



SECM and spectroscopic investigation of unwanted activity changes of metal electrodes observed during electrochemical CO₂ reduction

Researcher's Name

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Introduction

It is getting generally accepted that present level carbon dioxide emission can result in serious changes of the climate of our planet. Unfortunately the alternative zero CO₂ emission sources can provide only fractions of the energy needed. Therefore the complete replacement of the thermoelectric power plants in the near future has no reality. Another solution for this global problem can be the "recirculation" of the CO₂, the unwanted byproduct of energy production.

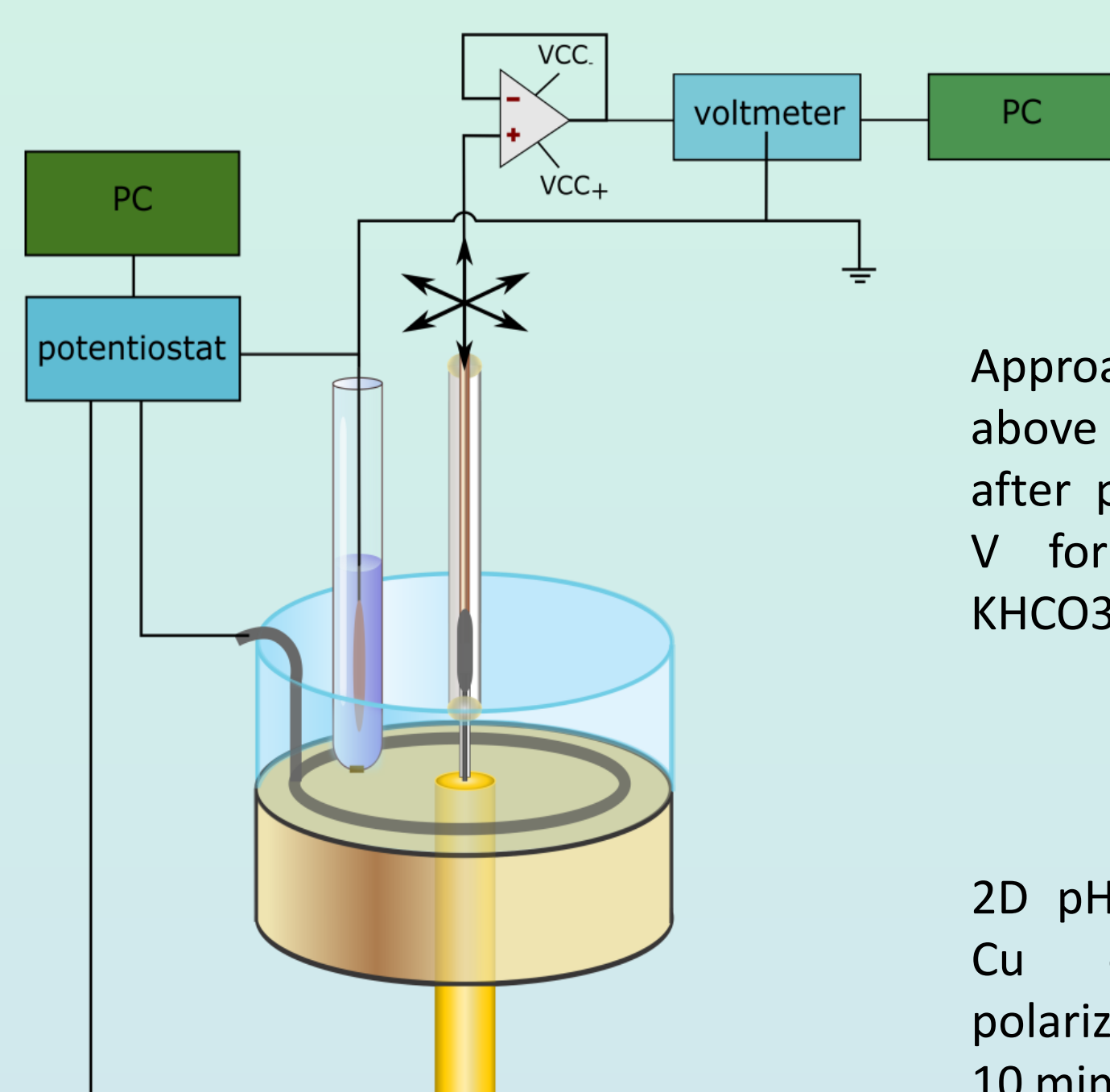
In this work, electrochemical reduction experiments are carried out in homemade cells supplied different metal electrodes. Electrolytes containing carbon dioxide absorbing components like monoethanolamine (MEA) or KHCO₃, KOH, and K₂CO₃ solutions are used.

Parallel to the electrochemical measurements the metal components originated from the possible degradation of the electrodematerials in the electrolyte were checked with atomic absorption methods for getting better insight to the nature of the electrode passivation.

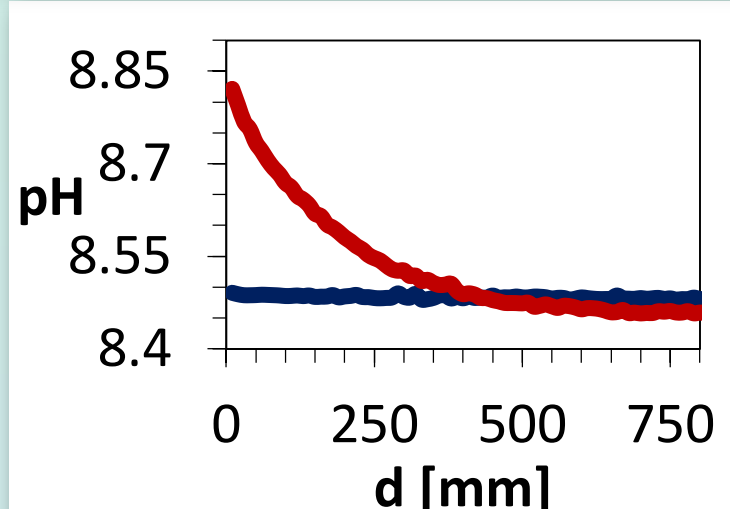
This contribution attempts to compare the behavior of different electrode materials (copper, nickel and their alloys) in CO₂ capturing media, and investigate of the products of the electrolysis using Scanning Electrochemical Microscopy (SECM), Atomic Absorption Spectroscopy (AAS) and other spectroscopic techniques.

SECM detection of product formation

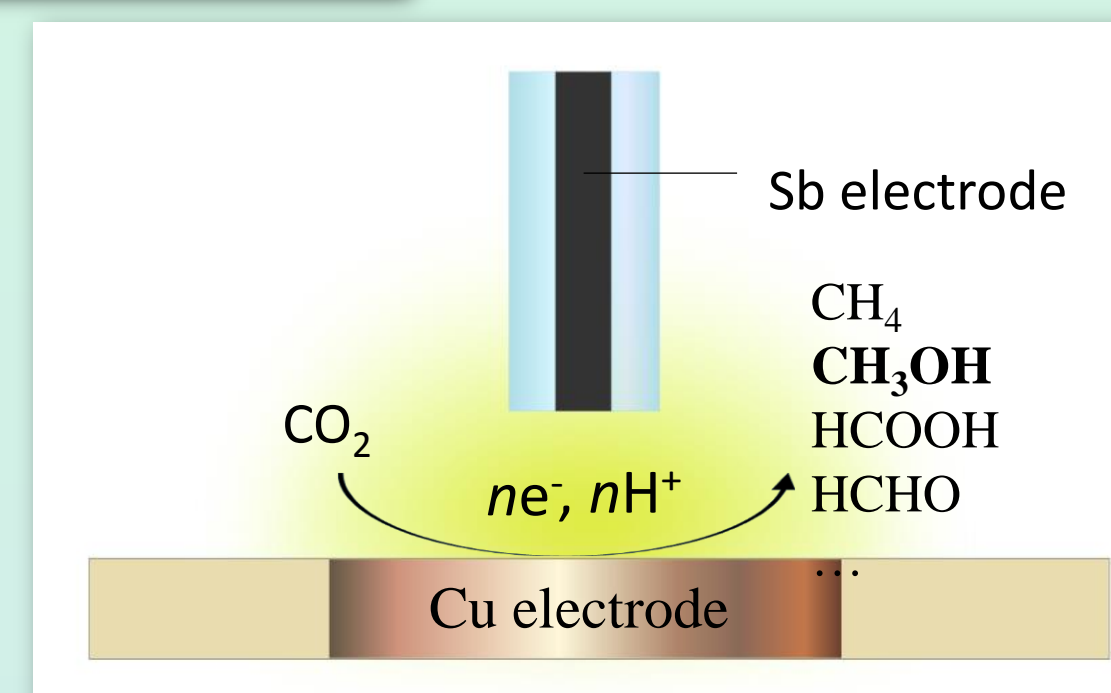
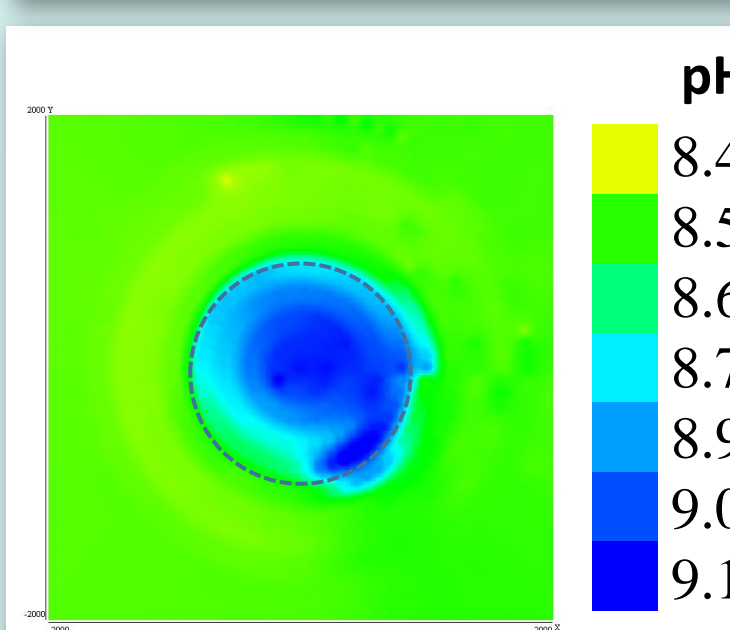
The local changes of the electrode where the conversion takes place can be monitored SECM with high resolution and sensitivity



Approaching pH curves above the Cu electrode after polarization at -0.5 V for 10 minutes in KHCO₃



2D pH scan above the Cu electrode after polarization at -0.5 V for 10 minutes



AAS measurements

The copper content of the electrolytes were measured with PerkinElmer PinAAcle 900T atomic absorption analysis at $\lambda=324.75$ nm, using acetylene-air flame (air 10 L/min, acetylene 2.5 L/min). The calibration was linear in the 0 - 5 ppm concentration range: $y=0.0664x+0.0006$ ($R^2=0.9991$).

Table 1. Measured Cu in different electrolytes CO₂ absorbed for 3 minute purging

Electrolyte	Basic solution/ppm	After CV/ppm	After CV and Absorbed CO ₂ /ppm
KOH	Under LML	1.345	3.554
KOH + KCl	Under LML	1.117	2.981
KHCO ₃	Under LML	0.065	0.073
Na ₂ CO ₃	Under LML	0.022	0.031
30% MEA	Under LML	6.769	11.778

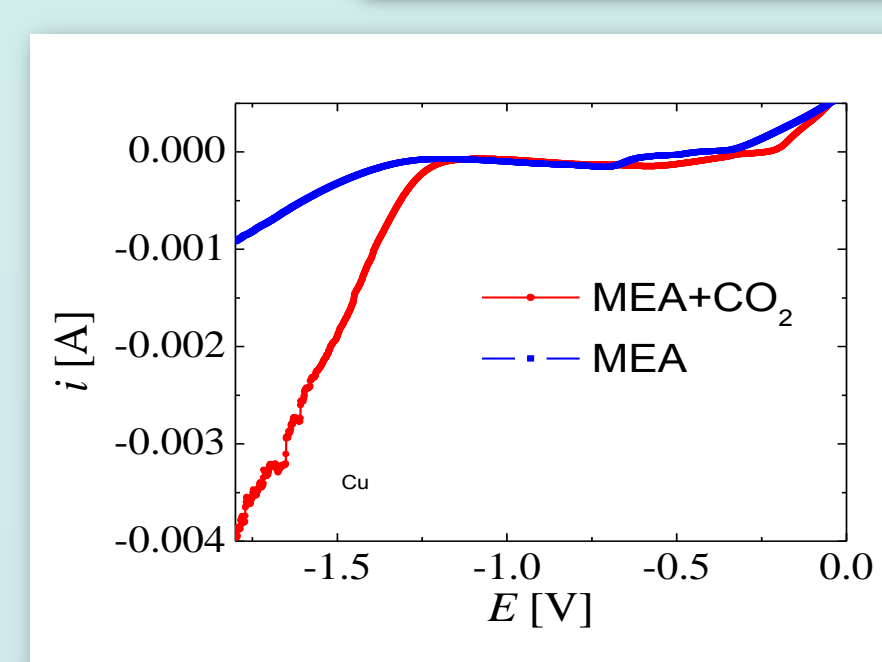
The data of Table 1. indicate the more absorbed CO₂ content of the electrolyte the bigger is the Cu content of the electrolyte. The KHCO₃ and Na₂CO₃ electrolytes absorb the less CO₂ amount. Considerable good absorbents are the 0.1 M KOH and 0.1 M KOH + 0.1M KCl solutions beside the 30% MEA.

Table 2. Measured Cu in 30% MEA

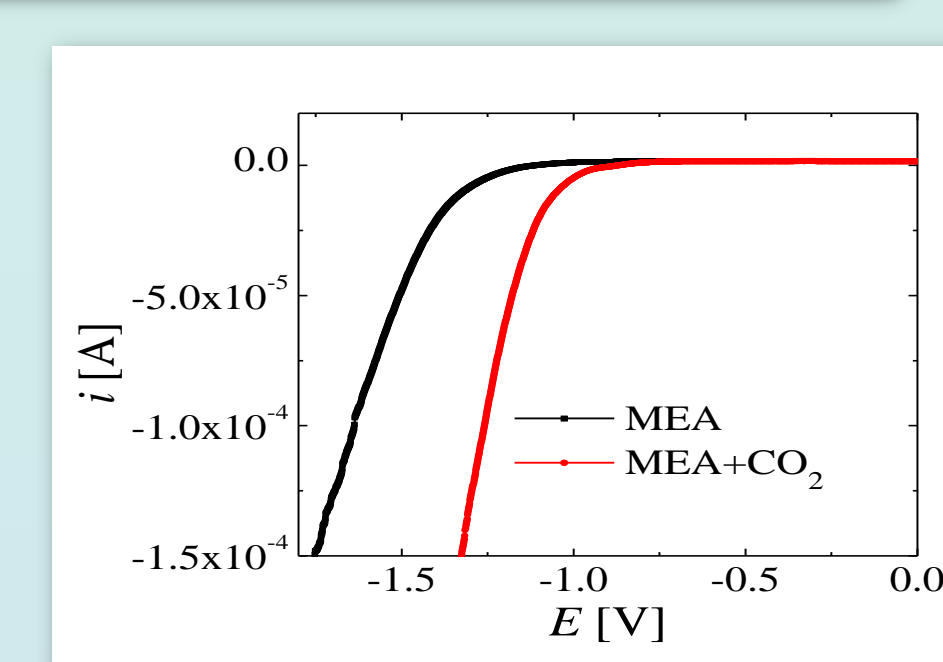
Absorbed CO ₂ mg	AAS measured Cu/ppm	Corrosion factor
0	0.202	-
100	2.837	0.142
170	4.136	0.122
400	8.489	0.106
507	12.553	0.125

The corrosion factor (AAS measured mg Cu/mgCO₂ in 5 ml electrolyte) is determined in 30 % MEA depending on the CO₂ content. It can be said that above 170 mg absorbed CO₂/5 ml MEA the corrosion factor can be regarded independent of the absorbed amount of CO₂. This feature of the system is promising considering the perspective industrial applications of the electrochemical reduction of CO₂ in MEA.

Cathodic polarization curves of Ni and Cu electrodes



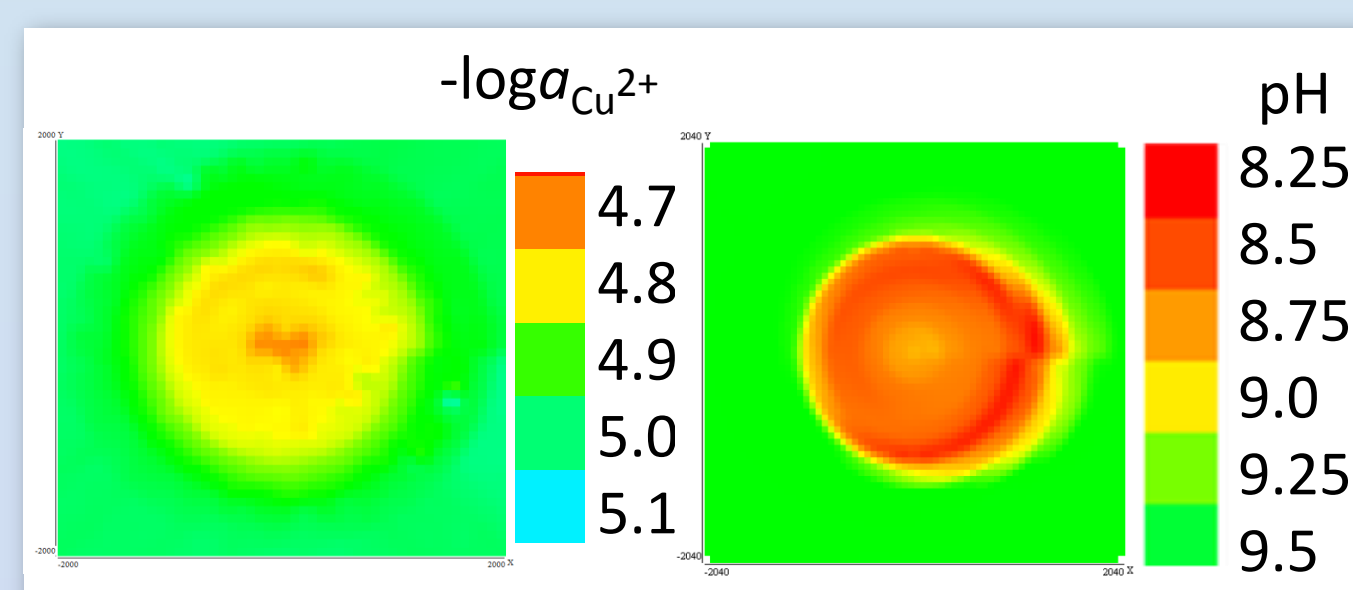
Cathodic polarization curves of the copper electrode in 30% MEA solution



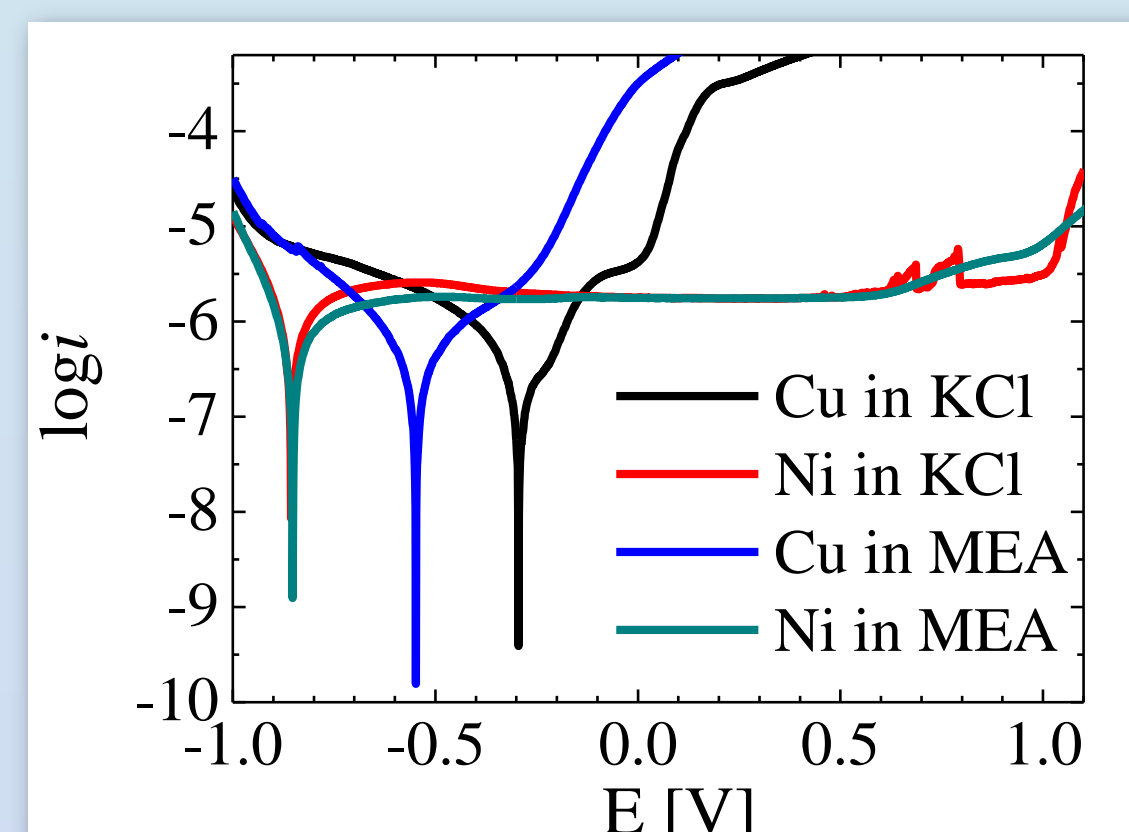
Cathodic polarization curves of the nickel electrode in 30% MEA solution black: pure solution, red: saturated with CO₂

Corrosion study of Ni and Cu electrodes

One of the most often used CO₂ capture absorbent in industrial scale is the aqueous solution of monoethanolamine (MEA)

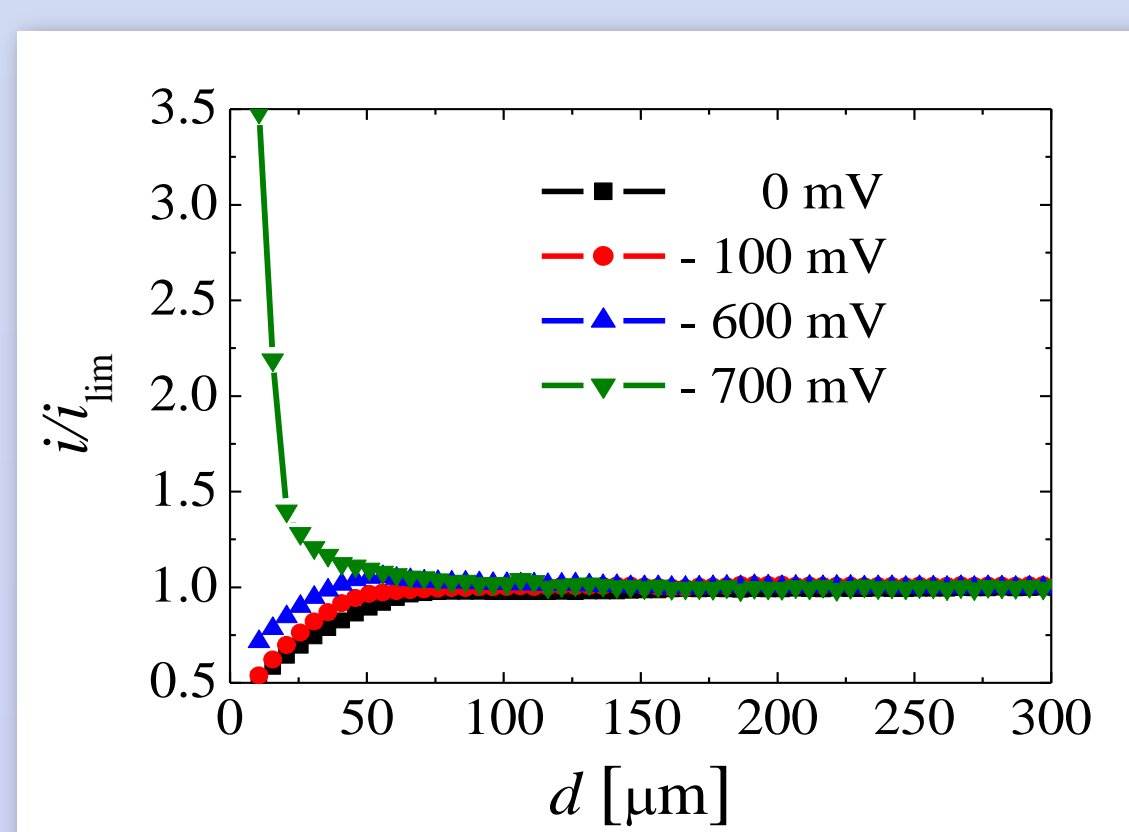
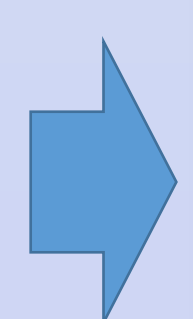


Distribution of Cu²⁺ (A) and pH (B) above the copper electrode measured with Cu²⁺ ISME and antimony microelectrodes after 30 minute exposure to 30% MEA solution.

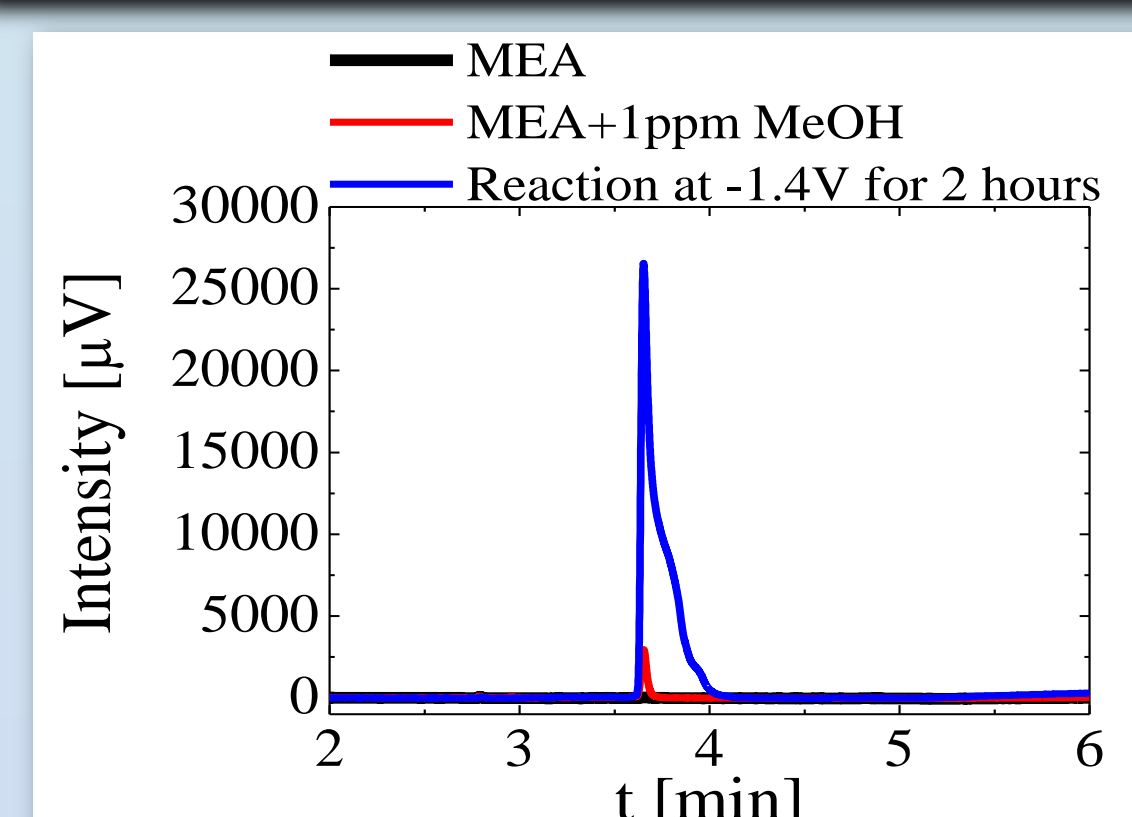


Tafel plot of Cu and Ni electrodes in different electrolytes

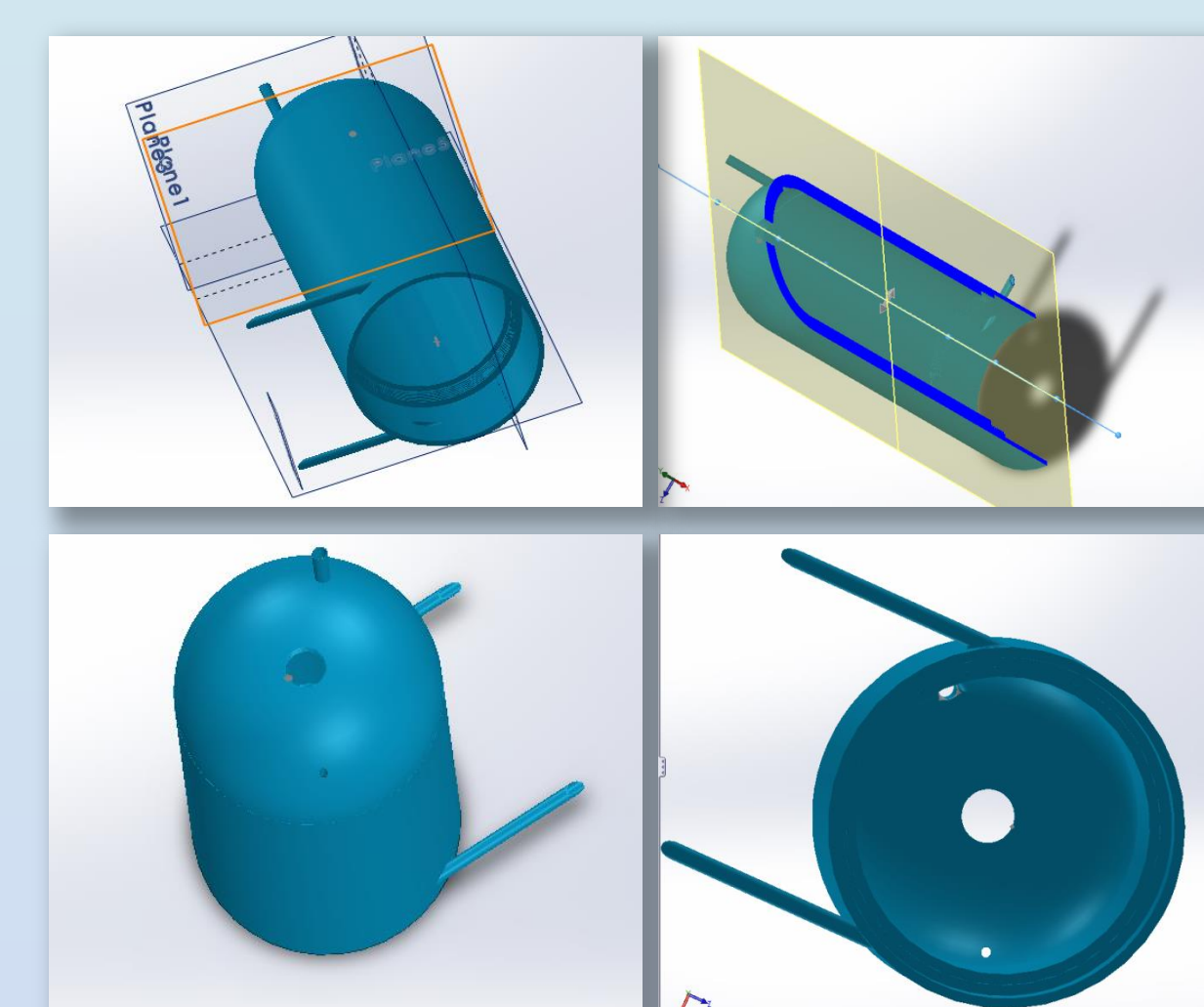
Vertical approaching curves with amperometric SECM. The tip was 25 μ m Pt, the sample is nickel in 30% MEA 0.1 M KCl, 1.25 mM Ferrocenemethanol. The Nickel specimen was polarized at different potentials whereas the tip was approaching its surface. The probe was biased at 600 mV.



Detection of products with gas chromatography



Detection of methanol in the reaction medium



Novel reactor facilitates to collect the gaseous products

Conclusions

The conversion of carbon-dioxide to reusable fuel is one of the greatest challenges of the century. The electrochemical CO₂ reduction has the advantage of the possibility to carry out the conversion in the capturing media broad-scale used in thermoelectric industries. In order to achieve efficient conversion, the selection of suitable electrode material electrode materials is crucial. Nickel and copper have catalytic effect on CO₂ reduction and their applicability in different media is tested with conventional electrochemical methods, SECM and AAS techniques. The detection of the products of the reduction can be performed with SECM and gas chromatography. The new reactor presented enhances the collection of gaseous and dissolved products for analysis.