

JKU
JOHANNES KEPLER
UNIVERSITY LINZ

Investigations of Polypyrrole based electrodes towards electrochemical reduction of CO₂

BACHELOR THESIS

to obtain the academic degree
Bachelor of Science (BSc.)

in the Bachelor program
Technical Chemistry

Author:

Dominik Wielend

Prepared at the:

Institute of Physical Chemistry - Linz Institute for Organic Solar Cells (LIOS)

Thesis supervisor:

o.Univ. Prof. Mag. Dr. DDr. h.c. Niyazi Serdar Sariciftci

Guidance:

Dogukan Hazar Apaydin MSc

Linz, June 2015

Abstract

Copper(I)oxide (Cu_2O) is known as catalyst towards electrochemical reducing of CO_2 to methanol. This work aims on depositing Cu_2O onto polypyrrole substrates and furthermore investigate their ability to CO_2 reduction.

For this purpose pyrrole was polymerised electrochemically and finalised by electrodeposition of copper and copper(I)oxide.

The electrochemical investigations are proceeded in an H-cell using 0.5 M KHCO_3 as electrolyte solution under nitrogen- and CO_2 -purged conditions. Determination of reduction products is proceeded using liquid and gas injection gas chromatography.

Statement of Authorship

I hereby confirm that this bachelor thesis was written autonomously by me and without foreign help. All the used references are cited in the bibliography in all conscience.

Linz, 22th of June 2015

Dominik Wielend

Table of Content

Abstract.....	i
Statement of Authorship.....	ii
Table of Content.....	iii
1. Introduction.....	1
2. Theoretical background.....	2
2.1 CO ₂ Reduction.....	2
2.2 Polypyrrole.....	3
2.2.1 Synthesis.....	4
2.2.2 Properties.....	4
2.3 CO ₂ reduction on Cu ₂ O surfaces.....	5
2.4 Copper deposition.....	7
3. Experimental Section.....	8
3.1 Copper plate with deposited Cu ₂ O.....	9
3.2 Polypyrrole on glassy carbon.....	13
3.3 Polypyrrole Film.....	19
3.3.1 Preparation of the polypyrrole film.....	19
3.3.2 Characterization of the polypyrrole film.....	21
3.3.3 Characterization of <i>PPy</i> /Cu/Cu ₂ O.....	24
4. Comparison of results.....	27
5. Conclusion.....	29
6. Bibliography.....	31
7. Acknowledgements.....	34

1. Introduction

Greenhouse effect is a well-known fact of today's world. The most prominent example for such greenhouse gas is carbon dioxide (CO₂). Nevertheless many more exist and methane (CH₄), nitrous oxide (N₂O), ozone (O₃), water (H₂O) and hydrofluorocarbons (HCFC) should also be mentioned.

Solomon et. al.^[1] stated that the amount of CO₂ in the atmosphere has increased since the beginning of industrialisation at 1750 until 2005 from 280 ppm to 379 ppm reaching up to 400 ppm level of a monthly global average value as of March 2015.^[2]

In this technical summary they also explain the consequences of this increasing amount of greenhouse gases like increased temperature on earth due to reflection of radiation and climate changes, which are not the aim of this work in greater detail.

For a scientific view on this topic the radiative efficiency of CO₂, CH₄ and N₂O is considered. When considering the effect over a period of 100 years, the radiative efficiency of CH₄ is 25 fold the value of CO₂ and N₂O even has the 300 fold effect.^[1]

Also taking water into account, Kiehl and Trenberth^[3] state that water is contributing in a greater part towards greenhouse effects than CO₂. The exact values differ when comparing a clear sky with cloudy conditions.

So why investigations for reducing the concentration of CO₂ should be done? First of all antropogenic CO₂ is contributing to some part to the greenhouse effect. The main source for this combustion are fossil fuels like oil, gas or coal which are known to be limited in quantity. Therefore investigations towards carbon dioxide capture and sequestration (CCS) and carbon dioxide capture and utilisation (CCU) are made.

Considering the very low overall amount of CO₂ in atmosphere such strategies are more straightforward when combined directly with combustion plants. CCS is an attempt to reduce the CO₂ emission evolving from companies using combustion of fossil fuels via compressing, liquefying and storing CO₂ in, for example geological formations.^[4] Examples for industries where high CO₂ emission is occurring are cement industries and

refineries.^[5] Combination of CCS with CCU, which aims at generating fuels out of CO₂ is the final task in this topic.^[5] For this reason catalysts for reducing CO₂ are needed. A couple of CCS with CCU supplying sufficient efficiency for reducing CO₂ to a fuel would not only reduce the emission of greenhouse gases but could furthermore reduce the dependency on fossil fuels.

2. Theoretical background

2.1 CO₂ Reduction

As explained before, the aim of carbon dioxide utilisation is to generate fuels out of CO₂. Various possible reaction products exist, whose redox potentials are summed up in table 1.

Table 1: Thermodynamic redox potentials (formal) of some CO₂ reduction products (vs. NHE, at pH =7)^[6]

$CO_2 + e^- \rightarrow CO_2^-$	$E^{\circ} = -1.90 \text{ V}$
$2 CO_2 + e^- \rightarrow CO + CO_3^{2-}$	$E^{\circ} = -0.65 \text{ V}$
$CO_2 + 2 H^+ + 2 e^- \rightarrow HCOOH$	$E^{\circ} = -0.61 \text{ V}$
$CO_2 + 2 H^+ + 2 e^- \rightarrow CO + H_2O$	$E^{\circ} = -0.53 \text{ V}$
$CO_2 + 4 H^+ + 4 e^- \rightarrow HCHO + H_2O$	$E^{\circ} = -0.48 \text{ V}$
$CO_2 + 6 H^+ + 6 e^- \rightarrow CH_3OH + H_2O$	$E^{\circ} = -0.38 \text{ V}$
$CO_2 + 8 H^+ + 8 e^- \rightarrow CH_4 + 2 H_2O$	$E^{\circ} = -0.24 \text{ V}$

It can be clearly seen that the insertion of the first electron into CO₂ shows the highest energy barrier of -1.90 V. This can be explained by the fact that upon taking up one electron the linear geometry has to be changed to a bent one containing an O-C-O angle of 133°.^[7] A scheme of this reaction is shown in figure 1.

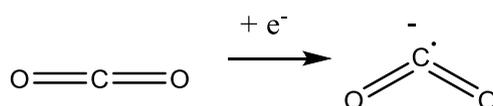


Figure 1: Scheme of a one electron CO₂ reduction

Following table 1, the reduction potentials for multi-election reductions are much lower. Nevertheless, the table only states the equilibrium potentials and not the real ones. Due to overpotentials on real electrodes the reduction potentials can be significantly higher.

In literature, the various mechanisms for reducing CO₂ to more energetically rich compounds are classified into the following three types: photochemical, electrochemical and the combination of those, photo-electrochemical reduction.

This thesis differs from the reducing materials from the previous research topic of the institute, reviewed from E. Portenkirchner et. al.^[6] They used rhenium and rhodium complexes for photo- and electrochemical reduction. In my case polymer films with deposited copper compounds as islands for electrochemical reduction are investigated.

2.2 Polypyrrole

Polypyrrole is assigned to the class of conducting polymers, which is a result of conjugated π system.^[8] Although the pioneers on this field and furthermore Nobel Prize laureates, H. Shirakawa, A. G. MacDiarmid and A. J. Heeger reported the general properties of conjugated polymers in 1977, polypyrrole has a quite longer history.^[9]

In 1888 for the first time the oxidative polymerization of pyrrole was reported.^[10] Since 1937 structural researches were as far to report that pyrrole units are linked via the α positions.

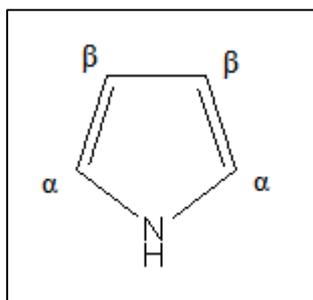


Figure 2: Scheme of pyrrole with α/β position

The result of polymerisation of pyrrole is a black substance which is insoluble in water.

2.2.1 Synthesis

For polypyrrole two general ways of syntheses are reported. In the first case, the chemical way, oxidative polymerization can be employed.^[8] For this route mainly FeCl₃ or other salts of iron or copper are used. Varying the solvent, reaction time and temperature and the monomer to oxidising agent has a great influence on the conductivity of the resulting polymer.

On the other hand polypyrrole films on metal electrodes can be achieved by electrochemical polymerization. Advantages of this method are that the mass and the thickness of the film can be regulated. The first one who reported this type of polypyrrole was Dall'Olio in 1968.^[8] They received a powder deposited on an electrode whereas Diaz et. al. in 1979 got a flexible film with improved conductivity.^[11]

2.2.2 Properties

Independent of the synthetic route, polypyrrole exists in an oxidized or p-type state.^[8] This results is observed as oxidation of pyrrole for the polymerisation and oxidation of just-built polypyrrole are competitive reactions which results in an incorporation of counter ions up to an ratio of pyrrole to counter ions of approximately 4:1.^{[8],[11]}

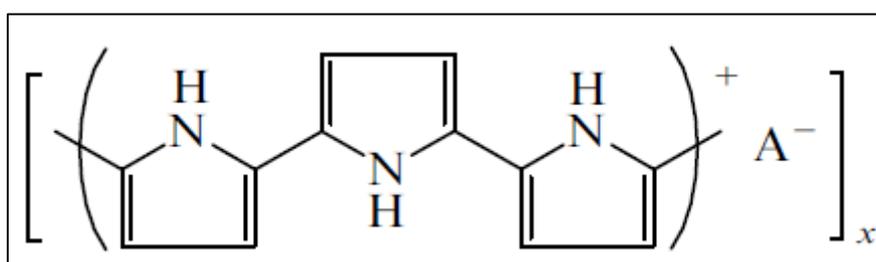


Figure 3: Scheme of an oxidised polypyrrole part^[8]

In figure 3 the A⁻ is standing for such a counter ion or so-called *dopant*. The exact level of oxidation can be modified by varying the relation between the reactants. In case of chemical polymerisation with FeCl₃, the FeCl₃ is not only the oxidising agent for the polymerisation but also dopant as [FeCl₄]⁻.^[10]

The final goal would be a flexible substrate for CO₂ reduction. As polypyrrole is a *p*-type semiconductor it is in general not the first choice for a substrate because CO₂ reduction as a reductive process would be better supported by an *n*-type substrate.^[12] The reason

for this is that *p*-type semiconductors are hole conducting while *n*-type semiconductors are electron conducting, which are needed for a reduction process.^[13]

However Cosnier, Deronzier and Moutet described polypyrrole immobilised on platinum as substrate for rhenium compounds towards CO₂ reduction and even reported a greater stability of the catalyst on the polypyrrole substrate.^[14]

In 2004 Köleli and Aydin^[15] reported the reduction of CO₂ to methanol using a polypyrrole coating on platinum as electrode. In their case high pressure was applied.

So in this work the attempt is made to synthesise a flexible free standing film of polypyrrole. Step by step depositions onto this substrates are performed and electrochemical studies under ambient atmospheric pressure performed.

2.3 CO₂ reduction on Cu₂O surfaces

The task of this thesis is to transfer the concept of reducing CO₂ to methanol (CH₃OH) at Cu₂O surfaces by Flake et. al.^[16] to a flexible substrate of polypyrrole. Cu(I) species are known for their catalytic activity towards several electrochemical reactions.

Flake et. al. assume that Cu₂O shows tendency towards selective reduction to methanol by two facts. They based their opinion on the work of Frese^[17].

Already the first step, adsorption of CO₂, shows one advantage of Cu(I) species. Following Frese, on Cu₂O surfaces this process is followed by the dissociation into CO_{ad} and O_{ad}, similar to chemisorption. Due to the strong affinity of copper towards oxygen, Frese suggests that the adsorbed O is getting absorbed by the matrix.

In aqueous solutions, the adsorbed CO is getting hydrated via adsorbed hydrogen on the surface. The adsorbed hydrogen atoms are produced by the reduction of water:



Those H_{ad} are supposed to reduce the CO_{ad} over formyl (HCO_{ad}) to finally methoxy (H₃CO_{ad}). This proposed mechanism is also consistent to the reduction of CO with H₂ on copper surfaces described by Yang et. al..^[18]

The second advantage of Cu(I) species is that Flake et. al. suggest that the adsorbed intermediate products are stabilised because of a high heat of adsorption.^[16]

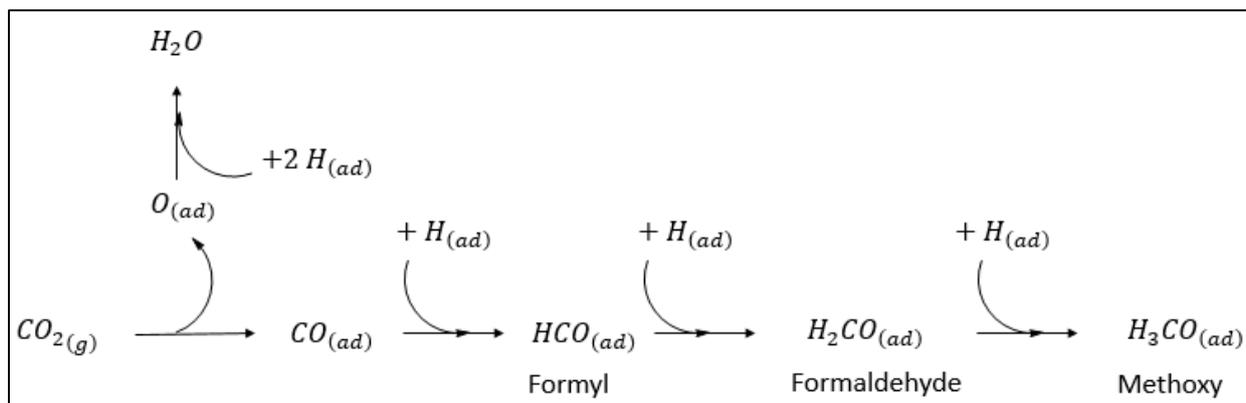


Figure 4: Schematic process of CO₂ reduction until methoxy intermediate

Based on descriptions of Frese^[17] and Yang et. al.^[18] the schematic, stepwise reduction of CO₂ is presented in figure 4. Taking the reduction of water to H_{ad} into account, the overall process has consumed 5 electrons up to the methoxy.

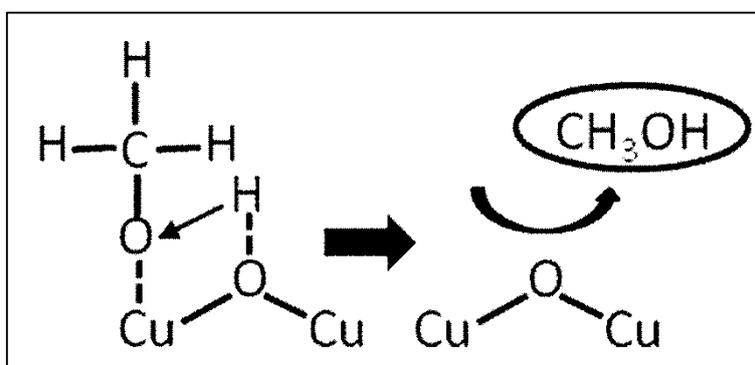


Figure 5: Scheme of methanol release from Cu₂O surface^[16]

Figure 5 shows the proposed last step on a Cu₂O surface - the release of methanol. By further addition of H_{ad} to the methoxy on the carbon atom, also methane (CH₄) could be released. Flake et. al. suggest that the release of methanol on Cu₂O surfaces is energetically favoured.^[16]

2.4 Copper deposition

As Flake et. al.^[16] describe the deposition on copper surfaces, also for the polypyrrole substrates comparable conditions are preferred. For this reason on top of the polypyrrole first a layer of metallic copper is deposited. Onto this copper layer then Cu_2O is deposited according to Flake et. al..

The copper deposition procedure is done related to the work of Grujicic and Pesic^[19]. A film only with deposited copper is also electrochemically characterised.

For deposition a 0.1 M CuCl_2 solution with a pH of 3.4 is prepared. Attention has to be paid to the special Cu/CuSO_4 reference electrode used in literature^[19], which shows a potential vs. *SHE* of +0.3 V. As in my systems an $\text{Ag}/\text{AgCl}/3\text{M NaCl}$ with a potential of +0.210 V is used this difference has to be considered.

Following the pourbaix diagram of copper species in figure 5 the correct potential for copper deposition in the pH range of the solution is determined.

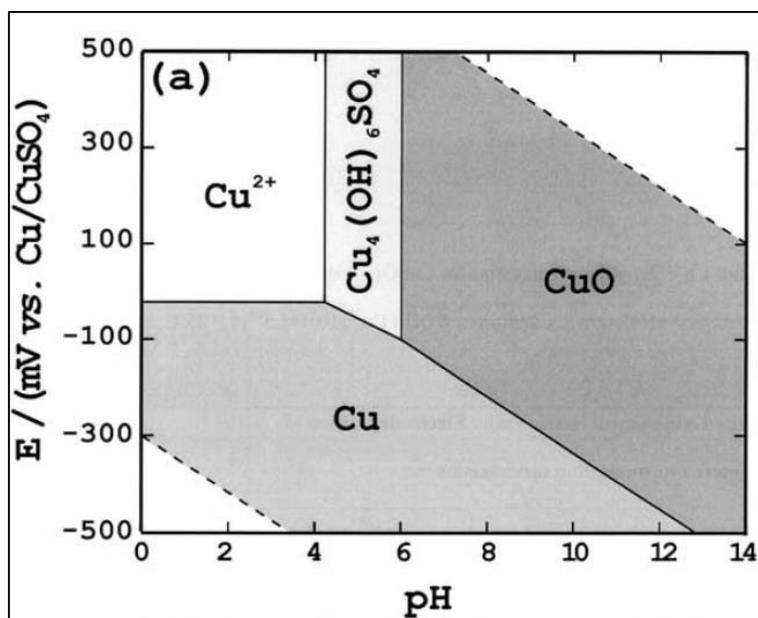


Figure 6: Pourbaix diagram of copper^[19]

For the deposition a three electrode system, like for the Cu_2O deposition, is used. -550 mV vs. $\text{Ag}/\text{AgCl}/3\text{M NaCl}$ are applied for 30 minutes. Although this is in a more negative area than showed in the diagram (-0.410 V vs. $\text{Ag}/\text{AgCl}/3\text{M NaCl}$), some over potential resulting from the electrode is expected.

3. Experimental Section

Cyclic voltammetry was employed throughout this study to characterise the electrochemical behaviour of the materials. For this method a setup containing a three electrode system is used. One is the working electrode (*WE*) covered or made out of the material to be analysed. Platinum or graphite rod was used as the counter electrode (*CE*) whereas the reference electrode (*RE*) was chosen as Ag/AgCl/3M NaCl which has a defined potential of 0.210 V vs. *NHE*.

Unless stated otherwise, when water is mentioned, purified water in a grade of Milli-Q or MQ, which corresponds to resistivity of 18 M Ω is meant. In all the experiments a comparison between cyclic voltammograms (*CV*) of N₂ and CO₂ purged solutions are made. The electrolyte solution is preliminarily purged with nitrogen for 30 minutes. All experiments recorded under purged CO₂ conditions are performed in a way that before measuring the electrolyte solution is purged with CO₂ for 15 minutes.

In all experiments a 0.5 M KHCO₃ solution with a pH value of 8.6 is used as electrolyte solution.

Unless stated otherwise all *CV* measurements are recorded under the following conditions:

Start Potential:	0 mV
1. Return Potential:	-1500 mV
2. Return Potential:	0 mV
Polarization Speed:	10 mV/s
Cycles:	2

For analysing headspace gas, a *Thermo Scientific Trace GC Ultra* containing a helium and a nitrogen channel with a thermal conductivity detector (*TCD*) is used.

For analysing electrolyte solutions, a *Thermo Scientific Trace 1310 Gas Chromatograph* for liquid injection with flame ionisation detector (*FID*) is used.

Unless stated otherwise the faradaic efficiency is calculated for all electrolyses after 1h including all detected products.

3.1 Copper plate with deposited Cu₂O

The first task is to prove the concept stated by Flake et. al.^[16] concerning the reduction of CO₂ to methanol. Their experiment is repeated in the same way as described.

A copper wire is fixed to a copper plate in a size of 0.7 x 2.5 cm. This plate is fixed in the plastic frame for reasons of stability.

The first step is the preparation of a solution with roughly comparable concentrations of 0.4 M Cu²⁺ species and 3 M lactate at a pH = 9. For this reason a 3 M lactate solution is prepared by dissolving 30.0289 g of a ~90% lactic acid solution in 60 mL of a 5 M NaOH solution in a 100 mL volumetric flask. Afterwards the flask is filled up with water and a pH value of approximately 5.5 is obtained. By adding drops of 5 M NaOH solution the pH is adjusted to 9.0.

4.6511 g of Cu(NO₃)₂ * 2.5 H₂O are filled up in a 50 mL volumetric flask with the ~3 M lactate solution which results in a pH of roughly 6. Also in this case the pH is adjusted to 9 by adding 5 M NaOH.

Due to this pH adjustments it is obvious that the concentrations are lower – but this error is negligible because the solution is only used for deposition.

Proceeding the deposition a three electrode system containing a platinum wire as *CE*, an Ag/AgCl/3M NaCl as *RE* and the *PPy* as *WE* is used.

In a water bath, the cell is firstly thermostatted to 60°C for 15 minutes. Afterwards +600 mV are applied at this temperature for 30 min. During the deposition, the liquid turns green and directly after this deposition a green coverage is visible but after rinsing with water the typical orange Cu₂O deposition is observed.

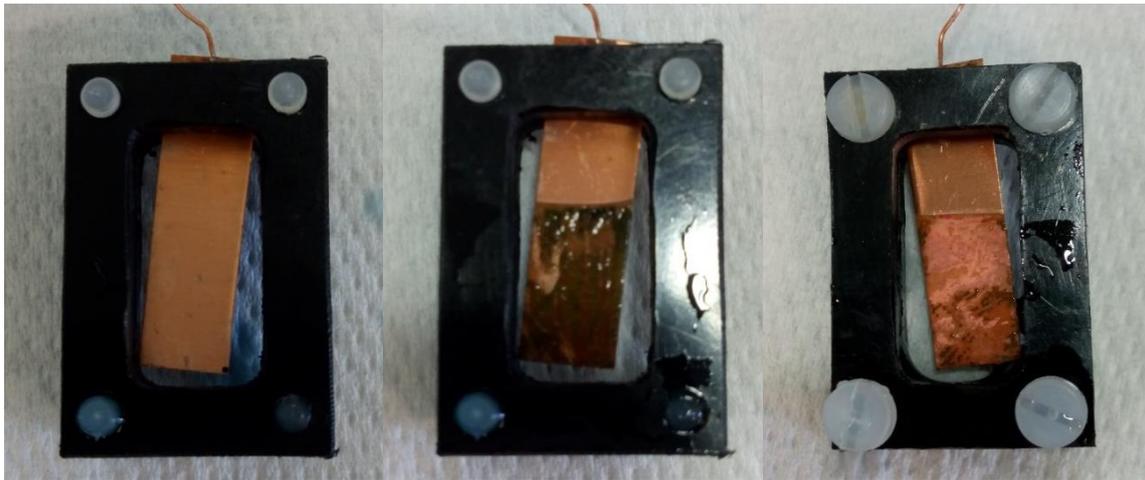


Figure 7: Copper plate before deposition, directly after and after rinsing

For electrochemical characterization, this plate is installed in an H-Cell using 0.5 M KHCO_3 solution as electrolyte.

WE ... Cu/ Cu_2O

RE ... Ag/AgCl/3M NaCl

CE ... platinum plate

When purging the cell at first the Cu_2O is quite resistant. Only during CV measurements the orange layer turns darker and fell off after measuring cycles under nitrogen purged conditions.

This can be used as explanation why the cycle under CO_2 shows a slightly more positive current than the one under nitrogen in figure 8.

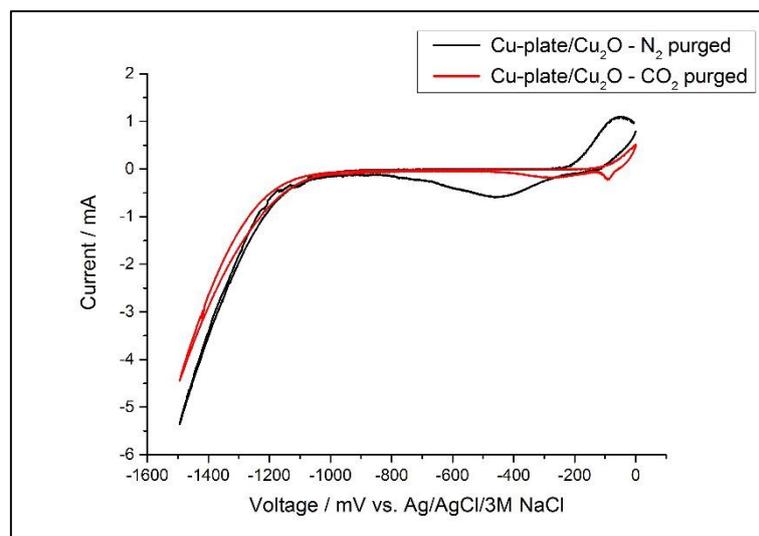


Figure 8: CV comparison of Cu/ Cu_2O

On the platinum *CE* and on the *WE* bubble evolution is observed. After the *CV* characterisation a 5 hours electrolysis is started at a potential of -1500 mV. Before starting this experiment, after 1 hour, after 5 hours and finally after 20h samples of electrolyte solution and the headspace are taken and analysed via GC. Before and after 20h the headspace is analysed in the nitrogen channel of the GC for hydrogen evolution. In this session samples are only taken from the *WE* side.

The analysis of the headspace revealed a constantly increasing amount of CO until 5 hours - which vanishes until 20 hours, seen in figure 9. After 1 hour the peak corresponds to an amount of 2.2 μL , after 5h to an amount of 9.4 μL and finally after 20h no CO can be detected any more.

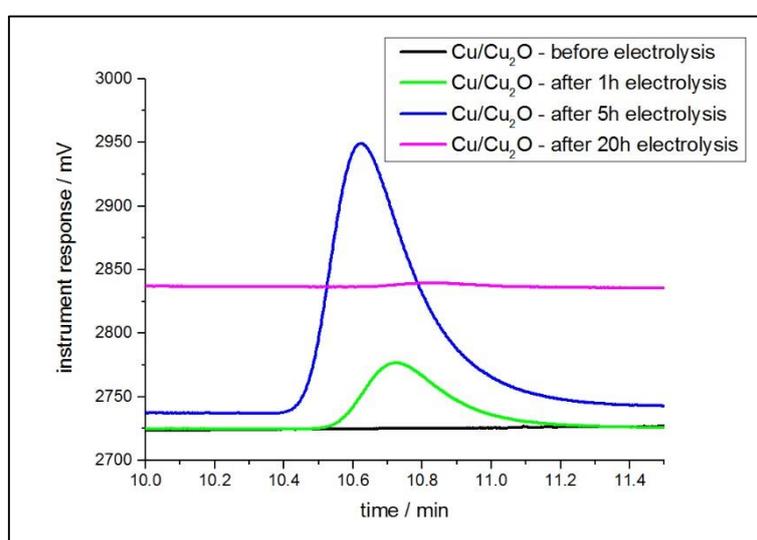


Figure 9: Comparison of the gas-GC (He channel) chromatograms during electrolysis

Considering the chromatogram of the nitrogen channel before the electrolysis a large amount of CO_2 is detected and some traces of oxygen.

After 20h no CO_2 can be detected any more whereas 51.2 μL of H_2 can be observed.

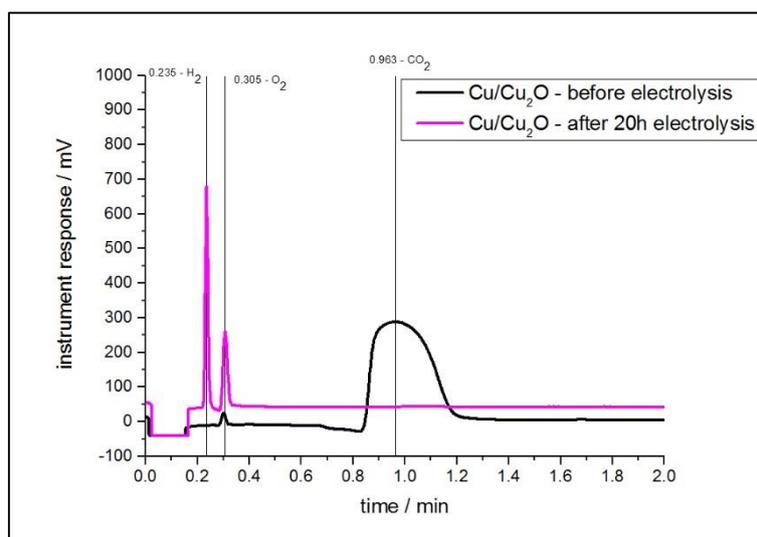


Figure 10: Comparison of the gas-GC (N_2 channel) chromatograms during electrolysis

Analysing the chromatograms of the liquid injection GC does not deliver as precise results as the gas GC. Very small peaks of methanol exist, as can be seen in figure 11, but as the signal to noise ratio is very low the amount of produced methanol is negligible.

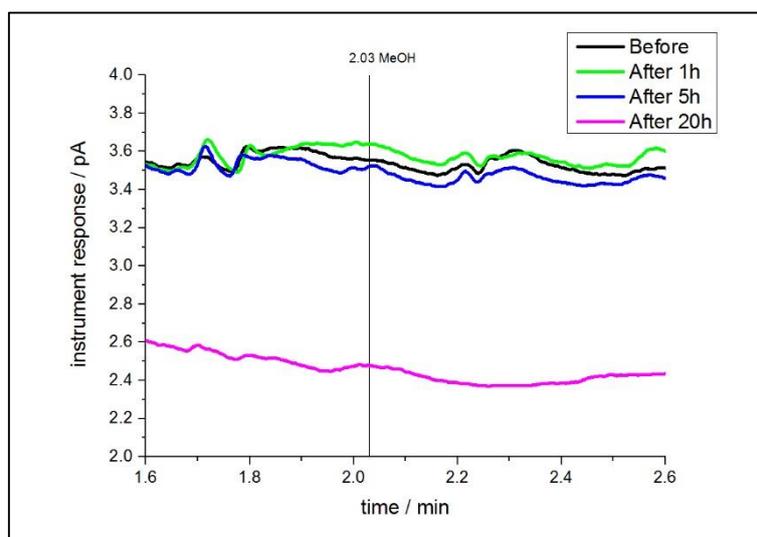


Figure 11: Comparison of the liquid GC during electrolysis

Although Flake et. al.^[16] stated a reduction of CO_2 to methanol in this experiment no methanol amounts as reported are found. Interestingly enough Flake et. al. only reported a minor amount of CO whereas in my case detectable amounts were clearly observed. The overall faradaic efficiency was calculated to be 1.5%.

3.2 Polypyrrole on glassy carbon

Before using the glassy carbon rod as working electrode, it is cleaned electrochemically by cyclic voltammetry in the ranges -500 mV to 500 mV for 20 cycles in 0.5 M H₂SO₄. Starting with the reference experiment, just the cleaned glassy carbon is used in 0.5 M KHCO₃ as electrolyte solution.

Selected electrodes:

WE ... glassy carbon rod

RE ... Ag/AgCl/3M NaCl

CE ... platinum plate

Under the usual settings CV is measured followed by a 20h electrolysis at -1500 mV.

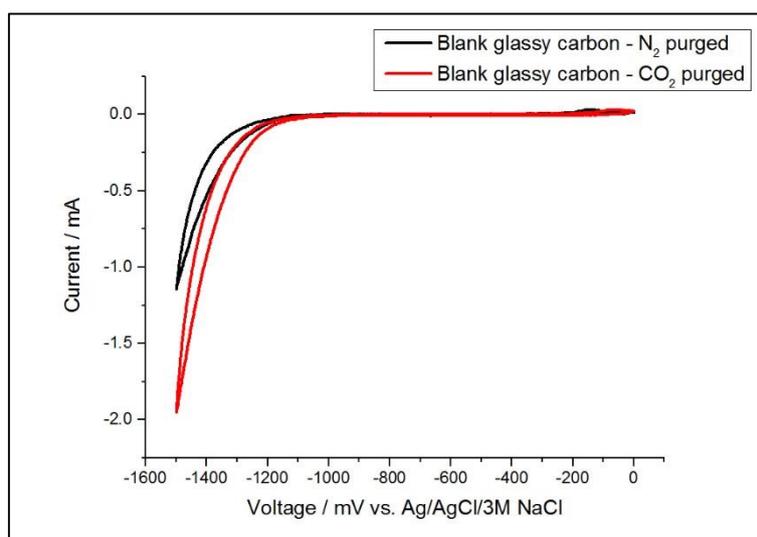


Figure 12: CV comparison of blank glassy carbon

During the experiment, before, after 1h and finally after 20h liquid and gaseous samples only from the WE side are taken and analysed:

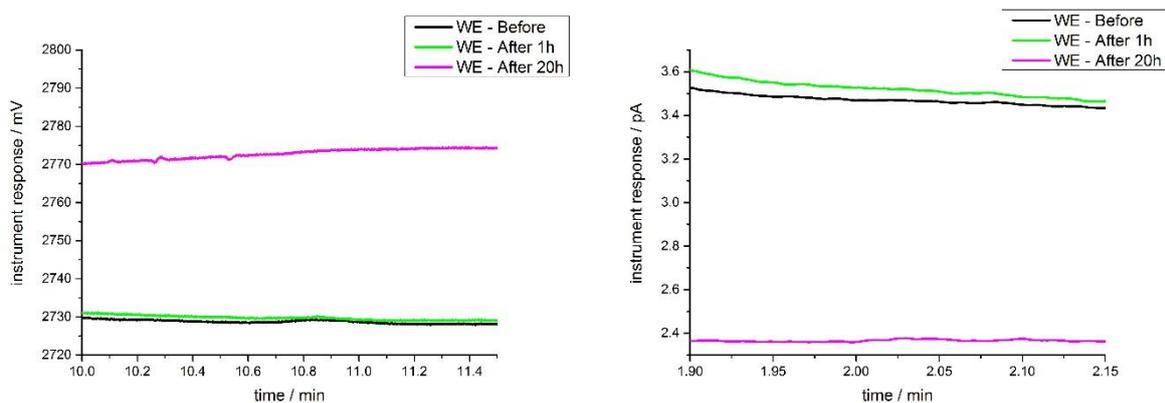


Figure 13: Gas and liquid GC analysis of blank glassy carbon

Not in the gas analysis (left side) CO nor in the liquid analysis (right side) methanol is detected. From this results a catalytic activity of glassy carbon towards CO₂ reduction can be excluded.

For the electrochemical polymerisation of pyrrole onto the glassy carbon electrode, a one-compartment cell is used (figure 14):

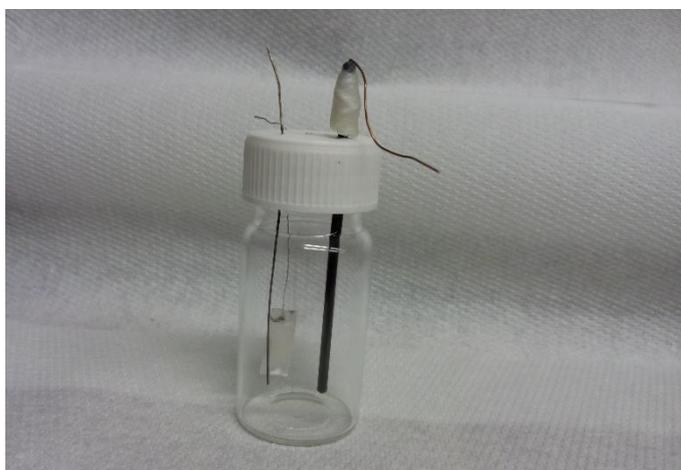


Figure 14: One-compartment cell for polymerisation

This cell is filled with 20 mL of a 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) solution in acetonitrile. 250 μL of pyrrole are added which results in a concentration of 0.18 M according to Diaz et. al.^[17]. Before starting the polymerisation the cell is purged with nitrogen for 45 minutes.

Potentiostat settings:

Start Potential: 0 mV
1. Return Potential: -900 mV
2. Return Potential: 900 mV
Polarization Speed: 100 mV/s
Cycles: 20

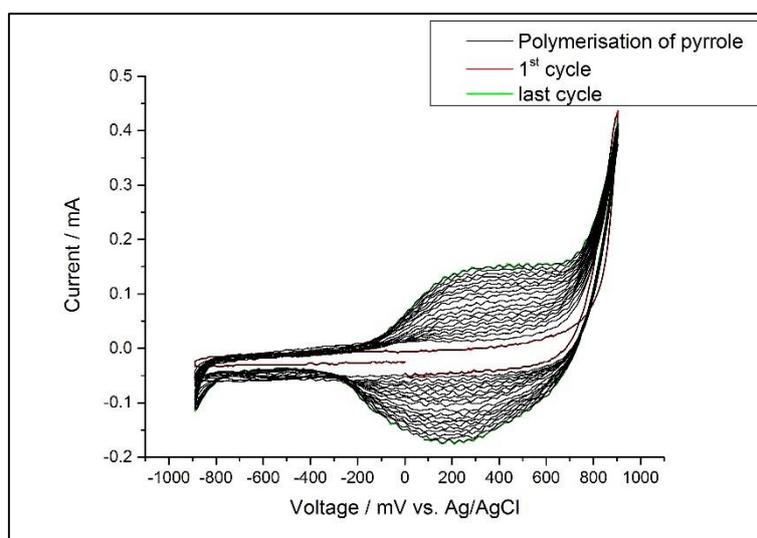


Figure 15: Polymerisation of pyrrole

Afterwards copper deposition according to page 7 followed by Cu_2O deposition according to page 9 which results in a robust-looking Cu_2O layer:



Figure 16: Glassy Carbon/ PPy / Cu / Cu_2O

This electrode is implemented as *WE* in an H-Cell which is filled with 0.5 M KHCO_3 as electrolyte solution.

Selected electrodes:

WE ... Glassy Carbon/*PPy*/Cu/Cu₂O

RE ... Ag/AgCl/3M NaCl

CE ... platinum plate

Then the usual N₂/CO₂ purging and CV measurement treatment followed by a 20h electrolysis at -1500 mV is done resulting in the following I-V-curves:

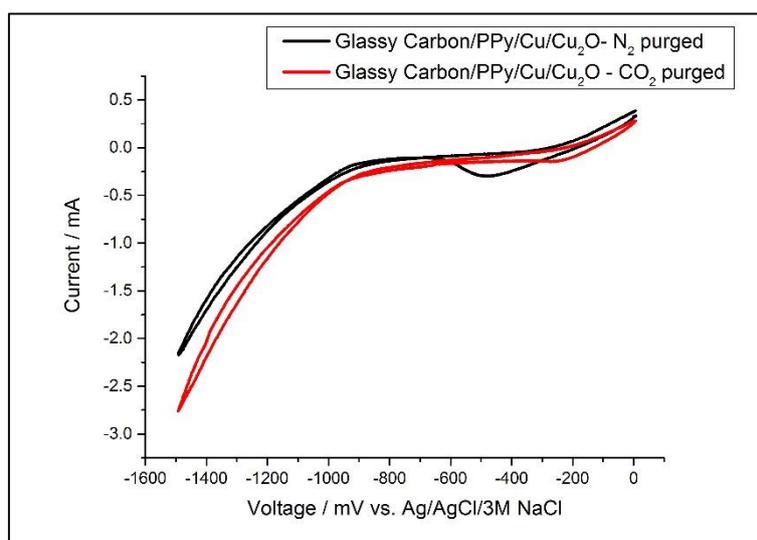


Figure 17: CV comparison 1 of the glassy carbon/*PPy*/ Cu/Cu₂O

During the experiment samples of the electrolyte solution and the headspace of the WE side are taken and analysed before, after 1h and finally after 20h. The liquid samples before injecting are diluted 1:4 to minimise errors occurring from changing the volume of the electrolyte solution.

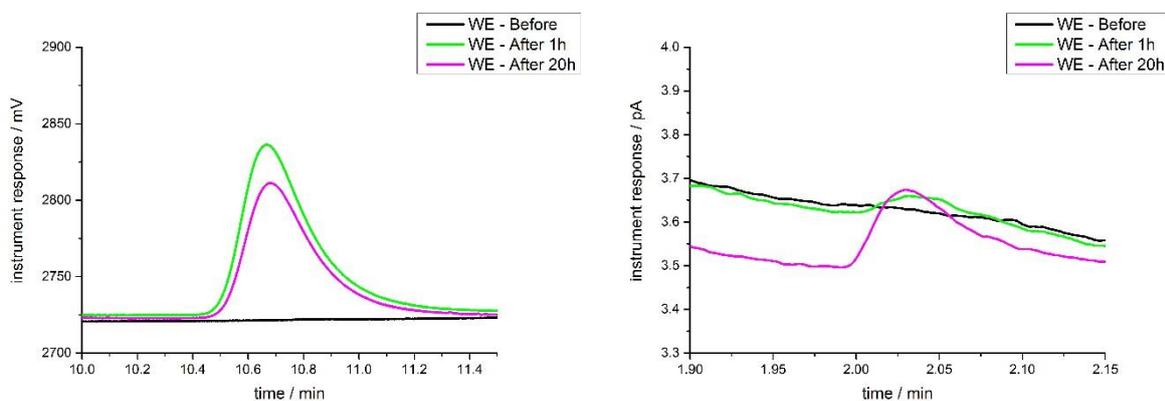


Figure 18: Gas and liquid GC analysis of Glassy Carbon/*PPy*/Cu/Cu₂O at -1500 mV

Deriving from the data from gas GC (left side) after 1h an amount of 4.8 μL CO is produced while after 20h an amount of 3.8 μL CO is produced. An untight H-Cell can also in this case be taken as reason for the decrease in the CO amount.

Deriving from the average values of the data from liquid GC (right side) after 1h an amount of 1.11 mg/L methanol is produced while after 20h an amount of 3.44 mg/L methanol is produced.

The overall faradaic efficiency was calculated to be 6.3 %.

As a final step for this experiment series a freshly prepared electrode as described before is prepared and an electrolysis at -1200 mV for 20h is proceeded. For making the cell more tight not only para film is used for isolating but also aluminium foil.

Selected electrodes:

WE ... Glassy Carbon/PPy/Cu/Cu₂O

RE ... Ag/AgCl/3M NaCl

CE ... platinum plate

The usual N₂/CO₂ purging and CV measurement treatment followed is done resulting in the following I-V-curves:

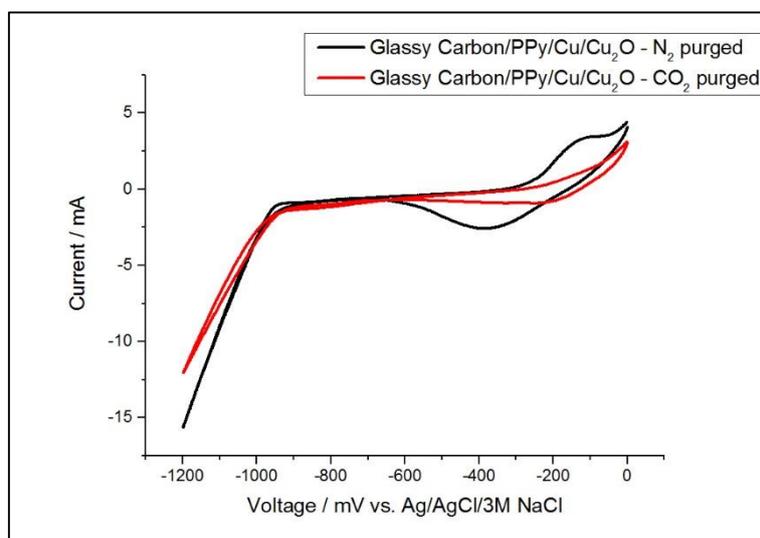


Figure 19: CV comparison 2 of the glassy carbon/PPy/ Cu/Cu₂O

Although the curves have a less smooth shape, the general shape is comparable to figure 17. Interestingly, more negative current values are reached than before.

For 20h electrolysis at -1200 mV is proceeded and monitored by liquid and gas GC. Samples are taken from the WE chamber before starting the electrolysis, after 1h and after 20h.

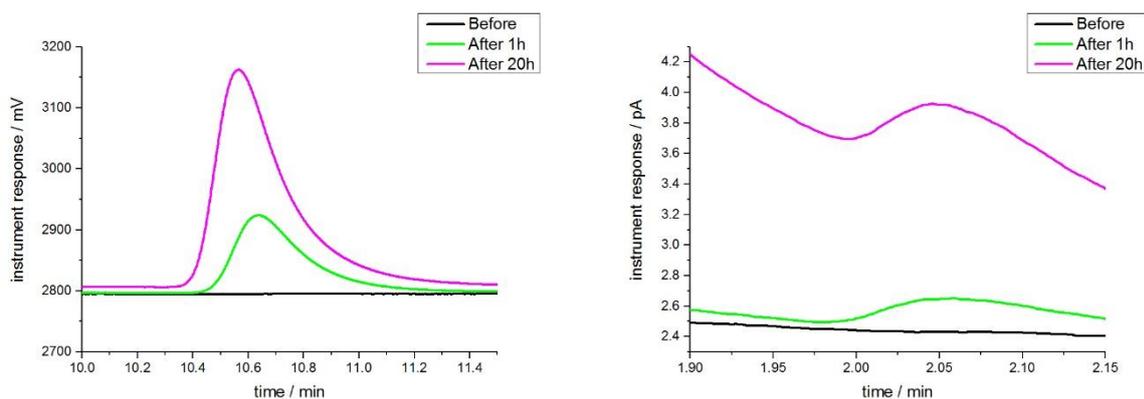


Figure 20: Gas and liquid GC analysis of Glassy Carbon/PPy/Cu/Cu₂O at -1200 mV

After 1h a CO amount (left chromatogram) of 5.6 μ L can be detected and after 20h 16.0 μ L. Following the liquid GC chromatogram (right side) after 1h a methanol concentration of 1.20 mg/L is detected and after 20h one of 3.06 mg/L.

Applying the less negative potential of -1200 mV slightly increased the overall faradaic efficiency to 7.1 %.

3.3 Polypyrrole Film

3.3.1 Preparation of the polypyrrole film

To purify the pyrrole immediately before using, a vacuum distillation is performed. Approximately 250 mL are heated in a 500 mL round bottom flask under reduced pressure up to 92 °C. The setup is shown in Figure 21:



Figure 21: Distillation setup

For the preparation of the free standing, flexible *PPy* film an electro-polymerisation method in style of Yilmaz et. al.^[20] was used. The reaction is operated in a ceramic pot. A stainless steel plate (10 x 11 cm) is used as anode whereas a stainless steel grid (14.4 x 14.4 cm) is used as cathode. The grid is placed on standing feet above the steel plate. In this pot, 900 mL of a 0.1 M *para*-toluolsulfonic acid (PTSA) are filled in and purged with nitrogen for one hour. Then exactly 10 mL of freshly distilled pyrrole are added, which results in a concentration of 0.17 M and homogenized with nitrogen bubbles.

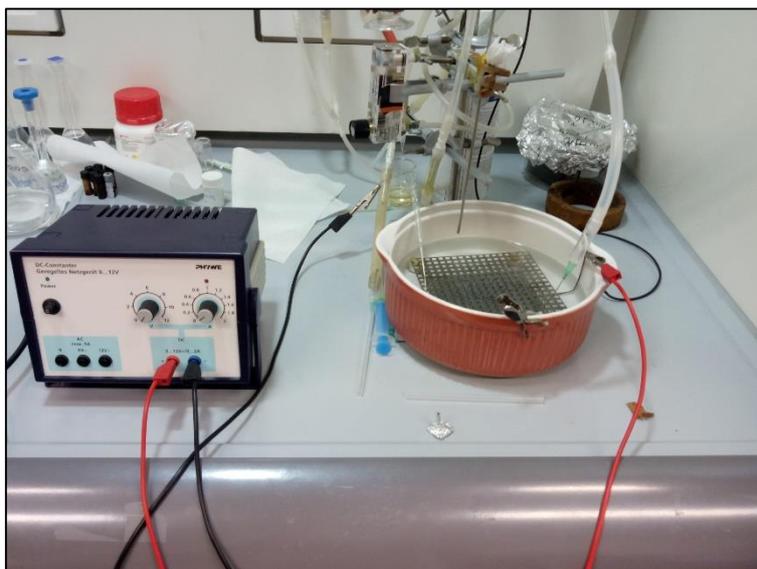


Figure 22: Setup for electro-polymerization

Galvanostatic polymerisation was employed with a current density of 2 mA cm^{-2} are applied for 17 hours.

After some minutes a black film is observed on the plate, which grows overnight.

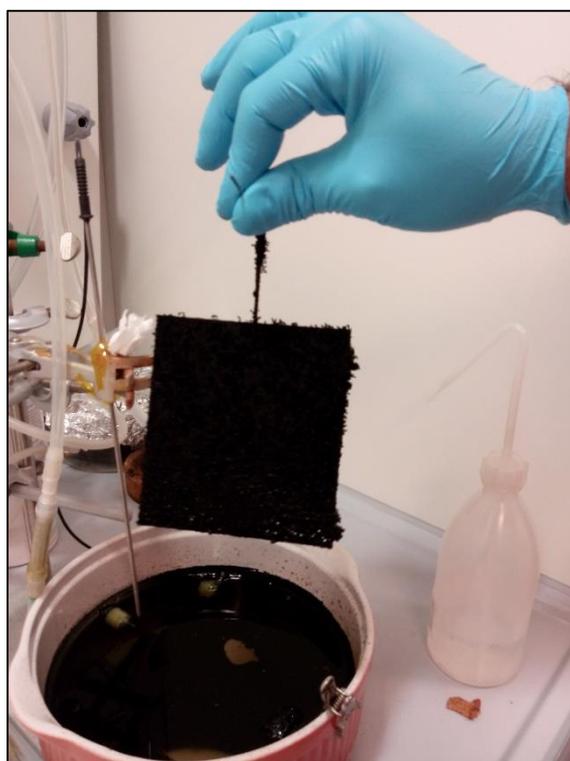


Figure 23: Black *PPy* film

This film is peeled off of the plate, rinsed with water and stored in a vessel with water inside for preventing it from drying out.

3.3.2 Characterization of the polypyrrole film

A piece of the film with dimensions of approximately 1 x 3 cm is put into a small plastic frame with aluminium foil (figure 24).

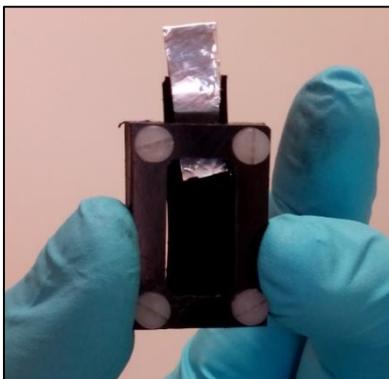


Figure 24: PPy film in the frame

Selected electrodes:

WE ... PPy film

RE ... Ag/AgCl/3M NaCl

CE ... platinum plate

For this characterisation again an H-Cell is used. Each chamber is filled with approximately 20 mL of 0.5 M KHCO_3 electrolyte solution and they are simultaneously purged with nitrogen. Then afterwards the usual N_2/CO_2 purging and CV measurement treatment is continued resulting in the following I-V-curves:

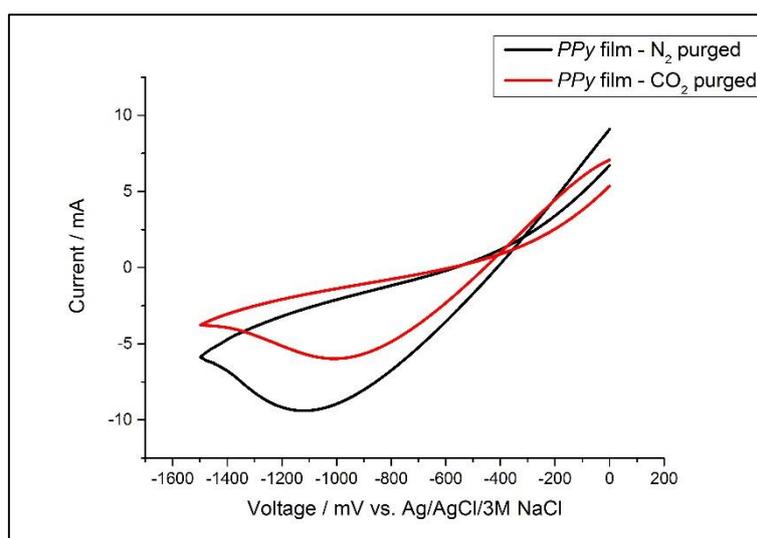


Figure 25: CV-Comparison of the PPy film

Like in case of the glassy carbon substrate, the two curves under N_2 and CO_2 show nearly the same behaviour. Interestingly, in both cases a “belly” at around -1000 mV is occurring.

Nevertheless afterwards an electrolysis at -1500 mV is proceeded for 22h monitored by liquid GC. Before the electrolysis, after 1h and after 22h samples are taken and analysed towards methanol.

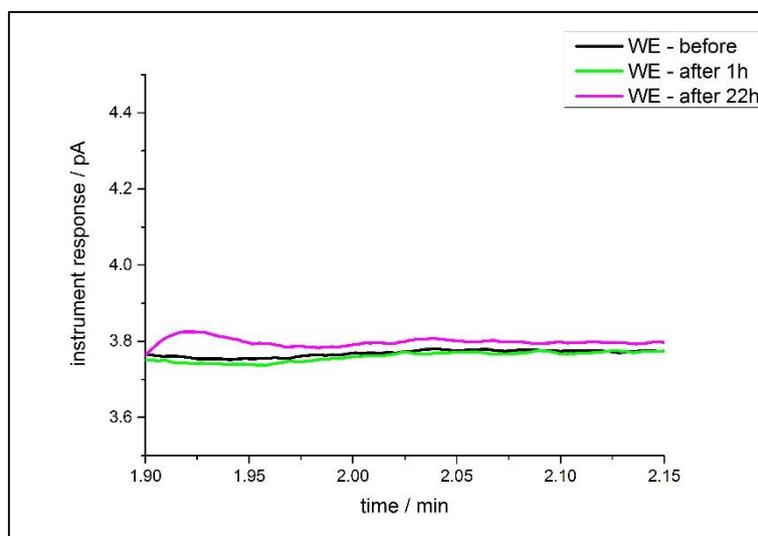


Figure 26: Liquid GC during 22h electrolysis

Beside some baseline fluctuation no peak resulting from methanol can be found.

Beside the study of the pure free standing *PPy* film, also *PPy*/*Cu* and *PPy*/*Cu*₂*O* films are studied. Like in the case of just *PPy* no clear reductive peak resulting from the influence of *CO*₂ in the electrolyte solution is visible. Electrolysis was performed at -1500 mV.

Furthermore in no case methanol or *CO* was observed in the *WE* chamber.

When metallic copper is deposited onto a *PPy* film and afterwards the film is exposed to air for one hour, the colour of the copper changes to green.

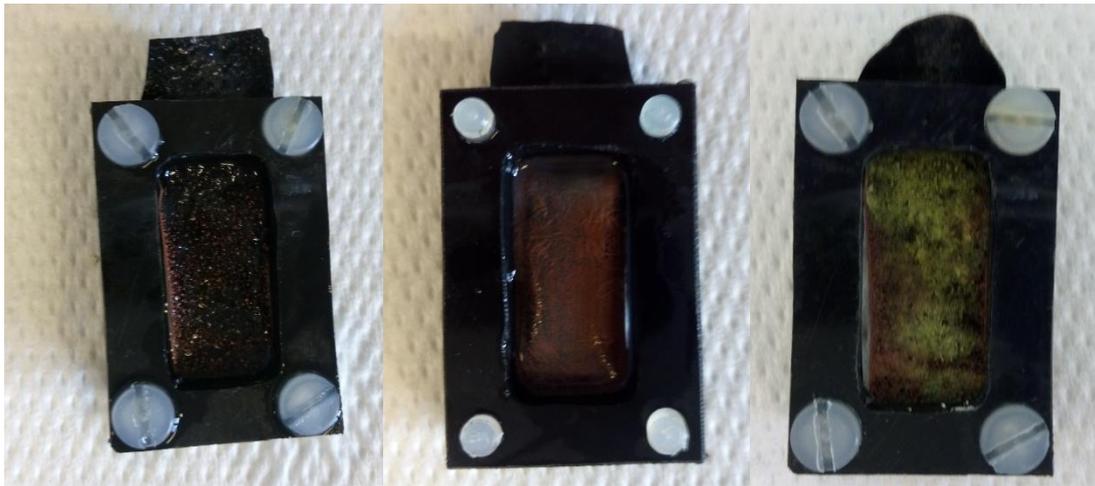


Figure 27: Left, Middle: PPy film directly after deposition. Right: after 1 hour

This can be explained by formation of a so-called copper patina. A picture from an optical microscope with 10 fold magnification is taken of this patina.

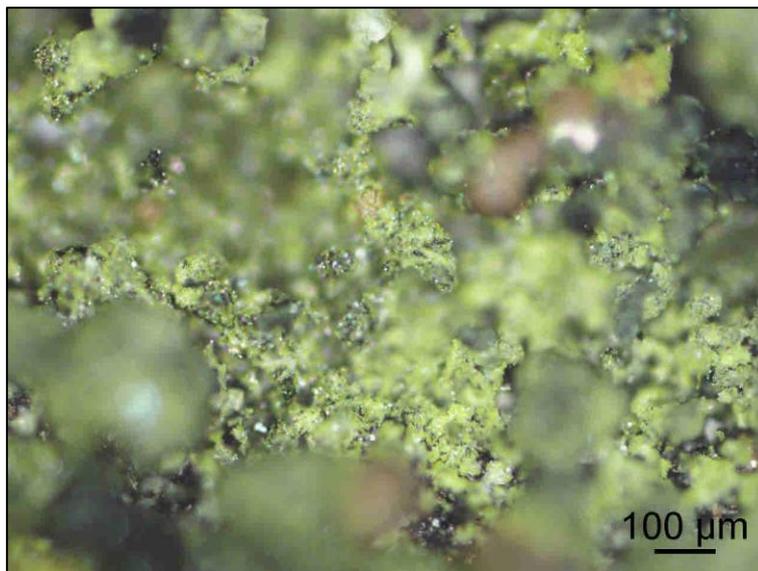


Figure 28: Copper patina on a PPy film

3.3.3 Characterization of *PPy*/Cu/Cu₂O

The final goal is now to first deposit metallic copper and on top deposit Cu₂O. Starting point is the deposition of metallic copper as described in chapter 2.4. Afterwards the film is shortly rinsed with water followed by the treatment for Cu₂O deposition explained in chapter 3.1.

After those two treatments a capable layer of orange Cu₂O is visible:



Figure 29: *PPy*/Cu/Cu₂O

This Cu/Cu₂O layer is very brittle and prone to delaminate upon rinsing with water. When installing this film in a small H-Cell it turns out that the layer is also frail towards purging the cell. Due to this reasons the bubbling rates while purging on the *WE* side have to be decreased to a low level.

Selected electrodes:

WE ... *PPy* film/Cu/Cu₂O

RE ... Ag/AgCl/3M NaCl

CE ... platinum plate

Again 0.5 M KHCO₃ solution is used as electrolyte solution and an H-Cell seen in figure 30 is used.



Figure 30: H-Cell setup with $PPy/Cu/Cu_2O$ film inside

The usual N_2/CO_2 purging and CV measurement treatment is proceeded.

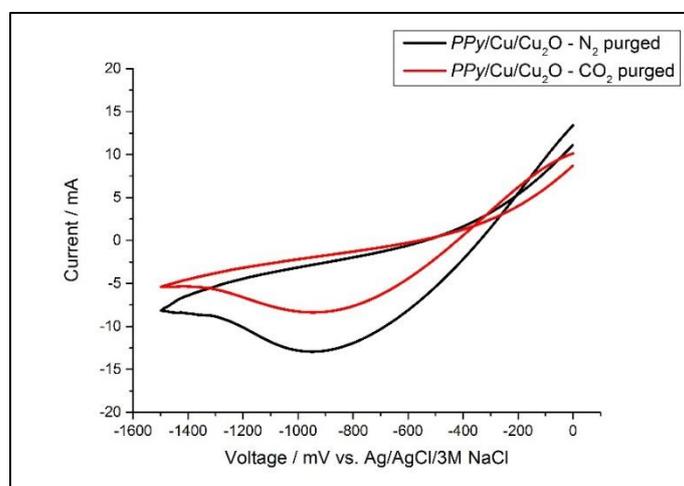


Figure 31: CV comparison of the $PPy/Cu/Cu_2O$ film

Also in this case, a similar behaviour like in the case of pure PPy (figure 25) is observed. After measuring the cyclic voltammograms a 20 hour electrolysis at -1500 mV is performed. During this measurement the liquid of the WE chamber is analysed via liquid injection GC after 20h of electrolysis. The headspace is analysed in the helium channel before, after 1h and finally after 20h.

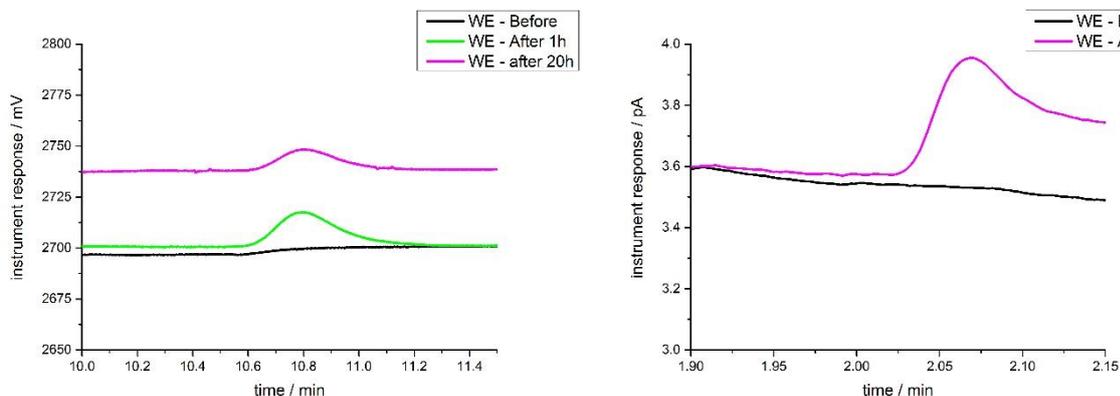


Figure 32: Gas and liquid GC analysis of $PPy/Cu/Cu_2O$ at -1500 mV

Following the results of figure 32, the slightly shifted methanol peak can be correlated to an amount of 0.79 mg/L.

After 1h an amount of 0.6 μL CO and after 20h an amount of 0.3 μL CO is observed. This decrease in amount from 1 to 20 hours can be explained in a way that the cell is not completely tight and CO is diffusing to the outside. The faradaic efficiency was calculated to be <1% for the whole process.

In another experiment an electrolysis at the “belly”, -1000 mV, was performed for 20h. Before, after 1h and finally after 20h samples of the headspace and the liquid are taken and analysed. In this case, the headspace was also analysed towards H₂ in the nitrogen channel.

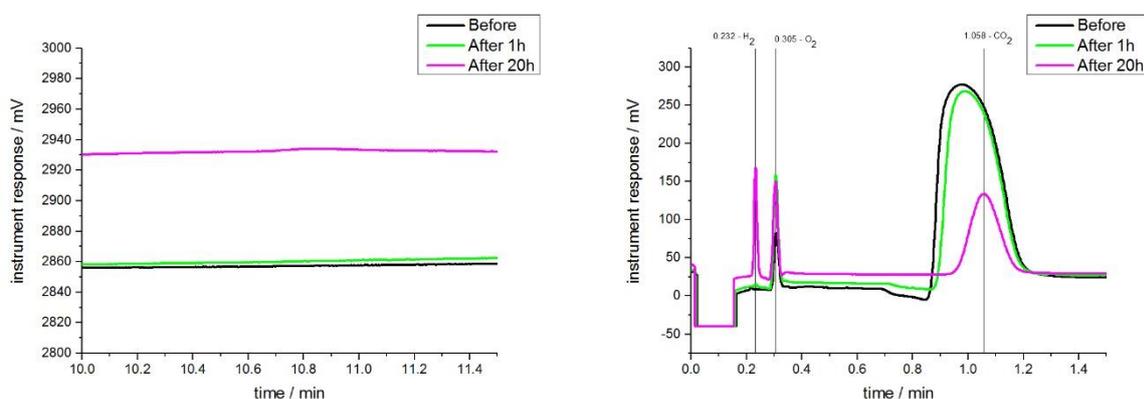


Figure 33: Gas GC analysis of *PPy/Cu/Cu₂O* at -1000 mV (left: He channel / right: N₂ channel)

Over the electrolysis time the CO₂ amount is decreasing, most likely diffusing out. After 1h, 0.1 μL of H₂ were detected and after 20h 5.7 μL H₂. In no case MeOH was observed.

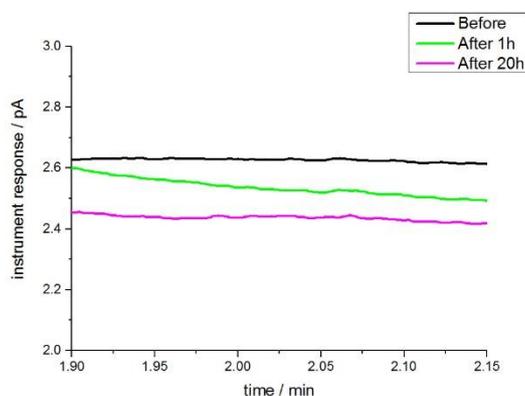


Figure 34: Liquid GC analysis of *PPy/Cu/Cu₂O* at -1000 mV

4. Comparison of results

In table 2 the results of methanol and CO in the *WE* chambers under different electrode conditions are compared.

Table 2: Comparison of the results

Electrode	Electrolysis duration / h	CO / μL	MeOH / mg L^{-1}	Faradaic efficiency
Cu_2O on copper plate	1	2.2	0	1.5 %
	5	9.4	0	
	20	0	0	
Glassy Carbon/ <i>PPy</i> /Cu/ Cu_2O (at -1500 mV)	1	4.8	1.11	6.3 %
	20	3.8	4.88	
Glassy Carbon/ <i>PPy</i> /Cu/ Cu_2O (at -1200 mV)	1	5.4	1.20	7.1 %
	20	16.0	3.06	
<i>PPy</i> /Cu/ Cu_2O	1	0.6	0	<1 %
	20	0.3	0.79	

The repetition of the experiment stated by Flake et. al.^[16] (chapter 3.1) showed that CO_2 was reduced – but only to CO and no traces of methanol were found. In this experiment the amount of CO increased nearly linearly until 5 hours and vanished after 20h. Furthermore the faradaic efficiency was very low.

Trying the same conditions on *PPy*-glassy carbon show a different picture (Chapter 3.2). At -1500 mV, after 1 and 20h a comparable concentration of CO was detected. The amount of methanol increased over the whole experiment. At -1200 mV the CO and the MeOH amount increased during the whole electrolysis time. Comparing just the absolute values, more CO was produced but less MeOH comparing the values to the electrolysis at -1500 mV.

Concerning the faradaic efficiencies, reducing the potential from -1500 mV to -1200 mV achieved a slightly higher efficiency.

In figure 35 the gas chromatograms (He channel) and the liquid chromatograms of the two different electrolysis potentials of Glassy Carbon/ *PPy*/Cu/ Cu_2O are compared:

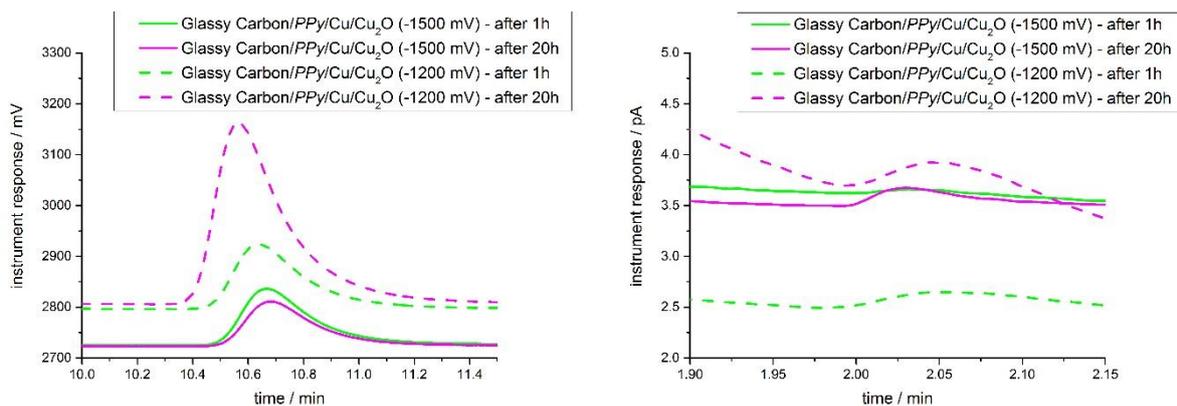


Figure 35: Gas and liquid GC comparison of $PPy/Cu/Cu_2O$ at -1500 mV vs. -1200 mV

When analysing the flexible film with Cu/Cu_2O deposition it showed a similar behaviour like in the case of PPy on glassy carbon. After 1h a higher CO level is reached than after 20h. After 20h an amount of 0.79 mg/L MeOH is detected.

5. Conclusion

As polypyrrole alone does not show a catalytic activity, a combination of Cu_2O and Cu is needed for reducing CO_2 .

The first peculiarity is that, if at all, only traces of methanol are produced. It has to be stated that in this work electrolysis times reached 20h whereas Flake et. al.^[16] stated reaction times of 10 to 30 minutes and that only traces of CO were found. They described a maximum faradaic efficiency of 38 % whereas I could only reach 7 %. However Frese^[17] described electrolysis times of 1 to 5 hours.

In my case small amounts of CO were produced and only traces of methanol. As could be seen by the experiment at -1200 mV at glassy carbon/*PPy*/ Cu / Cu_2O , using this less negative potential favours the CO evolution. On the other hand the methanol production was decreasing.

A suggestion for this reason is that in my case the adsorption of CO_2 is only followed by dissociation and desorption, following the “upper” way in figure 4. One reason for this short lifetime of the adsorbed state could be the heavy hydrogen evolution which is pulling the adsorbed CO molecules with them.

The greatest problem when working with the depositions on *PPy* is hydrogen evolution. All the reductive peaks occurring at -1500 mV are caused by water splitting. H_2 evolution is not only a competitive reaction – the evolving hydrogen bubbles also damage the depositions and lead them to fall off in nearly every case. If also reduction products are observed working at less negative potentials is recommendable.

One problem using a free standing *PPy* film might be conductivity. When deposited on glassy carbon, the micrometre thickness will not hinder the charge transport.

If the whole electrode is made of *PPy* one major problem might occur. As *PPy* is synthesised in the oxidised, conductive form it can be reduced to the neutral form at negative potentials. As a matter of fact, the neutral form shows significant lower electric conductivity which is handicapping reduction processes of CO_2 .

The shape of the *CV*'s of just *PPy* and *PPy*/ Cu / Cu_2O in figures 25 and 31 differs from the ones using glassy carbon or the copper plate as substrate as a “belly” is occurring.

John and Wallace^[21] studied the reduction and oxidation of polypyrrole and observed a quite similar shape for the reduction of oxidised *PPy* to the neutral form at - 800 mV.

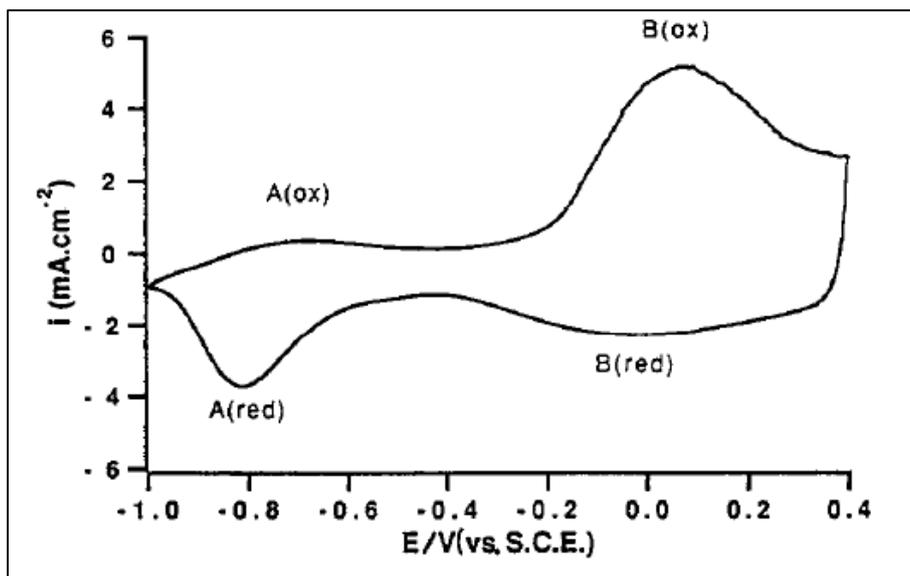


Figure 36: Reduction and oxidation of *PPy*^[21]

This can be seen as a proof that during reductive treatment of the *PPy* film the current flowing can be more dedicated to reducing the film than to reducing CO_2 .

A solution to this problem would be the use of an *n*-type semiconductor instead of a *p*-type. *N*-type semiconductors are capable of transporting electrons which are necessary for reduction processes and would stay in their conductive, reduced form over the treatment.

P-type semiconductors are the better choice for the opposite reaction type – for example water oxidation. In this case, a hole transporting layer is needed under oxidising environment.

6. Bibliography

[1] Solomon, S., D. Qin, M. Manning, R.B. Alley, T. Berntsen, N.L. Bindoff, Z. Chen, A. Chidthaisong, J.M. Gregory, G.C. Hegerl, M. Heimann, B. Hewitson, B.J. Hoskins, F. Joos, J. Jouzel, V. Kattsov, U. Lohmann, T. Matsuno, M. Molina, N. Nicholls, J. Overpeck, G. Raga, V. Ramaswamy, J. Ren, M. Rusticucci, R. Somerville, T.F. Stocker, P. Whetton, R.A. Wood and D. Wratt, 2007: Technical Summary. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

[2] National oceanic and atmospheric administration (NOAA): *Greenhouse gas benchmark reached*. 6th of March 2015. Internet link:

<http://research.noaa.gov/News/NewsArchive/LatestNews/TabId/684/ArtMID/1768/ArticleID/11153/Greenhouse-gas-benchmark-reached.aspx> (Last time opened: 14.06.2015)

[3] J. T. Kiehl and Kevin E. Trenberth: *Earth's Annual Global Mean Energy Budget*. Bulletin of the American Meteorological Society, 1997, Vol. 78, No. 2, 197 – 208

[4] K. M. K. Yu, I. Curcic, J. Gabriel, S. C. E. Tsang: *Recent Advances in CO₂ Capture and Utilization*. ChemSusChem, 2008, Vol. 1, 893 – 899

[5] P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, T. E. Müller: *Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂*. Energy & Environmental Science, 2012, Vol. 5, 7281–7305

[6] E. Portenkirchner, K. Oppelt, D. A. M. Egbe, G. Knör, N. S. Sariciftci: *Electro- and photochemistry of rhenium and rhodium complexes for carbon dioxide and proton reduction: a mini review*. Nanomaterials and Energy, 2014, Vol. 2, Issue 3, 134 – 147

[7] M. V. V. S. Reddy, K. V. Lingam, and T. K. G. Rao: *Studies of radicals in oxalate systems*. Molecular Physics, 1980, Vol. 41, No. 6, 1493 - 1500

- [8] T. V. Vernitskaya, O. N. Efimov: *Polypyrrole: a conducting polymer; its synthesis, properties and applications*. Russian Chemical Reviews, 2007, 66 (5), 443 – 457
- [9] H. Shirakawa, E. J. Louis, A. J. MacDiarmid, C. K. Chiang, A. J. Heeger: *Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, (CH)_x*. Journal of the Chemical Society, Chemical Communications, 1977, 578 - 580
- [10] R. E. Myers: *Chemical Oxidative Polymerization as a Synthetic Route to Electrically Conducting Polypyrroles*. Journal of Electronic Materials, 1986, Volume 15, Issue 2, 61 – 69
- [11] A. Diaz, K. K. Kanazawa, G. P. Gardini: *Electrochemical polymerization of pyrrole*. Journal of the Chemical Society, Chemical Communications, 1979, 635 – 636
- [12] A. J. Bard, S.N. Frank: *Semiconductor Electrodes. 11. Electrochemistry at n-Type TiO₂ Electrodes in Acetonitrile Solutions*. Journal of the American Chemical Society, 1975, Vol. 97, 26, 7427 – 7433
- [13] S. Günes, H. Neugebauer, N. S. Sariciftci: *Conjugated Polymer-Based Organic Solar Cells*. Chemical Reviews, 2007, Vol. 107, 1324-1338
- [14] S. Cosnier, A. Deronzier, J. Moutet: *Electrochemical coating of a platinum electrode by a poly(pyrrole) film containing fac-Re(2,2'-Bipyridine)(CO)₃Cl system application to electrocatalytic reduction of CO₂*. Journal of Electroanalytical Chemistry, 1986, Vol. 207, 315-321
- [15] R. Aydin, F. Köleli: *Electrocatalytic conversion of CO₂ on a polypyrrole electrode under high pressure in methanol*. Synthetic Metals, 2004, Vol. 144, 75–80
- [16] M. Le, M. Ren, Z. Zhang, P. T. Sprunger, R. L. Kurtz, J. C. Flake: *Electrochemical Reduction of CO₂ at Copper Oxide Surfaces*. Journal of The Electrochemical Society, 2011, Vol. 158, No. 5, E45 – E49
- [17] K. W. Frese: *Electrochemical Reduction of CO₂ at Intentionally Oxidized Copper Electrodes*. Journal of The Electrochemical Society, 1991, Vol. 138, No. 11, 3338 - 3344
- [18] Y. Yang, C. A. Mims, D. H. Mei, C. H. F. Peden, C. T. Campbell: *Mechanistic studies of methanol synthesis over Cu from CO/CO₂/H₂/H₂O mixtures: The source of C in methanol and the role of water*. Journal of Catalysis, 2013, Vol. 298, 10 -17

[19] D. Grujicic, B. Pesic: *Electrodeposition of copper: the nucleation mechanisms*. *Electrochimica Acta*, 2002, Vol. 47, 2901-2912

[20] P. Hacırlıođlu, L. Toppare, L. Yılmaz: *Polycarbonate-polypyrrole mixed matrix gas separation membranes*. *Journal of Membrane Science*, 2003, Vol. 225, 51-62

[21] R. John, G.G. Wallace: *Doping-dedoping of polypyrrole: a study using current-measuring and resistance-measuring techniques*. *Journal of Electroanalytical Chemistry*, 1993, Vol. 354, 145-160

7. Acknowledgements

First of all I want to express my special gratitude to o.Univ. Prof. Mag. Dr. DDr. h.c. Niyazi Serdar Sariciftci for giving me the opportunity to work at the LIOS and during this time receiving insight into the interesting field of science.

Special thanks to my supervisor Dogukan Hazar Apaydin, MSc for the excellent guidance throughout the whole time at LIOS. In my opinion the best didactic way of teaching is in the middle between just showing something and *learning by doing* - and you did a great job in guiding me with patience through the complex areas of analytics, CO₂ reduction and electrochemistry.

Finally I would like to thank all the members of LIOS for always providing help and the great time I had being part of this institute.