the selectivity and catalytic activity of the photoelectrodes and being decisive for efficiency. Also, the synthetic method is a crucial point because it affects the properties and structure of the catalyst, and manufacturing nanostructures with accurate morphology, size and composition can maximize the catalytic activity and the efficiency of the system.

3. Methodology

The HISRU approach involves the following methodology:

- Bibliographic research about optimal conditions of PVD and sol-gel synthesis of photoanode and cathode, to ensure which are the correct process parameters to be applied in order to achieve the right composition and catalyst structure to obtain the desired stability and efficiency.
- Optimizing process parameters to obtain the targeted structure. SEM, XRD or AFM techniques are used as methods of preliminary structural characterization. Also, electrochemical measurements as linear sweep voltammetry, cyclic voltammetry or EIS are performed in order to stablish relevant electrodes electrochemical parameters as density current or overpotential and partial validation of materials
- Proposed materials validation in a lab scale PEC system under visible light to see if the photoanode and the cathode work well all together in the PEC cell. Taking this into account, optimization of the electrodes, electrolyte or membrane if necessary.
- Design, manufacturing, mounting, testing, and verification of a PEC cell with stablished requirements.
- Definition and carry out of a test campaign with continuous on-line measuring of several parameters, using Mars level visible sunlight, producing CH_4 from CO_2 and verifying the PEC cell efficiency requirement value.
- Validation of the PEC system performance for future Mars ISRU activity.

4. Key Findings

Copper has been used as base material for the cathode, as copper is the element with the highest selectivity towards methane. Copper nanoparticles have been synthesized by following a sol-gel chemical reduction using copper sulphate or copper chloride as a copper precursor and ascorbic acid or acetic acid as reduction agent. The optimization of the sol gel process is crucial. Variables such as precursor types, the pH of the synthesis, the type of solvent or temperature and reaction time have been optimized during the project. The samples have been analysed in the XRD equipment, together with a commercial CuO reference. All the samples synthesized were crystalline and, compared to the commercial reference, nanoparticles with a higher degree of crystallinity than the reference sample can be produced. In the case of ascorbic acid, Cu metallic is obtained, and with acetic acid, CuO is produced. On the other hand, repeatable and reproducible samples have been obtained.

The selective Cu-based cathodes and light-responsive photoanodes have been manufactured by i) manual airbrushing, and ii) an optimized pyrolysis deposition technique with an automated spray. The second option resulted in a more homogeneous deposition of the materials onto porous carbon paper supports and in a more scalable and reproducible electrode fabrication.

The characterization of greywaters has been carried out by evaluating their main properties as a function of reaction time to confirm the stability of the photoanodes. In summary, the characteristics of the greywater with time, in terms of conductivity, chemical oxygen demand, suspended solids, and dissolved solids, among others, remains pseudo-stable up to 10 h of continuous operation. The control of dissolved solids evolution is essential because, although they might help in the oxidation reaction, they may also provoke a shielding effect in the photoanode surface. The evolution of both current density and production rate of methane in a greywater recirculation is slightly decreased after a certain time of operation, but it remains pseudo stable, demonstrating the feasibility of using greywater in the PEC system.

A breadboard of a reactor of 10 cm^2 has been assembled with the samples of all the elements manufactured during the trade-off activities. The results show that the continuous production of CH4 from CO2 photoelectroreduction using real greywaters as electrolyte in a gas-liquid photoanode/dark cathode configuration allowed to come closer to the project targets. In particular, the use of a metallic Cu (prepared by sol-gel) electrocatalyst as cathode results in higher CH4 production rates in comparison with the use of CuO-based cathodes (94.8 vs. 62.7 $\mu mol\ m^{-2}\ s^{-1}$). The photocurrent density achieved under the light is also higher at metallic Cu, reaching a value of 4.6 $mA\ cm^{-2}$, which is close with the target proposed in the project (> 5 $mA\ cm^{-2}$). Under visible light irradiation, the Faradaic Efficiency (FE) and Energy-to-Fuel (ETF) towards CH4 were 46.7 % and 6.55 %, respectively. Since the project goals are > 50 % (FE) and 5 % (ETF), it can be concluded that the results obtained with home-made synthesized metallic Cu (cathodes) and commercial BiVO4 photoanodes are promising. The metallic Cu represents the optimum electrocatalyst for the production of CH4 (continuous mode) in the PEC system. It should also be noted that the evolution of the current density with time (both under visible light and dark conditions) is pseudo-stable, which reveals the stability of the PEC system developed.

The incorporation of WO3 to BiVO4 surfaces in a multi-layered BiVO4/WO3 structure improves not only stability, but also visible light absorption and electron transport at the same time owing to their matched band edge positions compared to pure photocatalysts. The use of tailored BiVO4/WO3 (20:80) multi-layered photoanodes results in an improvement in the methane production rate (114.7 $\mu mol\ m^{-2}\ s^{-1}$), FE (65.2 %) and ETF (7.7 %), which can be explained by the effect of the current density reached with multi-layered or pure photoanodes (36 $mA\ cm^{-2}$ vs. 33.5 $mA\ cm^{-2}$, respectively). This is supported by the PEC characterization results achieved with multi-layered photoanodes in terms of improved electronic properties, visible light absorption, and charges separation. The improvement leads to a reduced overall cell potential (2 V) with the optimized multi-layered surfaces, which is crucial in practical applications from energy consumption viewpoint. Although hydrogen production significantly increased with $BiVO_4/WO_3$ photoanodes, ethylene generation also decreases, thus leading to an increase in FE (65.2 % vs. 46.7 %) and ETF (7.7 % vs 6.6 %) towards methane with multi-layered surfaces. Comparing the results with literature, it should be noted that the performance of photoanode-driven PEC systems in terms of j and FE to CH_4 are usually lower than 20 mA cm^{-2} and 60 %, respectively, which denotes the relevance of the present study, with a boosted PEC performance and simultaneous greywater co-valorisation.

Furthermore, an analysis focused on the effect of varying the applied voltage at the cathode under two different light intensities (59 mW cm^{-2} and 100 mW cm^{-2}, Mars and Earth conditions respectively) was carried out. The results showed that increasing the cathodic voltage led to a rise in current density. However, this increase did not favour methane production, as hydrogen became the predominant product, especially at higher voltages. The most favourable conditions for CH_4 production in terms of production rate, FE, and ETF were found at an applied voltage of -1.8 V vs. Ag/AgCl. Although the objective of the project is to produce space propellants based on CH_4, it is interesting to note that the system is also capable of producing hydrogen simply by increasing the applied potential at the cathode.

Taking into account the fluid recirculation requirements of the photoelectrochemical cell, the elements needed for the operation and monitoring of the system has been integrated into an autonomous system, designed and manufactured as a cylindrical vessel of Ø320 mm x 882 mm and 96 kg of weight, made of 7075 T6 SN aluminium with a protective Surtec 650 anodise and capable to withstand a pressure difference of 1 bar between the inside and the outside. The various electronic, pneumatic and hydraulic components have been placed on several floors inside the vessel and are controlled by the FW implemented in a Raspberry Pi Pico microcontroller, enabling the automated insertion and recirculation of greywater and CO_2 and controlling the inflow rates to the reactor and the adequate pH of the recirculating water.

5. Conclusion

This work covers the development of an innovative system for the generation of methane as space propellants from the photoelectrochemical reduction of CO_2 coupled to astronauts' greywater oxidation in an in-situ resource utilization approach for future Martian habitats. This technological strategy takes advantage of the abundant CO_2 concentration in Mars atmosphere and sunlight to yield chemicals and fuels.

The effect of the metallic Cu cathode composition using pure $BiVO_4$ surfaces as the photoanode shows an enhanced CH_4 production rate in comparison with the results reached with CuO cathodes at the same operating conditions. The incorporation of WO_3 to $BiVO_4$ surfaces in a multi-layered $BiVO_4/WO_3$ structure improves the methane production rate, FE and ETF compared to pure photoanode. Both current density and CH_4 production are pseudo-stable up to 10 h of continuous operation under visible light irradiation.

On the other hand, the possibility of greywater recirculation operation is also demonstrated, providing an appealing option to close the greywater cycle in the photoelectrochemical system.

Furthermore, the components needed for the operation and monitoring of the photoelectrochemical system has been integrated into an autonomous system, working together to drive the photoelectrochemical process, with careful monitoring and control over greywater quality and fluid flows.

Overall, this project represents a first approach in promoting the ISRU concept for the generation of a sustainable space propellant in continuous mode from CO_2, water, and sunlight by means of a robust, efficient and autonomous photoelectrochemical system that could be applied in future space missions.

6. Future Work

The project posed a significant challenge in both the development and optimization of the reactor (and each of its components) to achieve the expected methane production rate, FE and ETF, as well as in the design and manufacture of a system capable of controlling and automating the insertion and recirculation of greywater and CO2 through the reactor.

However, some activities could not be carried out during the project. In the next points, these elements/tests are detailed:

- Revision of the scaled reactor from 10 cm^2 to 100 cm^2 to solve the leakages and to obtain the methane production expected: the CO2 leakages need to be removed and then, more tests must be carried out to achieve the voltage and current density values as the ones obtained with the lab scale PEC.
- Investigate power options for the system: the selection of an integrable potentiostat to power the cell is still a pending step towards the total automatization of the system.
- Investigate CO2 pumps able to insert pressure with a 10-mbar source: different tests with the actual selected pump (and/or with other new options) and CO2 pressure conditions around 10 mbar should be performed to confirm the feasibility of inserting pressure into the vessel in a real environment.
- Investigate methane sensor and flowmeter that can be integrated into the vessel: during the project period, we could not find a methane sensor and flowmeter of the dimension and characteristics needed to be integrated into the system. The electronics market is moving fast and there may soon be elements that fit into this development.
- Integrate communications to connect the system with external main control: the implemented control is launched by some shell commands, which is a perfect option to verify the correct performance of the system; however, the final operation should be controlled by an external main control via a dedicated communication, e.g. CAN bus.
- Demonstrate the complete system in an operational environment

These issues should be taken into account as a starting point to be analysed and improved for the development of a second version of the system.