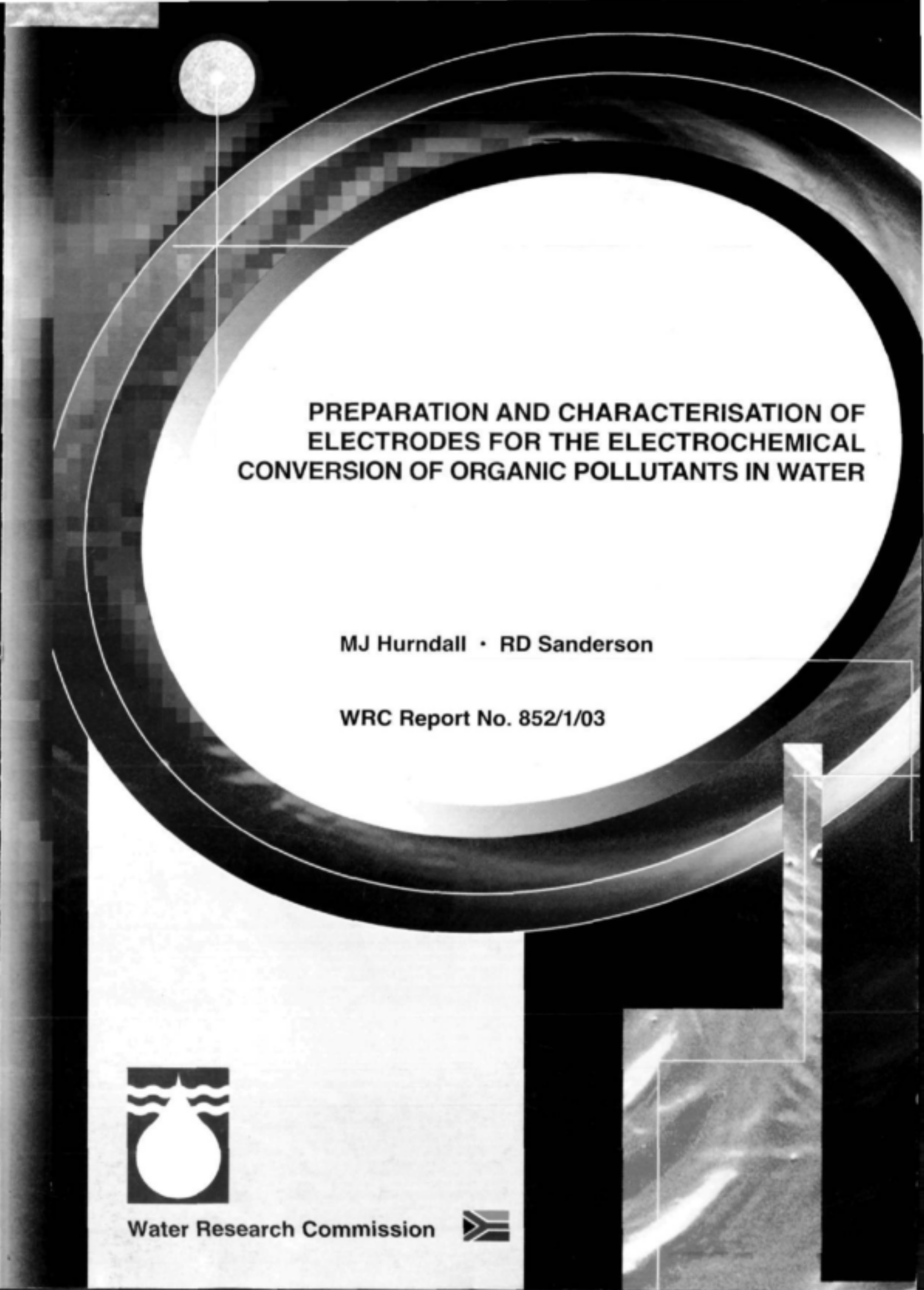

PREPARATION AND CHARACTERISATION OF ELECTRODES FOR THE ELECTROCHEMICAL CONVERSION OF ORGANIC POLLUTANTS IN WATER

MJ Hurndall · RD Sanderson

WRC Report No. 852/1/03

Water Research Commission

PREPARATION AND CHARACTERISATION OF ELECTRODES FOR THE ELECTROCHEMICAL CONVERSION OF ORGANIC POLLUTANTS IN WATER

Final Report

to the
Water Research Commission

by

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EXECUTIVE SUMMARY

Preparation and characterisation of electrodes for the electrochemical conversion of organic pollutants in water

Introduction

Many different methods for improving the quality of wastewater, such as pressure-driven membrane-based methods, biological treatment, chemical treatment and treatment with chlorine are ozone are already established.

Elecrochemical oxidation has recently been proposed as an alternate method for the removal of organic pollutants from water, especially for dilute solutions of biorefractory organics. The use of high oxygen-overvoltage anodes for the direct oxidation of refractory organic chemicals is of great potential value in wastewater treatment.

The economic feasibility of this type of process is associated with its ability to limit side reactions and its good current efficiency. Anodic oxidation does not release undesirable chemicals into the water (as chlorination does).

For the efficient use of the above process, two areas required close attention:

- the choice of electrode material and
- the design of the electrode system for the maximum contact of impurities onto the electrode.

To increase energy efficiency per unit volume of water treated, anodic electrocatalysts are required to hinder the oxygen evolution reaction and yet be electrocatalytically active towards the oxidation of dissolved organics.

Research in the field of material science, for better and more cost-effective electrodes that could improve existing water purification processes was undertaken. Attention was to be paid to the improvement of existing electrocatalytic systems by creating novel and potentially useful metal oxide electrocatalysts (subsequently based on SnO_2). A further way in which the efficiency of electrochemical methods for wastewater treatment could be increased was by supporting the system on solid polymer electrolytes (SPE). An SPE system thus makes possible electro-organic reactions at an electrode on the surface of an ion-exchange membrane, without the need for addition of a supporting electrolyte

Broadly speaking, the project was to address the design, preparation, characterisation and evaluation of new and improved electrodes for the electrochemical conversion (oxidation) of hazardous organic pollutants in water. The oxidation (conversion and combustion) of phenol, considered a standard/model contaminant for hazardous organic compounds in water, and widely used as a model compound to asess methods of treating aqueous soultions containing organic waste, was to be investigated.

Objectives

The main objectives of this project were:

1 To create a document describing the state-of-the-art in electrolytic processes, other than electrodialysis, in water treatment.

2 To design and prepare novel electrode materials for the electrocatalytic oxidation of phenol in water, by optimising the •OH radical production electrochemically. This included the preparation of new doped SnO_2 sol-gel layers.

3 To characterise the above electrodes, by various methods, including: surface analysis by microprobe and by XPS.

4 To determine the electrochemical oxidation of phenol by cyclic voltammetry and conductivity measurements of the electrode materials.

5 To use a novel electrode material in a SPE reactor for the electrocatalytic oxidation of phenol, without the addition of salt to the electrolyte solution.

Overview of the project

With the assistance of technology available at Max Planck, Germany, we learnt how to make sol-gel electrode materials of tin oxide and with the assistance of Essen University (Germany), the electro-deposition of lead oxide electrodes. This progress then brought us in-line with the existing American technology. However, although tin oxide is conductive, it does not have the conductivity of a good electrode material. Both our group and overseas experts in the field then deemed it necessary to increase the overpotential further. Hence, we were to aim at making electrodes from materials that do not desire to have extra oxygen in the ceramic lattice.

Towards this aim, antimony oxide, Sb_2O_3, was copolymerised with tin oxide, by sol-gel synthesis, from its metal salts. This put excess oxygen into the lattice and did indeed increase the overpotential for oxygen generation, while the increased conductivity of the electrode allowed more efficient hydroxyl radical generation on the electrode surface.

This report describes progress made with the design and preparation of new SnO_2-based electrodes for the electro-catalytic oxidation of hazardous organic contaminants in water, the characterisation of the electrode materials and determination of the electrochemical oxidation of phenol by cyclic voltammetry. The following electrodes were evaluated for oxidation of phenol: Ebonex, Ebonex/PbO_2 and Ti/SnO_2 and Sn-doped Ti/SnO_2.

Phenol is considered to be a major water pollutant and phenol oxidation can be used as a model reaction to assess methods for treating aqueous organic waste. The oxidation (conversion and combustion) of phenol, considered a standard/model contaminant for hazardous organic compounds in water, was chosen as the model pollutant with which to evaluate the new electrode materials in this study.

Good results were obtained with the new electrodes, especially the Sb-doped ones The cyclic voltammograms revealed a high overpotential for oxygen evolution, resulting in well-separated peaks for the oxidation of phenol. (Good separation of the peaks for oxygen evolution from water and from organics, respectively, is required). Improvements in the conductivities of above films and higher current densities for the oxidation reaction were obtained by doping the film sol-gel solution with 10% Sb. Doping with fluoride increased the conductivity, but decreased the oxidation peaks.

These electrodes were fully characterised by advanced techniques, both in South Africa and Germany. What was desired was indeed synthesised. In an electrolytic cell, using sulphuric acid as electrolyte, the combustion of phenol was proved beyond doubt. The organics were combusted very rapidly, even from solutions with concentrations as high as 1g per litre. Hence the concept of anodic oxidation and the use of the new membrane materials was proved.

For the kinetic measurements of the reactions by which •OH radicals were formed at the anodes, the PbO_2-based electrode material on the Ebonex and the $Ti/SnO_2/Sb_2O_5$ anode material were compared. RNO was used as a spin trap for the •OH radicals.

One way in which the efficiency of electrochemical methods for wastewater treatment can be futher increased is by supporting the system on a solid polymer electrolyte (SPE). As organic pollutants do not form sufficiently conductive electrolytes for electrochemcial treatment without the addition of supporting salts, an SPE reactor was designed. This meant that we were able to move away from using an aqueous electrolyte to using a solid polymer electrolyte (SPE), namely Nafion, which requires no salt in the water to be treated.

Since perflourinated ion-exchange membranes such as Nafion as an SPE are use to separate the anode and the cathode in the electrochemical oxidation process, no conductive liquid is required in the cell. This is feasible since the fixed sulphonoic acid groups in the polymer, similar to the immobilised sulphuric acid, provide the conductivity through proton mobility inside the membrane. Hydrogen ions are formed at the anode during oxidation and migrate through the cation-exchange membrane.

Sb-doped SnO_2 anodes were coupled with a perfluorinated cation-exchange membrane to build a system for the anodic oxidation, and evaluated.

Porous titanium electrodes of up to 50 cm^3 in size were coated with doped SnO_2 for a SPE galvanostatic solid polymer electrolyte (SPE) application. Results indicated very low voltage across the stack, even without adding supporting electrolytes to the water. Once again, phenol breakdown was achieved.

There were however problems with the cell design. The first cell design was rather simple and the water to be combusted, or rid of organics, needed to be in total contact with the electrode. Unfortunately, mass transport problems and current deficiency limited the total efficiency of contact as the liquid flowed past the flat electrode in a cell designed for gaseous reactions ie. a fuel cell. A standard laboratory test system, a reversed fuel cell, had been used [Grimm, 2000].

Although good progress was made on the materials side of the project, in terms of the preparation of new and efficient electrode materials and assessment of their efficiency in the electrocatalytic conversion of phenol in wastewater, further work is strongly recommended. It should focus on even newer and improved electrode materials and, most importantly, on the improvement of the cell design. A better understanding of the mass-transport limitations of the reactor is also required.

Conclusions

The main conclusions of this project were:

- A written review of electro-assisted methods for water purification was compiled, and subsequently published. (Desalination **115**, 1998, 285-294)

- Various electrode materials (anodes) were prepared, characterised and evaluated for their catalytic potential as oxidation catalysts for the electrochemical oxidation of phenol, a model of organic pollutants in water. These electrodes were to have well separated peaks for the overpotential and the oxidation peak, in the cyclic voltammograms, for the oxidation of phenol.

- Determination of the electrochemical oxidation of phenol was successfully carried by means of cyclic voltammetry.

- Most favourable results were obtained with the new Sb-doped films on Ti foil, $Ti/SnO_2/Sb_2O_5$, prepared by a special sol-gel dip-coating technique. This new electrode material had a high overpotential for oxygen evolution, resulting in a well-separated peak in the cyclic voltammogram.

- Kinetic measurements, confirmed by UV/Vis spectroscopy, revealed that •OH radicals were formed as intermediates during the combustion of phenol in a second order rate-determining step. Using an on-line technique, the combustion of phenol in an electrolytic cell, using sulphuric acid as electrolyte, was established. This proved the concept of anodic oxidation and the suitability of the new membrane material.

- *The Ebonex® electrode did not absorb the phenol on the electrode, hence the* electrochemical reaction took place at a very much lower potential, much lower than the overpotential for oxygen evolution.

- With the $Ebonex/PbO_2$ electrode the oxygen overpotential interfered with the oxygen evolution peak.

- Overall, a new electrode material that separates the overpotential from the oxidation peak, while maintaining excellent kinetics at the electrode surface, has been prepared. With increasing current densities, increasing degrees of oxidation were obtained.

- Further, instead of using an aqueous electrolyte, a solid polymer electrolyte (SPE) reactor was designed. It required no salt in the water to be treated. Nafion was used to separate the anode and cathode in the electrochemical oxidation process. The new electrodes in the SPE for the combustion of phenol were efficient.

Unfortunately, with the simple cell design used there were mass-transfer problems. Current deficiency limited the total efficiency of contact as the solution flowed past the flat electrode in a cell designed for gaseous reactions ie. a fuel cell. The present cell design used had poor current efficiency and conversion.

In order to improve the current efficiency it is necessary to improve on reactor design. It is envisaged that with the design of a suitable commercial reactor, this technology could be effectively used. Such a design was, however, considered to be beyond the scope of this present research project (which focuses on the materials science aspects of a novel electrode materials). It should be undertaken by chemical engineers.

Lastly, the development and use of improved analytical techniques for the more accurate determination of the products of phenol oxxidation should be considered.

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Preparation and characterisation of electrodes for the electrochemical conversion of organic pollutants in water

The steering committee responsible for the project comprised the following persons:

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1 INTRODUCTION

1.1 Introduction

Many different methods for improving the acceptable quality of water, for both human consumption and industrial purposes, are already established. These include the pressure-driven, membrane-based methods of: reverse osmosis, ultrafiltration and microfiltration, biological treatment and treatment by means of various chemicals such as ozone or chlorine, and treatment with UV-radiation. The rising demand for water of acceptable quality can, however, only be met if we consider applying other suitable scientific and technical resources available to us, in stepping up the productivity of process technologies for converting low-grade water into water of better quality.

Electrochemistry, a branch of physical chemistry, is now playing an increasingly important role in numerous areas of science and technology, especially in the treatment of waste streams [Murphy, 1992]. Electrochemistry is concerned with the properties of solutions and electrolytes, such as: resistance and electrolytic conductivity, and with processes that occur at the electrodes. Briefly, electrochemistry deals with the charge transfer at the interface between an electrically conductive (or semi-conductive) material and an ionic conductor (e.g. liquids, melts or solid electrolytes) as well as with the reactions within the electrolytes and the resulting equilibria.

Recently, electrochemical oxidation has been proposed as an alternate method for the removal of organic pollutants [Comninellis, 1993; Murphy, 1992]. The economic feasibility of this type of process is associated with its ability to limit side reactions, especially oxygen formation from water, and have good current efficiency. The choice of anode material plays an important role – it should be stable over a wide range of anodic potentials and have a high overpotential for oxygen evolution, which constitutes the main side reaction in anodic oxidation [Polcaro, 1999]. Electrodes of metal dioxides such as PbO_2 and SnO_2 are useful. The former has high oxygen overpotential and the latter is a useful material due to its catalytic properties in organic oxidation.

Electrochemical methods for water treatment can, in principle, offer the potential advantage in that they can bring about the complete decomposition of organic waste to carbon dioxide and water [Comninellis, 1993], or other less harmful compounds. (See Figure 2.1.) Electrochemical combustion is presented as a clean and versatile method. It can be applied directly to an aqueous effluent, it requires few added chemicals and can be applied at very low concentrations. The process can, in principal, run at high electrochemical efficiency and combustion. It can also be used/operated under essentially similar conditions for a wide variety of wastes [Grimm et al.,1998].

Electrochemical methods of water treatment may benefit from the relatively low cost of electricity in South Africa, but the environmental burdens created by consuming more electricity do need to be taken into account.

1.2 Tin dioxide and lead dioxide electrodes for the anodic oxidation of organic compounds in aqueous media.

Although several research groups have developed anodic materials for electrochemical oxidation, the electrical current efficiency of the materials is, to date, unsatisfactory. Tin dioxide and lead dioxide were used by Comninelis [1993] to prepare electrodes for the anodic oxidation of organics compounds in aqueous media. Platinum (Pt) was the initial choice for the working electrode of both anodic and cathodic electrocatalysis [Murphy 1992]. Problems can, however, be encountered when it is used as the electrocatalyst for organic oxidation reactions because of the predominance of oxygen formation from water as an unwanted side reaction. On Pt electrodes, in a acidic environment, oxygen is formed at about 0.3V higher than the standard reversible potential for oxygen formation, which is 1,23v vs NHE. This overpotential is significantly lower than for the same reaction on most other meals. High overpotentials are less beneficial on platinum because a higher proportion of the current is consumed in water oxidation, therefore decreasing energy efficiency.

Alternatives to platinum anode electrocatalysis are desired. Ideally the electrocatalyst should have a significantly higher oxygen overpotential than Pt does. This will allow the electrode potential to be increased for enhanced rates of organic-impurity oxidation, without excessive oxygen formation. Furthermore, the anodic electrocatalyst should be at least as stable as platinum. Many metals are inherently reactive and subject to dissolution and corrosion when used as electrocatalysts, while others form stable corrosion-resistant ceramic-type oxide layers at their surfaces. The latter are usually electronically insulating and hence no use as electrode materials. Nevertheless, some do have highly conducting and stable oxide layers that are effective electrocatalytic materials.

Of overall importance is to increase the current efficiency (by maximising the anodic potential), over the formation of oxygen from water as an unwanted side reaction, and in so doing minimise the oxygen-evolution reaction [Murphy, 1992]. To increase energy efficiency per unit volume of water treated, anodic electrocatalysts are required to hinder the oxygen evolution reaction and yet be electrocatalytically active towards the oxidation of dissolved organics. Separation of the two peaks in the cyclic voltammograms of electrocatalytic reactions (see section 4.1 for a discussion on the use of cyclic voltammetry and cyclic voltammograms) is a good sign that there is opportunity to increase the current efficiency.

Improvements in reactor design can also contribute to improved current efficiency. Contact of the organic waste molecules with the electrode surface, in order to allow electro-oxidative catalysis, must be taken into acount.

1.3 Phenol, as model organic pollutant

Phenols, defined as hydroxy derivatives of benzene, occur in domestic and industrial wastewater, natural waters and potable water supplies. Phenol is considered to be a major water pollutant. Maximum permissible phenol concentrations of 0.05 mg dm^{-3} have been proposed [Comninellis, 1991]. Phenol oxidation can be used as a model reaction to assess methods for treating aqueous organic waste. The oxidation (conversion and combustion) of phenol, considered a standard and model contaminant for hazardous organic compounds in water, was chosen as the model pollutant with which to evaluate the new electrode materials in this study. It is a very common pollutant, yet one very difficult to destroy.

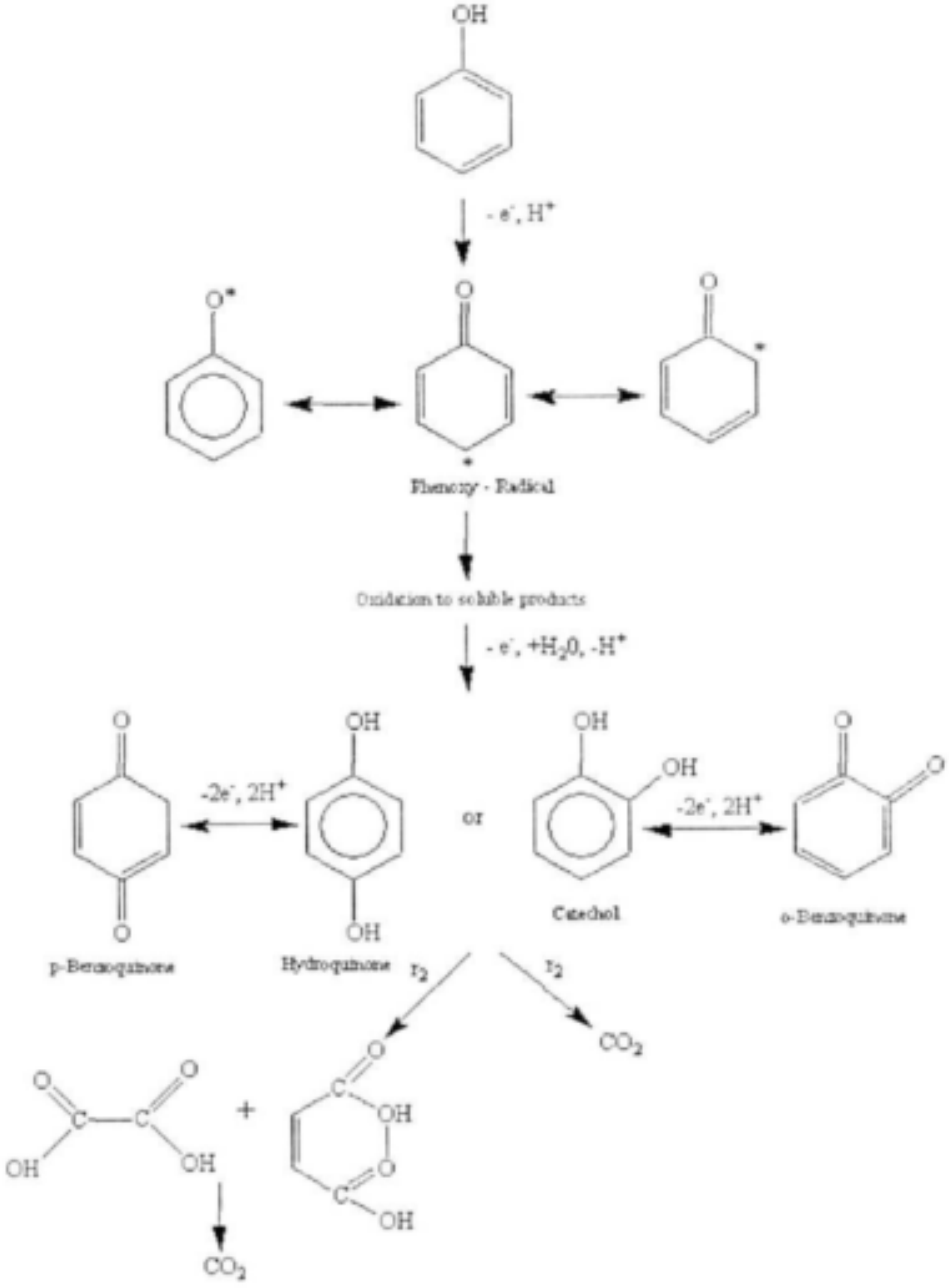

Fig 1.1: Proposed mechanism for the electrochemical oxidation of phenol [from Linkov, 2001]

1.4 Objectives

The many ways in which electrochemistry can be applied to the purification of polluted water demonstrates that research in this field is important. In 1997, when this project commenced, water-treatment purification systems based on anodic oxidation were emerging and becoming commercially available (eg. that of AEG, Electrosynth), but were very costly.

Research in the field of material science, for better and more cost-effective electrodes that could improve existing water purification processes was undertaken. The new materials were required to: enhance the rates of the organic oxidation reactions, and to increase energy eficiency by suppressing unwanted side reactions eg. oxygen evollution from water.

Attention was to be paid to the improvement of electrocatalytic systems by examining novel and potentially useful metal oxide electrocatalysts, especially those based on SnO_2. A further way in which the efficiency of electrochemical methods for wastewater treatment was to be increased was by supporting the system on solid polymer electrolytes (SPE).

Broadly speaking, the project was to address the design, preparation, characterisation and evaluation of improved electrodes, for the electrochemical conversion (oxidation) of hazardous organic pollutants in water. A key factor leading to complete anodic oxidation is the choice and design of a suitable electrode material. Evaluation was to be carried out by cyclic voltammetry (CV) and conductivity measurements.

The oxidation (conversion and combustion) of phenol, considered a standard/model contaminant for hazardous organic compounds in water, was to be investigated. According to literature, it was assumed that the oxidation of phenol lead to the formation of oxygen and carbon dioxide. (It was later seen that the oxidative peak in the cyclic voltammogram is completely removed, ie. total oxidation occurs. With •OH radicals this usually signifies combustion to CO_2 or small organic acids.).

The main objectives were therefore as follows:

1. To create a document describing the state-of-the-art in electrolytic processes, other than electrodialysis, in water treatment.
2. To design and prepare novel electrode materials for the electrocatalytic oxidation of phenol in water, by optimising the •OH radical production electrochemically. This included the preparation of new SnO_2-based materials and Sb-doped SnO_2 sol-gel layers.
3. To characterise the above electrodes, by various methods, including: surface analysis by microprobe and by XPS.
4. To determine the electrochemical oxidation of phenol by cyclic voltammetry and conductivity measurements of the films.

5. To apply novel electrode materials in a SPE reactor for the electrocatalytic oxidation of phenol.

Technology to more adequately analyze the disappearance of phenol needed to be developed, however the analysis of phenol degradation products by Gas Chromatography/Mass Spectroscopy (GC/MS) was not able to be undertaken.

1.5 General approach and methodology

Novel electrode materials were to be prepared, characterised and evaluated for the electrochemical oxidation of phenol, considered to be a standard organic contaminant in water and the most standard compound with which to study combustion. Chemically-stable and electrically-reactive catalytic surfaces on the electrodes were to be created by the sol-gel technique.

Both tin oxide and lead oxide have very high overpotentials for water splitting and therefore allow complete combustion of organics [Polcaro, 1999]. Taking this into consideration, and after discussions with experts on field of catalytic materials [Maier, 1996], research was to be conducted to prepare electrodes containing these materials. Although tin oxide is conductive, it does not have the conductivity of a good electrode material. It was then deemed necessary to further increase the overpotential. Focus was to be on preparing electrodes that do not desire to have extra oxygen in the ceramic lattice (see section 2.2.3).

The sol-gel dip-coating method was chosen for the preparation of SnO_2 films on Ti substrates. It has been shown to be well suited for the preparation of defect-free films [Maier, 1993]. In the past this procedure was used in the preparation of catalytically-active membrane films [Maier, 1995]. The method has several advantages [Chaleton, 1994]: high purity of starting materials, ease of coating large and complex-shaped substrates, low cost. The large variety of synthetic parameters provides control over the structural and chemical properties of catalysts. Sol-gel synthesis offers better control over pore volume, surface area, porosity and pore-size distribution. The sol-gel process provides a new approach to the preparation of catalysts, membranes, thin layers (catalytic films) etc. The sol-gel dipping technique leads to well prepared SnO_2 layers with respect to structure and morphology.

Antimony oxide, Sb_2O_3, was to be copolymerised with tin oxide, by sol-gel synthesis, from its metal salts. This would put excess oxygen into the lattice and lead to an increase in overpotential for oxygen generation, while the increased conductivity of the electrode should lead to more effective hydroxyl radical generation on the electrode surface.

Technology required to prepare sol-gel electrode materials of tin oxide was made available to us by the Max Planck Institute (Germany). Technology required to carry out the electrodeposition of lead oxide electrodes was made available by the University of Essen (Germany). Work was carried out locally and overseas.

Characterisation of the electrode materials was to be carried out by the following advanced techniques: impedance spectroscopy, X-ray photo-spectroscopy (XPS) surface analysis and microprobe surface analysis.

Characterisation of the electrode materials for the electrochemical oxidation of phenol was to be determined by cyclic voltammetry and conductivity measurements of the film

The electrochemical performance of the electrode was also to be determined by fibre-optics UV/Vis determination of hydroxyl radicals (determination of the phenol concentration by UV/Vis analysis).

The complete oxidation (combustion) of phenol was first to be determined in an electrolytic cell, using sulphuric acid as electrolyte. Later, it was intended to progress from using an aqueous electrolyte to using a solid polymer electrolyte (SPE), namely Nafion, which requires no salt in the water to be treated [Murphy, 1992].

1.6 Outline of the structure of the report

Chapter 1 introduces the area of research, lists the objectives of the project and discusses the methodology followed.

Chapter 2 contains a survey of information gathered from the literature, relevant to this project.

Chapter 3 describes the preparation of the various novel electrodes for the electro-catalytic oxidation of hazardous organic contaminants in water and their characterisation: Ebonex®, Ebonex/PbO_2 and Ti/SnO_2. The latter was doped with Sb, and henceforth referred to as Ti/SnO_2/Sb_2O_5. Characterisation of the electrodes by various methods is also described.

Chapter 4 describes the evaluation of the electrode material for the electrochemical oxidation of phenol by cyclic voltammetry and conductivity measurements. Further characterisation in terms of kinetic measurements, with a redox couple, is also discussed.

Chapter 5 addressed the cell performance.

Chapter 6 describes the characterisation of the new Sb-doped SnO_2 electrode material by electro-impedance spectroscopy.

Chapter 7 discusses the application of the above electrode material in a Solid Polymer Electrolyte (SPE) reactor for the electrocatalytic oxidation of phenol.

Chapter 8 contains the conclusions to the project and recommendations for future research.

Chapter 9 lists the publications, posters and presentations that emnated from this research.

2 HISTORICAL AND THEORETICAL BACKGROUND

2.1 HISTORICAL BACKGROUND

2.1.1 Introduction

Electrochemical oxidation has recently been proposed as an alternative method for the removal of organic pollutants [Comninellis, 1993: Murphy, 1992], especially from solutions of biorefractory organics. The economic feasibility of this process is associated with its ability to limit side reactions and its good current efficiency. The choice of anodic material plays an important role; it should be stable over a wide range of anodic potentials, and should present high overpotential for oxygen evolution, which constitutes the main side reaction in organic oxidation. Metallic dioxide electrodes such as PbO_2 and SnO_2 are suitable. The former has a high oxygen overpotential and the latter is useful because of its catalytic properties in organic oxidation. Both types of electrode have been studied for the oxidation of organic compounds [Smith, 1981; Chiang, 1995; Comninellis 1991 and 1995; Kötz and Stucki 1991].

2.1.2 Electrode materials for the oxidation of hazardous organic compounds in water

The first high-performing electrode material successfully investigated for the oxidation of hazardous organic compounds in water was lead dioxide (PbO_2) [Kirk, 1984; Wabner, 1985]. Lead dioxide is of great practical importance, firstly as the positive plate in the lead-acid battery [Randle, 1979] and secondly as an inert electrode for different anodic processes. This is because noble metal electrodes, e.g. platinum electrodes, used for anodic electrosynthesis, are expensive, inherently only slightly stable and chemically as well as electrochemically less noble than is generally assumed. PbO_2 electrodes are relatively stable from the mechanical, chemical and electrochemical point of view, and they are comparatively cheap. These electrodes have another very interesting advantage, namely anodic oxygen evolution at the PbO_2 surface takes place at an essentially more positive potential than on, for example, a platinum electrode [Wabner, 1985].

PbO_2 was deposited galvanostatically on a suitable Ebonex substrate [Wabner, 1974; Fleischmann, 1958]. Ebonex, as Magneli phase titanium suboxides which are blue-black in colour and electrically conductive, are known to be excellent supports for any kind of electrocatalytic coating [Park, 1995]. The remarkable combination of its electrical conductivity and very high corrosion resistance makes this material most suitable for use in electrochemical cells with particularly corrosive electrolytes [Graves, 1992]. Additionally, the ceramic-rutile based structure of Ebonex makes it very compatible with rutile-structured surface coatings such as iridium dioxide, ruthenium dioxide and lead dioxide.

Comninellis [1994] found that SnO_2 is an excellent electrode material with high stability and radical output. SnO_2 is intrinsically a large band-gap (3.7 eV) semiconductor whose resistance may be decreased enormously by doping. The conductivity and the electrocatalytic properties of electrodes were improved by the introduction of traces of Sb_2O_5 to the SnO_2 films as a dopant. Incorporation of the former in the SnO_2 matrix, by isomorphis of Sn atoms, is relatively easy and leads to a low lattice-parameter modification [Boudeulle, 1983]. The preferred material described in the literature as a substrate for the electrocatalytic SnO_2 films is titanium.

Comninellis [1993] also discovered that hydroxyl radicals (•OH radicals), as intermediates on the electrode's surface, are the driving force for the complete oxidation (combustion) of even very stable organic compounds in water, such as phenol. As a detection method for the •OH radicals, Comninellis used a method well established in biology and biochemistry, i.e. spin-trapping with p-nitrosodimethylaniline (RNO).

2.1.3 Coating methods

There are a variety of methods available for coating the catalyst support to obtain dimensionally stable anodes. Methods of film preparation include:

- Chemical vapour deposition [Kadam, 1990; Popova, 1990],
- Reactive sputtering [Czapla, 1989],
- Sol-gel dip coating [Arfsten, 1984], (see section 2.1.6)
- Spray-pyrolysis [Popova, 1990; Chaudhuri, 1990; Karlsson, 1992; Comninellis, 1993].

For the purpose of the present project the sol-gel dip-coating method for the preparation of SnO_2 films on Ti substrates was chosen. Interest in the sol-gel processing of inorganic ceramic and glass materials began as early as the mid-1800s with Ebelman and Graham's studies on silica gels. These early investigations showed that the hydrolysis of tetraethyl orthosilicate (TEOS), $Si(OC_2H_5)_4$, under acidic conditions, yielded SiO_2 in the form of a glass-like material [Ebelmen, 1846; Ebelmen, 1847]. However, extremely long drying times of a year or more were necessary to prevent the silica gels from fracturing into a fine powder and, consequently, there was little technological interest. For a period from the late 1800s to the 1920s chemists became very interested in gels. This was stimulated by the phenomenon of Liesegang Rings [Liesegang, 1896; Heinisch, 1970] formed from gels. A huge volume of descriptive literature resulted from these studies [Lloyd, 1926; Holmes, 1926; Stern, 1967], but there was a relatively sparse understanding of the physical-chemical principles.

Roy and co-workers [Roy, 1954; Roy, 1956; Roy, 1969; McCarthy, 1969] recognised the potential for achieving very high levels of chemical homogeneity in colloidal gels. In the 1950s and 1960s they used the sol-gel method to synthesise numerous novel ceramic oxide compositions, involving Al, Si, Ti, Zr, etc., that could not be made using traditional ceramic powder methods. The motivation for sol-gel processing is primarily the potentially higher purity and improved homogeneity and the lower processing temperatures associated with sol-gel compared with traditional glass melting or ceramic powder methods. During the past decade there has been an enormous growth in interest in the sol-gel process. This growth has been stimulated by several factors. On the basis of Kistler's early work [Kistler, 1931], several teams have produced very low-density silica monoliths, called aerogels, by hypercritical point drying [Fricke, 1986].

It has been shown that the dip-coating method is well-suited for the preparation of defect-free films [Maier, 1993]. In the past this procedure has been used for the preparation of catalytically-active membrane films [Maier, 1995]. The method has major advantages [Chaleton, 1994]: starting materials of high purity, ease of coating of large and complex-shaped substrates and low cost. The sol-gel dipping technique leads to very high-quality SnO_2 layers with respect to structure and morphology. Chemical modifications, achieved readily by the addition of selected dopants, like antimony alkoxides, antimony chlorides, $K_2[PtCl_6]$ or fluoride to the sol, should reduce the band gap between the valence- and conducting bands as an n-donor in the oxide and thus increase conductivity.

As mentioned above, a special feature of a SnO_2-based electrode material is the high anodic overpotential for the oxygen evolution reaction. Consequently, the material should also be useful for other electrochemical reactions running at high anodic potentials, such as perchlorate production. The common industrial method of producing perchlorate is the electrochemical oxidation of aqueous chlorate solutions [Ibl, 1981]. The anode material is crucial to obtain a high current efficiency for the formation of perchlorate. To data only two materials, smooth platinum and lead dioxide, are used industrially [Ibl, 1981]. Munichandraiah et al. suggested a one-electron-transfer step, to give an adsorbed hydroxyl radical, as the rate-determining step for the overall reaction [Munichandraiah, 1987]. Tin dioxide produces high hydroxyl concentrations on the surface and is thus a potentially useful system for perchlorate production.

2.1.4 Solid Polymer Electrolytes

Ion-exchange membranes can function as Solid Polymer Electrolytes (SPE) in non-conductive liquids. Hence electro-organic synthesis as well as the electrochemical combustion of organic compounds in water are feasible without supporting electrolytes. The SPE process was initially developed by industry for the electrolysis of pure water and for fuel cells (now usually referred to as Proton Exchange Membrane, PEM, fuel cells). The first applications of the SPE process for electro-organic synthesis were published by Ogumi et al. in Japan and by Sarrazin and Tallec in France and Grinberg et al. in Russia [Ogumi, 1981; Sarrazin, 1982; Grinberg, 1983]. Further investigations were published more recently by Liu and Fedkiw [1992] and by Chen and Chou [1993].

A different approach to a reactor system is the principle of fluidised-bed electrolysis, designed by Goodridge and Fleischmann [Backhurst, 1969]. The electrolyte flows from bottom to top through a loose bed of particles thus fluidising the particles. The fluidised particles are charged via a feeder electrode. This provides a large surface area for the reaction zone, described as a three-dimensional electrode.

2.2 THEORETICAL BACKGROUND

2.2.1 Electrochemistry

Briefly, electrochemistry deals with the charge transfer at the interface between an electrically conductive (or semi-conductive) material and an ionic conductor (e.g. liquids, melts or solid electrolytes) as well as with the reactions within the electrolytes and the resulting equilibrium. Electrochemical waste destruction shows potentially several benefits in terms of costs and safety over other methods of waste destruction [Grimm, 1998]. Operation at room temperature and atmospheric pressure reduces the possibility of volatilisation and the discharge of unreacted waste. The waste treatment can be terminated within seconds by simply cutting off power to the electrodes. Electrochemical combustion is presented as a clean and versatile method.

The following electrochemical approaches may be distinguished:

- indirect electrochemical oxidation of inorganic or organic contaminants;
- direct electrochemical oxidation of the contaminants;
- cathodic removal of metal-cations (mostly heavy metals)
- separation through membranes using an electric field.

The removal of undesired components from aqueous phases is based on the choice of the appropriate electrode material and potential, or by a membrane-assisted system to drive the electrode processes selectively.

2.2.2 Electrochemical Methods

2.2.2.1 Mechanism of the oxidation of organics in water

Two different pathways are described in the literature for the anodic oxidation of undesired organics [Comninellis, 1994, 1996]: electrochemical conversion and electrochemical combustion (Fig. 2.1).

Electrochemical conversion transforms only the toxic and non-biocompatible pollutants into biocompatible organics, so that biological treatment is still required after the electrochemical oxidation.

In contrast, electrochemical combustion yields water and CO_2 and no further purification is necessary.

Experimental results indicate the accumulation of $\cdot OH$ radicals favours the combustion reaction, while introduction of oxygen into the electrode lattice results in conversion.

Electrochemical combustion can be described by the following equations:

$$MO_x + H_2O \xrightarrow{k_{OH}} MO_x(\bullet OH) + H^+ + e- \qquad (2\text{-}1)$$

This step involves the physisorption of $\bullet OH$ radicals on the electrode surface.

$$R + MO_x(\bullet OH)_z \xrightarrow{k_C} (CO_2 + ZH^+ + Ze- + MO_x) \qquad (2\text{-}2)$$

Anodes with a high oxygen overpotential, such as Ti/SnO_2, Ti/PbO_2 and graphite-felt, favour the electrochemcial combustion [Comninellis, 1991, 1993, 1988].

2.2.2.2 Anodic Oxidation

Anodic oxidation is considered to be very useful for the treatment of organic compounds in water, especially as far as the removal of organic wastes in industrial effluents is concerned. The main objective of the process is to oxidize any organics to H_2O and CO_2.

Two different approaches may be distinguished:

I. direct anodic oxidation, where the organics are destroyed at the electrode's surface, or
II. indirect oxidation, where a mediator, for example Ag^{2+}, is electrochemically generated to carry out the oxidation.

i) Direct oxidation

Two different pathways are described in the literature for the anodic oxidation of undesired organics [Comninellis, 1993]:

I. electrochemical conversion and
II. electrochemical combustion.

Electrochemical conversion transforms only the toxic and non-biocompatible pollutants into biocompatible organics, so that biological treatment is still required after the electrochemical oxidation. In contrast, electrochemical combustion yields water and CO_2 and no further purification is necessary. This means that research should rather focus on studies of the mechanisms of the anodic combustion. Fig. 2.1 is a schematic representation of the electrochemical conversion/combustion, adopted from Comninellis [Comninellis, 1993].

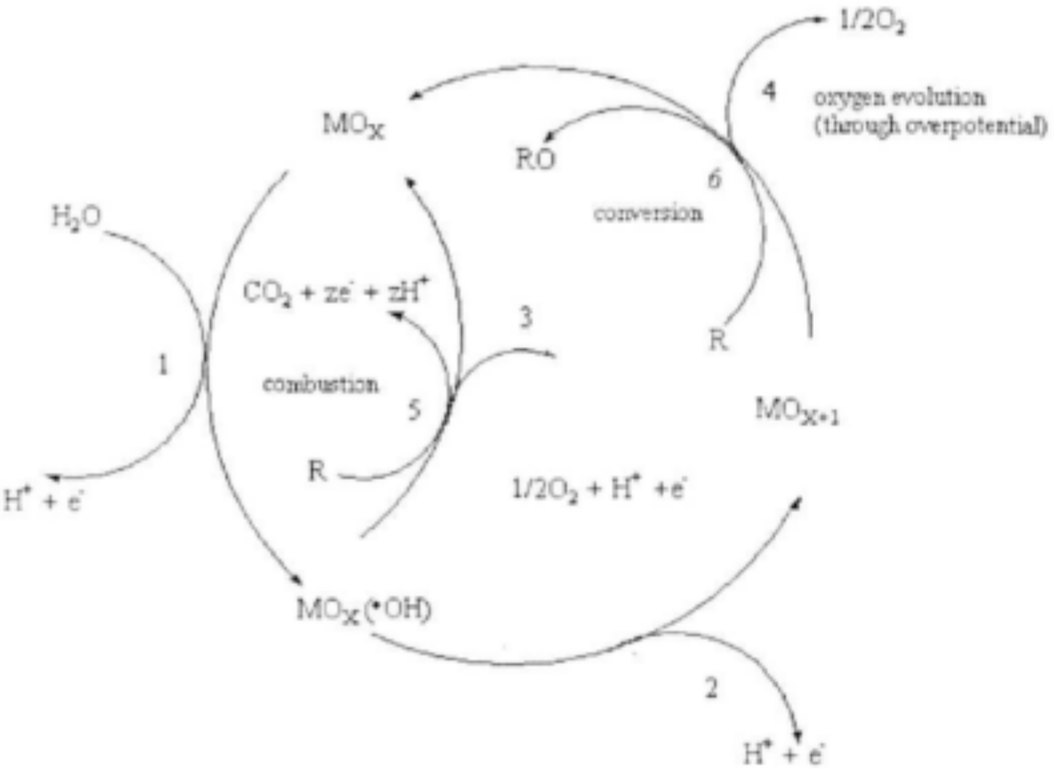

Fig 2.1: Pathway of electrochemical combustion/conversion (scheme adopted from Comninellis, 1993). R represents an organic compound.

Experimental results indicate that the accumulation of •OH radicals favours the combustion reaction. Introduction of oxygen into the electrode's lattice results in conversion. This opens a challenging field for materials science, for the creation of novel and more efficient electrodes.

ii) Indirect oxidation

During indirect electrochemical oxidation, the organic pollutants are destroyed by an electron-transfer agent, such as ClO^-/Cl^- or Ag^{2+}/Ag^+ [Almon, 1992]. The extremely high standard potential of the reaction (1.96V/NHE, in nitric acid medium): $Ag^+ \rightarrow Ag^{2+}$, establishes silver ions as the ideal mediator which attack organic species such as tributylphosphate (TBP), tetraphenylborate (TPB) and benzene [Almon, 1986]. The process is potentially useful in waste-water treatment as well as even for the disposal of radioactive organic waste. When used as an electron-transfer agent, silver acts as a reusable catalyst, and no silver waste is generated. The anodic reaction is balanced by the cathodic reduction of nitric acid,

$$HNO_3 + 2\,H^+ + 2e^- \rightarrow HNO_2 + H_2O \qquad (2\text{-}3)$$

nitric acid must be regenerated by the chemical reaction of nitrous acid with oxygen. Furthermore, separators must be inserted into the cell to prevent the HNO_2 from migrating to the anolyte compartment and reducing the Ag^{2+}. The mechanism has been studied by means of spectroscopic and potentiometric methods [Lehmani, 1996].

2.2.3 Electrode materials

The choice of an effective electrode material is based on high activation energies for undesired side-reactions. If side-reactions are to be reduced, then cathode materials should have high overvoltages for hydrogen-evolution. Materials such the dioxides of Pb or Sn are suitable. The anodes should preferably show high overvoltages [Bard and Faulkner, 1980] for the evolution of oxygen. Fluoride addition should furthermore reduce the surface polarity of the electrodes and thus improve the adsorption of organics on the electrode surface.

Stannic oxide (SnO_2) is an important oxide semi-conductor [Polcaro, 1999.] It has a high oxygen overpotential and its properties are well known. Stannic oxide has a wide band gap and is one of the oxides with the highest mobilities of electrons. Its semi-conductance can be controlled by doping with antimony and/or fluorine. Besides being useful as electrode materials, tin oxide semi-conductors with dopants and additives are widely used as transparent, electronically-conductive electrodes in electrochromic devices (ECD), low emitting (i.e. heat reflection) coatings and as conductance-type, gas-sensitive detectors [Granqvist, 1990].

Chemical modifications, readily achieved by the addition of selected dopants such as antimony alkoxides, antimony chlorides $K_2[PtCl]_6$ or flouride to the sol, should reduce the band gap between the valence- and conducting bands, and thus increase conductivity.

Fig 2.2 is a schematic representation of the band structure for the rutile modification of SnO_2 and PbO_2 [Wabner, 1985], where the 26 valence electrons just fill all anionic, all t -, and e - type energy states.

Since a gap is expected to occur between the e-type and s-type energy states, these materials should, according to the literature, be insulators or semi-conductors [Wabner, 1985]. N- or p-doping with fluoride or antimony can convert SnO_2 to a conductor. This means that the $e\sigma - s\sigma$ gap has been totally eliminated, by doping, and that very broad bands have formed, facilitating electron movement.

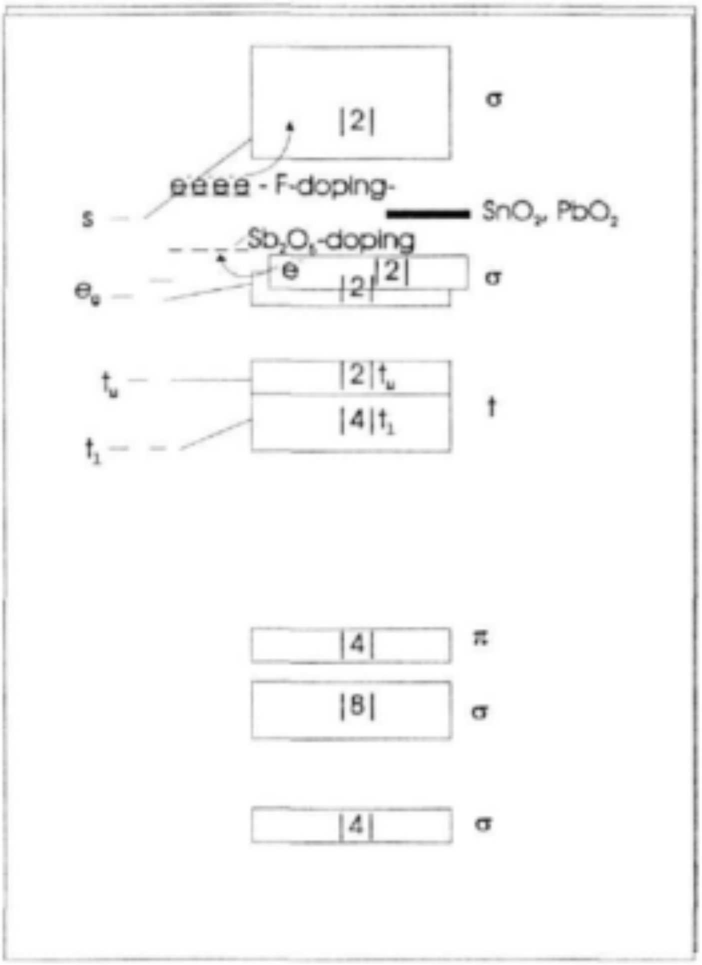

Fig 2.2: Model of the band structure scheme of the rutile lattice of SnO_2 and PbO_2

Sharifan and Kirk [1986] described the use of PbO_2 as electrode material, while Comninellis et al. [1996] focused their research on SnO_2 coatings obtained by spray pyrolysis.

Surface properties of the electrodes, such as pore-size, roughness and catalytic activity, can be measured by electrochemical methods, such as impedance spectroscopy and cyclic voltammetry.

Favoured goals of electrode design include high surface roughness with many catalytic sites (that might be smoothed during application), high exchange current densities, high Tafel slopes and a high electron-transfer rate [Bard and Faulkner, 1980]. High porosity provides a large surface area and the pore sizes must not be too small, to allow for a rapid mass transport. Surface properties of the electrodes, such as pore-size, roughness and catalytic activity can be examined by electrochemical methods such as impedance spectroscopy or cyclic voltammetry. Catalytic activity should be at a maximum, if the undesired molecules fit closely into the pores.

2.2.4 Ebonex®, as a support for electrocatalytic coatings

Chemically stable and electrically conductive materials must be selected as carriers for electrocatalytic materials. Titanium (Ti) is usually used as the base material. Recently, Ebonex®, as a Magneli phase titanium suboxide, blue-black in colour and electrically conductive, has been reported to be an excellent support for any kind of electrocatalytic coating [Park, 1995]. (Ebonex®, is a registered trademank of Atraverda, Ltd., USA.) The remarkable combination of its electrical conductivity and very high corrosion resistance makes this material most suitable for use in electrochemical cells with particularly corrosive electrolytes [Graves,1992]. Additionally, the ceramic/rutile-based structure of Ebonex ceramic makes it very compatible with rutile-structured surface coatings such as iridium dioxide, ruthenium dioxide and lead dioxide. For example, Heraeus has reported that lead-dioxide coated Ebonex electrodes have projected lifetimes of at least four years, at 1 kA/m^2 in fluorine-containing electrolytes [Mayr, 1990].

PbO_2 layers were to be galvanostatically deposited on an Ebonex electrode material from a $PbNO_3$ solution.

2.2.5 The sol-gel process, for the preparation of catalytic materials

Sol-gel chemistry is a very versatile method for the preparation of catalytic materials. [Wabner, 1985, Spiker, 1992, Park, 1995]. A number of different synthetic parameters provide control over the structural and chemical properties of catalysts thus formed. Sol-gel synthesis offers better control over pore volume, surface area, porosity and pore-size determination than other preparation procedures do. Sol-gel can also facilitate multi-element systems in as single step. The sol-gel process provides a new approach to the preparation of catalysts and membranes.

Starting from molecular precursors, an oxide network is obtained by the hydrolysis and polycondensation of alkoxides. The solution chemistry of alkoxides has been investigated and the precursors used in most studies are generally commercially available.

Sol-gel synthesis involves the formation of a sol followed by the formation of a gel. A gel is a diphasic material with a solid encapsulating a liquid. These polymerised alkoxides are dried to remove the encapsulating liquid, leaving a porous network. The external surface of the sol-gel catalyst is relatively small compared to the internal surface area. Thus, sufficient diffusion of molecules through the pores of the active catalyst centres is crucial and requires a proper design of the pore structure.

Sol-gel chemistry is based on the hydrolysis of a precursor and the condensation of partially hydrolysed species to form a three-dimensional network. These two reactions can be represented as:

$$\text{Hydrolysis:} \quad \text{-M-OR} + H_2O \rightarrow \text{-M-OH} + ROH \qquad (2\text{-}4)$$

$$\text{Condensation: } -\text{M-OH} + \text{R-M} \rightarrow \text{M-O-M} + \text{ROH} \qquad (2\text{-}5)$$

The basic premise is that the sol-gel product depends on the relative rates of hydrolysis and condensation. For example, precipitates form if the hydrolysis rate is low and the condensation rate is fast. Controlling these rates can change the characteristics of the product for specific applications. Factors that can be also varied include: acid or water content, the type of precursor, the type of solvent, precursor concentration and temperature.

Three approaches are used to make sol-gels:

- Method 1: gelation of a solution of colloidal powders,
- Method 2: hydrolysis and polycondensation of alkoxide or nitrate precursors, followed by supercritical drying of gels,
- Method 3: hydrolysis and polycondensation of alkoxide precursors followed by ageing and drying under ambient conditions.

Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with diameters of 1–100 nm [Davis, 1963]. A gel is an interconnected, rigid network with pores of sub-micrometer dimensions and polymeric chains whose average length is greater than a micrometer. The term gel embraces a diversity of combinations of substances that can be classified in four categories:

- well-ordered lamellar structures;
- covalent polymeric networks, completely disordered;
- polymer networks formed through physical aggregation, predominantly disordered;
- particular disordered structures.

A gel is formed by network growth from discrete colloidal particles (Method 1) or by formation of an interconnected 3-D network, by the simultaneous hydrolysis and polycondensation of an organometallic precursor (Methods 2 and 3). When the pore liquid is removed as a gas phase under supercritical conditions (critical-point drying, Method 2), the network does not collapse and a low density aerogel is produced. Aerogels can have pore volumes up to 98% and densities as low as 80 kg/m^3 [Yoldas, 1975; Fricke, 1988].

When the pore liquid is removed by thermal evaporation at near ambient pressure (drying), as used in Methods 1 and 3, and shrinkage occurs, the monolith is termed a xerogel. If the pore liquid is primarily alcohol-based, the monoliths are often termed alcogels. The generic term gel usually applies to either xerogels or alcogels, whereas aerogels are usually designated as such. A gel is defined as dried when the physically absorbed water is completely evacuated. This occurs between 100 and 180 °C. A dried gel may still contain a very large concentration of chemisorbed hydroxyls on the surface of the pores. Thermal treatment in the range 500 – 800 ° C desorbs the hydroxyls and thereby decreases the contact angle and the sensitivity of the gel to rehydration stresses and results therefore in a stabilised gel.

2.2.6 Electrochemical reactor design

In porous electrodes, reactions occur inside the pores of a porous bulk. Unfortunately, such configurations are of little use for water treatment because the mass transport of the contaminants to the inside of the pores is slow. This can be improved by arranging thin, porous layers of electrodes, as in fuel cells. Particle electrodes have been extensively studied for their use in the deposition of heavy metals from waste waters [Kreysa and Heitz, 1986]. The two different types of construction are:

- an electrochemical packed-bed reactor, and
- an electrochemical fluidised-bed reactor.

An electrochemical packed-bed reactor is shown schematically in Fig. 2.3. A bed of conductive and non-conductive spherical particles, such as graphite and synthetics, is situated between two electrodes, and the contaminated water flows through it.

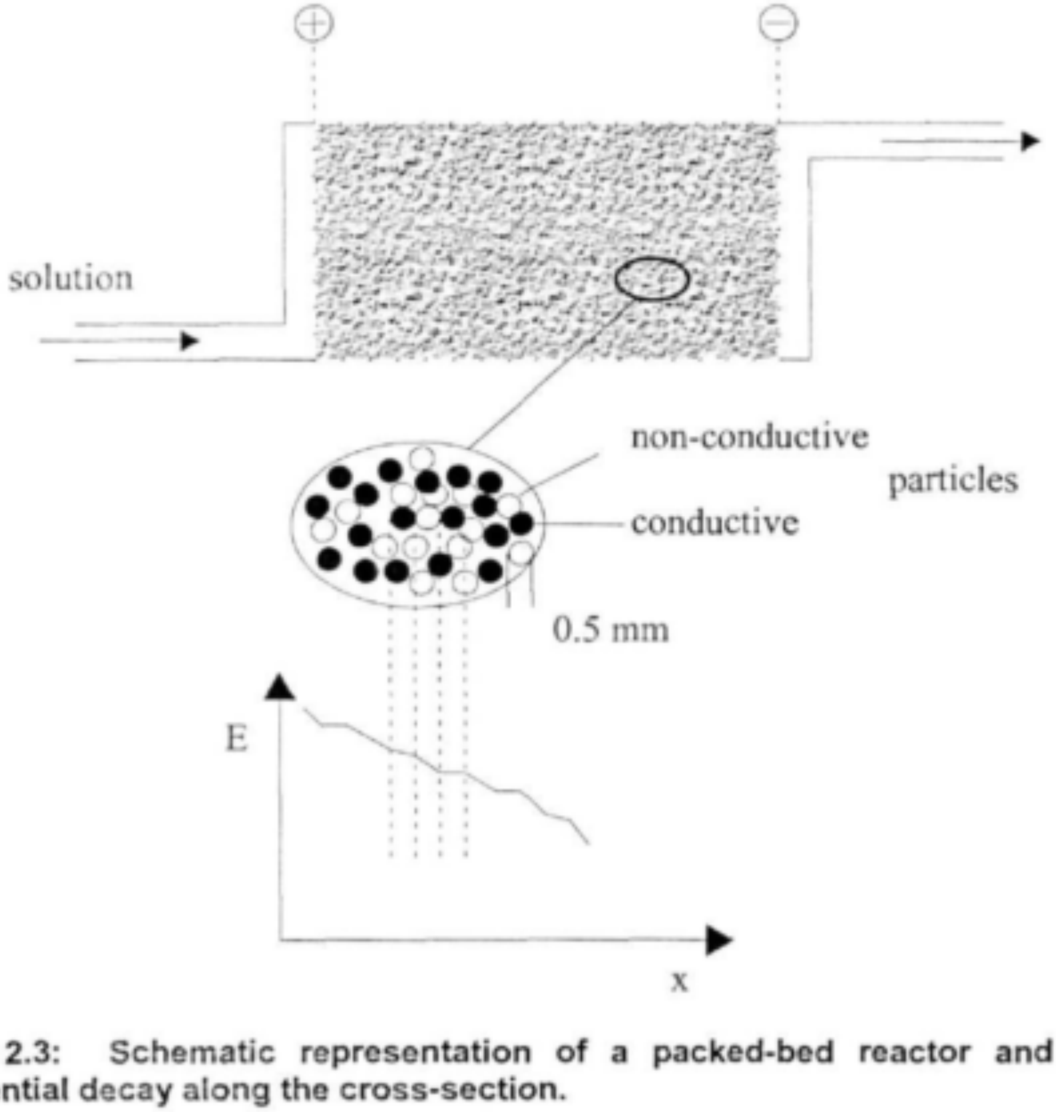

Fig 2.3: Schematic representation of a packed-bed reactor and the potential decay along the cross-section.

If the conductivity of the solution is not too high and the voltage across it is sufficiently high, the conductive particles will act as a multitude of bipolar electrodes. In three-dimensional electrodes the penetration depth of the current in a direction parallel to the current flow is limited. Ohmic losses in the electrolyte are the main cause of the decrease in local current density. The penetration depth of the limiting current density increases with decreasing concentration of the metal ions. Application of this principle has led to the design of the Enviro-Cell®, shown schematically in Fig. 2.4. The penetration depth of the bed increases as the metal ion concentration decreases. The metal concentration can be reduced to a low as 1/1000 of the initial concentration.

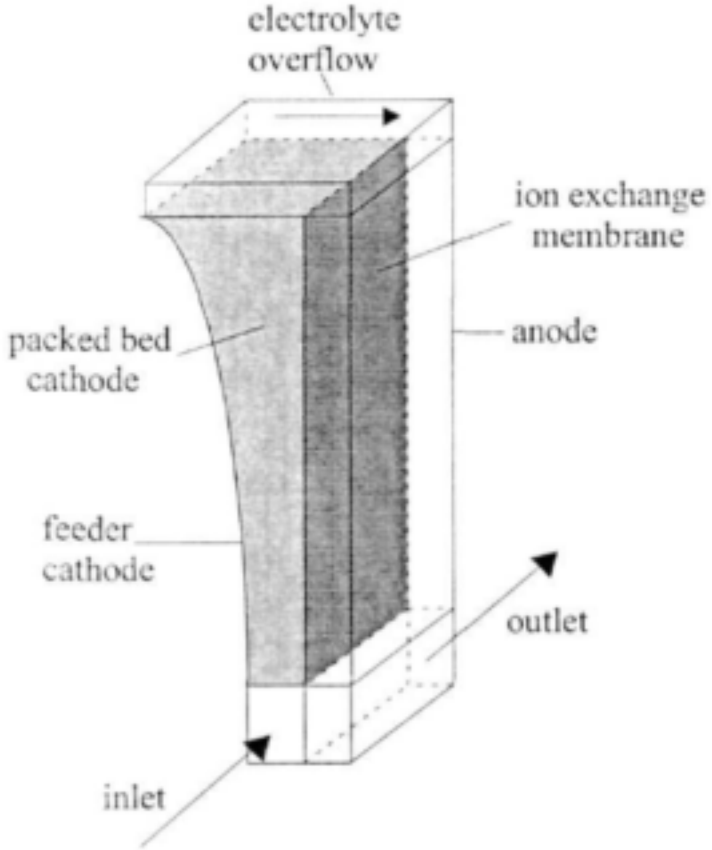

Fig 2.4: Schematic representation of the Enviro cell®

This principle design of a fluidised-bed reactor is illustrated in Fig. 2.5. *In* this reactor a loose bed of particles of size diameter 0.1-1 mm is flooded upwards, from the bottom. The fluidised particles are charged cathodically by a feeder electrode. Metal ions are adsorbed at the surface of the particles and once the particles contact the working-electrode its potential drives the charge-transfer reaction and the discharged metal is deposited. When the metals lose contact with the electrode they either desorb, and collect at the bottom of the reactor, or the particles grow and the larger ones sink to the bottom and are replaced by fresh particles.

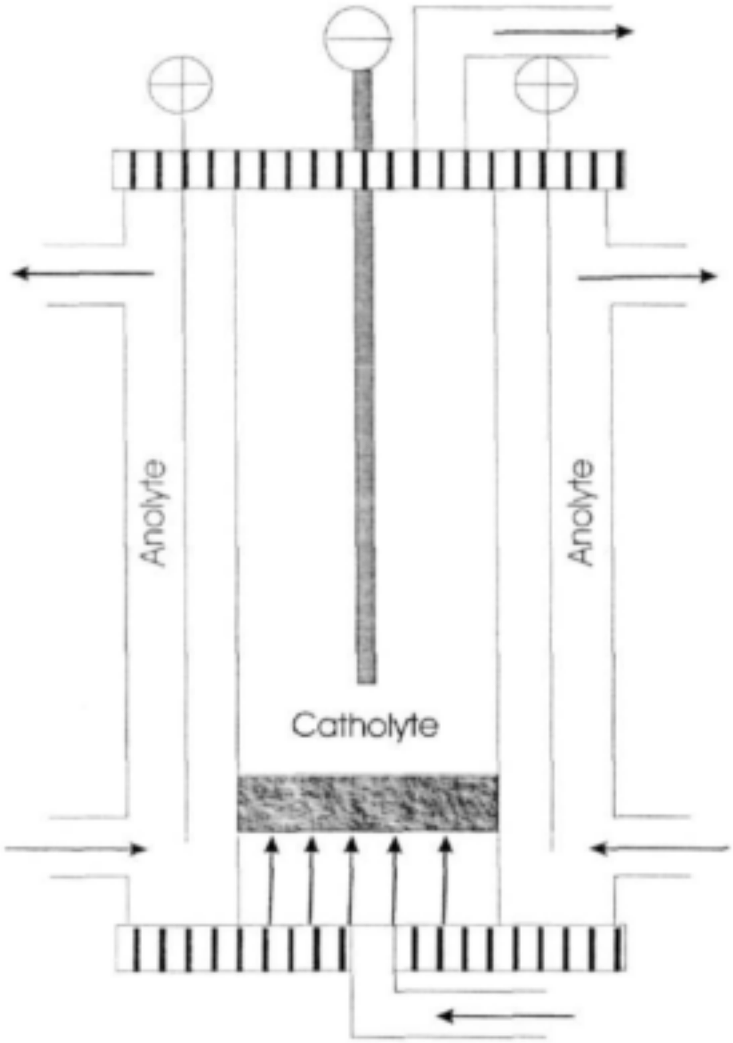

Fig 2.5: The principle design of a fluidised-bed reactor

The principle has been widely studied and purification by this means has been carried out on an industrial scale [Kreysa, 1981]. For hydraulic reasons, the height of such a cell is usually restricted to 2 m. Consequently, only a limited concentration drop per pass can be achieved. Continuous operation and serial arrangement of the cells can reduce these problems. Advantages of a fluidised-bed reactor include: the rapid mass-transport and the low real-current density, meaning that even very low concentrations of metals can be removed from the wastewater.

2.2.7 Membrane-assisted methods of water purification

Membranes serve as separators and solid electrolytes in many fields of applied electrochemistry. For the treatment of polluted water the two main principles are:

- Electrodialysis, and

- Solid-Polymer-Electrolyte (SPE) applications.

2.2.7.1 Electrodialysis

The use of direct-current electricity to increase the rate of dialysis of electrolytes or to produce demineralised water from potable water has been known for about 100 years. Electrodialysis is an electrically-driven, ion-exchange membrane-separation technology that is capable of separating selected ions from aqueous mixtures and concentrating them. Electrodialysis, like evaporation or reverse osmosis, can recover pure water from a salt solution or concentrate the total dissolved solids in a waste stream. [Davis, 1990].

The electrodialysis stack consists of both anion- and cation-exchange membranes, assembled alternately and separated by a proprietary gasket-spacer that directs the flow of solution into designated chambers and distributes flow. The driving force in an electrodialysis stack is electricity, applied as direct current flowing from an anode at one end of the stack, through the stack, to the cathode at the other end of the stack. The ion-exchange membrane, the current density and the electrolyte to be processed all play important roles in the electrodialysis system. [Davis, 1990].

The direct current causes the positively charged cations to migrate toward the cathode, and the negatively charged anions to migrate towards the anode. When an ion contacts an anion-exchange membrane surface, the properties of the membrane determine whether the ion is rejected or allowed to pass through it. The ion-exchange membranes are thin-film polymers containing electrically charged functional sites. These selectively charged membrane barriers thus affect a separation. This ability of the membrane to separate ions is called permselectivity, which can be custom-designed to meet specific demands. [Davis, 1990].

The construction an operation of a large-scale ED water desalination plant has been described by Kawahara. [Kawahara, 1994].

2.2.7.2 Solid-Polymer-Electrolyte (SPE) applications

The literature describes both oxidative and reductive treatment for water purification by SPE [Grimm, 2000].

An adverse effect of using an electrochemical oxidation approach for water purification is the low ionic conductivity of many types of wastewater. For the electro-oxidation process to be effective for the removal of organic contaminants, an acid, base or salt must be added to the water to form an electrolyte. This is impractical for many purposes. Ion-exchange membranes work as solid polymer electrolytes (SPE), even in non-conductive fluids. Of special importance in the SPE process is the electro-osmotic transport through the membrane, which can be utilised, during design, to enhance the mass transfer at the electrodes and thus improve selectivity and yield. Electro-osmotic transport can increase mass transfer and must therefore be considered in the design of reactors.

The direction of the mass transport is determined by the choice of a cation- or an anion-exchange membrane. Fig. 2.6 illustrates the principle of an SPE configuration, supporting a cation-exchange membrane. The ionic flux is maintained by the protons, and the electrodialytic removal of heavy metals takes place simultaneously. When an anion-exchange membrane is used for separation, the organics are ionised at the cathode and driven through the membrane to the anode, where electrochemical oxidation takes place, as illustrated in Fig. 2.7.

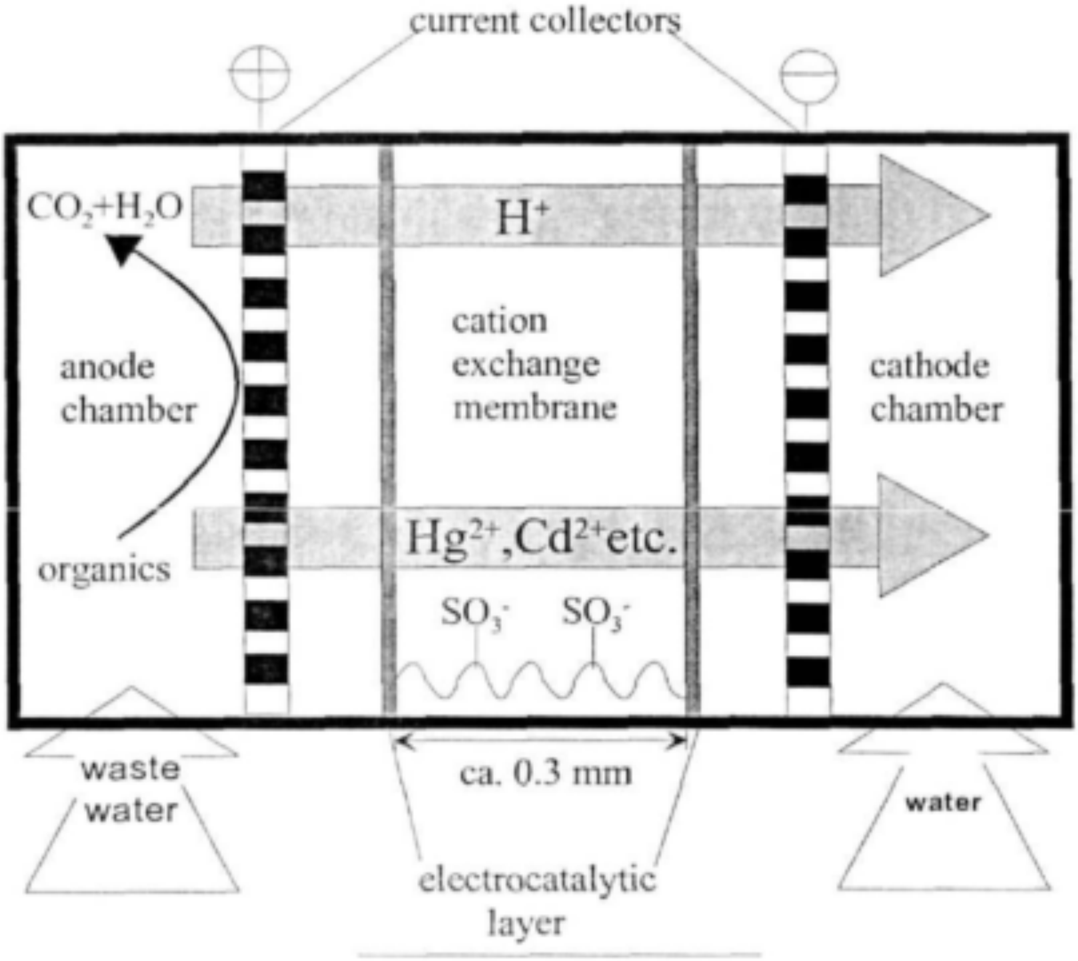

Fig 2.6: SPE configuration, supporting a cation-exchange membrane, for combustion and heavy-metal removal

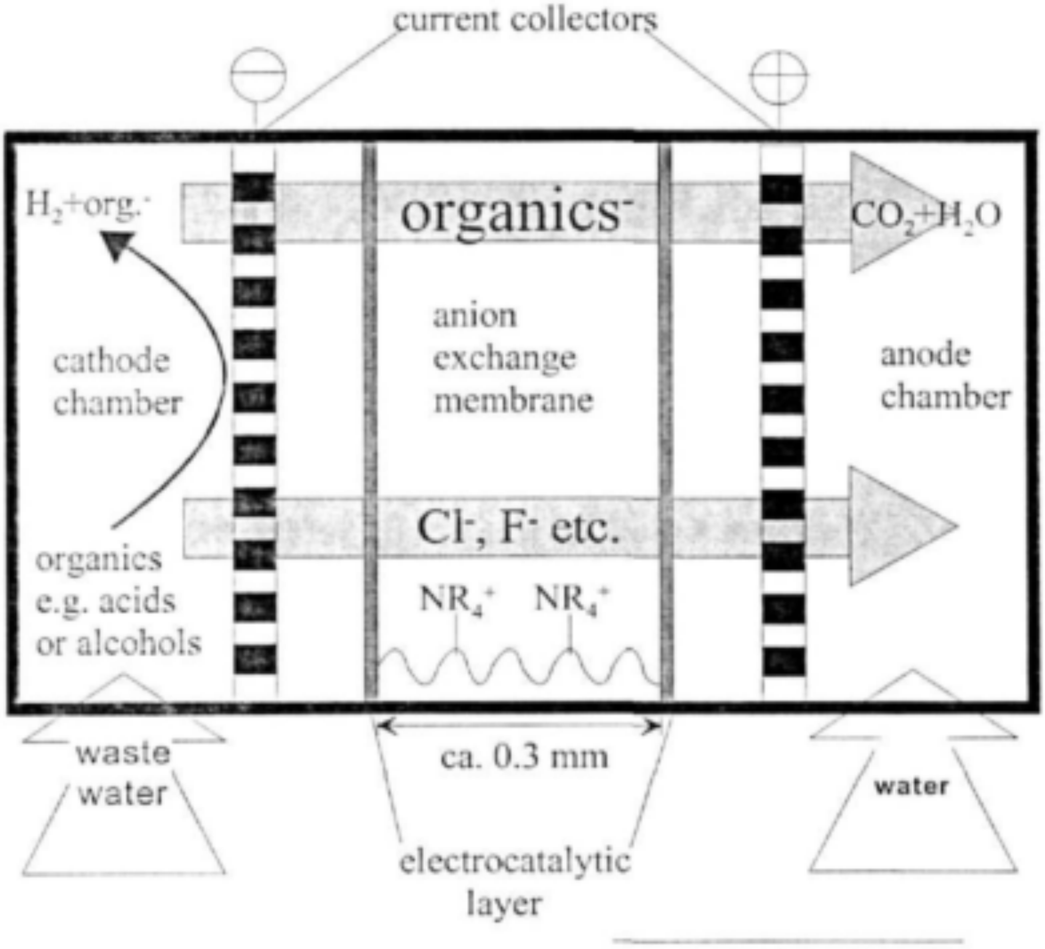

Fig 2.7: SPE configuration, supporting an anion-exchange membrane, for combustion and anion removal

3. PREPARATION AND CHARACTERISATION OF ELECTRODE MATERIALS

3.1 Introduction

Various electrode materials were prepared and studied for the electrochemical oxidation of phenol. These included: Ebonex, Ebonex/PbO_2 and Ti/SnO_2 doped with 10% Sb to yield Ti/SnO_2/Sb_2O_5. The effect of fluorine and antimony doping on the conductivity of the films was also investigated.

The new electrode materials were then characterised by: determination of the hydrophobicity index (as indicator of whether the electrode had a hydrophobic or hydrophilic surface), conductivity measurements (to determine the efficiency of the electrode in an electrochemical oxidation reaction) and surface-analysis by microprobe

3.2 Experimental

3.2.1 Tin dioxide (SnO_2) prepared by sol-gel

Stannic oxide (SnO_2) is an important oxide semiconductor [Polcaro, 1999]. It has a high oxygen overpotential and its properties are well known. Stannic oxide has a wide band gap and one of the highest mobilities of the carriers (electrons) among oxides. Its semi-conductance can be controlled by doping with antimony and/or fluorine. Besides being useful as electrode materials, tin oxide semiconductors with dopants and additives are widely used as transparent, electronically-conductive electrodes in electrochromic devices (ECD), low emitting (i.e. heat reflection) coatings and as conductance-type, gas-sensitive detectors [Granqvist, 1990]. Although various techniques can be used for their fabrication, the sol-gel route in combination with a dip-coating technique is particularly attractive because it is possible to already tailor the properties of the final oxide at the beginning or the production process i.e. in solution. Generally, the sols can be produced either directly from inorganic salt solutions or from the metal alkoxides, after which hydrolysis and polymerisation yield the gels and xerogels. Conversion of xerogels into final oxides requires removal of organic residues. This is done by heat-treatment of the xerogel films at temperatures of up to 500°C.

It is generally accepted that the alkoxide route is more appropriate for the fabrication of films. The yield of the corresponding dip-coating process is quite high and the dip-coated films exhibit high compactness and low porosity. However, the inorganic route has also been successfully used for film-preparation, although it is known that films are less homogeneous and more porous when they are deposited from the aqueous colloidal inorganic solutions [Brinker, 1990]. In the study being reported on, electrode materials were produced by both an inorganic and an organic sol-gel dip-coating routes.

3.2.2 Preparation of doped SnO_2 sol-gel layers

3.2.2.1 Preparation of doped SnO_2 sol-gel layers, via the inorganic route

The doped SnO_2 solutions were prepared according to the method described by Chaleton [1994] from two alkoxides, obtained directly from chlorides. 8.37g of $SnCl_2.2H_2O$ was dissolved in 100 ml absolute ethanol. The antimony solution was simultaneously prepared from a given amount of $SbCl_3$, dissolved in 20 ml absolute ethanol. Both mixtures were separately stirred, heated and in a closed vessel. The vessels were then opened, the solutions stirred again and then heated until the solvents had completely evaporated, to yield two powders. They were mixed together in 50 ml of absolute ethanol, in accordance with the desired doping level. For fluoride doping, triethoxyfluorosilane ($FSn(OEt)_3$) was added under a nitrogen-atmosphere. For Pt doping, Na_2PtCl_6 was added to the solution. The dope solution was finally stirred then heated to 50 °C for 2 h. The doping level (Dp_{sol} ratio = $n_i/\sum n$) in the initial antimony solution was kept constant at 5% (while the doping level for the fluoride ranged from 0-2.5%. Caution was required to accurately control the percentage of antimony introduced in the final solution used for the sol-gel dip-coating. Potential complications could stem from not knowing to what extent the dopant was correctly mixed and also if, owing to any possible time- (or temperature-) dependent reaction, partial precipitation of Sb or other dopants occured.

3.2.2.2 Preparation of SnO_2 solution via the organic route

Commercial Sn(2-ethylhexanoate)$_2$, extra pure triethanolamine (TEA) and hexanol were used without further purification. To an hexanol solution of the alkoxide (0.5M) one molar equivalent TEA was added at room temperature and the mixture stirred for 2 h. Then 20 ml of deionised water, diluted with hexanol, was added drop-wise to the solution and the mixture stirred again at room temperature for 2 h. The resultant clear solution was used for the dip-coating of films.

For the preparation of Sb-doped films, a mixture of the tin alkoxide and Sb(butanoate)$_3$, for a doping level of 5%, were used. For the Pt-modification the amount of $Na_2(PtCl_6)$ necessary to achieve a doping level of 5% was added. The procedure followed to prepare the final solution was the same as described above.

3.2.3 The dip-coating process

All substrates were pre-treated with nitric acid and rinsed with absolute ethanol prior to dip-coating. The beaker containing the sol was placed in a large glass container that was covered with a glass plate designed with a hole (Fig. 3.1). The substrate was attached to a string passing through the hole in the glass plate and connected to a vibration-free motor (Wemo). Plates of quartz glass were used as substrates for the conductivity measurements. Plates of titanium foil served as substrates for the electrodes. Before dip-coating, the atmosphere in the container was saturated with ethanol. The substrate was immersed and then pulled out of the sol, continuously, at a constant speed of 3 mm/min. Once the plate was finally removed from the solution the motor was stopped. The hanging substrate was allowed to dry for 6 h, whereafter it was dried at 100 °C for 15 min in air. This coating procedure was carried out twice, to heal cracks and defects in the film. Calcination was carried out in air by heating the substrate to 600 °C, at a rate of 1 °C/min.

After the calcination process the electrode material maintained its porous structure and was still permeable to water.

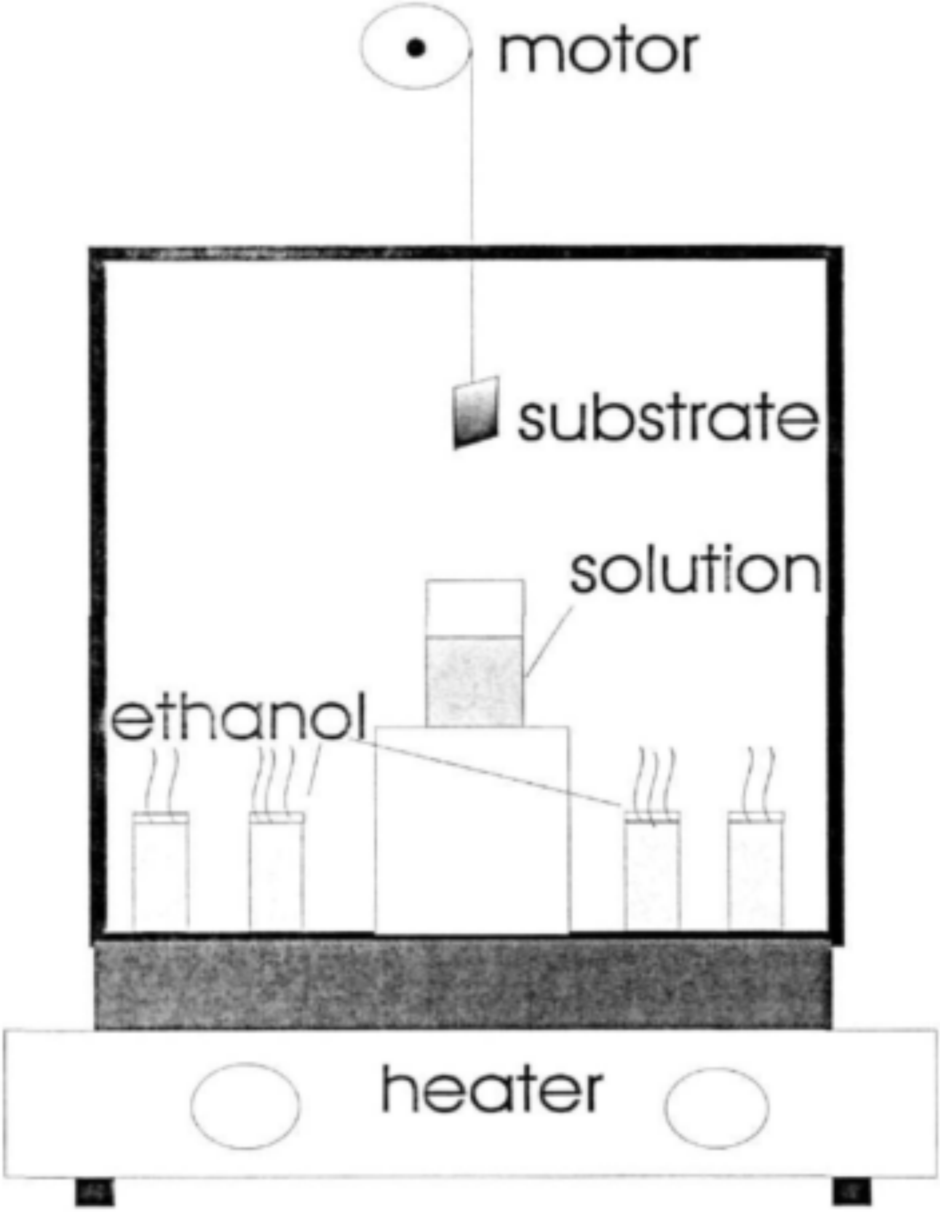

Fig 3.1: Schematic representation of dip-coating equipment, with atmospheric control, used in the dip-coating process to prepare doped SnO_2 sol-gel layers.

3.2.4 Galvanostatic deposition of PbO_2

Plates of Ebonex were coated anodically for 30 min with PbO_2 in an acid solution of $Pb(NO_3)_2$ (c.d. = 10 mA cm^{-1}, electrolyte: 0.4 mol l^{-1} $Pb(NO_3)_2$ [Trassati, 1980].

3.2.5 Determination of the hydrophobicity index

The hydrophobicity index is defined as the ratio of adsorbed n-octane over adsorbed water. A HI>1 indicates a hydrophobic surface and a HI<1 an hydrophilic surface. Determination of the modified hydrophobicity index is a simple method by which to estimate the surface polarity. It is based on the competitive adsorption of n-octane and water from the gas phase [Grimm, 2000]. The surface polarity (hydrophobicity) of the bulk materials were measured by competitive adsorption [Weitkamp, 1992] with especially built equipment [Klein, 1996]. Surface areas of the powdered materials were measured by adsorption isotherms in liquid Ar.

Ideally, electrodes should not be too hydrophobic or hydrophilic. Electrodes should 'like' the organic molecules to be oxidised. They should tend to adsorb the reaction intermediates to the electrode surface, to ensure the maximum number of oxidation steps before releasing the product back into the solution. Electrode reactions involving adsorbed species have been discussed in the Appendix.

3.2.5.1 Experimental set-up for measurement of the hydrophobicity index

Hydrophobicity measurements were conducted on products obtained from the inorganic sol-gel synthetic route. Two samples were doped with antimony (doping level of 5%). The second sample was additionally doped with 5% fluorine. The hydrophobicity measurements were carried out to determine if the fluorine doping had an effect on the surface polarity of the powders, as this would be expected to enhance adsorption of organics on the surface of the electrodes.

Surface polarity measurements were carried out at the Max-Planck-Instiut für Kohlenforschung at Mülheim, Germany. A weighed sample was placed in a protective gas stream and heated to 300 °C for desorption and the removal of impurities. After cooling to 30 °C, the sample was exposed to a stream of argon, containing defined and similar concentrations of water and octane. The water and octane contents of the gas streams are dependent on the flow-rate of the argon passing through the particle-packed vessel. Accurate control of the flow-rate was crucial for correct measurements The final ratio of the single components (water and octane) was determined by gas chromatography (GC).

A schematic representation of the assembly of the apparatus used to determine surface polarity has been presented by Grimm [Grimm, 2000].

3.2.5.2 Procedure

A known mass of a solid sample, normally a powder, was placed in the reactor, which was then closed by screwing on the lid. A moderate high temperature-resistant copper paste was used on the threads to assist subsequent dismantlings. The reactor was installed into the metal heating block and secured by a clip-lock (Swagelok) fitting. To obtain a powdered sample, part of the sol-gel solution was allowed to dry without a dip-coating step involved. Thereafter, the sample was placed into the furnace and underwent the same temperature programme as the electrodes for calcination, as described in section 3.2.3. The surface polarity of the powdered material was thus identical to that of the coated films.

To desorb any contaminants on the sample, it was purged with an argon stream at 400 °C for 12 hours. After that the temperature was set to 35 °C, while the argon flow was continued. A heating band was wrapped around the capillary wires. The GC was set to a temperature of 50 °C and the main valve to the helium flask opened. After confirmation of the helium stream (approximately 5 min) the TCD could be switched on. Subsequently, the weighed saturation bubblers were inserted in the line, containing water and octane respectively. The saturation bath was kept at 25 °C and the argon valve opened. After switching on the flow controllers the argon began flowing through the saturation flasks. This was recorded as the starting time of the measurement. To avoid high pressure in the saturation section, provision had to be made for outlet of the gas through the bypass. After cooling the reactor to 30 °C, the recording of measurements could commence.

First, the background water-peak value in the chromatogram (of the argon that purged the reactor) had to be determined. This was done by simultaneously pressing the start button of the integrator and opening the 6-way valve for 8 seconds. In subsequent calculations, the obtained value was subtracted from the water peak. After turning the valves (1) and (2) (saturation flow from the bypass through the reactor and argon through the saturation section, respectively), the initial chromatogram at t=0 was recorded. The same procedure was repeated every 3.5 min, until saturation of the sample with water and octanol was achieved. The reactor was heated to 323 K to avoid condensation. Quantitative calculation of the process curve was done with the numerical calculation programme TABLECURVE 3.0 (Jandelscientific).

3.2.6 Determination of conductivity measurements

Conductivity measurements were carried out on SnO_2 films deposited on quartz plates, using the four-probe method across the surface. Pt foil was used for contact. The antimony content was kept constant at 10%. The flouride content was 2,5% while the Pt content reached 5%.

3.2.7 Surface analysis by microprobe

The surface of the anode was investigated by X-ray spectroscopy at the National Accelerator Centre. The X–rays were activated by a proton beam. The XPS analyses were carried out at the Institut für Physicalische und Elektrochemie at the Heinrich-Heine-Universität, Dusseldorf.

An electrode with a doping level (Dp_{sol} ratio = $n_i/\Sigma n$) of 10% Sb was investigated by microprobe analysis. A sample was bombarded by protons and the resulting X-ray spectra analysed.

3.2.8 XPS Spectroscopy

The ionisation energies of electrons in compounds can be measured by photoelectron spectroscopy. From the results, a picture of the energies of the orbitals are obtained. X-ray photoelectron spectroscopy (XPS) provides the photons with enough energy to knock out the core electrons. The energy of the core shells is to a large degree independent of the chemical environment of the atom. Consequently, the resulting absorption lines are characteristic for distinct elements in a film, molecule or alloy. Elementary analysis of films is thus possible.

The value of the absorbing energy can furthermore help to determine the oxidation state of the analysed element. This is why this method is also often referred to as ESCA (electron spectroscopy for chemical analysis).

ESCA is limited to investigations of surfaces because, while only the X-rays can penetrate thicker samples, the resulting expelled electrons can only pass a few nanometers through a compact sample.

3.3 Results and Discussion

3.3.1 Hydrophobicity measurements

An increase in the hydrophobicity index (HI) of the Sb-doped SnO_2 material from 0.70 to 0.79 was observed upon addition of 2,5 % fluorine-containing alkoxide.

The surface areas of the powdered materials were between 100 and $120 m^2/g$, with a broad pore size distribution around a pore diameter of 0,80 nm.

3.3.2 Conductivity measurements

The tems used in this section are explained as follows:

- Resistance and resistivity is used interchangeably.

- The specific resitance of a membrane is the resistance of a membrane multiplied by the area of the membrane, divided by the thickness is the membrane.

Increased conductivity results in a decrease in resistance.

The specific resistances of the films were calculated, with the assumption that one layer of the film, after each calcination, had a thickness of 100 nm. This film thickness is based on AFM investigations of the films (film edge height) and a gravimetric measurement, carried out at the MPI-Mülheim, Germany. The specific resistance of the fluoride films was 0,0048 ohm cm.

In Figures 3.2 and 3.3 the effects of various dopants on the resistances of SnO_2 films are plotted against the number of sequential dip-coatings (calcinations). The dopants were: SnSb: 10% Sb; SnSbPt: 10% Sb, 5% Pt; SnSbF: 10% Sb, 2.5% F. (The index 'in' stands for the inorganic route, 'org' for the organic route.)

A change in the resistance (conductivity) was observed when the fluoride was added as a dopant, while the addition of Pt did not seem to influence the conductivity of the films.

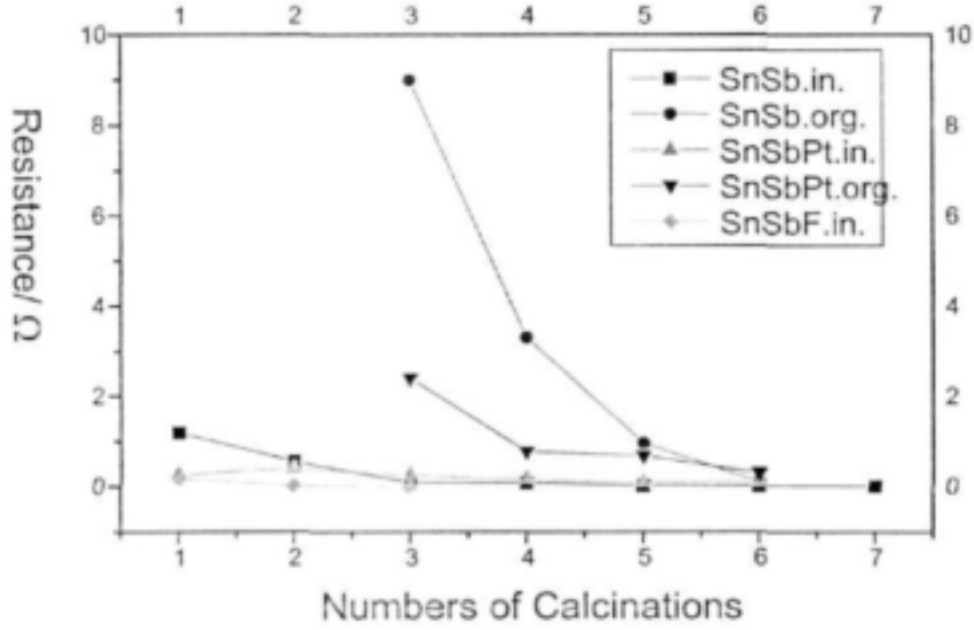

Fig 3.2: The effect of the various dopants on the resisances of the SnO_2 films, plotted against the number of calcinations: SnSb: 10% Sb; SnSbPt: 10% Sb, 5% Pt; SnSbF: 10% Sb, 2.5% F.

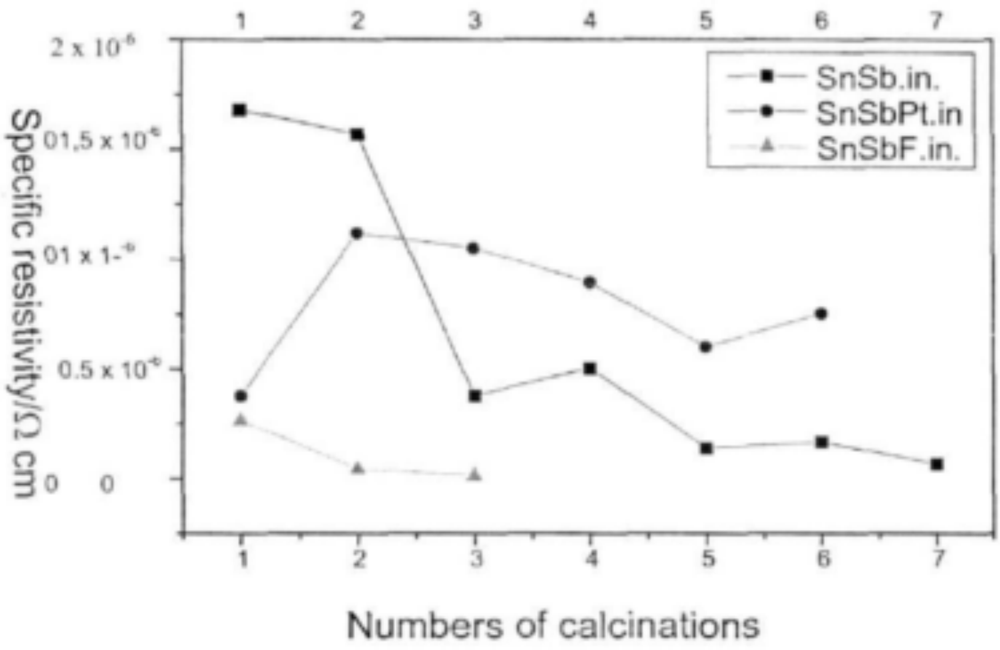

Fig 3.3: The effect of the various dopants on the resistances of the SnO_2-films, plotted against the number of calcinations: SnSb: 10% Sb; SnSbPt: 10% Sb, 5% Pt; SnSbF: 10% Sb, 2.5% F.

The incorporation of fluoride into the SnO_2 film decreased the resistance (improved the conductivity), by reducing the band-gap between the valence and the conducting band of the oxide. The specific resistance of the fluoride films (0.0048 Ohm cm) is in the range of metallic conductivity. The results of the first two calcination steps were omitted, because their resistances were 'out of range' (they could not be displayed on the multimeter). The incorporation of Pt into the matrix resulted in only a slight decrease in the resistance (slight increase in conductivity). Although the specific resistances should remain constant over time, a slight shift to lower values with increasing numbers of calcinations was observed. This indicated that the films became increasingly dense during calcination. Conductivity values for the undoped SnO_2 could also not be obtained as the resistances were out of range.

From the three curves it was obvious that after three calcinations (which are necessary for good densification) results obtained for the experiments with platinum were the poorest. Results obtained with the Sn/Sb membranes were much better. There was however a major improvement when fluorine was included in the structure (this was, however, not the original idea - fluorine was added to add hydrophobicity in order to create better adsorption of organics to the reactive catalytic surface).

3.3.3 Surface analysis of the Ti/SnO_2/Sb_2O_5 by microprobe

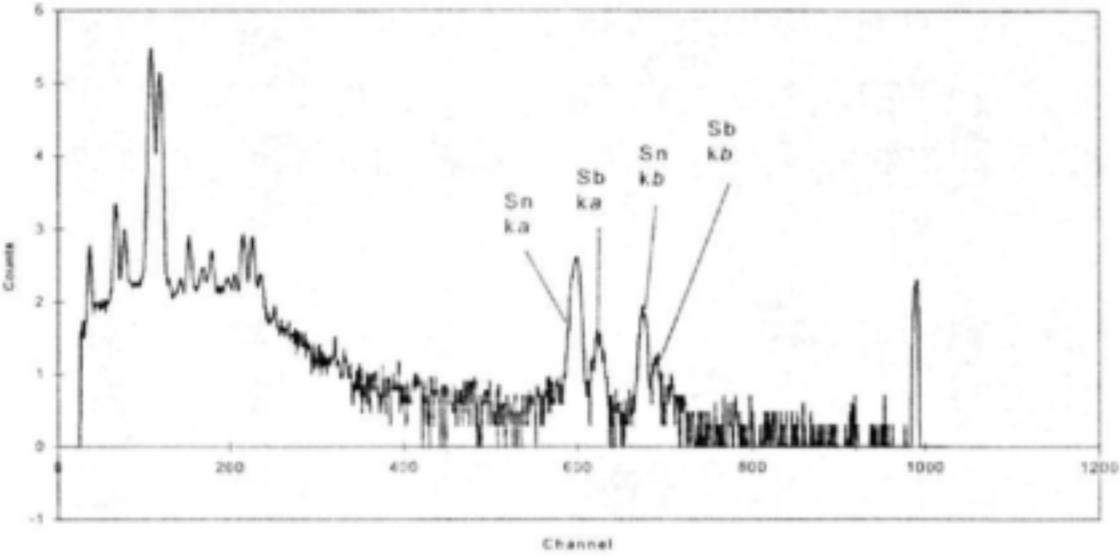

Fig 3.4: X-ray spectrum of surface of Ti/SnO_2/Sb_2O_5, showing Sn and Sb peaks.

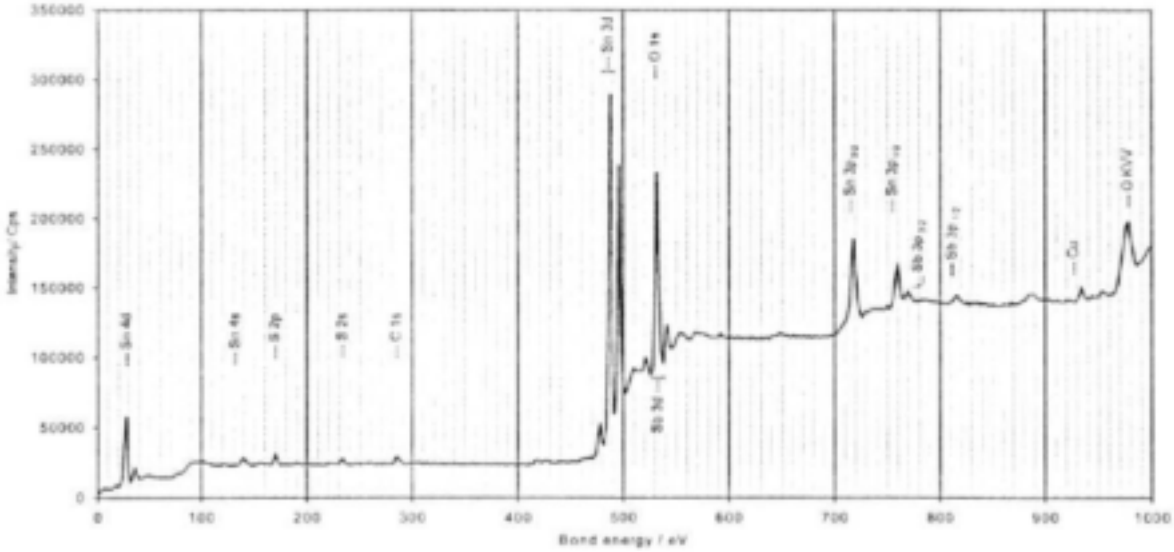

Fig 3.5: XPS-spectrum of the Ti/SnO_2/Sb_2O_5 electrode, prepared by the inorganic route

The surface of the electrode with a doping level (Dp_{sol} ratio = $n_i/\sum n$) of 10% Sb was investigated by microprobe analysis. A sample was bombarded by protons and the resulting X-ray spectra analysed. The X-ray spectrum of the surface of $Ti/SnO_2/Sb_2O_5$ is shown in Fig. 3.4. The ratio of Sn/Sb, calculated by integration methods, ranged from 9.9-12.8% for the Sb content, thus confirming that the dopant had been well mixed in the sol, without detectable precipitation taking place. Unfortunately, no information on the oxidation states of the elements could be obtained by this analytical method.

3.3.4 Analysis by XPS spectroscopy

To confirm the results from the microprobe analysis, further surface analysis was undertaken with XPS. Additional information on the oxidation states of the coatings was obtained. The entire spectrum of the $Ti/SnO_2/Sb_2O_5$ electrode prepared by the inorganic route is shown in Fig. 3.5.

The catalytic layer of the electrode material was investigated and information on the distribution of the elements and the oxidation state of the elements was obtained. Determination of the antimony was not straightforward as its signal appears at the same binding energy as that of the oxygen peak. The peak at 532 eV had to be separated into an oxygen peak and an antimony peak. Here this was done by making use of the relation between the pre-wave (Sb $3d_{5/2}$) at 532 eV and the wave at 541 eV (Sb $3d_{3/2}$) for antimony was fixed at 1.44. This precondition was used for the fit in Fig. 3.6.

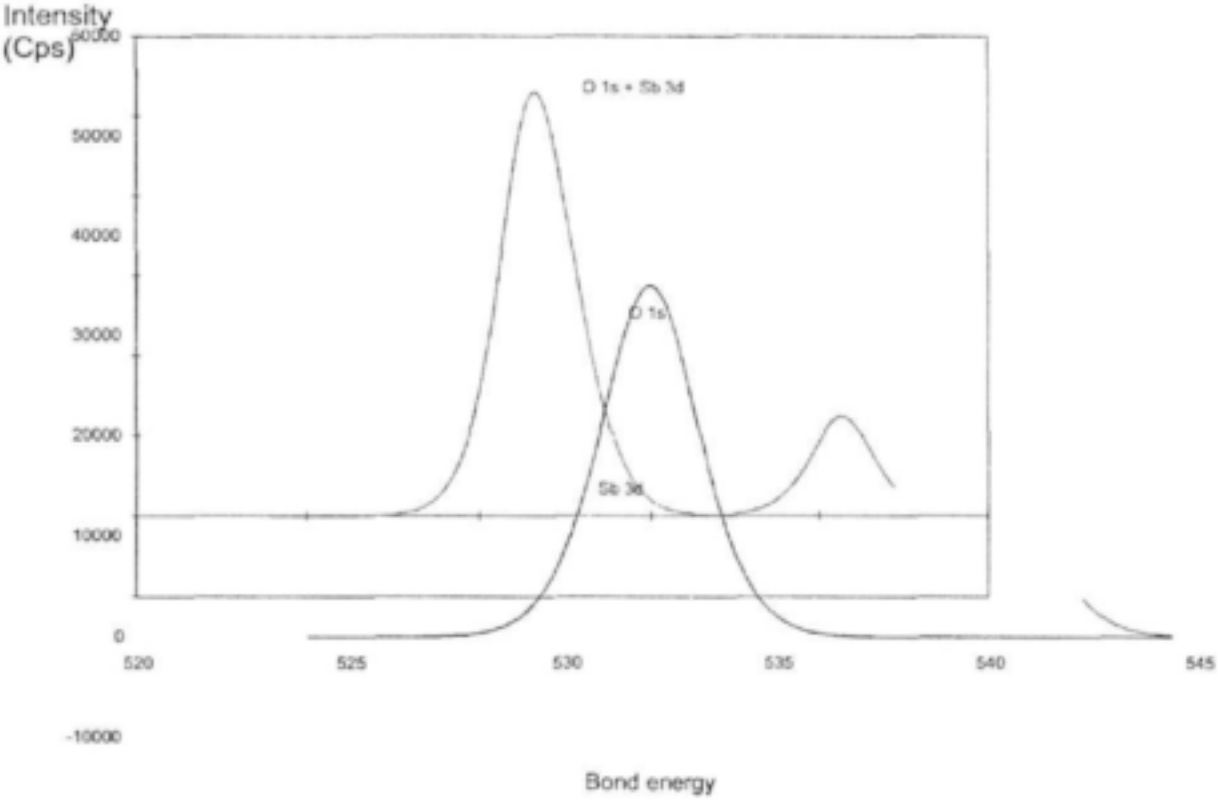

Fig 3.6: Curve fitting for the separation of the oxygen and the antimony peaks

The real areas of the peaks had to be calibrated according to the sensitivity of the instrumentation towards the particular elements. The atomic ratio between Sn and Sb was found to be 4:1. Since the doping level (Dp_{sol} ratio = $n_i/\sum n$) of Sb in the initial solution was 10%, part of the Sn must have precipitated out of the solution prior to the process of dip-coating. The shift in the binding energy of the elements determined the oxidation number. Sn was found to have the oxidation number 4, while the shift for Sb indicated an oxidation number of 5, corresponding to the oxides SnO_2 and Sb_2O_5. The fact that traces of sulphur and copper were detected on the surface is explained by the treatment of the samples prior to before the XPS-analysis. The samples and sample-holders (Cu) were purified with 2 M H_2SO_4. Obviously, despite attempt made to remove them in an ultrasonic bath, small amounts of S and Cu had remained on the surface.

The samples prepared via the organic sol-gel route revealed a high Ti peak, obviously arising from the titanium foil-based substrate (Fig 3.7). This indicated defects in the film as the substrate was not completely coated. (This "inefficient" coating would contribute to the poor catalytic performance of this electrode material.)

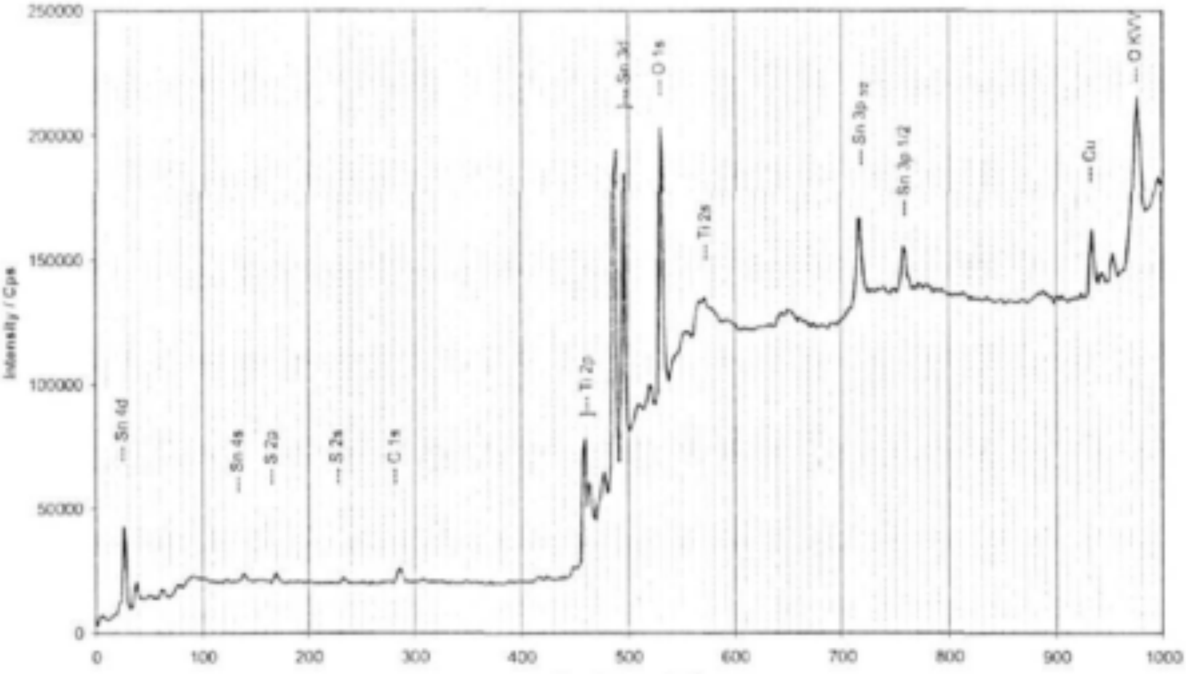

Fig 3.7: XPS spectrum of the Ti/SnO_2 electrode, prepared by the organic route

4 DETERMINATION OF THE CATALYTIC ACTIVITY OF THE NEW ELECTRODE MATERIALS TOWARDS PHENOL, BY CYCLIC VOLTAMMETRY

4.1 Introduction

The electrochemical oxidation of aqueous solutions of phenol was studied, using different electrode materials (Ebonex, Ebonex/PbO_2, Ti/SnO_2 and Sb-doped Ti/SnO_2). Cyclic voltammetry was used to investigate the catalytic activity of the electrode materials. Best results were obtained with Sb-doped SnO_2 films on titanium foil, prepared by the sol-gel dip-coating technique. Cyclic voltammograms revealed a high overpotential for oxygen evolution, resulting in a well-separated peak for the oxidation of phenol. Improvements in the conductivities of the films and higher current densities for the oxidation were obtained by doping the film in a sol-gel solution with 5% Sb. Doping with fluoride increased the conductivity and hydrophobicity, but decreased the oxidation peaks. Upon the addition of phenol to the electrolyte, however, the electrodes did not show a separated oxidation peak. The oxidation peak was partially hidden by oxygen evolution. The electrochemical characteristics of the electrode material Ebonex were not significantly changed by the addition of phenol to the electrolyte.

4.2 Cyclic voltammetry

Electrochemical techniques in which a potential (E) is imposed upon an electrochemical cell and the resulting current (i) is measured are categorised as voltammetric methods. Generally speaking, voltammetry is very useful for analysing dilute solutions both qualitatively and quantitatively for inorganic, organic and biological components, measuring thermodynamic parameters for metal-ion complexes and oxidation-reduction systems and studying the kinetics of chemical reactions. Cyclic voltammetry (CV) is a versatile electro-analytical technique for the study of electroactive species. The effectiveness of CV results from its capability for rapidly observing redox behaviour over a wide potential range.

CV entails of cycling of the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of this working electrode is controlled, relative to a reference electrode such as a SCE or Ag/AgCl electrode. The controlling potential that is applied across these two electrodes can be considered as an excitation signal. The excitation signal for CV is a linear potential scan with a triangular waveform. The triangular potential excitation signal sweeps the potential of the electrode between two values (called the switching potentials) at a certain scan rate. Single or multiple cycles can be used.

For the choice of the reference system, compatibility with the various components in the solution is crucial. In this study, either a mercury sulphate electrode ($Hg/HgSO_4/K_2SO_4$) or Reversible Hydrogen Electrode (RHE) was used.

With cyclic voltammetry it is possible too investigate complex chemistry and to distinguish between similar mechanisms. The form of a cyclic voltammogram will depend on the value of the rate k constant for the following reaction and the potential scan rate v.

According to Pletcher (1991, section 6.8), for a very simple system involving an electrochemical process:

$$R - e^- \leftrightarrow O$$

$$O \xrightarrow{k} P$$

4.1.2 Cyclic voltammograms

Cyclic voltammetry is a very popular technique with which to study the mechanism and kinetics of coupled homogeneous chemical reactions (see also the Appendix). It is particularly useful for initial studies of a new system. The data is presented in the form of a cyclic voltammogram, which allows rapid qualitative interpretation without recourse to calculate data. The insight gained from one experiment may immediately be used in the design of the next.

A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered as the response signal to the potential excitation signal. The voltammogram is a display of current (vertical axis) versus potential (horizontal axis).

Prior to measurement the electrode is scanned between the oxygen and hydrogen potential until the cyclic voltammogram remains unchanged. The activity of a catalytic film towards combustion is indicated by the appearance of an additional peak or increase in the current in the anodic range after the addition of phenol to the electrolyte. The theory behind this is discussed in more detail in the Appendix.

At slow scan rates: at each potential, the current density will be higher in the presence of the chemical process and the peak will appear at less positive potentials. Where the scan rates lead to changes in both peak current density and the peak potential, it is generally indicative of the reaction having intermediate state, i.e. oxidation taking place in more than one single step, which is what one expects from the combustion of phenol.

The cyclic voltammagrams in this oxidative process are irreversible. Their shapes are dependent on the potential scan rates, concentrations of ingredients and certain other parameters. They are not repeatable, as a second scan on the irreversible system will be different to the first scan. The deviation on the scans when a reagent is added, which can be oxidized, gives information as to the amount of the oxidation and the nature of the interaction. It can be seen when the reagent is strongly absorbed to the electrode or when oxygen is strongly absorbed to the electrode [Pletcher, 1991].

The activity of a catalytic film towards combustion is indiated by the appearance of an additional peak or an increase in the curent in the anodic range after the addition of phenol to the electrolyte.

A very brief explanation of a cyclic voltammogram is given here, using Fig. 4.8 as an example. In this particular cyclic voltammagram the sharp peak indicates a strongly absorbed reagent, i.e. phenol, and its oxidation on the forward sweep, but no reduction on the return sweep, indicating that it is irreversibly destroyed. The overpotential for oxygen pollution occurs at a slightly higher potential, which is the slight peak at the end of the cyclic voltammagram.

4.2 Experimental

All electrochemical measurements were carried out with a Solartron SI 1280B electrochemical measurement unit with a three-electrode cell. The reference electrode was based on a $Hg/HgSO_4/K_2SO_4$ (sat.) system. The electrolyte consisted either of 1M H_2SO_4 or 1M H_2SO_4 + 5 mM phenol (standard contaminant). The solution temperature was maintained at 25 °C. Prior to any measurements being made, nitrogen was bubbled through the electrolyte and the electrode was scanned between the oxygen and hydrogen potential until the cyclic voltammogram remained unchanged. The activity of a catalytic film towards combustion is indicated by the appearance of an additional peak in the CV or an increase in the current in the anodic range after the addition of phenol to the electrolyte.

4.3 Results of determinations of electrocatalytic oxidation

4.3.1 Cyclic voltammograms of pure Ebonex

The cyclovoltammic scans of Ebonex were carried out in 1 M sulfuric acid and 1 M sulfuric acid plus 5 mM phenol. Results are shown in Figures 4.1 and 4.2, respectively. The activity of the catalytic film towards combustion is indicated by the appearance of an additional peak, or increase in the current in the anodic range, after the addition of phenol to the electrolyte. The hydrogen adsorption and desorption can be attributed to the respective peaks between -0.5 V (NHE) and +0.7 V (NHE). The hydrogen and oxygen evolution reactions are shifted to high overpotentials. The hydrogen evolution starts at 0.650 V (NHE), whereas the oxygen evolution begins at 2.7 V (NHE). The addition of phenol to the electrolyte of sulfuric acid does not have a great impact on the shape of the cyclic voltammograms of Ebonex. A slight increase in the anodic current density was observed and this was attributed to the oxidation of phenol, although Ebonex is reported in the literature to be electrocatalytically inactive [Park, 1995]. Ebonex favourably adsorbed the oxygen.

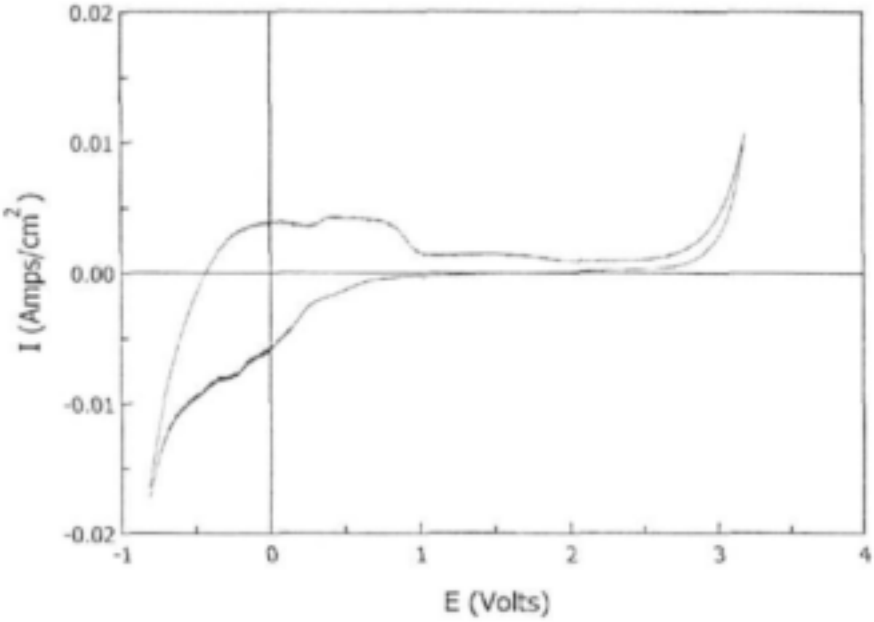

Fig 4.1: Cyclic voltammogram of pure Ebonex, V = 20 mV/sec, Electrolyte: 1 M H_2SO_4, plotted versus NHE

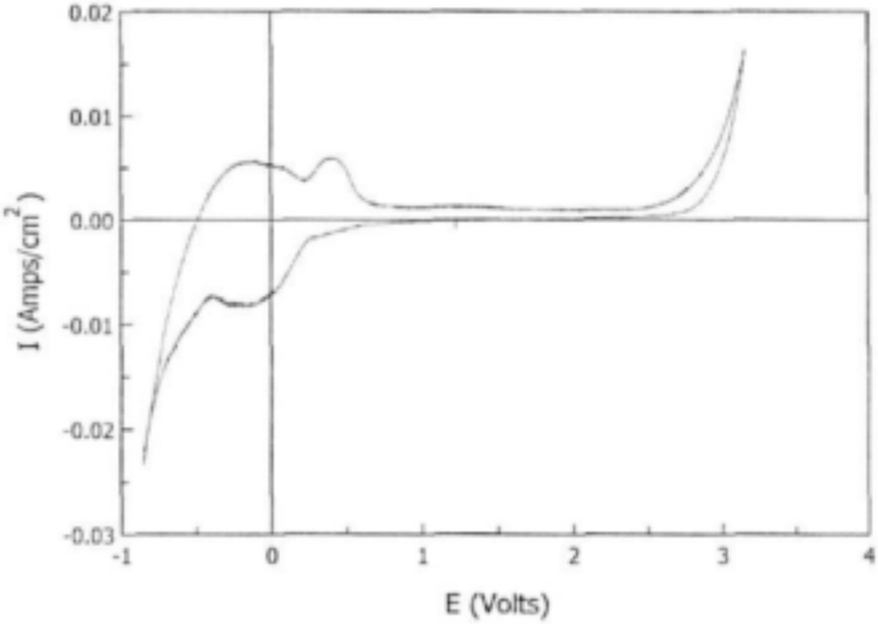

Fig 4.2: Cyclic voltammogram of pure Ebonex V = 20 mV/sec, Electrolyte: 1 M H_2SO_4 + 5 mM phenol, plotted versus NHE.

That small hump (at about 0,5 eV) indicated the oxidative conversion of phenol, although it was not not very efficient. There was strong oxygen absorption onto the Ebonex.

4.3.2 Cyclic voltammograms of Ebonex® coated with PbO_2

After coating the Ebonex® with PbO_2 the CV completely changed. The PbO_2 only seemed to be stable towards reduction at potentials above 1.5 V versus NHE. Below that, potential reduction peaks were observed and these shifted to lower voltages with an increasing numbers of scans, as seen in Fig. 4.3.

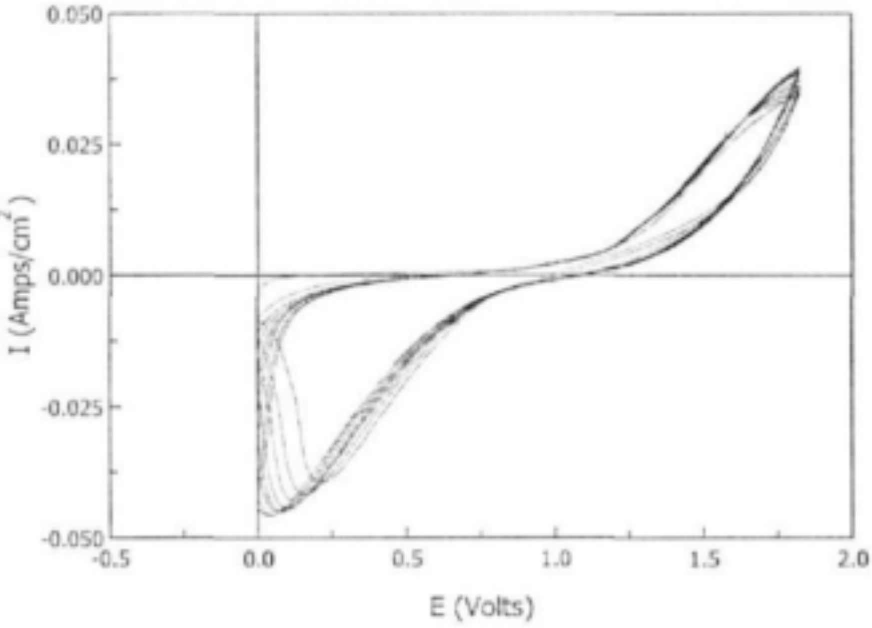

Fig 4.3: Ebonex® electrode, coated with PbO_2. Electrolyte: 1 M H_2SO_4 v = 20 mV/s, 10 scans

Fig. 4.4 shows that after the addition of 5 mM phenol to the electrolyte there appeared no additional, clearly separated oxidation peaks, but there was a significant increase in the anodic current in the range of 1.2 V-1.5 V, indicating the destruction of phenol. The anodic current was partially obscured by the oxygen evolution peak, which meant that at the potential of the combustion, oxygen evolution had also taken place. As the concentration of phenol decreased with each scan so the anodic current also decreased.

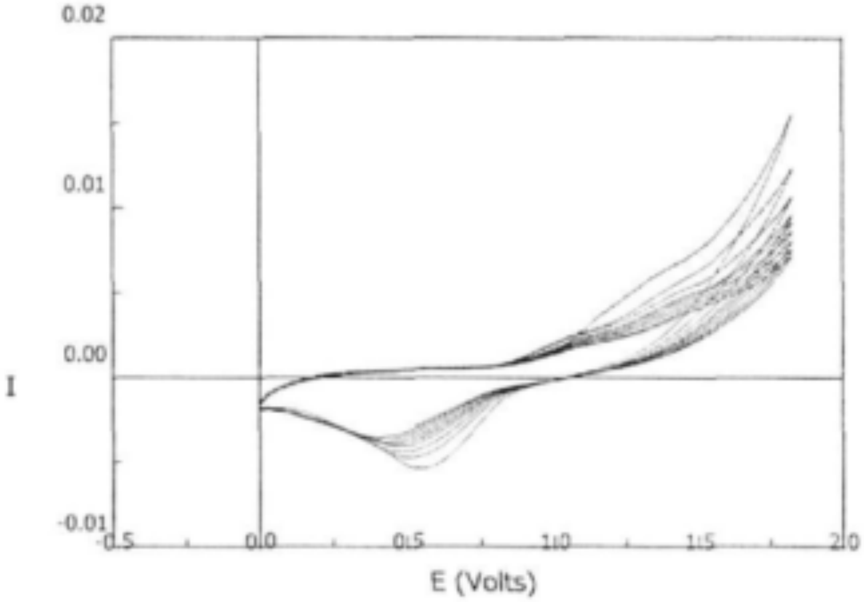

Fig 4.4: Ebonex electrode®, coated with PbO_2. Electrolyte: 1 M H_2SO_4 + 5 mM Phenol, v = 20 mV/s, 10 scans

With the PbO_2 coating on the Ebonex there was a widening of a broad peak at a potential of 1.2 to 1.6 volts, which indicates absorption of the phenol to the electrode and subsequent oxidation.

4.3.3 Cyclic voltammograms of titanium coated with SnO_2

Without the addition of any dopants to the sol-gel solution the Ti electrode did not show any catalytic activity for the oxidation reaction, as illustrated by the comparison between Figures 4.5 and 4.6. The addition of phenol to the electrolyte did not change the shapes of the cyclic voltammograms. Both voltammograms remained featureless - there was no indication of combustion. The peak for the oxygen-evolution reaction appeared at a high overpotential of 2.3 V (NHE).

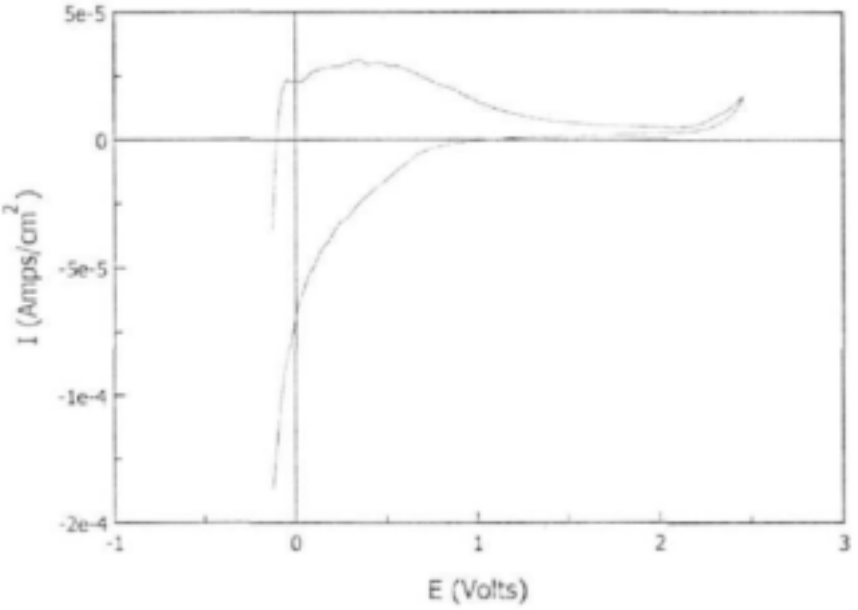

Fig 4.5: Ti coated with pure SnO_2. Electrolyte: 1 M H_2SO_4, v = 20 mV/sec

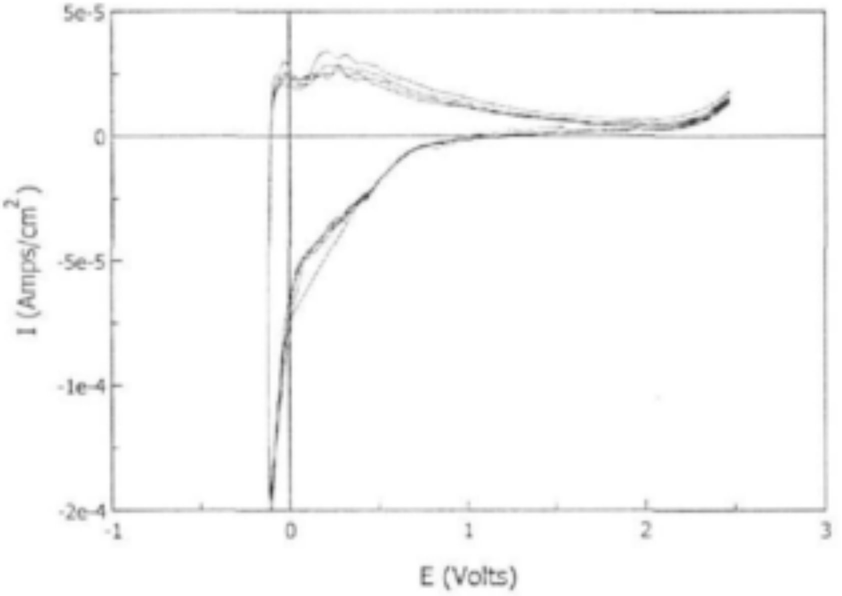

Fig 4.6: Ti coated with pure SnO_2. Electrolyte: 1 M H_2SO_4 + 5 mM phenol, v = 20 mV/sec

In contrast to this, the doping with Sb resulted in a new combustion peak after the addition of phenol to the electrolyte. This can be seen in Figures 4.7 and 4.8. Fig 4.7 shows the cyclic voltammogram in 1 M H_2SO_4. In Fig 4.8 after the addition of phenol, a new combustion peak appears. The peak was well separated, and thus at its maximum of 1.5 V (NHE) it could be assumed that combustion took place, without any side reactions. The oxygen evolution takes place at a high overpotential of 2,2V vs NHE.

By doping the sol-gel solution with fluoride, additionally, the shape of the CV remained the same but the combustion peak reached a current density lower than that obtained after Sb-doping only. After the addition of 10% fluoride the peak totally disappeared. The peak current for pure Sb-doping was 1 mA cm^{-1}, 0.81 mA cm^{-1} for 2.5 % F^- and 0.14 mA cm^{-1} for 5% F^-. Although the doping with fluoride improved the conductivity of the film it seemed to lower the electrode's capacity for combustion.

Similar experiments with PbO_2-coated Ebonex® did not result in a separated combustion peak. There was still a high overpotential for the oxygen evolution, but upon the addition of phenol an increase of the anodic current density was observed.

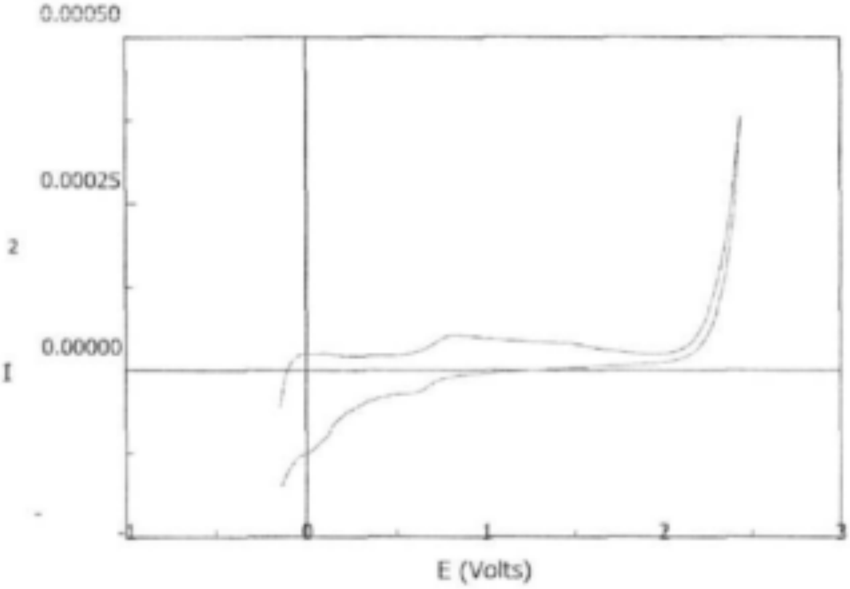

Fig 4.7: Ti coated with SnO_2 + 10% Sb-content ($Ti/SnO_2/Sb_2O_5$,). Electrolyte: 1 M H_2SO_4, v = 20 mV/sec

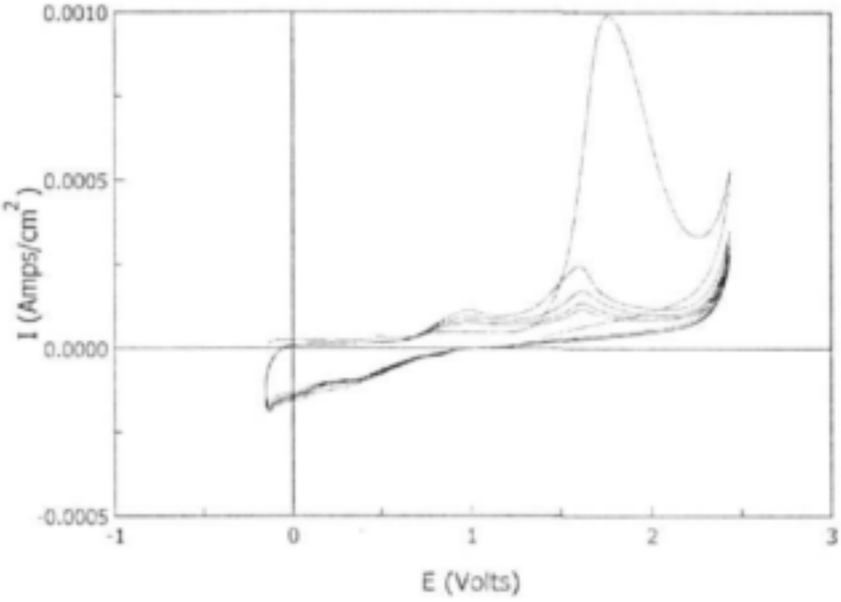

Fig 4.8: Ti coated with SnO_2 + 10% Sb-content ($Ti/SnO_2/Sb_2O_5$). Electrolyte: 1 M H_2SO_4 + 5 mM phenol, v = 20 mV/sec

The beneficial effect of Sb-doping can be attributed to the incorporation of an element with a higher oxidation number (Sb^5) into the film, to create electron vacancies in the lattice that make the electron transfer from the organic pollutant to the electrode for the oxidation easier. In addition, the introduction of Sb_2O_5 results in a higher oxide present in the film. The electrochemical conversion pathway is consequently suppressed, as the chemisorptions of oxygen (MO_{x+1}) into the lattice is less likely to occur.

4.4 Further characterisation of the $Ti/SnO_2/Sb_2O_5$ material by kinetic measurements with the redox couple $K_4[Fe(CN)_6]/K_2[Fe(CN)_6]$

Cyclic voltammetry on the redox couple $K_4[Fe(CN)_6]/K_2[Fe(CN)_6]$ was carried out at different scan rates. This was done to further characterise the $Ti/SnO_2/Sb_2O_5$ material. It is especially the value of the peak current that gives an indication of the electron transfer rate on the electrode's surface. Moreover, the diffusion coefficient of the active species in the electrolyte can be calculated and compared to results from the literature. The electrolyte consisted of 10 mM of each ferri- and ferro-cyanide. The supporting electrolyte was 0.1 M H_2SO_4. The scan rates ranged from 1–100 mV (1, 5, 10, 50 and 100 mV/s). Fig. 4.9 shows all the cyclic voltammograms combined in one plot, at different scan rates.

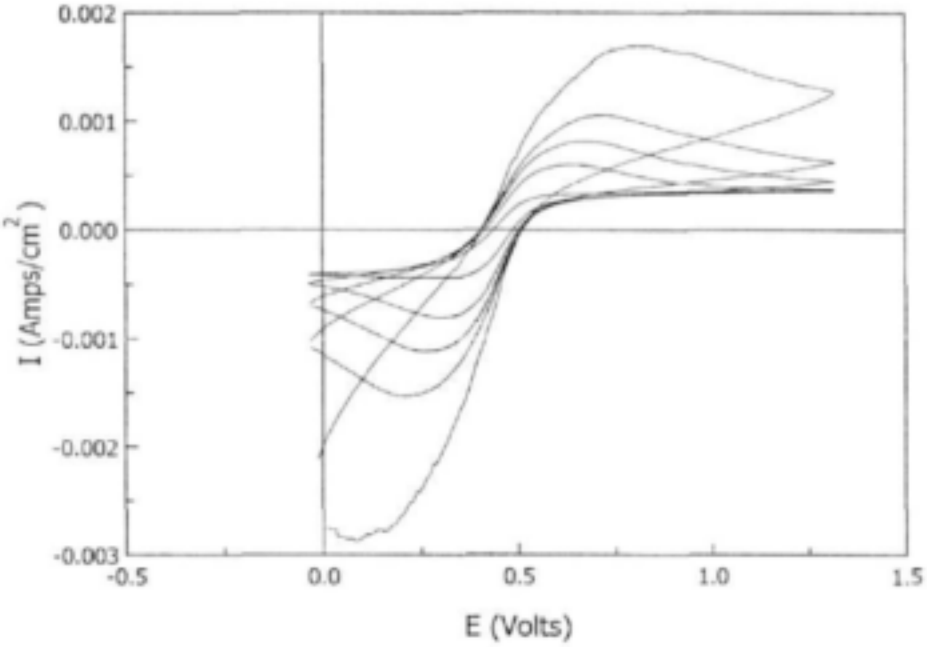

Fig 4.10: Cyclic voltammograms the Ti/SnO_2/Sb_2O_5, with different scan rates (1, 5, 10, 20, 50, 100 mV/s). Electrolyte: 10 mM $K_4[Fe(CN)_6]$, 10 mM $K_2[Fe(CN)_6]$.

Table 4.1 presents an overview of the resulting peak currents and shift in peak potentials.

Table 4.1: Peak current and shifts in peak potentials for different scan rates.

Scan rate (mv/sec)	Square root of scan rate $v^{½}$ (Vs^{-1})	Peak current I_p (mA/cm^2)	Shifts in peak Potential E (volts)
1		0.357	0.013
5		0.600	0.032
10		0.817	0.061
20		1.057	0.111
50		1.406	0.136
100		1.701	0.232

Fig. 4.11 is a plot of the square route of the scan rate versus the peak potential to confirm the linearity between $v^{1/2}$ and I_P.

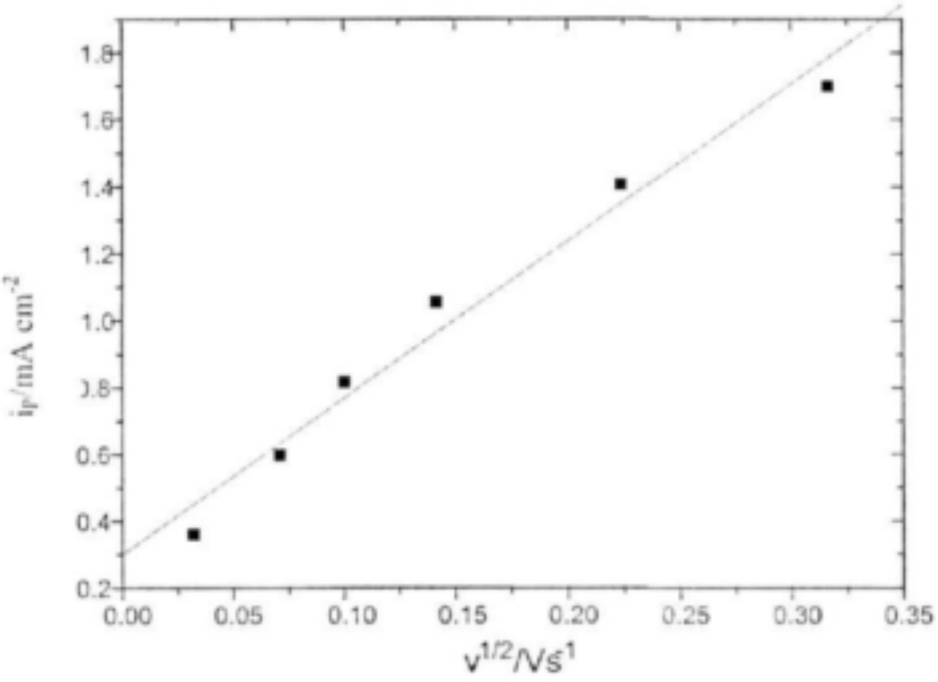

Fig 4.11: Plot of the square root of the scan rate ($v^{1/2}$) versus the peak current i_P

This proves the linearity of the square root of the scan rate ($v^{½}$) vs peak current density (I_p)

The peak currents i_P from Table 4.1 are rather low, which indicates problems with the charge transfer on the electrode's surface. This is possibly due to oxidation reactions that the electrode material is subjected to at high potentials. The linearity between $v^{1/2}$ and i_P has been predicted for a simple reaction and is clearly seen in Fig. 4.11. The linear regression resulted in a standard error coefficient of r = 0.98815. As the potential changes with the scan rate, the reaction is inhibited on the surface of the electrode. From the slope of the plot in Fig. 4.11 a diffusion coefficient of $D = 4.9 \times 10^{-9}$ m^2 s^{-1} for phenol was obtained. This value is close to the value reported in literature (1.178×10^{-9}) [Hamed, 1951].

4.5 Conclusions

Several different electrode materials were prepared and tested for their catalytic potential as oxidation catalysts for phenol, by cyclovoltammetry. With the Ebonex/PbO_2 electrodes the oxidation did not appear to be specific, as oxygen evolution occurred as a side reaction at the same electrochemical potential as the combustion reaction.

In contrast, the Sb-doped Ti/SnO_2 electrodes proved to be capable of specific oxidations of phenol in the water, indicated by a well-separated anodic peak in the CV. The electrodes were only active when doped with antimony, because the n-donor provides for the conductivity of the film. Catalytic activity of the coating was enhanced as Sb_2O_5 forms a higher oxide than SnO_2 does. Thus, the incorporation of oxygen into the film is reduced and the combustion reaction favoured.

Doping with fluoride had a reverse effect on the oxidation efficiency, although this modification did improve the hydrophobicity of the films.

The kinetic experiments have given a diffusion coefficient for the electro-active species that is close to the literature value.

A further point emerging from the cyclic voltammograms was that there was no reduction reaction, indicating the irreversibility of the oxidation. Lastly, the oxidation peak decreased until it was no longer visible

5 ASSESSMENT OF CELL PERFORMANCE AND KINETIC STUDIES

5.1 Introduction

Assessment of the cell performance was carried out using N,N-dimethyl-p-nitrosoaniline (RNO) as a spin trap for •OH-radicals. Kinetic studies were done for the formation of the •OH-radicals. For the kinetic measurements of the reactions by which •OH-radicals were formed at the anodes, the PbO_2-based electrode material on Ebonex and the new $Ti/SnO_2/Sb_2O_5$ anode material were compared.

As mentioned in section 2, there are two different pathways for the anodic oxidation of undesired organics described in the literature [Simond, 1997; Arfsten, 1984; Chaudhuri, 1990] (see also Fig. 2.1):

(i) electrochemical conversion – during which only the non-biocompatible pollutants are transformed into biocompatible organics, and biological treatment is still required after the electrochemical oxidation, and

(ii) electrochemical combustion – that yields carbon ddioxide and water, and no further purification is necessary.

The accumulation of •OH radicals favours the combustion reaction, while the introduction of oxygen into the electrode lattice results in conversion. Anodes with a high oxygen overpotential, such as Ti/SnO_2, Ti/PbO_2 and graphite-felt, favour electrochemical combustion [Arfsten, 1984; Chaudhuri, 1990; Karlsson, 1992]. The following mechanism for the formation of •OH radicals on an oxide anode (MO_x) has been suggested by Comninellis [Simond, 1997]:

$$MO_x + H_2O \xrightarrow{k_{OH}} MO_x(\bullet OH) + H^+ + e^- \qquad (5\text{-}1)$$

The destruction of organics proceeds by the reaction:

$$R + MO_x(\bullet OH)_z \xrightarrow{k_C} Z/2\ CO_2 + Z\ H^+ + Z\ e^- + MO_x \qquad (5\text{-}2)$$

The •OH radicals were detected by a method which is already well established in biology and biochemistry, that is, spin-trapping with N,N-dimethyl-p-nitrosoaniline (RNO) [Maier, 1993]. RNO has a sensitive absorption band at 440 nm ($\varepsilon = 3.44 \times 10^4\ M^{-1}cm^{-1}$), and its bleaching upon acceptance of an electron from an •OH-radical can easily be observed by means of UV/Vis spectrophotometry.

Thus, the rate of the bleaching reaction in the presence of N,N-dimethy-p-nitrosoaniline (RNO) is determined by k_{RNO}.

$$RNO + \bullet OH \xrightarrow{k_{RNO}} \text{spin-adduct} \qquad (5\text{-}3)$$

5.2 Nitrosodimethylaniline (RNO) as scavenger for •OH radicals

p-Nitrosodimethylaniline (RNO) is a selective scavenger for •OH-radicals [Wabner, 1985]. A number of •OH-radical spin traps are described in the literature [Bors, 1978], but RNO has the following advantages.

(i) The reaction of RNO has been reported to be selective [Comninellis, 1993] as niether singlet oxygen ($^1O_2$) nor various "peroxo" compounds destroy the chromophoric group of RNO [Kvaljic, 1965].

(ii) It has a high rate of reaction with •OH-radicals ($k = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$).

(iii) RNO is easy to use, one merely observes the bleaching of the sensitive adsorption band at 440 nm ($\varepsilon = 34\ 200\ M^{-1}cm^{-1}$).

Another advantage of RNO for the detection of •OH radicals formed by the hydrolysis of water is that RNO is electrochemically inactive at Pt, IrO_2 and SnO_2 anodes, as has been shown by cyclic voltammetry measurements [Comninellis, 1993]. Similar results have been reported in literature at Pt and PbO_2 anodes [Wabner, 1985].

In this research RNO was used as a spin trap and the bleaching of the yellow colour was measured during electrolysis:

$$RNO + \bullet OH \rightarrow R\text{-}(OH)\,NO\bullet \qquad (5\text{-}4)$$

5.3 Experimental

The electrolytic cell, shown in Fig. 5.1 was specially constructed to afford direct spectroscopic observation of electrolysis at the anode. For the electrolysis, the electrochemical cell consisted of a chamber with a working and a counter electrode, and was equipped with a fibre-optic sensor for spectrophotometric UV/Vis analysis. The fibre-optic sensor is illustrated in Fig. 5.2. This set-up was used for the kinetic studies with RNO. The •OH radical trapping was measured in a phosphate buffer (pH = 7.0) containing 2×10^{-5} mol/l RNO ($\varepsilon = 34\ 200\ M^{-1}cm^{-1}$ at 440 nm).

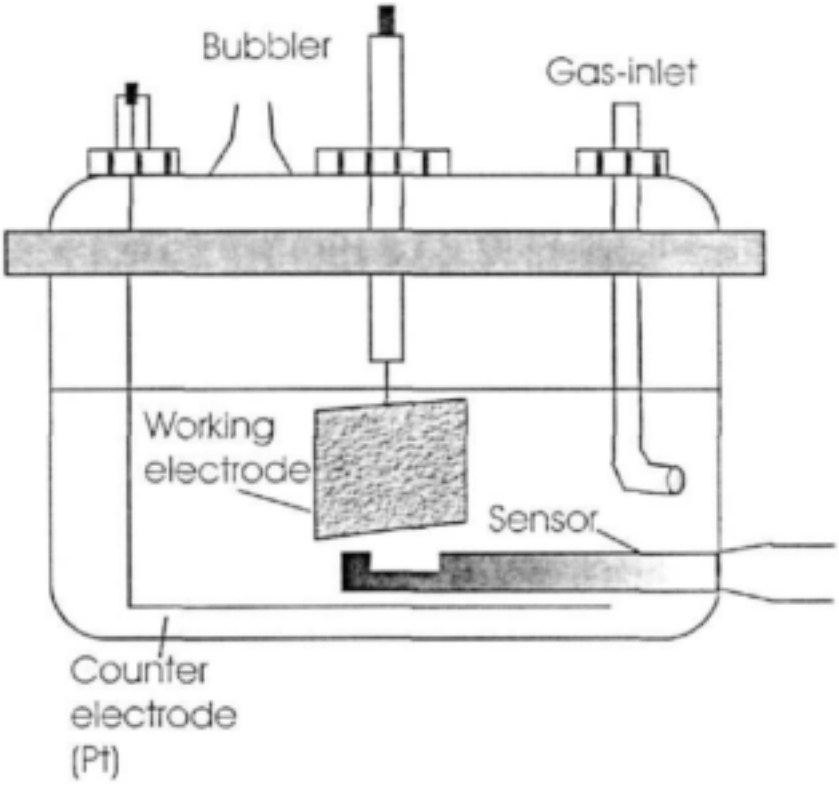

Fig 5.1: Set-up of the electrochemical cell used for the spectroscopic observation of electrolysis at the anode

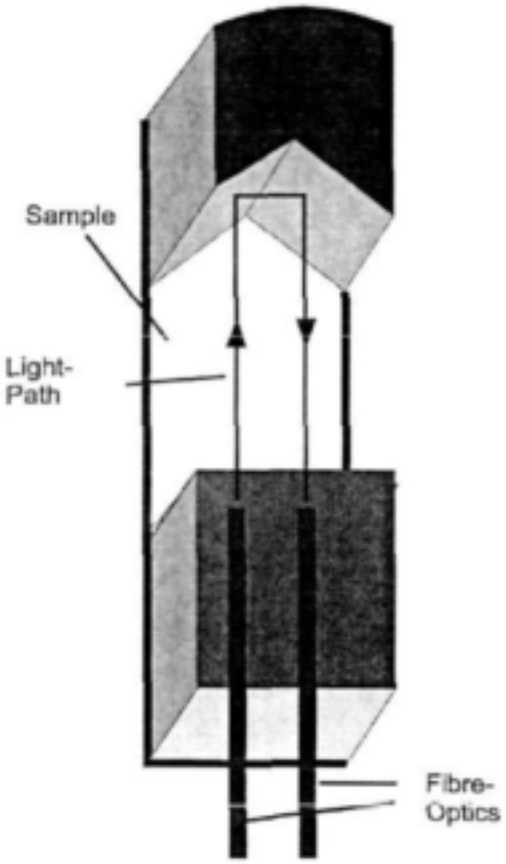

Fig 5.2: Sensor used for the RNO-determination

5.4 Results

After the galvanostatic electrolysis on Ti/SnO_2/Sb_2O_5 and Ebonex/PbO_2 in a phosphate buffer solution with $2x10^{-5}$ M RNO, absorption curves were obtained for the bleaching of RNO (Figure 5.3). The software program 'Mathcad 5.0 Plus' was used to determine the rate constants of Equations 5.1 or 5.3 and the order of the reaction. The program permitted the estimates of the reaction order and the rate constant, the differential method being used to analyse the reaction data. Interpolation was carried out by spline function, to generate equally spaced points.

Kinetic data obtained for the PbO_2-based electrodes were: Reaction order: a = 2.4; specific velocity for a rate equation $dC/dt = k \times C^a$; $k = 0.134\ M^{-1}\ s^{-1}$; correlation: 0.967.

Kinetic data obtained for the SO_2-based electrode were: Reaction order = 1.92; $k = 0.155M^{-1}\ s^{-1}$; r = 0.959.

The reaction order of 2 is valid for both electrode materials.

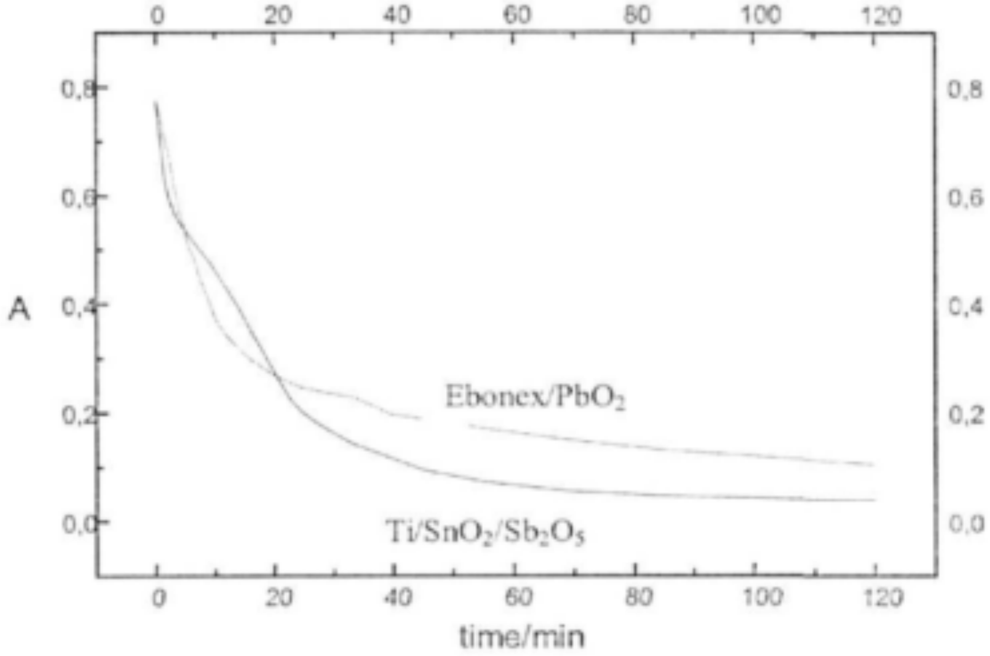

Fig 5.3: Absorption against time of electrolysis for Ebonex/PbO$_2$ and Ti/SnO$_2$/Sb$_2$O$_5$. Current density: $i = 20$ mA cm^{-2}, electrolyte: Phosphate buffer (pH7) + 2×10^{-5} M RNO.

5.5 Discussion

The pathway of the electrochemical combustion was confirmed by the detection of •OH-radicals by spin trapping by RNO during electrolysis. The reaction order of the overall reaction is 2. Unfortunately, this reaction order could satisfy either of the second-order equations, equation (5-1) or equation (5-3), ie. two successive reactions. One of them must be predominately rate-determining, meaning that either $k_{OH} >> k_{RNO}$ or $k_{OH} << k_{RNO}$. Equation (5-1) was independent of the electrode material, because the radical reacted directly with the RNO. The *difference in the rate constants could thus be explained only by the initial reaction* during which the radicals are formed.

Consequently, equation (5-1) must be the rate-determining step of the whole reaction, and the calculated data valid for that particular step. This was in accordance with the literature [Comninellis, 1994]. Therefore, the overall reaction was assumed to be second order, with $k_{RNO} >> k_{OH}$, and the first equation is the rate-determining step.

The absorption curves in Fig. 5.3 further indicate that •OH radical production is kinetically increased by the SnO_2-based material, which lead also to a lower final concentration of RNO.

6 CHARACTERISATION OF THE Sb-DOPED SnO_2 ELECTRODE MATERIAL BY ELECTRIC IMPEDANCE SPECTROSCOPY

6.1 Introduction

The kinetics of electrode processes can be determined by Electric Impedance Spectroscopy (EIS) [Wien, 1896; Warburg, 1899].

6.2 Instrumentation

A phase-sensitive voltmeter was used to study the electrochemical response of the interphase is an accurate method for the determination of the double layer capacitance of an electrode system. From results, By combining a phase-sensitive voltmeter (also called a lock-in amplifier) or a Frequency Response Analyser (FRA) with a variable frequency sine-wave generator, one obtains an electrochemical impedance spectrometer [Randles, 1947; Ershler, 1947; Gerischer, 1951]. Such instruments are commonly combined with a microcomputer, which makes it relatively easy to probe the interphase over a wide range of frequencies, and to record and analyse data [MacDonald, 1986; Gabrielli, 1980; Sluyters-Rehbach, 1984]. Modern instrumentation, which is commercially available, covers a frequency range of about 12 orders of magnitude, from10^{-5} Hz to 10^7 Hz. The range of frequencies that can be employed in electric impedance spectroscopy (EIS) measurement is limited more by the electrochemical aspects of the system than by the instrumentation. Thus, measurements at very low frequencies take a long time, during which the interphase may change chemically. The minimum time needed to make a measurement at any frequency is the inverse of the frequency (i.e. the period) of the perturbing wave. EIS experiments are usually conducted in the 10^{-3} to 10^{-5} Hz range. The results of EIS can be displayed in a number of different forms; the most common of which is probably the complex-plane impedance plot [Grimm, 2000].

6.3 Experimental – determination of impedance measurements

Impedance measurements were carried out at the Institute for Inorganic Chemistry at the University of Essen, Germany. A strip of $Ti/SnO_2/Sb_2O_5$ (0.3 cm wide), was cut out and exposed to the electrolyte 1 M H_2SO_4. The electrode material was pre-treated at 2 V, versus a Reversible Hydrogen Electrode (RHE) as a reference, for 60 s. Impedance measurements were then made over the entire frequency range of 10^5 Hz–0.01 Hz. The potential at the working electrode ($Ti/SnO_2/Sb_2O_5$) for the different impedance measurements ranged between 0 V (RHE) and 2 V. The potential was raised in small increments, as follows: 0 V; 0.5 V; 1.0 V; 1.3 V; 1.4 V; 1.45 V; 1.5 V; 1.55 V; 1.6 V; 1.7 V; 1.8 V; 1.9 V; 2.0 V. The steps were chosen to be particularly small around 1.5 V (RHE) because, according to the results of cyclic voltammetry, the combustion reaction of phenol is expected to emerge in this potential region. In order to observe the influence of the diffusional Warburg term on the measurements, the experiments were repeatedly carried out with the electrode emerged to different depths (3 cm, 2 cm and 1 cm). The smaller the exposed electrode area to the electrolyte, the less diffusional interference to the measurement is expected. The entire procedure was repeated after adding 5mmol/l of phenol to the electrolyte, to examine the different responses due to the combustion reaction.

The experiments were conducted in an electrochemical cell equipped with a Pt-wire as a counter electrode and an RHE electrode as reference system. The Pt-wire surrounded the working electrode as a cylinder, to provide an even current distribution to the working electrode. The experimental set-up is shown in Fig. 6.1. An EG&G potentiostat 273 connected to a Solartron 1260 frequency response analyser was used as an electrochemical interface.

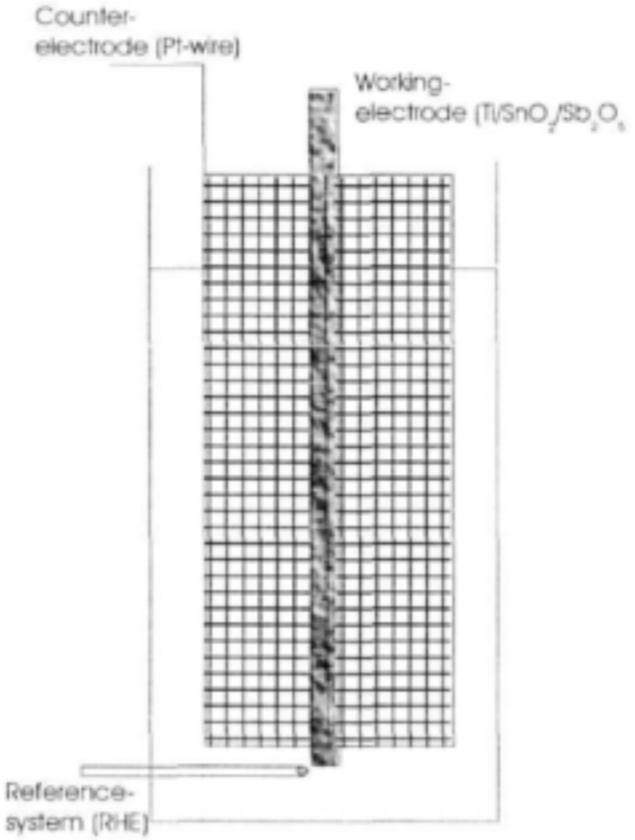

Fig 6.1: Experimental set-up used for determining impedance measurements

6.4 Results and discussion of impedance measurements

Two series of measurements were carried out. The first comprised frequency scans in 1 M H_2SO_4, whereas for the second sequence of measurements 5 mmol/l of phenol was added to the electrolyte.

6.4.1 With 1 M H_2SO_4 as electrolyte

The impedance measurements in sulphuric acid only were merely employed for the sake of general characterisation. At higher potentials, seen in Fig. 6.3 and Fig. 6.4, there is a change from mass transport limitation to charge transfer, from the •OH-radical production and the oxygen evolution reactions. The figures only display the data of the measurements at a penetration depth of three cm of the electrode. In Fig. 6.2 it can already be observed that the curves become less

steep with rising potential due to a decreasing effect of mass-transport limitation on the system. (Z is an impedance vector.)

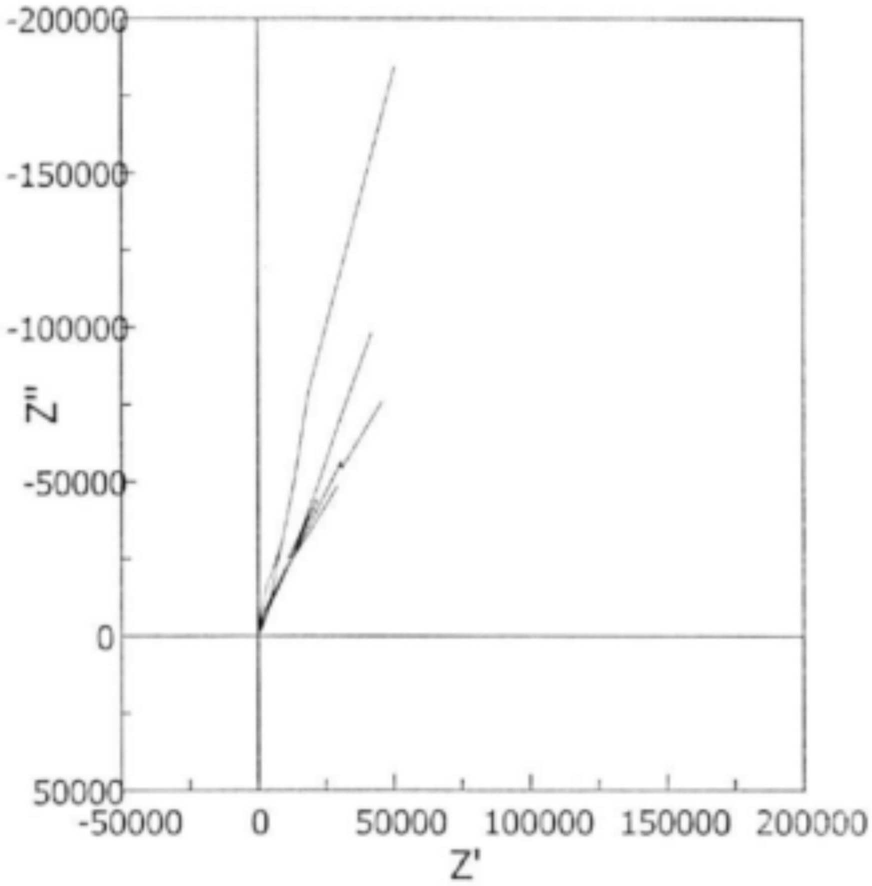

Fig. 6.2: Impedance measurements of the Ti/SnO_2/Sb_2O_5 electrode in 1 M H_2SO_4. Penetration depth of the electrode into the electrolyte: 3 cm, potentials: 0 V; 0.5 V; 1.4 V; 1.55 V and 1.6 V versus RHE.

6.4.2 With 1 M H_2SO_4 and 5 mM phenol as electrolyte

Phenol (5 mmol/l) was added to the electrolyte of 1 M sulphuric acid before starting the second sequence of measurements. Kinetic studies had led to the conclusion that the overall combustion reaction comprised one initial rate-determining step of the •OH-radical production, prior to the following reaction between the •OH-radical and the phenol, which is second order (sectiom 5.3). This reaction does not necessarily take place directly at the electrode's surface nor involve a charge-transfer from the electrode to the electrolyte. Thus, one could expect that the addition of phenol to the electrolyte does not influence the charge-transfer step manifested in the impedance spectrum.

The addition of the phenol to the electrolyte did not significantly change the electrochemical response of the interphase

6.5 Conclusions

Consequently, the proposed mechanism was confirmed and the formation of •OH-radicals is the crucial step for the combustion reaction.

7 APPLICATION OF A Sb-DOPED ELECTRODE MATERIAL IN A SOLID POLYMER ELECTROLYTE (SPE) REACTOR FOR THE ELECTROCATALYTIC OXIDATION OF PHENOL

7.1 Introduction

One way in which the efficiency of electrochemical methods for wastewater treatment can be increased is by supporting the system on solid polymer electrolytes (SPE). Sb-doped SnO_2 anodes were coupled with a perfluorinated cation-exchange membrane to build a system for the anodic oxidation of hazardous organics in water (phenol).

As organic pollutants do not form sufficiently conductive electrolytes for the electrochemcial treatment without the addition of supporting salts, an SPE reactor was designed. When perfluorinated ion-exchange membranes such as Nafion as an SPE are used to separate the anode and the cathode in the electrochemical oxidation process, no conductive liquid is required in the cell. A SPE system thus makes possible electro-organic reactions at an electrode, on the surface of an ion-exchange membrane, without the need for addition of a supporting electrolyte. [Chen and Chou, 1993]. This is feasible because of the fixed sulphonic acid groups in the polymer, similar to immobilised sulphuric acid, provide the ionic conductivity through proton mobility inside the membrane. Hydrogen ions are formed at the anode during oxidation and migrate through the cation-exchange membrane.

Large-scale porous titanium electrodes, up to 100 cm^2, were coated with Sn-doped SnO_2, for a galvanostatic solid polymer electrolyte (SPE) application. This resulted in very low voltage across the stack, even without adding supporting electrolytes to the water. Phenol was used as a standard contaminant throughout all experiments. A new method for online analysis of the phenol by fibre-optics UV/Vis spectroscopy was designed and the results compared to those obtained using a well-established standard colorimetric method for the determination of phenol.

7.2 Experimental

7.2.1 Electrode preparation for the SPE-reactor

The Sn-doped SnO_2 solutions for the dip-coating were prepared from two alkoxides obtained directly from chlorides, according to the method described by Chaleton [Chaleton, 1995]. A porous, circular titanium plate, with a total area of 100 cm^2, was used as a substrate for the catalyst. It was placed in a clean chamber saturated with ethanol vapour. The sol was pipetted onto the substrate through a hole in the top of the chamber, coating both sides of the electrode. The substrate was then allowed to dry for 6 h, after which it was dried in air at 100°C for 15 min. This coating procedure was carried out twice, to close cracks and heal defects in the film. Calcination was then carried out in air, by heating the substrate to 600°C at a rate of 1 °C/min. After the calcination process the electrode maintained its porous structure and was still permeable to water.

7.2.2 Set-up of the SPE-reactor

A porous Ti plate, coated with Pt by means of magnetron sputtering on the surface and identical in shape to the anode, was used as a cathode. The two electrodes were mounted in the SPE reactor [Bessarabov, 1998; Sanderson, 1997], sandwiching a perfluorinated Nafion-like cation-exchange membrane in H^+-ionic form ('Plastpolymer', St. Petersburg, Russia), as shown in Fig. 7.1. The membrane was prepared from a blend of the copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-5-methyl-1-octene-8-sulfonyl fluoride. The thickness of the membrane was 230 μm, and the equivalent mass was 1120.

The electrolyte (500 ml) was pumped through the reactor by means of a peristaltic pump, passing the anode- and cathode chambers in series, without separation of the two chambers. The cation-exchange membrane ensured the ionic migration between the two electrodes. The anodic and the cathodic chambers did not have to be separated, because total oxidation was expected by •OH radicals that only exist at the electrode surface. The total area of the electrodes was 100 cm^2.

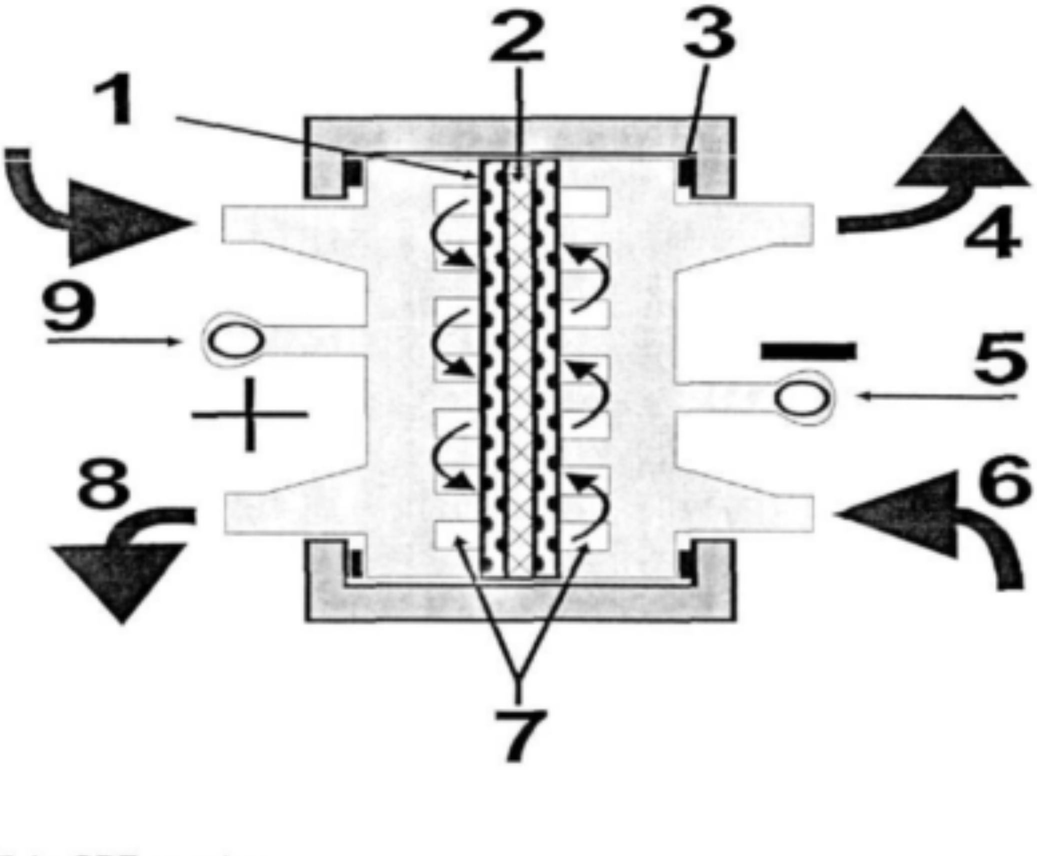

Fig 7.1: SPE-reactor

(1) porous Ti, coated with SnO_2/Sb_2O_5, (2) Nafion membrane, (3) isolators between electrodes and reactor, (4) outlet for water, (5) cathode side, (6) cathodic inlet for water, (7) distribution channels for cathode and anode, (8) anodic outlet, (9) anode.

7.2.3 On-line analysis of phenol during electrolysis in the SPE reactor (by means of fibre-optics spectrophotometry)

For better monitoring of the process of the oxidation of phenol in an SPE-reactor, a direct online method for the phenol detection in water by fibre-optics spectrophotometry was conceived. The direct detection of the phenol concentration at 270 nm by means of UV/VIS spectrophotometry was interfered with by the noise caused by the electrolysis process itself. In order to overcome this problem an antipyrine dye was formed with 4-aminoantipyrine in the presence of hexacyanoferrate (III), with the maximum of absorbance at 510 nm. 4-aminoantipyrine exerts an electrophilic attack upon the para-position of the phenol to form a quinone structure [Spiker, 1992].

To confirm results obtained from the above method, the phenol index was additionally determined by the well-established colorimetric method. [DEU. 1984].

The UV/VIS analysis was carried out with a Perkin Elmer Lamda 20 spectrophotometer attached to a fibre optics sensor placed inside the flow of the electrolyte (Fig. 7.2). The electrolyte for the phenol determination comprised: 0.1 mol l^{-1} 4-aminoantipyrine, 2 mM $K_3[Fe(CN)_6]$, 1.3 mM NH_4Cl 0.03 mol/l NH_4OH, 1.4 mM potassium sodium tartrate tetrahydrate and 0.1 mM phenol. The red absorption band was monitored at 510 nm.

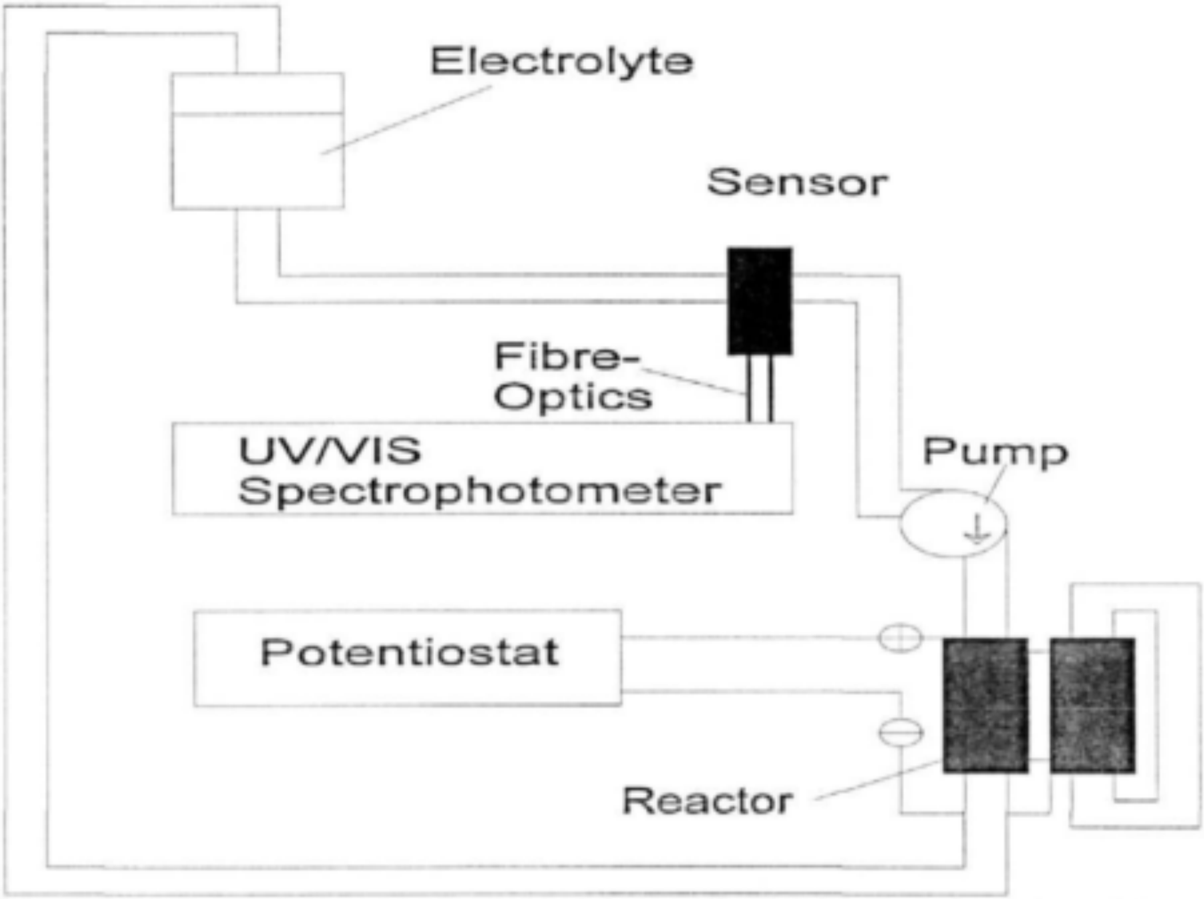

Fig 7.2: Schematic representation of the on-line phenol analysis by a fibre-optics spectrophotometer.

7.2.4 Electrochemical equipment

All electrochemical measurements were carried out with a Solartron SI 1280B. Electrolysis was performed galvanostatically, with a current density of i: 20 mA cm^{-2}. The determination of the phenol index was carried out at the Private Institut für Umweltanalytik in Flöha, Germany.

7.3 Results

7.3.1 Determination of the phenol index starting with high concentrations (1g/l phenol)

Electrolyte (100 ml) containing 1g l^{-1} of phenol, was pumped through the SPE reactor during electrolysis at a current density of 20 mA cm^{-2} for 1200 min. Analysis was carried out every 15, 30, 60, 120, 240, 480, 720 and 1200 min. After a preliminary distillation and extraction with chloroform, the test samples were analysed [Murphy, 1992]. The concentration of the phenol decreased from 1g l^{-1} to 0.22g l^{-1} after 960 min of electrolysis. Further electrolysis could not significantly decrease that concentration.

Fig. 7.3 shows the decrease in phenol concentration versus time.

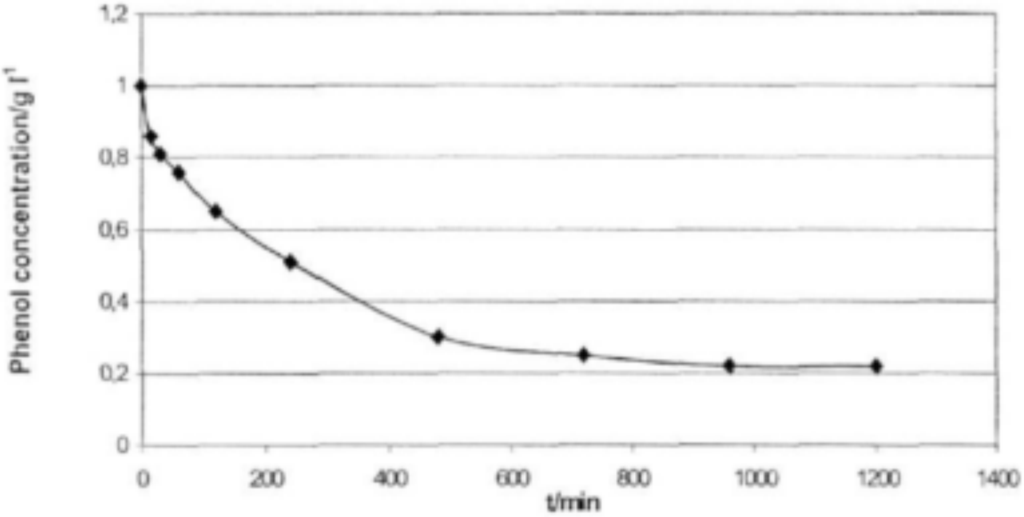

Fig 7.3: Phenol concentration (g l^{-1}) versus electrolysis time in the SPE-reactor. Current density: 20 mA cm^{-2}

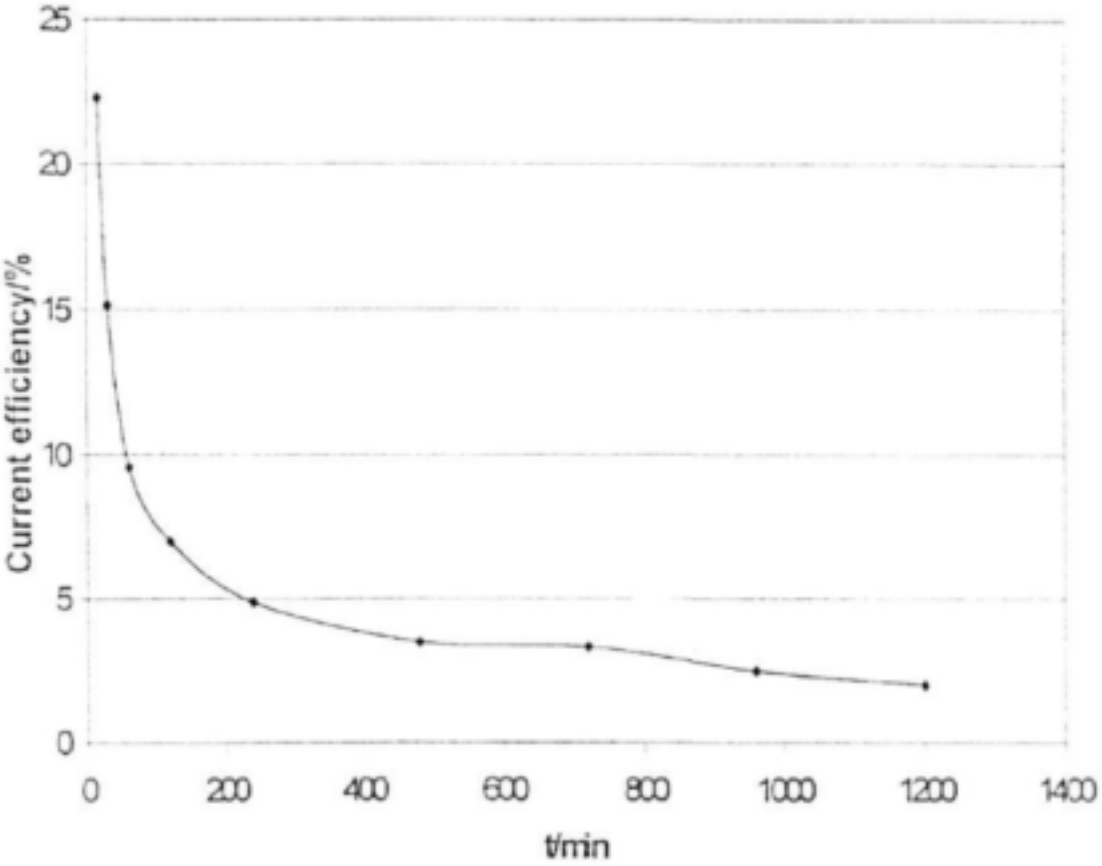

Fig. 7.4: Current efficiency versus time of electrolysis

The current efficiency was calculated under the assumption that 28 electrons are required for the complete oxidation of 1 molecule of phenol. With the phenol concentration decreasing, the current efficiency also decreased. After 15 min of electrolysis the current efficiency reached 22.3%, decreasing to 7% after 120 min and finally reaching 2% after 1200 min of electrolysis, as shown in Fig 7.4. (The measurements are based on a calibration curve obtained from standardised measurements.)

7.3.2 Determination of the phenol index starting with very low concentrations (1mg/l phenol)

To illustrate the effect of mass-transport limitation on the current efficiency and performance of the entire process, electrolysis was carried out with very low starting concentrations of phenol. Electrolyte (500 ml), containing 1mg/l of phenol, was pumped through the SPE reactor during electrolysis, at a current density of 20 mA/cm^2 for 240 min. The pumping rate was 70 ml/min. Analysis was carried out every 30 min. The test samples were analysed after a preliminary distillation.

The concentration of the phenol decreased from 1 mg/l to 0.02 mg/l after 240 min of electrolysis. Fig. 7.5 shows the decrease in phenol concentration versus time.

The entire process consumed 2.98×10^{-3} moles, while only 5.19×10^{-6} moles of phenol were converted.

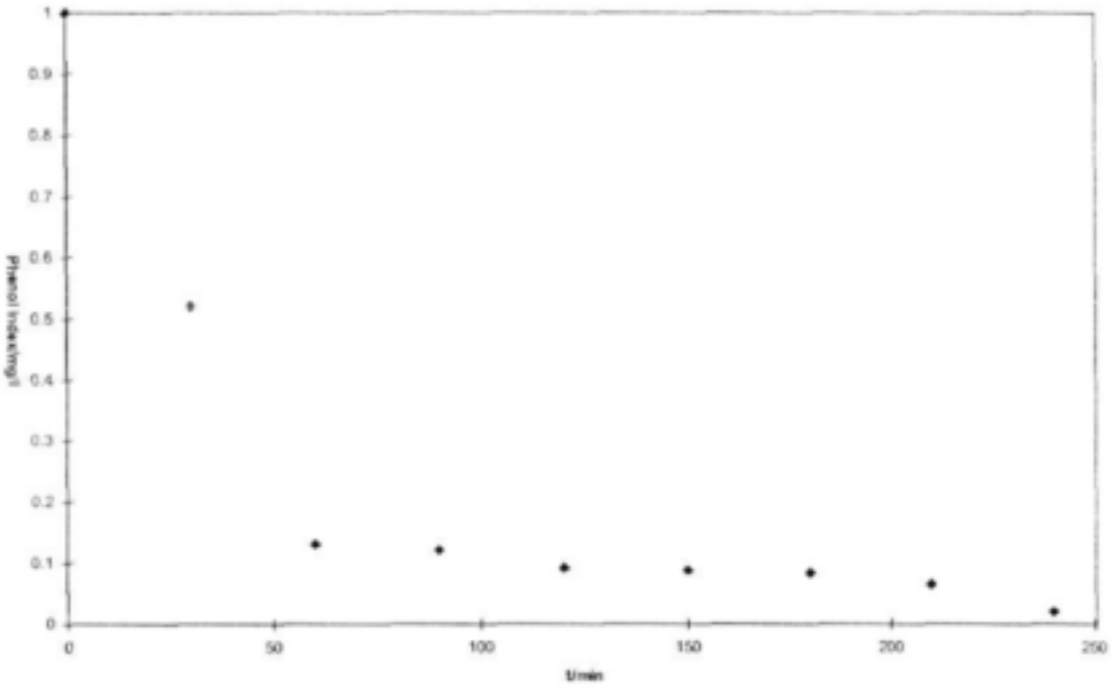

Fig 7.5: Phenol index (mg/l) versus time during electrolysis in the SPE-reactor. Current density: 20 mA/cm^2.

7.3.3 Voltage across the reactor using the proton exchange membrane compared to a simple separator

By using the cation exchange membrane inside the reactor the voltage dropped from 25V, using a simple separator between cathode and anode, to about 3.4 V, as shown in Fig. 7.6. The application of the proton exchange membrane thus made it unnecessary to add supporting electrolytes.

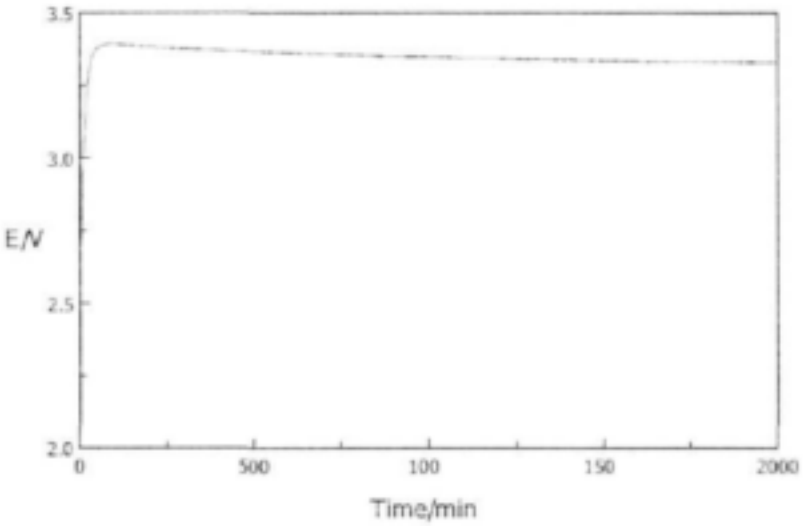

Fig. 7.6. Voltage across the stack, versus time, during electrolysis, with a Nafion-type membrane between cathode and anode.

7.3.4 Online phenol analysis with 4-aminoantipyrine by fibre-optics

For the online determination of phenol, 0.1 mM of phenol was mixed with 0.1 mol l^{-1} 4-aminoantipyrine, 2 mM $K_3[Fe(CN)_6]$, 1.3 mM NH_4Cl 0.03 mol l^{-1} NH_4OH and 1.4 mM potassium sodium tartrate tetrahydrate, to form 0.5 l of the coloured antipyrine dye. This was pumped through the reactor at a current density of 20 mA cm^{-2}. The concentration of the phenol was determined by the fibre-optics spectrophotometer at a wavelength of 510 nm. Fig. 7.7 illustrates the decrease of the phenol concentration, versus time, during electrolysis.

Using the perfluorinated cation-exchange membrane inside the reactor, the voltage dropped from 17 to 3.35V. The concentration drop was not as rapid as shown for the accurate determination, but was nonetheless similar. This indicated that the quinone structure formed between phenol and 4-aminoantipyrine was much more stable than the phenol itself, and that a more accurate and direct assessment of the phenol combustion process was not possible. Part of the inaccuracy was attributed to mass transport limitation to the fibre-optic sensor.

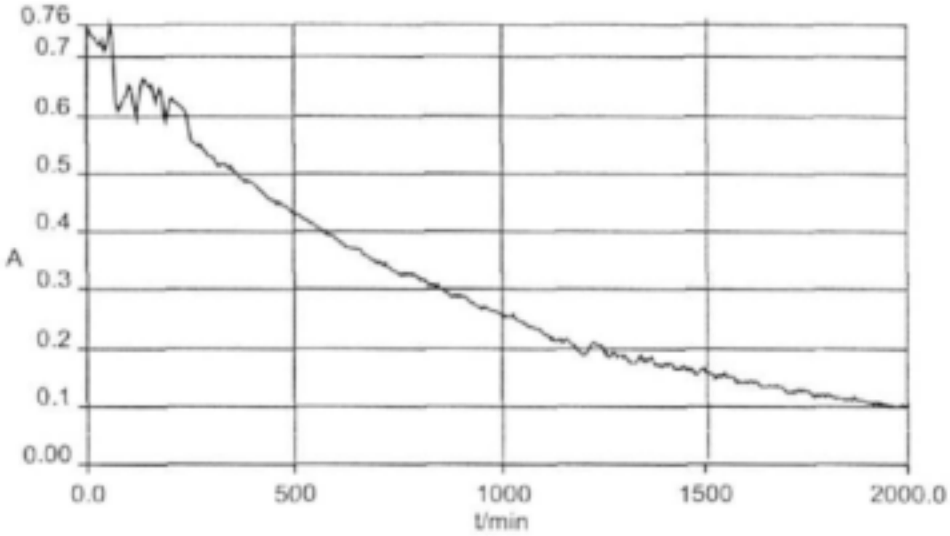

Fig 7.7: Decrease in the phenol concentration, versus time, during electrolysis in a SPE reactor. Initial phenol concentration: 0.01g l^{-1}, complexing agent: 4-aminoantipyrine, online-detection at 510 nm, i = 20 mA cm^{-2}

7.4 Discussion

The SPE reactor design, using the Nafion membrane to separate anode and cathode, proved to be very effective; it delivered very low voltage.

Direct phenol determination by fibre-optics was possible only with loss of accuracy, because the quinone structure formed between the 4-aminoantipyrine and the phenol seems to be more stable to electrocatalytic attack than the phenol alone is. Furthermore, mass transportation limits to the fibre-optics sensor must be considered.

The efficiency of the $Ti/SnO_2/Sb_2O_5$ electrodes in a SPE reactor, for the efficient electrochemical destruction of phenol in water, has been demonstrated.

The loss in current efficiency can be explained by side reactions, such as oxygen evolution. The cyclic voltammograms have, however, shown a clearly separated and sharp phenol peak. Thus, further study should focus on finding the suitable current density for a variety of phenol concentrations, so that at any point, side reactions can be kept to a minimum.

Upscaling the system would entail a number of stacks of the described reactor design, mounted together as required.

8 CONCLUSIONS

Introduction

The recent trend, internationally, has been to look at oxidative systems to remove the organic burden from effluent streams or from polluted water for drinking. Chlorination has been the method most widely used to treat water, but undesirable chloramines are obtained. Ozonolysis has gained some attention because its organic products are less harmful than the chloramines. Ozonolysis is however not a simple process and the ozone needs to be destroyed before the treated water is made available. It is dangerous in its raw form and highly corrosive to metals and oxidative to other materials.

Elecrochemical oxidation has recently been proposed as an alternate method for the removal of organic polutants from water, especially for dilute solutions of biorefractory organics. The economic fesibility of this type of process is associated with its ability to limit side reactions, and its good current efficiency. Anodic oxidation is considered to be a clean process and does not release undesirable chemicals into the water (as chlorination does).

For the efficient use of the above process, two areas required close attention:

- the choice of electrode material and
- the design of the electrode system for the maximum contact of impurities onto the electrode.

The choice of anodic material plays an important role: it should be stable over a wide range of anodic potentials and have a high overpotential for oxygen evolution (which is the main side reaction in anodic oxidation). The impurities in the water need to contact the electrodes in the electrochemical process.

Phenol is known to be a major organic water-pollutant that needs to be removed or destroyed. It reacts with chlorine during water treatment and produces carcinogenic products. Phenol oxidation has frequently been used a model reaction to assess methods of treating organic wastes. Hence, it was also used as a model organic pollutant in this study.

Overview of progress made during the present study

In the present project a protocol was developed for making new and useful electrode materials by sol-gel methods for the electrochemical oxidation of phenol. It did not include optimisation of the process.

The study has been successful in addressing the first area, ie. the creation, characterisation and evaluation of new an effective electrode materials for the elctrochemical oxidation of phenol. It did not include detailed consideration of the engineering aspects of the design of an electrode reactor. If, however, there are salts present in the water to be treated, eg. brack water, then the electrode system developed in this research can be used. If not, then a specifically engineered (designed) cell structure is required.

Very early in this research programme it was proved conclusively that the American technology, available at the time, potentially useful for the oxidative removal of organics from wastewaters showed low efficiency (as determined by cyclic voltammetry) for the oxidation of phenol. New and improved materials for use in electrochemical cells had to be found. Whereas the existing systems used ruthenium oxide, platinum, lead oxide and carbon, much water splitting and only partial oxidation takes place.

Results of the present project have shown the advantage of the newly developed tin/antimony electrode material - it exhibits good conductivity and strong organic oxidation, prior to the overpotential for water splitting. It is also different to other electrodes, which often work by absorbing the oxygen intermediate, as the electrode works by absorbing the impurities onto the electrode. The oxidation is very rapid and, on completion, there are no more oxidative organics remain. This is indicative of combustion to carbon dioxide. It had been assumed, based on available literature, that the only oxidation product of phenol was carbon dioxide. Unfortunately mass spectroscopy data could not be obtained to confirm this ourselves.

Conclusions

Specific conclusions to this project on the preparation and characterisation of electrodes for the electrochemical conversion of pollutants in water were as follows:

- Various electrode materials (anodes) were prepared, characterised and evaluated for their catalytic potential as oxidation catalysts for the electrochemical oxidation of phenol, a model of organic pollutants in water. These included Ebonex, Ebonex/PbO_2, Ti/SnO_2 and Sn-doped Ti/SnO_2 (Ti/SnO_2/Sb_2O_5).
  (These new electrodes were to have well separated peaks for the overpotential and the oxidation peak, in the cyclic voltammograms, for the oxidation of phenol.)

- Determination of the electrochemical oxidation of phenol was successfully carried by means of cyclic voltammetry (CV).

- Most favourable results were obtained with the new Sb-doped films on Ti foil, Ti/SnO_2/Sb_2O_5, prepared by a special sol-gel dip-coating technique. This new electrodes had indeed a high overpotential for oxygen evolution, resulting in well-separated peaks in the CV.

- Kinetic measurements, confirmed by UV/Vis spectroscopy, revealed that •OH radicals were formed as intermediates during the combustion of phenol in a second order rate-determining step. Using an on-line technique, the combustion of phenol in an electrolytic cell, using sulphuric acid as electrolyte, was proved. This proved the concept of anodic oxidation and the suitability of the new membrane material.

- The Ebonex electrode did not absorb the phenol on the electrode, hence the electrochemical reaction took place at a very much lower potential, much lower than the overpotential for oxygen evolution.

- With the Ebonex/PbO_2 electrode the oxygen overpotential interfered with the oxygen evolution peak.

- Overall, a new electrode material that separates the overpotential from the oxidation peak, while maintaining excellent kinetics at the electrode surface, has been prepared. With increasing current densities, increasing degrees of oxidation were obtained.

- Further, instead of having to use an aqueous electrolyte, a solid polymer electrolyte (SPE) reactor was designed. It required no salt in the water to be treated. Nafion was used to separate the anode and cathode in the electrochemical oxidation process. The efficiency of the new electrodes in the SPE for the combustion of phenol was demonstrated.

Unfortunately, with the simple cell design used, there were mass-transfer problems. Current deficiency limited the total efficiency of contact as the solution flowed past the flat electrode in a cell designed for gaseous reactions ie. a fuel cell. The cell design used had poor current efficiency and conversion, although it did have the advantage that there was no 'secondary pollution'.

Recommendations for future research

In order to improve the current efficiency it is necessary to improve on the reactor design. It is envisaged that with the design of a suitable commercial reactor, this technology could be effectively used. This design was, however, considered to be beyond the scope of this present research project on the materials science aspect of a novel electrode material. It should be undertaken by Chemical Engineers. Further, improved analytical techniques for the oxidation of phenol should be considered.

It is further recommended that still newer and more effective electrodes, in newer forms, be developed and optimised. They should be used in a fixed-bed reactor.

Future practical applications of this technology will largely depend on the designs of the new cell/s and applications in niche markets.

In the latest issue of Modern Plastics International (November 2001) there is an article "New water treatment concepts proliferate". Two non-chemical methods of water treatment are discussed: by ozone and •OH radicals. The latter method is used by Innovation Water Technologies, in their TowerKlean® system, to treat water with an electric field. It is time that South Africa moves further into these concepts that are proliferating and hold the key to future water treatment without chemical addition.

Technology never stands still - it always advances, and the man in the street will always be offered new technology to improve his quality of life.

9 PUBLICATIONS, POSTERS AND ORAL PRESENTATIONS EMANATING FROM THIS RESEARCH PROJECT

9.1 List of publications

J. Grimm, D. Bessarabov and R. Sanderson, Desalination **115** (1998) 285 -294, Review of electro-assisted methods for water purification.

J. Grimm, D. Bessarabov, R Sanderson, W. Maier and S. Storck, Desalination **115** (1998) 295-302, Sol-gel film preparation of novel electrodes for the electrocatalytic oxidation of organic pollutants in water.

J. Grimm, D. Bessarabov, U. Simon and R Sanderson, J. Appl. Electrochem., **30**(3) (2000) 293 – 303, Characterisation of doped tin dioxide anodes prepared by a sol-gel technique and their application in an SPE-reactor.

9.2 Oral presentations

- Water purification by electro-assisted membrane systems, 2nd WISA-MTD-Workshop on membrane technology: New Developments in Membrane Process, Badplaas, South Africa, 21 – 24 October 1998
- SPE-membranes – application of doped tin dioxide anodes prepared by a sol-gel technique. ICOM 99, Toronto, Canada, 12 – 18 June 1999.

9.3 Poster presentations

- Electrochemical ozone generator based on solid polyelectrolyte (SPE) membrane technology for water disinfection, WISA 98, Cape Town, South Africa, 4 – 7 May, 1998.
- Preparation and characterisation of novel thin-film electrode material for anodic oxidation of organics in water, WISA 98, Cape Town, South Africa, 4 – 7 May, 1998.
- Sol-gel film preparation of novel electrodes for the electrochemical oxidation of organic pollutants in water, First International Conference on Inorganic Materials, Palais de Congres de Versailles, France, 16–19 September, 1998.
- Preparation of inorganic electrode materials, Inorganic 98, Stellenbosch, South Africa, 1998.

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APPENDIX

ELECTRODE REACTIONS INVOLVING ADSORBED SPECIES AND CHARACTERISATION BY CYCLIC VOLTAMMETRY

A.1 Cyclic voltammetry and electrode reactions involving adsorbd species

Cyclic voltammetry is particularly well suited to the study of the mechanism and kinetics of coupled homogenous chemical reactions. It is now possible to investigate very complex chemistry and distinguish between similar mechanisms. [Pletcher, 1991, p 171].

An electrode reaction which involves the oxidation of an adsorbed layer, eg

$$R_{ADS} - n e^- \leftrightarrow O$$

will give a cyclic voltammogram with quite different characteristics to one where the electrode reaction is an oxidation. The properties of the voltammogram largely arise because the amount of reaction is determined by the number of sites on the electrode surface where adsorption can occur (not in any way by diffusion of the substrate R in solution).

Generally, peaks with totally different characteristics for the oxidation of both adsorbed and solution-free R will be observed on a cyclic voltammogram. The formation of a bond between R and the surface stabilises the reactant and therefore makes it more difficult to oxidise. The adsorbtion peak must therefore occur at a more positive potential and this implies that the oxidation of solution-free reactant ooccurs while there is a layer of R adsorbed on the surface. Conversely, if it is the product which is adsorbed, the formation of the adsorbed layer will occur more readily than the solution-free product and the adsorption peak will occur at less positive potentials. Again, the solution reaction will take place in the presence of the adsorbed layer. The different shapes of the peaks and the very different dependence of their peak currents on potential scan rate readily allows for the recognition of such situations. Typical types of voltammograms are illustrated in Figure A1.

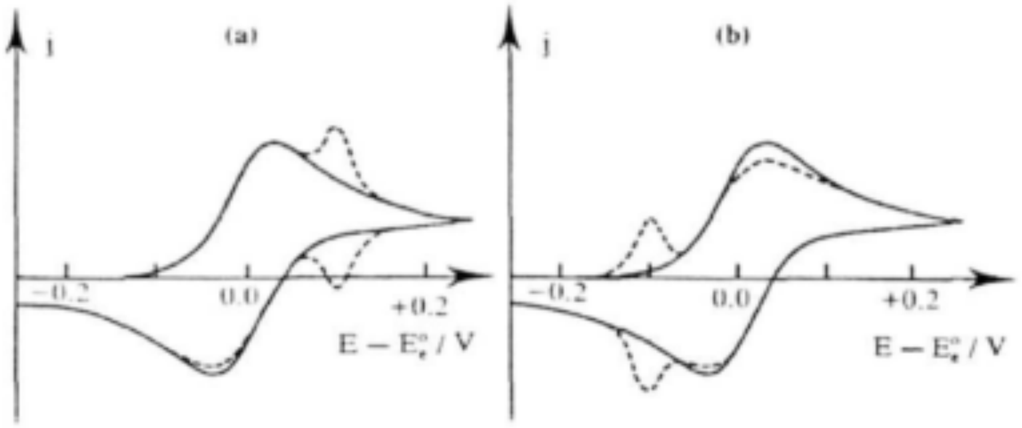

Fig A1: Theoretical cyclic voltammograms for the oxidation of R when (a) R is strongly adsorbed and (b) when O is strongly adsorbed. (The dashed line shows the response with adsorption and the solid line that for a simple process without adsorption). [Taken from Pletcher, 1991, p 173]

A.2 Instrumentation of voltammetry

The potentiostat is the main instrument used in voltammetry. The potentiostat applies a potential to the electrochemical cell between the working and reference electrodes. A current-to-voltage converter measures the resulting current between the working and counter electrodes. The current is typically displayed on a recorder as a function of the applied potential. Many types of voltammetry require that the potentiostat be capable of scanning from one potential to another.

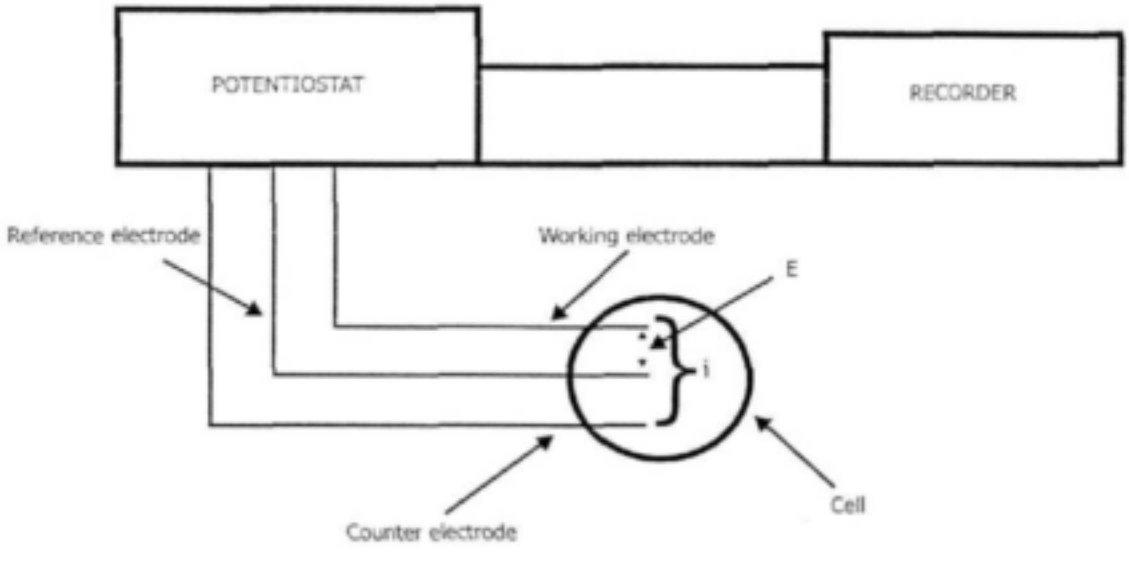

Fig A.2 Instrumentation of voltammetry

Modern potentiostats use a three-electrode configuration (see below and Figure A 2 above). The three-electrode arrangement prevents the reference electrode from being subjected to large currents that could change its potential. The working electrode is the electrode at which the electrolysis process of interest takes place. Different types of working electrodes are used in voltammetry. These include the following: (a) hanging drop (usually mercury), (b) mercury film and (c) solid (platinum, gold, glassy carbon and wax-impregnated graphite) electrodes. The current required to sustain electrolysis at the working electrode is provided by the counter electrode. The counter electrode is generally a platinum wire (coiled or uncoiled) that is often placed directly into the solution. The reference electrode is typically a saturated calomel electrode (SCE) or a Ag/AgCl electrode, which is often isolated from the solution by a tube of electrolyte called a salt bridge.

A typical electrochemical cell usually consists of a glass container with a cap having holes for introducing electrodes and nitrogen. Provision is made for oxygen removal from the solution by bubbling with nitrogen gas. The cell is then kept oxygen-free by passing nitrogen over the solution. Since the limiting (or peak) current in any type of voltammetry is temperature-dependent, the cell should be thermostated.

A.3 Linear potential sweep and cyclic voltammetry

Linear potential sweep is a potentiostatic technique, in the sense that the potential is the externally controlled parameter. The potential is changed at a constant rate

$$v = dE/dt$$

and the resulting current is followed as a function of time.

When the potential is swept forward and backward between two fixed values, the technique is referred to as cyclic voltammetry. In this way the current measured at a particular potential on the anodic sweep can readily be compared with the current measured at the same potential on the anodic sweep. Almost all literature data are presented in this form. Linear potential sweep measurements are generally of three types [Grimm, 1999]. Only two of the three are relevant here:

A.3.1 Very slow sweeps.

When the sweep rate is very low, in the range $v = 0.1 - 2$ mV, the system can be considered to be almost in equilibrium and measurements are conducted under quasi steady-state conditions.

A.3.2 Oxidation or reduction of species in the bulk.

In this case, the sweep rate is usually in the range of 0.01–100 V/s. The lower limit is determined by the need to maintain the total time of the experiment below

10–50 seconds (i.e. before mass transport by convection becomes important). The upper limit is determined by the double layer charging current and by the uncompensated solution resistance.

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