

Influence of the electrochemical cell configuration over the stability of tunable and stable production of syngas for efficient coupling with hydroformylation reaction.

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1. Introduction

In this study, the electrochemical reduction of carbon dioxide (eCO₂RR) to syngas is investigated through optimization in three distinct **electrochemical configurations**. Notably, the study demonstrates the effectiveness of **tuning syngas selectivity** by varying reactor configurations. This is essential for integrating eCO₂RR with other industrially relevant processes for sustainable resource conversion as hydroformylation. The **coupling** of carbon dioxide reduction with organic molecule synthesis holds paramount significance in tackling critical challenges [1]. Firstly, it serves as a strategic tool in the fight against climate change by harnessing CO₂, a major greenhouse gas, and converting it into valuable organic compounds. This not only reduces net CO₂ emissions but also transforms CO₂ into feedstock for industries, adding economic value. Moreover, it aligns with the circular carbon economy concept, reintegrating CO₂ into industrial processes, creating a closed-loop system, and decreasing environmental impact while lowering fossil resource dependency. Additionally, the diverse range of products obtained through CO₂ reduction, from biofuels to specialty chemicals, promotes a sustainable and resilient economy [2]. This study endeavors to elucidate the mechanisms and processes promoting selectivity towards the desired product while investigating the influence of the reactor configuration on these aspects.

2. Methods

The **eCO₂RR to syngas** was optimized in three main electrochemical configurations: a single compartment electrochemical cell and a h-type cell equipped with an anionic membrane (AEM) and a bipolar membrane (BPM). For what concerns the electrodes, an Ag foil was employed as working electrode in an ionic liquid based 3-methoxypropionitrile (3-MPN) solution and water as proton source for H₂ evolution reaction (HER); a Pt foil has been employed as counter electrode. The gaseous products were collected and quantified using an online micro-gas chromatograph. Electrochemical characterizations have been carried out by means of conductivity, electrochemical impedance spectroscopy (EIS) and ECSA measurements. Electrochemical CO₂ reduction tests at constant current densities (chronopotentiometry) were conducted to produce syngas. To get mechanistic insights on the eCO₂RR process, a multi-physics model was implemented based on the experimental data. Physical characterization of the electrode and electrolyte has been investigated *via* XPS spectroscopy.

3. Results and discussion

To produce a stable and tunable syngas stream from CO₂ a single compartment electrochemical cell was employed. However, with this configuration, the HER takes advantage over the eCO₂RR in a minute's time scale, changing the selectivity of the system dramatically. When a H-type cell equipped with a AEM is employed, a stable stream of syngas is produced with a long-term stability over a period of several hours. Different behavior is seen when the same cell is equipped with a BPM. The protons generated by the water dissociation process at the interface of the BPM in fact provide a higher amount of protons to the cathode. The reduction of these protons requires a lower overpotential compared to CO₂ reduction, yet with a higher diffusion coefficient. Engineering of the electrolyte also permits the fine tuning of the syngas composition at the outlet of the **electrochemical reactor** in terms of CO/H₂ ratio. Moreover, to get mechanistic insights on the eCO₂RR process, a multi-physics model was implemented based on the experimental data, demonstrating a strong correlation with the observed

trends. This is pivotal for the effective integration of the process with other industrially relevant thermocatalytic reactions as the hydroformylation.

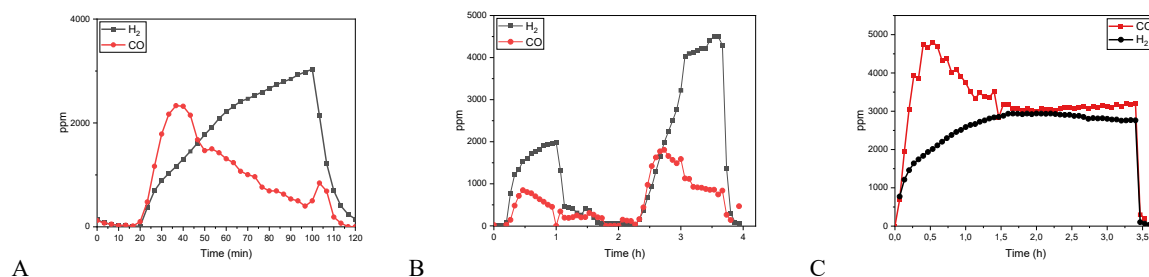


Figure 1. Different selectivity of the system using three different configurations. A) Single compartment electrochemical reactor; B) H-type cell equipped with BPM; C) H-type cell equipped with AEM.

4. Conclusions

The results exposed address the challenge of enlighten the mechanisms and processes that foster selectivity toward the desired product, as well as examining how the reactor configuration can influence these aspects. The electrochemical reactor set-up has been demonstrated to be dramatically effective in tuning the selectivity of CO₂ reduction to syngas and other valuable products. Changing the configuration from a single cell reactor to a double compartment cell, and choosing the appropriate membrane permit a stable and tunable production of syngas. It comes easier to think about an integrated process able to couple the electrochemical reduction of CO₂ with other industrially relevant reactions as hydroformylation and carbonylation. The coupling of these processes is crucial for **sustainability**, enabling the conversion of **waste materials** into valuable resources, in harmony with environmental responsibility and a sustainable future.

References

- [1] Figueiredo, M. C., Trieu, V. & Koper, M. T. M.. ACS Sustain Chem Eng 7, 10716–10723 (2019).
- [2] Zhang, B., Peña Fuentes, D. & Börner, A. ChemTexts 8, (2022).

Keywords

Integrated process; electrochemical reactor; eCO₂RR; syngas.