STRATEGIES AND PROBLEMS DURING CO₂ ELECTROCHEMICAL REDUCTION EXPERIMENTS

Sasho Stojkovikj, Matthew T. Mayer

Young Investigator Group: Electrochemical Conversion of Carbon Dioxide (EE-NECC), Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Lise-Meitner-Campus in Wannsee, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

**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 as a consequence of the great oil crisis and 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:**

**ELECTROLYTES:**
- Aqueous vs. non-aqueous electrolytes.
- Influence from trace impurities like trace metals that can catalyse CO₂/ER (Purification using electrolysis or chelating agents like EDTA, Chelex... [1, 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 labelling with ¹³C - “golden standard” [5] (will prove or disprove whether the products are generated by CO₂/ER).
- CO₂/HCOO⁻ equilibrium [6, 7].

**STABILITY/DURABILITY OF THE CATALYSTS DURING THE CO₂/ER 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-CO₂/ER experiment can give significant information about the catalyst stability.

**CO₂ GAS PURITY:**
99.999 vs. >99.999% [1] Important or not?

**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...;
- Clearly stating how the electrode surface area was measured (Imp meas. vs. Imp theo);
- 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.

**KEY REFERENCES:**

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**MORE INFORMATION:**
Sasho Stojkovikj, PhD Student, EE-NECC
Tel.: +49 (0)30 8062 - 45613
E-mail: sasho.stojkovikj@helmholtz-berlin.de

Dr. Matthew T. Mayer, EE-NECC Group Leader
Tel.: +49 (0)30 8062 - 43232
E-mail: matthew.mayer@helmholtz-berlin.de

https://www.helmholtz-berlin.de/for-sucht/science/ee-neecc/index_de.html