Nanoscaled Structures of Chlorate Producing Electrodes

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Till Ingrid
Abstract

SODIUM CHLORATE IS MAINLY USED for production of chlorine dioxide (a pulp bleaching agent). Sodium chlorate is produced by an electrochemical process where chloride ions (from sodium chloride dissolved in water) are oxidized to chlorine on the anodes and hydrogen is evolved on the cathodes. The anode of this process consists of a metal plate coated with a catalytically active metal oxide film. The electrocatalytic properties of the anode coating film have been widely investigated due to the great importance of these electrodes in the electrochemical industry. The material properties are, however, not as well investigated, and the studies described in this thesis are an attempt to remedy this.

Several standard material characterization methods were used, such as SEM, TEM, AFM, EDX, XRD, porosimetry and DSC. Also, a novel model system based on spin coated electrode films on smooth substrates was developed. The model system provided a way to design samples suitable for e.g. TEM, where the sample thickness is limited to maximum of 100 nm. This is possible due to the ability to control the film thickness by the spinning velocity when using the spin coating technique.

It was shown here that the anode coating has a nanostructure. It consists of grains, a few tens of nanometers across. The nanostructure leads to a large effective area and thus provides an explanation of the supe-
rior catalytic properties of these coatings. The grains were also shown to be monocrystalline.

The size of these grains and its origin was investigated. The calcination temperature, the precursor salt and (if any) doping material all affected the grain size. A higher calcination temperature yielded larger grains and doping with cobalt resulted in smaller grains and therefore a larger real area of the coating. Some preparation conditions also affected the microstructure of the coating; such as substrate roughness. The microstructure is for example the cracked-mud structure. A smoother substrate gave a lower crack density.

The cathode of chlorate production is usually an uncoated metal plate, therefore ‘less catalytically active’. It is, however, possible to activate the cathode by for example in situ additions to the electrolyte. It was shown here that sufficient addition of molybdate to the electrolyte resulted in a molybdenum film deposited on the cathode and thereby an increase of its surface area and an activation the hydrogen evolution reaction.

**Keywords:** Sodium chlorate, ruthenium dioxide, titanium dioxide, ternary mixed oxides, cobalt doping, electrodes, nanowires, crystallites, cracked-mud structure, microscopy, diffraction, elemental analysis, calorimetry, spin coating, active area, in situ activation, molybdenum, DSA®, cathodes
Sammanfattning

Natriumklorat (NaClO₃) används främst för framställning av klor-dioxid, vilket är en blekningskemikalie för pappersmassa. Klorat tillverkas genom en elektrokemisk process där kloridjoner från koksalt (NaCl) löst i vatten oxideras till klorgas på anoden och vätska bildas på katoden (genom sönderdelning av vatten).


Två parameterar som undersökts visade sig ha inverkan på kornstorleken: bakningstemperatur, och dopning med kobolt. Om ursprungsaltet för ruteniumdioxid är ruteniumnitrosynitrat \((\text{RuNO(NO}_3)_3\)) ger en högre bakningstemperatur större korn och därmed mindre yta (per volymenhet). Om ursprungssaltet istället är ruteniumklorid \((\text{RuCl}_3)\) har inte bakningstemperaturen någon större inverkan på kornstorleken. Koboltdoping leder till mindre korn och därmed större aktiv yta.

Anodbeläggningen har även en mikrostruktur som är känd sedan länge. Också mikrostrukturen påverkas av vissa tillverkningsparametrar, exempelvis substratets ytråhet och dopning med kobolt. Ett slätare substrat ger en lägre sprickdensitet (färre sprickor per ytenhet, och här avses makroskopisk yta). Koboltdoping ger en högre sprickdensitet.


Tillverkning av klorat är en energikrävande process, och en hel del arbete har under årens lopp lagts ner på att effektivisera både elektroderna och processen som helhet. Eftersom anoden är ‘aktiv’ har en större ansträngning lagts på att effektivisera den, katoden består vanligen av en obelagd stål- eller titanplåt och är därmed ‘mindre aktiv’. Det har gjorts försök att ersätta katoden med en aktiv variant. En annan metod att aktivera katoden är att tillsätta någon substans till elektroyten, en substans som exempelvis fäller ut som en katalytiskt aktiv film på katoden och därmed aktiverar den. Det skulle kunna göras
under drift utan att de befintliga katoderna behöver bytas ut. Molybd- 
dat (MoO$_4^{2-}$) har visat sig vara en intressant kandidat – som fäller ut 
på katoden. Här visades att den utfallda filmen både ökar katodytan 
(på samma sätt som anoden har en större aktiv yta än dess makro-
skopiska) och aktiverar vätsgasutvecklingen. I dagsläget tillsätts redan 
’hjälpemikalier’, bland annat natriumdikromat (NaCr$_2$O$_7$), till elekt-
trolyten. Det gör molybdat till en ännu mer intressant tillsats. Molyb-
dat har nämligen även egenskaper som liknar kromatets och mångden 
kromat skulle då samtidigt kunna minska, eller helt uteslutas, vilket är 
positivt eftersom natriumdikromat bland annat är cancerogent.
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Christine Hummelgård
Ortsjön
October, 2012
List of Papers

1. Nanoscale characterization of crystallinity in DSA® coating
   C. Malmgren, M. Hummelgård, J. Bäckström, A. Cornell and H. Olin

2. Nanocrystallinity in RuO₂ coatings – Influence of precursor and preparation temperature
   C. Malmgren, A. K. Eriksson, A. Cornell, J. Bäckström, S. Eriksson and H. Olin

3. Spin coated titanium-ruthenium oxide thin films
   C. Hummelgård, J. Gustavsson, J. Bäckström, A. Cornell and H. Olin
   Manuscript submitted.

4. Physical and electrochemical properties of cobalt doped (Ti,Ru)O₂ electrode coatings
   C. Hummelgård, R. Karlsson, J. Bäckström, S. M. Habibur Rahman, A. Cornell, S. Eriksson and H. Olin
   Manuscript submitted.

5. In-situ activated hydrogen evolution by molybdate addition to neutral and alkaline electrolytes
6. On the suppression of cathodic hypochlorite reduction by electrolyte additions of molybdate and chromate ions
J. Gustavsson, G. Li, C. Hummelgård, J. Bäckström and A. Cornell

Comments on the papers and my contribution
In 2010, I changed my familyname from Malmgren to Hummelgård

Paper I
The idea was developed by HO and JB. I did most of the experimental work and analysis and wrote the main bulk of the paper. All authors discussed and commented on the paper

Paper II and III
The idea was developed by HO, JB and me. I did most of the experimental work and wrote the main bulk of the paper. All authors contributed to the analysis and commented on the paper.

Paper IV
The idea was developed by JB and me. I performed SEM, AFM, TEM and EDX measurements and wrote the main bulk of the paper. I did not perform the electrochemical measurements. All authors contributed to the analysis and commented on the paper.

Paper V and VI
I carried out the SEM and EDX measurements, contributed to the analysis and commented on the paper. I did not contribute to the wet chemistry.
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Wisest are those who are aware of their ignorance.
Chapter 1

Introduction

SODIUM CHLORATE (NaClO₃) is mainly used for production of chlorine dioxide, an environmentally compatible bleaching agent for pulp.¹ Sodium chlorate is produced by electrolysis of sodium chloride. Since the beginning of the 1970s, the anode of this process is a so-called dimensionally stable anode (DSA®) that consists of a metal plate coated with a catalytic metal oxide film (most commonly a titanium/ruthenium mixed oxide, Ti₀.₇Ru₀.₃O₂, on a titanium plate [1]), and the cathode is made of low carbon steel or titanium [2].

These mixed metal oxides have been used for over 40 years in the electrochemical industry as catalytically active coatings on electrodes for production of chlorine gas or sodium chlorate, electrolytic metal refinement and water electrolysis, but also as gas sensors and supercapacitors due to their excellent electro-catalytic activity, high thermal and chemical stability, low resistivity, and remarkable redox properties [1, 3–7]. The electrocatalytic properties of a metal oxide depends on both its electronic parameters and its morphology. The electronic parameters are related to the physical and chemical properties of the material, such as electronic structure and crystallinity etc. Characterization of the surface properties of the electrodes are thus of fundamental importance for understanding their electrochemical behavior [8].

There is an abundance of scientific papers about the performance and electrochemical properties of anodes coated with (Ti,Ru)O₂ and related

¹The environmental issues of paper bleaching was given much attention twenty years ago, which promoted the use of chlorate. See the fourth paragraph of section 2.1.
oxides, but the electrochemical data are rarely connected to the nature of the anode itself and there are still gaps in the knowledge about the fundamental understanding of these materials and their behavior. My ambition for the last six years has been to fill some of these gaps. The goal of my work has been to understand (and develop) the anode material, from a physical point of view. Work on the cathode have been done alongside, focusing on the reactions and electrochemical part. And of course, collaboration between the two; I have performed microscopy and material analysis on the cathodes and the anodes have been tested electrochemically.

For the cathode, the present work has been focused on in situa activation (addition of a compound to the electrolyte that enhances the electrocatalytic properties of the cathodes) of the chlorate process. The energy consumed when using a titanium cathode is higher than when a steel cathode is used, but the titanium is more corrosion resistant [2]. Much effort was put into finding a better cathode material, but none is commonly used in the industry yet. Activation of the existing cathodes has several advantages over cathode replacement. The electric energy used for electrolysis accounts for up to 80% of the variable production cost of chlorate, and with rising costs for electricity, any reduction of the cathode energy consumption is valuable.

This thesis has the following structure. First, the history and live settings of the chemistry in which these electrodes are used is presented, then, there is a short description of the material and the scientific background, this is followed by a brief presentation of sample preparation and analysis techniques. The following three chapters describe the results; Surface and near surface views, Morphology, and Bulk composition, elements and crystal structure. The order is not chronological, neither strictly paper-oriented, but rather according to question. Each chapter mainly deals with a small part of analysis and each subchapter describe an answer to a question (sometimes a whole series of measurement and an arsenal of instruments are used to answer a single question, and sometimes there are questions asked to which no answer was found). The results mainly deal with the material analysis and physical part. The electrochemical results are certainly an important part of the published (and yet to be published) papers, but is only mentioned briefly in the thesis. Finally, there is some concluding remarks including conclusion, outlook and a summary of the appended papers.
Chapter 2

Electrochemical chlorate production: past and present

Chlorine gas was first proposed as a bleaching agent in 1785. A hundred years later sodium chlorate was commercially produced. The type of electrochemical cell most commonly used for bleaching agent production today was, however, not commercially used until the beginning of the 1970s.

This chapter describes of the production of chlorine based chemicals, and specific pulp bleaching; how it was done in the past and how it is done today.

2.1 The history of bleaching textiles and pulp


The use of wood as a fibre supply for paper was not introduced until the mid 1800s. Before that, paper in the western hemisphere was almost exclusively made from rags of linen and cotton. White paper was made from rags derived from white textiles; bleaching the rags were too dif-
CHAPTER 2. ELECTROCHEMICAL CHLORATE PRODUCTION

Difficult. During this time textiles were bleached by sunlight and urine, later on a multistage process with lye, boiling water, sunlight and lactic acid was used. In 1774 chlorine gas was discovered (by C. W. Scheele) and in 1785 it was proposed as a bleaching agent. The chlorine was used in the form of an alkaline solution. Unfortunately, this chlorine solution was unstable and difficult to transport, but a major improvement was achieved in 1799 when the production of a bleaching powder – hypochlorite, began. Hypochlorite became the dominant bleaching agent for textiles, and later wood pulp, and remained dominant until the beginning of the 1900s. In the 1920s chlorine dioxide (first reported by Humphrey Davy in 1811) proved to be capable of delignification without having any negative effects on the cellulose itself (which had been a problem with chlorine gas).

Chlorine dioxide, once again, is difficult to transport (it is explosive in higher concentrations). The bleaching agent is therefore produced in two steps, first NaCl is oxidized to NaClO\(_3\), which can be transported as a dry powder, and is reduced to ClO\(_2\) at the paper mill.

The older type of bleaching, using chlorine gas (elemental chlorine) produces large amounts of chlorinated organic compounds, which are considered very toxic. In Sweden and Finland, the chlorine gas bleaching was being phased out in the 1970s and was completely abandoned in 1993, in favor of the elemental chlorine free process (using chlorine dioxide) and the totally chlorine free process (using hydrogen peroxide and ozone) [12]. Modern copy paper is also crispy white mostly due to a coating of kaolin clay [13]. However, the use of chlorine gas as a bleaching agent still (2005) stands for about 10% of the bleaching worldwide [14].

The history of chlorate

Chlorate was produced by electrosynthesis for the first time by Wilhelm von Hisinger and Jöns Jakob Berzelius in 1802. They were performing “experiments relating to the effect of the electrical pile on salts and their bases”. In one of the series, sodium chloride solution was electrolyzed between silver wires. In the remaining clear solution they found sodium chloride, silver chloride and “perhaps, hyperoxygenized muriatic sodium and a formerly unknown silver salt”. In fact, the salts were sodium chlorate and silver chlorate. Earlier electrolysis of chlo-
2.2. CHLORATE PRODUCTION CONDITIONS

Ridge did probably also lead to formation of chlorate, but Hisinger and Berzelius were the first who recognized having prepared chlorate. A definite proof of the formation of chlorate through electrolysis of chloride solutions was given by Kolbe in 1847. In 1886 H. Gall and A. de Montlaur started the first plant with an industrial-sized chlorate production. For a more detailed account of the history of chlorate, see the 1981 review by Vogt [15].

2.2 Chlorate production conditions

The environment of the electrochemical is quite aggressive, pushing the standards of the materials in the system to the limit. In production of chlorate, the electrolyte contains, in addition to brine (NaCl (aq)), hydrochloric acid (HCl) to maintain a proper pH and sodium dichromate (NaCr₂O₇) which forms a protective film on the cathode [16, 17]. Chromate also functions as a buffer to keep the electrolyte pH at an optimum level. Titanium is usually used as substrate of the anodes. The most well known chemical property of titanium is its excellent resistance to corrosion. Titanium is very easily oxidized and it is this oxide that protects the rest of the metal from corrosion. For the catalytic coating of the anode, metal oxide from the platinum group metals is mainly used, such as ruthenium dioxide and iridium dioxide. Titanium is however vulnerable to hydrogen as it penetrates into the metal and forms titanium hydride which causes embrittlement of the construction. Since the cathode is producing hydrogen gas from splitting water, there might be problems with a titanium cathode; a steel cathode corrodes if not kept under cathodic protection (negatively charged) [18].

Apart from the material in the electrodes, some other parameters are of importance for the process; the electrolyte pH and temperature, the salt concentrations and the electrode gap. The average electrolyte pH should be between 5.9 and 6.7 [19] (the local pH value varies form 4 close to the anode up to 13 – 14 close to the cathode). An elevated temperature is important for the chlorate formation and it should be at around 70°C [18]. The electrode gap (the gap between anode and cathode) needs to be smaller than approximately 0.5 cm [20]. A high chlorate concentration is essential for the crystallization of NaClO₃ and a high chloride concentration is important for the anode operation. The salt concentration, however, must have a margin to the solubility lim-
2.3 Electrochemical reactions

The electrolyte contains sodium chlorate at a concentration just below the crystallization level, and the electrolyte is circulated. To the electrolyte pumped in at one end of the chlorate cell, sodium chloride dissolved in water is added (figure 2.1). The electrolyte pumped out in the other end has a higher chlorate concentration, still under the crystallization level. In the next step some of the sodium chlorate is extracted, and dried while the remaining electrolyte returns for another cycle. At the anode, chlorine gas is made from sodium chloride (NaCl), while the
2.3. ELECTROCHEMICAL REACTIONS

cathode splits water into hydrogen gas and hydroxide ions (OH⁻);

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-, \]  
\[ (2.1) \]

and

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- . \]  
\[ (2.2) \]

If the anode and the cathode are not kept apart, the hydroxide will react with the chlorine and form hypochlorite (\(\text{ClO}^-\)) [11], or (if the electrolyte temperature is higher than 60 °C) a stable salt - sodium chlorate;

\[ \text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O} \]  
\[ (2.3) \]

or

\[ 3\text{Cl}_2 + 6\text{OH}^- \rightarrow 5\text{Cl}^- + 3\text{ClO}^- + 3\text{H}_2\text{O} . \]  
\[ (2.4) \]

To avoid that the intermediate hypochlorite and the product chlorate are reduced on the cathode;

\[ \text{ClO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^- \]  
\[ (2.5a) \]

\[ \text{HClO} + \text{H}^+ + 2e^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \]  
\[ (2.5b) \]

\[ \text{ClO}_3^- + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Cl}^- + 6\text{OH}^- , \]  
\[ (2.5c) \]

hexavalent chromium, \(\text{Cr(VI)}\), is added to the electrolyte in the form of sodium dichromate. The sodium dichromate forms a protective film of chromium (III) hydroxide \((\text{Cr(OH)}_3)\) on the cathode surface [2,21,22].

There are a number of possible anodic side reactions leading to formation of oxygen gas [16]. In the absence of hypochlorite, at a potential\(^1\) lower than the reversible potential for chlorine evolution, the main reaction is oxygen evolution from water discharge;

\[ 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4e^- . \]  
\[ (2.6) \]

\(^1\)Voltage between the working electrode, in this case the anode, and a reference electrode.
Hypochlorite in combination with water [23] can also be a source of oxygen evolution;

\[
12\text{ClO}^{-} + 6\text{H}_2\text{O} \rightarrow 4\text{ClO}_3^{-} + 8\text{Cl}^{-} + 24\text{H}^{+} + 3\text{O}_2 + 12\text{e}^{-} \quad (2.7a)
\]

\[
\text{ClO}^{-} + \text{H}_2\text{O} \rightarrow \text{Cl}^{-} + 2\text{H}^{+} + \text{O}_2 + 2\text{e}^{-}. \quad (2.7b)
\]
Chapter 3

Electrode fabrication and materials

The most common electrode manufacturing process is pyrolytic treatment of a gel-like precursor solution deposited on a metal substrate. The production method is simple, economical and allows tuning of a wide range of parameters.

The manufacturing process of the anode is described in this chapter, together with a short history of development. A review of the research field of these materials is presented as background in order to place this thesis in its scientific context together with some open problems.

3.1 Industrial anode manufacturing

The standard anode\(^1\) consists of a titanium plate coated with a catalytic metal oxide, usually containing RuO\(_2\) and/or IrO\(_2\). The coating is applied as a precursor solution of metal salts dissolved in a solvent (alcohol or acidified water is commonly used). One of the most commonly used application technique is spray coating.\(^2\) The concept is simple; a spray robot creates a mist of the coating solution that is then attracted to the substrate by an electrical field applied between the nozzle and the substrate [24]. The coated substrate is then dried (in air, typically

---

\(^1\)Dimensionally Stable Anode (DSA\(^\text{®}\)), described in section 3.2.

\(^2\)Not to be confused with spray pyrolysis. More coating and application techniques are described in section 4.1.
80 – 110 °C) and annealed at a higher temperature (350 – 500 °C) to calcine the amorphous coating to a crystalline oxide. This coat-dry-anneal procedure is repeated until a desired thickness is obtained. A typical coating of a commercial DSA® is around 10 µm thick. Parameters involved during coating preparation such as solvent, deposition technique, precursor, and calcination atmosphere and temperature are known to influence the physical and electrochemical properties of the coatings. [4]

In order to obtain a uniform precursor solution, all the salts should be completely dissolved. In the literature, the composition of the coating is always calculated from the components dissolved in the painting solution, thus assuming that all the applied material is transformed to the corresponding oxides, with a deposition yield of 100 %. The deposition yield of some metal salts is not always 100 %, and the actual coating composition on the calcined anode, can be different from the composition of the painting solution. [25]

The economical and simple method of thermal decomposition of an aqueous salt solution creates a film that is stable during gas evolution reactions in aggressive environments.

3.2 The history and development of the DSA®

In 1998, Hayfield published a series of articles summarizing the history and development of the DSA® [26–28]. The DSA® as it is known today was patented by Beer [29] in 1965. The invention provided lower cell-voltage, longer electrode lifetime, better product quality and mostly, more stable production conditions, for the chlor-alkali and chlorate industry. The name ‘dimensionally stable’ originates from the electrodes used in chlorate production prior to the invention of the DSA®: graphite blocks. In use, the graphite block is slowly consumed to form CO₂ and therefore the electrode gap is not constant, but has to be adjusted many times.³ The invention of the DSA® gave the advantage of an electrode that is not consumed during the process and an electrode gap that does not needs to be adjusted. The coating of the DSA® eventually stops working (a typical lifetime is about ten years) and has to be replaced,

³In order to keep the electrolysis conditions constant the electrode gap needs to be constant, see the second paragraph of section 2.2.
3.2. THE HISTORY AND DEVELOPMENT OF THE DSA®

Figure 3.1: Photo of anode assembly for chlorate production. The electrodes are usually assembled in electrode packages with anodes on one side and cathodes on the other side, or just the anodes in the package using the cell-box as cathode. In the electrode package case, a couple of packages are stacked in one cell, and in addition, there is also an anode end-package (photo) in one end and a cathode end-package in the other. The typical chlorate plant contains several cells. Photo reproduced with permission from Permascand.
CHAPTER 3. ELECTRODE FABRICATION AND MATERIALS

but the dimensions of the anode are constant. Figure 3.1 shows a photo of an anode assembly.

By the mid 1950s high quality titanium started to be produced and it was discovered that it had good electrochemical properties and good corrosion resistance. However, in some environments titanium shows a tendency to corrode. J.B. Cotton (head of research and development at a British company called ICI) experimented with attaching other metals to the titanium in order to minimize the risk and in 1958 he found that when spot welding a small piece of platinum wire to the titanium, current passed through the platinum. The concept of the platinum coated titanium bielectrode had thus been recognized. Totally independent of the ICI work, an employee of Magneto Chemie in The Netherlands, H.B. Beer, had taken out a patent on rhodium-plated titanium. Its priority was just a few weeks before that of the ICI patent. Two years later Angell (ICI) proposed an alternative to electrodeposition of coatings. His method was to take a solution containing a soluble noble metal salt, apply it as paint to the titanium surface and then heat it in air to transform the salts to oxide. The consequence of the two 1958 patents was an agreement between Magneto Chemie and ICI, under which the development of titanium-based electrodes to replace graphite electrodes in chlorine cells was going to be shared. Beer was going to work on coating formulations, while others were going to concentrate on assessing the commercial viability of the coatings on titanium electrodes. The agreement stayed in force for several years, not being terminated until 1965, when Beer filed the patent of ruthenium oxide coating.

3.3 Open problems

The introduction of DSA® was nothing less than a technological revolution at the time [1], and the electrochemical properties of the anode oxide have been widely investigated [30]. The effects of precursor and preparation temperature have been studied [31–34] as well as the electrochemical properties of mixed oxides of different kinds [35–40]. The morphology of the anode is sometimes investigated [41–43], but is seldom analyzed in terms of origin.

Despite that the material systems having been industrially important for a long time, the fundamental material properties are largely unex-
3.3. OPEN PROBLEMS

Pure TiO$_2$ is by contrast very well studied [44–46]. Also studies of pure RuO$_2$ can be found, but for the mixed oxide the research is limited. The field has lately become mature enough to allow for a microscopic understanding of what the structure and fundamental properties are, and how they connect to electrochemical performance. To some extent, research about the connection between microscopic structure, electronic properties and electrochemical performance of oxides have started to emerge [47–50].

The two oxides TiO$_2$ and RuO$_2$ is crystallographically very similar and a solid solution of the rutile$^4$ titanium-ruthenium oxide system is expected, although a small amount of pure TiO$_2$ in anatase form is common [51]. Separation into two separate rutile structures has been hinted [52], and phase separation between main and additional catalytic oxides are also discussed in the literature [40, 50], but the number of publications is limited.

Also, the metal substrate has to be considered a part of the system. Ions from the substrate might enter the coating film and affect its electrochemical properties [53]. This effect decreases the possibility to investigate the electrochemical properties intrinsic to the coating, but can be circumvented by replacing the metal substrate with an inert one [54]. Contamination from the substrate has also been suggested as cause for deactivation or passivation of the electrode during long time use [55]. Another characteristic of a metal substrate is the surface roughness, that causes the coating film to be of uneven thickness and also complicating the determination of the film thickness.

Addressing the cathode, many attempts have been made to replace the cathode material in the chlorate process with coatings containing ruthenium compounds as electrocatalyst [56, 57]. In situ activation has several advantages over cathode replacement. Molybdate (MoO$_4^{2-}$) has shown some promising features as in situ activator for hydrogen evolution, both in chlorate electrolyte [58, 59] and in strongly alkaline solution [60–65].

To prevent the intermediate hypochlorite and the product chlorate from being reduced on the cathode, sodium dichromate is added to the electrolyte. The chromate forms a blocking film on the cathode surface.

$^4$Rutile and anatase are possible crystal structures of titanium dioxide. Ruthenium dioxide only crystallizes in rutile.
[21, 22]. Molybdate is, as opposed to dichromate, not very toxic and is used as an environmentally friendly alternative to dichromate in corrosion applications [66]. Molybdate also buffers in a pH region close to that of dichromate [59]. At low levels of molybdate or dichromate, an additional buffer may be needed to stabilize the electrolyte pH in the chlorate process at 6 – 7. Phosphate (PO$_4^{3-}$) is a possible buffer alternative, which may also form cathode films that can affect the current efficiency [67] and thus the current efficiency in electrolytes containing combinations of molybdate, dichromate and phosphate are of interest.
Chapter 4

Methods

To provide a greater understanding of the material characteristics of these materials, a long list of measurement techniques were used. In this chapter, the basics of sample preparation and the analysis techniques used are briefly described. The interested reader is referred to the literature for each section (and to Wikipedia for a more popular version; en.wikipedia.org). For measurement details, see the individual papers.

4.1 Sample preparation

In laboratory scale (in contrast to industrial manufacturing), many more application and coating techniques are available, since only a limited number of small sized samples are studied. Table 4.1 summarizes some of the alternative deposition techniques available in laboratory scale, some of which are also possible to use in large scale industrial production. Commonly used are brush or dip coating in which the losses of active material is minimized [25, 68]. However, there is an uncertainty in obtaining a desired film thickness with these techniques. By spin coating on a flat substrate, films of uniform and accurately controlled thickness can be reproducibly prepared.

Spin coating can be used under large scale industrial conditions provided that each unit is quite small (less than 15 cm in diameter), as is done in the electronics industry e.g. for photoresist application, but can not be used for industrial electrode manufacturing due to material
**Table 4.1: Different coating techniques**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolytic</td>
<td>A precursor salt is dissolved in a solvent (alcohol or acidified water). The solution is applied to the substrate using one of several available techniques. The substrate is then heat-treated in two steps; to dry out the solvent at a mediate temperature and to calcine the coating at an elevated temperature.</td>
<td>[68–70]</td>
</tr>
<tr>
<td></td>
<td>**</td>
<td>Solvent</td>
</tr>
<tr>
<td>Aqueous</td>
<td>Spray*</td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td>Dip*</td>
<td></td>
</tr>
<tr>
<td>Sol – gel</td>
<td>Brush*</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>d</em></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spin</td>
<td></td>
</tr>
<tr>
<td></td>
<td>up to 600 °C</td>
<td></td>
</tr>
<tr>
<td>Spray pyrolysis*</td>
<td>The same coating solution as described above is applied by spraying onto a preheated substrate (300 - 600 °C). The coating is then immediately calcined.</td>
<td>[71]</td>
</tr>
<tr>
<td>Reactive sputtering</td>
<td>Metallic precursor is sputtered onto the substrate in vacuum. Results in a metallic, rather than oxide coating.</td>
<td>[72]</td>
</tr>
<tr>
<td>Chemical vapor deposition (CVD)</td>
<td>A precursor is vaporized using heat and blown onto the substrate using a flow of e.g. O₂. Low pressure is needed. The precursor is metallic, the obtained coating becomes an oxide.</td>
<td>[6]</td>
</tr>
<tr>
<td>Electro-deposition</td>
<td>The substrate is placed in the precursor solution and the metal is forced to deposit on the substrate by polarization.</td>
<td>[7]</td>
</tr>
</tbody>
</table>

* Suitable to use also in industrial production.
4.1. SAMPLE PREPARATION

Figure 4.1: Schematic picture of spin coating process.

Figure 4.2: Coating weight as a function of $1/\sqrt{\omega}$ with $\omega$ given in revolutions per minute (rpm) for a silicon wafer of 10 cm in diameter. The blue line is a linear regression fit to data. Spin coating is usually performed with polymer solutions with a rather high viscosity, however the measurements agree well with the model even though the n-propanol based ruthenium-titanium solution used here is of low viscosity.
losses. The spin coating technique has been known for decades, it is an excellent method for making high quality thin films and has been proven a good technique for making long lasting electrodes for oxygen evolution [68].

The principle of spin coating is that a circular substrate is placed on a vacuum chuck that can rotate in high speed (typically 6000 rpm). A liquid solution is dripped onto the substrate, and while it then spins the liquid is caused to form a thin layer of very homogenous thickness on the substrate. The redundant solution is spun off (figure 4.1). Schubert and Dunkel [73] presented a simplified model for prediction of the film thickness in spin coating:

\[ h_\infty \sim \omega^{-1/2} \eta^{1/3} c_0, \] (4.1)

where \( h_\infty \) is the coating thickness after infinite spinning time, \( \omega \) is the spinning velocity, \( \eta \) the viscosity of the solution, and \( c_0 \) the concentration of film-forming material in the initial coating solution. For a fixed solution the thickness is proportional to \( 1/\sqrt{\omega} \). The coating weight is proportional to the coating thickness, provided homogeneous composition of the calcined coating and equal size of the coated wafers (figure 4.2).

4.2 Atomic force microscopy

Atomic force microscopy (AFM) is a technique to obtain information about the topography of a small part of the sample (the maximum scanning area is around 100 \( \mu m \) by 100 \( \mu m \)). The AFM consists of a microscale cantilever with a sharp tip at its end, that is used to sense the specimen surface. When the tip is brought close to a sample surface, forces between the tip and the sample lead to a deflection of the cantilever. The deflection is measured using a laser spot reflected from the cantilever into a position sensitive photodiode. A disadvantage of AFM is the scan size, and maximum scannable height (around 5 \( \mu m \)). The operator therefore needs to have some knowledge about the surface roughness beforehand. Another inconvenience is that an incorrect choice of tip for the required resolution can lead to image artifacts. Another common artifact is the double tip (figure 4.3), it occurs when the
4.2. ATOMIC FORCE MICROSCOPY

Figure 4.3: (a) Example AFM image and (b) same sample with double tip artifact. With a double tip, all features of the sample surface are registered twice and appear in the image with a ‘shadow’.

tip is damaged or some particle has attached to it. The atomic force microscope can provide good images of very small features on the sample surface but is not recommended as the first instrument to use when examining an unknown sample. [74, 77]

There are some different modes in which the AFM can work. The first mode invented was contact mode. The tip is dragged along the surface and the static tip deflection is used as a feedback signal. The problem with this technique is that a soft sample could be damaged by the tip, a very hard sample on the other hand might break the tip. Non-contact modes were therefore invented, using the interaction forces between the tip and the sample to regulate the frequency or amplitude of the oscillating tip when it approaches the sample surface.

In tapping mode, the cantilever is driven to oscillate up and down at near its resonance frequency by a small piezoelectric element mounted in the AFM tip holder. The amplitude of this oscillation is typically 100 to 200 nm. Due to the interaction of forces acting on the cantilever when the tip comes close to the surface, the amplitude of this oscillation decreases as the tip gets closer to the sample. The height of the cantilever above the sample is then corrected to maintain a set cantilever oscilla-
tion amplitude as it is scanned over the sample. A tapping AFM image is therefore produced by imaging the force of the intermittent contacts of the tip with the sample surface. [74]

4.3 Electron microscopy

Scanning electron microscopy (SEM) is primarily used to study surfaces. It can be used in the same ways as an optical microscope, or to get information about relative atomic weight in the sample. The transmission electron microscope (TEM) is used to study the interior and structure of a sample.

Simply put, the electron microscope consists of an electron gun, a few magnetic lenses and scanning coils, and a detector. The electron gun emits the electrons and accelerates them (typically up to 20 kV in SEM and 200 kV in TEM), creating an electron beam directed at the specimen. In the SEM, the sample is placed at the bottom of the column. The electron beam is scanned across the specimen and the detector counts the number of scattered electrons from each point on the surface. In the TEM, the sample is placed in the middle of the column with magnetic lenses both above and below it. A fluorescent imaging disc, placed at the bottom serve as detector. Unlike SEM, that can analyze bulky samples, TEM requires a very thin sample (less than 100 nm) which almost always means complicated sample preparation. The sample is normally placed on a TEM-grid with a diameter of 3 mm. A disadvantage of the SEM is the requirement of electrically conductive samples, otherwise the electron beam will charge the sample and essentially decrease the quality of the image. If the sample is not conductive, a thin conductive layer of graphite or gold can be deposited on it, to avoid charging. As an electron gun requires vacuum, the sample in both SEM and TEM can not usually contain gas or water as it would contaminate the system. [75–78].

Electron-specimen interaction

When an electron beam hits a solid material, electrons (secondary electrons) as well as x-rays are released from the specimen. The electrons from the primary beam can be back-scattered (back-scattered electrons),
4.3. ELECTRON MICROSCOPY

The primary beam can be back-scattered, diffracted or pass through the specimen. On its way it releases secondary electrons and x-rays from the specimen.

diffracted or pass through the specimen as a transmitted beam (figure 4.4).

The number of secondary electrons emitted per second is high, and secondary electrons are therefore the most commonly used imaging signal in SEM (secondary electron mode). As the secondary electrons have low energy (less than 50 eV) they interact strongly with the atoms of the sample material. The detected secondary electrons usually comes from the immediate surface of the specimen as those created deeper into the material are absorbed on their way out. Due to their low energy, the secondary electrons need to be accelerated into the detector, which means that the detector also detects electrons that were not initially traveling
towards it. This in turn means that the image is given perspective and an illusion of being three-dimensional.

**Back-scattered electrons** have lost some of their energy when colliding with the specimen and therefore contain information of the surface material. These electrons may be used in SEM (*back-scatter mode*) to produce an image that shows relative atomic weights in the specimen, as a heavier atom scatter more electrons from the beam than a light one. A light spot on a back-scatter mode image indicates an area with heavier atoms than the surrounding area, and vice versa. Back-scattered electrons come from the near surface region (a fraction of a micrometer down in the specimen). They have to be directed towards the detector to be caught (unlike the secondary electrons that are attracted by the high potential accelerator of the detector) and a shadow-effect can be obtained by tilting the sample, providing typographic information.

The **transmitted beam** is used for imaging in TEM. There are two types of contrast mechanisms in TEM. *Mass-thickness contrast* means that a thick sample or a sample containing heavy atoms will transmit fewer primary electrons than a thin sample containing light atoms. *Diffraction contrast* occurs in crystalline samples. The diffracted electrons will not hit the imaging disc in imaging-mode, the diffraction will therefore cause the image to be darker. Different orientation of the crystals in the sample will cause more or less of the primary beam to be diffracted. An image of a sample of uniform thickness, containing just one atom type, could still show grain boundaries as a result of different grains oriented in different ways. One or both of these contrast mechanisms may contribute to the appearance on the TEM image. The diffracted electrons contain information on crystal structure of the specimen and is used in TEM for electron diffraction.\(^1\)

The **x-rays** emitted from the specimen arise when excited atoms are relaxed. Excitation of atoms occur when the incoming electron knocks out one of the inner electrons. The x-rays contain information about the chemical composition of the sample and can be used for elemental analysis.\(^2\) [75–77]

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1 The electron diffraction technique is presented in section 4.4.
2 A couple of examples of elemental analysis techniques are presented in section 4.5.
4.4 Resolution in electron microscopy

Since the electrons used in SEM and TEM have shorter wavelength than photons in the visible range, the resolution of an electron microscope is better than of an optical one. The wavelength depends on the acceleration voltage and is calculated by the de Broglie equation:

$$\lambda = \frac{h}{p} \Rightarrow \lambda = \frac{h}{\sqrt{2m_0eU}}.$$  \hspace{1cm} (4.2)

The energy used in an electron microscope is several kilovolts, causing the electrons to travel at an appreciable fraction of the speed of light, therefore relativistic effects has to be taken into account;

$$\lambda = \frac{h}{\sqrt{2m_0eU}} \frac{1}{\sqrt{1 + \frac{eU}{2m_0c^2}}}.$$ \hspace{1cm} (4.3)

In a SEM with an acceleration voltage of 20 kV, $\lambda$ is 8.5 pm and in a TEM with $U = 160$ kV, $\lambda$ is 2.9 pm.

If all parts of an imaging system are considered to be perfect, then the resolution of any imaging process will be limited by diffraction. This leads to the simplified statement that the limit of resolution of any imaging process is going to be on the order of the wavelength of the wave used to image it. However, the resolution in the TEM is lowered by aberration resulting in a (line)resolution\(^3\) of about 3 Å. In the SEM the resolution depends both on the spotsize (which in turn depends on i.a. the wavelength) and the “large” volume of the sample that is affected by the primary beam (figure 4.4) which lowers the resolution to approximately 10 nm. [76–78]

4.4 Diffraction

Electron diffraction is a mode in transmission electron microscopy, focusing the primary beam to a minimal spot. A diffraction pattern with spots evince that the material is crystalline. For each crystal direction, a set of spots will appear in the pattern, rotated compared to the previous. A powder, or poly-crystalline sample, would therefore be represented

\(^3\)Data for a JEOL 2000fx [80].
by a pattern of circles. Just one set of spots in the diffraction pattern is evidence of monocrystallinity (figure 4.5). The pattern itself is unique for each type of crystal structure and can be compared to a theoretical pattern found in a database to determine the crystal type in the sample. [77–79]

X-ray diffraction gives about the same information about the specimen as electron diffraction, but can be performed on a bulk sample. It is a technique where the crystal structure of a sample is obtained by analyzing the angles at which the peaks of the diffractogram appear. It can also be used to estimate the average crystal size as it is a volume averaging technique. This is done by measuring the width of the peaks; the larger the crystallites, the narrower the peak. The estimation is valid under the assumption that all line broadening is due to finite crystallite sizes. Calculations are made using the Scherrer equation;

\[
L = \frac{K \lambda}{\beta \cos \theta},
\]  

(4.4)

where \( L \) is the mean size of the crystallites in the sample, \( K \) a constant approximately equal to unity, \( \beta \) is the width of the peak (at half maximum intensity) in the diffraction profile (measured in radians) and \( \theta \) is the angle at which the peak appears. [79,81]
4.5 Elemental analysis

When materials are exposed to short-wavelength x-rays, gamma rays or a high energy electron beam, ionization (ejection of one or more electrons from the atom) may take place. The removal of an electron from an inner orbital make the electronic structure of the atom unstable, and electrons in higher orbitals “drops” into the lower orbital to fill the hole left behind. Transition from one orbital to a lower one generates a release of energy in the form of a photon. Thus, the material emits radiation, which has an energy characteristic of the atoms present (the energy difference between the two orbitals involved). The emitted radiation is detected and presented as a spectrum of intensity versus photon energy. The number of photons of each characteristic radiation is directly related to the amount of the corresponding element in the sample.

When the primary beam is electrons (in an electron microscope) the technique is called energy dispersive x-ray spectroscopy (EDX) and when the primary beam is x-rays the technique is called x-ray fluorescence (XRF). The maximum energy of the emitted x-rays is limited by primary beam energy. Heavier elements generally have larger energy gaps between the orbitals than lighter elements and thus require higher acceleration voltage of the instrument to be detected. Also, the lowest energy detectable is limited by the detector window (protection of the detector). A window made of beryllium (common) limits the detectable elements to nothing lighter than sodium ($Z = 11$). An ultra thin window (made of a polymer) allows for detection of elements heavier than boron ($Z = 5$). [76]

Using x-ray photoelectron spectroscopy (XPS) it is possible to determine not only the elemental composition of a specimen, but also the chemical and electronic state of those elements. For XPS, the primary beam is x-rays, which knocks out electrons from the specimen (photoelectric effect). XPS requires ultra-high vacuum conditions and detects only those electrons that have actually escaped into the vacuum of the instrument (originated from within the top 10 nm of the material). The kinetic energy of the emitted electrons is measured and the electron binding energy of each of them is then calculated. Each element produces a set of XPS peaks at characteristic binding energies. The intensity of each of the characteristic peaks is proportional to the amount of the corresponding element within the irradiated area. XPS can detect
Figure 4.6: Schematic DSC curve demonstrating the appearance of some common features. (a) Evaporation of solvent (or melting), (b) glass transition, (c) oxidation or crystallization. Exothermic reaction upwards.

elements heavier than lithium (Z = 3). [82]

4.6 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique, other examples are Differential thermal analysis or Thermogravimetric analysis. In DSC, the temperature of the sample holder is increased linearly with time, and the difference in the amount of heat required to increase the temperature of a sample and a reference (empty crucible) is measured. The resulting curve of heat flux is plotted either versus temperature or versus time. The basic principle is that when the sample undergoes a physical transformation, more or less heat will need to flow to it than to the reference to maintain both at the same tem-
4.7 Porosimetry

Porosimetry is used to analyze a porous material, to determine average pore diameter, total pore volume, surface area, etc. A non-wetting liquid (often mercury) is pushed into the material using high pressure. In case of a fully wettable capillary, the pore size can be calculated using Washburn’s equation;

\[ L^2 = \frac{\gamma D t}{4\eta}, \]

where \( t \) is the time for a liquid of dynamic viscosity \( \eta \) and surface tension \( \gamma \) to penetrate a distance \( L \) into the capillary whose pore diameter is \( D \). Washburn’s equation is based on the external pressure needed to force the liquid into a pore against the force of the liquid’s surface.
tension and describes capillary flow in a bundle of parallel cylindrical
tubes. [87]

A variation of the technique is to use liquid nitrogen instead of mer-
curry as the nitrogen can penetrate deeper into the material and thus
measure smaller pores (less than 6 nm in diameter, which is the limit for
mercury). The calculations in this case are based on adsorption and des-
orption isotherms of the nitrogen using the Barrett, Joyner, Halenda model
[88]. Knowing the pore size distribution, the surface area of the sample
can be calculated using the Brunauer, Emmet, Teller function (BET) [89].
In case of a porous material, many issues have been raised both about
the physical meaning of the calculated pore diameter. [90]

4.8 Electrochemical measurements

Cyclic voltammetry is a type of potentiodynamic electrochemical mea-
urement (this means varying the voltage and measuring the current).
In cyclic voltammetry the working electrode potential is ramped lin-
early versus time, when the potential reaches the set point the potential
ramp is inverted, creating a cycle. This is repeated multiple times dur-
ing an experiment [91]. The current will (if there is a double layer capac-
itance of the electrode) create a hysteresis depending on the number of
chargeable sites on the electrode surface [92]. The more sites, the larger
the hysteresis. The voltammetric charge (q*) is obtained by integrating
the current with respect to time and is an estimate of the active surface
area of the electrode [93]. The voltammetric charge is larger for slower
sweep rates [94] as there is a diffusion limitation of electrolytes species
and a slower sweep rate gives the species more time to penetrate into
the electrode.

A Polarization curve is a series of galvanostatic measurements, mean-
ing setting the current density and measuring the potential. The current
densities are often logarithmically spaced over the total measurement
range (typically 1 to 1000 A/m², with ten current densities per decade).
All these potential values are then plotted against the current density.
The gradient of the resulting curve is called Tafel slope (measured in
mV/decade) and gives an indication of reaction speed. There can be

\[\text{The voltage is applied between anode and cathode, but the feedback is a measurement of voltage between the working electrode and a reference electrode.}\]
4.8. ELECTROCHEMICAL MEASUREMENTS

several intervals with different Tafel slope values. The potential difference between each point and the a half-reaction’s thermodynamically determined reduction potential is called the overpotential in that point. The overpotential is the ‘cost’ for the electrode, and a higher overpotential indicates a larger energy consumption [95]. Polarization curves can be obtained either anodically (positive current) or cathodically (negative current).

These measurement are often stated to be iR-corrected (any effect of a serial resistance in the system is excluded from the result). One way to do this is by current interrupt [96], which means that the current is very quickly turned off and the potential change during some tenth of a millisecond after the cutoff is recorded. Galvanostatic polarization is also used as a single measurement to investigate long term physical change on the electrode surface, or to place the electrode in steady state (charge the double layer capacitance of the electrode) prior to an experiment.

When performing a galvanostatic polarization of an electrode, the current efficiency (how much of the applied current is actually consumed by the desired reaction) can be obtained by measuring the amount of evolved gas per time unit. For this experiment, the anode and cathode has to be separated using a divided cell [97]. The current used for the desired reaction can be calculated from the reaction rate (the number of electrons needed per mole evolved gas is known) and is converted to current efficiency by dividing by total applied current. [98]

A Polarization sweep on the other hand is a potentiodynamic measurement, simply explained as one half cycle in cyclic voltammetry. This is used to see any limiting current, i.e. there is a terrace point in the IV-curve where the potential has to be substantially increased in order for the current to start increasing again. A limiting current is an evidence of a reaction taken place (and can be used to detect an undesired side reaction based on the current where it appears). [91]
Chapter 5

Surface and near-surface views

To the naked eye, an anode looks unreflectingly dark gray or, if the coating is thin, tinged with yellow, red, green or blue. By zooming in just a couple of hundred times, using an optical microscope, a different world appears. A spiderweb of lines stretches across the surface. Some thousand times of magnification makes the thin lines feel like canyons and a hundred thousand times of magnification revels the very heart of the coating structure.

This chapter deals with imaging of the anode and cathode; commercial, model and manipulated systems. Imaging means viewing and measuring in the obtained images without analyzing. The analyses of the structures are described in the next two chapters.

5.1 Cracked-mud structure

Dimensionally stable anodes consist of a catalytically active metal oxide film on a metal support. Solvent leaving the coating, and tensions in the substrate, cause the coating to crack during drying and calcination. The surface will then look a bit like the surface of a dried river course. This is called the ‘cracked-mud’ structure (figure 5.1) and was first described by Pizzini et al. [99] in 1972. The cracks, observed in cross section SEM (figure 5.2), was seen to pass through several layers in the
32

CHAPTER 5. SURFACE AND NEAR-SURFACE VIEWS

Figure 5.1: SEM image of DSA® coating. Solvent leaving the coating, and tensions in the substrate cause the coating to crack during drying and calcination. Through the cracks, the layers underneath can be seen.

Figure 5.2: Cross section image of a DSA® coating. (a) SEM image. The cracks is seen to pass several microns down the coating. Inset: The separate layers are visible as altering dark (titanium-rich) and bright (ruthenium-rich) lines. (b) TEM image. The structure of each layer can be seen, with a dark ruthenium-rich core flanked by brighter titanium-rich stripes on both sides.
Figure 5.3: SEM image of 500 nm thick coating (Ti$_{0.7}$Ru$_{0.3}$O$_2$) spin coated onto (a) silicon wafer, (b) mirror polished titanium plate and (c) grit-blasted titanium plate. The smoother the substrate, the lower the crack density in the coating.

cracking. The separate layers can be seen as altering bright (ruthenium-rich) and dark (titanium-rich) lines. In cross section TEM (looking at a thin slice of the coating) the structure of each layer were revealed, with a dark ruthenium-rich core flanked by brighter titanium-rich stripes on both sides.

5.2 Substrate impact on the microstructure

The cracked-mud structure is not uniform across the surface of a standard anode, as the crack density varies. This might be due to a varying coating thickness. With spin coating, the coating thickness is controlled...
by the spinning velocity [73].

In the present study, the differences of the crack density was shown to be dependent on the substrate roughness for a given coating thickness. The almost atomically flat surface of the silicon substrate gave a coating with very few cracks and the plaquettes in this case became several millimeters across. Figure 5.3a shows a portion of a surface where two cracks meet. On a polished titanium plate (figure 5.3b) the plaquettes were also large, typically 100 µm across. On a rough surface, e.g. a grit blasted titanium plate (figure 5.3c), coating solution accumulated in the valleys and resulted in non-uniform thickness and, consequently, areas with more or less cracked-mud microstructure. The coating plaquettes also became quite small. Therefore, the smoother the substrate, the lower the crack density in the coating.

5.3 Increased crack density when doping with cobalt

The cracking of the coating might also depend on the coating itself and its contents. By making two samples with the same coating thickness on the same type of substrate, it was possible to see the effects of an extra component in the coating. Doping with cobalt affected the cracked-
mud structure of the (Ti,Ru)O$_2$ mixed oxide in that the crack density increased (figure 5.4). With 10 mol% of cobalt in the mixture, the increased crack density was most distinct for thin coatings and had almost vanished when the coating thickness reached 3 μm. This effect have been noted by da Silva et al. [100], but only if the amount of cobalt in the mix is larger than 50 mol%.

5.4 Coating grains

DSA® coatings has an effective surface area that is 10 – 1000 times larger than the visible surface [1]. However, the high increase in surface area cannot be explained by the cracked-mud structure alone. A closeup on the top of a plaquette using an atomic force microscope, revealed a rough surface at the nanoscale (figure 5.5a). Transmission electron microscopy showed that this was not just a surface phenomenon, but the entire coating is built up of 20 – 30 nm sized grains (figure 5.5b). The grains are visible in the image as irregular, facetted “circles” (a two-dimensional image of a three-dimensional “spherical” structure) of different intensity of gray. The bumps in the AFM image are the tops of the close packed grains on an electrode surface.

By electron diffraction in the electron microscope, the sample was discovered to be crystalline. The beam can also be focused on a single grain, which revealed a monocrystalline rutile structure (figure 5.6). That is, each grain is a single crystal and if measuring the average crystallite size of a sample the number would also be the average grain diameter.

5.5 Thin film electrodes

The sample preparation of an anode for cross section imaging is quite complicated as it consists of moulding in epoxy, extensive cutting, grinding and polishing. It is also difficult to measure and define the obtained coating thickness if the substrate is rough, which is usually the case for a titanium plate. An average value for the whole electrode does not
CHAPTER 5. SURFACE AND NEAR-SURFACE VIEWS

Figure 5.5: (a) AFM image of the top of a plaquette. 30 nm wide grains are closely packed together all over the plaquette top surface. The grayscale represents a height difference of 10 nm. (b) TEM image of coating scraped off the substrate and placed on a TEM grid. The entire coating consists of 20 – 30 nm grains. (The sharp, black, slightly elliptical spot in the centre is an artifact. It originates from the non-fluorescent centre spot on the imaging disc.)

Figure 5.6: (a) Electron diffraction from one coating grains. (b) Theoretical diffraction pattern from rutile. The extra set of spots in the diffraction pattern (marked with an arrow) could be due to double diffraction or superlattice reflection [78].
Figure 5.7: Cross section SEM image of a silicon wafer spin coated with 450 nm of Ti$_{0.7}$Ru$_{0.3}$O$_2$. Prior to the coating the wafer was deposited with 150 nm of titanium.

Figure 5.8: TEM image of Ti$_{0.7}$Ru$_{0.3}$O$_2$ spin coated onto a silicon nitride TEM grids at 5500 rpm. The individual grains in the coating can be seen as gray spots. (The larger black spot just below the center is an imaging artifact.)
say much about the actual case. To simplify cross section imaging, the titanium substrate was replaced by a single crystal silicon wafer. The silicon wafer is easily broken, and if the coating is not too thick it follows the breaking direction of the wafer. The piece was then placed standing in a spring (coil) on a SEM holder. This method was shown to be a quick and uncomplicated way of studying the film thickness. The sample in figure 5.7 consists of a silicon wafer coated with an about 450 nm thick layer of (Ti,Ru)O$_2$ (measured in the image). Between the wafer and the coating is a 150 nm layer of titanium that was evaporated onto the wafer prior to the coating. The titanium layer is clearly visible as a brighter line. Calculations of the film thickness were made based on the weight increase according to:

$$h = \frac{m}{\rho A}$$

(5.1)

where $h$ is the film thickness, $m$ the weight increase, $\rho$ the density of the oxide and $A$ the sample area. The calculated thickness was for this sample 414 nm.$^1$ The difference derive from the porosity in the coating and the uncertainty of the density of the mixed oxide. Knowledge about the actual film thickness makes studies on loading versus activity as well as electrolyte penetration depth less complicated.

When instead studying a sample in TEM, other issues occur. A limitation of the TEM is the maximum sample thickness of just 100 nm. To be able to use TEM to study the grains of a standard anode, the substrate has to be removed and just a thin layer of the coating placed on the TEM grid. The easiest way to do this is to scrape the coating off the substrate with a sharp knife and place the crumbs on the TEM grid.

Using the spin coating technique, with high spinning velocity, to apply the coating and a silicon nitride TEM grid as substrate it was here shown that the coating could be made thin enough to be examined in TEM without need of tedious sample preparation (figure 5.8). The size of the individual grains can be seen, as well as how the grains are bound together.

$^1$For detailed calculation and specific numbers, see paper III.
5.5. THIN FILM ELECTRODES

Figure 5.9: SEM images of titanium cathode after polarization at -3 kA/m², 70°C for 30 minutes in 2 M NaCl, pH 6.5 (a) without any addition, (b) and (c) with addition of 4 mM Mo(VI) in the electrolyte. The molybdate deposits on the cathode surface either as a cracked film or as feather-like crystals. There is a detectable amount of molybdenum also in-between the crystals.
Figure 5.10: XRF spectra of titanium cathodes polarized in pH-neutral or alkaline electrolyte containing 4 mM Mo(VI). Polarization conditions: 30 minutes at -3 kA/m², 70°C, rotation rate: 3000 rpm, pH-neutral electrolyte: 2 M NaCl (pH ≈ 6.5), alkaline electrolyte: 1 M NaOH (pH ≈ 13.7).

5.6 Molybdenum oxide film in situ deposited on the cathode

Molybdate has shown some promising features as in situ activator for hydrogen evolution [59–65], as it forms a molybdenum oxide film on the cathode. In this study, sodium molybdate dihydrate was added to a model system electrolyte with a neutral pH (5 M NaCl, pH ≈ 7). The molybdate deposited on the cathode surface either as a cracked film or as feather-like crystals (figure 5.9). There was also a thinner, non-cracked molybdenum containing film in-between the crystals. The cracks are most likely due to the drying of the thicker film. The large, square shaped particles on the reference sample is residue NaCl. According to the electrochemical measurements, there was a considerable enlargement of the electrode surface due to the deposited film.

The bulk pH of the electrolyte appeared to have had a significant effect
on the build up of the molybdenum based film, as the films formed in alkaline electrolyte (pH $> 7$) were thinner than the films formed in neutral electrolyte. Analyses by XRF showed that there was significantly more molybdenum on electrodes polarized in neutral media than in alkaline (figure 5.10). This was further confirmed by XPS measurements. Signals from the titanium substrate was only observed for the alkaline sample, indicating a very thin or not fully covering cathode film. The hydrogen evolution reaction was, however, activated by the molybdenum addition in both electrolytes.

The XPS measurements further indicated that the film formed in neutral electrolyte was more complex than the film formed from alkaline electrolyte and probably consisted of a mix of different molybdenum oxides. This is in agreement with the multiple film types and surface crystals observed on that sample (figure 5.9). The sample polarized in alkaline electrolyte revealed only two different oxidation states, most probably assigned to MoO$_3$ and MoO$_2$ [103]. The film formed at alkaline conditions also contained a considerable amount of iron impurities. The solubility for Fe(III) is quite low in pH neutral electrolytes and the probability of iron and molybdenum co-deposition is low.

5.7 Summary of chapter 5

The standard DSA$^\text{®}$ coating is cracked and the crack density increases by increased substrate roughness and by addition of cobalt to the coating solution. However, the cracked-mud structure alone can not explain the thousand fold increase of the surface area. Even though the cracks most likely play a role in mass transport, the dominating source of surface enlargement is the nanocrystallinity as the anode coating consists of faceted monocrystalline grains of rutile structure. When using a metal plate as substrate the coating has to be viewed from the top, or the electrode molded into epoxy and polished to be viewed in cross section. If, instead, using a silicon wafer as substrate, cross section sample preparation becomes less complicated. To be able to study the grains of a standard anode using TEM, the coating has to be scraped of or prepared without substrate. Using spin coating onto a silicon nitride TEM grid, the coating can be made thin enough to be studied as whole. Spin coating allows control over the coating thickness and accurate predictions of it may be done.
In situ addition of molybdate to the electrolyte deposits as a catalytically active film on the cathode, it enlarges the surface area and activates the hydrogen evolution reaction. The deposition of the film is highly dependent on the electrolyte pH, as a much thinner film is deposited in alkaline than in pH-neutral electrolyte.
Chapter 6

Morphology

The world as we know it is (at least) three-dimensional, while a microscopy image is two-dimensional. The viewing horizon is also further limited by increasing order of magnification. AFM, as a microscopy technique, senses the surface rather than views it, giving height and slope values of the imaged area. Volume averaging measurement techniques give size estimations for the whole sample and are in some way also three-dimensional.

This chapter deals with measuring of size and shape. The average grain and crystallite size, as well as the height, width and depth of the coating features.

6.1 Area, volume and cavities

The average size of monocrystalline grains observed in section 5.4 could be obtained by estimating the average crystallite size from XRD measurements using the Scherrer equation. The grains were shown to be between 20 and 30 nm. With knowledge of the grain size, a model for calculating the real area of the coating was obtained as follows. Assuming the grains to be spheres and that the real area of the coating is a simple sum of the area of each grain (assuming a loosely packed structure) means an area increase of \( \pi \) for each layer of grains. Grains 30 nm in diameter \((10 \mu m \approx 300 \text{ layers of grains in a common coating})\) resulted in a real area of the whole coating about a thousand times larger than the geometrical area, in agreement with experimental data [1]. Under
a few assumptions [88] the real area measured by gas porosimetry can be used to calculate the average pore diameter (figure 6.1). Under the same assumptions, and still assuming the grains to be spheres the average pore diameter can be calculated from grain size for comparison. For grains 30 nm in diameter the calculated pore diameter was 13 nm, in agreement with porosimetry estimations.

### 6.2 Process parameter impact on crystallite size

The size of the grains affects the real area of the coating (smaller grains create a larger real area), thus a way to control the nanoscopic grain structure is also a way to control the electrochemical properties of the coating.

A model coating of pure RuO$_2$ was prepared from ruthenium nitrosyl nitrate (Ru(NO(NO$_3$)$_3$) and ruthenium chloride (RuCl$_3$), at calcination temperatures 350 to 550 °C. The obtained coating grains had a rather uniform size distribution for each sample and were smaller for lower calcination temperatures. Typically large and small grains are shown in figure 6.2.

As shown in figure 6.3b the average crystallite size (estimated from XRD measurements using the Scherrer equation) increased with increas-
6.2. PROCESS PARAMETER IMPACT ON CRYSTALLITE SIZE

Figure 6.2: TEM image of small and large grains due to different preparation. RuO$_2$ prepared from 100% ruthenium nitrosyl nitrate calcined at (a) 350 °C, and (b) 550 °C. The black spot in the middle is an imaging artifact.

Figure 6.2: TEM image of small and large grains due to different preparation. RuO$_2$ prepared from 100% ruthenium nitrosyl nitrate calcined at (a) 350 °C, and (b) 550 °C. The black spot in the middle is an imaging artifact.

The trend was clearer for the samples prepared from ruthenium nitrosyl nitrate, with a four-fold increase of crystallite size while for the samples prepared from ruthenium chloride the trend was more vague.

Using BET surface area measurement, the mean diameter of the grains can be estimated under the assumption that the coating consists of loosely packed spherical grains with uniform size distribution. The so-estimated grain sizes can be compared with the crystallite sizes estimated from XRD measurements. The calculated grain sizes from XRD and BET agreed qualitatively in the sense that samples prepared from RuCl$_3$ displayed grain sizes almost independent of preparation temperature, while RuNO(NO$_3$)$_3$ yielded highly temperature dependent grain diameters. However, quantitatively, there was about a one order-of-magnitude discrepancy between the sizes estimated from porosimetry and diffraction data. The explanation was most likely that the crystallite grains are not loosely packed. They are rather sintered or clustered together in such a way that only a fraction of the boundary surface of the crystallites is accessible for the gaseous probe of the porosimetry.
Figure 6.3: (a) X-ray diffraction patterns of RuO$_2$ coating prepared from RuNO(NO$_3$)$_3$ at different temperatures, illustrating the varying peak width. Curves are offset for clarity. (b) The crystallite size in the sample calculated from the width of the diffraction peak, using the Scherrer equation. (c) Crystallite size calculated from BET surface area.
6.3. CRYSSTALLITE SIZE AND ACTIVITY FOR DOPED COATINGS

Another parameter that might affect the grain size is doping materials. About one third of the ruthenium of the standard 70:30 titanium/ruthenium dioxide mixture was replaced by cobalt. The doped oxide showed smaller grains compared to the undoped oxide. Average crystallite size was 10 nm for the sample with cobalt and 20 nm for the sample without. The size estimation was confirmed by measurements in TEM (figure 6.4) and AFM images. This gave a real area for the doped sample that was about twice the area of the undoped. The area enlargement is calculated under the assumption of monocrystalline symmetrical grains of homogeneous size in each sample. Determination of the electrochemically active surface area using cyclic voltammetry confirmed that the surface area of the doped samples was approximately twice the size of the undoped samples. The smaller grains of the doped sample was in contradiction with Jirkovský et al. [49] who found that RuO$_2$ doped with cobalt in fact have larger grains than the undoped RuO$_2$. Their study is, however, of a binary oxide without titanium and with nitrate precursors which could explain the difference. In the cobalt doped TiO$_2$ binary oxide case [110] the doping does not affect the parti-

Figure 6.4: TEM image of small and large grains due to doping with cobalt. (a) Ti$_{0.7}$Ru$_{0.3}$O$_2$ with an average grain size of 20 nm, (b) Ti$_{0.7}$Ru$_{0.2}$Co$_{0.1}$O$_2$ with an average grain size of 10 nm. The black elliptic spot in the middle is an imaging artifact.
The increased voltammetric charge for the doped samples are however in agreement with previous reports on ruthenium-cobalt mixed oxides [40]. The doped samples, with one third of the ruthenium substituted with cobalt, exhibited no loss in activity for anodic chlorine evolution compared to the undoped samples. And for cathodic hydrogen evolution the activity of the doped electrodes was even higher than for the undoped electrodes. The activity was preserved (or increased) most likely due to the surface enlargement of the doped electrode coatings.

6.4 Benefits of a flat substrate

A characteristic of a metal substrate is the surface roughness on the microscale. This roughness is often wanted, helping the adhesion of the coating to the substrate [104], but can be a limitation for some characterization methods such as AFM [74].

If the crack density is high, some caution must be taken when approaching the sample surface with the AFM tip. The AFM is limited to measure the top of the plaquettes, since the tip cannot go down in the cracks as they are too deep and narrow. The almost atomically flat surface of the silicon substrate, on the other hand, allows the coating to be studied with AFM regardless of the roughness (figure 6.5). The nanosized grains were, however, shown to be independent of the microstructure of the substrate, in agreement with the findings of Shrivastava and Moats [68]. When the coating was made thin (less than 400 nm) it curled up and looked a bit like worm-eaten wood. The grains could still be seen as 30 nm wide spots (figure 6.6).

6.5 Titania nanowires

Titanium is rapidly oxidized when exposed to air, even at room temperature. Under some conditions this spontaneous oxidation generates elevated structures, like wires, instead of the common more or less smooth film. Titania nanowires, nano-wiskers and nano-flowers grown from a titanium substrate are reported in the literature [105–107] as routs to generate templates for other structures. Here, titania nanowires have been grown by annealing a titanium plate under low pressure and by
Figure 6.5: AFM image of coating (approximately 500 nm thick, (Ti,Ru)O₂) spun onto (a) and (c) a silicon wafer, (b) and (d) a titanium disc (image (d) is taken on top of a plaquette). The cracked-mud structure of the coating on titanium substrate inhibits the whole area from being examined using the AFM.
Figure 6.6: Images of “worm structure” on thin Ti$_{0.7}$Ru$_{0.3}$O$_2$ coating. (a) SEM image of thin film coating on polished titanium, coating thickness approximately 400 nm), (b) and (c) AFM images of thin film coating on silicon, coating thickness approximately 200 nm.
6.5. TITANIA NANOWIRES

Figure 6.7: SEM images of spontaneously grown nanowires. (a) Titania wires grown on titanium plate polarized for 30 minutes in 5 M NaCl, 70 °C at -3 kA/m². (b) Titania wires grown on titanium plate annealed at 1200 °C for 30 minutes in 0.02 mbar of air, under argon flow of 150 ml/min. (c) Possible titania wires (that could also be wires of e.g. Ca₃(PO₄)₂) grown on a titanium plate polarized in 5 M NaCl + 32 mM NaH₂PO₄, 70 °C at -3 kA/m².
cathodic polarization in brine (figure 6.7). The exact composition of the wires shown in figure 6.7c was hard to determine, nor was it possible to determine if they were titania wires at all. EDX measurement showed, besides titanium, measurable amounts of calcium and phosphorus and it is possible that those wires were made of e.g. calcium phosphate rather than of titania.

### 6.6 Summary of chapter 6

Area calculations using a simple model gives an increase of the surface area by approximately three times for every layer of grains. The model can also be used for estimations of average pore diameter based on the grain size. Area and pore size calculations agree with experimental data.

RuO$_2$ grains made from RuNO(NO$_3$)$_3$ become smaller when prepared at lower temperatures. Smaller grains result in larger real area and larger voltammetric charge. Grains made from RuCl$_3$ prepared at temperatures 350 – 550 °C showed almost constant grain size, real area, and voltammetric charge.

The grain size and distribution of a coating is independent of the microstructure of the electrode and its substrate. A thin coating does not crack but curls up in new features. Under some conditions the spontaneous oxidation of titanium creates titania nanowires rather than a smooth film.
Chapter 7

Bulk composition, elements and crystal structure

First impressions are always based on the appearance, but as everyone knows, it is what is on the inside that really counts. To look beyond the hills and canyons, mysterious features and simple size measuring and find out what coatings and depositions are made of, how they are built and how well a sample contains what it is supposed to contain.

This chapter deals with material analysis; crystal structure determinations, elemental analysis, oxidation state measurements and transition enthalpy estimations.

7.1 Growth of TiO$_2$ from the substrate

Spontaneous oxidation of the substrate can contaminate the coating [53, 108]. The coating composition might then not be the intended or the coating might contain titanium when it was supposed to be pure ruthenium dioxide.

The tendency for titanium migration was discovered to depend on both temperature and properties of the coating solution. In the case of RuO$_2$ made from RuCl$_3$ calcined at 550°C, a double peak was observed in the XRD spectrum at 2$\theta$ = 27° (figure 7.1c), representing the rutile phase of
Figure 7.1: XRD spectra of Ti$_{0.7}$Ru$_{0.3}$O$_2$ spin coated on silicon and polished titanium, respectively. (a) Whole spectra, (b) magnification of the first rutile peak (at 27.4 - 28.1 $^\circ$) and expected TiO$_2$ and RuO$_2$ rutile peaks marked with vertical lines. (c) The growth of titanium oxide during calcination is visible in the ruthenium dioxide prepared from ruthenium chloride calcined at 550 $^\circ$C, as a double peak at 2$\theta = 27^\circ$, representing the rutile phase of titanium and ruthenium dioxide, respectively, and at the titanium dioxide anatase phase peak at 2$\theta = 25^\circ$. 
titanium and ruthenium dioxide, respectively. A small titanium dioxide anatase peak at $2\theta = 25^\circ$ was also observed. The only available source of titanium, in this case, was the substrate. This was noticed for all chloride originated RuO$_2$ samples calcined at a temperature above 450°C and also for nitrate (RuNO(NO$_3$)$_3$) originated RuO$_2$ samples calcined at 550°C but the effect was most clear in the first sample mentioned above. A similar double peak was observed for thin film coating of (Ti,Ru)O$_2$ prepared at 470°C (figure 7.1b). There is an indication of a shoulder on the high-angle side of the peak in the titanium-substrate sample data. Since the shoulder appears at the position of RuO$_2$ it is not easily explained by oxidation of the substrate and the phase-separation explanation is also unlikely since it is reported to occur only for calcination temperatures above 700°C [109]. The cell parameters derived from the peak positions in the diffractograms indicated a slightly higher titanium dioxide concentration in the coating on the titanium substrate, which in turn could be explained by titanium migrating into the coating from the substrate. Compared to the same coating on silicon, both patterns display strong reflections from the respective substrate materials (figure 7.1a). Reflections originating from the metallic titanium interlayer can be seen from the sample prepared on silicon substrate. The presence of a titanium diffraction pattern showed that the titanium metal on the silicon substrate was not transformed (at least not fully) to titanium dioxide in the process. Moreover, it can be noted that none of the patterns display any reflection attributable to TiO$_2$ in anatase form.

7.2 Mix of rutile and spinel, doping with cobalt

The undoped (Ti,Ru)O$_2$ oxide is mainly of rutile structure with TiO$_2$ in anatase structure as a minority phase. Mixed oxides of ruthenium and cobalt are in the literature reported as RuO$_2$ + Co$_3$O$_4$ [40,100–102] or as a single phase rutile [49,50,110]. However, evidence of phase separation into both rutile and spinel (crystal structure of Co$_3$O$_4$) only exists for high calcination temperatures (> 900°C [50]) or high cobalt concentrations (> 70 mol % [49]).

The doped sample (Ti$_{0.7}$Ru$_{0.3-x}$Co$_x$O$_2$, x = 0.093, figure 7.2) in this study, exhibited one unidentified peak at $2\theta = 26^\circ$ (marked with an *) that was not present in the undoped sample (x = 0), but there was no evidence of spinel. The unidentified peak could be attributed to Co$_3$O$_4$ or CoTi$_2$O$_5$. 


Figure 7.2: XRD spectra of Ti$_{0.7}$Ru$_{0.3-x}$Co$_x$O$_2$ (x = 0 and 0.093) spin coated onto titanium discs. Coating thickness was approximately 3400 nm (7 layers). The text Spi marks the angles where the spinel peaks should have appeared.

However, there were no other visible peaks in the pattern that could confirm these assignments. Da Silva et al. [40] explains the lack of spinel peaks in the diffractogram for high ruthenium concentration mixtures (> 70 mol %) by the highly amorphous nature of their film (which also hides a possible peak at $2\theta = 26^\circ$). Since the oxide film presented here was not highly amorphous that explanation of the non-existing spinel peaks is unlikely. They interpret the amorphous nature of their film as an indication of insolubility of Co$_3$O$_4$ in RuO$_2$. It was however shown that it is possible to dissolve cobalt in ruthenium-titanium dioxide in another crystalline form than Co$_3$O$_4$. Jirkovský et al. [49] found spinel in samples calcined at 400 $^\circ$C only when the Co:Ru ratio is larger than 2:1.

### 7.3 Heat flow of coating solution calcination

The heat flux curve of the calcination process of a solution can reveal the steps in which the transformation occurs. It might also give an in-
7.3. HEAT FLOW OF COATING SOLUTION CALCINATION

Figure 7.3: DSC curves of coating solution (RuCl$_3$ + TBOT in 1-propanol) with and without addition of cobalt (CoCl$_2$), as a function of reference temperature. Measurement performed using a gold crucible. Exotherm reaction upwards. Inset: Integral of heat flux vs time for measurement in both gold and aluminum crucibles, the highest value in each category is for the gold crucible.

Figure 7.4: DSC curves of one precursor at the time in 1-propanol, solutions with the same molar amount of precursor per volume solvent as before. Curves are offset for clarity. Measurement performed in aluminum crucible. Exotherm reaction upwards.
dication of what oxide the process resulted in. DSC curves of coating solutions with and without the addition of cobalt is shown in figure 7.3. The endothermic feature below 100°C is present in both curves, and could be directly attributed to the evaporation of the solvent. The main features of the curves can be found in the temperature interval 270 – 380 °C, and were attributed to oxidation of the precursors and formation of the oxide coating material. The curves exhibited the same features when obtained using both gold and aluminum crucibles, so no part of the curve could be explained as reactions between the solution and the crucible material. The oxidation of the solution doped with cobalt peaked at a slightly higher temperature than the oxidation of the undoped coating solution ($T_c$ increased from 338 °C to 341 °C). Further, it can be noted that the oxidation took place over a greater temperature interval and had lower enthalpy in the presence of cobalt.

The lower enthalpy of the oxidation of the cobalt containing solution was not surprising. The oxidation reaction $3\text{CoCl}_2 + 2\text{O}_2 \rightarrow \text{Co}_3\text{O}_4 + 3\text{Cl}_2$ is endothermic ($\Delta H = +46 \text{ kJ/mol}$), as is the reaction $\text{CoCl}_2 + 0.5\text{O}_2 \rightarrow \text{CoO} + \text{Cl}_2$ ($\Delta H = +74 \text{ kJ/mol}$). Conversely, the corresponding reaction for ruthenium, $\text{RuCl}_3 + \text{O}_2 \rightarrow \text{RuO}_2 + 1.5\text{Cl}_2$ is exothermic ($\Delta H = -100 \text{ kJ/mol}$). Therefore, it was expected that the formation of a mixture of titanium, ruthenium and cobalt oxides should release less heat than the formation of a mixture of only titanium and ruthenium oxides.

DSC experiments on solutions containing only one precursor salt using the same procedure were performed for comparison (figure 7.4). Coating solutions contained 5.351 g RuCl$_3$·nH$_2$O, 14.929 g titanium (IV) n-butoxide (TBOT) and 1.387 g CoCl$_2$·6H$_2$O, respectively, dissolved in 1-propanol to a 50 ml final volume. The cobalt solution curve displayed the same initial solvent evaporation, but was then completely flat for all temperatures up to 600°C. In other words, CoCl$_2$ in propanol did not oxidize in the range of less than 600°C. The TBOT curve exhibited a small oxidation peak at about 250°C but the main oxidation peak was not shown until just above 500°C, while the RuCl$_3$ curve only had one peak at about 370°C. The mix of RuCl$_3$ and TBOT had no peaks after 350°C (maximum at about the same temperature as pure RuCl$_3$). Consequently, the addition of ruthenium to TBOT lowers the oxidation temperature.
Hexavalent chromium (dichromate) is added to the chlorate production electrolyte to prevent the intermediate hypochlorite and the chlorate from being reduced on the cathode. The dichromate forms a film of chromium (III) hydroxide on the cathode surface [21]. As dichromate is toxic and carcinogenic, molybdate can be used as an environmentally friendly alternative. Molybdate also forms a film on the cathodes surface, buffers in a pH region close to that of chromate and activated the hydrogen evolution reaction. An additional buffer may be needed to stabilize the electrolyte pH, when using low levels of molybdate or dichromate [67].

1 The reaction equations are summarized in section 2.3.
Figure 7.6: (a) SEM image of DSA-type anode after polarization at 3 kA/m², 70 °C for 30 minutes in 2 M NaCl, pH 6.5 with addition of 4 mM Mo(VI) in the electrolyte, image taken using backscatter electrons. (b) EDX spectrum of area marked in figure a.
The films formed on the cathode by co-additions of molybdate and phosphate were investigated. The molybdenum-containing cathode films became thinner if the electrolyte during the film build-up also contained phosphate. With 80 mM molybdate in the electrolyte a cracked film was formed on the cathode surface. The cathode film that was formed in presence of both molybdate and phosphate, looked similar but was thinner. The activation of hydrogen evolution was still as effective. If the amount of molybdate was low (4 mM) and the electrolyte also contained between 10 and 40 mM phosphate no molybdenum film was visible with SEM or detectable with EDX on the cathode surface (figure 7.5). This may be due to competitive adsorption of molybdate and phosphate, where the higher molybdate concentration is necessary for the molybdate to be favored. Addition of molybdate was found to activate the hydrogen evolution reaction even when no film could be detected, obviously a catalytic film was formed which then dissolved, detached or was too thin to be detected by EDX.

7.5 Effect on the anode by addition of molybdate to the electrolyte

In chlorate production, the anode and cathode coexist in the same electrolyte. An addition to the electrolyte which is supposed to activate the cathode, naturally, would also affect the anode. A potential anode problem is increased oxygen level in the hydrogen cell gas [59] as this would reduce the efficiency of chlorate production as well as being a safety risk if the oxygen/hydrogen mixture reaches an explosive composition. In the present study, molybdenum could be detected on the anode by EDX, but no visible changes of the surface morphology was noticed by SEM. The anode has a high surface roughness due to the cracked-mud structure of the coating and it is highly likely that the deposited molybdenum was hidden in the cracks (Figure 7.6).

Addition of molybdate to the electrolyte appeared to have a damaging effect on the anode potential. It is therefore likely that the increased oxygen level is caused by precipitation of molybdenum on the anode surface.
7.6 Summary of chapter 7

Spontaneous oxidation of the substrate can contaminate the coating through titanium atoms from the substrate migrating into the coating. The resulting titanium/ruthenium ratio will then no longer be as designed. Migrating titanium atoms might also enhance phase separation of ruthenium and titanium in the coating.

Pure cobalt oxide is commonly Co$_3$O$_4$ in spinel structure. A ternary mixed oxide of titanium, ruthenium and cobalt, containing ∼ 10 mol % cobalt does not give any indication of spinel. Instead the cobalt is most likely incorporated in the overall rutile structure. The oxidation of the cobalt doped mixed oxide peak at a slightly higher temperature than the undoped solution and it also has lower enthalpy.

Co-addition of molybdate and phosphate makes the deposited molybdenum film on the cathode become thinner and if the molybdenum content is too low no film at all is formed, the activation is however as efficient. Molybdenum from the electrolyte is also detectable on the anode, even though no deposit is visible.
Chapter 8

Concluding remarks

This concluding chapter contains the conclusions and outlook, and a short summary of the appended papers.

8.1 Conclusion

The superior catalytic properties of the DSA® is due to the large electrocatalytic area of the coating, which is attributed to the nanocrystallinity. The entire coating is built up of grains, some tens of nanometers across. The size of the grains directly affects the real area of the coating; smaller grains result in a larger real area. The real area of the coating is naturally connected to the active area of the same and therefore has an influence on the electrochemical properties of the electrode. The size of the grains is controlled by the processing parameters such as precursor salt and calcination temperature. For RuO$_2$ made from Ru(NO(NO$_3$)$_3$ a higher calcination temperature yields larger grains (and smaller area). RuO$_2$ prepared from RuCl$_3$, on the other hand, is not as sensitive to calcination temperature. The grain size is also influenced by the coating solution contents and additives. Doping with cobalt decreases the grain size and therefore increases the real area of the coating.

The grains are monocrystalline and crystallite size measuring techniques such as x-ray diffraction could be used to determine the average grain size. Also the substrate plays a large role in the appearance of the coating even though it has a limited effect on the grain size.
Besides the nanostructure, the coating has a well known microstructure (cracked-mud structure), and it is shaped by conditions such as substrate roughness and coating solution content. A smoother substrate decreases the crack density while addition of cobalt instead results in a higher crack density.

The model system developed is based on spin coating on a smooth substrate. It provides a way to design samples suitable for e.g. TEM, where the sample thickness is limited to a maximum of 100 nm. This is possible due to the ability to control the film thickness by the spinning velocity when using the spin coating technique. An easily broken silicon wafer as substrate renders a quick and uncomplicated route for cross section SEM sample preparation.

It is possible to activate the otherwise less active (hydrogen evolving) chlorate cathode by in situ additions of molybdate to the electrolyte. The addition of molybdate to a pH neutral electrolyte results in a molybdenum oxide film deposited on the cathode, as too, with the co-addition of molybdate and phosphate if the molybdate concentration is large enough. Even in cases where no film is visible (alkaline electrolyte or insufficient amount of molybdate together with the phosphate) the activation of the hydrogen evolution reaction is as efficient.

8.2 Outlook

During my six years at Mid Sweden University a lot of different approaches have been tested and considered, that have not yet resulted in published papers. Some of them have been cancelled, some put on hold and some is still in the “to do”-bin. The purpose of this section is to give a short summary of the things that currently are hot, up at the nano-attic.

Speaking of additives, there are of course other metal oxides besides cobalt that could be used. For example and to name just one, binary Ru-Ni [48] oxides have shown interesting results that might be possible to turn into ternary mixed oxides of ruthenium, titanium and nickel, and there are certainly many more. For material analysis some techniques not used here could give new input. Techniques like Raman Spectroscopy [111], Scanning Electrochemical Microscopy [112], Electrochemical Impedance Spectroscopy [113] to mention some.
Soap-bubbles are also interesting, in several ways. Using foam coating very thin layers of graphite have been coated on different substrates and it might be possible to transfer the techniques to ceramic coatings. Also, adding surfactants to the coating solution in such way that micelles are formed [114] (these are later burnt away during calcination, leaving holes behind) could be a way to increase the accessibility to the deeper parts of the coating oxide. Instead of micelles, some sort of polymer nano-spheres could be used [115] in the same way. Another idea on the same theme is to fill the coating with pieces or particles of a material that is corroded away during use of the electrode, gradually giving access to the deeper layers of the coating.

The nanowire technique is still interesting even though it has been on hold for a while. A nanowire forest theoretically would increase the surface area several hundred times [116, 117]. Growing nanowires on a pre-coated electrode is however not a good idea as the ruthenium deposits as a film, and not as nanowires.

Capacitive behavior and double layer capacitance of catalytic materials is well known [5] and the closeness between electrocatalytic electrodes and capacitors is established [4]. To therefore take the knowledge achieved for ruthenium dioxide coatings as anodes for electrolysis and use it for supercapacitor applications opens many interesting doors. And also, so far my research has focused on the chlorate production; chlorine, oxygen and hydrogen evolution. It would also be interesting to expand the horizon a bit and try the same materials for other reactions.

8.3 Summary of appended papers

As all results have been described previously, in no chronological or paper oriented order, this section aims to clarify which results are presented in which of the six appended papers.

Paper I – Nanoscaled characterisation of DSA® coating

This paper describes the finding of the grains, that more accurately explained the large surface area of the DSA®. The grains were investigated in terms of size and crystallinity (and found to be monocristalline
rutile) and the porosity of the coating was measured. A simple model was shown to explain both the area increase and pore size distribution, at least to an acceptable level.

**Paper II – Influence of precursor and preparation temperature**

For simplicity, the DSA\textsuperscript{®} coating in this paper, was replaced by a model system of pure ruthenium dioxide. The effect on the grain size of precursor and preparation temperature was investigated. The grain size calculated from porosity measurements and from x-ray diffraction was compared and shown to be qualitatively in agreement, although not quantitative. A growth of titanium dioxide (titanium from the substrate migrating into the coating) was also shown.

**Paper III – Spin coated titanium/ruthenium oxide thin films**

The effect of substrate was further investigated. The crack density of the cracked-mud structure was shown to increase by increased surface roughness. The nanocrystallinity was however not affected by the substrate, even though migration of titanium from the substrate is known. Simple routes for sample preparation of cross section SEM and TEM was shown using a model system.

**Paper IV – Effects on the coating by cobalt doping**

In this paper a ternary mixed oxide was compared to the standard binary mixed oxide. Cobalt was chosen as doping agent. Both the cracked-mud structure and the nanocrystallinity was affected by the doping. The crack density increased and the grain size decreased with the addition of cobalt. Also the electrocatalytic activity for chlorine evolution was affected - it decreased, but was compensated for by the increased active area (due to increased real area).
Paper V – Molybdenum cathode film; effect of electrolyte pH

The deposition of a molybdenum oxide film on the cathode was shown for electrodes polarized in pH-neutral electrolyte containing molybdate. The effect of electrolyte pH was discussed, as there was no molybdenum detectable on the cathode after polarization if the electrolyte had been alkaline. The effect of co-addition of phosphate to the electrolyte was also investigated.

Paper VI – Molybdenum cathode film; replacement of sodium dichromate

In this paper the effect of co-addition of molybdate and phosphate as a replacement of the dichromate used today was further investigated. The phosphate decreased the thickness of the precipitated molybdenum film on the cathode and also cleaned out just two molybdenum oxides, whilst the molybdenum film precipitated without phosphate present was more complex. There was also a needle-like structure to be seen on the cathode if polarized with only sodium chloride and phosphate in the electrolyte. The effect on the anode was also investigated, both electrochemically and in terms of precipitation.
Bibliography


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