

Submitted by

Stefan Pöllner

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**Linz Institute for Organic
Solar Cells (LIOS)/ Institute
of Physical Chemistry (IPC)**

Thesis supervisor

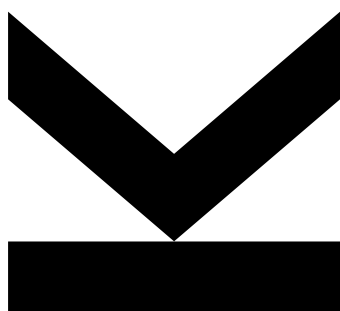
**o. Univ. Prof. Mag. Dr. DDr.
h.c. Niyazi Serdar Sariciftci**

Guidance

DI Dr. Philipp Stadler

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Investigation of Polydopamine as a Catalyst for Oxygen Evolution Reaction



Bachelor thesis

to obtain the academic degree of

Bachelor of Science

in the Bachelor program

Technical Chemistry

Statement of Authorship

I hereby declare this bachelor thesis was entirely written by me and without foreign help. No other person's work has been used without due acknowledgement in this thesis. All used references are cited in the bibliography in all conscience.

Linz, 12.08.2019

Stefan Pöllner

Tasks

The conducting biopolymer polydopamine (PDA) is known as a catalyst for CO₂ reduction and for hydrogen evolution. Here in this work, the electrocatalytic oxygen evolution reaction (OER) was investigated.

PDA was synthesized on various substrates including carbon felt, fluorine doped tin oxide (FTO), titanium mesh and gold using oxidative chemical vapor deposition (o-CVD). The deposited thin films were characterized by fourier-transform infrared spectroscopy (FTIR), UV/Vis spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM). These PDA-coated electrodes were characterized electrochemically for OER using cyclic voltammetry (CV). An online gas chromatography (GC) was performed to examine the evolution of oxygen and high performance liquid chromatography (HPLC) and ion chromatography (IC) were executed on the electrolyte to check if PDA is decomposing during water oxidation.

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1. State-of-the-art and theory concept

As renewable energy production has fluctuations, there is the need for energy storage and conversion [1]. A possible way of storage is (photo)electrochemical energy conversion to fuels e.g. by splitting H_2O to H_2 and H_2O_2 or CO_2 to hydrocarbons and CO as shown in Figure 1. However, these redox reductions require efficient kinetics in the oxygen evolution reaction. It is obligatory to optimize the OER by electrocatalysts to receive an overall high energy efficiency (EE).

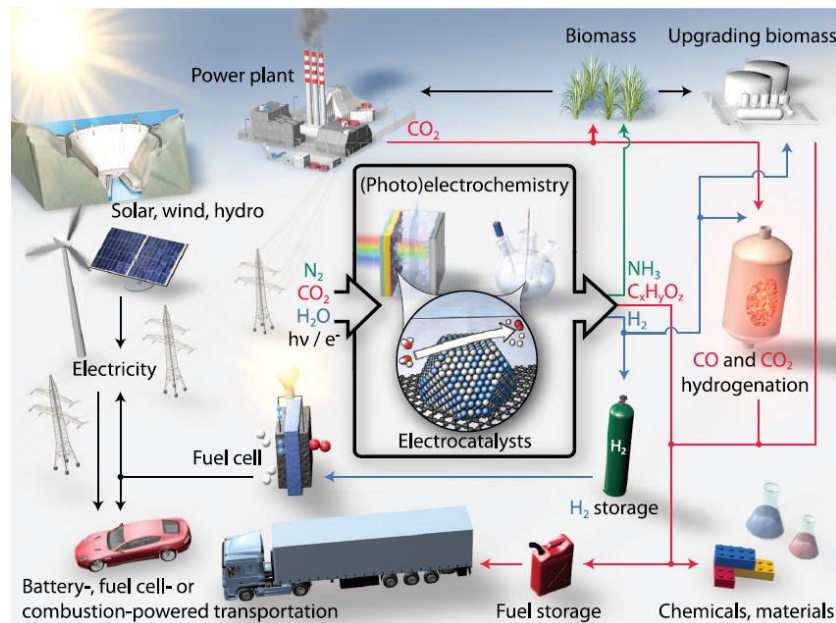


Figure 1: Concept for electrochemical energy storage [2]

Currently noble metal containing materials such as IrO_2 and RuO_2 are the state-of-the-art catalysts for OER and will be discussed in 1.1. .

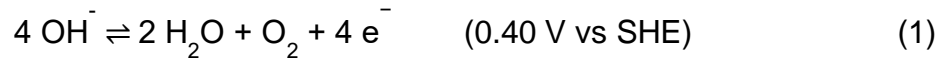
In this thesis polydopamine, a non-metal functional polymer, was investigated with regard to catalytical activity on OER.

The tasks of this thesis are:

- Synthesis of PDA by o-CVD on CF, Au, titanium mesh and FTO
- Analysis of PDA by FTIR, UV/Vis, SEM and AFM
- Characterizing PDA-coated electrodes with cyclic voltammetry under electrolyte variation
- O_2 analysis via GC during OER
- High performance liquid chromatography (HPLC) and ion chromatography (IC) of the electrolyte to check PDA for decomposition

1.1. OER catalysis

As shown in Formula 1, the OER is a 4-electron process consisting of two steps (adsorption and recombination). Because of the reaction mechanism, in particular the recombination, the OER can be kinetically hindered with the consequence of high overpotentials [3].



The aim of my research in this thesis is to develop a polymer catalyst which facilitates the water adsorption and the recombination process with the target to reduce overpotentials. Common OER-catalysts are measured at a current density of 10 mA cm^{-2} (area is normalized as electrochemical active surface).

Currently noble metal containing materials such as IrO_2 and RuO_2 are the state-of-the-art catalysts for OER due to their high electrocatalytical activity. However, metals like Ir and Ru are scarce and expensive. Therefore, novel approaches for electrocatalysts for OER are required.

In 2008, a formation of a non-noble electrocatalyst for OER in phosphate buffered water containing Co^{2+} ions was reported [4]. Currently, a huge variety of transition metal-oxide-based catalysts (mostly Ni, Co, Fe) are under investigation [5]. In Figure 2 the volcano plot summarizes the catalytic performance of best-in-class metal oxides regarding to their overpotential and binding energy of the intermediate oxygen on the surface. To enable accelerated kinetics, it is essential to reduce the oxygen binding energy.

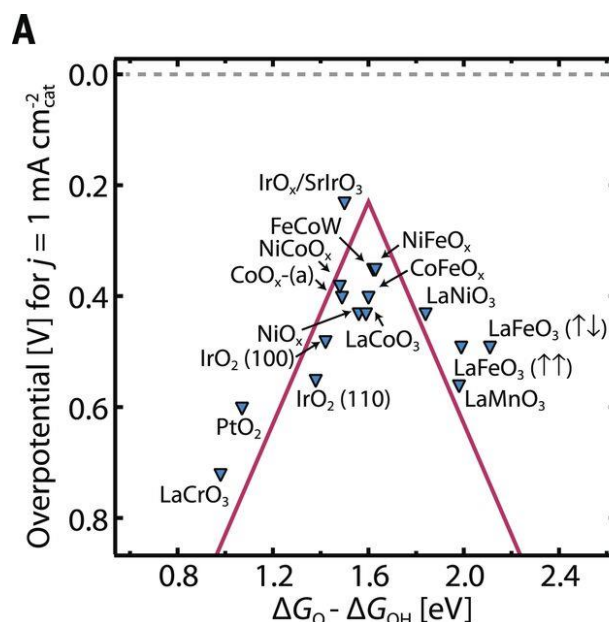


Figure 2: OER volcano plot for various metal oxides [2]

It is evident that metal oxides have a decent performance in OER, however oxide catalysts often experience stability problems such as dissolution in the electrolyte due to oxidation, especially in acidic media [6]. Also, the high cost of metal oxides is noticeable.

I first use PDA as an organic OER catalyst, representing a novel approach for sustainable and inexpensive OER.

1.2. PDA

As mentioned before, I investigate the effect of polydopamine for electrocatalytic OER. PDA is synthesized using o-CVD in a tube furnace starting from monomeric dopamine in presence of sulfuric acid as oxidizing agent (Figure 3).

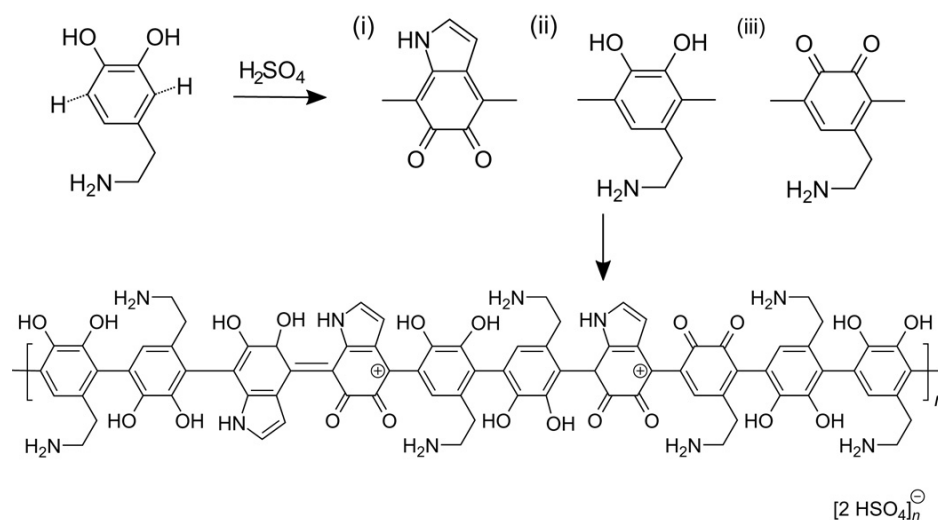


Figure 3: Synthesis path for PDA, with (i) condensed and oxidized diketoindeole, (ii) dopamine, and (iii) oxidized dopamine as intermediate monomers [7]

By using CVD an oxidative polymerisation occurs. This chemically polymerizes p-doped PDA in one step and generates a conductive and conjugated system consisting of a p-doped polymer [8].

Generally, p-doped systems/semiconductors promote the electrocatalytic OER and lead to high surface activity [9]. Therefore, a positive effect of PDA on OER was hypothesized.

2. Experimental

Four types of materials were tested as electrode-substrates for OER: gold (Au), fluorinated tin oxide (FTO), titanium mesh (Ti) and carbon felt (CF). The aim was to find a substrate, which binds the PDA effectively and is stable during the harsh conditions during synthesis and electrochemistry.

Also, the effect of various electrolytes (KOH, NaOH, $\text{KHCO}_3/\text{K}_2\text{CO}_3$) and pH on the stability of the working electrodes and the efficiency of OER was investigated.

2.1. Preparation of electrodes

Au has been directly deposited on glass with/without adhesion layers (chromium and polyethyleneimine (PEI)). The glass substrates were prepared by cutting 3.8 x 1.0 cm substrates. Afterwards they were cleaned by sonification in a detergent (Hellmanex) for 15 min and then washed with deionized water. Further the glasses were purified using a *Plasma ETCH P25* plasma oven for 5 min at 50 W and O_2 atmosphere.

The PEI electrodes were produced by spin coating with a solution of Polyethylenimine in 1-butanol (0.033 %) and 84 rps for 30 s, right after the substrates were dried on a heating plate at 110 °C for 10 min. Then they were again purified in the plasma oven. 7 nm of chromium was evaporated onto the glass substrates by thermal, vapor desorption in high vacuum. 100 nm of gold were evaporated onto to the glass, the PEI and the chromium substrates. The tops of the electrodes were covered with silver paste and were wrapped with aluminium foil for connection with a crocodile clip.

The FTO coated glass substrates were cleaned by sonification in a detergent (Hellmanex) for 15 min and then washed with deionized water and dried with N_2 . The titanium meshes were also washed with deionized water and dried with N_2 . For the carbon felt electrodes no preparation steps before synthesis were applied.

2.2. Synthesis of PDA by o-CVD



Figure 4: Tube furnace connected with N₂ supply and gas washing bottle

For the synthesis of PDA, a tube furnace (Carbolite, Type: MTF 12/38/400, Max. Temp: 1200 °C, Performance: 1600 W) with a glass tube inside (outer diameter: 3.2 cm, inner diameter: 2.8 cm) was used (Figure 4). Dopamine hydrochloride was dried in a furnace at 150 °C in a glovebox overnight in presence of CaH₂. For synthesis 500 mg of Na₂SO₄ mixed with 500 μL of H₂SO₄ (95-97 %) and 500 mg of dopamine hydrochloride have been positioned in two separate vials in the tube according to Figure 5 (sodium sulphate increases the amount of SO₃ in the vapour and therefore improves the oxidation power of sulfuric acid).

The substrates were positioned on a slide glass in the glass tube. The tube was connected to a nitrogen line on the inlet side and to a gas washing bottle containing 1 M NaOH on the outlet side. A fume hood was positioned over the outlet to ensure that there is no release of sulfuric acid. The polymerization reaction was carried out at 350 °C for 30 min with a nitrogen flow of 2.5 L min⁻¹. Before that the materials were heated at 150 °C for 30 min in the tube furnace to ensure that the volatile compounds were evaporated.

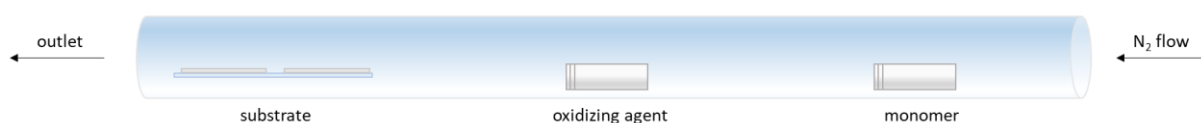


Figure 5: Schematic drawing of the reactants inside the glass tube

The CVD deposition was performed using carbon felt, FTO glass, glass, titanium mesh and on gold. About 0.75 mg PDA per cm² projected area were obtained on titanium

mesh and about 1 mg per cm² projected area on the other substrates. Figure 6 shows four kinds of electrodes after the synthesis with PDA containing carbon felt, FTO on glass, titanium mesh and Au/Cr on glass.

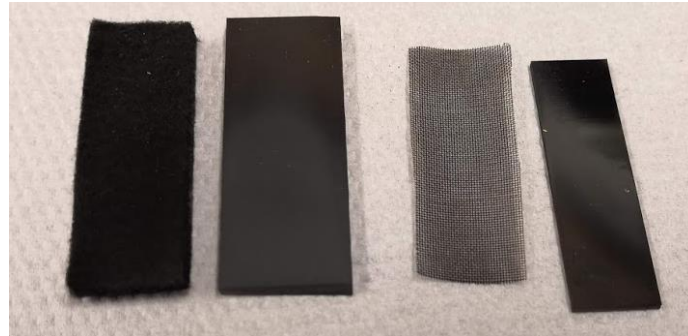


Figure 6: Beginning from left: PDA on CF, FTO, TM and Au/Cr

2.3. Characterization of PDA film

2.3.1. ATR-FTIR

For the FTIR measurements a Bruker Vertex 80 spectrophotometer was used. The samples were placed and clamped directly on a platinum attenuated total reflection (ATR) module pointing with the PDA side to the ATR-diamond crystal, to minimize the gap between substrate and crystal. The interferometer uses a KBr beam splitter and a liquid N₂-cooled mercury cadmium telluride (MCT) detector. The background measurement was performed using air as a reference.

The advantage of the ATR method allows to measure the reflectance (internal reflection) of the PDA. The infrared light is reflected at the diamond surface since the crystal is in direct contact with the sample. An evanescent IR-wave forms and thus the fingerprint spectroscopic absorption can be measured directly [10].

The time for synthesis of the PDA in the furnace was reduced from 30 min at 350 °C to 5 min to receive a thinner film ("Thickness control over time").

Figure 7 shows the spectrum of PDA thin film synthesized on glass substrate (calibration: air). The broad absorption band between 3300 cm⁻¹ and 1800 cm⁻¹ relates to O-H and N-H vibrations. These are broadened by hydrogen bonds. The bands at 2320 cm⁻¹ are related to CO₂ in the atmosphere. Vibrations between 1650 cm⁻¹ and 1421 cm⁻¹ are a characteristic fingerprint of cyclic C=N groups [11]. The band at 1578 cm⁻¹ represents carbonyl vibrations. The intense bands starting from 1162 cm⁻¹ to

859 cm^{-1} provide evidence of the p-doping of the PDA (infrared-activated vibrations, see [11]).

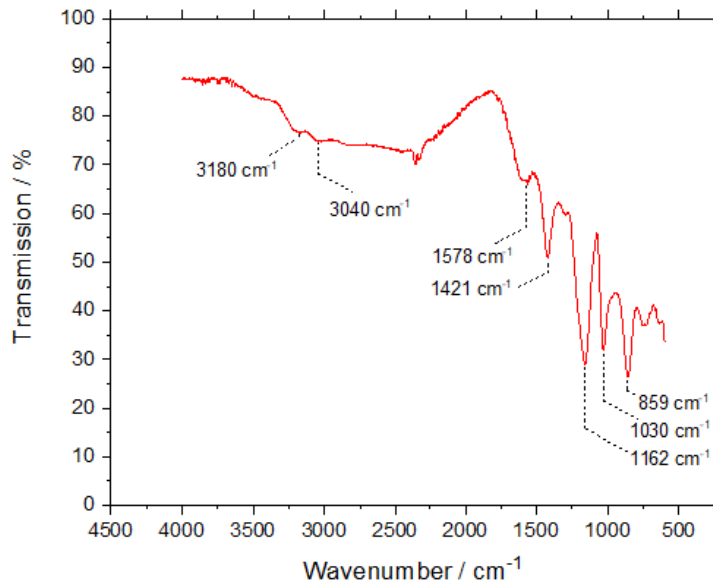


Figure 7: FTIR spectrum of PDA thin film on glass substrate

In Figure 8 a FTIR spectrum obtained from literature of, inter alia, PDA prepared by o-CVD is shown. It is noticeable that the absorption bands in the fingerprint region are similar to the ones in Figure 7. However, the broad absorption band between 3700 cm^{-1} and 1900 cm^{-1} is more intensive than the one observed in the here synthesized PDA. This implies that the O-H / N-H valence vibrations are broadened in the PDA thin film. This phenomenon could be a result of the different reaction time during synthesis.

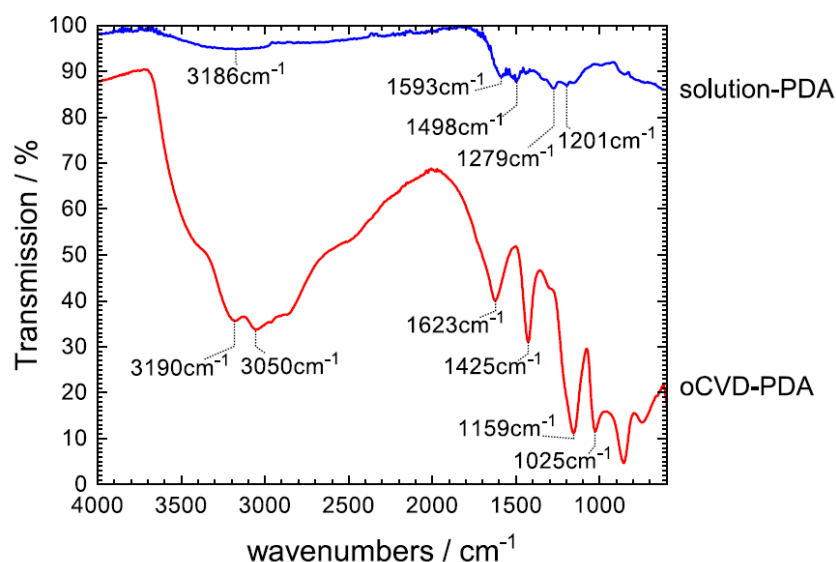


Figure 8: FTIR spectrum PDA prepared by o-CVD and in solution [Fehler! Textmarke nicht definiert.]

2.3.2. UV-Vis

For the UV-Vis measurements a Lambda 1050 spectrometer has been used. A D₂ lamp and a tungsten-halogen lamp serve as light sources. The data interval is 2 nm. The monochromator is set to 850 nm. Slits are configured for photomultiplier tube (PMT) at 4 nm and for InGaAs and PbS at 2 nm. PMT, InGaAs and PbS (3-detector module) are used for detection.

For UV/Vis transmission PDA-films with 0.4 mg PDA per cm² substrate have been produced (this has been achieved by using 100 mg dopamine instead of 500 mg for synthesis).

Figure 9 shows the transmission and absorbance spectrum of PDA-on-glass substrates. The PDA films show intense, broad spectral absorption starting from 800 nm to 350 nm.

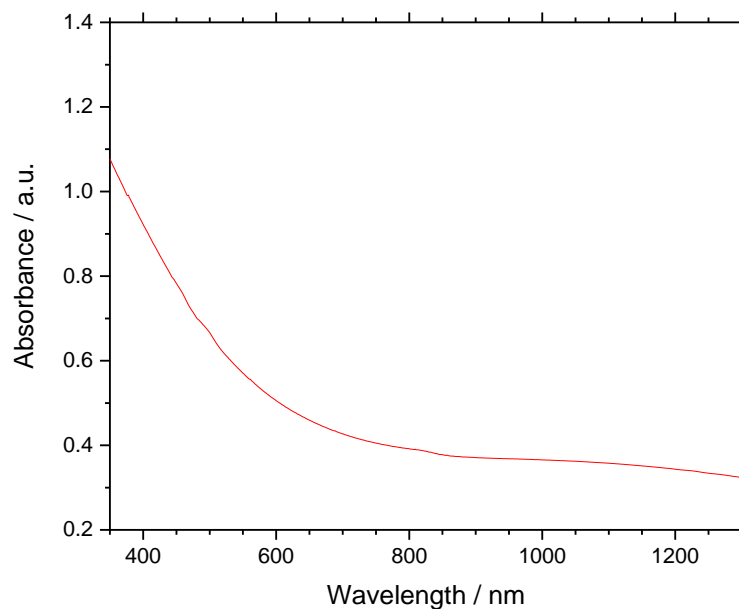


Figure 9: Absorbance spectrum of PDA on glass starting from 1300 nm to 350 nm

2.3.3. SEM

To obtain information of topography and visualization of the PDA films, images with a scanning electron microscope (SEM) have been taken using a JEOL JSM-6360LV SEM. The acceleration voltage was 9 kV and a working distance between 20 mm and 21 mm was implemented.

For the SEM images titanium mesh as reference and titanium mesh coated with PDA were compared. It is visible in Figure 10 that the titanium mesh was completely coated with PDA.

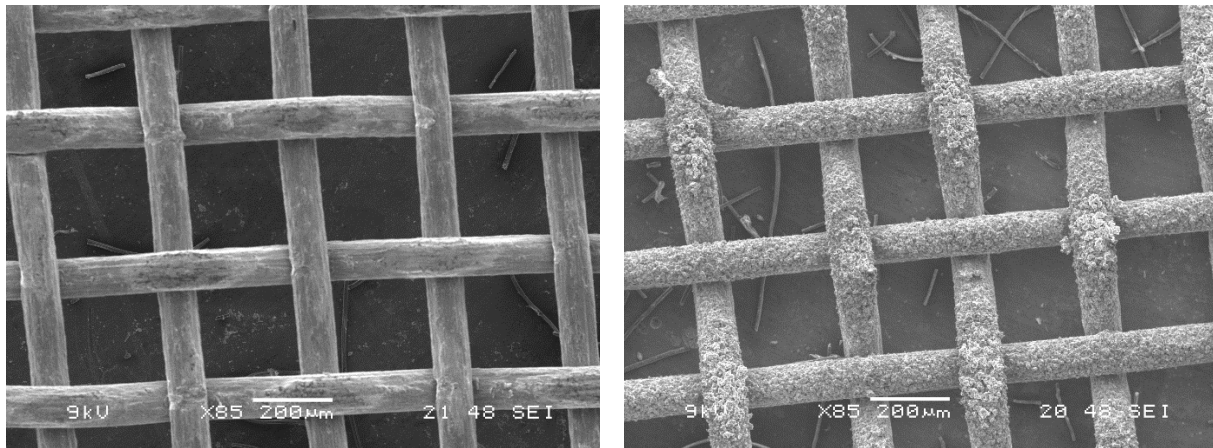


Figure 10: (left) titanium mesh reference (right) PDA coated titanium mesh, 85-fold magnification

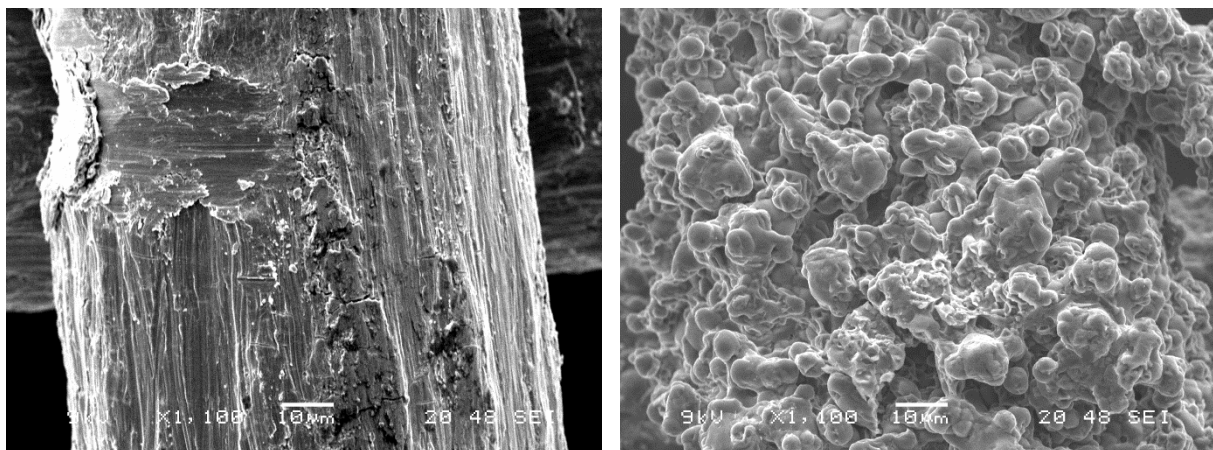


Figure 11: (left) titanium mesh reference (right) PDA coated titanium mesh, 1100-fold magnification

Figure 11 shows that the surface of the PDA is rough (400 rms), therefore enlarging the catalytically active surface area for the oxygen evolution reaction.

2.3.4. AFM

To receive more detailed information about the topography of the PDA films, the substrate was investigated with atomic force microscopy (AFM). A microscope called Innova provided by Bruker was used. The AFM was operated in tapping mode with a scan rate of 0.5 Hz. The measurement was carried out with a μ -masch ultrasharp NSC15/AIBS cantilever.

A PDA thin film on glass substrate produced by the method described in 2.2. with the deviation of 3 min synthesis time instead of 30 min was used. The observed film

(Figure 12) has a high root mean square roughness of 400 nm. This is in agreement to the roughness observed in SEM.

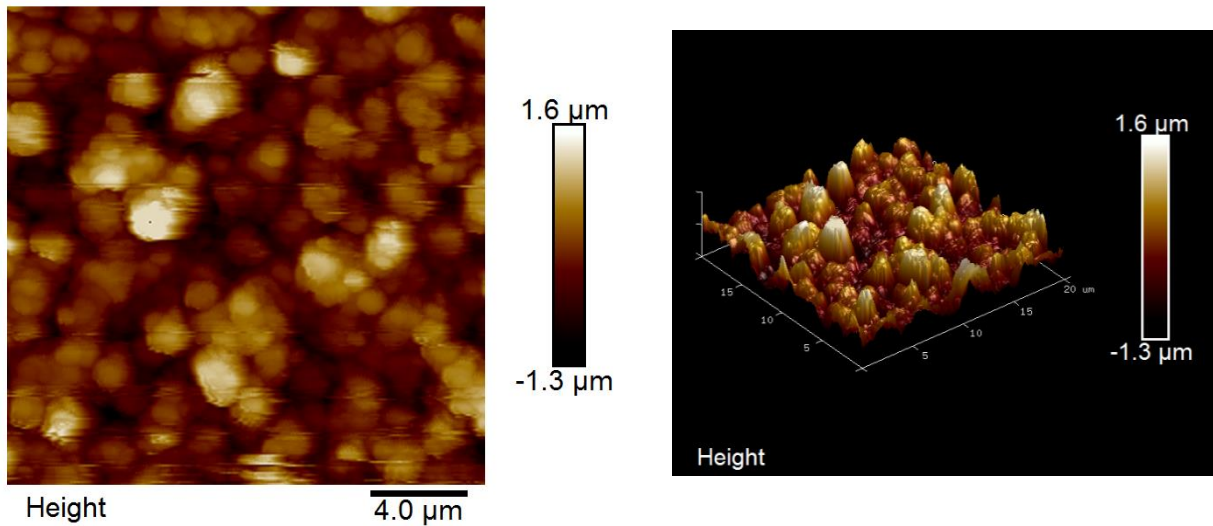


Figure 12: AFM image of thin film PDA on glass substrate

2.4. Electrochemistry

For characterization of OER cyclic voltammetry was performed. The various PDA coated electrodes served as working electrodes (WE), platinum and nickel sheet were used as counter electrodes (CE). For CV's I used a Ag|AgCl|3M KCl electrode as reference electrode (RE). The reference electrode delivers a constant potential of 210 mV vs standard hydrogen electrode (SHE). A glass frit separates the two compartments. For long-term experiments (chronoamperometry/chronopotentiometry) a 2-electrode setup without a reference electrode was implemented. All electrodes were connected to a potentiostat (Jaissle Potentiostat-Galvanostat IMP 88 PC-R). In Figure 13 a schematic drawing of the setups are shown.

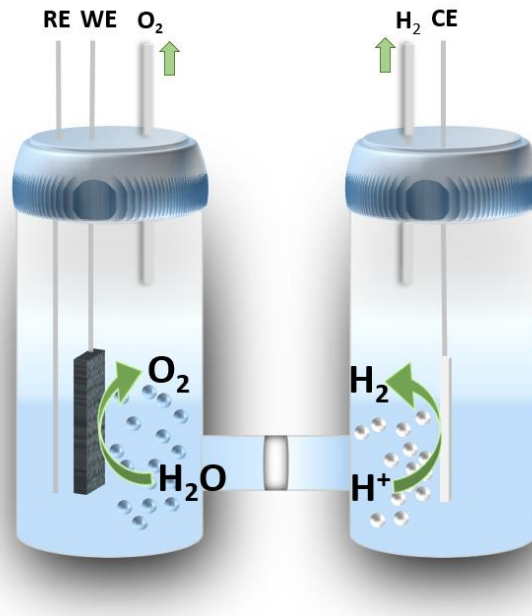
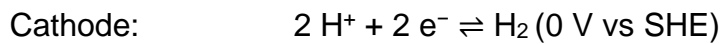
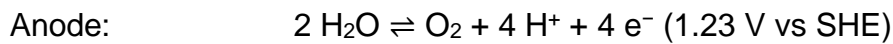


Figure 13: Schematic drawing of the 2-compartment cell used for OER

There are two half reactions taking place in the cell:



The potential delivered by the Ag/AgCl reference electrode is converted into reversible hydrogen electrode (RHE) potential to enable to compare different measurements independent of type of reference electrode and pH of the electrolyte:

$$\text{RHE} = \text{SHE} + 0.210 \text{ V} + 0.059 \text{ V} \cdot \text{pH} \quad (2)$$

2.5. Online GC analysis

To test if any decomposition of PDA occurs in oxidative conditions a chronopotentiometry in an electrochemical cell with simultaneous online GC measurement has been performed. For chronopotentiometry a 2-compartment cell with a glass frit and an air bridge was used (the air bridge served to equalize the pressure). The cell was sealed tightly, so that there was no release of analyte gas. A nickel sheet served as counter electrode and PDA coated on platinum served as working electrode (2-electrode setup). As seen in Figure 14, the electrolyte was purged with nitrogen (with 10 mL min^{-1}) delivered from a supply line. This led to a gas flow from the cell directly to the 6-port valve of the GC with a volume of 1.5 mL. For the measurement the Trace GC Valve Oven from Thermo Scientific was used. A temperature program starting from $40 \text{ }^\circ\text{C}$ and with a final temperature of $130 \text{ }^\circ\text{C}$ was

performed. Every 30 min a measurement was started (20 min measurement time, 10 min idle time).

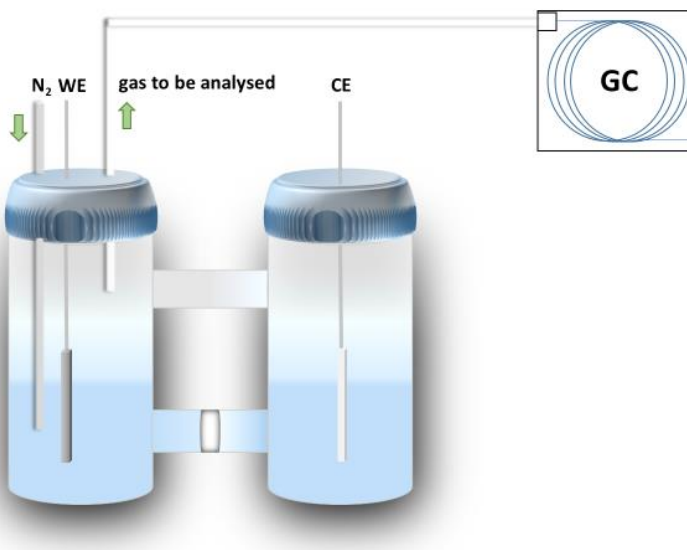


Figure 14: Schematic drawing of the on-line GC analysis

2.6. HPLC, IC

After 24 h of chronopotentiometry with PDA synthesized on platinum the electrolyte was analysed by HPLC and IC to check if decomposition of the catalyst occurs.

For IC, the sample was diluted by the factor of 40 with 18 MΩ cm water. The analysis was performed with an *ICS-5000 Dionex* ion chromatograph equipped with a *Dionex Ion Pac AS19* column. The operation temperature in the column was 30 °C and an eluent flow rate of 0.25 mL/min was applied. A conductivity detector was used for detection of the analytes and KOH (0-7 min, 14-27 min 10mM KOH; 7-14 min 100 mM KOH) served as eluent.

For HPLC, the sample was diluted by the factor of 100 with 18 MΩ cm water. The analysis was performed with a *Dionex HPLC* chromatograph (column: *HyperREZxP Carbohydrate Ca²⁺*, 8 μm particle size, 300 x 7.7 mm). The operation temperature in the column was 70 °C and 3 mM H₂SO₄ served as mobile phase. The detection was carried out with a UV/Vis detector at a wavelength of 210 nm.

2.7. Chemicals

Table 1: Used Chemicals

| Materials | Purity | Company |
|--|-----------|---------------|
| Sodium sulfate | ≥ 99 % | Sigma Aldrich |
| Sulfuric acid | 95 – 98 % | J.T.Baker |
| Dopamine hydrochloride | 98 % | Sigma Aldrich |
| Calcium hydride | 95 % | Sigma Aldrich |
| Sodium hydroxide | 99 % | Merck |
| Potassium hydroxide | 85 % | Alfa Aesar |
| Potassium bicarbonate | ≥ 99.7 % | Fluka |
| Potassium carbonate | 99 % | Alfa Aesar |
| Polyethylenimine, branched, in 1-butanol (0.2 %) | ≥ 99 % | Sigma Aldrich |
| 1-Butanol | ≥ 99 % | Sigma Aldrich |
| Oxalic acid | ≥ 99 % | Sigma Aldrich |
| Sodium acetate | ≥ 99 % | SigmaUltra |
| Sodium formate | ≥ 99 % | Sigma Aldrich |

3. Results and Discussion

3.1. Chromatography / PDA stability

3.1.1. Online GC analysis

For the online GC analysis, a PDA coated platinum electrode was used to study the stability and possible degradation products. A chronopotentiometric scan at a constant current was performed. The Faradaic efficiency is the efficiency with which charge is transferred into the chemical reaction of water splitting. The calculated amount of oxygen produced in 30 min is:

$$n = \frac{I \cdot t}{z \cdot F} = \frac{0.8 \cdot 10^{-3} \text{ A} \cdot 1800 \text{ s}}{4 \cdot 96485 \text{ s A mol}^{-1}} = 3.73 \mu\text{mol O}_2 \hat{=} 83.6 \mu\text{L O}_2 \quad (3)$$

n ... produced oxygen [mol]

I ... current [A]

t ... time [s]

z ... number of electrons

F ... faraday constant (96485.3 A s mol⁻¹)

In Figure 15 the performance of PDA coated platinum and blank platinum are compared. In the CV's, it is noticeable that the platinum electrode has a lower overpotential compared to the PDA coated one, implying that Pt is a better catalyst than PDA for OER. But as mentioned before, the purpose of this experiment was to test the stability of PDA.

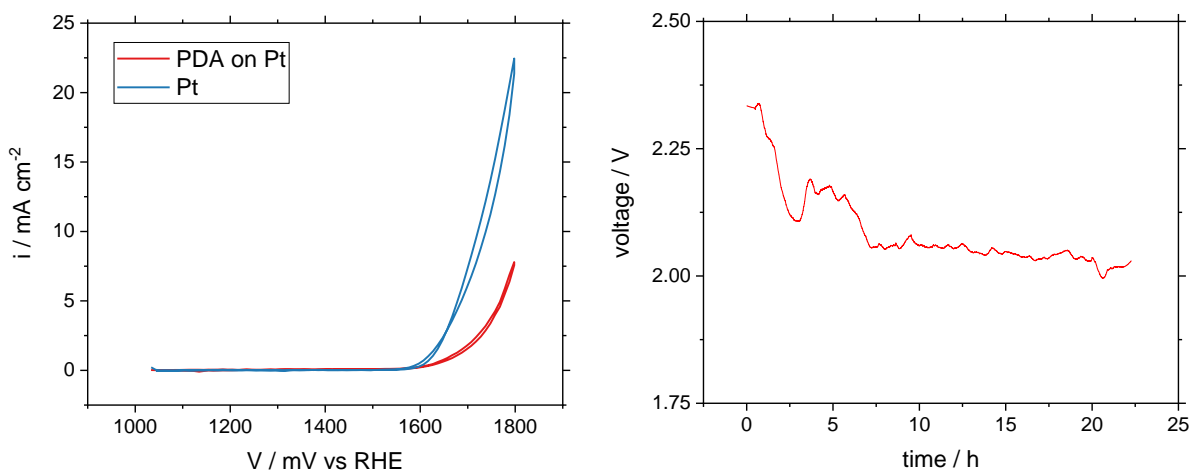


Figure 15: (left) comparison of PDA on titanium mesh and blank titanium mesh in 1 M KOH at a scan rate of 10 mV s⁻¹ (right) chronopotentiometry of PDA on titanium mesh at 0.8 mA during online gas chromatography

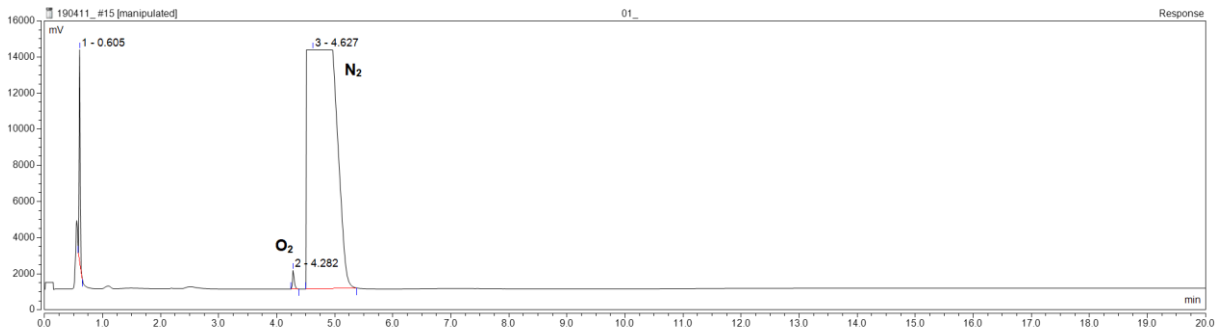


Figure 16: online gas chromatography after 5 h 26 min

Figure 16 shows a GC chromatogram after 5 h 26 min and at 4.282 min a peak of O₂ was observed. However, in the N₂ supply line an oxygen content of 0.22 % was detected, leading to a total amount of 0.65 mL O₂ delivered by the supply line in 30 min. This is a difference of more than the factor 7 to the 83.6 μL theoretically produced oxygen.

This shows that this type of measurement is not suitable for detecting small oxygen amounts precisely, however the peaks of the chromatograms during the chronopotentiometry were larger than the one from the N₂ supply line reference measurement, implying that there was evolution of O₂.

The GC chromatograms were further investigated for CO peaks, which is a possible decomposition product of PDA. When compared to reference measurements with CO found at 7.42 min, no indicational carbon monoxide was observed after 24 h electrolysis.

Figure 17 shows that there was delamination of the PDA during electrolysis after 23 h.

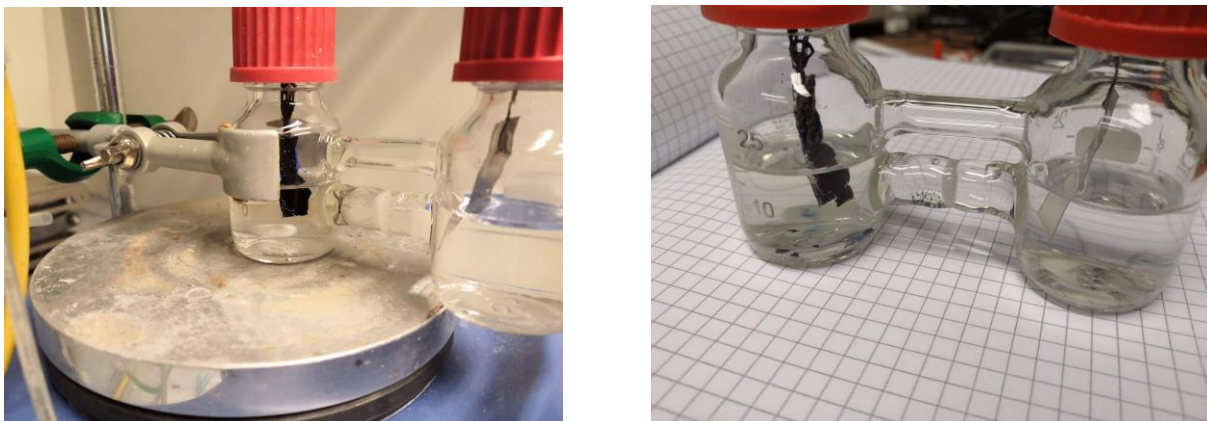


Figure 17: (left) Electrochemical cell after 4 h chronopotentiometry (right) Delamination of the PDA film after 23 h chronopotentiometry

3.1.2. HPLC

After 24 h the electrolyte was analysed with HPLC to check for further decomposition products. As seen in Figure 18 no decomposition products were found.

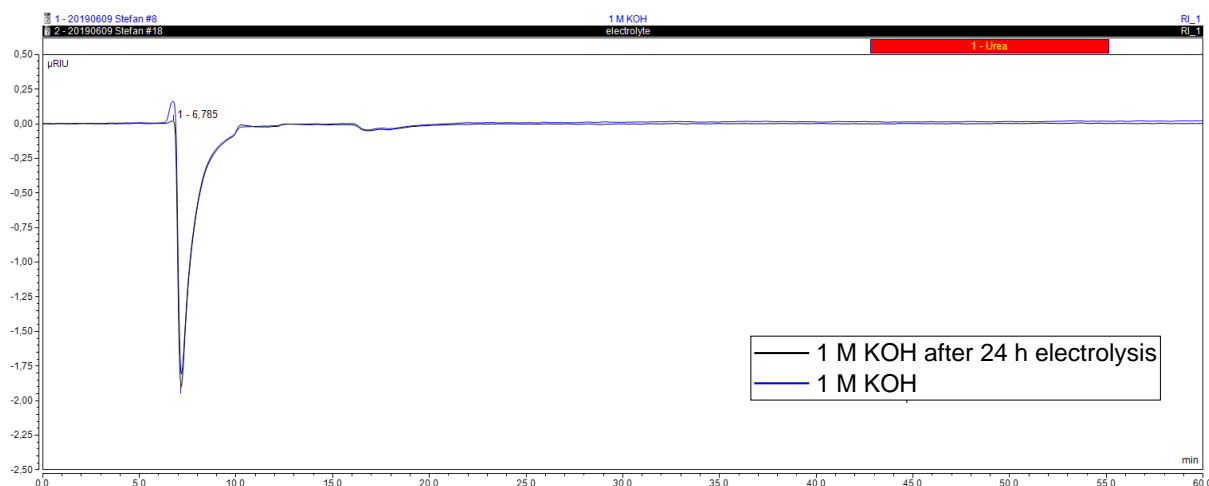


Figure 18: Comparison of 1 M KOH after 24 h electrolysis and 1 M KOH as reference with HPLC

3.1.3. IC

The electrolyte was also checked by IC for following possible decomposition products: acetate, formate, oxalate. For identification of the peaks measurements with 5 ppm of internal standards were performed, including oxalic acid, sodium acetate and sodium formate.

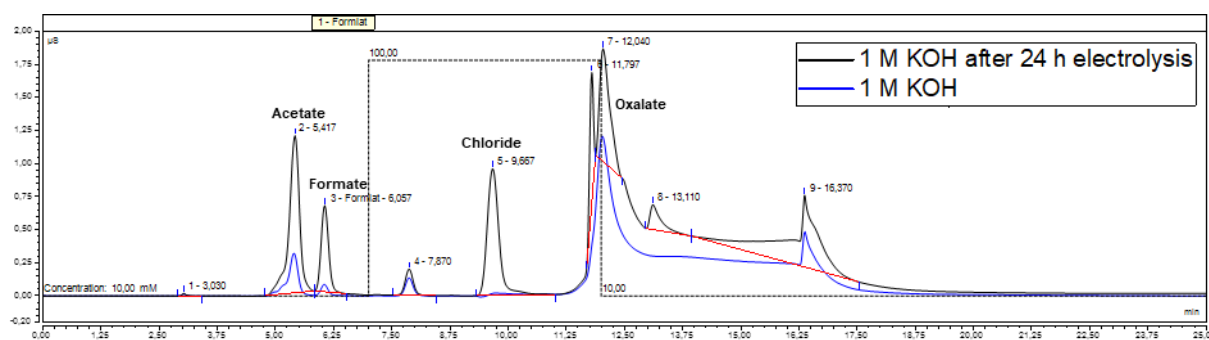


Figure 19: Comparison of 1 M KOH after 24 h electrolysis and 1 M KOH as reference with IC

Figure 19 shows that all three possible decomposition products of PDA (acetate at 5.417 min, formate at 6.057 min and oxalate at 12.040 min) were found in the electrolyte. Also, chloride at 9.667 min was found, implying that there was diffusion of chloride ions through the glass frit of the reference electrode.

This experiment shows that there is decomposition of PDA during applying positive potentials in alkaline media. However, with these chromatographic techniques the possible catalytic effect of PDA cannot be investigated, for this purpose cyclic voltammetry has been performed.

3.2. Proof of principle: Is PDA a catalyst for OER?

The main target of this section is to investigate by cyclic voltammetry if PDA has an catalytic effect on OER.

In Figure 20 a gold/chromium/glass electrode covered with PDA is compared to a gold/glass electrode. It can be clearly seen that PDA has a positive effect on OER. The electrode with the catalyst has with 3 mA cm⁻² at 568 mV overpotential a more than three times higher current compared to the reference electrode with 0.85 mA cm⁻². With the PDA coated electrode a tafel slope of 469 mV dec⁻¹ was received.

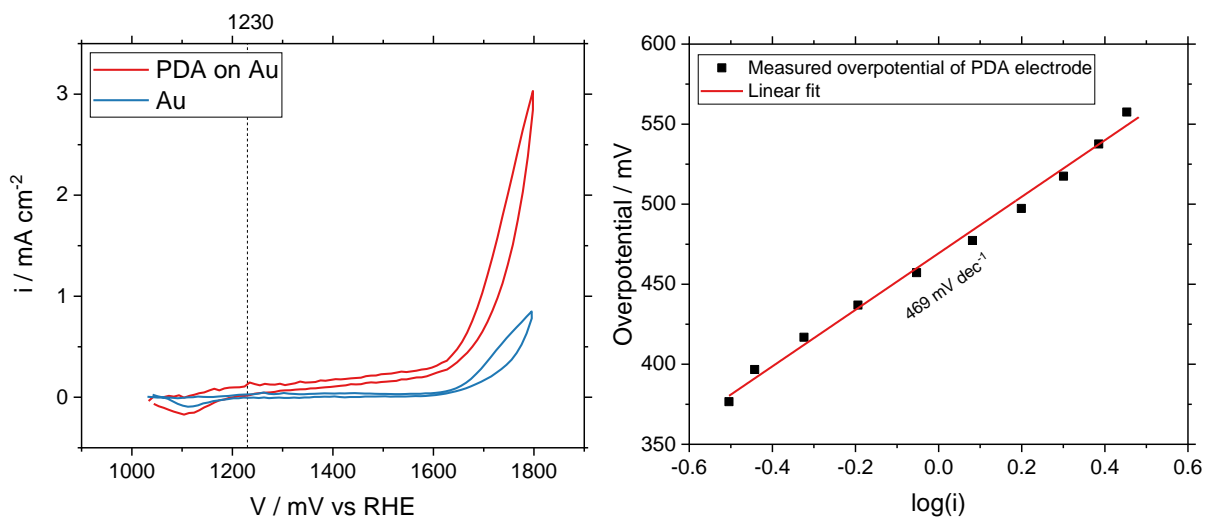


Figure 20: (left) Comparison of PDA on gold/chromium electrode and gold on glass reference in 1 M KOH at a scan rate of 10 mV s⁻¹ (b) tafel plot of PDA covered electrode

Since the transition of using sulfuric acid in synthesis and using strongly, alkaline electrolytes for OER is pretty harsh, a pretreatment program has been performed before performing water oxidation. After synthesis the electrodes were washed with MQ water, 0.01 M KOH and 1 M KOH gradually and were dried with air between the steps.

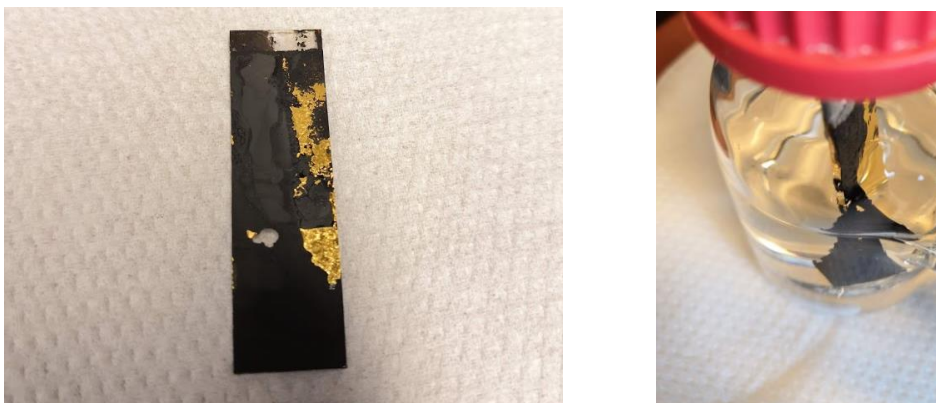


Figure 21: (left) PDA on Au/Cr after treatment (right) PDA on Au/Cr after CV

However, for all three types of electrodes delamination of the PDA film occurred during the pretreatment or after a period of approximately 30 min in the electrolyte performing cyclic voltammetry (Figure 21).

3.3. PDA on FTO glass

Alternatively to Au, FTO is stable in acid and base, therefore PDA has been synthesized on FTO glass substrates according to 2.2. with a synthesis time of 15 min. Before the electrochemical experiments, the PDA electrode was pre-treated with the electrolyte (0.01 M KOH) and washed with 18 M Ω cm water to prevent delamination by too harsh change from acidic to basic conditions.

Figure 22 shows the first ten cycles of a cyclic voltammogram of the PDA coated FTO electrode in 0.5 M K₂CO₃/KHCO₃. It was examined whether the change in electrolyte and pH has a positive effect on stability of the PDA electrode. However, a decrease of the current with every cycle was observed due to the delamination of the PDA film.

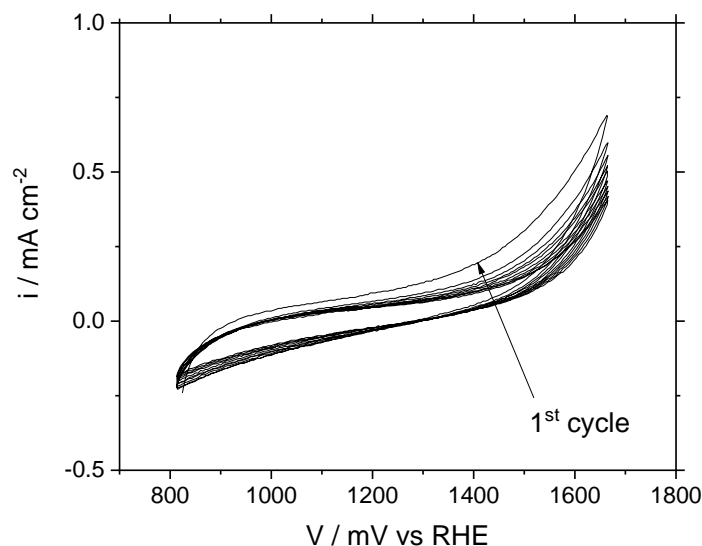


Figure 22: 10 cycles cyclic voltammetry of PDA on FTO glass with a scan rate of 50 mV s⁻¹

After 100 cycles of cyclic voltammetry the current was nearly 0 mA for the whole potential range. Delamination of the PDA film of the electrode occurred (Figure 23). This leads to the conclusion that FTO glass is no suitable substrate for PDA in the harsh conditions of PDA synthesis and OER.



Figure 23: Delamination of PDA film of FTO glass after 100 cycles cyclic voltammetry

3.4. PDA on titanium mesh

3.4.1. OER in 0.5M $K_2CO_3/KHCO_3$

In this section the effect of a $K_2CO_3/KHCO_3$ buffer solution and therefore a different type of electrolyte and a significantly lower pH value on the stability of the working electrode was investigated.

In Figure 24 the cyclic voltammogram of PDA covered titanium mesh in 0.5 M $K_2CO_3/KHCO_3$ can be seen. A decrease of current with increasing number of cycles was observed. Delamination of the PDA occurred, which was visible through appearance of black flakes in the electrolyte, which explains the decreasing current. A current of 0.58 mA cm^{-2} at 400 mV overpotential was received at the first cycle.

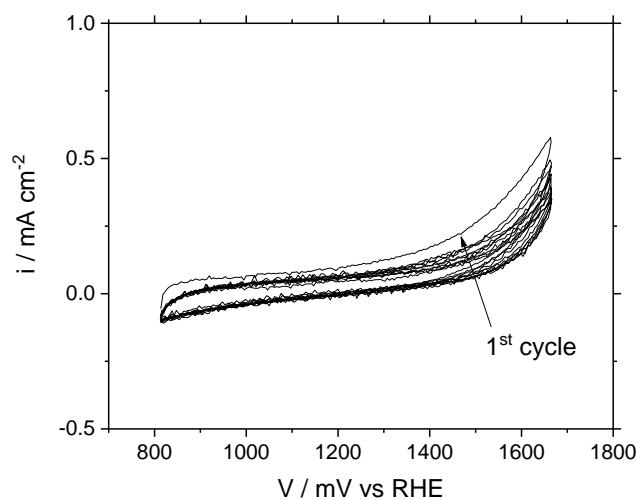


Figure 24: 10 cycles cyclic voltammetry of PDA on titanium mesh with a scan rate of 50 mV s^{-1}

3.4.2. OER in 1 M KOH

In 1 M KOH again a catalytic effect of PDA on OER was observed. An overpotential of 557 mV was apparent at 5 mA cm⁻² for the PDA covered titanium mesh, whereas a current of 0.92 mA cm⁻² was received at the same overpotential for the electrode without catalyst (Figure 25 a). A tafel plot with a slope of 426 mV dec⁻¹ was received for the PDA coated electrode (Figure b).

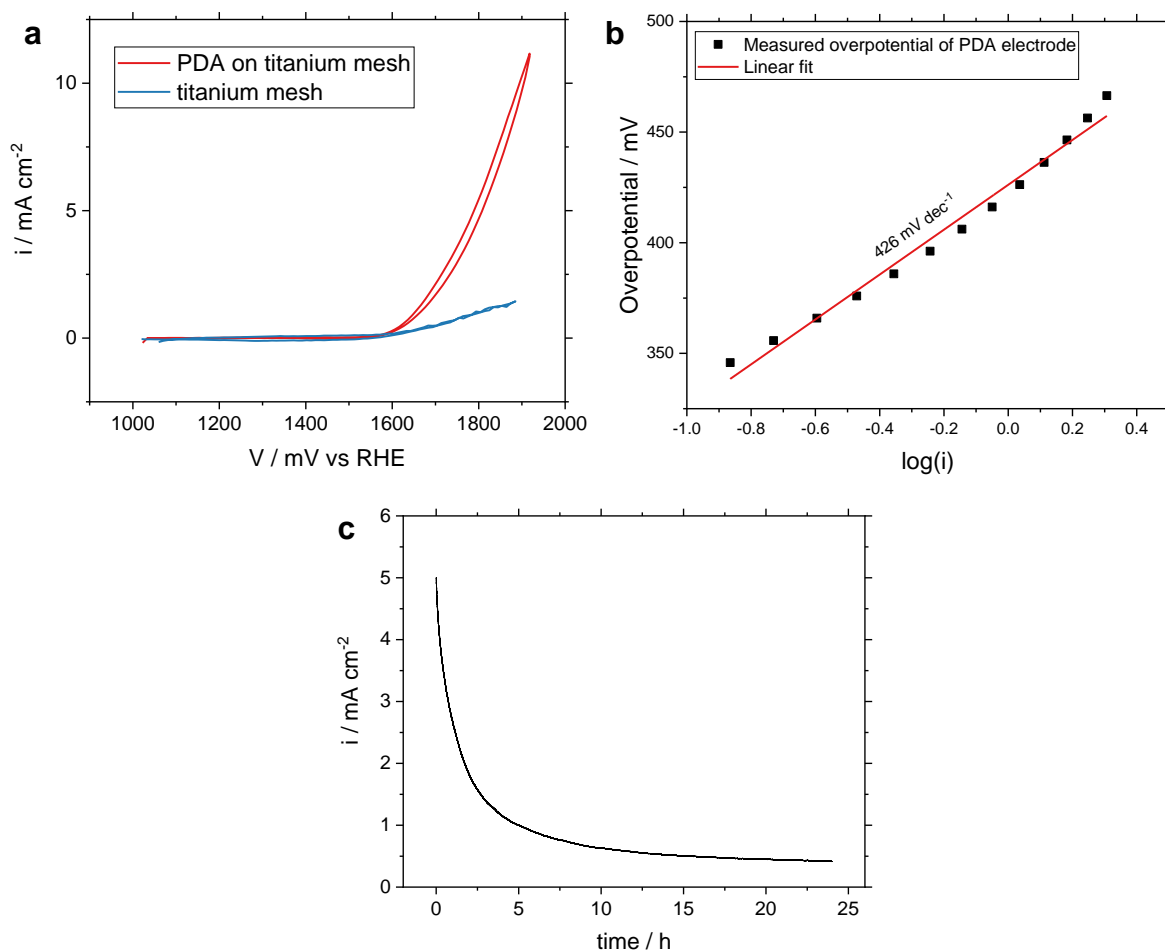


Figure 25: (a) Comparison of PDA on titanium mesh and blank titanium mesh in 1 M KOH at a scan rate of 10 mV s⁻¹ (b) tafel plot of PDA on titanium mesh (c) 24 h chronoamperometry of PDA covered titanium mesh with two-electrode setup and 557 mV overpotential

Also, a chronoamperometry with 557 mV overpotential using a two-electrode setup was implemented (Figure c). For this purpose, the current at 557 mV overpotential in CV was observed, then for chronoamperometry the potential was modified until the same current between working and counter electrode was received. After 5 h the current was decreasing from 5 mA cm⁻² at the start to approximately 1 mA cm⁻².

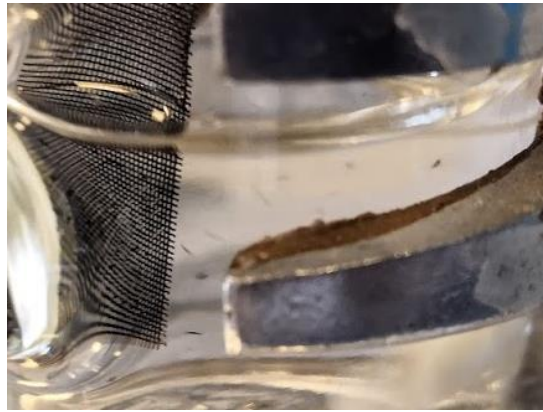


Figure 26: Occurrence of PDA flakes in electrolyte during chronoamperometry

In Figure 26 the occurrence of PDA flakes in the electrolyte during chronoamperometry is shown, leading to the conclusion that on titanium mesh also delamination occurs.

In Figure 27 the effect of catalyst loading on titanium mesh was examined. The performances of a PDA coated electrode with 0.75 mg PDA per cm^2 projected area and an electrode with 0.3 mg PDA per cm^2 projected area were compared. The thinner film was produced by using 100 mg dopamine hydrochloride instead of 500 mg (conventional method) during synthesis. It is evident that the more coated electrode has with 557 mV overpotential at 5 mA cm^{-2} a much better performance than the less coated electrode with 746 mV overpotential at 5 mA cm^{-2} . This leads to the result that PDA thin films produced by decreasing the amount of dopamine hydrochloride for synthesis have a worse performance than the catalyst synthesized by the conventional method.

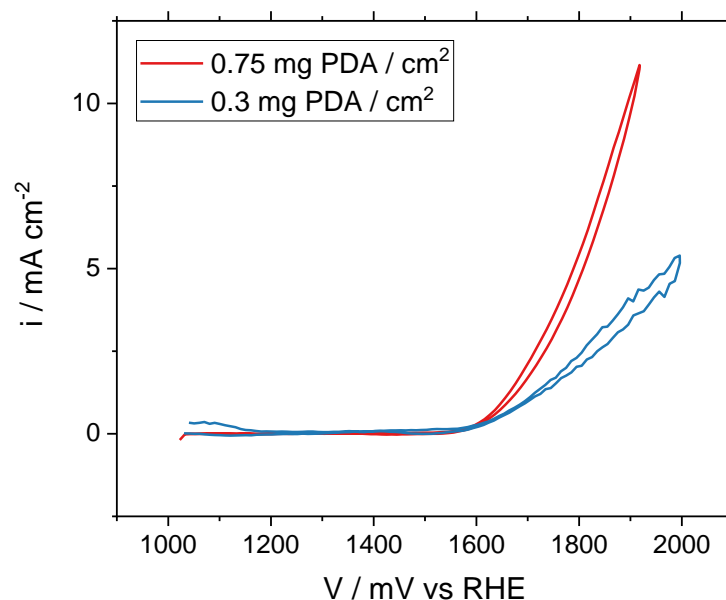


Figure 27: Comparison of PDA coated Ti with 0.75 mg PDA per cm^2 projected area and Ti with 0.3 mg PDA per cm^2 projected area

3.5. PDA on carbon felt

3.5.1. OER in 1M KOH

In Figure 28 the cyclic voltammograms of PDA synthesized on carbon felt and carbon felt as reference in 1M KOH (pH = 13.70) are compared, also the tafel plot of the PDA coated electrode is shown. It is recognizable that the PDA electrode has an overpotential of 478 mV at a current of 5.00 mA cm^{-2} and the reference electrode has a current of 0.62 mA cm^{-2} at 478 mV overpotential. This is a difference of a factor larger than 8 and the best result so far. For the PDA coated electrode, a tafel plot with a slope of 357 mV dec^{-1} was received. Also Figure c shows that the current is nearly equivalent during the runtime of 10 cycles with 100 mV s^{-1} .

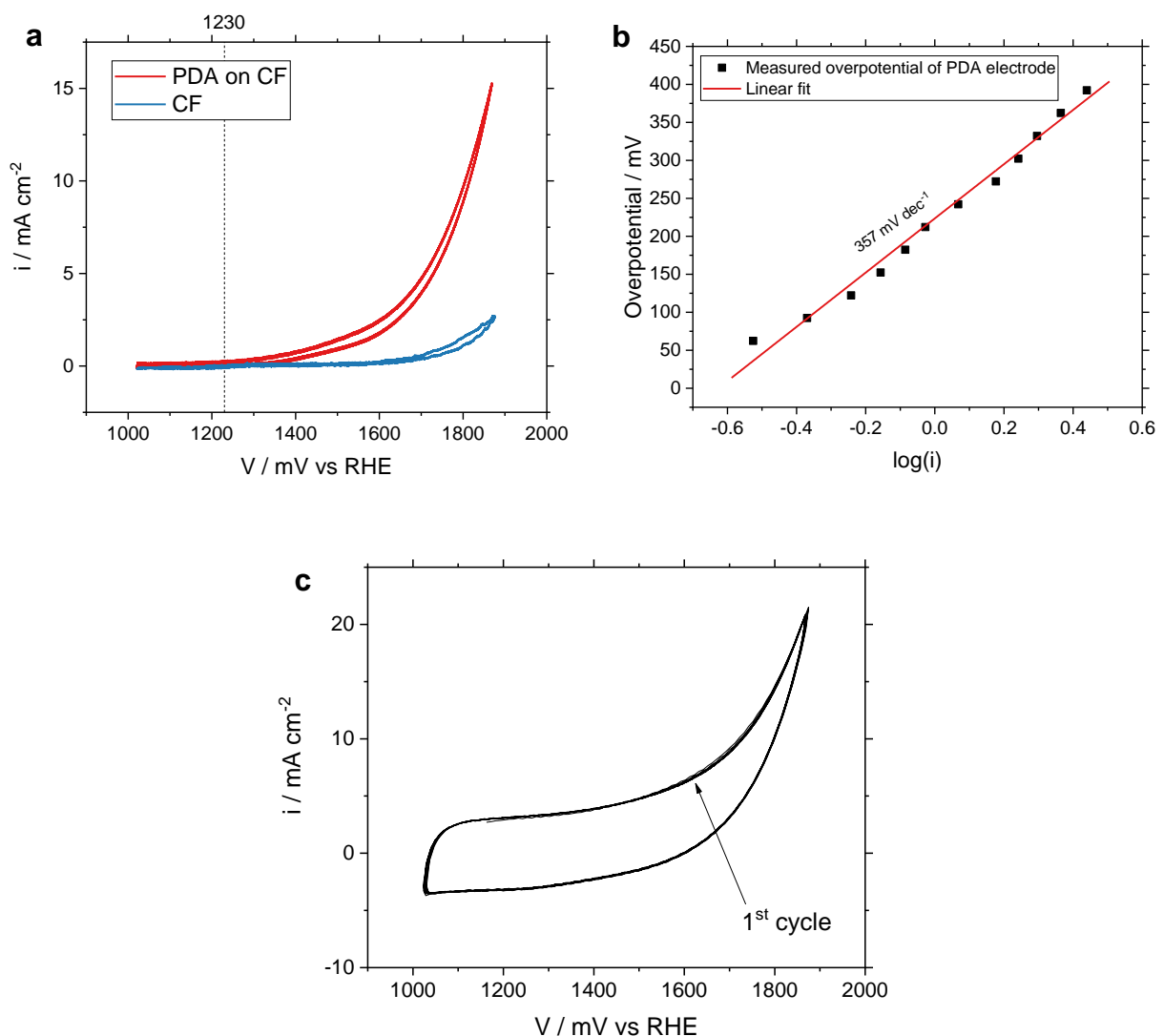


Figure 28: (a) Comparison of PDA on CF and CF in 1M KOH at a scan rate of 1 mV s^{-1} (b) tafel plot of PDA on CF (c) 10 cycles cyclic voltammetry of PDA on CF with a scan rate of 100 mV s^{-1}

For both electrodes a long term chronoamperometry with 1620 mV vs RHE was performed to test the stability of PDA and the substrate material. In both cases a strong,

brown discoloration of the electrolyte occurred (Figure 29). From this it can be concluded that carbon felt decomposes oxidatively in 1M KOH during after application of positive voltage [2]. There is no discoloration of 1M KOH when carbon felt is put into the electrolyte for 1 week without any performance of electrochemistry, so the observed colour change is related to the oxidative potential. In 3.1. we see that PDA does decompose as well to acetate, formate and oxalate as well.



Figure 29: (left) cell with PDA on CF as working electrode after 48 h chronoamperometry in 1M KOH (right) cell with CF as working electrode after 70 h chronoamperometry in 1M KOH

3.5.2. OER in 1M NaOH

The catalytic effect of PDA is evident in Figure 30 (1M NaOH, pH = 13.25). The PDA electrode has an overpotential of 481 mV at a current of 5.00 mA cm⁻² and the reference electrode has a current of 0.84 mA cm⁻² at 478 mV overpotential. The received tafel plot has a smaller slope of 267 mV dec⁻¹ compared to the one observed in 1 M KOH.

Figure c shows that the performance of the catalyst was relatively constant over the application of 100 cycles cyclic voltammetry with a scan rate of 100 mV s⁻¹. There was a small rise of observed current during the various cyclic voltammograms which was due to the rising electrochemical active surface of the electrode over time which in turn was due to the wetting and suction of the CF with electrolyte.

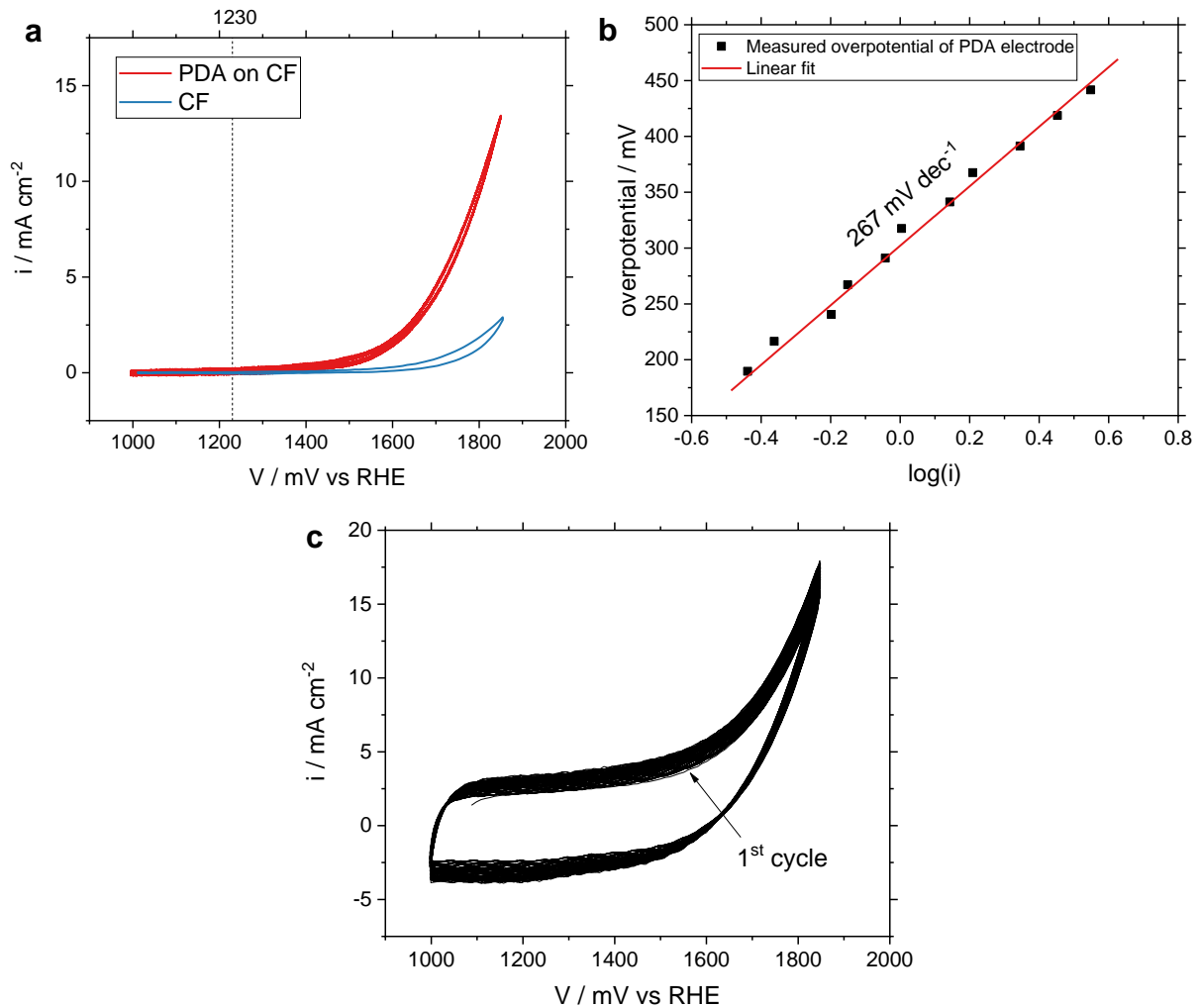


Figure 30: (a) Comparison of PDA on CF and CF in 1M NaOH at a scan rate of 1 mV s^{-1} (b) tafel plot of PDA on CF (c) 100 cycles cyclic voltammetry of PDA on CF with a scan rate of 100 mV s^{-1}

For the cell with the PDA coated working electrode a chronoamperometry with 1590 mV vs RHE for 48 h was performed and again a strong discoloration of the electrolyte similar to the one in Figure 29 appeared. Only for the tafel slope there is distinction between the electrolytes 1 M KOH and 1 M NaOH in OER.

3.5.3. OER in $0.5 \text{ M K}_2\text{CO}_3/\text{KHCO}_3$

In Figure 31 the results of the experiments in $0.5 \text{ M K}_2\text{CO}_3/\text{KHCO}_3$ ($\text{pH} = 10.15$) are shown. The slope of the CV of the reference CF electrode is nearly 0, which indicates that there is only capacitive current occurring. The received tafel plot has with 341 mV dec^{-1} a slope between the ones observed in 1 M KOH and 1 M NaOH .

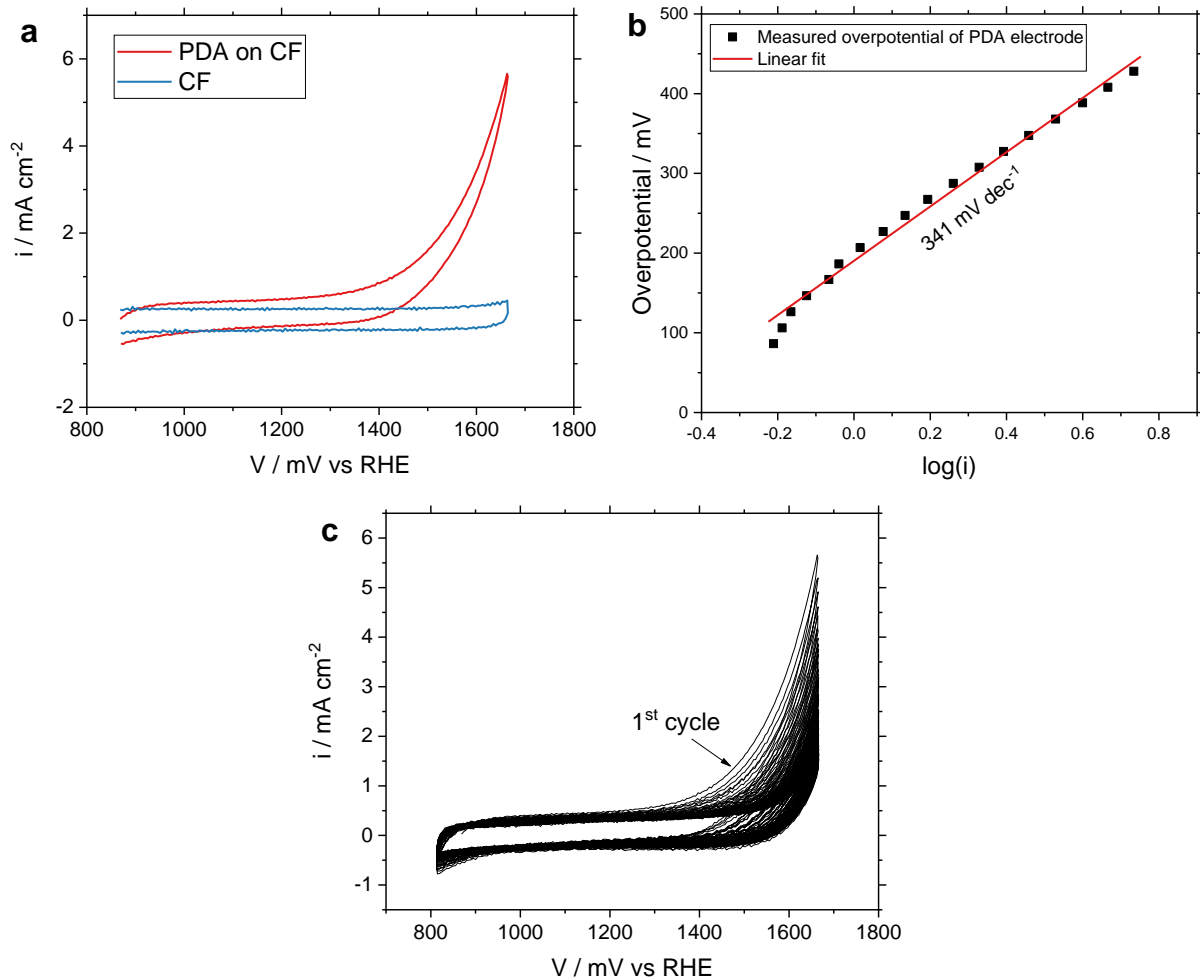


Figure 31: (a) Comparison of PDA on CF and CF in 0.5M $K_2CO_3/KHCO_3$ at a scan rate of 50 mV s^{-1} (b) tafel plot of PDA on CF (c) 100 cycles cyclic voltammetry of PDA on CF with a scan rate of 50 mV s^{-1}

However, as seen in Figure 31 c the OER diminishes over time as the current decreases. An explanation for this phenomenon is the delamination of PDA of CF. Similar to the experiments in 1M KOH and 1M NaOH a yellow discoloration of the electrolytes has been observed in the electrochemical cells, however this time lighter due to the lower applied currents.

3.5.4. Determination of electrochemical active surface area (ECSA) of PDA on CF

The electrochemical active surface area of PDA on CF was determined by calculating the capacitance of the electrode surface in the “double layer region” (working and counter electrode behaving like a capacitor). In this region of low potential there are only capacitive currents and no faradic currents. Plotting the currents of various scanrates gives a straight line, whose slope is equal to the double layer capacitance:

$$i = \frac{dQ}{dt} = \frac{dQ}{dV} * \frac{dV}{dt} = C * v \quad (4)$$

i ... current [A] Q ... electrical charge [C] t ... time [s]
 V ... voltage [V] C ... capacitance [F] v ... scan rate [mV s⁻¹]

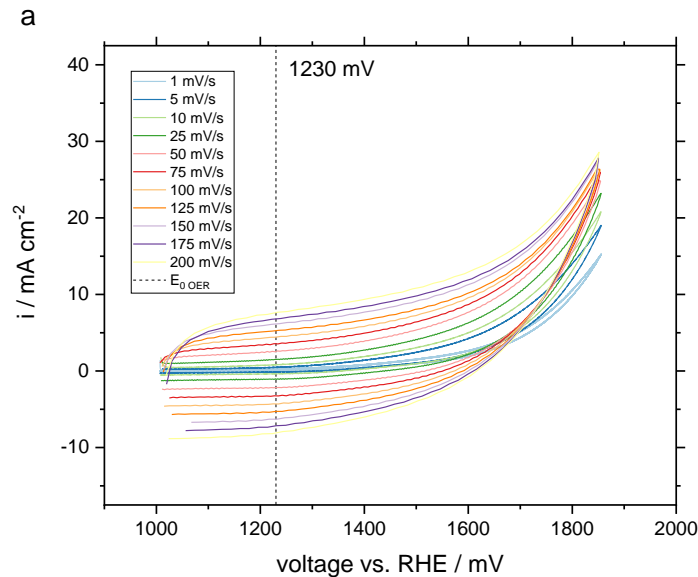
The electrochemical active surface area can be calculated by dividing the double layer capacitance through the reference value of capacity per the unit area, which is typically between 20 and 40 μF cm⁻² [12]:

$$ECSA = \frac{C}{C_{ref}} \quad (5)$$

In the experiment the received slope for the forward scans was 37.1 mF cm⁻² and for the backward scans -41.3 mF cm⁻² (Figure 32). The average of these absolute values has been taken for determination of ECSA:

$$ECSA = \frac{39.2 \text{ mF cm}^{-2}}{40 \text{ μF cm}^{-2} \text{ per cm}^2_{ECSA}} = \mathbf{980 \text{ cm}^2_{ECSA}} \quad (6)$$

The high result of 980 cm²_{ECSA} per cm² electrode in solution indicates that carbon felt is an attractive choice for electrochemical reactions, due to high currents because of the large, effective surface area.



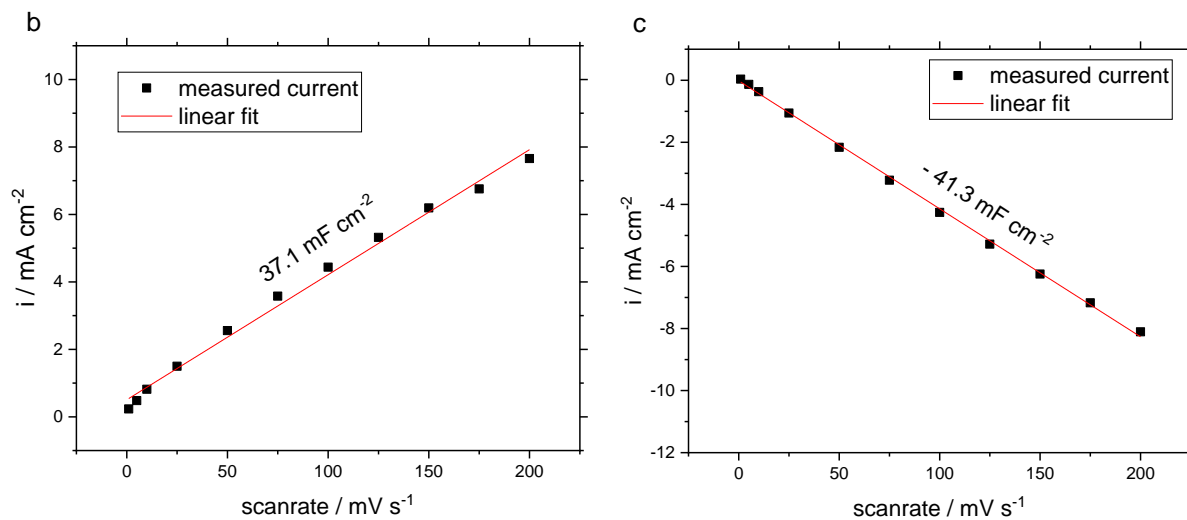


Figure 32: (a) cyclic voltammograms of OER with various scan rates of PDA coated CF in 1M KOH (b) assignment of currents against scan rate during forward scan (c) assignment of currents against scan rate during backward scan

4. Results and conclusion

PDA was synthesized on Au, FTO, titanium mesh and carbon felt and was tested electrochemically for OER under variation of electrolytes, though mainly 1 M KOH was used, since this is the most frequent used electrolyte in literature.

The polymer was analysed and characterised by UV/Vis spectroscopy, FTIR spectroscopy, AFM and SEM. Also, gases were analysed by GC and the electrolyte by HPLC and IC.

It was found out that PDA has a catalytic effect on OER.

In Table 2 the results of the cyclic voltammograms in this thesis are summarized. The lowest overpotential for 5 mA cm⁻² current was achieved with PDA on carbon felt in 0.5 M K₂CO₃/KHCO₃. The lowest tafel slope and therefore highest activity for OER was attained with PDA on carbon felt in 1 M NaOH.

Table 2: Comparison of results of PDA coated electrodes

| Substrate | Electrolyte | Current / mA cm ⁻² | Overpotential / mV | Tafel slope / mV dec ⁻¹ |
|---------------|--|-------------------------------|--------------------|------------------------------------|
| Carbon felt | 1M KOH | 5 | 478 | 357 |
| Carbon felt | 1M NaOH | 5 | 481 | 267 |
| Carbon felt | 0.5M K ₂ CO ₃ /KHCO ₃ | 5 | 418 | 341 |
| FTO glass | 0.5M K ₂ CO ₃ /KHCO ₃ | - | - | - |
| Titanium mesh | 1M KOH | 5 | 557 | 426 |
| Gold | 1M KOH | 3 | 568 | 469 |

In Table 3 the performance of PDA is compared to some common catalysts found in the literature. It is noticeable that the tafel slope of PDA is factor three to six times higher than the tafel slopes from the compared catalysts, concluding that PDA cannot compete with metal catalysts in performance. The overpotentials have not been compared, since in this thesis for current density the projected area of the electrode was used and not the electrochemical active surface area.

Table 3: Comparison of PDA to state-of-the-art catalysts

| Catalyst | Electrolyte | Tafel slope / mV dec ⁻¹ |
|---------------------------|-------------|---------------------------------------|
| PDA | 1M NaOH | 267 |
| IrO ₂ [13] | 1M KOH | 79 |
| RuO ₂ [14] | 1M KOH | 90 |
| α-Co(OH) ₂ [5] | 1M KOH | 67 |
| α-Ni(OH) ₂ [5] | 1M KOH | 42 |

In all tested electrolytes decomposition of carbon felt occurred, making it not suitable for OER. Also, delamination of the PDA happened on FTO, titanium mesh and on gold. Finally, it was seen that PDA decomposes during OER to formate, oxalate and acetate, which means that PDA in the way synthesized in this thesis is not stable during OER.

This leads to the conclusion that the PDA synthesis method and therefore the structure of PDA has to be modified to receive a more stable and more effective catalyst for OER. Also, a different carrier electrolyte has to be found to prevent the PDA electrode from delaminating of the electrode substrate.

5. Literature

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Finally, I want to thank the whole LIOS team for the nice atmosphere in this institute and making my stay here a great time.

7. List of Abbreviations

Table 4: List of Abbreviations

| Abbreviation | Full form |
|--------------|---|
| PDA | Polydopamine |
| OER | Oxygen evolution reaction |
| FTO | Fluorine doped tin oxide |
| FTIR | Fourier-transform infrared spectroscopy |
| SEM | Scanning electron microscopy |
| AFM | Atomic force microscopy |
| CV | Cyclic voltammetry |
| GC | Gas chromatography |
| HPLC | High performance liquid chromatography |
| IC | Ion chromatography |
| ECSA | Electrochemical active surface area |
| EE | Energy efficiency |
| CF | Carbon felt |
| PEI | Polyethyleneimine |
| ATR | Attenuated total reflection |
| WE | Working electrode |
| CE | Counter electrode |
| RE | Reference electrode |
| SHE | Standard hydrogen electrode |
| RHE | Reversible hydrogen electrode |