

## Solar-driven CO<sub>2</sub> electroreduction with direct-coupled PV-EC in realistic operating cycles

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#### Significance and Relevance

In this work we design, and test direct-coupled PV-EC device for converting  $CO_2$  into chemical products with emulated PV devices reproducing IV characteristics of real PV modules in the field at most relevant irradiance/temperature combinations with precision and accuracy on par with class A+ solar simulator [1]. The emulated PV of the PV-EC device can be adjusted to the required size of the lab scale EC cell used for  $CO_2$  electroreduction. PV emulation offers stable operation of the PV-EC system over diurnal cycles allowing to establish correlation between performance, coupling factor and solar-to-fuel efficiency. This is of importance for future improvements of the electrical design of such systems and their performance in realistic cycles.

Preferred and 2<sup>nd</sup> choice for the topic: Photocatalysis and photoelectrocatalytic approaches, solar energy utilization

# Preferred presentation: (Oral only)

### Introduction and Motivations

The rising levels of  $CO_2$  in the atmosphere require the development of novel approaches to carbon management. Moreover, the installed capacity of photovoltaic (PV) systems is expanding at a considerable rate, resulting in a significant discrepancy between the generation of electricity from PV sources and the actual demand for electricity. The long-term storage of energy in molecules such as fuels or other industrially useful chemicals is of particular significance in counterbalancing the seasonal variations in photovoltaic power generation. The direct-coupled photovoltaic-electrochemical (PV-EC) system addresses these issues by converting excess PV energy into chemicals prior to feeding it to the grid. This enhances the utilization of photovoltaic power and improves grid stability.

### **Materials and Methods**

In this study, we have designed and tested a direct-coupled photovoltaic (PV) electrocatalytic (EC) device for the conversion of carbon dioxide (CO<sub>2</sub>) into carbon monoxide (CO) and hydrogen (H<sub>2</sub>) (see Figure 1). The device employs emulated PV that reproduces the IV characteristics of real PV modules in the field at the most relevant irradiance and temperature combinations (Figure 1(a)). The characteristic operating points of the PV-EC were obtained using the NREL public database for silicon heterojunction (SHJ) modules installed in specific regions of the USA. The newly developed PV emulator routine enables the precise and accurate reproduction of any IV characteristic of a PV module, at a level comparable to that of a Class A+ solar simulator [2]. In our study, a SHJ module with an emulated area of 44.5cm<sup>2</sup> drives a flow-type stack EC cell (area  $9.5cm^2$ ) with a silver/gas diffusion layer (GDL) cathode [3] and an iridium oxide anode (see Figure 1(b)).

### **Results and Discussion**

The operation of the PV-EC system was evaluated under dynamic conditions, represented by three sunny days in a cycling procedure. This procedure involved eleven steps of irradiance-temperature pairs, ranging from 0.2 Sun to 1.1 Sun and 20°C to 54°C, followed by idle 'night' periods (see Figure 2(a)). The operating voltages achieved were in the range of 2.4 to 3.2V, while the operating currents were between 70 and 335mA corresponding to current densities of 7.4 to 35.2mA/cm<sup>2</sup> (see Figure 2(b)). The solar-to-chemical efficiency was observed to range between 8.7 and 10.8% at a high degree of coupling (0.85 to 1) in the absence of power electronics. Finally, a consistent and stable dynamic operation towards CO as the primary product with 75% faradaic efficiency and H<sub>2</sub> (25%) as a by-product over one to three-day cycles was demonstrated. This coupling, in conjunction with the high selectivity



towards CO, renders the approach an attractive one for the decentralized storage of excess PV energy, offering a material-saving route.



**Figure 1** (a) PV emulation is realized with a custom PYTHON script controlling a standard source measure unit (SMU), whereby the emulator program takes the IV characteristics of the PV device of interest and controls the SMU output to reproduce the behavior of the PV device at the terminals of the SMU. (b) An EC cell with a gas chamber next to Ag/GDL electrode and 2 electrode chambers separated by a cation exchange membrane CEM (Nafion N117, thickness 0.007 inch) and a 1M KHCO3 electrolyte saturated with CO<sub>2</sub> (20 cm<sup>3</sup>min<sup>-1</sup>) flowing in both chambers. Both devices are in direct connection without power electronics in between.



**Figure 2** (a) Time profile of a summer day realized on shorter timescale with 16 hours of real time emulated in 5 hours of experiment. (b) Voltage, current, coupling factor, Faradaic efficiency and solar-to-chemical efficiency of the PV-EC investigated over 5 hours of dynamic operation.

### References

- 1. T. Cibaka et al., Energy Env. Sci., 2024 submitted.
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- 3. G. Liu et al., Chemical Engineering Journal 2023, 40, 141757.

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