Comparison of Electrodes for Application in Anodic Oxidation of Wastewater Constituents

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Abstract

Since new electrode materials such as glassy carbon, several metal oxides and diamond doped titanium electrodes have established in industrial application and research, electrochemical oxidation in synthesis as well as wastewater treatment offers several new applications for EAOPs (Electrochemical Advanced Oxidation Processes).

For both applications, anodic synthesis as well as wastewater treatment, detailed knowledge of the operation set up and the operation conditions is needed to enable feasible operation.

Target of this project has been the comparison of iridium oxide doped DSA, glassy carbon and diamond electrodes in oxidative wastewater treatment. Investigation has considered the correlation of current density and anode potential for specified electrolyte composition and temperature of operation. Investigation has been carried out for open cell as well as membrane cell applications.

Basically stable operation conditions in practical application are expected from this detailed analysis of operation. Investigation has therefore considered the current/ potential characteristic of the basic electrolyte as well as different states of conversion.

Investigation has been carried out with ethylenediaminetetraacetic acid (EDTA) and the conductance electrolyte sodium sulphate. EDTA has been selected because of its broad application and its properties. Sodium sulphate has been chosen to avoid unwanted interaction of the electrolyte and the anode. Under anodic charge EDTA can undergo cleavage as well as oxidation. Rate and efficiency of both routes strongly depend on the current density and the corresponding anode potential.

Cleavage has been analysed through the complexation properties of the synthetic effluent. Oxidation has been quantified through TOC-analysis.

Based on the current/potential correlation and batch conversion tests in bench scale the specific energy consumption has been determined.

1 Introduction

EAOPs (Electrochemical Advanced Oxidation Processes), such as anodic oxidation of wastewater constituents, will increasingly obtain an important role in the environmental technologies.[Schmidt 2003] In degradation of persistent organic pollutants and preparation for biological wastewater treatment EAOP-systems are expected to offer a powerful tool. Through the electric current the oxidant can be produced and oxidation of constituents can be carried out directly in a controlled way with less need of chemicals for the oxidation process. Compared with chemical oxidation processes simple handling and high efficiency is expected from EAOPs.

Since new electrode materials such as glassy carbon, several metal oxides and diamond doped titanium electrodes have established in industrial application and research electrochemical oxidation in synthesis as well as wastewater treatment offer several new applications for EAOPs.

For both applications, anodic synthesis as well as wastewater treatment, detailed knowledge of the operation set up and the operation conditions is needed to enable feasible operation.

Targeting high process efficiency, optimisation of the electrocatalytically active surface of electrodes and the geometric set-up are vitally important.

Aim of this project has been the comparison of iridium oxide doped DSA and diamond doped titanium electrodes in oxidative wastewater treatment.

Experimental investigation was carried out with Ethylendiaminetetraacetic acid (EDTA). EDTA is a strong chelating agent, applied to enforce the solubility of metal cations by forming strong metal complexes. This organic pollutant is widely used in industrial and consumer applications for preventing formation of scales and for increasing the solubility of heavy metal cations. In European rivers and lakes you can find high concentrations of EDTA and other aminopolycarboxylic acids [Sörensen *et al.*, 1998].

Due to its complexation properties, EDTA has a negative effect on the separation of several heavy metal ions from aqueous effluents. Depending on the chemical nature of the metal cation and the applied precipitation or separation route, precipitation can be suppressed seriously [Vohra and Davis, 1999].

2 Experimental Setup and Analysis

For all investigations a batch electrolysis cell, equipped with a DC power supply, potential record, pH record, temperature record and temperature control unit was used.

2.1 Experimental setup

The schematic of electrochemical cell arrangement used for investigations is presented in figure 1.

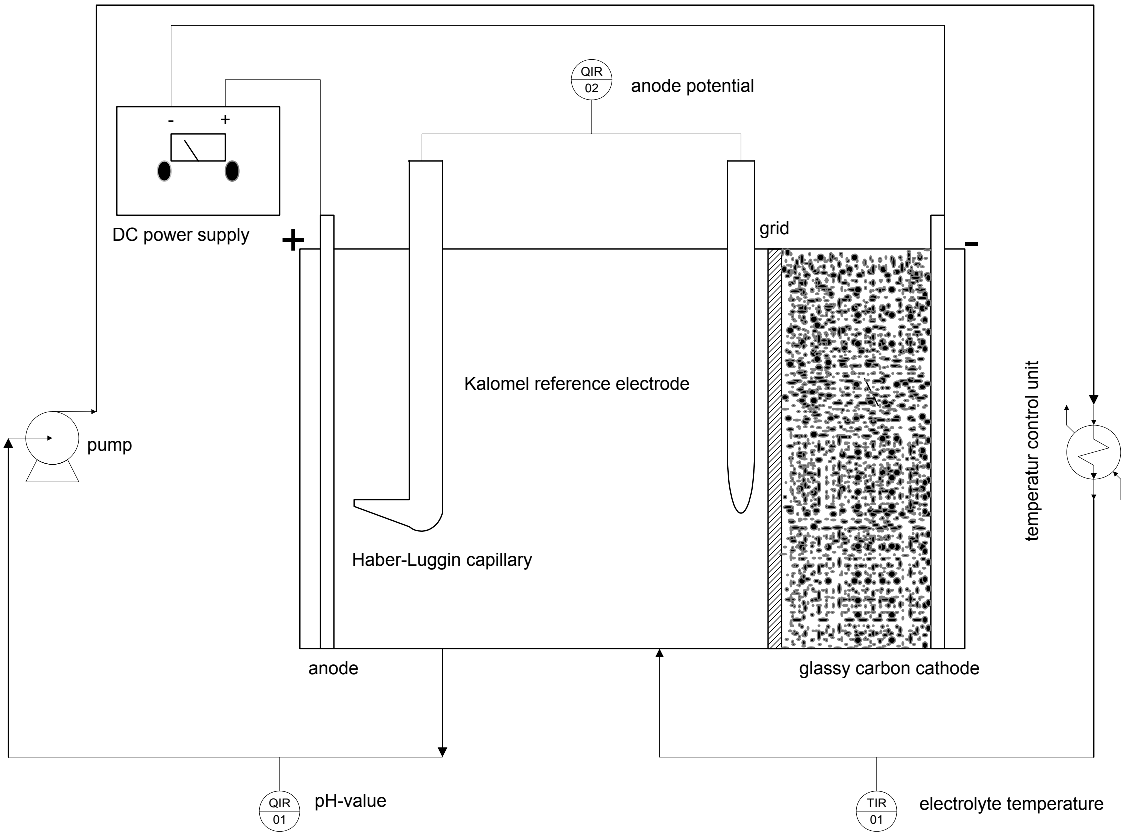

Figure 1: Experimental setup

The electrocatalytic effect of Iridium oxide doped DSA and diamond doped titanium electrode on EDTA degradation and TOC depletion was compared. Figure 2 shows the different surface structure of the electrodes with the iridium oxide doped DSA on the left and the diamond doped titanium electrode on the right hand side of the figure.

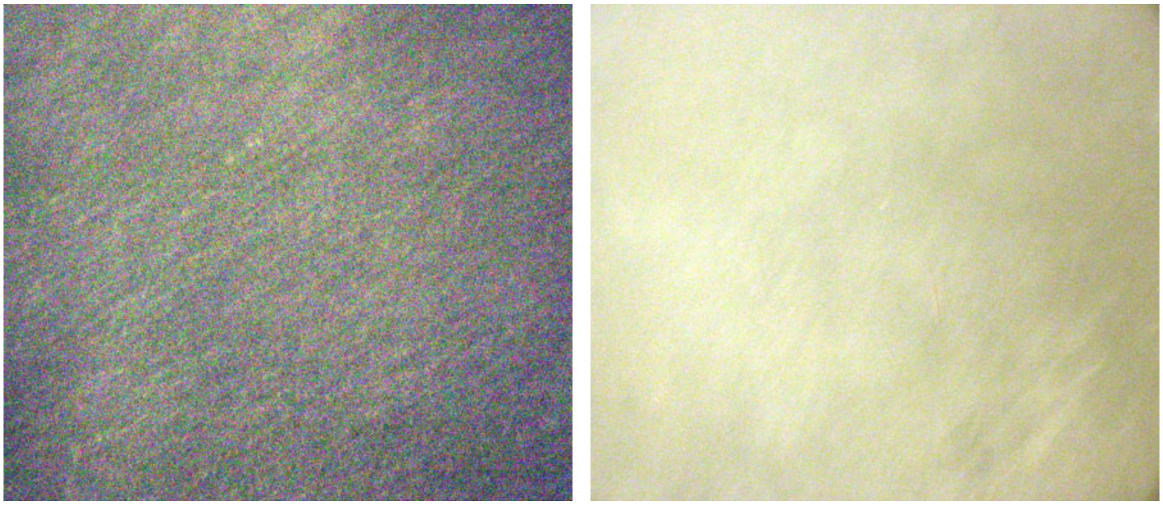

Figure 2: Surface structure of the iridium oxide doped DSA electrode (left) and the diamond doped titanium electrode (right)

Although specified by a significant resistance contribution glassy carbon was the favoured cathode material because of its role in a complementary programme. The electrolyte temperature was kept constant at 297 K with a temperature control unit.

2.2 Analysis and quality of chemicals

For analytical purposes several samples of the electrolyte were collected during each experimental run.

The concentration of EDTA was determined with an ion pair chromatographic method [German standard methods for water control, waste water and sludge analysis] employing a Dionex DX500 HPLC system with a Lee Scientific Series 600 UV/Vis detector. A reversed phase analytical column (Agilent C12) served as the stationary phase and the mobile phase was a solution of Tetrabutylammoniumhydrogensulfate and Tetrabutylammoniumhydroxide. Prior to analysis the EDTA samples were chelated with Fe(III)-ions and absorption was measured by UV-photometry at a wavelength of 260 nm.

Electrooxidative conversion of EDTA was quantified through TOC-analysis with a Shimadzu TOC 5000 analyzer.

Several chemicals were dissolved in RO-grade water. EDTA (Ethylenediamineteraacetic acid Disodium Salt Dihydrate) was purum (≥ 97 % (KT)) grade (FLUKA Chemika # 03685) and Na_2SO_4 (Sodium Sulphate anhydrous) was pro analysis grade (Merck #1.06649.1000).

3 Results and discussion

First step of this project was investigation and record of the anode potential for both anodes. The electrochemical potentials were recorded via a Haber-Luggin-capillary arrangement in parallel to the determination of the current/voltage characteristic. Investigation was carried out with the conductance electrolyte sodium sulphate 0.05 M/l as sodium sulphate is expected not to undergo unwanted interaction with either electrode. Figure 3 shows the current density/potential graph for both anode materials. For better interpretation the voltage drop due to ohmic resistance of the electrolyte was subtracted from the recorded electrode-potential data.

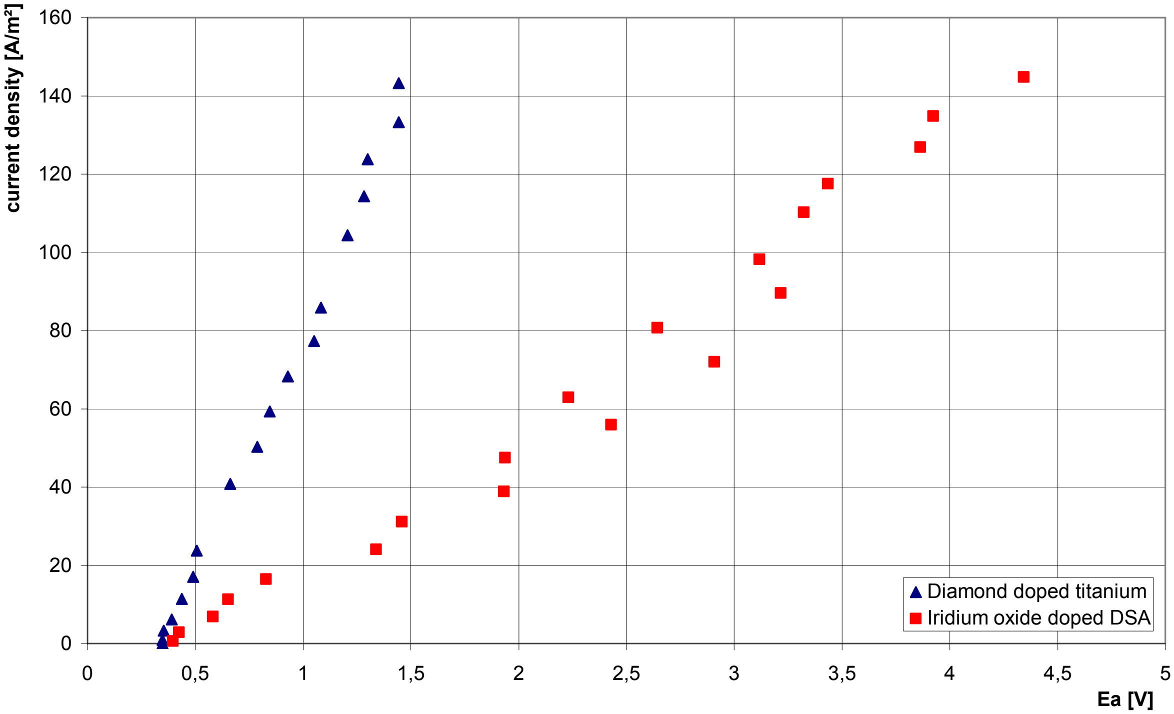

Figure 3: Current density vs. anode potential Ea; comparison of the iridium oxide doped DSA anode and the diamond doped titanium anode versus glassy carbon cathode at 297 K and constant electrolyte concentration of 0.05M/l Na_2SO_4.

Figure 4 shows the comparison of the anode potential/operation voltage characteristic for both anode materials after subtraction of the ohm resistance of the electrolyte

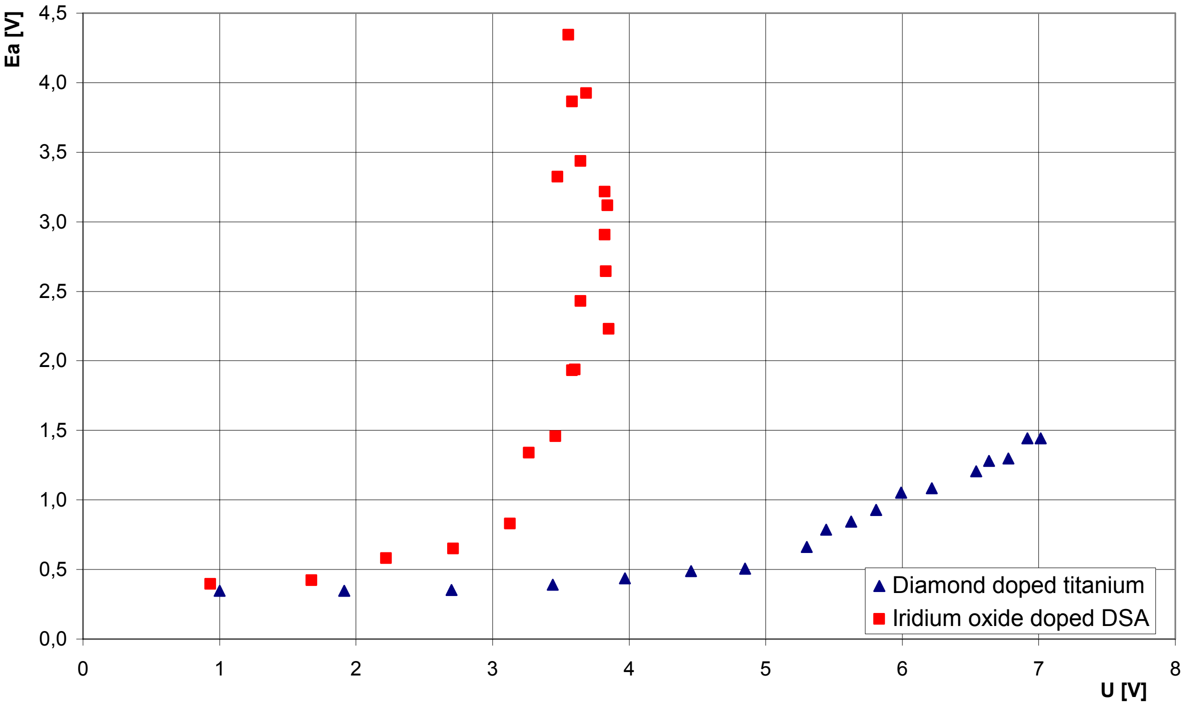

Figure 4: Anode potential Ea vs. operation voltage for the iridium oxide doped DSA anode and the diamond doped titanium anode versus glassy carbon cathode at 297 K and 0.05M/l Na_2SO_4 electrolyte

In a next step the current voltage curves for the conductance electrolyte sodium sulphate plus EDTA were recorded. Figure 5 shows the current density/potential plot for the working anode iridium oxide doped DSA.

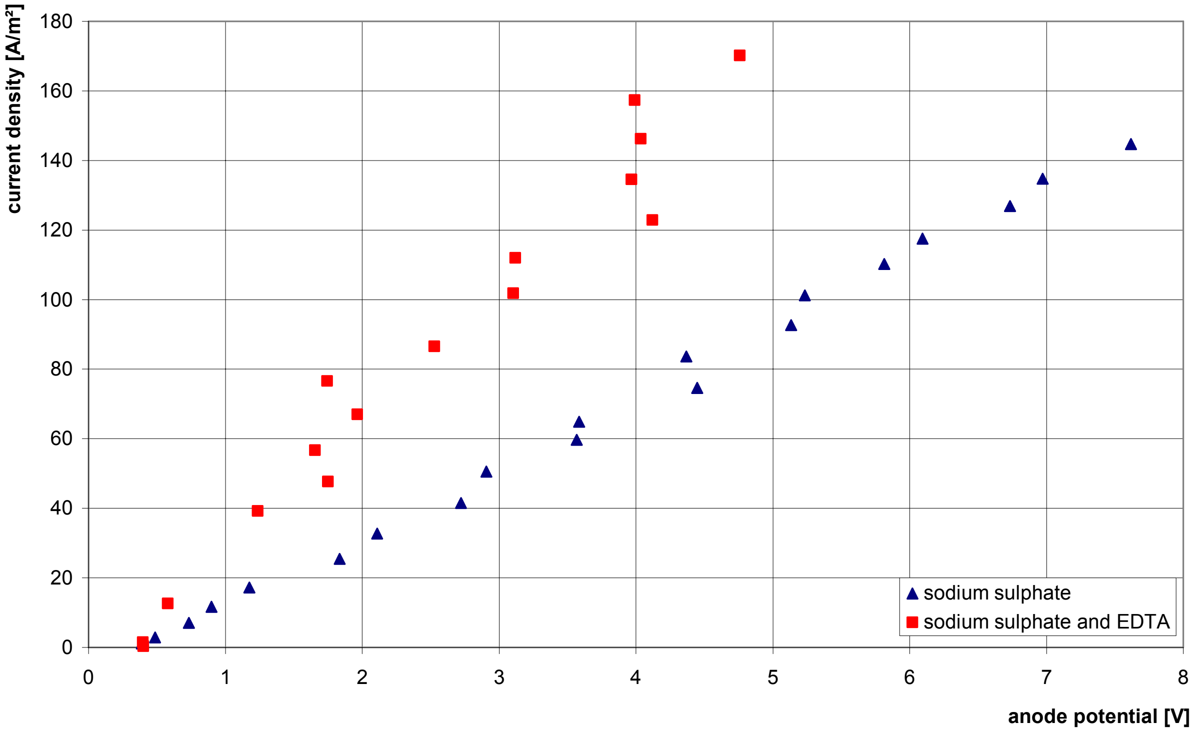

Figure 5: Current density vs. anode potential for the iridium oxide doped DSA anode versus glassy carbon cathode at 296 K, 0.05M/l Na_2SO_4 and 1.34 mM/l EDTA electrolyte concentration.

Then degradation of EDTA and TOC depletion by anodic oxidation for several current density levels was investigated. As mentioned above, EDTA was selected because of its broad application and its properties. The basic conductance electrolyte sodium sulphate was chosen to avoid unwanted interaction with the anode. Under anodic charge EDTA can undergo cleavage as well as oxidation. Rate and current efficiency of degradation by cleavage and oxidation strongly depend on the current density. Cleavage was analysed through the change of the complexation properties and oxidation was analysed through TOC determination within each run.

The effect of the iridium doped DSA electrode on cleavage and oxidation was investigated for different current densities in open cell electrolysis with a glassy carbon cathode. Figure 6 shows the loss of complexation activity of EDTA. The experiments were carried out at 297 K; sodium sulphate concentration was 0.05 M/l and EDTA start concentration was 1.34 mM/l.

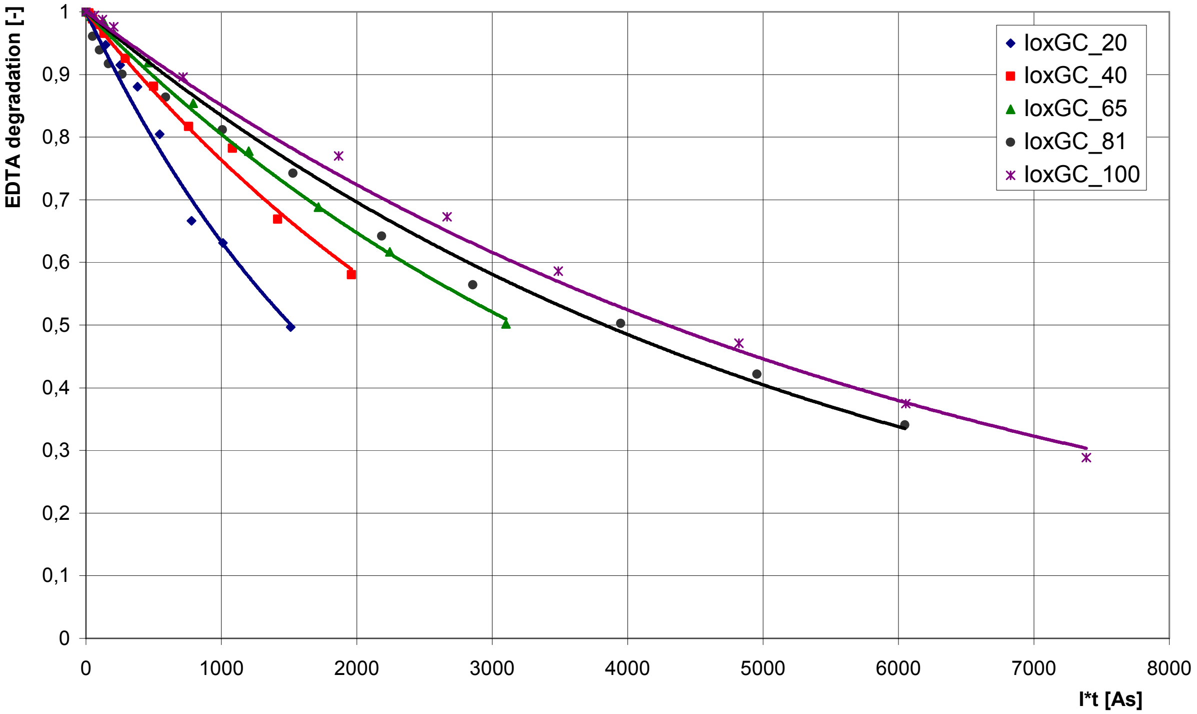

Figure 6: EDTA degradation vs. Coulomb during batch open cell electrolysis with an iridium doped DSA and glassy carbon cathode at 297 K. Electrolyte start composition: 0.05 M/l Na_2SO_4 and 1.34 mM/l EDTA. Parameter: current density 20 (IoxGC_20), 40 (IoxGC_40), 65 (IoxGC_65), 81 (IoxGC_81) and 100 (IoxGC_100) A/m²

Figure 6 shows that increasing current density has a negative effect on the current efficiency for degradation because of rising oxygen evolution.

Figure 7 indicates a maximum nitrogen-acetate cleavage for current density of about 40 A/m^2 according to the observed increase of the pH-value, while operation at lower current density results in nearly constant pH-value. At elevated current density the electrolyte is acidified during operation, while finally at current density of 100 A/m^2 the pH remains nearly constant again. Deduced from the results of qualitative investigation of products during photochemical degradation of EDTA, acidification is probably caused by cleavage of the ethylene-nitrogen bond with consecutive formation of oxalic acid in a multistep oxidation process. Cleavage of the nitrogen-acetate bond by forming ethylenediaminetriacetate and ethylenediaminediacetate during photochemical degradation results in an elevation of the pH value. Although not confirmed by separate qualitative determination of the composition of degradation products during open cell electrolysis it is concluded from the pH trends that the mechansim of degradation must be similar to photochemical degradation and oxidation. Independent of the missing confirmation of the assumed mechanism the different pH trends show a severe effect of the current density on EDTA degradation.

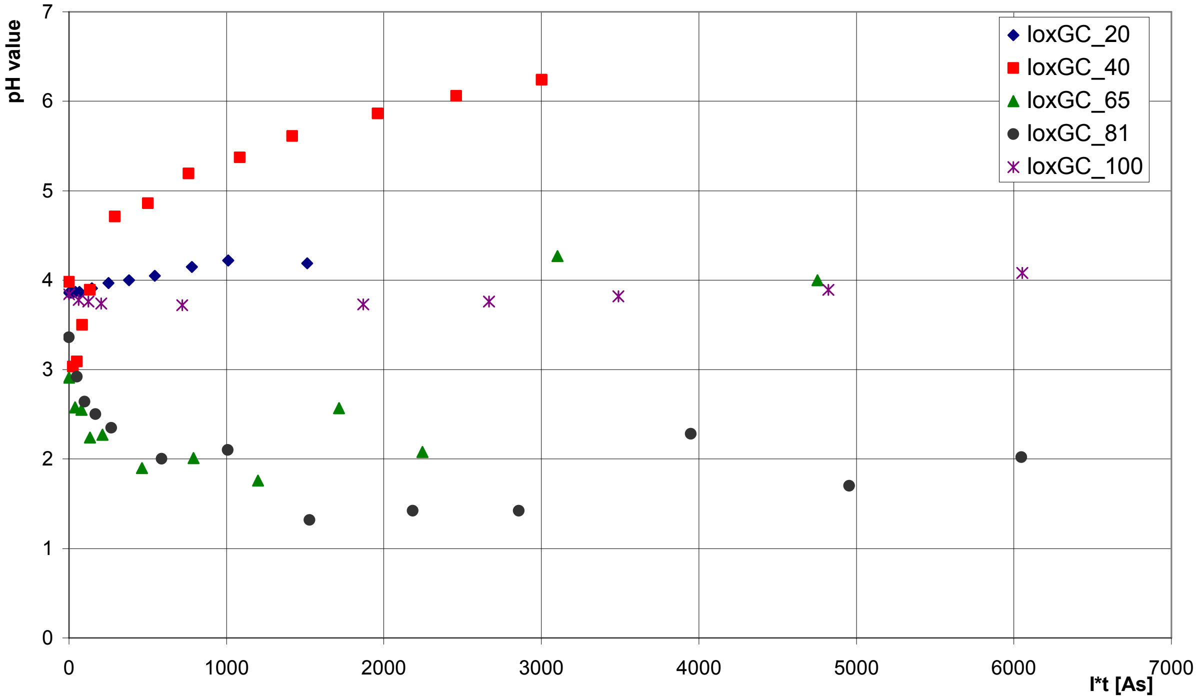

Figure 7: pH value vs. I*t for open cell EDTA electrolysis with iridium oxide doped DSA electrode and glassy carbon cathode at 297 K, 0.05 M/l Na_2SO_4 and 1.34 mM/l EDTA electrolyte start concentration. Parameter: current density 20 (IoxGC_20), 40 (IoxGC_40), 65 (IoxGC_65), 81 (IoxGC_81) and 100 (IoxGC_100) A/m²

EDTA degradation for open cell electrolysis with iridium oxide doped DSA and diamond doped titanium anode was then compared with TOC depletion. The experiments were carried out at current density of 81 A/m², operation temperature of 297 K, and 0.05 M/l sodium sulphate and 1.34 mM/l EDTA electrolyte composition.

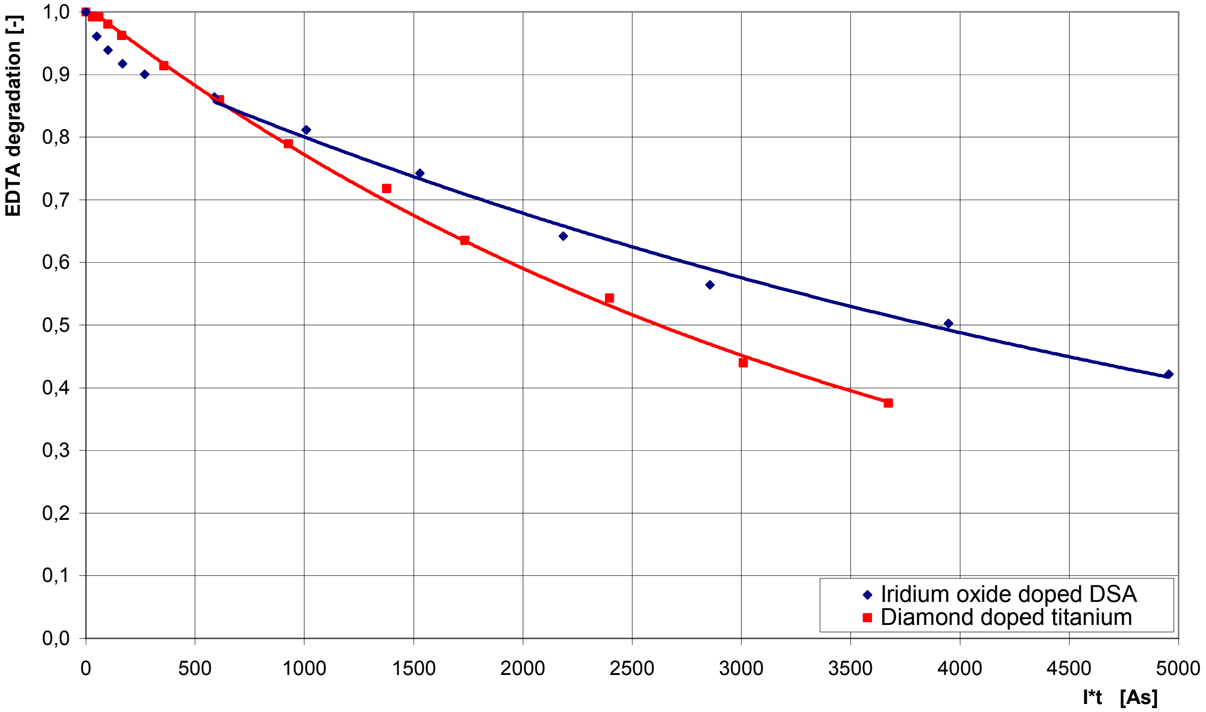

Figure 8: EDTA degradation vs. I*t for open cell electrolysis with iridium oxide doped DSA electrode and diamond doped titanium anode and glassy carbon cathode at 297 K, electrolyte start concentration 0.05 M/l Na_2SO_4 and 1.34 mM/l EDTA, current density: 81 A/m²

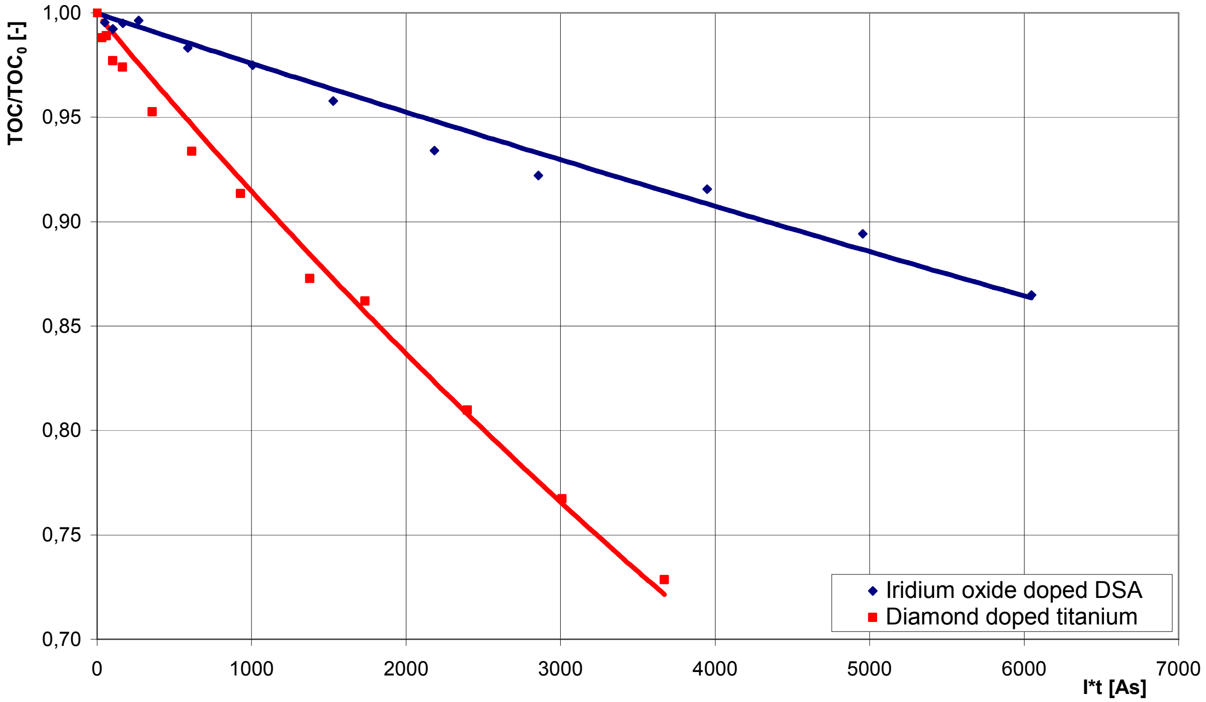

Figure 9: TOC depletion vs I*t [As] for open cell electrolysis with iridium oxide doped DSA electrode and diamond doped titanium anode and glassy carbon cathode at 297 K, electrolyte start concentration 0.05 M/l Na_2SO_4 and 1.34 mM/l EDTA, current density: 81 A/m²

According to the specification of diamond doped electrodes the results shown in figure 8 and 9 have been expected because of the much higher overvoltage for oxygen charge transfer. As shown in figure 9 the overvoltage for oxygen charge transfer has a trementous impact on the rate of TOC depletion and the current efficiency.

4 Summary

Target of the project was to investigate the current density'/potential characteristic of the basic electrolyte sodium sulphate with the electrode combination iridium oxide doped DSA and glassy carbon cathode in comparison with a diamond doped titanium anode and the same cathode material.

The investigated anode materials differ significantly in the current/voltage characteristic. In comparison the diamond doped anode shows the better efficiency for EDTA mineralization and degradation.

Demonstrated with the iridium oxide doped DSA the current density has an important effect on the route of degradation, shown by the pH characteristic, and the current efficiency.

Symbols

Ea	Anode potential [V]
U	Operation voltage [V]
I	current [A]
t	time [sec]

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