Doctoral Dissertation
Doctoral Program in Physics

Integration of Photovoltaic Systems and Electrochemical Technologies Toward Carbon Neutrality: Experimental and Modeling Study

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Introduction

The present work falls within the framework of Carbon Capture, Utilization and Storage (CCUS) technologies, in particular in the field of solar-driven electrochemical CO_2 reduction. Toward decarbonization and the net-zero emission goals set for 2050, the electrochemical conversion of CO_2 into added-value products is one of the best solutions for cutting carbon emissions, ensuring a carbon neutral loop in which the CO_2 is valorized and utilized as source for molecules of interest (e.g., Carbon Monoxide). Furthermore, the adoption of renewable energy makes this technology completely sustainable.

Within this context, the present work adopts a dual approach: (1) the experimental investigation of devices coupling dye-sensitized solar cells (DSSCs) and electrochemical (EC) cell, (2) the development of mathematical models to describe and optimize the operation of both individual components and the integrated Photovoltaic (PV)-EC system and (3) the exploration of the possibility to obtain a bicarbonate electrolyzer (BE) fully powered by PV systems, thus creating a PV-BE device. The thesis is structured to systematically address these objectives. It begins with a review of the fundamental principles and current state of the art, followed by a detailed account of the experimental methods and materials used. Subsequently, the development and validation of a comprehensive mathematical model are presented. The results are analyzed in depth, with a focus on their implications for the design and operation of efficient and scalable PV-EC systems.

An additional section explores the integration of photovoltaic devices with bicarbonate electrolyzers. This part investigates the potential of developing a system capable of converting captured CO_2 into valuable products using solar energy.

Overall, this work aims to contribute to the advancement of sustainable technologies for CO_2 utilization and renewable energy integration, laying the groundwork for future innovations in the field.

Methods

Concerning the mathematical model, it has been developed on COMSOL Multiphysics, by solving the constituting equations with a Finite Element Method approach. The mathematical modeling contains a 2D representation of the batch cell reactor for CO_2 conversion in CO, in which electrolyte/membrane/cathode and anode are inserted. Thanks to the insertion of equations that express the kinetics of the electrochemical reactions occurring at the electrodes (Oxygen Evolution Reaction at the anode, Hydrogen Evolution Reaction and CO_2 conversion to CO reaction at the cathode), it has been possible to both validate the model with experimental results and obtain important parametric results for the optimization of the process.

The experimental work centers on the design and characterization of an integrated PV-EC system for CO_2 conversion. First, a commercial batch-type electrochemical reactor was employed for CO_2 electroreduction, featuring separate anodic and cathodic compartments sealed with polymeric gaskets and separated by a Nafion N117 proton-exchange membrane to ensure selective ion transport. Both compartments were filled with 0.1 M $KHCO_3$ electrolyte, recirculated via peristaltic pumps at 1.547 mL/min. CO_2 was supplied to the cathode at a controlled flow of 15 mL/min using mass flow controllers.

The anode consisted of a platinum foil (9.9 cm^2), while the cathode was prepared by sputtering silver nanoparticles onto carbon paper, with electrode areas ranging from 1.2 to 1.9 cm^2. A two-electrode configuration was used with a potentiostat to perform chronoamperometry, typically over one-hour intervals. Gaseous products were analyzed via micro-GC, and possible liquid products were examined using HPLC.

To supply the required electrical energy, a photovoltaic module composed of six dye-sensitized solar cells connected in series was fabricated. The photoanodes were based on TiO_2 layers sensitized with commercial N719 dye, and counter-electrodes consisted of sputtered platinum on Fluorine-doped Tin Oxide glass. The cells were filled with an iodide/triiodide redox electrolyte and sealed using a thermoplastic film. I–V curves were recorded under simulated solar light to evaluate module performance and its compatibility with the electrolyzer for integrated solar-driven CO_2 conversion. The module is finally integrated with the EC cell through a Pt foil that serves as anode the EC and cathode for the PV system.

In parallel, a custom bicarbonate electrolyzer was developed with stainless steel flow plates (2 cm^2) and a bipolar membrane. The anode used Ni foam, and the same silver-based cathode was adopted. Electrochemical tests were performed using 1 M KOH as anolyte and 2 M $KHCO_3$ as catholyte, with N_2 gas (20 mL/min) used as a carrier instead of CO_2. In this case, the PV-BE system is also studied, with coupling through external electrical connections.

Results

The experimental results confirmed the feasibility of integrating dye-sensitized solar cells with an electrochemical cell for CO production, demonstrating promising performance under simulated solar illumination and weather conditions ($FE_{CO} \approx 80\%$ at 1 kW/m^2 illumination, $FE_{CO} \approx 60\%$ at 0.6 kW/m^2 illumination).

In parallel, the developed mathematical model offered valuable predictive insights into the influence of key operational parameters (such as electrolyte flow rate, membrane characteristics, and system geometry) on current density and Faradaic efficiency. The strong correlation between experimental data and simulation outcomes highlights the reliability of the modeling approach and its effectiveness as a tool for optimizing the design and operation of integrated PV-EC systems.

The preliminary study for PV-BE devices reported a $FE_{CO} \approx 62\%$ at 1 kW/m^2 illumination, assessing the feasibility of both capturing and converting the CO_2 through solar energy, reducing the costs of separation of inlet gases.

Appendix: Electrochemical Urea production from Nitrate and CO_2

A supplementary study has been conducted throughout the thesis work, in which it has been explored the electrochemical co-reduction of nitrogen oxides and CO_2 toward urea formation, an attractive molecule for fertilizers. In this case, the development and validation of a reliable colorimetric assay has been addressed, to push the standardization of valid detection assays for urea through electrolysis. Different colorimetric methods used in literature have been studied, confirming that colorimetric assays (classic Diacetyl Monoxime method, DAMO) report apparent urea concentrations that are not supported by structural methods (urease-based enzymatic assay and NMR spectroscopy).

From a catalytic perspective, precise control of the cathodic potential is essential to manage competing processes such as hydrogen evolution, nitrite accumulation, and C–N coupling kinetics.