Plan Overview

A Data Management Plan created using DMPonline

Title: Photoelectrochemical system design for CO_2 and CH_4 conversion to valuable products

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Template: DMPOnline Template (NWU)

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Project abstract:

Agribusiness is one of the main financial activities in Brazil, especially the sugar and alcohol sector. Despite the economic relevance of this industrial complex, there is an environmental concern associated to the release of tons of carbon dioxide (CO_2) and biomethane (CH_4) per year. As these gases are the main causes of the greenhouse effect, it is necessary to develop technologies and processes to minimize its emission. Photocatalytic processes may be an alternative since they can convert CO_2 and CH_4 into important organic molecules. The photocatalysis efficiency can be further improved by photoelectrocatalytic processes, which separate more efficiently the photogenerated charges. Although there are several studies related to photoelectrocatalysts synthesis, there are few efforts to apply these materials in photoelectrocatalytic reactors with high performance industrial design. In this context, this postdoctoral project has as main objective the development of a photoelectrocatalytic reactor for simultaneous CO_2 and CH_4 conversion to valuable compounds. It will be used a photoanode/photocathode system (TiO_2/Cu_2O) and the new reactor will be studied considering micro fluid dynamics elements and process intensification. The reactor will be operated in potentiostatic mode and different process parameters will be analyzed, such as flow, applied potential, and the effects of turbulence promoters, giving special attention to the mass transfer phenomena. Thus, it is expected to be established the best process parameters that provide high selectivity for more valuable products, faster photoelectrocatalysis kinetics, and lower energy consumption.

ID: 92223

Start date: 01-06-2021

End date: 01-06-2024

Last modified: 01-02-2024

Grant number / URL: FAPESP 2019/21496-0

Copyright information:

Photoelectrochemical system design for CO_2 and CH_4 conversion to valuable products

Data Collection

What data will you be collecting ?

In the Project Scope, data will refer to any equipment result, including those intended for graphical plots (e.g., spectroscopic data) or images (e.g. transmission electron microscopy). These data will be collected in different experiments regarding the produced samples and their characterizations, mainly in digital format.

How will the data be collected or created?

- Catalyst characterizations: scanning and transmission electron microscopies; X-ray diffraction patterns; infrared, Raman, and UV-Vis spectroscopies; analytical elemental determination; etc.
- Catalysis-related data: CH_4 reforming, CO_2 conversion, and N_2 reduction in experimental reactors; temperature-programmed gas desorption; surface-acidity titration, etc.

How will the data be stored and backed up during the research?

All produced data will be stored in a Data Repository, based on digital servers (to be acquired using Technical Reserve resources) provided by the Project Coordination and located in Embrapa Instrumentation TI Support. For data organization, project management software will be provided to all users keeping basic information about acquisition date, equipment, and measurement conditions. Free software alternatives will be analyzed by Project Coordination but keeping all the information encrypted in a physical server, for data reliability and confidentiality. Management software will include a digital Laboratory Notebook, which will be used by all project members. Related sub-projects (e.g. Ph.D. thesis, postdoc projects, etc) will be registered using the same system. Raw data from equipment will be linked to the digital Notebook and physical versions (paper-based) will be scanned and also stored in digital format. Project Coordination will keep physical notebooks after each sub-project ending at least 3 years after Project completion.

Who will be involved in your data collection ?

The data collection will be made mainly by the Principal Investigator (Dr. Jéssica Ariane de Oliveira) but it can also be made by other members of the research group depending on the required equipment since some of them have restricted access.

What documentation and metadata will accompany the data?

Along with Storage, Backup, Selection, and Preservation procedures, all information about equipment model, experiment setup, calibration, and accessory data will be kept in the Repository. Information management will be done by the Project software using the structure of Laboratory digital notebooks.

How will you manage access and security?

All data will be registered in a standard Laboratory Notebook, to be provided by the Project Coordination to all project members. This Laboratory Notebook (see below), in both physical and digital format, is aimed to keep all the information protected and easily available for Coordinators (for checking or validation).

Which data are of long-term value and should be retained, shared, and/or preserved?

Several experiments proposed in this Project are destructive analyses and, in some cases, as-produced catalysts are unstable for long-term storage. Therefore, methods for sample preparation and characterization will be preserved in a digital server for experiment reproduction in a detailed format. When possible, representative samples will be stored and classified by Project Coordination for cross-checking and validation if necessary. As described above, data and methods should be preserved in the Repository at least for 10 years.

What is the long-term preservation plan for the dataset?

A Project webpage will be built for public information about the main proposal, members, subproposals, and achievements. A contact email will be provided on the webpage. This webpage will be prepared using support from UFSCar and Embrapa TI services and features will be used to help access project members in restricted areas.

Ethics

Give a description of your Ethics

How will you manage any ethical issues?

Each project member should sign an Ethical and Legal Responsibility term, which will be kept by Project Coordination. This term will follow the general guidelines promoted by FAPESP, including data ownership, responsibility, and absence of plagiarism declarations. Plagiarism software support will be provided by Project Coordination using Technical Reserve resources. Plagiarism reports for each produced document will be kept together with the final documents in the Data Repository.

How will you manage copyright and Intellectual Property Rights (IPR) issues?

Core IT systems to secure IP, including all input/output devices that store the documents they process. They are typically networked and connected to remote management systems. Also, cloud applications and file-sharing services.

How will you share the data?

Papers and published content will be freely provided on the Project webpage using preprint documents or final papers in case of open access options. These will strictly follow Journals' policies and, in cases of restricted data access, Project Coordination will ask FAPESP about any specific event. Raw data will be provided by request to Project Coordination, in the Project contact email.
To access information about each Project's achievement, Public Yearly Meetings will be promoted, and structured for 2-day meetings. Each principal investigator will be invited to present to the general public the main achievements through oral presentations and poster discussions about specific topics. The events will follow the general structure of scientific meetings, with invited presentations (generally by important researchers in related areas, not necessarily working on the project) and regular talks. A public document will be produced reporting the main achievements and highlights of the research, such as important papers (in high-impact factor journals), patents, or technology transfer processes. In this document, only the public information will be widespread taking care of language (intended to be accessible to all publics) and structure (visually attractive).
The Public Yearly Meetings will be important to start cooperation among groups but this will be stimulated by other means, such as regular web-based forums. To that, a project webpage will be developed with thematic forums to promote continuous discussion about specific topics and sharing of research results. The presence in social media will be stimulated, starting a project Facebook page and
YouTube channel. These platforms will also help with project webpage development (see above) since information posted there may be widespread by the page and vice-versa.
Especially for the YouTube channel, the researchers will be invited to post short videos and short tutorial videos aimed at the general public. Each investigator will be stimulated to offer short web courses and webinars on related topics using the platform. These platforms will also be useful for widespread information about yearly meetings, such as posting news or recorded presentations.

Are any restrictions on data sharing required?

Access will be restricted to project members until paper publication or any other information disclosure (patent, meetings, etc). As published, raw data will be available to anyone who formally requests Project Coordination. Raw data will be stored in digital format at least 10 years after Project completion

Who will be responsible for data management?

Data management will be the responsibility of Project Coordination (Coordinator and PIs). TI support from institutions will be provided as Institutional Support. A Data curator will be yearly indicated by the Project Coordinator as a contact point for TI support, researchers, and the community. To help the Proponent organize information about equipment and data sources, a project secretariat will be provided with general support for project management (acquisitions, payments, etc) and to provide information about the multiuser facility. All the equipment acquired in this proposal will be asked to operate as multiuser facilities and the Secretariat will be responsible for proposing and managing a system for easy access. The involved costs (including maintenance, consumables, and operational people) of each technique will be studied by the Secretariat aiming to support researchers to propose sustainable conditions for shared usage. A general web-based scheduling system for equipment access will be discussed with all investigators. The previous experience of Embrapa Instrumentation in the management of LNNA (Nanotechnology
National Laboratory for Agriculture) as a member of SISNano (Brazilian System of Nanotechnology Laboratories) will support this discussion.
The equipment, book, and database acquisition processes will be preferably done by the project secretariat. The Secretariat will be supported by the previous experience of FAI-UFSCar and Embrapa Instrumentation Project Management Office in
international acquisitions. In any case, all the equipment financed by this proposal will be offered as a multiuser facility according to FAPESP guidance lines.

What resources will you require to deliver your plan?

The approval of the 1-year extension of the postdoc fellowship, funded by FAPESP, will be enough to achieve the mentioned goals

Planned Research Outputs

Book Chapter - "New Photoelectrochemical Processes for Small Molecule Activation: The Case of Methane"

The high stability of the C–H bonds makes methane reform a difficult reaction. Thus, high temperatures and pressures are required for the industrial conversion of CH_4 into syngas, making the process pricy. This chapter introduces the challenges for partial methane oxidation as well as presents photoelectrocatalysis (PEC) as a sustainable approach for controlled methanol production from CH_4 under mild conditions. By the end of the chapter the main bottleneck for the PEC CH_4 conversion is explained, including a full discussion about the parameters required to efficiently control the methane conversion that includes (i) the role of oxygen species, such as hydroxyl radicals, dissolved molecular oxygen, and oxygen vacancies; (ii) the ability of metals to change the oxidation state; and (c) the importance of adequate band edge positions in the semiconductor.

Data paper - " Evaluation of the activity and selectivity of mesoporous composites of MCM-41 and CuO in the CO2 photoreduction process"

The conversion of CO2 into valuable chemical feedstock through photocatalysis is considered an effective strategy to mitigate global warming and energy supply problems. Among the challenges for CO2 photoreduction are the design and synthesis of active photocatalysts with high affinity for the CO2 molecule and suitable reduction potentials of valence and conduction bands to promote the reduction of the CO2 molecule. Molecular sieves (MCM-41) with semiconductors, such as copper oxide, are alternatives to the traditional semiconductors (TiO2 and ZnO) with high CO2 adsorption capacity, high specific surface area, and good stability, making them perfect candidates for photocatalysis. Therefore, in this work, mesoporous composite materials based on MCM-41 and CuO were synthesized via the impregnation method. The synthesized materials were chemically, structur
ally, and morphologically characterized by XRD, SEM, FTIR, XPS, DRS, N2 adsorption and desorption, and atomic absorption spectroscopy techniques, and the photocatalytic activity in the reduction of CO2 was evaluated under visible radiation. We show that MCM-41 and the composite MCM-41/CuO have significant potential for use in the CO2 photoreduction process, where the composition and different active sites in the photocatalysts play an important role in the activity and selectivity of the products formed. The results showed that the MCM-41 and the
composite with 1 % (w/w%) CuO presented high selectivity and production of methanol, with 585.88 and 267.05 µmol.gcatalyst-1 , respectively. Thus, the findings demonstrated the versatility of the MCM-41 to form composites with semiconductors, as well as the need to comprehend the main aspects that influence CO2 photoreduction activities and the selectivity of the composites, including their surface, structural, and electrical features.

Data paper - "Selective CH4 reform to methanol through partial oxidation over Bi2O3 at room temperature and pressure"

Herein, we propose that an efficient CH4 partial photooxidation to methanol depends on appropriate band edge positions in photocatalysts. We demonstrated our hypothesis using Bi2O3 since this semiconductor have a valence band favorable to produce •OH and a conduction band not advantageous to O2•- which is crucial to keep O2 available for •CH3 capture and CH3OH formation. A notably and selective partial photooxidation of methane to methanol was observed under visible light at room temperature and pressure. As a result, the productivity of methanol over Bi2O3 can reach approximately 3771 µmol g 1 h 1 with c.a. 65% selectivity avoiding overoxidation to CO2. Isotope labeling experiment (13CH4) confirmed that methane acts as the carbon source of methanol and ESR measurements proved the •CH3 and •OH generation. Besides, Bi2O3 exhibited good stability after 5 cycles maintaining a high and selective methanol production. These results provide insight into critical photocatalyst properties for the partial photooxidation of methane to methanol.

Data paper - " Role of Cu0-TiO2 interaction in catalyst stability in CO2 photoreduction process"

The application of copper-based semiconductors for CO2 photoreduction has been limited by the poor stability of these catalysts in aqueous solutions due to parallel oxidation reactions. Thus, here we discussed the role of the Cu0-TiO2 interaction in catalyst stability, where the semiconductor acts as a charge separator and support for Cu0. Cu0 nanoparticles were deposited on the surface of TiO2 by reducing copper nitrate using a sodium borohydride solution. The metallic copper presents a higher selectivity in CO production (82.32%), while pure TiO2 presents a selectivity for CH4 (62.44%). However, with the heterostructure formation, the photocatalyst activity increases and the selectivity changes with copper amount variation over TiO2. In addition to the obtained C1 products (CH4, CO, and CH3OH), products containing two or more carbons (C2+) were also generated, such as acetic acid (C2H4O2), acetone (C3H6O), and isopropanol (C3H8O). H2 was also produced, although the selectivity for products derived from the photoreduction of CO2 was significantly greater. The sample TiO2/Cu 30% was significantly stable, which indicated the importance of an adequate heterojunction in the catalyst activity. These results demonstrate the synergistic effect between different copper species over TiO2, in which both materials play a role in the catalytic event.

Data paper - "Preparation and Application of Nb2O5 Nanofibers in CO2 Photoconversion"

Increasing global warming due to NOx, CO2, and CH4, is significantly harming ecosystems and life worldwide. One promising methodology is converting pollutants into valuable chemicals via photocatalytic processes (by reusable photocatalysts). In this context, the present work aimed to produce a Nb2O5 photocatalyst nanofiber system by electrospinning to convert CO2. Based on the collected data, the calcination at 600 C for 2 h resulted in the best condition to obtain nanofibers with homogeneous surfaces and an average diameter of 84 nm. As a result, the Nb2O5 nanofibers converted CO2 mostly into CO and CH4, reaching values around 8.5 mol g 1 and 0.55 mol g 1, respectively.

Data paper - "Copper vanadates: Targeted synthesis of two pure phases and use in a photoanode/cathode setup for selective photoelectrochemical conversion of carbon dioxide to liquid fuel"

Durable photocathodes are a matter of crucial concern in photoelectrochemical (PEC) CO2 reduction and a photoanode/dark cathode configuration is a viable strategy to circumvent this stability issue. In this vein, this study addresses a literature gap related to emerging photoelectrode materials for solar fuel generation. First is the perennial problem of securing a pure phase in the ternary copper vanadate (Cu-V-O) family of inorganic semiconductors. An optimized synthesis route was developed to prepare two copper vanadates with distinct morphological and optical properties. The copper site valence in the precursor influenced the semiconductor composition type: a Cu(II) source led to n-type β-Cu2V2O7 while employing a Cu(I) source and an inert, deoxygenated environment, p-type α-CuVO3 was obtained. The α-CuVO3 photoelectrode was unstable and easily converted to β-Cu2V2O7. Therefore, only the PEC performance of β-Cu2V2O7 towards CO2 reduction was evaluated in this study, demonstrating that mainly methanol (generation flux: ~236 µmol cm-2 h 1) was selectively formed.

Planned research output details

Title	Type	Anticipated release date	Initial access level	Intended repository(ies)	Anticipated file size	License	Metadata standard(s)	May contain sensitive data?	May contain PII?
New Photoelectrochemical Processes for Small Molec ...	Book Chapter	Unspecified	Open	None specified		None specified	None specified	No	No
Evaluation of the activity and selectivity of mes ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Selective CH4 reform to methanol through partial o ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Role of Cu0-TiO2 interaction in catalyst stabilit ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Preparation and Application of Nb2O5 Nanofibers in ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Copper vanadates: Targeted synthesis of two pure p ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No