# OXIDATION OF GLYCEROL ON DIAMOND COATED ELECTRODES

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## Introduction

On the background of rising prices for fossil fuel and the implementation of the EU Directive 2003/30/EC "on the promotion of the use of biofuels or other renewable fuels for transport" the importance of alternative fuels like biodiesel or bioethanol increases.

Increasing production of biodiesel needs exploitation of byproducts. In case of biodiesel process the most important byproduct is glycerol[1]. Its price is subject of significant fluctuations because of a surplus of non food quality product. Several oxidation routes, especially the electrochemical oxidation, which enables formation of value added oxidation products for the chemical industry, seem to be a promising utilization.

Electrochemical oxidation is known as an environment-friendly ("green") process because chemical oxidation agents are substituted by electrons.

## Target

Glycerol oxidation, subject of this ongoing project, has been widely investigated in the past. Several electrode materials, electrolyte compositions, pH-regions and temperature fields have been investigated by different research groups. To briefly sum up the results, the expected optimum set up for highly selective synthesis of a specific product has still not been found. Most electrode materials which have been tested in the past are not stable (e.g. silver [1], even gold anodes have limited stability [1]) or generate only cleavage products (e. g. nickel [1]). Only the use of a platinum anode in combination with a huge excess of sodium hydroxide as electrolyte provided acceptable yields of sodium lactate as product [2]. At our department [3] several electrode materials (e. g. DSA, glassy carbon) have been tested. Only diamond coated electrodes seem to be a promising choice for obtaining "better" results.

In the past mainly acids (like sulfuric acid) and alkali hydroxides were used as electrolytes. The use of acids is the easiest way, because acids are not consumed during the electrolysis and they provide good electric conductivity. So electrolysis works with low concentration of acid. Unfortunately at strong acidic conditions the cleavage of glycerol is the main anodic reaction and current yields are low. Alkali hydroxides provides better current yields but large excess is needed because alkali hydroxides are consumed by many reactions (aldol reaction, Cannizzaro reaction, $CO_2$-fixing …) which lead to a complex product mixture. This complex product mixture and the huge amount of surplus sodium hydroxide make downstream processing a very difficult and expensive procedure. In conclusion metal salt electrolytes have been tested for their capability.

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[1] In the biodiesel production there is a yield of about 100 g glycerol per kg biodiesel.

## Method and experimental setup

The electrochemical oxidation was carried out in batch operation in a thin layer pump cell (Figure 1). Anode and cathode compartment were separated by an anion exchange membrane. Anolyte and catholyte were pumped through the cell by peristaltic pumps (with a volume flow of 4 ml/s) in order to increase the mass transfer and to take the hydrogen out of the cell. The temperature was measured with a Pt100 resistance temperature detector and controlled with heat exchangers between pump and cell.

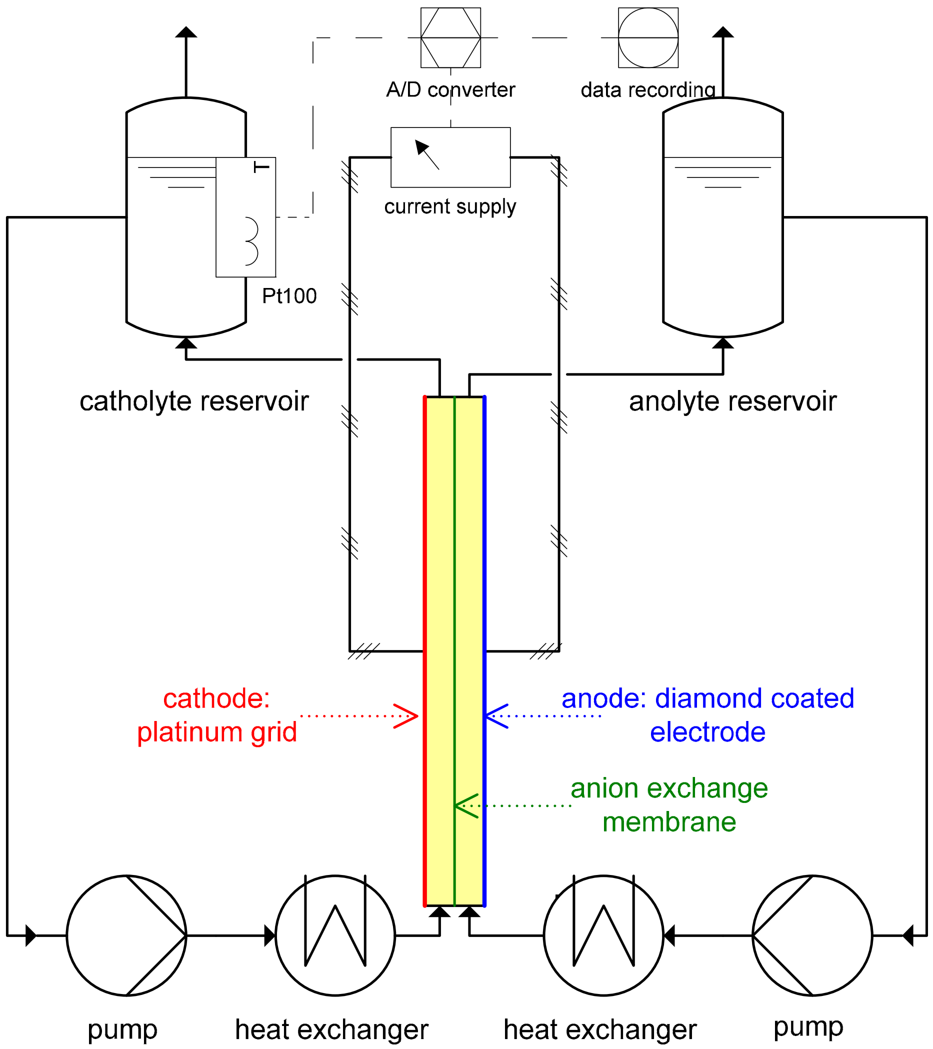

**Figure 1.** Sketch of the electrolysis cell

A diamond coated electrode (Fraunhofer IST) was used as anode. This electrode consists of a boron doped polycrystalline diamond layer on a niobium carrier.

Diamond coated electrodes have high chemical, mechanical, and thermal stability. The main advantage of diamond coated electrodes for anodic synthesis reactions is the distinct oxygen overvoltage. A platinum grid was used as cathode because of its very low overvoltage for hydrogen evolution, the only cathode product. All experiments were carried out with aqueous anolyte mixtures of glycerol ($c_{\mathrm{glycerol}}$ = 0.25–2 mol/dm³).

a b c

**Figure 2.** Images of the platinum anode (a), the anion exchange membrane (b) and the diamond coated anode (c)

The electrocatalytic activity of various electrolytes which provide different pH regions such as sodium sulfate ($Na_2SO_4$, moderate acidic because of organic acids which were formed during the glycerol electrolysis), *di*-potassium hydrogen phosphate ($K_2HPO_4$, neutral, buffer [$pK_A(H_2PO_4^-) = 7.207$]) and sodium carbonate ($Na_2CO_3$, alkaline) were investigated. Aqueous solutions of sodium hydroxide ($c_{NaOH} = 0.1$ mol/dm³) were used as catholyte. Thus charge transfer through the membrane was based on hydroxide ion transfer. During process optimization the current density ($j$ = 75–305 A/m²), temperature ($\theta$ = 20–50 °C), glycerol concentration and electrolyte concentration were varied. All experiments were carried out with constant current, flow and temperature. Cell voltage, current and temperature were recorded.

After specified time intervals samples were taken, acidified with dilute sulfuric acid and analyzed by HPLC.

## Results

At the beginning of the electrolysis the desired products (glyceraldehyde and dihydroxyacetone) are formed with good selectivity and current yield. With ongoing process the fraction of cleavage products (glycolaldehyde and formic acid/formate) increases (**Figure 4**, **Figure 5**, and **Figure 6**). On a limited scale—especially at alkaline conditions—the oxidation of glyceraldehyde to glyceric acid and the oxidation of glycolaldehyde to glycolic acid take place (**Figure 3**). Through formation of acids during the electrolysis process the pH value decreases. The ratio between glyceraldehyde and dihydroxyacetone depends strongly on the pH value: At acidic conditions ($Na_2SO_4$ as electrolyte) only glyceraldehyde is formed, at neutral ($K_2HPO_4$ as electrolyte) and moderate alkaline ($Na_2CO_3$ as electrolyte) conditions mixtures of glyceraldehyde and dihydroxyacetone were formed.

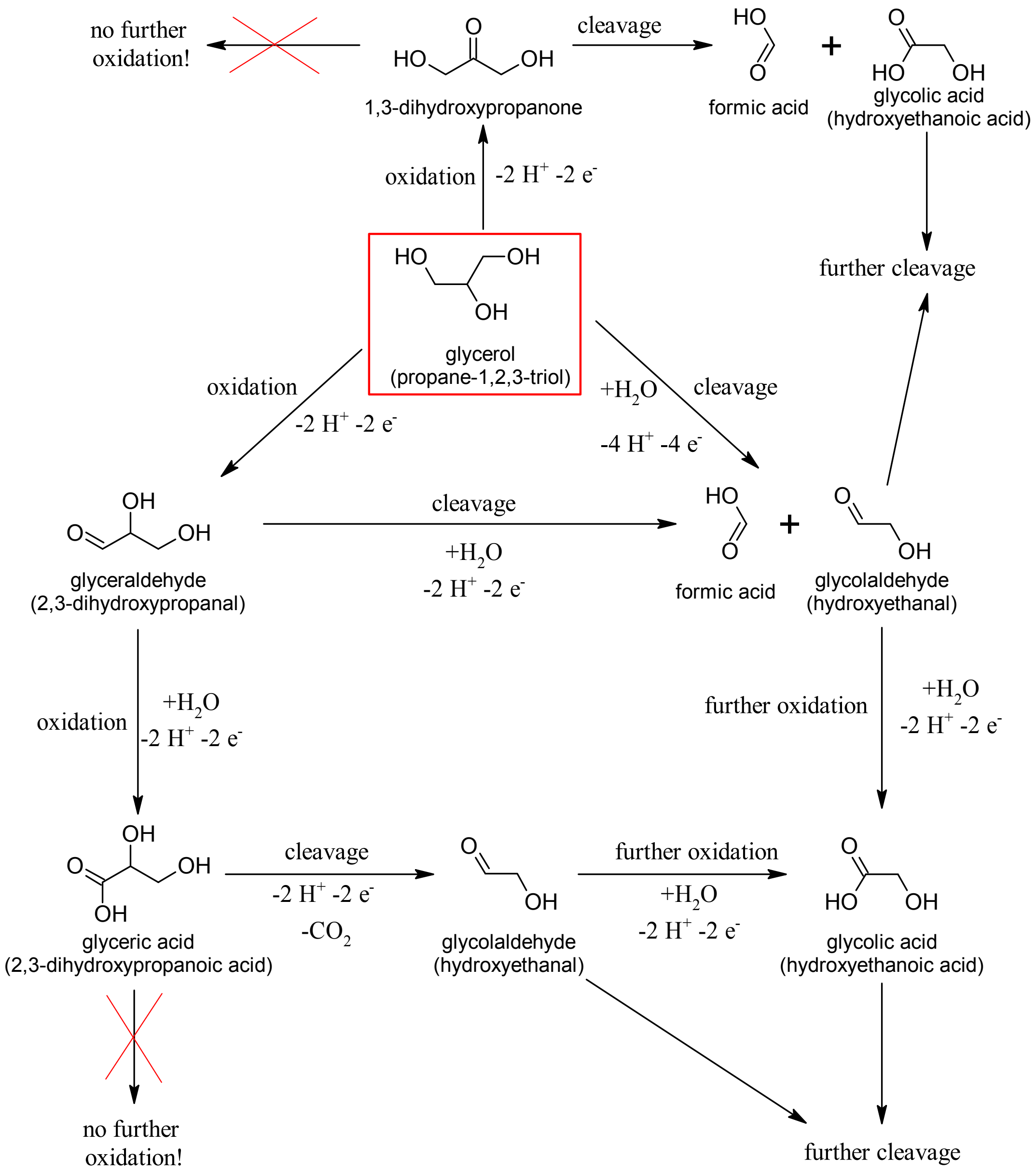

**Figure 3.** Overview of the anodic reactions of glycerol and its oxidation products without consideration of deprotonation reactions of the carboxylic acids

As a result of the cleavage reaction the concentration of glyceraldehyde and dihydroxyacetone reach a maximum. Through the decrease of the pH value dihydroxyacetone reaches its maximum prior to glyceraldehyde (cf. **Figure 5** and **Figure 6**).

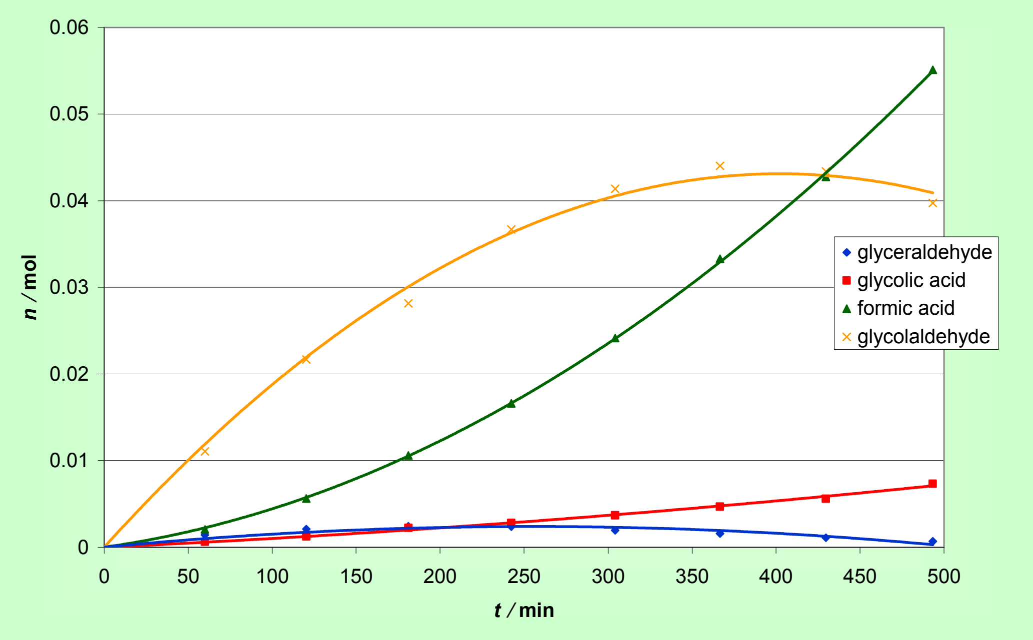

**Figure 4.** Formation of oxidation products versus time; electrolyte: $Na_2SO_4$, $\theta = 20$ °C, $j = 300$ A/m²

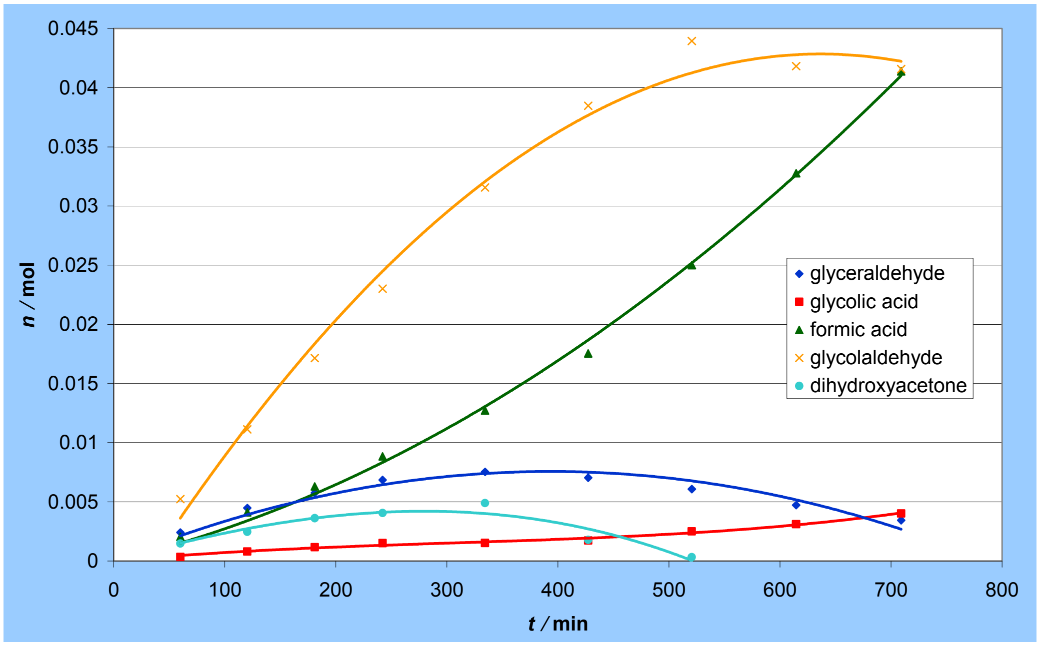

**Figure 5.** Formation of oxidation products versus time; electrolyte: $K_2HPO_4$, $\theta = 20$ °C, $j = 200$ A/m²

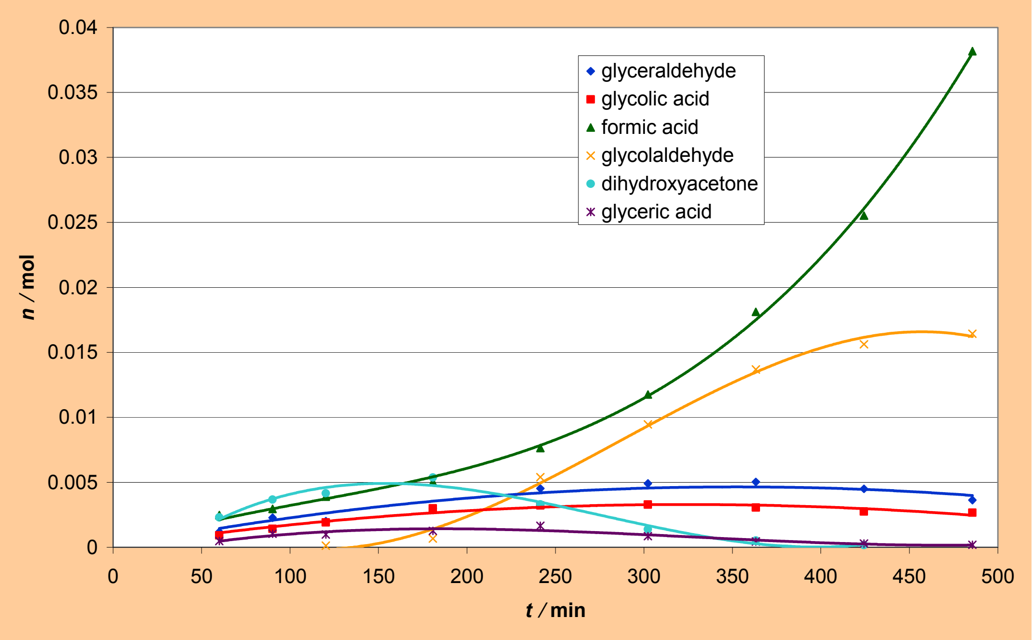

**Figure 6.** Formation of oxidation products versus time; electrolyte: $Na_2CO_3$, $\theta = 20$ °C, $j = 305$ A/m²

The reaction kinetics of glycerol oxidation was determined (**Figure 7**). At the beginning of the process the degradation of glycerol follows zero-order rate law (electron transfer controlled reaction), with increasing electrolysis time a change to first order rate of degradation can be observed (mass transport controlled reaction). Formation of gaseous decomposition products (oxygen or carbon dioxide) is negligible.

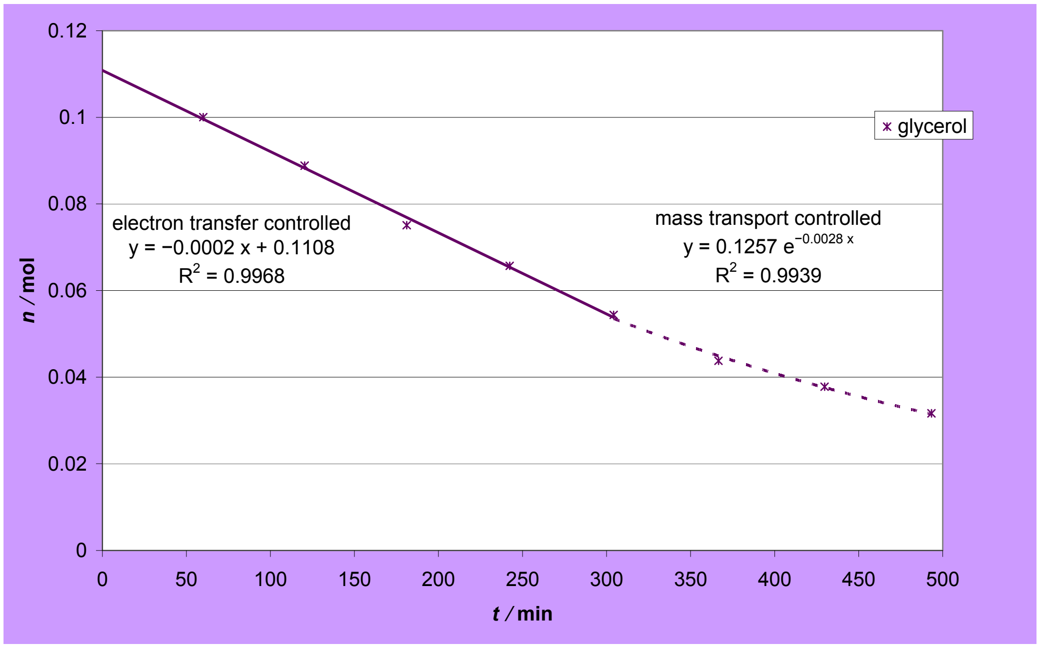

**Figure 7.** Glycerol versus time plot indicating electron transfer controlled reaction at the beginning and mass transport controlled reaction with ongoing time. Electrolyte: $Na_2SO_4$, $\theta = 20$ °C, $j = 300$ A/m²

# References

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2. Tkaczuk, Piotr (1993), *"Elektrochemische Oxidation von Glycerin und Glycerinderivaten an einer Platin-Anode in verschiedenen Zelltypen,"* Ph.D. Dissertation, University of Dortmund, Germany.
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