

STRATEGIES AND PROBLEMS DURING CO₂ ELECTROCHEMICAL REDUCTION EXPERIMENTS

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Goal: Main requirements for performing robust, reproducible experiments in order to help elucidate structure-activity relationships toward advancing catalyst design!

ABSTRACT:

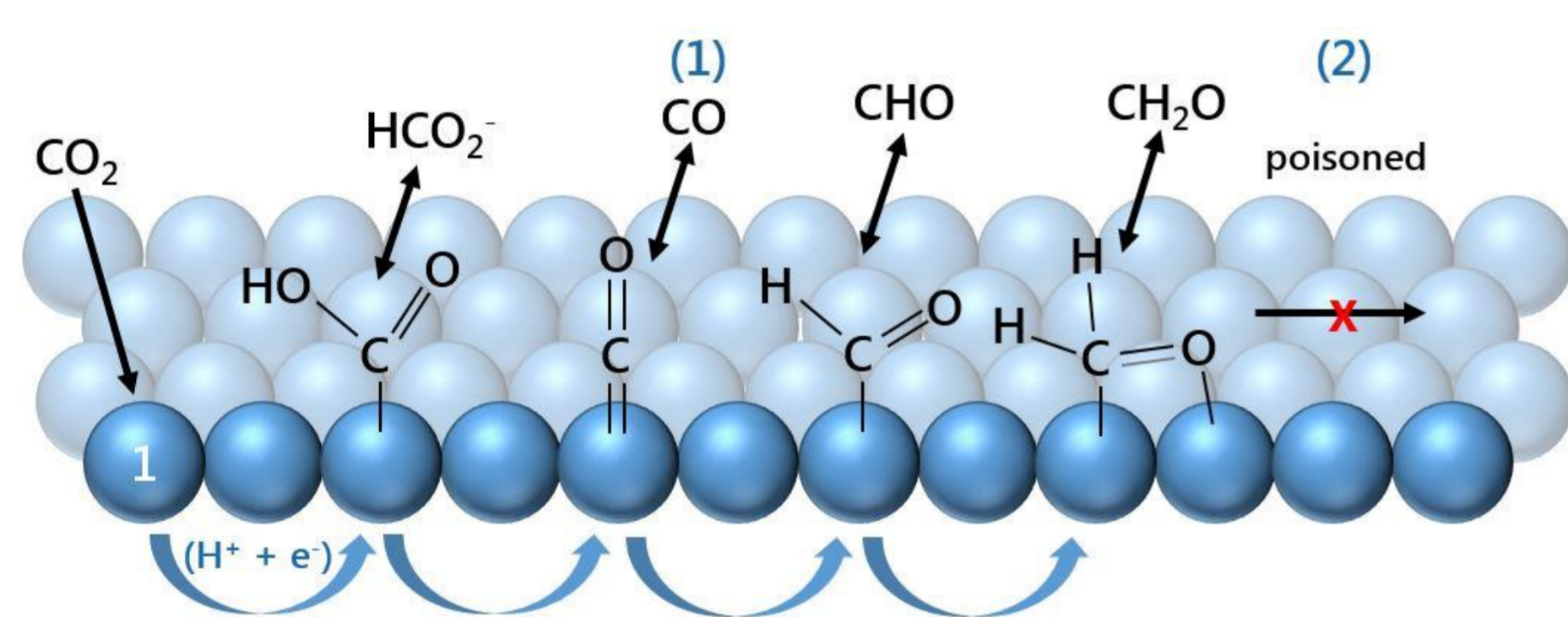
With the global consensus that anthropogenic CO₂ emissions are dangerous and should be mitigated, utilizing CO₂ as feedstock for synthesis of chemicals and fuels represents an important strategy. A promising approach is to electrochemically reduce CO₂ into value-added products such as carbon monoxide, formate/formic acid, alcohols, aldehydes and hydrocarbons, using renewable electricity to drive electrocatalysts that will mediate this reduction efficiently and selectively.

The first electrochemical reduction of CO₂ was introduced back in the 19th century (when only CO was detected as a product), but it became more popularized in the 1980s of the 20th century as a consequence of the great oil crisis and the awareness of global warming in the 1970s. The number of publications in this topic is rapidly

increasing every year, but experimental methods and data representation frequently differ from publication to publication, potentially leading to confusion and misunderstanding.

There are several important parameters and conditions that should be standard issue in every publication. These parameters include [1]: Onset potential for the corresponding electrocatalyst, Faradaic Efficiency for each product, partial current for each product, stability (durability) and turnover number of the used electrocatalyst, and furthermore the experimental conditions in terms of the: purity of the used chemicals, purity of the carbon dioxide, electrolyte preparation, etc.

General electrochemical CO₂ reduction mechanism:



Reduction potentials of CO ₂	E* (V) vs SHE at pH = 7 [2]
CO ₂ + e ⁻ → CO ₂ ⁻	-1.90
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.61
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	-0.52
2CO ₂ + 12H ⁺ + 12e ⁻ → C ₂ H ₄ + 4H ₂ O	-0.34
CO ₂ + 4H ⁺ + 4e ⁻ → HCHO + H ₂ O	-0.51
CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH + H ₂ O	-0.38
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O	-0.24
2H ⁺ + 2e ⁻ → H ₂	-0.42

CONCLUSION

- Careful design of the electrochemical experiment including the cell and all of the connections;
- Usage of chemicals with the highest possible purity;
- Compulsory performance of control experiments (substrate testing, isotopic labeling, analysis at multiple points, performing experiments by purging inert gases like Ar or N₂, comparison of the Faradaic efficiencies of the newly developed catalysts with the known ones like Cu, Au, Ag, Pt...);
- Clearly stating how the electrode surface area was measured (*j_{geom.}* vs. *j_{ECSA}*);
- The total Faradaic efficiency of the products should add up to 100% (if not: possibility of non-quantified products, competitive non-Faradaic reactions...);
- Measuring the stability (durability) of the electrocatalyst;
- Application of as much as possible *in situ* methods for both product and catalyst characterization

ELECTROLYTES:

- Aqueous vs. non-aqueous electrolytes.
- Influence from trace impurities like trace metals that can catalyse CO₂ER (Purification using electrolysis or chelating agents like EDTA, Chelex...[1, 3])

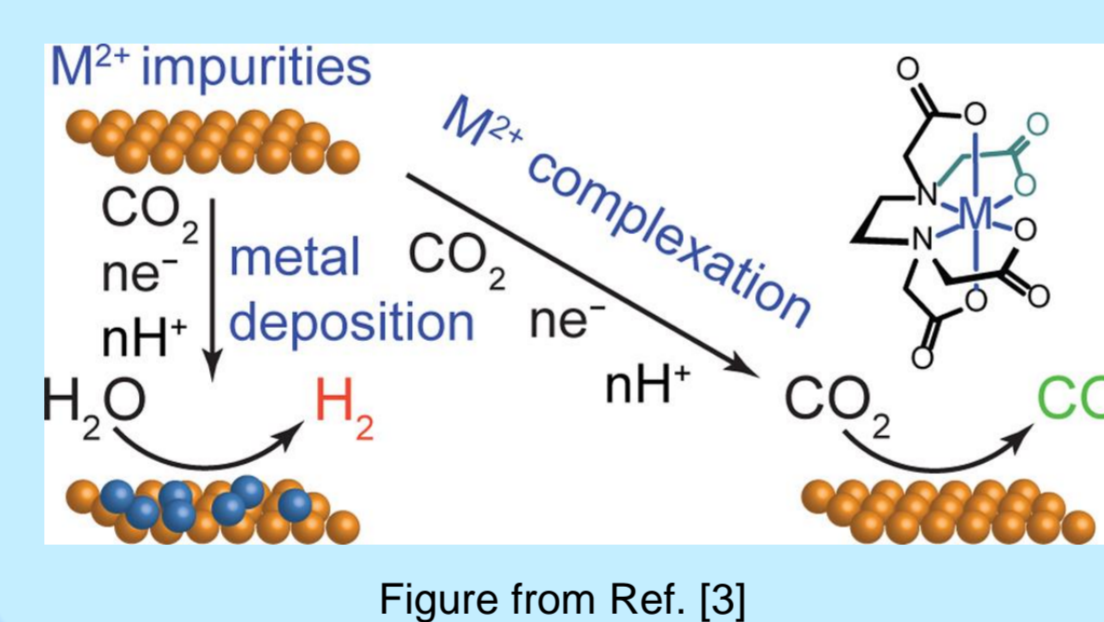
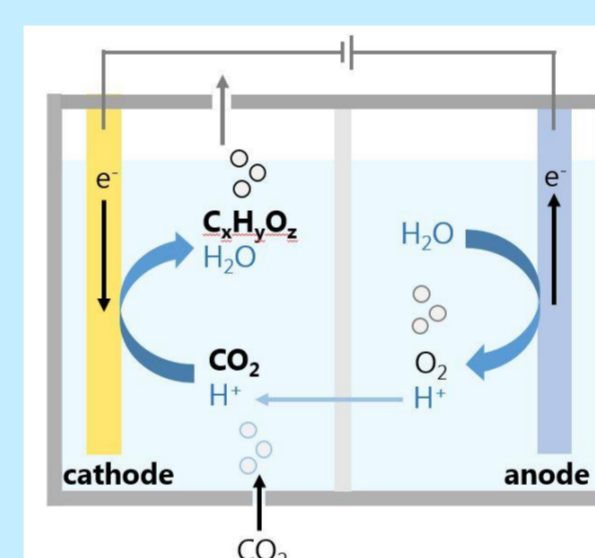


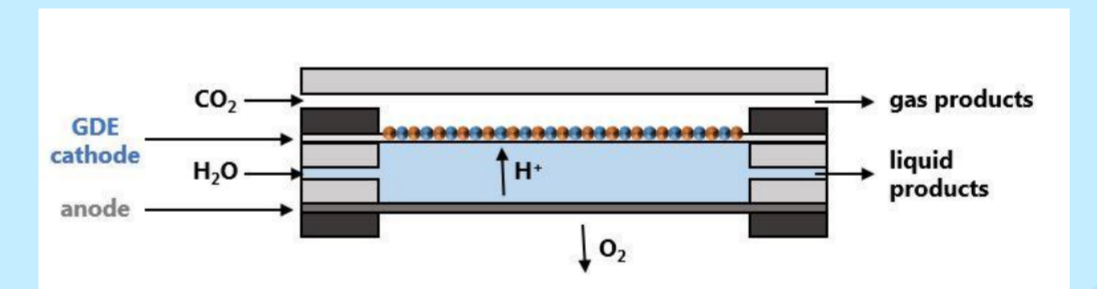
Figure from Ref. [3]

ELECTROCHEMICAL CELL DESIGN:

- (a) Gas flow cell (more applicable for thin film electrodes)



- (b) Cell with gas diffusion electrode (more applicable for porous catalysts)



CONTROL EXPERIMENTS:

- Per se* catalysis by the substrate (especially if contaminated with trace metals [4])
- Isotopic labeling with ¹³C - "golden standard" [5] (will prove or disprove whether the products are generated by CO₂ER)
- CO₂/HCO₃⁻ equilibrium [6, 7]

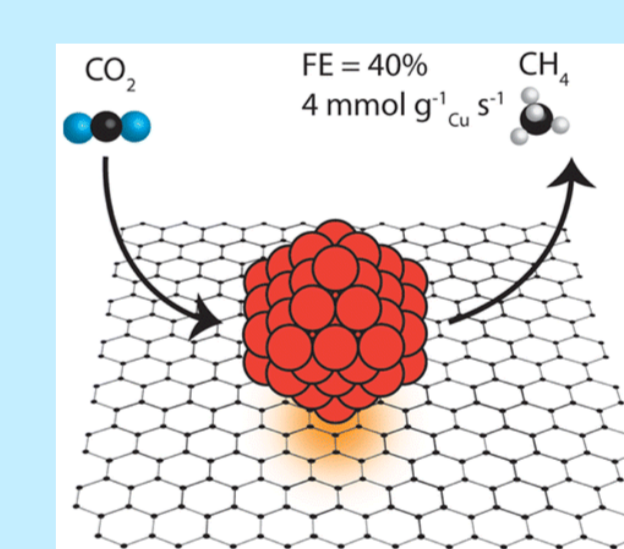


Figure from Ref. [4]

STABILITY/DURABILITY OF THE CATALYSTS DURING THE CO₂ER EXPERIMENT:

- In theory the catalyst should not be consumed, in practice it is!
- The stability of the catalyst during time can be quantified by expressing the turnover number TON.
- The chemical analysis of the electrolyte pre- and post- CO₂ER experiment can give significant information about the catalyst stability.

CO₂ ELECTROCHEMICAL REDUCTION

Strategies and problems during the experiment design

CO₂ GAS PURITY:

99.999 vs. <99.999% [1]
Important or not?

RELEVANT ANALYTICAL METHODS [1]:

- Analysis of the catalyst (*Ex situ*: before and after the CO₂ER experiment; *In situ*: real time tracking of any change in composition, structure, morphology...).
- CO₂ER products analysis (analysis of gaseous and liquid products)



KEY REFERENCES

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