Electrochemical setup for online FTIR and Differential Electrochemical Mass Spectrometry studies of CO₂-electroreduction on model metal surfaces

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Carbon dioxide is a major contributor to global warming and, beyond the mandatory reduction of our emissions, the possibility of recycling this greenhouse gas is becoming increasingly attractive. The electrochemical reduction of CO₂ is an interesting pathway since a broad range of useful products can be formed such as methanol and formic acid (fuels for PEMFC), methane and ethylene (reactants for synthesis or combustion process). CO and H₂ (syngas) etc. [1]. Nevertheless, on top of the high overpotential required to drive this reaction, the electrochemical reduction of CO₂ suffers from a poor yield/selectivity of valuable products [2, 3]. In order to overcome these two barriers, a better fundamental understanding of this reaction is urgently needed. For this purpose, we have designed a Differential Electrochemical Mass Spectrometry (DEMS) setup coupled with an electrochemical flow cell that allows the in-operando quantification of the volatile species produced in the course of the reaction. The behavior of copper, gold and platinum single-/poly-crystalline electrodes toward the CO₂ electrochemical reduction will be studied in order to better understand the origin of the different selective formation of specific products on these materials.

**Custom-made DEMS setup**

**Electrochemical cell**

DEMS Measurements can be done either with a standard three-electrode electrochemical cell (not shown here) or a dual thin-layer flow cell.

**Electrolyte flow path**

- Design adapted from Jusys et al. work [5]
- A syringe pump injects the electrolyte through FEP tubes.
- Common flow rate range: 0.5 – 1.5 mL/min
- The tubes are plugged in the flow distributor (Fig. 2)
- Electrolyte flows through upper and lower compartments via capillaries
- The volatile products cross through the porous membrane -> MS

**Preliminary results**

Electrochemical measurements were done using chronoamperometry coupled with mass spectrometry.

- **Experimental conditions:**
  - WE: Polycrystalline Cu disk
  - RE: Hg/HgSO₄
  - CE: Pt-mesh
  - Electrolyte: CO₂ sat. 0.1M KHCO₃
  - Potential steps (a):
  - starting at -0.51 V/RHE
  - steps of -0.05V, holding potential for 5 min
  - back to -0.51V/RHE for 5 min between each step

- Hydrogen evolution reaction clearly identified (b)
- Correlation between potential steps and increase of methane signal (c)
- CO₂ signal decreases during potential steps and increases during potential rests (d)

**Conclusions and outlooks**

The preliminary results of this work show the production and the detection of hydrocarbons from the electroreduction of CO₂ with a DEMS setup. The results have been obtained with a Cu polycrystalline electrode. Further studies will be done using different electrolytes, different pH conditions and single crystal electrodes. Moreover, the setup is adapted to FTIR characterization and the technique will be used in a future work for the identification of adsorbed species on electrode surface. Improvements on both the flow cell and the three-electrode cell setups are ongoing to maximize the reliability of the results.

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**References**