Understanding selective oxide films in the chlorate process

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Vera Smulders

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It is my pleasure to
invite you to attend the
public defense of my
PhD thesis:

Understanding selective oxide films in the chlorate process

by
Vera Smulders

Friday September 4th
at 14:45
in the Waaier 4
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Understanding selective oxide films in the chlorate process

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UNDERSTANDING SELECTIVE OXIDE FILMS IN THE CHLORATE PROCESS

PROEFSCHRIFT

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UNDERSTANDING SELECTIVE OXIDE FILMS IN THE CHLORATE PROCESS

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Cover: Chromate and permanganate in water, by Vera Smulders

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Chapter 1

An introduction to the chlorate process

Abstract

This chapter provides context and background information for the work in this thesis. First, chlorate is introduced and its applications are described. Then, an overview of the chlorate production process is provided, describing the reactions involved, the conditions in the industrial process, and a history of its development.

Next, the crucial functions of the sodium dichromate additive in the chlorate process are explained. Particular attention is paid to the function that is the subject of this thesis: the formation of a film on the cathode that causes suppression of hypochlorite reduction in favor of hydrogen evolution. The carcinogenic nature of chromate is then explained, followed by an overview of the existing literature aiming to find a replacement, once again with a focus on the cathodic film.

Finally, the aims and research questions of this thesis are defined: how does the formation of a selective cathode film from chromate proceed, and how can we replicate this functionality using a non-toxic alternative? An overview of all the chapters is provided, describing the approach to answer this question.

1.1 Sodium chlorate

1.1.1 Use of chlorate

Approximately 3,6 million tons of chlorate (ClO_3^-) are produced annually, consuming 20 TWh, making it the third-largest electrochemical process by energy consumption [1].

The primary application of chlorate, requiring 3,2 million tons a year, is for on-site production of chlorine dioxide (ClO_2). This is used in environmentally friendly Elemental Chlorine Free (ECF) bleaching of pulp [1]. By using ClO_2 instead of Cl_2 gas during the bleaching process, this process avoids the formation of carcinogenic dioxins and dioxin-like compounds.

The second application is in chemical oxygen generation [2], for example in emergency breathing masks used in commercial aircraft in case of loss of cabin pressure. Oxygen is generated by decomposition of the chlorate at high temperature, following the reaction:

The third application is in agriculture, as a herbicide, defoliant and desiccator. However, the European Union (EU) has unauthorized its use in agriculture since 2010, stating long-term health concerns from food contamination, associated with a decreased iodine uptake in children [3]. Rather more short-term health concerns are injuries from exploding clothes, as described by James Watson in his Ig Nobel Prize-winning [4] “The Significance of Mr. Richard Buckley’s Exploding Trousers” [5] and demonstrated in the Mythbusters “Exploding Pants” episode in 2006.

1.1.2 Reactions to make chlorate

Chlorate is formed in an undivided electrochemical cell by oxidation of NaCl , following the overall reaction:

The actual reaction mechanism probably involves the electrochemical formation of Cl_2 at the anode (Eq. 1.3), which dissolves (Eq. 1.5) and reacts to chlorate following a series of solution-based processes (Eq. 1.6 and 1.7) [6]. The hydrogen evolution reaction (HER) is used to close the electron circuit at

the cathode (Eq. 1.4). Note that the HER is strongly pH dependent, and the E^0 provided here assumes a pH of 14. See section 1.2.1.3 for additional information.

1.1.3 Chlorate process overview

Figure 1.1: Schematic of a chlorate plant [7].

A large scale chlorate plant contains a multitude of parts in addition to those present in the various electrochemical cells used in laboratories. NaCl is

purified and dissolved into a brine, which is fed to the electrolyzers. Here, the electrochemical reactions in Equation 1.3 and 1.4 are performed. Because the homogeneous reactions in Equation 1.6 and 1.7 are slower than the electrochemical reactions, a reactor tank, separate from the electrolyzers, is used to extend the residence time of the electrolyte. Chlorate is formed in this reactor tank, and extracted using a crystallizer. The electrolyte is then recycled in a closed loop system. The process conditions are summarized in Table 1.1.

Table 1.1: Typical conditions in a chlorate electrolyzer [8].

Process conditions		
<i>Chlorate</i>	450 – 630	g dm ⁻³
<i>Chloride</i>	80 – 110	g dm ⁻³
<i>Dichromate</i>	2 – 7	g dm ⁻³
<i>pH</i>	5.8 – 6.5	
<i>Temperature</i>	70 – 85	°C
<i>Current density</i>	3	kA m ⁻²
<i>Cell Potential</i>	2.8 – 3.3	V

These conditions are chosen to maximize efficiency. The pH provides the optimal 2:1 HClO:ClO⁻ ratio for chlorate production that is required by Equation 1.7. This reaction faces competition from the decomposition of the the intermediates, hypochlorite and hypochlorous acid, according to Equation 1.8 and 1.9. Compared to these reactions, chlorate decomposition is kinetically very unfavorable, so by maximizing the rate of reaction 1.7 losses due to backreaction can be prevented [9].

The decomposition reactions in Equation 1.8 and 1.9 are a problem both because they reduce efficiency through a loss of intermediate products, and because they introduce O₂ into the cell gas. Because the cell gas consists of H₂ and O₂, this forms an explosive risk, in particular when O₂ is in excess of 4%.

Careful choices are made not only about the conditions, but also about the electrodes used. Currently, about 6000 kWh ton⁻¹ of chlorate is required, and electricity is a major component in the manufacturing costs [10]. This figure, known as the energy consumption, is derived from the cell potential and the overall losses. The electrode material has a large influence on cell potential and energy losses. Using the current state-of-the-art, roughly half of the 5000 kWh actually goes to chlorate formation, the rest is lost as low-value heat [10]. Figure 1.2 shows the distribution of potential in a state-of-the-art cell. The electrode reactions require a fixed thermodynamic potential, shown in black, but there are also significant losses on the cathode due to overpotential, shown in red. The other potential losses are mass transport near the electrode surfaces (yellow), and the iR-drop (or Ohmic drop) across the cell gap due to solution resistance (blue).

Figure 1.2: Cell potential across a typical cell gap. From left to right: thermodynamic potential for chloride oxidation, anodic overpotential, mass transport, iR-drop, mass transport, cathodic overpotential, thermodynamic potential for water reduction. Adapted from [8].

In addition, electrodes with long lifetimes of up to 10 years and affordable material costs are essential. On the anodic side there is not much room for improvement, as the Dimensionally Stable Anode (DSA) used here provides high selectivity and stability at low overpotential, offsetting its high initial cost [11]. On the cathodic side mild steel or, less commonly, titanium is used. Both provide a low-cost option with good mechanical properties and a reasonable

overpotential for water reduction, on the order of 350 mV. Selectivity, stability, and overpotential all do leave something to be desired, however, and sodium dichromate is an essential electrolyte additive to overcome these shortcomings. This will be discussed in detail in Section 1.2.

1.1.4 History of chlorate production and research

Chlorate is one of the oldest electrochemical processes, with the first confirmed electrosynthesis dating back to 1802 [12]. The process was discovered by Wilhelm von Hisinger and Jöns Jakob Berzelius [12], hobbyist scientists, only two years after Alessandro Volta first invented the pile, a source of electrical current [13].

The first electrochemical plant opened in 1886 in Villers-St. Sépulcre, Switzerland, using a diaphragm setup in a reactor made of wood. It was not very successful due to cathodic losses, and production ended in 1898 [12]. Around the same year, plants opened in Buckingham and Niagara in Quebec, Canada. These had no diaphragm and used bipolar electrodes with a small cell gap (1.5 to 3 mm), already remarkably similar to today's designs [14]. At the turn of century there were also factories in Switzerland, Sweden, and France. Surprisingly, there were no factories in Germany, despite most chlorate research being performed there [12].

Research focused on developing an understanding of the formation of chlorate. Initially it was believed that the formation was a purely chemical process, but within a few years this theory was completely upended several times. The revisions were driven by thorough experiments and reportedly accompanied by "sometimes violent discussions" [12]. Several papers and discussions in rude tones were exchanged between Foerster and Wohlwill [15], [16] in particular. Foerster insisted there was no electrochemical aspect to chlorate formation, while Wohlwill, a student of Nernst, held that there was. The matter was eventually clarified in 1900 when Lorenz and Wehrlin published extensive experimental results that showed chlorate could be formed electrochemically under certain circumstances [17], although Foerster nevertheless maintained his stance [12].

Regardless of the exact mechanism, it was generally agreed that hypochlorite plays an important part in chlorate formation, and that its

reduction at the cathode is undesirable. The solution for this was found in 1897, when Landin proposed the use of additives of compounds that can have changing oxidation states, particularly chromate [18]. The addition of chromate improved the efficiency of the chlorate process drastically, and investigating its workings is central to this thesis.

Müller was the first to suggest the formation of a film from this chromate additive as an explanation for the increase in current efficiency. He came up with his theory shortly after the discovery of chromate's effect [19], but it wasn't until 60 years later that a mechanism was proposed. This was by Wagner, in 1954, who described a porous Cr(III) film that electrostatically repulsed negatively charged ions from its pores [20]. There was limited knowledge about the film at this point, and his proposal was challenged less than a year later by Kolthoff and Shams El Din, who showed that the film did not inhibit the reduction of other negative ions such as permanganate and iodine [21].

On the anodic side, a breakthrough of similar magnitude to the chromate additive was made in 1965, when the graphite anodes were replaced by the recently invented dimensionally stable anode[22]. This electrode, made of a RuO₂ coating on Ti, manages to perform the anodic chlorine evolution with excellent selectivity at low overpotential, greatly improving the chlorate and chlor-alkali industries [22].

On the cathodic side, there was little interest in further investigation for the next few decades. This changed in the early 90's, when a partnership between Nouryon (formerly AkzoNobel), Permascend AB, and the Royal Institute of Technology in Stockholm (KTH) produced a slew of publications within a few years, all investigating the workings of the chromate additive. Certainly our understanding improved, but no comprehensive understanding was reached. These results are summarized in Section 1.2.

The latest, still on-going wave of research started in the 2010's, prompted by the inclusion of the toxic dichromate in the European Union's REACH program [23]. This means use of dichromate requires special authorization, and a replacement is sorely needed to continue chlorate production within the EU. Recent research has focused not only on understanding chromate, but also

on finding a replacement. An overview of the current progress in this direction is provided in Section 1.3.

1.2 Sodium dichromate in the chlorate process

1.2.1 The functions of chromate

Chromate fulfills multiple functions in the chlorate process, and an understanding of these is crucial to replacing it with something less carcinogenic. The main effects associated with chromate are:

- Catalysis of the homogeneous reaction from hypochlorite to chlorate;
- Cathodic corrosion protection;
- Electrolyte buffering;
- Induction of cathodic selectivity.

Its effects have been studied in detail over the last decades. A summary of the literature is provided below for each function, with emphasis on the last one, the focus of this thesis: inducing cathodic selectivity.

1.2.1.1 Homogeneous catalyst for chlorate formation

Dichromate was shown to improve rate of chlorate formation by catalyzing the reaction in Equation 1.7 [24]–[26]. It is not a particularly good catalyst, increasing the rate of chlorate formation by only a factor of 2. However, an increase in chlorate formation means a decrease in the steady-state hypochlorite concentration [27], in turn decreasing the rate of hypochlorite decomposition as described in Section 1.1.3. The combination means this catalytic effect is a significant contribution to industrial efficiency.

1.2.1.2 Cathode corrosion protection

The film that is formed from the chromate additive on the cathode surface during electrolysis may protect the mild steel surface from corrosion during shut down. Alternatively, the film may dissolve when a cathodic potential is no longer applied [28]. Corrosion is a serious problem during shutdowns [10]. Shutdowns occur for maintenance, when electricity prices rise too high, or whenever there is a problem somewhere in the system.

1.2.1.3 pH buffering

The overall reaction of chlorate electrolysis is pH neutral (Eq. 1.1). There is however a steep pH gradient across the cell gap when operating at high current density, as illustrated in Figure 1.3. This is because the individual electrode reactions are not pH neutral: the anode becomes acidic due to Cl_2 dissolution (Eq. 1.5), and the cathode alkaline due to the HER (Eq. 1.4).

Figure 1.3: pH distribution across a chlorate cell operating at 3 kA m^{-2} [8].

Chrome-6 (Cr^{VI} or Cr(VI)) exists as three different species in the electrolyte: dichromate ($\text{Cr}_2\text{O}_7^{2-}$), chromate (CrO_4^{2-}) and hydrogen chromate (HCrO_4^-). The equilibrium between them helps to stabilize the pH according to the buffering reaction in Equation 1.10:

Equation 1.10 occurs rapidly in the diffusion layer near the cathode surface, where it enhances the HER by providing additional H^+ to the reaction layer, as illustrated in Figure 1.4 [29]. Near the anode, the equilibrium favors CrO_4^{2-} , which can dimerize to dichromate following Equation 1.11:

Figure 1.4: Schematic concentration profiles near the cathode. Adapted from [29].

1.2.1.4 Cathode selectivity

Reduction of ClO^- and HClO intermediates proceed by Equation 1.12 and 1.13 respectively, and both are kinetically favorable on mild steel electrodes.

Chromate forms a thin film of $\text{Cr(III)(hydr)oxide}$ (denoted from here on out as $\text{Cr}^{\text{III}}\text{O}_x$ or CrO_x) on the cathode during operation [30], eliminating these unwanted reactions and providing selectivity towards the HER [20], [28], [31], [32]. The resulting overall reaction scheme is visualized in Figure 1.5. Interestingly, a similar functionality has been reported in the field of photocatalysis [33]–[37].

Figure 1.5: Schematic view of reactions in the chlorate process. The $\text{Cr}^{\text{III}}\text{O}_x$ film is shown in orange, blocking the undesired reaction pathways that are marked in red.

Exactly how the chromate film accomplishes this selectivity remains an active research topic in the community. Experimental work has focused on several aspects of the film, including its structure [30], [38], thickness [39], the mechanism of selectivity [31], [32], [38], [40], the effect of the underlying electrode [30], [38], [39], [41]–[43], and the improved current efficiency induced by the film [44].

The very first theory about the mechanism by which the chromate film achieves its remarkable effect was proposed in 1954, when knowledge was still very limited. It supposes the film functions as a diaphragm, blocking oxychloride access to the buried electrode interface through electrostatic repulsion in the pores [20]. However, this theory has been repeatedly shown to not fully explain the behavior of the film [31], [32]. Most importantly, other negative ions, such as permanganate and iodine, can be reduced even when the film is present [21].

The next theory considers that the film physically blocks transport of hypochlorite to the electrode surface [32]. This was supported by the discovery that other trivalent metal ions can also make selective electrodes [45]–[47]. In addition, chromate films could be applied to other electrodes to produce a similar effect: Pt and Fe [31], [32], [41], or even RuO₂ [48] and Rh [34] all show selectivity towards HER accompanied by a slight increase in overpotential. However, Au does not follow this pattern: on Au the addition of chromate actually leads to a decrease in overpotential, although selectivity is still acquired [32].

This prompted the proposal of the third theory: that the chrome film itself plays a catalytic role in the HER [32]. One of the reasons for the lack of clarity concerning the mechanism is that the *in situ* structure of the film is not known. By examining *ex situ* deposited Cr(OH)₃ and Cr₂O₃ films this uncertainty was circumvented to some extent, and experimental work combined with density functional theory (DFT) modelling has recently led to some new insights [8], [38], [42]. Most interesting is the observation that the increase in overpotential caused by the chromate film does not occur in the absence of hypochlorite [8]. This is explained by DFT results that show that hydrogen evolution takes place on Cr-OH sites. Hypochlorite reduction requires free Cr sites, which are not available at the potential at which hydrogen evolution takes place. Instead Cr-Cl is formed, which is inactive for both hypochlorite

reduction and HER, causing the increase in overpotential [8]. However, this theory of catalytic Cr films does not explain why the underlying electrode material still influences the overpotential for HER. It is possible that reality lies somewhere in the middle, and facets of all three theories combine to form the remarkable properties of the film formed by the chromate additive.

Another question that does not have a satisfactory answer is the film growth. The film forms rapidly at the lab scale [39] but can take much longer industrially [8]. It is known that the film is extremely thin, on the order of a few nanometers [39]. Why growth is self-limiting to this thickness is not known. On polished substrates, μM amounts of dichromate are sufficient to induce complete inhibition of hypochlorite reduction [49]. However, in the industrial process much larger concentrations of 2 to 8 g dm^{-3} are needed [50]. In a pilot plant, the cathodic current efficiency scaled with chromate concentration up to 5 g dm^{-3} [51]. These concentrations are much higher than required for the formation of a few monolayers, even when taking into account that some chromate is incorporated into the Fe during shutdowns [8], [51]. These discrepancies in concentration indicate that the film growth process is influenced by the process conditions, and possibly also that the film formation by itself is not sufficient to achieve state-of-the-art efficiency.

Because the film is extremely thin and the electrolyte highly oxidative, it was thought that the film would be unstable when cathodic protection is removed, but recent work shows chromium remaining on the surface even after shut down [51].

Of particular note for the work in Chapter 3 of this thesis is that while it is known that chromium reduction produces more charge than the corresponding oxidation, and it has been proposed that an excess of reduced chromium goes into solution as Cr(OH)_4^- [31], this mechanism was never demonstrated or quantified. The mechanism of reduction has been proposed as a direct 3-electron reduction of Cr(VI) to Cr(III) [12], although work on the reverse process, oxidation of Cr(III) to Cr(VI), suggests a series of 1-electron steps including formation of Cr(V) and Cr(IV) [52].

1.2.2 The problem of chromate

Figure 1.6: Hazard symbols for sodium dichromate, from left to right: oxidizing; toxic; carcinogenic, mutagenic and reprotoxic; corrosive; and toxic to the environment.

A container of sodium dichromate boasts five different hazard symbols as shown in Figure 1.6. Even if it is initially added as a safe three-valence oxide [53], chromate will always be present in its highly carcinogenic, six-valence state in the electrolyte. Because of this, it falls under REACH legislation and is listed in Annex XIV, meaning authorization is needed for usage within the EU per September 2017 [23]. For chlorate production, an alternative must be found urgently so chlorate plants can remain operational within the EU [50].

The carcinogenic nature of chromate is due to two factors. First, its structural similarity to sulfate means that once ingested or inhaled, it will be transported into cells by means of sulfate channels [54]. Second, once inside the cell, hexavalent chromate is reduced to trivalent chromium, which then forms complexes with proteins and nucleic acids [54]. These Cr-DNA complexes then cause mutations during DNA replication [54].

1.3 Alternatives to chromate

Numerous alternative additives to dichromate have been proposed, including rare-earth metal (REM) salts [45]–[47], permanganate [55], [56], vanadate [57], and molybdate [49], [58]–[61]. Alloys of Fe and Cr were also investigated [43]. Other solutions involve more fundamental changes to the way the chlorate process is operated, such as the introduction of a membrane or diaphragm. However, those involve a tremendous investment and re-development of currently operating plants, so a slot-in replacement additive would be preferable [50]. The two most promising candidates, which are also investigated in this thesis, are molybdate and permanganate. They will be discussed in more detail below.

1.3.1 Molybdate

Studies on molybdate have revealed great promise for its application in place of dichromate. The search for an alternative to chromate is also occurring in the field of corrosion protection [62]. Chromate and molybdate were found to have similar properties in this field, too [62], [63], where molybdate has long been applied [64]. Although effects are similar, the underlying mechanisms were not found to be identical [65]. Molybdenum films are not typically electrodeposited [66], except as alloys with iron-group metals [59], [67], but molybdenum oxide films can be deposited from aqueous molybdate solutions [68].

The main features that make molybdate a possible candidate for the chlorate process are:

- It activates the cathode for HER in alkaline media [49], [60], [69];
- It undergoes in situ film formation [70];
- It inhibits corrosion of the cathode [64], [69];
- It has a similar buffering range, suitable for chlorate formation [60];
- It inhibits the oxygen reduction reaction [70], and thus possibly also oxychloride reduction [49];
- It is safer and more environmentally friendly than chromate.

Indeed molybdate has been studied for the chlorate process [49], [60], [61], [71]. Unfortunately, molybdate was shown to increase O_2 in the cell gas to an unacceptable 4.6% in the absence of dichromate [60], [71]. This is a serious problem because the cell gas consists primarily of H_2 , and the introduction of more than 4% O_2 leads to an explosive mixture. However, because the level depends on molybdate concentration the danger can be ameliorated by limiting the amount of MoO_4^{2-} [60]. 7 to 70 μM was found to activate the HER without increasing the oxygen in the cell gas much when using a Maxphase cathode [71], but this patent does not show reference data for the electrode without additives. In addition, it is unclear if the activation of the cathode is partially due to incomplete blocking of hypochlorite reduction.

The activating effect on the HER may be promoted by combining molybdate with a second additive. This has been successfully proven for Cr [61], but Fe [49] may also be an option. Unfortunately, literature is still lacking a rigorous

study of the combined effect of chromate and molybdate on the oxygen content [61].

A final aspect that has not yet been fully investigated is the transition from benchtop laboratory experiments to pilot plants, let alone much larger industrial plants. This scale-up step is far from trivial, and trends don't always translate well due to differences in geometry, time scale, mass transport, and reactor volume-to-electrode surface ratio [72], [73].

Overall, although it shows promise, more evidence is required to clarify if molybdate is a viable co-additive to decrease chromate use.

1.3.2 Permanganate

Of the alternatives to chromate proposed [40], [45], [46], [55], [74] MnO_x containing films seem very promising owing to the fact that they can be deposited *in situ* from non-toxic permanganate solutions, and have shown very similar selectivity towards H_2 production [55], [56]. MnO_x is also used as a selectivity-inducing film for the oxygen evolution reaction [75]. Unfortunately, contrary to chromate, film growth from a permanganate solution is not limited to the nanometer range. Unlimited film growth would cause various problems in an industrial electrochemical reactor, ranging from larger resistances and higher cell potentials to short-circuiting and cell clogging [55]. However, a recent publication shows that thermally deposited MnO_x films also induce excellent selectivity towards the HER in solutions containing hypochlorite [56].

Such films are extremely promising for chlorate applications, but thermal decomposition requires high temperatures and requires films with a thickness of several μm . However, the rich redox chemistry of manganese also allows carefully controlled electrodeposition. Film properties can be tuned through the solution pH and concentration, as well as through the deposition potential [76].

This is well-studied for anodic deposition from Mn^{2+} [77], [78], but cathodic deposition is rarely discussed in literature. Still, cathodic deposition from permanganate to birnessite and amorphous MnO_2 has received some attention in recent years in the context of superconductors [79]. Deposition was primarily studied in neutral conditions [80], [81]. Though alkaline

environments have been used for MnO_x deposition [82], and corresponding films have been optimized for capacitance [83] and the oxygen reduction reaction [79], the deposition mechanism has not been investigated. pH plays an important role as the mechanism involves different soluble and insoluble intermediates [78], [80], and the instability of Mn^{2+} ions at high pH suggests fundamentally different pathways in highly alkaline conditions. However, work into the dissolution of metallic manganese suggests that Mn^{2+} and even Mn^{3+} can be present in significant amounts in a highly alkaline environment, despite their relative insolubility [80], [84]. Another factor of importance to film morphology is the counter ion. For electrochemical purposes only the Na^+ cation is of interest, as this induces deposition of an amorphous film instead of the less conductive layered birnessite formed from K^+ -containing solutions [78], [81].

In short, despite an increasing number of publications on cathodic permanganate deposition in recent years, the deposition mechanism in highly alkaline media remains poorly understood. However, it is clear that the deposition conditions greatly influence the electrochemical and mechanical properties of the film [85]–[87]. Morphology, phase, and composition are all pH and potential dependent, so the exact origin of the varying properties remains unclear. Controlling the film properties is crucial to achieving complete inhibition of hypochlorite reduction, and more knowledge is required to link the deposition parameters to the resulting film properties.

1.4 Aims and outline of this thesis

The aim of this thesis is to ameliorate the use of the carcinogenic chromate additive in chlorate processes. The overarching research question is: how does the formation of a selective cathode film from chromate proceed, and how can we replicate this functionality using a non-toxic alternative?

To understand the outstanding properties of the buried interfaces obtained at the interface between electrode and film, I first study film formation from chromate on a fundamental level. I use a simplified model system, and propose a deposition mechanism. With this knowledge I can introduce complexity, achieving parameters closer to the industrial process. In these conditions I also investigate the limitations of film growth and selective

blocking of the hypochlorite reduction for ultra-low μM chromate concentrations. I enhance the performance at this concentration through a comprehensive investigation of the promising co-additive molybdate. I validate these results by scaling up to a pilot reactor, to bridge the gap between fundamental studies and industrial operation. Finally, I remove chromate altogether, and investigate film deposition from permanganate as a replacement for chromate.

In **Chapter 2**, I describe the experimental procedures and equipment used. I also provide a theoretical background for our primary techniques: the Rotating Ring Disc Electrode (RRDE), and the Electrochemical Quartz Crystal Microbalance (QCM or eQCM).

In **Chapter 3**, I study the deposition mechanism of thin films from dichromate solutions on Au electrodes, specifically the mismatch between reductive and oxidative current. The RRDE and QCM provide me with information about the soluble species formed, and the mass of the film deposited on the electrode, respectively. I demonstrate that only a minor fraction of current is related to the formation of a film, and that the film is at most three monolayers thick. Based on my results I propose a mechanism explaining the self-limiting growth of the film, wherein the first monolayer inhibits further chromate reduction.

In **Chapter 4**, I expand the results of Chapter 3 to Pt electrodes. This allows the introduction of high concentrations of NaCl to the electrolyte, so that I can more closely mimic the industrial conditions. I confirm that Pt develops an even thinner film than Au, and I discover that NaCl does not influence the deposition. I use low concentrations of chromate to control the film thickness, allowing me to disentangle the mechanistic steps proposed in Chapter 3. I find a nicely closed charge balance again, but a slightly different deposition and oxidation mechanism compared to Au.

In **Chapter 5**, I expand my investigation into chromate deposition by testing a third substrate material, Ti, and by reducing the chromate concentration 2000-fold. I also introduce molybdate as a co-additive, to improve the performance at these low concentrations. I find that chromate deposition is different on Ti than on Pt or Au, involving no soluble intermediates. I find that molybdate deposition is concentration dependent, and that molybdate

activates the cathode for the HER. By mixing the two additives a hybrid system can be formed, which performs better than the sum of the individual additives would suggest. To validate my results I scale up the experiments to a lab pilot plant, and I discuss the discrepancies between the two experimental scales.

In **Chapter 6**, I eliminate dichromate entirely and exchange it for permanganate. I study its deposition on Au, and I find a complicated deposition mechanism with no inherent limit to film growth. I study the influence of deposition potential by analyzing the films using SEM and XPS. Although the oxidation state is independent of deposition potential, morphology varies wildly. I evaluate film performance in permanganate-free solutions of hypochlorite, and I find a correlation between deposition potential and cathode selectivity. I discover a remarkable, narrow potential window that is exempt from this trend and results in virtually perfect selectivity. DFT calculations confirm that the reduction of hypochlorite on manganese oxides contains significant energetical barriers.

Finally, **Chapter 7** summarizes my findings and provides a perspective on the future of this topic.

Chapter 2

Theory and experimental methods

Abstract

This chapter describes the experimental materials and procedures that are applied in this thesis. It also provides basic theory on potential and current in electrochemistry, as well as on the most important techniques used: the rotating ring disc electrode and the quartz crystal microbalance.

2.1 Electrochemical theory [88]

One of the major expenses in electrochemical processes is the electricity which is used to drive the reactions, expressed in power consumption in kWh. Power is determined by the necessary cell voltage, which consists of the thermodynamically required voltage, overpotentials, and Ohmic losses as discussed in Chapter 1, multiplied by the current. The current is determined by the Faradaic efficiency, i.e. the amount of current which is actually used for the desired electrochemical reaction as compared to undesired electrochemical reactions. In the following I will discuss this in more detail.

As indicated previously, for any given electrochemical reaction, a certain thermodynamic standard potential E° (V) is required, but generally an additional overpotential η (V) must also be applied. η is the difference between E° and the experimentally required potential to perform the reaction, E (V). This means the cell requires extra power to drive the reaction, and this power is lost as low-value heat. The overpotential increases with increasing current density j (A) as described by the Butler-Volmer equation:

$$j = j_0 \left\{ \exp\left(\frac{\alpha_a z F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c z F \eta}{RT}\right) \right\} \quad (2.1)$$

Where j_0 is the exchange current density (A m^{-2}); z is the number of electrons transferred; F is Faraday's constant ($9.65 \cdot 10^4 \text{ C mol}^{-1}$); R is the universal gas constant (8.314 J K^{-1}); T is the temperature (298 K); and α_a and α_c are the anodic and cathodic charge transfer coefficients, respectively. Equation 2.1 describes both the anodic and cathodic reaction simultaneously, but at high j we can assume the contribution from the opposing reaction is negligible. Equation 2.1 can then be simplified to determine η :

$$\eta = A \log_{10} \left(\frac{j}{j_0} \right) \quad (2.2)$$

Equation 2.2 is known as the Tafel equation, and hence A (V decade^{-1}) is known as the Tafel slope. By plotting $\log(j)$ versus E , *e.g.* in polarization curves, the Tafel slope and j_0 can be found experimentally. In addition to providing information about overpotential and energy losses, the Tafel slope can also be used to discern information about the reaction mechanism. For a simple one-electron reversible reaction, the Tafel slope is 120 mV dec^{-1} , but for a more complex mechanism it can for example provide information about

the number of electrons participating in the rate-determining step. However, this approach is not applied in this work so it will not be discussed here.

In our experiments we measure $E_{Ag/AgCl}$ (V), which is the potential difference between the working electrode and the reference electrode, a stable Ag/AgCl redox couple placed close to the working electrode surface. However, we need to compare potentials between different solutions and reference electrodes. This is accommodated by reporting voltages versus the Reversible Hydrogen Electrode (RHE) instead. The RHE is based on the Normal Hydrogen Electrode (NHE). This is a standardized reference electrode defined by the potential of a Pt electrode in 1 M H^+ at 1 atm. To convert $E_{Ag/AgCl}$ we first determine $E^\circ_{Ag/AgCl}$ (0.196 V), the equilibrium potential of our reference electrode relative to the NHE. We then convert $E_{Ag/AgCl}$ to a potential versus NHE, E_{NHE} (V):

$$E_{NHE} = E_{Ag/AgCl} + E^\circ_{Ag/AgCl} \quad (2.3)$$

To correct for the pH, the Nernst equation is used. This is shown in Equation 2.4 and describes the potential of an electrochemical half-reaction in relation to the activities of the reduced and oxidized species, α_{red} and α_{ox} respectively.

$$E = E^\circ - \frac{RT}{zF} \ln \left(\frac{\alpha_{red}}{\alpha_{ox}} \right) \quad (2.4)$$

Here E° is the half-reaction standard potential (V). To use the Nernst equation to compensate a potential for pH, we can approximate the activities using the concentrations to calculate the potential required for the reduction of H^+ to H_2 :

$$E_{H^+/H_2} = E^\circ - \frac{RT}{zF} \ln \left(\frac{P_{H_2}}{[H^+]^2} \right) \quad (2.5)$$

In Equation 2.5, P_{H_2} is the hydrogen partial pressure (1 atm), and $[H^+]$ is the concentration of protons. *Per* definition the pH equals zero at which the standard redox potential E° is 0 V, and z is 2. After filling in the values we find the equation:

$$E_{H^+/H_2} = -0,059 \text{ pH} \quad (2.6)$$

By combining Equations 2.3 and 2.6, we can convert our measured potential to V vs RHE:

$$E_{RHE} = E_{Ag/AgCl} + 0,059 \text{ pH} + E^\circ_{Ag/AgCl} \quad (2.7)$$

It is worth noting that both the Butler-Volmer and the Nernst equation include the temperature. Lab-scale experiments in this thesis were all performed at room temperature (20 °C), with the exception of the QCM experiments, which were performed at 15 °C. The temperature dependence can be neglected for this 5 degree difference, but the industrial chlorate process is operated at 80 °C, leading to a significant difference. This is why the pilot scale validation experiments were performed at 80 °C.

2.2 General procedure

The following details regarding cleaning procedure and electrolyte preparation apply to all experiments in this thesis.

Solutions were made using Milli-Q water (18.2 Ω , Millipore). Experiments were performed at room temperature in solutions that were de-aerated by bubbling N₂ for 45 minutes prior to the experiment. Electrochemical techniques were controlled using a Biologic VSP potentiostat and the accompanying EC-lab software. The Ag/AgCl reference electrode, with $E^{\circ}_{Ag/AgCl} = 0.1976$ V vs NHE, was homemade using 3 M NaCl (Sigma Aldrich, >99,8%) and Ag wire (Alfa Aesar, >99,98%). pH was measured using a Hanna Edge pH meter equipped with an HI11310 electrode.

Electrodes and cell were cleaned by thoroughly rinsing with 10% nitric acid and then Milli-Q water. Pt and Au electrodes were additionally cleaned electrochemically in a 0.1 M NaOH (Sigma Aldrich, >99%) solution by cycling 5 times from +0.9 to +1.65 V vs RHE at 100 mV s⁻¹.

2.3 Rotating ring disc

Au and Pt rotating ring disc electrode (RRDE) experiments were performed using a Metrohm Autolab RRDE using a solid Au disc as working electrode with a Pt ring, or a solid Pt disc with a Pt ring. The counter electrode (CE) was a 2 cm² Pt flag electrode.

Ti RRDE experiments were performed using a PINE research WaveVortex 10 RRDE, with a ChangeDisc tip containing a Pt ring electrode and interchangeable Ti or Pt discs. The discs were polished with 5; 0.3; and then 0.05 μ M Al polishing compound between experiments, to remove the

deposited films, then rinsed and sonicated for 10 minutes in Milli-Q to remove the polishing compound.

The collection efficiency of the Pt ring electrodes was determined to be 25% from the data in Figure 2.1, using $K_4Fe(CN)_6$ (Sigma Aldrich, >99,95%) and KNO_3 (Sigma Aldrich, >99,99%) as redox couple and electrolyte, respectively. This calibration was repeated monthly to ensure an accurate collection efficiency for calculations.

Figure 2.1: Cyclic voltammogram of a Au disc, Pt ring RRDE at 100 mV s^{-1} in $10 \text{ mM } K_4Fe(CN)_6$ and $1 \text{ M } KNO_3$, $E_{\text{ring}} = +0.1 \text{ V}$.

2.3.1 RRDE theory [88]

A rotating disc electrode works by inserting a disc-shaped working electrode into a tip made of inert material as shown in Figure 2.2. This tip is then rotated in an electrolyte bath, with two interesting consequences.

Figure 2.2: Cross section (left) and bottom view (right) of an RRDE tip.

Firstly, the rotation of the tip transports electrolyte from the middle of the tip towards the edges, as illustrated in Figure 2.2b. One can insert a second, ring-shaped electrode around the first, separated by a nonconducting material. By keeping this ring at an opposing potential to the disc, products formed at the disc can undergo the opposing redox reaction at the ring. This leads to a current on the ring that is the inverse of that on the disc. The ring has a limited efficiency, however, so its current has a maximum theoretical value of 25% compared to the disc. To determine this efficiency, known as the collection factor, the currents must be quantified.

The limiting current density of each electrode j_{lim} (A m^{-2}), indicated by a plateau such as between 1.1 and 1.8 V in Figure 2.1, can be used to calculate the collection efficiency N using Equation 2.8:

$$N = \frac{j_{\text{lim ring}}}{j_{\text{lim disc}}} 100\% \quad (2.8)$$

After correcting for the collection efficiency the difference between ring and disc current can be used to determine the amount of soluble species formed on the disc. Solid films that remain attached to the disc will not move to the ring, and so simultaneous reactions on the disc can be disentangled.

The second effect of rotating the electrode is the forced convection that is created, transporting electrolyte from the bulk to the tip (Figure 2.2a). So long as turbulent flow is avoided, this convection decreases the thickness of the stagnant layer at the electrode surface, known as the diffusion layer. For a kinetically rapid reaction, j_{lim} becomes mass transport limited according to:

$$j_{\text{lim}} = \frac{zFD}{\delta} C \quad (2.9)$$

Where D is the diffusion coefficient ($\text{m}^2 \text{s}^{-1}$) and C is the reagent concentration (mol). From Equation 2.9 it is clear that even a small decrease in diffusion layer thickness has a major effect on the surface concentration of ions. And indeed, larger mass transport leads to increased currents, as shown in Figure 2.3a. This figure uses the rapid ferro-ferricyanide reaction as a model system:

The increase of j_{lim} as a function of rotation rate can be quantified in more detail by applying the Levich equation [88]:

$$j_{\text{lim}} = (0.620)zFAD^{2/3}\nu^{-1/6}C\omega^{1/2} \quad (2.12)$$

Where A is the electrode area; ν is the kinematic viscosity; and ω is the angular velocity of the tip. This equation is based on hydrodynamics, and most of these variables remain constant within a given experiment. Therefore they can be simplified to a single constant B_L , known as the Levich constant:

$$j_{\text{lim}} = B_L\omega^{1/2} \quad (2.13)$$

Equation 2.13 shows that j_{lim} scales with the square root of the angular velocity, as demonstrated in Figure 2.3b.

Figure 2.3: (a): Cyclic voltammogram using a Pt RDE and 10 mM $\text{Fe}(\text{CN})_6$ in 1 M KNO_3 at 50 mV s^{-1} as a function of rotation rate; and (b) a Levich plot showing the limiting current density (taken at 1.3 V) as a function of the square root of rotation rate.

Further analysis of these results can also provide information regarding the reaction mechanism. The details of this are not straightforward and we refer the reader to the work of Treimer *et al* for a complete explanation [89]. Relevant for the work in this thesis is the inverse relation between rotation rate and current, *i.e.* an increase in mass transport results in a decrease in current density. This is a clear sign that the electrochemical process consists of multiple steps, and there is a soluble intermediate required for a slow subsequent electrochemical step. For such a reaction pathway, a higher rotation rate causes the intermediate to be transported away from the electrode surface more efficiently, decreasing the probability for further reaction, and thus causing a decrease in reaction rate and current.

2.4 Quartz crystal microbalance

eQCM experiments were performed using a Gamry eQCM 10M at 5 MHz. The sensors were Au-coated AT-cut crystals from Gamry and Q-sense, Pt-Au crystals from Q-sense, and Au-Ti crystals from MicroVacuum. The CE was a Pt wire (Alpha Aesar, >99,99%). The cell was cooled to 15 °C using a Julabo F12 water bath.

The quartz crystal was cut using the so-called AT-cut, which is designed to minimize temperature-frequency coupling. Nevertheless, accuracy was improved by cooling the cell during experiments, because the slight heat associated with losses from the electrochemical reaction leads to degassing of the solution near the electrode, causing bubbles to form on its surface over time, affecting the accuracy of the measurements.

2.4.1 QCM theory [4]

The QCM utilizes the piezoelectric effect to oscillate a quartz crystal and measure the mass difference Δm (g) of its surface as compared to a standard condition. An alternating potential is applied to each face of the crystal, causing it to oscillate as shown in Figure 2.4. The QCM equipment measures the response of the crystal to the potential. One of the electrodes used for this is exposed to the solution and can be used to perform electrochemistry.

Figure 2.4: A quartz crystal with Au electrodes on top and bottom. (a) shows the crystal at open circuit potential, (b) is deformed as a result of an applied potential.

The response to the applied potential is greatest when the period of the oscillations matches the fundamental frequency (f_0 , MHz) of the crystal. This is the case when the thickness of the crystal (t_q , cm) is twice the acoustic wavelength, and a standing wave with a period equal to the inverse of the frequency is formed. For a given crystal, f_0 can be found using its shear modulus (μ_q , g cm⁻¹ s⁻², a ratio of sheer stress to sheer strain) and density (ρ_q , g cm⁻³):

$$f_0 = \sqrt{\frac{\mu_q}{\rho_q}} / 2t_q \quad (2.11)$$

However, the measured resonance frequency (f_s , Hz) is not only a function of the mechanical properties of the crystal, but also of any mass deposited onto the face of the crystal. The Sauerbrey equation [90] can be used to determine Δm based on the shift in f_s :

$$\Delta f_s = -\frac{2f_0^2 n}{A(\mu_q \rho_q)^{1/2}} \Delta m \quad (2.12)$$

In this equation n is the harmonic number (*i.e.* 1), and A the piezoelectrically active area (cm^2). For a given type of crystal these constants can be summarized into the calibration constant C_f ($\text{cm}^2 \text{ g}^{-1}$), giving Equation 2.13:

$$\Delta f = -C_f \Delta m \quad (2.13)$$

C_f can also be determined using copper deposition as a calibration [91]. This calibration was performed after experiments were completed to avoid Cu contamination. Values found are close to the theoretical of 56.6 for $f_0 = 5$ MHz, with calibrations giving on average $54 \pm 3 \text{ Hz cm}^2 \text{ g}^{-1}$. Variation can be explained by roughening through oxidation and reduction during the experiments.

The Sauerbrey equation treats the mass as an extension of the crystal itself. This means it only holds for uniformly distributed, rigid, thin-film deposits. For thicker or more flexible films such as polymer layers, dampening can occur. In this scenario only the material close to the surface oscillates with the crystal, while material further away remains stagnant, leading to an underestimation of the mass difference. The films in this work are expected to be uniformly deposited films with a thickness on the nanometer scale, and so within the constraints of the Sauerbrey equation. The validity of the Sauerbrey equation can be judged by the symmetry of the response around the resonance frequency [91]. No asymmetry was observed in any experiment, so indeed we can safely apply the Sauerbrey equation.

2.5 Raman spectroscopy

Raman spectra were recorded using an Avantes AvaRaman spectrometer with Intertec $\lambda = 785$ nm laser wavelength. *In situ* Raman experiments were performed on Au foil (Alfa Aesar, >99,95%), roughened as described in 2.7.1. The CE was a platinized Ti mesh (Magneto Special Anodes).

The reactor was a homemade flow cell shown in Figure 2.5, made of Teflon and brass, with a quartz glass window, and PEEK electrolyte lines. The electrolyte was pumped using a Watson-Marlow 101U pump at 0.8 mL min^{-1} . The Raman probe, with a focal distance of 10 mm, was mounted on a μm optical screw to optimize the distance to the electrode surface. The beam travels through 4 mm of solution to get to the electrode surface.

Figure 2.5: Expanded view and cross section of the Raman flow cell. Not shown are the connectors for the electrolyte lines.

2.6 Pilot plant trials

Scaled-up experiments were performed using a pilot plant at Nouryon R&D in Bohus, Sweden. Figure 2.6 shows a schematic representation of the plant and electrode stack, and Figure 2.7 shows a photograph of the setup in use.

Figure 2.6: Schematic of the pilot plant and electrode stack.

The anode was a Dimensionally Stable Anode (DSA) and the cathode a Ti plate, each with an exposed area of 30 cm^2 . Both electrodes were cleaned by rinsing with acetone prior to first use. Gaskets (Si, DensiQ) were cleaned with water prior to first use. Experiments were performed while circulating 1.1 dm^3 of electrolyte with a temperature of 348 K , controlled by a Laude Eco Silver thermostatic bath. The pH was regulated to 6.5 using a Mettler Toledo pH 2100e pH meter and Grundfos Alldos DDA acid pump with 2 M HCl (Scharlau, reagent grade). The current density was 3 kA m^{-2} . The electrolyte was circulated at 160 mL min^{-1} using an Iwaki Magnet Pump. The reactor was

flushed with 60 mL min^{-1} N_2 and the gas was analyzed for O_2 content using a Servomex Series 1100 paramagnetic oxygen transducer.

Figure 2.7: Photograph of the pilot plant at Nouryon's Bohus laboratory, with major components labeled.

The electrolyte was composed of 5.5 M (580 g dm^{-3}) NaClO_3 (Nouryon, recrystallized) and 2 M (120 g dm^{-3}) NaCl (Scharlau, ExpertQ grade) in deionized water. For experiments with 0, 2.7, 27 and $270 \text{ }\mu\text{M}$ $\text{Na}_2\text{Cr}_2\text{O}_7$ the chlorate was recrystallized to remove all chromate contamination. Na_2MoO_4 (Sigma, 99.5%) was added to the electrolyte in the desired concentration, after which experiments were run for 90 minutes. Then $\text{Na}_2\text{Cr}_2\text{O}_7$ (Sigma Aldrich, 99.5%) was added directly to the reactor using a syringe. Insertion was performed in a 10 minute long break, during which current was stopped and the cell was flushed with 150 mL min^{-1} of N_2 . Current could then be started again for a further experiment.

Hypochlorite concentration was determined by extracting 19 mL of electrolyte into a syringe that contained 5 mL 5 M NaOH (Scharlau, reagent grade) to prevent hypochlorite decomposition. 5 mL of this mixture was

combined with 10 mL 0.5 M acetate buffer (HAc, Scharlau 99.8%, and NaAc, Merck, 99-101%), 10 mL 0.1 M KI (Scharlau, reagent grade) and 50 mL H₂O. Thiosulfate (Merck, p. a.) was used to perform a titration using a Metrohm 775 Dosimat with starch (Sigma Aldrich, ACS reagent) as an indicator. Each titration was performed in triplicate.

2.7 Electrode preparation

2.7.1 Electrochemical roughening for SERS

The Au foil was electrochemically roughened to achieve SERS using the method established by Weaver *et al* [92]. The method consists of polishing the Au foil to a mirror finish, using 1 μm MicroPolish followed by 0.3 μm MicroPolish. They were then rinsed and sonicated twice in milli-Q for 10 minutes, rinsing again in between. Next, the polished electrodes were submersed in 0.1 M NaCl with a Pt mesh CE. 25 potential cycles were performed by first maintaining the potential for 1.3 s at +2.15 V, then sweeping at 500 mV s^{-1} to +0.65 V and holding for 30 s. This causes repeated oxidative Au dissolution followed by reductive Au deposition, leading to increased surface roughness. Figure 2.8 shows SEM pictures of the electrode before and after roughening.

Figure 2.8: SEM images of Au foil electrodes, scalebar shows 200 nm. (a) shows a polished surface, (b) shows a surface after roughening.

2.7.2 Pt deposition onto Au

Thin films of Pt, on the order of 5 monolayers, were deposited on Au using the method described by Weaver *et al* [93]. Deposition was performed in a solution of 0.7 M Na₂HPO₄ (Sigma Aldrich, >99%) and 4 mM H₂PtCl₆ (Alfa

Aesar, >99.9%) and applying -0.4 mA cm^{-2} for 40 seconds. The area used here is not the geometric electrode area but the electrochemically active surface area. This was determined using the method described by Petrii *et al* [94]. This method assumes a monolayer of oxygen adsorbed on the surface of the electrode after applying an oxidative potential with a 1:1 ratio of oxygen to surface atoms. The amount of oxygen can be found by determining the charge of the peak corresponding to the reduction of this oxygen, which is found on Au at +1 V. A conversion ratio of $390 \pm 10 \text{ } \mu\text{C cm}^{-2}$ has been determined empirically [94].

By using this approach a very thin layer of Pt was deposited, so the SERS effect was maintained but the surface was fully covered by Pt. Complete Pt coverage was confirmed using cyclic voltammetry, which showed no peaks related to Au after Pt deposition.

2.8 Scanning electron microscopy

Scanning electron microscopy (SEM) was performed using a Zeiss MERLIN HR-SEM system at the MESA+ Institute for Technology NanoLab facility. Secondary electron detection was used to gather topological information. Both low (HE-SE2) and high (Inlens) electrons could be detected. Energy selective backscatter (ESB) was used to map compositional contrast. In cases where sufficient material was present, compositional differences were quantified using energy dispersive x-rays (EDX).

2.9 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was performed using a PHI Quantera SXM – XPS system using a $600 \times 300 \text{ } \mu\text{m}^2$ scanning x-ray bundle. After determining the composition of the top 3-5 nm, samples were sputtered for 1 minute using a 3kV $3 \times 3 \text{ mm}^2$ Ar-ion bundle to remove around 11 nm of material. Then a second spectrum was recorded to determine sub-surface composition.

Chapter 3

Electrochemical formation of Cr(III)-based films on Au electrodes

Abstract

Using an electrochemical Quartz Crystal Microbalance (eQCM) and a Rotating Ring Disk Electrode (RRDE; Au disk, Pt ring), we analyzed the deposition of reduced Cr-species formed from reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ on Au electrodes. Generally, the current induced by reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ is significantly larger than the accumulated amount of weight deposited on the Au electrode. Deconvolution of the reductive peak reveals two processes that can be differentiated by varying rotation speed. We therefore propose soluble $\text{Cr}^{\text{V}}\text{O}_4^{3-}$ is formed by reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$, followed by consecutive reduction of $\text{Cr}^{\text{V}}\text{O}_4^{3-}$ to primarily soluble $\text{Cr}^{\text{III}}(\text{OH})_4^-$. Simultaneously, reduction of $\text{Cr}^{\text{V}}\text{O}_4^{3-}$ also leads to the formation of a monolayer of $\text{Cr}^{\text{III}}(\text{hydr})\text{oxide}$. This monolayer significantly inhibits the further reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$, but allows the film to reach a maximum thickness of approximately 1.85 nm by reduction of surface adsorbed $\text{Cr}^{\text{V}}\text{O}_4^{3-}$ and/or de-hydroxylation of $\text{Cr}^{\text{III}}(\text{OH})_4^-$.

Note: this chapter is an adaptation of the publication with the same name: V. Smulders, N. Simic, A. S. O. Gomes, B. Mei, and G. Mul, "Electrochemical formation of Cr(III)-based films on Au electrodes," *Electrochim. Acta*, vol. 296, pp. 1115–1121, Feb. 2019.

3.1 Introduction

In Chapter 1 we discuss in detail the chlorate process and the crucial role the chromate additive ($\text{Na}_2\text{Cr}_2\text{VIO}_7$) has in chlorate production. Briefly, a Cr(III) film is deposited *in situ* on the cathode, which creates superb selectivity. However, due to the highly carcinogenic nature of chrome(VI), a safer alternative for cathodic protection against reduction of oxychlorides is needed.

Briefly, the properties of the $\text{Cr}^{\text{III}}\text{O}_x$ film have been studied extensively, with a focus on its structure [30], [38], thickness [39], and the effect of the underlying electrode [31], [32], [41], [42]. We note that, while it is known that chromium reduction produces more charge than the corresponding oxidation, and it has been proposed that an excess of reduced chromium goes into solution as $\text{Cr}(\text{OH})_4^-$ [31], this mechanism was not demonstrated or quantified. In addition the reductive pathway is unclear. A direct 3-electron reduction of Cr(VI) to Cr(III) has been proposed [12], although work on the reverse process, oxidation of Cr(III) to Cr(VI), suggests a series of 1-electron steps including formation of Cr(V) and Cr(IV) [52].

We therefore focus in this chapter on understanding the origin of the limited growth of a protective film from $\text{Na}_2\text{Cr}_2\text{O}_7$ ($\text{Cr}^{\text{VI}}\text{O}_4^{2-}$) on Au electrodes in a highly alkaline environment, designed to simulate the pH of the electrolyte close to the cathode in an industrial chlorate process. By comparing the increase in mass of the chromium-oxide film, determined using an electrochemical quartz crystal microbalance (eQCM), and the electrochemical response on a rotating ring disc electrode (RRDE), we demonstrate that reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ leads to a variety of soluble species, explaining the mismatch between oxidative and reductive charges. We propose a novel mechanism for deposition and growth termination of protective chromium films, which might contribute to the ongoing search for Cr(VI) replacements.

3.2 Results and discussion

For a description of the materials and methods used, as well as theoretical background for the QCM and RRDE techniques, please see Chapter 2.

3.2.1 Mass vs charge determined by eQCM

Initially, eQCM measurements were used to determine the quantity of $\text{Cr}^{\text{III}}\text{O}_x$ deposited on the Au electrode during electrochemical reduction of dichromate. The potential was cycled from -0.5 to 1.8 V vs. RHE, starting from 0.75 V (close to open circuit potential). The weight changes and the current response observed were measured: a representative cyclic voltammogram (CV) in the presence of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ is shown in Figure 3.1, and a reference CV in the absence of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ is provided in Figure A3.1.

Figure 3.1: (a) Cyclic voltammogram (on Au, at 50 mV s^{-1}) and corresponding Δm vs E in $10 \text{ mM Na}_2\text{Cr}_2\text{O}_7$ at pH 13.8. (b) Shows the oxidative range in more detail. Dashed grey lines are a guide showing the onset of mass change. The dashed red lines indicate linear mass change rates.

In the absence of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ (Figure A3.1) the expected currents due to hydrogen ($< -0.5 \text{ V}$ vs. RHE) and oxygen evolution ($> 1.5 \text{ V}$ vs. RHE) on the Au working electrode were observed, as well as peaks related to the formation (peak IIa and d) and reduction (peak III) of surface Au_2O_3 [52]. Accordingly, only a small, reversible mass difference of $0.2 \mu\text{g cm}^{-2}$ was detected at +1.0 to 1.5 V (peak III). When $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ is added (Figure 3.1), a much larger but equally reversible mass difference appears (see Figure A3.2 for reproducibility). Mass gain, which takes place only during the cathodic sweep, is initiated simultaneously with $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ reduction (Peak I), and continues at slower growth rate at more negative potentials (0.17 to -0.5 V). At these potentials a small, but not so obvious current is generated due to the continued reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$, likely to (solid) $\text{Cr}^{\text{III}}\text{O}_x$. Similarly, mass loss during the anodic sweep corresponds to the oxidation of $\text{Cr}^{\text{III}}\text{O}_x$ to soluble species (peak IIa and IIc, 1.0V

- 1.5V vs. RHE), as observed in the accompanying CV. Usually, the deposition of $\text{Cr}^{\text{III}}\text{O}_x$ films on the surface of the electrode is only discussed on the basis of the large reduction peak [30], [32], however as suggested by the eQCM results, film growth continues beyond this potential. Chrono-amperometric measurements (at -0.5 V vs. RHE) revealed that the total mass deposited after 20 minutes levels off at $0.58 \mu\text{g cm}^{-2}$, in good agreement with the calculated mass gain on the basis of measured anodic currents in cyclic voltammetry. The composition of an electrochemically deposited $\text{Cr}^{\text{III}}\text{O}_x$ film has been previously proposed, with suggestions being (hydrated) $\text{Cr}(\text{OH})_3$ [30], Cr_2O_3 [95], or a mixture of the two [41], [42]. Assuming the film is composed of $\text{Cr}(\text{OH})_3$, a mass of $0.58 \mu\text{g cm}^{-2}$ would require 1.6 mC cm^{-2} to reduce sufficient Cr^{VI} to Cr^{III} (Table 3.1, Q_{eQCM}). Using a density of 3.11 g cm^{-3} for $\text{Cr}(\text{OH})_3$, the film can be estimated to be 1,85 nm thick. This corresponds to 1 to 3 monolayers, depending on the method used: assuming the Cr_2O_3 unit cell, it is 1-2 monolayers, but for $\text{Cr}(\text{OH})_3$ it would be 2-3. This thickness is smaller than found in literature, where it is estimated by XPS to be in the order of 8 nm [30] and by ellipsometry to be 2-4 nm [39]. However, since the $\text{Cr}^{\text{III}}\text{O}_x$ film is likely not composed of stoichiometric $\text{Cr}(\text{OH})_3$ but rather similar to a gel-like layer including OH^- and H_2O moieties [10], [30], the discrepancy in reported thickness might be explained. Hydration of $\text{Cr}(\text{OH})_3$ will add significant volume without causing dramatic changes in film weight. In addition, the finding that 1-3 monolayers of chromium are involved is consistent with previous studies [31], [32], [40], [41]. It should also be mentioned that the mass gain appears to be independent of the concentration of sodium dichromate for concentrations between 10 and 40 mM (see Figure A3.3). This result deviates from previous studies, which have shown a dependence of film mass on concentration (in a large concentration range, 0.15 to 15 mM) as well as potential range (-0.6 to -1.7 V vs SCE) [30], [39]. Applied experimental conditions and differences in analytical methodology might explain the observed differences.

From the eQCM response it is obvious that there is a clear difference in rate between film formation (marked in Figure 3.1a by dashed red lines) and dissolution (region II): the mass gain region during the cathodic sweep contains two clearly distinct linear deposition rates suggesting a two-step

process, whereas the mass loss by oxidation of the chromium oxide film happens in a single, rapid step.

Because there are two distinct and linear regions of mass increase, it seems unlikely that the film is self-limiting simply due to its own increased resistance, or that the decrease in deposition rate is due to depletion of Cr(VI) near the electrode; one would expect the mass change to taper off gradually in those scenarios. Instead the distinct change in mass increase observed at approximately $0.38 \mu\text{g cm}^{-2}$ suggests that there is an abrupt transition in the deposition mechanism. Assuming reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ to $\text{Cr}(\text{OH})_3$, the mass ($0.38 \mu\text{g cm}^{-2}$) appears to be sufficient for a complete monolayer coverage. Since no major changes in the electrolyte or in the Au surface appear during deposition, it seems likely that complete coverage of the Au surface by $\text{Cr}(\text{OH})_3$ (or $\text{Cr}^{\text{III}}\text{O}_x$) is the trigger for the decreased deposition rate, before eventually, at $0.58 \mu\text{g cm}^{-2}$, the film growth is terminated. This is also indicated by the identical mass change found for different scan speeds, over a range of 5 to 100 mV s^{-1} (Figure A3.4), suggesting film thickness is primarily potential-dependent.

3.2.2 Characterization of the system using the RRDE

As analysis of the eQCM data shows that reductive current is significantly larger than the oxidative current (Figure 3.1a), a Rotating Ring Disc Electrode (RRDE) was used to further analyze the reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$.

Figure 3.2 shows cyclic voltammograms (CV) of a gold electrode (Au disk/Pt ring RRDE) at pH 13,8 and room temperature, with and without 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$. $E_{\text{Au,disc}}$ is scanned between -0.5 and + 2.25 V vs RHE, starting from close to the open circuit potential at +0.75 V. The electrode rotation rate was maintained at 4000 rpm, thereby reducing mass transfer limitations. These are inevitable in the eQCM setup, and explain discrepancies in voltammograms between Figure 3.1 and Figure 3.2.

The Pt ring electrode, E_{ring} , was kept at a constant oxidative potential of +1.5 V vs RHE. The measured ring current was approximately 0 mA in the absence of $\text{Na}_2\text{Cr}_2\text{O}_7$ during the entire sweep (not shown). In the presence of $\text{Na}_2\text{Cr}_2\text{O}_7$ a strong oxidative ring current, represented by the red line in Figure 3.2a, was detected matching the reductive current associated with the reduction of

$\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ observed on the disk. This result—the observation of an oxidative current on the ring—is strong evidence that besides the formation of a $\text{Cr}^{\text{III}}\text{O}_x$ film, soluble, reduced CrO_x -species are formed.

Figure 3.2: Cyclic voltammogram at 4000 rpm and 100 mV s⁻¹, RRDE with Au disc working electrode and Pt ring, $E_{\text{ring}} + 1.5$ V vs RHE, without (dotted black line) and with 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ (solid black line) at pH 13.8. The red line shows the oxidative current on the Pt ring electrode, during the Cr-containing experiment. It has been corrected for the collection efficiency and inverted to allow comparison to the j_{disc} (see Chapter 2 for details) (a) Shows peaks labeled with letters to aid in discussion. (b) Shows the oxidative region of (a) in more detail.

The most pronounced difference when comparing RRDE and eQCM measurements is observed in the oxidative region: as shown in Figure 3.1, for the eQCM significantly higher current is obtained in an oxidative scan, as compared to an electrode rotating at 4000 rpm. In the absence of rotation (Figure A3.5, solid red), the features of the CV of the disk appear very similar to the data obtained with the eQCM. Holding the disk at the potential of +0.6 V vs RHE for 30 minutes (without rotation, Figure A3.5, dashed red), reduces the intensity of oxidative current in a scan continued in the positive direction, matching the intensities observed at 4000 rpm. This suggests that aqueous reduced CrO_x -species, formed during the scan in the negative direction, are still in close proximity to the electrode surface, and can be easily re-oxidized in the return sweep. Providing time, or increasing mass transport away from the electrode using rotation, allows us to exclusively detect oxidation of the reduced CrO_x film.

The RRDE experiment confirms that reduction and oxidation of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ occurs in several steps. In Figure 3.2, the negatively-going scan shows a large reduction peak at around +0.4 V (peak I). Because we exclude substantial

mass transport limitations at 4000 rpm, we can attribute the decrease in reductive current at potentials more negative than +0.4 V (forming a peak, as opposed to a plateau for a continuous process) purely to inhibition of reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ by the *in situ* formed $\text{Cr}^{\text{III}}\text{O}_x$ film, in perfect agreement with the results previously discussed by Lindbergh and Simonsson [32], [41].

Detailed analysis of the charges involved in each of the peaks was performed (for more information see Figure A3.6). The obtained charges are summarized in Table 3.1, which also includes the charges calculated from the mass gain during the eQCM experiment. The $Q_{\text{eQCM}} = 1.6 \text{ mC cm}^{-2}$, mentioned above, is in good agreement with the oxidation of Cr(III) $Q_{\text{disc ox}} = 1.7 \text{ mC cm}^{-2}$, but much smaller than the charge associated with reduction of Cr(VI) $Q_{\text{disc red}} = -45.9 \text{ mC cm}^{-2}$. From our eQCM experiments, we assume that $Q_{\text{disc ox}}$ corresponds to the complete stripping of the $\text{Cr}^{\text{III}}\text{O}_x$ film, also in agreement with recent findings [32]. The reductive charge not accounted for by $Q_{\text{disc ox}}$ is associated with the current detected at the ring electrode: the corrected ring charge $Q_{\text{ring}} = 43.4 \text{ mC cm}^{-2}$. Since solid products cannot be detected at the ring, this charge can be attributed solely to the formation of soluble products. Subtracting Q_{ring} from $Q_{\text{disc red}}$ leaves a net difference $Q_{\text{RRDE net}} = -2.5 \text{ mC cm}^{-2}$, which is of the same order of magnitude as Q_{eQCM} and $Q_{\text{disc,ox}}$. This clearly demonstrates that the majority of the reductive current is used to produce soluble CrO_x species, and only a small fraction can be attributed to film formation.

Table 3.1 Charges corresponding to redox processes. Values displayed in italics should correspond to the Cr(III)-(hydr)oxide film growth.

Source	Charge (mC/cm ²)
Q_{eQCM} : Charge needed for mass gain found in QCM, for Cr(VI) to Cr(OH) ₃	-1.6
$Q_{\text{disc ox}}$: disc oxidation minus Au oxidation +0,75 V through +1,6 V	-1.7
$Q_{\text{disc red}}$: total disc reduction +0,6 V through -0,1 V	-45.9
Q_{ring} : ring oxidation, after efficiency correction, +0,6 V through -0,1 V	43.4

$$Q_{RRDE \text{ net}}: Q_{\text{disc red}} - Q_{\text{ring}}$$

-2,5

Although it is not so obvious in Figures 3.1 and 3.2, the chromium reduction peak is likely the result of multiple reductive processes. This is confirmed by varying the rotation speed of the electrode. The shape of the reduction peak is asymmetrical at low rotation speeds (see Figure A3.7). Deconvolution of the peak obtained at 100 rpm, using a semi-quantitative fit, is shown in Figure 3.3a.

Figure 3.3: a) Deconvolution of the reduction peak, CV at 100 rpm, 100 mV s⁻¹; b) Area of fitted peaks vs rotation speed. For duplicate measurement see Figure A3.8.

The plateau current of a mass-transport limited reaction should be linearly dependent on the square root of the angular rotation velocity according to the Levich equation [88]. As previously discussed, there is no mass transport limited current plateau, since an oxide-film is formed at the electrode. Nevertheless, the peak current for the two deconvoluted peaks in Figure 3.3a has been used to construct the graph shown in Figure 3.3b. Peak Ia shows a linear decrease with rotation rate, suggesting that a mass transfer limited reaction takes place, *prior* to film growth. Peak Ib seems independent of, or even inversely correlated to rotation rate. Independence would suggest the reaction is kinetically controlled, whereas an inverse correlation suggests there is an aqueous intermediate involved in the second reductive process: increased mass transport by higher rotation rates causes this intermediate to be moved away from the electrode surface before it can react further, decreasing the rate and associated current of the consecutive electrochemical reaction [89].

Given the different apparent mass transfer dependencies, the ring current was also analyzed in further depth. Figure 3.4a shows a more detailed view of the ring current as a function of disk potential. Several peaks are observed. Their positions and relative intensities vary based on the applied ring potential.

Figure 3.4: (a) Ring current versus disc potential, for decreasing ring potentials, during disc cathodic sweep with 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, pH 13.8, 4000 rpm and 200 mV s^{-1} , RRDE with Au disc working electrode and Pt ring (as in Figure 2); b) Shows a detail of a).

It is difficult to identify the number and origin of the oxidation reactions occurring on the ring with certainty, but at the two most oxidative ring potentials used (+1.5 V and +1.2 V vs RHE), the peak-shape of the oxidation current on the ring is similar to that of the reduction current on the disc (which is much more asymmetrical at the 200 mV s^{-1} used in Figure 3.4). The ring peaks are centered at $E_{\text{disc}} +0.37$ V and $+0.13$ V vs. RHE. This is slightly shifted compared to the reduction peaks of Cr(VI) detected on the disc ($+0.33$ and $+0.27$ V vs. RHE); this may be partly attributed to the time delay it takes for the species to move from the disc to the ring, and partly to kinetic effects, either due to different kinetics for oxidation versus reduction, or because the disc is Au while the ring is Pt.

At less positive ring potentials, $E_{\text{Pt,ring}} < +1.2$ V, significantly smaller currents are obtained, as shown in Figure 3.4b. Interestingly, the oxidation process belonging to the detected current that peaks at $E_{\text{disc}} +0.37$ V almost disappears, suggesting that $E_{\text{ring}} +1.2$ V is the minimum potential required for the oxidation of this particular species. For even lower applied potentials an oxidative current can still be detected at the ring and it seems as though as

many as three peaks may be present. However, only two distinct oxidative reactions dominate, whose peak-overlap results in a variety of peak shapes. At the lowest ring potential used, $E_{\text{Pt,ring}} = +0.7$ V, only a single peak is visible at $+0.22$ V vs RHE, a good match for peak Ia. The various peak shapes can then be explained by a narrow peak at $+0.22$ V overlapping with a broad peak, that for sufficiently high potentials dominates the $+0.37$ V region. It is interesting to note that the lowest investigated ring potential, $+0.7$ V, is well below the onset potential of chromium oxidation on Pt, and in fact only barely more oxidative than required for reduction of Cr(VI) (see Figure A3.9). This is in contrast to Au electrodes, where the oxidation of the soluble species occurs in the same potential region, as film oxidation (see also Figure A3.5). Figure A3.9 also shows that any Pt contamination from the CE [96] should result in a visibly different $\text{Cr}^{\text{III}}\text{O}_x$ formation-mechanism. Since all measurements are consistent with the behavior of Au, Pt contamination of the disk can be safely assumed to be absent.

Thermodynamic data relating to Cr-electrolyte systems can be summarized in a Pourbaix diagram (see Figure A3.10, adapted from [97]). A slight mismatch between actual values of the experiments and the Pourbaix diagram is not surprising because electrode overpotentials and the iR drop of the cell have not been taken into consideration in constructing the Pourbaix diagram. Experiments were performed at pH 13.8, where thermodynamics suggest chromium exists as chromate, $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$. As a negative potential is applied, $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ is reduced in a fast, mass transfer limited 1-electron reaction to soluble $\text{Cr}^{\text{VO}}\text{O}_4^{3-}$ [52], [97], explaining the rotation rate dependence of peak Ia (Figure 3.3 and A3.8), and the accompanying signal on the ring induced by re-oxidation of $\text{Cr}^{\text{VO}}\text{O}_4^{3-}$ to $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$. A consecutive, kinetically limited reduction of $\text{Cr}^{\text{VO}}\text{O}_4^{3-}$ leads to formation of lower valence CrO_x species, most likely $\text{Cr}^{\text{III}}(\text{OH})_4^-$ [31], [97]. This is again a soluble species that can be detected on the ring. In addition, solid $\text{Cr}^{\text{III}}\text{O}_x$ is deposited [97], explaining film formation observed by eQCM. Once a monolayer of $\text{Cr}^{\text{III}}\text{O}_x$ is formed, the reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ to $\text{Cr}^{\text{VO}}\text{O}_4^{3-}$ is inhibited (similar to inhibition of oxychloride reduction) and the remaining current, quickly decreasing in quantity, is due to the kinetically limited reduction of (surface adsorbed) $\text{Cr}^{\text{VO}}\text{O}_4^{3-}$ to $\text{Cr}^{\text{III}}(\text{OH})_4^-$ and some additional $\text{Cr}^{\text{III}}\text{O}_x$. This theory is also supported by work on the oxidation of Cr(III) to

Cr(VI), where a three-step mechanism was proposed involving similar intermediates [52].

The slower, but still significant mass gain observed by eQCM in the potential region where almost no reduction currents are recorded (Figure 3.1a; $E_{Au} = +0.17$ to -0.5 V), suggests previously proposed direct reduction of $Cr^{VI}O_4^{2-}$ to $Cr^{III}O_x(s)$ is improbable [30]–[32]. We propose that an outer-sphere reduction of $Cr^{VI}O_4^{3-}$, likely present as surface-bound intermediate, leads to film formation, which is increasingly hampered as the film grows thicker, until the growth is finally terminated entirely. In addition, there could be a direct chemical deposition from the previously formed $Cr^{III}(OH)_4^-(aq)$ to $Cr^{III}O_x(s)$. However, a small current not present without chromium can be observed in this region (Figure A3.1c), corresponding to the current required to deposit the small mass gain (0.05 mA cm^{-2}). QCM measurements at different scan speeds all show the same trend (Figure A3.4), indicating a link between film mass and potential, rather than film mass and time. Both these observations point towards the Faradaic mechanism being dominant, but a chemical deposition cannot be excluded.

In summary, the following electrochemical reduction reactions of $Cr^{VI}O_4^{2-}$ occur on Au electrodes. Please note that the notation above the arrows simply indicates the electrode surface during the reaction, not necessarily the catalytic involvement of this surface.

For the first monolayer $E_{Au} = +0.5$ to $+0.17$ V (peak I):

(mass-transfer limited - rotation dependence of peak Ia)

(kinetically controlled, analysis of peak Ib)

(kinetically controlled, analysis of peak Ib)

Then deposition of the subsequent layer occurs at $E_{Au} = +0.17$ to -0.5 V, where reduction of Cr(VI) is almost entirely suppressed:

The reverse reactions of (3.6) and (3.7) probably cause the current detected on the Pt ring of the RRDE, whereas the reverse reactions of Equations (3.8), (3.9) and (3.10) give rise to the oxidative features during film stripping (see Figure 1, peak II). The mechanism has also been schematically summarized in Figure 3.5.

Figure 3.5: Schematic overview of the processes occurring on the Au electrode upon reduction of chromate at alkaline pH.

3.3 Conclusions

We investigated the dynamics of formation of a film of $\text{Cr}^{\text{III}}\text{O}_x$ from sodium dichromate on Au, using electrochemical and gravimetric methods.

Only a small fraction of reductive charge can be attributed to film growth; the remainder appears to be related to the formation of soluble products. From eQCM data, we find a $\text{Cr}^{\text{III}}\text{O}_x$ film of approximately 1.85 nm in thickness. We propose that reductive deposition of Cr(III) from (di)chromate is preceded by reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ to soluble $\text{Cr}^{\text{V}}\text{O}_4^{3-}$, which forms primarily soluble $\text{Cr}^{\text{III}}(\text{OH})_4^-$ but also a monolayer of $\text{Cr}^{\text{III}}\text{O}_x$. This layer inhibits the further reduction of $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$, similar to the inhibition of reduction of oxychlorides.

Appendix 3

Figure A3.1: (a) Cyclic voltammogram (at 50 mV s^{-1}) and corresponding Δm vs E without (blue line) with 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ (black line, same as Figure 1) pH 13.8. (b) Shows the oxidative range in more detail. Dashed grey lines are a guide showing the onset of mass change. The dashed red lines indicate linear mass change rates. (c) Shows the far reductive region in more detail. Dashed lines are a guide to read the current density.

Figure A3.2: Three consecutive cyclic voltammograms (dotted lines) (on Au, at 50 mV s^{-1}) and corresponding Δm vs E (solid lines) in 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, pH 13.8. Scans were taken in order black, red, blue.

Figure A3.3: Δm vs $[\text{Cr}]$ for $[\text{Cr}] = 10, 20, 30$ and 40 mM after 20 minutes chronoamperometry at -0.5 V vs RHE .

Figure A3.4: Cyclic voltammograms (on Au) (dotted line) and corresponding Δm vs E (solid line) in 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, pH 13.8, at different scan speeds. The red line shows 5 mV s^{-1} , black 50 mV s^{-1} , blue 100 mV s^{-1} .

Figure A3.4 shows that at all scan speeds the same mass is achieved, despite the vastly different current densities. The rate of mass gain also changes at roughly the same potential, and exactly the same film mass. As higher scan speeds lead to more cathodic transitions, a kinetic limitation to the film formation seems likely. The fact that the rate transition occurs at the same film mass confirms the film thickness as the trigger for the change in mass change rate.

Figure A3.5: Cyclic voltammogram, 100 mV s^{-1} , RDE with Au disc working electrode, without (grey dotted line) and with 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, pH 13.8. Electrode was stationary (red lines) or rotating at 4000 rpm (black lines). Solid lines indicate continuous scans, dashed lines show scans which were paused during the oxidative sweep at $+0.6 \text{ V vs RHE}$ for 30 minutes.

The oxidative region of the CV looks different when comparing a stationary to a rotating electrode (Figure A3.5 solid red vs solid black). By pausing the voltammogram for 30 minutes during the oxidative sweep, at a potential where no current was flowing (+0.6 V vs RHE) the electrolyte near the electrode was equalized to the bulk electrolyte by diffusion. The resulting voltammograms (Figure A3.5 dashed red and black lines) are very similar to the continuous cycle measured at 4000 rpm, regardless of rotation speed. This shows that the increased and shifted oxidative current in the stationary CV is the result of aqueous products still in solution near the electrode, and only the underlying peaks revealed at high rotation speed (or after pausing to allow time for diffusion) can be attributed to film oxidation.

Figure A3.6: (a) Cyclic voltammogram at 4000 rpm and 100 mV s⁻¹, RRDE with Au disc working electrode and Pt ring, E_{ring} 1.7 V vs RHE, without (dotted grey line) and with 10 mM $Na_2Cr_2O_7$ (solid black line), pH 13.8. The dashed blue line shows the current on the Pt ring electrode, during the Cr-containing experiment. The ring is kept at a constant potential of +1.5 V vs RHE. Colored areas show the integration areas used to calculate the charges that are given in Table 1. The solid blue line shows the ring current, corrected for the collection factor (see experimental section). (b) Shows the oxidative region of (a) in more detail.

Figure A3.7: Cyclic voltammogram, 100 mV s^{-1} , RDE with Au disc working electrode in $10 \text{ mM Na}_2\text{Cr}_2\text{O}_7$, pH 13.8. Rotation speed varied from 100 to 4000 rpm.

Peak Ib was centered on $+0.27 \text{ V vs RHE}$. Peak Ia was given as a starting point a center of $+0.33 \text{ V vs RHE}$, which at high rotation speeds was accurate. However, it was not constrained to this center value and at lower rotation speeds. Peak Ia shifts to more positive potentials up to $+0.39 \text{ V vs RHE}$. No other constraints were applied to the fit.

Figure A3.8: Duplicate measurements of Figure 3b. Area of fitted peaks vs rotation speed after deconvolution of the reduction peak of a CV recorded at 100 mV s^{-1} , RRDE with Au disc working electrode and Pt ring, $E_{\text{ring}} + 1.5 \text{ V vs RHE}$ in $10 \text{ mM Na}_2\text{Cr}_2\text{O}_7$ at pH 13.8.

The maximum current density was not the same between the three experiments, possibly due to the effects of polishing between experiments.

However, the trend itself is very reproducible and only qualitative conclusions are drawn from these trends, so the exact values are of lesser importance.

Figure A3.9: Cyclic voltammogram, 4000 rpm and 100 mV s^{-1} , RDE with Pt disc working electrode in without (blue) and with (black) 10 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, pH 13.8.

Figure A3.9 shows a Pt in the absence (blue) and presence (black) of chromium. The deposition of chromium on Pt proceeds in a distinctly different manner to that on Au. There is no trace of the Pt deposition mechanism during experiments using Au electrodes. Therefore Pt contamination from the CE [96] can be safely excluded as a factor in this work.

Figure A3.10: Pourbaix diagram of Cr, focusing on formation of hydroxide. The arrow indicates the phase transitions proposed, occurring at the applied pH of ~ 14 (1 M NaOH). Adapted from [97].

Chapter 4

Films on Pt from low-concentration chromate and molybdate solutions

Abstract

The deposition of $\text{Cr}^{\text{III}}\text{O}_x$ on Pt has been studied using RRDE and QCM. We show that much less charge is associated with the formation of soluble intermediates than on Au (See Chapter 3). Overall, a similar but slightly thinner film is formed than on Au. However, oxidation is markedly different, being also accompanied by small amounts of soluble species, which were not observed on Au electrodes. In addition, film oxidation occurs in an earlier potential region. By limiting the chromate concentration we can manipulate the film thickness, allowing us to distinguish different phases of film growth. We discuss several theories to explain the altered processes as compared to Au electrodes.

In addition, we study the kinetics of the cathode reactions as a function of chromate concentration. We then introduce molybdate as a co-additive in solutions containing ultra-low chromate concentrations, and find that molybdate enhances the HER, improves hypochlorite reduction inhibition, and creates high film stability. Finally, we show that these properties are due to the cathodic oxide film, not the chromate and molybdate in solution.

4.1 Introduction

The deposition of a cathodic $\text{Cr}^{\text{III}}\text{O}_x$ film from alkaline dichromate solutions was investigated in Chapter 3. Based on those results we cannot exclude chemical oxidation of reduced Cr-species by oxychlorides during chlorate production. However, interaction of CrO_x -species with (oxy)chlorides requires further assessment because the industrial chlorate electrolyte contains an excess of 100 g dm^{-3} of NaCl and high concentrations of oxychlorides. Cl is a reactive molecule, and is known to occupy surface sites on many materials [98], so there is a possibility that chloride affects surface processes such as deposition of $\text{Cr}^{\text{III}}\text{O}_x$. The Au electrode used in Chapter 3 is unsuitable for this purpose, because it can dissolve through the formation of Au chlorides [98].

From literature it is known that a similar $\text{Cr}^{\text{III}}\text{O}_x$ film as we reported for Au, also forms on other noble metals [30], [38], [39], [41]–[43]. In this chapter we continue our investigation of the $\text{Cr}^{\text{III}}\text{O}_x$ film on Pt electrodes to verify this hypothesis, and moreover this allows us to introduce and study the effect of NaCl on deposition. In addition, we expand our investigation to μM concentrations of chromate, down from the industrial 20 mM used in Chapter 3. By understanding the limiting factors at these ultra-low concentrations we may be able to decrease the amount of chromate required industrially. Using this newly developed understanding we introduce molybdate as a co-additive. This has been shown to increase the performance of chlorate cells at low chromate concentrations [49], [60], [61], [71], but the mechanism is still poorly understood. The literature regarding molybdate is discussed in detail in Chapter 1.

We find that the CrO_x film is slightly thinner on Pt than on Au, as expected from literature. The deposition process is similar to that on Au, but there are some significant differences, most notably a much smaller production of soluble intermediates, and a different oxidative process. We find that molybdate activates the cathode for the HER, and enhances the chromate film by improving its stability and selectivity.

4.2 Results and discussion

4.2.1 Chromate on Pt

For a description of the materials and methods used, as well as theoretical background for the QCM and RRDE techniques, please see Chapter 2.

Figure 4.1 shows the RRDE (a) and QCM (b) results for a Pt electrode in a solution of 0.1 M NaOH and 5 mM $\text{Na}_2\text{Cr}_2\text{O}_7$. Experiments without chromate are shown in Figure A4.1. Comparative experiments with 2 M NaCl are shown in Figure A4.2, but the addition of salt to the electrolyte did not result in notable changes.

Figure 4.1: Cyclic voltammetry of a Pt electrode in 0.1 M NaOH, 5 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ at 50 mV s^{-1} . (a) shows RRDE data at 4000 rpm, $E_{\text{ring}} + 1.4 \text{ V}$, corrected for 25% collection efficiency. The inset shows a detail of the ring current density in $\mu\text{A cm}^{-2}$. (b) Shows QCM data with current density (top) and mass difference (bottom).

Figure 4.1a shows the current from the disc (black) and ring (red) electrode. The ring was held at a constant potential of +1.4 V. The ring current in the figure has been corrected assuming a theoretical collection efficiency of 25%, and has been inverted in order to allow direct comparison between ring and disc current. In the reductive scan, the disc current shows a reductive peak associated with surface PtO reduction at +0.6 V, and a large current due to the HER at -0.1 V. Peaks relating to chromate have been labeled as peaks Ia, Ib, IIa, and IIc in line with the nomenclature from Chapter 3. Chromate reduction is evident from the reductive current starting at +0.55 V (shallow

peak Ia) and cumulating in a clear peak at around +0.1 V (peak Ib). An oxidative ring current is observed during reduction of chromate, which extends from +0.4 V to +0.1 V, giving it a distinctive shape that is very similar in appearance to that found on Au electrodes. PtO reduction and HER are not significantly affected by the $\text{Cr}^{\text{III}}\text{O}_x$ film, in agreement with literature [37], [40], [44], suggesting the underlying Pt surface is not much affected by the film.

In the anodic sweep the typical oxidative peaks related to Pt-H oxidation can be seen at +0.2 and +0.3 V. The oxidation peaks at +1.1 (IIa) and +1.3 V (IIc) can be assigned to the oxidation of the $\text{Cr}^{\text{III}}\text{O}_x$ film, superimposed on a small current due to Pt oxidation (Figure A4.1).

Figure 4.1b shows the QCM results. The top figure shows the voltammetry, which is qualitatively similar to the scan recorded in the RRDE. Quantitative differences can be explained by the different mass transport conditions: the QCM electrode is stationary whereas the RRDE is rotated at 4000 rpm. The potential range used with the QCM is narrower than for the RRDE, to avoid the HER and oxidation of Pt. The bottom figure shows the mass difference throughout the experiment. Mass gain is visible starting at +0.35 V in the cathodic scan, 200 mV more negative than the onset of disc and ring current in the cathodic sweep of the RRDE. The mass reaches a value of $0.41 \mu\text{g cm}^{-2}$ at the most negative potential of 0 V. Chronoamperometry performed at this potential hardly shows additional mass gain, indicating that the $\text{Cr}^{\text{III}}\text{O}_x$ film growth self-terminates at $0.46 \mu\text{g cm}^{-2}$ at 0 V (Figure A4.3a). Assuming a density of 3.11 g cm^{-3} for $\text{Cr}(\text{OH})_3$, this mass gain suggests a film thickness of only $\sim 1.5 \text{ nm}$. In the anodic scan the film is stable up to +1.3 V, where, concomitantly with the second oxidative peak, rapid mass loss can be observed leading to full removal of the film.

The total charges related to chromate reduction and oxidation are shown in Table 4.1. By comparing the ring and disc charges, the charge related to the formation of solid $\text{Cr}^{\text{III}}\text{O}_x$ can be isolated from that related to soluble products. Table 4.1 shows that, like on Au, the charge balance is closed during deposition: the difference in charge between ring and disc is 1.3 mC cm^{-3} , matching precisely to the charge required to create $1.46 \mu\text{g Cr}(\text{OH})_3$ from CrO_4^{2-} . In good agreement +1.1 mC is found during film oxidation.

Table 4.1: Charges corresponding to potential regions associated with the reduction of chromate (+0.35 V to 0 V), and the oxidation of the deposited $\text{Cr}^{\text{III}}\text{O}_x$ film (+0.95 to +1.35 V). Charges have been corrected for the charge in that region on Pt in the absence of chromate, extracted from Figure A4.1.

Source	Q (mC cm ⁻²)
Disc charge (reduction)	-2.0
Ring charge (solution)	+0.74
Difference disc-ring (deposition)	+1.3
Disc charge (oxidation)	+1.1
Charge needed for 0.46 $\mu\text{g Cr}(\text{OH})_3$ from CrO_4^{2-}	-1.3

To gain further insight into the Pt film, experiments were also performed at lower chromate concentrations. Lowering the concentration results in the formation of an incomplete film, which in turn leads to changes in the oxidative region of the voltammogram. The results are shown in Figure 4.2.

Figure 4.2a shows the development of a voltammogram on a stationary RDE as a function of chromate concentration. The chromate reduction regions at +0.4 and +0.1 V grow with the chromate concentration, as the supply of reactant near the electrode surface increases. Similarly, the current in the film oxidation region also increases with chromate concentration. However, the oxidation also shows a clear peak shift. At 2 μM chromate the oxidation peak is hard to observe. At 20 μM it appears at +1.0 V, shifting to +1.1 at 200 μM . At 2000 μM , a second peak appears at +1.25 V, still 50 mV short of the +1.3 V observed at 5 mM chromate in Figure 4.1.

Figure 4.2b shows the corresponding QCM experiment. The mass difference increases with chromate concentration. However, it should be noted that this is simply a matter of mass transfer limitation, as maintaining a reductive potential results in continuous, albeit slow, film growth until it terminates at a similar value as when using 5 mM chromate (Figure A4.3b).

The oxidation peaks develop at slightly lower concentration on the QCM than on the RDE, possibly due to the different geometry and surface-to-volume ratio of the cells. At 200 μM chromate, mass loss begins at +1.15 V, 150 mV lower than for 5 mM chromate. However, in both cases the mass loss is clearly concomitant with the onset of the second oxidation peak.

Figure 4.2: Cyclic voltammetry of a Pt electrode 0 rpm in 0.1 M NaOH at 50 mV s⁻¹ (a) shows an RDE electrode at 0 rpm with chromate concentration of 2; 20; 200; and 2000 μ M. (b) Shows the mass difference recorded using QCM with chromate concentration of 2; 20; and 200 μ M.

At 20 μ M chromate, the oxidative mass loss is less abrupt, although a region of increased mass loss can be observed between +0.9 and +1.15 V (grey dashed line in Figure 4.2b), coinciding with the first oxidation peak. However, in contrast to the higher concentrations, a continuous mass loss can be observed between 0 and +0.9 V. At 2 μ M chromate, this effect is sufficient to lose all mass before the oxidative region is reached, explaining why there are no peaks there: there is no film left to reduce. This effect is also present at 20 μ M, although in this case it is less pronounced and a distinct oxidation peak with associated mass loss can be seen. The peak and mass change amount to less than a full monolayer. Since the continuous mass loss is absent at 200 μ M, when there is more mass than a single monolayer, the second layer may be protecting the first.

By combining the information from Figure 4.1 and Figure 4.2, we can now interpret the differences between Au and Pt. At first glance these figures may look similar to those found on Au: a ring current indicating soluble products accompanies the deposition, along with a mass increase that is fully removed at oxidative potentials. However, there are several important differences.

First, the onset potentials for the various processes are different on Au and Pt, and they are not always accompanied by mass change in the same manner.

The potentials have been summarized in Table 4.2. In the cathodic scan, mass gain requires less positive potential (reduction is less favorable) for Pt than for Au, whereas in the anodic scan a more positive potential is required to induce oxidation of the film (oxidation is again less favorable). For Pt, the first oxidation peak (IIa) does not result in mass loss, whereas for Au this is the case.

Table 4.2: Summary of onset potentials and their accompanying qualitatively indicated mass change type, relating to deposition from chromate.

Peak	E_{Au} (V)	Δm_{Au}	E_{Pt} (V)	Δm_{Pt}
Ia	+0.55	Gain	+0.55	-
Ib	+0.50	Gain	+0.35	Gain
IIa	+1.0	Loss	+1.0	-
IIc	+1.35	-	+1.15	Loss

Second, there is a difference in total mass, which is smaller for Pt than the $0.58 \mu\text{g cm}^{-2}$ found on Au [99] by 20%. This is in accordance with literature [30], but has not been previously explained.

Third, and most significant, the ring charge during deposition on Pt is only $+0.73 \text{ mC cm}^{-3}$, two orders of magnitude smaller than that found for Au (43 mC cm^{-3} [99]), so although film thickness is comparable for Au and Pt, the production of soluble species is not.

Various hypotheses are possible to explain the differences, but we believe the underlying surface plays a role. The 150 mV region where only soluble products are formed ($\text{Cr}^{\text{VO}}_4^{2-}$) occurs only on bare Pt, and film deposition starts concomitantly with the formation of a Pt-H surface. This might result in a different nature of the (monolayer) CrO_x film on Pt than on Au, and explain why the ring current is so much lower for Pt than for Au as the rate of formation of $\text{Cr}^{\text{III}}(\text{OH})_4^-$ may be much lower. This may also mean the charge permeability of the CrO_x film is lower for Pt than for Au, indicating a difference in chemical structure.

The theory of a different chemical structure of the film and lower charge permeability for Pt is in agreement with the different overpotential for oxidation of CrO_x , and the absence of mass loss in peak IIa for Pt. The first

monolayer on Pt is unstable at any potential more oxidative than its deposition potential (peak Ib), as evident from Figure 4.2, and has a lower oxidation potential than the layers on top. It apparently can undergo bottom-up oxidation without going into solution, explaining the current in peak IIa, which does not result in mass loss. Apparently on Au the first monolayer CrO_x film has a better charge permeability. This logically results in top-down oxidation (oxidation of the film in contact with the electrolyte), explaining the immediate mass loss upon oxidation of the CrO_x film on Au.

4.2.2 Film-induced kinetics and molybdate co-additive

Molybdate is known to enhance the effect of the chromate additive at ultra-low chromate concentrations such as those studied here [49], [60], [61], [71]. However, molybdate deposition occurs in the HER regime on Pt, so bubbles caused too much interference to investigate molybdate film growth using the QCM. Instead, polarization curves were used to determine the effectiveness of the partially-formed $\text{Cr}^{\text{III}}\text{O}_x$ films for hypochlorite reduction as a function of chromate and molybdate concentration. The results are shown in Figure 4.3. In Figure 4.3a the black curve shows a reference experiment using a Pt electrode in an alkaline solution without hypochlorite. It shows only the HER, evident as a monotonic increase in potential at high current densities. An identical experiment in the presence of 80 mM hypochlorite is shown using the open red markers, and this additionally shows a potential plateau between +0.1 and 0 V vs RHE, indicating that a mass transport limited process occurs, *i.e.* hypochlorite reduction.

The addition of 1, 6 and 27 μM chromate is shown in the open green, blue and turquoise curves respectively. At 1 μM the reduction of hypochlorite is partially inhibited, as evident from the shift of the plateau edge to lower current densities. At 6 and 27 μM no hypochlorite reduction is visible at all, and the curves match the black reference curve. For all concentrations the HER is unaffected.

The effect of 10 mM of molybdate on this series of experiments is shown by the solid markers for the different chromate concentrations. For all chromate concentrations, an activation of the electrode in the HER region can be observed by the shift of the curve at high current density to smaller potentials. In addition, a small inhibition of the hypochlorite reduction is observed, again

indicated by a shift in the plateau edge. This effect stacks with the inhibition caused by chromate.

Figure 4.3: *iR*-corrected polarization curve in 0.1 M NaOH, 2 M NaCl at 2500 rpm. Electrodes were pre-polarized at -0.1 V vs RHE for 5 minutes before measuring the polarization curve from high to low current density. The grey dashed line indicates the current density typically used to run the industrial chlorate process. The black squares show reference experiments without additives (a): Curves measured in solutions containing 80 mM ClO⁻, and without (open markers) or with (solid markers) 10 mM MoO₄²⁻. CrO₄²⁻ was present at 0; 1; 6; or 27 μM. (b): Dark blue curves show electrodes that have been transferred to a solution without additives, after prepolarization in solutions with 27 μM chromate, both without (open markers) and with (solid markers) 80 mM molybdate.

The activating effect of the molybdate could be caused either by activation of the HER by the MoO_x film [49], [60], or by continuous reduction of molybdate. To determine if the activation observed for molybdate is related to the film or the additive, an experiment was performed wherein a cathode was pre-polarized in an additive-containing solution, then transferred to a solution containing only the background electrolyte. The results are shown in Figure 4.3b. The curves representing the mixed additive films (solid diamonds and triangles) match perfectly for *in situ* and *ex situ* films. This shows that the activation is due to activation of the HER by the film rather than the solution additive.

In addition, Figure 4.3b shows that the presence of molybdate also enhances the stability of the film. Even at the highest chromate concentration studied, 27 μM, the film's selectivity-inducing effect is not maintained after transfer as evident by the obvious hypochlorite reduction. However, a film that was deposited in the presence of molybdate still inhibits hypochlorite

reduction even after transfer. This clearly shows molybdate enhances the lifetime of the film in an alkaline environment at open circuit conditions, greatly enhancing the corrosion protection.

4.3 Conclusions

First, we have investigated the deposition of a thin film of $\text{Cr}^{\text{III}}\text{O}_x$ from sodium dichromate on a Pt electrode using RRDE and QCM. We can account for all charge transferred, and we find a mechanism similar to that on Au electrodes proposed in Chapter 3, although there are significant differences. Although the deposition of a film is accompanied by the production of soluble products in both cases, on Pt the amount of these is two orders of magnitude smaller than on Au. This can be explained by a different $\text{Cr}^{\text{III}}\text{O}_x$ on Pt compared to Au. This theory is further supported by the earlier mass loss and the less oxidative potential required for film deposition and oxidation on Pt. Overall, the mechanism proposed in Chapter 3 is able to explain the observation on Pt, suggesting applicability to a wider array of substrates.

Second, we have investigated the performance in terms of suppressing hypochlorite reduction on films deposited from ultra-low μM chromate solutions. We found complete blocking at $27\ \mu\text{M}$, but film stability was limited. We also investigated the influence of molybdate, and found that it activates the cathode for HER, improves film stability and enhances the hypochlorite suppression, making it an exemplary co-additive. We believe the origin of the effect should lie in the formation of a different, mixed Mo-CrO_x composite, of which the composition and formation mechanism requires further investigation.

Appendix 4

Figure A4.1: Cyclic Voltammogram using a Pt in 0.1 M NaOH at 50 mV s^{-1} using (a) Pt ring, Pt disc RRDE at 4000 rpm, $E_{\text{ring}} + 1.4 \text{ V}$; and (b) QCM.

Figure A4.1 shows an RRDE and QCM voltammogram in the absence of chromate in the electrolyte. No ring current was observed.

Figure A4.2: Cyclic voltammetry of a Pt electrode in 0.1 M NaOH, 2 M NaCl, 5 mM $\text{Na}_2\text{Cr}_2\text{O}_7$ at 50 mV s^{-1} . (a) shows RRDE data at 4000 rpm, $E_{\text{ring}} + 1.4 \text{ V}$, corrected for 25% collection efficiency. The inset shows a detail of the ring current density in $\mu\text{A cm}^{-1}$. (b) Shows QCM data with current density (top) and mass difference (bottom).

Figure A4.2 Shows RRDE and QCM experiments on a Pt electrode in the absence of NaCl. No major differences are observed compared to Figure 4.1.

Figure A4.3: Mass difference recorded during chronoamperometry on a Pt electrode in 0.1 M NaOH, 2 M NaCl, at 50 mV s^{-1} at 0 V vs RHE, in the presence of (a) 5 mM and (b) 20 μM $\text{Na}_2\text{Cr}_2\text{O}_7$.

Chapter 5

Mixed chromate and molybdate additives for cathodic enhancement

Abstract

This chapter investigates the effect of μM concentrations of chromate at the pilot scale using a Ti cathode. We find that chromate at such low concentrations does not provide sufficient energy efficiency. Based on the results in Chapter 4 we therefore introduce molybdate as a co-additive to improve performance, and we find an optimum energy improvement of 4% when combining 0.8 mM molybdate and 27 μM chromate. Minimal molybdate addition is preferable because while the presence of any molybdate improves the cathodic current efficiency, the detrimental effects from homogenous hypochlorite decomposition to oxygen scale with molybdate concentration. A detailed investigation using a quartz crystal microbalance reveals a hybrid film deposition process at the applied molybdate concentrations. Molybdate and hybrid film growth were not found to be self-limiting, although no detrimental effects from excessive film growth were detected during the pilot trials. RDE polarization curves show hybrid behavior in line with that found in the pilot cell. Discrepancies between lab and pilot arise, as individual cell geometries influence the effective additive concentration at the electrode surface, shedding light on the subtleties of the concentrations involved.

5.1 Introduction

In Chapter 4 we studied film growth from solutions containing μM concentrations of chromate, both with and without molybdate as a co-additive on Pt surfaces. We found that molybdate activates the electrode for the HER and improves the inhibition of hypochlorite reduction provided by chromate, in agreement with literature [49], [60], [61], [71]. We also found it improves film stability. Unfortunately, literature shows molybdate will increase the percentage of O_2 in the cell gas [60], [71]. However, a rigorous study of the combined effect of chromate and molybdate is still lacking [61]. A further aspect not yet thoroughly investigated is the transition from benchtop laboratory experiments to pilot plants, let alone much larger industrial plants. This scale-up step is far from trivial: trends don't always translate well due to differences in geometry, time scale, mass transport, and reactor volume-to-electrode surface ratio [72], [73]. A full overview of the available literature is given in Chapter 1, but in short, more evidence is required to clarify if molybdate is a viable candidate for (partial) chromate replacement.

In this chapter, we do a thorough study of both the lab scale and pilot scale influence of small amounts of chromate, molybdate, and mixtures of the two. We use Ti as a cathode material because it is already applied in the industrial chlorate process. The impact of the combined additives on the performance of the pilot cell was determined using several measures: the cathodic and anodic current efficiency; the oxygen and hypochlorite production; and the cell potential. To understand the trends observed, the film deposition is discussed using the data of a quartz crystal microbalance (QCM), and the kinetics using a rotating ring disc electrode (RRDE). The knowledge from lab scale experiments can then be fundamentally connected to the process performance from the pilot cell.

We find that small chromate concentrations do not have the same effect on a pilot scale reactor as on a more idealized lab scale reactor. Molybdate addition has beneficial as well as detrimental effects on the cell performance. However, the different effects do not scale equally with molybdate concentration, so we find an optimum. Additionally, molybdate deposition at the cathode is suppressed when chromate is also present, leading to a hybrid

behavior. Using this information we define the most promising concentration range for both additives.

5.2 Results and discussion

For a description of the materials and methods used, as well as theoretical background for the QCM and RRDE techniques, please see Chapter 2.

5.2.1 Pilot plant cell

The effectiveness of the molybdate and chromate additives in the chlorate process was studied at the pilot-plant scale to closely match industrial conditions. Most notably, a circulating, high-temperature (80 °C), pH controlled (pH 6.5) electrolyte is used with a large electrode stack (30 cm²) at high current density (300 mA cm⁻², or 3 kA m⁻²). A detailed description with schematics of the plant and electrode stack can be found in Section 2.5.

Performance was evaluated by comparing each measurement to the current state-of-the-art, containing 5 g dm⁻³ sodium dichromate, which is summarized in Table 5.1.

Table 5.1: performance parameters measured in the pilot plant for the current state-of-the-art chlorate electrolyte containing 21 mM (5 g dm⁻³) dichromate.

Parameter	Value
Cathodic current efficiency (%)	97.0
Anodic current efficiency (%)	96.3
Cell potential (V)	3.38
Energy efficiency (kWh ton ⁻¹)	5470
[NaClO] (mM (g dm ⁻³))	18 (1.3)
O ₂ formation (μM s ⁻¹)	0.71

The influence of chromate was studied for the concentrations 0, 2.7; 27; and 270 μM Cr^{VI}, in the absence and presence of 80 mM Mo^{VI}, in a set of experiments performed in triplicate. Similarly, the amount of molybdate was varied from 0; 0.8; 8; and 40 mM at a fixed Cr^{VI} concentration of 27 μM Cr^{VI}. An overview of the results is shown in Figure 5.4.

Figure 5.1: Measurements of pilot cell performance using a Ti cathode: (a) cathodic current efficiency (CCE); (b) O_2 formation rate, (c) $[ClO^-]$; (d) anodic current efficiency (ACE); (e) cell potential; and (f) energy consumption. All were measured after a steady state was achieved. Along the bottom x-axis, values are shown as a function of Cr^{VI} concentration with 80 mM molybdate (black ▲) and without molybdate (grey □). The top x-axis shows values indicating molybdate concentration at a fixed Cr^{VI} concentration of 27 μM (blue ★).

The dashed red lines indicate the measured state-of-the art value as listed in Table 5.1 for reference. The black lines relate to the bottom x-axis and show the performance of the pilot cell as a function of chromate concentration. The grey line indicates results collected with no molybdate in the electrolyte, whereas the black line indicates measurements with 80 mM molybdate present. Conversely, the blue lines, relating to the top x-axis, show the performance of the pilot cell as a function of molybdate concentration, with a constant chromate concentration of 27 μM .

Figure 5.1a shows the measured cathodic current efficiency (CCE). The CCE increases with increasing chromate concentration, as expected from literature [44], as the cathodic film is established. Also in accordance with literature, the CCE increases when molybdate is present [49]. The blue line shows that this improvement is established even at 0.8 mM molybdate, and that it seems to be independent of molybdate concentration. Moreover, at high chromate concentration (270 μM) the CCE is unaffected by molybdate.

The oxygen production, displayed in Figure 5.1b, shows unexpected behavior. Chromate addition in the concentration range studied here slightly increased the O_2 production from 1.2 to 1.5 $\mu M s^{-1}$, in contrast to the low O_2 rate of 0.7 $\mu M s^{-1}$ observed at industrial chromate concentration (table 5.1). Literature also indicates a lowering of O_2 production as an effect of chromate [51]. The cause of this deviation may not lie in any catalytic effect, but simply in the lack of buffering at the anode at these low chromate concentrations. This leads to a higher pH at the anode, and thus more O_2 production [100].

The presence of 80 mM molybdate causes an additional 1.1 $\mu M s^{-1}$ of O_2 , almost doubling the rate of O_2 formation. Beyond that, the trend found for chromate addition is maintained. Still in Figure 5.1b, the blue line clearly shows that the O_2 formation rate increases as a function of increasing molybdate concentration. This indicates that molybdate catalyzes the

undesired homogeneous decomposition of hypochlorite to oxygen [60], according to the equations (also shown as Eq. 1.8 and 1.9):

The hypochlorite concentration $[\text{ClO}^-]$, shown in Figure 5.1c, confirms this as it follows an opposite trend mirroring that found for O_2 production. Note that hypochlorite concentration $[\text{ClO}^-]$ represents the total amount of ClO^- and HClO in the electrolyte, which is converted to ClO^- in order to be titrated. As discussed in Chapter 1, chromate is known to catalyze the desired hypochlorite decomposition pathway (eq. 5.3, also shown as Eq. 1.7), which results in chlorate formation [26], [27], [101], [102]. However, this effect is not yet apparent at the chromate concentrations used in these trials.

The anodic current efficiency (ACE), shown in Figure 5.4d, shows a trend identical to that for $[\text{ClO}^-]$. The ACE is calculated from the current and the O_2 production, as detailed in Appendix 5.

Figure 5.1e shows the overall cell potential, which is one of the most important parameters when it comes to saving power in a chlorate cell. The cell potential increases as a function of chromate concentration, which is related to the Cr^{III} film formed on the cathode [38]. The film increases the overpotential for the HER, but the major contribution to the increase in cell potential is that as the film forms, hypochlorite reduction is inhibited, and water reduction becomes the sole reaction governing the cathode potential.

In the presence of 80 mM molybdate the cell potential decreases due to the activating effect molybdate has for the HER [49], and it maintains a value of 3.17 V independently of chromate concentration. At 27 μM of chromate the cell potential falls within the error bar both with and without molybdate. The error bars represent absolute offsets between duplicate experiments, but not variations in trend. Therefore the trends can be assumed to be valid, even when they fall within the error bars. From the blue line in Figure 5.4e it is evident that at 0.8 mM the cell potential decreases to 3.08 V, but the decrease does not follow further molybdate additions. On the contrary, with increasing molybdate concentration the cell potential increases.

It is important to mention that a low cell potential, *e.g.* at low chromate concentrations while in the absence of molybdate, can be caused by unwanted hypochlorite reduction still occurring on the cathode, and this reaction has a lower equilibrium potential than the HER. Thus, a lower cell potential does not necessarily translate to net gains for the process. This is demonstrated in Figure 5.1f.

The best way to compare the efficiency of chlorate cells operating under different conditions is by comparing the energy consumption, in kWh ton⁻¹. The calculation of energy consumption takes into account the cell potential and the losses expressed by the CCE and the ACE [51]. This value is calculated according to:

$$\text{Energy consumption} = \frac{mzFV}{Mt\varepsilon} = \frac{10^6 \times 6 \times 96485 \times V}{106.44 \times 3600 \times \varepsilon} = \frac{1511 V}{\varepsilon} \quad (5.4)$$

Where m is the mass of chlorate (g), z is the number of electrons needed per chlorate ion, F is Faraday's constant (C mol⁻¹); V is the cell potential (V); M is the molar mass of sodium chlorate (mol g⁻¹); t is time (s); and ε is the total current efficiency (%), calculated using:

$$\varepsilon = \frac{\text{ACE} - (100 - \text{CCE})}{100} \quad (5.5)$$

In Figure 5.1f the energy consumptions obtained for the conditions studied in this work are summarized and compared. The blank lines show that the energy consumption at low chromate concentrations (<270 μM) is better when molybdate is absent, partially due to higher cell potential but primarily due to the extremely detrimental effect on the ACE. At the highest chromate concentration (270 μM), however, the energy consumption with or without molybdate in the electrolyte are the same, showing that the Cr^{III} film dominates the electrochemistry of the cathode. As for the molybdate concentration, the blue line shows that at low molybdate concentrations the beneficial effects molybdate has on the CCE and cell potential dominate the energy consumption. The beneficial effect of molybdate on CCE does not scale with concentration, but its negative effect on hypochlorite decomposition does. This leads to a decrease in energy efficiency with increasing molybdate concentration as homogeneous decomposition starts to dominate.

Overall, the optimal energy consumption was found at 27 μM chromate and 0.8 mM molybdate.

5.2.2 Lab scale

To further understand film growth and kinetics we performed RRDE and QCM experiments. Figure 5.2 shows the QCM results.

For a Ti-coated QCM electrode no mass change was observed in an electrolyte free of additives (Figure A5.4a). When adding chromate, no mass change was observed on the 1 minute time scale for low concentrations (Figure A5.4b and c). In a cycle of +0.35 V to -0.5 V and reverse, approximately $0.5 \mu\text{g cm}^{-2}$ of CrOx is deposited (see Figure A5.2a). In a second cycle an approximately similar amount of CrOx was deposited (not shown). The same electrode was finally used in a chronoamperometry experiment, shown in Figure 5.2a. At 270 μM chromate rapid mass gain can be seen at -0.5 V, terminating at $0.9 \mu\text{g cm}^{-2}$. The total mass gain thus amounts to $1.9 \mu\text{g cm}^{-2}$. This is 3 times as much as found on Au ($0.58 \mu\text{g cm}^{-2}$, Chapter 3), and 4.5 times as much as for Pt ($0.41 \mu\text{g cm}^{-2}$, Chapter 4) electrodes. This may be due to a fundamental difference in the exact $\text{Cr}^{\text{III}}\text{O}_x$ composition, as discussed in Chapter 4, suggesting a better charge permeability of the film on Ti than on Au and Pt. The difference may also be due to a larger real surface area of the Ti electrode.

In the presence of 80 mM of molybdate there was clear mass gain on short timescales starting from -0.3 V, with the rate depending on the applied potential (Figure 5.2b). Note that for each potential, the mass gain was reset to 0 (the order in experiments is indicated by the sequence arrow). A linear, but different slope in mass gain can be observed for each potential. The total mass gain at the end of several experiments was $5.9 \mu\text{g cm}^{-2}$, although the growth rate shows no indication of termination.

When mixing concentrated molybdate and chromate (Figure A 5.1d), the mass gain behavior is identical to that found for only a high concentration of chromate. This is also the case when a film has already been deposited on the electrode. After depositing a chromate film, adding molybdate to the solution does not lead to any additional mass gain (Figure A5.6a), clearly proving that the Cr^{III} film blocks molybdate reduction. When doing the reverse, depositing chromate onto an already formed molybdenum film, a limited mass gain equal to that found for chromate on bare Ti was found, suggesting a Cr^{III} film

deposits on top of the molybdate film (Figure A5.5e). This deposition also terminates further film formation (Figure A5.6b), as expected on a Cr^{III} surface.

The study using lower molybdate concentration (Figure A5.4d), revealed no mass gain at the lowest concentration, 0.8 mM, on a short timescale. However, mass gain was evident after extended deposition time (Figure 5.2c). The deposition rate improved once the potential was increased to -0.6 V (not shown), into the HER regime, and this improvement was maintained even when the potential was stepped back to -0.5 V. No such effect was observed at 80 mM molybdate.

Figure 5.2: Mass change over time as a function of deposition potential. The legend shows the deposition potential in V vs RHE, the arrow indicates the sequence of measurements. Electrolyte additive was (a) 270 μM Cr^{VI} ; (b) 80 mM molybdate; (c) 270 μM Cr^{VI} and 80 mM molybdate (d) 0.8 mM molybdate before and after stepping into the HER regime; and (e) 0.8 mM molybdate and 27 μM Cr^{VI} , on clean Ti and after 4 minutes deposition with only 0.8 mM molybdate at -0.5 V after HER.

When mixing molybdate and chromate in low concentrations, a mixed behavior is observed (Figure 5.2d), where the addition of chromate partially inhibits continued film growth. The deposition rate is decreased compared to the case where only molybdate is present, and increasing the potential into the HER regime does not boost the deposition rate.

At 27 μM chromate does not dominate the mixed additive film growth as it does at 270 μM , because growth is not self-terminating. But neither does the film growth resemble that found in the absence of chromate, suggesting a different film structure altogether. Thus the film itself must be of a hybrid nature, and in fact molybdate is known to favor co-deposition [49]. If the hybrid film formation requires a specific balance of additives, that can also explain the phenomenon that the chromate film appears complete at a lower concentration in the QCM than in the pilot. The relative mole ratio between additive and surface area of the electrode is different in the different setups, and geometry and mass transfer conditions will also play a large role [72], [73].

To gain further insight into the kinetics of the system, experiments were performed on a RRDE. During polarization using a Ti disc with a Pt ring, the ring potential was maintained at +0.7 V to detect soluble reduced species on the disc. However, no current signal was detected on the ring, neither during tests performed with molybdate nor in tests with chromate. The lack of soluble intermediates is a clear distinction from the deposition of $\text{Cr}^{\text{III}}\text{O}_x$ on Au in similar circumstances, where obvious oxidation currents were observed [99].

To investigate the half-cell potential of the cathode, polarization curves were measured and are presented in Figure 5.3. To achieve the full effect of the film deposited from the additive, the cathode was pre-polarized for 5 minutes at -0.6 V before the polarization curve was recorded.

Figure 5.3a shows curves recorded in 27 μM chromate and 0.8 mM molybdate. Increasing the concentrations to 270 μM chromate and 80 mM molybdate results in similar polarization curves, shown in Figure A5.4. This is in contrast to the QCM measurements, where concentrations played an

important role, but this can likely be attributed to the vastly increased mass transport at the RDE compared to the QCM electrode.

Polarization curves of *ex situ* films recorded in additive-free solutions, shown in Figure A5.5, also closely match those in Figure 5.3. This indicates that the observed effects are due to the film rather than the additive, in agreement with the results from Chapter 4 on Pt electrodes.

Figure 5.3a shows polarization curves recorded without hypochlorite in solution. The black lines indicate the polarization of a Ti cathode without additives, shows only the HER at -1.0 V. In the presence of molybdate, the cathode shows a change in potential to -0.5 V, in line with the cell potential in Figure 5.1e, and as expected from literature [49], [60]. Upon the addition of chromate, the cathodic polarization shows a small decrease in potential at high current densities, contrary to what was observed in the overall cell potential in the pilot plant (Figure 5.1e). This is unexpected and not in line with literature [38], but consistent throughout our results. A mixture of both additives behaves much like chromate, as expected from previous experiments.

Figure 5.3: *iR*-drop corrected polarization curves at 2500 rpm in 0.1 M NaOH, 2 M NaCl, 27 μM chromate and 0.8 mM molybdate. The grey dashed line indicates the current density industrial setups operate at. The electrode was polished Ti, pre-polarized for 5 minutes at -0.6 V vs RHE. (a) without hypochlorite; (b) with 80 mM hypochlorite.

Figure 5.3b shows polarization curves in the presence of 80 mM NaClO. The hypochlorite reduction was in a kinetically controlled regime on Ti at the rotation rate used (Figure A5.6). On Ti without any additives, a clear shift to more positive potential can be seen upon the introduction of hypochlorite (grey line) compared to an electrolyte without hypochlorite (black line), related to hypochlorite reduction [55]. At high current densities this process becomes mass transport limited, and the HER also occurs. Hypochlorite reduction continues into this regime, though, as indicated by the decrease in potential required from 2 to 2.5 log|j|.

In the presence of molybdate, the activation of the cathode is superimposed on the hypochlorite reduction, which continues without inhibition. In the presence of chromate the hypochlorite reduction is suppressed due to formation of the CrO_x film, resulting in a polarization curve similar to that of bare Ti without hypochlorite. A mixture of additives behaves again similarly to chromate.

Taking the values from the RRDE at 300 mA cm^{-2} we find that the addition of 0.8 mM molybdate co-additive to $27 \text{ }\mu\text{M}$ chromate results in a 290 mV decrease in cathodic potential. This is significantly more than the 90 mV decrease in cell potential measured in the pilot plant at this current density. Comparing the half-cell potential from the RRDE to the full cell potential from the pilot cell is not straightforward, not only due to the influence of the anode, but also because of the different operating conditions, *e.g.* temperature, mass transport and pH. Nevertheless, this result suggests further tweaking of the (co-)additive ratio may result in bigger improvements.

5.3 Conclusions

We have studied the effect of low concentrations of chromate and molybdate on a titanium cathode, both on pilot and lab scale. In the pilot cell we found that at μM concentrations chromate cannot match the current state-of-the-art. Molybdate influences the cell potential, improves the CCE and catalyzes the homogeneous decomposition of hypochlorite to oxygen. The effects of molybdate are negated at $270 \text{ }\mu\text{M}$ chromate. Crucially, the beneficial effects of molybdate addition are fully present at low concentration of molybdate, whereas the negative effects scale with concentration.

QCM experiments revealed that film deposition from molybdate is not self-limiting, whereas from chromate a $1.9 \mu\text{g cm}^{-2}$ film is formed. Molybdate film growth does not occur in the presence of $270 \mu\text{M}$ chromate or more, but at low additive concentrations a hybrid film growth dynamic was observed, in accordance with pilot plant experiments. RRDE polarization curves show trends generally matching the pilot plant trials.

Overall, $27 \mu\text{M}$ chromate and 0.8 mM molybdate was the optimal ratio for cathodic protection. Compared to additive-free operation, it resulted in an improvement in energy consumption of 2%, versus 7% using 20 mM chromate. Small concentration differences have a large impact, and cell characteristics such as mass transport and volume-to-area ratio influence the effective concentration. With further optimization, it may be possible to optimize the hybrid film more and approach the cell performance required for industrial application, while maintaining a 2000-fold reduction in chromate concentration compared to the current state-of-the-art.

Appendix 5

Calculation of the values in Figure 5.1:

The nitrogen flow was set to 60 mL min⁻¹, and the actual flow (V_{N_2} , mL min⁻¹) was determined after 15 minutes of stabilization. This was used together with the total gas flow (V_{tot} , mL min⁻¹) and the measured oxygen fraction ($V_{O_2 \text{ measured}}$, %) to determine the H₂ flow (V_{H_2} , mL min⁻¹) according to:

$$V_{H_2} = 1.006 V_{tot} \left(1 - \frac{V_{O_2 \text{ measured}}}{100\%}\right) - V_{N_2} \quad (\text{A5.1})$$

The real oxygen fraction (V_{O_2} , %) can then be calculated using:

$$V_{O_2} = \frac{V_{tot}}{V_{tot} - V_{N_2}} V_{O_2 \text{ measured}} + 0.26 \frac{V_{N_2}}{V_{H_2} + V_{N_2}} \quad (\text{A5.2})$$

V_{H_2} and V_{O_2} can be converted to moles (M_{H_2} and M_{O_2} , mol sec⁻¹). M_{H_2} can be used together with the current (I , A) and Faraday's constant (F , C mol⁻¹) to find the cathodic current efficiency (CCE, %):

$$\text{CCE} = \frac{2F}{I} M_{H_2} 100\% \quad (\text{A5.3})$$

Similarly, the anodic current efficiency (ACE, %) can be calculated using:

$$\text{ACE} = 100\% - 2V_{O_2} \quad (\text{A5.4})$$

Figure A5.4: Mass change over time as a function of deposition potential for (a) background electrolyte 2 M NaCl, 0.1 M NaOH; (b) 2.7 μM Cr; (c) 27 μM Cr; (d) 270 μM Cr and 80 mM Mo; and (e) 0.8 mM Mo. In (d), the legend shows the sequence of the experiments from top to bottom.

Figure A5.5: Cyclic voltammogram and mass change, in a solution of 0.1 M NaOH and 2 M NaCl at 50 mV s^{-1} on bare Ti for: (a) no additives; (b) $270 \text{ } \mu\text{M}$ Cr; (c) 80 mM molybdate; and (d) $270 \text{ } \mu\text{M}$ and 80 mM molybdate on an electrode coated with $5.9 \text{ } \mu\text{g cm}^{-2}$ of MoO_x after the experiments in Figure 5.2b.

Figure A5.5 shows cyclic voltammograms of bare Ti electrode in an electrolytes containing different additives. Figure A5.5a shows no additives, and no mass change. Figure A5.5b has $270 \text{ } \mu\text{M}$ chromate and rapid deposition can be clearly seen starting at -0.35 V . Figure A5.5c has 80 mM molybdate and show $0.1 \text{ } \mu\text{g cm}^{-2}$ deposition. Figure A5.5d shows an electrode pre-coated with $5.9 \text{ } \mu\text{g cm}^{-2}$ of a molybdate film. $270 \text{ } \mu\text{M}$ chromate was added to the electrolyte before this CV was made. Note how similar the mass gain behavior looks to Figure A5.5c, indicating a chromate film is depositing on top of the molybdate.

Figure A5.6: Mass change over time as a function of deposition potential and time. (a) 270 μM Cr and 80 mM Mo, on an electrode coated with $1.9 \mu\text{g cm}^{-2}$ of $\text{Cr}^{\text{III}}\text{O}_x$ film. (b) 270 μM Cr and 80 mM Mo, on an electrode coated with $5.2 \mu\text{g cm}^{-2}$ of molybdate film.

Figure A5.6 shows the mass of electrodes in an electrolyte that contains 270 μM chromate and 80 mM molybdate. Figure A5.6a shows no mass gain on an electrode that has been coated with $1.9 \mu\text{g cm}^{-2}$ $\text{Cr}^{\text{III}}\text{O}_x$ previously. The noise is related to H_2 formation, not film deposition. Figure A5.6b shows an electrode on which $5.9 \mu\text{g cm}^{-2}$ of molybdate was deposited, before being inserted into a solution containing 270 μM chromate. Initial mass deposition was observed in the CV shown in Figure A5.5d, but after a total mass increase of $1.4 \mu\text{g cm}^{-2}$ no further deposition is observed.

Figure A5.4: iR-drop corrected polarization curves at 2500 rpm in 0.1 M NaOH, 2 M NaCl, 270 μM chromate and 80 mM molybdate. The grey dashed line indicates the current density industrial setups operate at. The electrode was polished Ti, pre-polarized for 5 minutes at -0.6 V vs RHE. (a) without hypochlorite; (b) with 80 mM hypochlorite.

Figure A5.5: iR-drop corrected polarization curves at 2500 rpm in 0.1 M NaOH, 2 M NaCl and 80 mM NaClO (unless otherwise noted). The grey dashed line indicates the current density industrial setups operate at. The electrode was polished Ti, pre-polarized for 5 minutes at -0.6 V vs RHE, then transferred to a solution without additives. The additive concentrations for deposition were 27 μM chromate and 0.8 mM molybdate. (a) without hypochlorite; (b) with 80 mM hypochlorite.

Figure A5.6: Levich plot of current density versus rotation rate on a Ti disc in 0.1 M NaOH, 2 M NaCl and 80 mM NaClO. Current was sampled at -0.9 V vs RHE.

Figure A5.6 shows the current density at -0.9 V vs RHE, where hypochlorite reduction occurs but not the HER. It displays a linear correlation with the square root of the rotation rate, indicating a fully mass transport limited reaction without kinetic limitations.

Chapter 6

Cathodic deposition of Mn-based thin films for selective electrochemistry

Abstract

To fully eliminate chromate from the chlorate process, we evaluate the effect of potential on the deposition of MnO_x films from alkaline permanganate solutions on Au electrodes. Like chromate, deposition reactions from permanganate involve both soluble and solid species, but we also observe homogeneous redox chemistry in the electrolyte. Because permanganate films display uninhibited growth, we study *ex situ* prepared film selectivity. Overall, selectivity scales with deposition potential. Crucially, however, we discover a remarkable deposition potential window wherein a stable thin film is formed that suppresses an exceptional 98% of hypochlorite reduction. On the basis of Raman and SEM analyses, the morphology (thin platelet containing films) and crystal phase of these films is distinct, but the chemical composition difficult to identify. XPS characterization suggests the elemental surface composition is dominated by the formation of $\text{Mn}^{\text{II}}\text{O}$ and $\text{Mn}^{\text{II}}(\text{OH})_2$. Using these compositions, DFT modeling demonstrates that reduction of hypochlorite contains significant energetic barriers. These results demonstrate that cathodic alkaline permanganate deposition is a suitable technique for creating selective films.

Note: this chapter is the result of a collaboration. DFT calculations were contributed by Michael Busch, Department of Chemistry and Materials Science, Aalto University, Kemistintie 1, 02150 Espoo, Finland.

6.1 Introduction

To fully eliminate chromate from the chlorate process we must move beyond the molybdate co-additive studied in Chapters 4 and 5, as molybdate by itself cannot create sufficient inhibition of hypochlorite reduction. Instead, we turn now to permanganate, which has shown great promise as a replacement for chromate, except that film growth is problematically not self-limiting [55]. An overview of existing literature is provided in Chapter 1. Briefly, cathodic deposition from permanganate to birnessite and amorphous MnO_2 has received some attention in recent years, but the deposition mechanism is yet unclear. pH and potential likely play an important role in the nature and chemical composition of the film.

In this chapter, we focus on the cathodic deposition of MnO_x thin films on Au electrodes from permanganate in a highly alkaline environment. We evaluate the properties of the MnO_x films and show that the rich chemistry of manganese allows for tuning of the properties of the MnO_x films through the deposition potential. Using QCM, SEM, Raman and XPS we characterize thickness, morphology and (surface) composition of the MnO_x thin films. The inhibiting nature of MnO_x films for hypochlorite reduction is assessed. Although all films are amorphous in nature regardless of the deposition potential, a clear correlation of deposition potential with electrode selectivity will be demonstrated. Finally, we apply density-functional theory (DFT) in order to further evaluate the origin of the selectivity. In line with earlier work [40] we discuss that from a purely thermodynamic perspective hypochlorite reduction is fully inhibited by surface $-\text{OH}$ and $=\text{O}$ groups, but this blocking may be circumvented by a ligand exchange mechanism.

6.2 Computational details

For a description of the materials and methods used, as well as theoretical background for the QCM and RRDE techniques, please see Chapter 2.

All DFT computations were performed using GPAW (version 1.3.0) in combination with the Atomic-Simulation Environment [103], [104] (ASE; Version: 3.15.0 [105]). Valence electrons were modelled with the generalized gradient approximation (GGA) using the PBE [106] functional. No Hubbard-U

corrections were added since a recent study showed that U parameters, which are typically obtained by fitting to bulk properties, are not necessarily applicable when modelling species adsorbed at the surface [107]. This is further justified when considering the good accuracy of GGA functionals when modelling electrochemical reactions over transition metal oxide surfaces [43], [108], [109]. Core electrons were treated within the projector augmented wavefunctions (PAW) method [110]. Spin was fixed assuming a high spin electron configuration and ferromagnetic coupling between the Mn ions. The structures were considered to be converged when the largest force on any atom was below $0.05 \text{ eV } \text{\AA}^{-1}$.

The initial convergence of the lattice parameters was performed using the minimal unit cell in combination with $7 \times 7 \times 1$ ($\text{Mn}(\text{OH})_2$) and $7 \times 7 \times 7$ (MnO) k-point sets. Considering the failure of pure GGA functionals to properly account for van-der-Waals interactions, the interlayer spacing was fixed to the experimental value of $c = 0.468 \text{ nm}$ [111], [112]. The hypochlorite reduction over MnO was modelled at the (100) surface using a 2×1 surface unit cell and a 3 monolayer thick slab where the lowest monolayer was fixed to the bulk value. A $3 \times 3 \times 1$ k-point set was used. For $\text{Mn}(\text{OH})_2$ both the (110) and (100) surfaces were considered. For the (110) surface a 4 monolayer thick slab with a 4×1 surface was used. Equivalent to MnO , the lowest monolayer was fixed to the bulk values. The k-point set contained only the gamma-point. Considering that only weak van-der-Waals interactions are present between the layers, the chemistry of the (100) surface was modelled using a single $\text{Mn}(\text{OH})_2$ layer with a 2×2 surface unit cell. A $7 \times 7 \times 1$ k-point set was used in this case. In all cases the backside of the slab was terminated such, that it displays the bulk oxidation state.

6.3 Results and Discussion

6.3.1 Thin film deposition

Suitable deposition potentials have been identified using cyclic voltammetry. Specifically, redox processes and thin film growth occurring on an Au electrode in permanganate solution were identified using RRDE and eQCM, respectively. The potential of the Au WE was cycled at 100 mV s^{-1} from

open circuit potential (+1.6 V), to -0.75 V before the potential was reversed and swept from -0.75 to +1.8 V. During RRDE measurements the Pt ring electrode was kept at a constant potential of +1.5 V throughout the scan, and a constant rotation rate of 4000 rpm was maintained. The first cycle is shown in Figure 6.1a, and a reference experiment in the absence of permanganate is shown in Figure A6.1 The second cycle is shown and discussed in Figure A6.2.

Figure 6.1: Cyclic voltammograms in 5 mM NaMnO₄ pH 14, first cycles. (a) RRDE with Au disc working electrode and Pt ring at constant potential, $E_{\text{ring}} +1.5$ V vs RHE, at 4000 rpm and 100 mV s^{-1} . The red line shows the current on the Pt ring electrode, inverted from positive to negative and corrected for the collection efficiency to allow for direct comparison to the disc current. (b) Δm vs E on a stationary QCM electrode at 50 mV s^{-1} , arrows denote scan direction.

A reductive current develops as soon as the cathodic sweep starts, with three distinct peaks of increasing current density centered at +1.3 V, +1.1 V and +0.75 V. Generally, the observed CV closely resembles the data reported by Donne *et al.* [80] showing three distinct regimes. Particularly at potentials negative of +0.75, a close resemblance regardless of pH is observed [80]. Moreover, our measurements suggest that current associated with the first two peaks measured at the Au disk electrode is accompanied by an oxidative current on the Pt ring that, once corrected for the collection efficiency (see Chapter 2), closely matches the disc current. This suggests the first two reductive peaks relate primarily to reactions producing soluble products that can be oxidized at the ring. Nevertheless, the difference between ring and disc at +1.1 V reveals a minor charge discrepancy of -1.2 mC cm^{-2} , suggesting MnO_4^- adsorption or MnO_x deposition, *i.e.* film formation. Given that the ring potential is set to be at +1.5 V E_{ring} , which is as oxidative as possible without continuous oxygen evolution and well beyond the potential associated with

MnO_x oxidation at the Pt electrode (Figure A6.3), it is unlikely that any soluble Mn-products would not be oxidized at the ring [80]. The non-sigmoidal shape of the peaks also suggests the products are not exclusively soluble [80]. The self-terminating nature of these peaks also points to the deposition of a passivating film, which is further corroborated using eQCM.

In the anodic sweep the current gradually decreases, accompanied by an additional decrease in ring current, although the ratio of ring to disc current increases. At +1.0 V an oxidative peak current at the disc is observed related to oxidation of the film. Subsequently (above +1.5 V) oxidation of the Au disc surface (Figure A6.1) and O₂ production occurs.

To determine the film mass, Au-coated eQCM crystals have been used and cyclic voltammetry has been performed as described above (Figure 6.1b and 1c). Discrepancies in current-voltage response between eQCM and RRDE measurements are caused by the poor mass-transport conditions in the eQCM cell, and indeed CVs recorded using a stationary RRDE (Figure A6.4) are in excellent agreement with the eQCM data. A reference eQCM experiment in the absence of permanganate (Figure A6.1) revealed only minor mass changes associated with reduction of the Au₂O₃ surface at +1.0 V. Therefore we assign the mass gain in the presence of permanganate exclusively to film deposition. For a permanganate-containing electrolyte a minor mass gain of 0.57 µg cm⁻² is already observed during the cathodic scan at +1.1 V in agreement with the unaccounted charge determined by RRDE. Estimated film masses corresponding to 1.2 mC cm⁻² have been summarized in Table 6.1. More mass gain is to be expected on the QCM due to the lower scan speed used, extending the growth time in this regime, so QCM and RRDE are in good agreement.

Table 6.1: Δm calculated from the molar mass of MnO_x compounds assuming 1.2 mC cm⁻² of charge.

	mm (g mol ⁻¹)	e ⁻	Δm (µg cm ⁻²)
<i>MnO</i>	70.937	5	0.22
<i>Mn(OH)₂</i>	88.952	5	0.27
<i>MnOOH</i>	87.945	4	0.34
<i>MnO₂</i>	86.936	3	0.45

This initial mass gain is minimal compared to the major mass gain observed at potentials negative of +0.75 V, where a continuous mass gain of $1.2 \mu\text{g cm}^{-2} \text{C}^{-1}$ is observed during the cathodic sweep (Figure A6.5) until mass gain levels out at +1.0 V in the anodic sweep, in agreement with observations of film deposition in a neutral environment [80]. The overall mass gain is large, on the order of $60 \mu\text{g cm}^{-2}$ per cycle, strengthening the importance of *ex situ* MnO_x film preparation.

6.3.2 Electrochemical Selectivity

Based on our observations we identified six different potential regimes to electrodeposit MnO_x -films on Au electrodes and studied their selectivity for hydrogen evolution over the hypochlorite reduction reaction. All films were deposited for 20 minutes at the respective deposition potentials highlighted in Figure 6.1a.

Ex situ prepared electrodes were transferred to an alkaline solution containing hypochlorite (no permanganate) resembling the conditions at the cathode of the electrochemical chlorate cell. The current density at a constant polarization of -0.1 V is summarized in Figure 6.2a. It is worth noting that here, a lower current density indicates inhibition of ClO^- reduction. For comparison, the reductive current obtained at a bare Au electrode is shown.

Figure 6.2: a) Hypochlorite reduction current densities at Mn films deposited at different deposition potentials (a) and different deposition times at +0.9 V (b). In (a), colors match the arrows in Figure 6.1. For more details, see Figure A6.6. Experimental conditions: potentiostatic polarization at -0.1 V in 80 mM NaClO , pH 14, 4000 rpm.

Overall, Figure 6.2 shows that films deposited at more cathodic potentials more effectively inhibit the reduction of hypochlorite, showing a linear correlation. There is one exception, however. Interestingly, the MnO_x film deposited at +0.9 V fully inhibits the ClO^- reduction. To determine if this inhibition is dependent on film thickness, the ClO^- reduction current was investigated as a function of deposition time at this favorable potential (Fig. 2b). Inhibition of ClO^- reduction is already evident after 1 second of deposition at +0.9 V. The inhibiting nature of the produced film increases rapidly to 80% after 60 seconds of deposition, and after 5 minutes the reduction of ClO^- is reduced by 98%.

Extrapolating the mass gain rate from the QCM data (Figure A6.5), the film mass after 5 minutes is estimated to be roughly $60 \mu\text{g cm}^{-2}$ or between 110 and 190 nm, for MnO and Mn(OH)_2 assuming 5.37 and 3.26 g cm^{-3} , respectively. Although this is two orders of magnitude thicker than a similarly selective CrO_x film [99], it is much thinner than the MnO_x films deposited at more negative potentials, which still display markedly poorer reduction selectivity. The 150 nm film is also much thinner than the optimum found for *ex situ* thermally formed MnO_x films, which is 2-3 μm [56]. The remarkable inhibition of films deposited at +0.9 V is not merely a function of film thickness but might also depend on composition and morphology. It is worth noting that this deposition potential is extremely close to the deposition potential reported to provide optimal oxygen reduction performance, +0.88 V vs RHE [79]. That is further evidence that this potential window produces a unique film.

The stability of the film during reduction in a hypochlorite solution in the absence of permanganate was investigated using chronoamperometry (Figure A6.7). The film proved stable under reduction conditions, initially inhibiting ClO^- reduction by 98% compared to bare Au and with only a slight decrease in inhibition to 94% after 1 hour of constant operation. The decrease in inhibition could be due to reduction of the film to a different phase, or due to a change in morphology, possibly exposing Au, although no visual change of the electrode surface could be observed. The stability during potential cycling was also investigated, and the selectivity was found to drop rapidly when the film was exposed to oxidative potentials greater than +0.85 V (Figure A6.8). This potential matches the maximum mass gained in Figure 6.1, suggesting that

film oxidation and potentially crack formation, exposing the Au substrate, starts at this potential.

To confirm that only hypochlorite reduction is suppressed by the MnO_x film prepared at +0.9 V, but not the hydrogen evolution, kinetics were thoroughly analyzed using IR-corrected polarization curve measurements, shown in Figure 6.3. In the absence of any Mn-based film, OCl^- reduction can be seen starting at +0.5 V, and hydrogen evolution dominates at potentials negative of -1.5 V. With the Mn film present, the OCl^- reduction is absent and hydrogen evolution kinetics match perfectly, both with and without the film.

Figure 6.3: *iR*-corrected polarization curves recorded at 4000 rpm in 80 mM NaClO, pH 14. The Mn film was deposited in 5 mM NaMnO_4 , pH 14, for 20 minutes at +0.9 V vs RHE.

6.3.3 Characterization of MnO_x

To identify the MnO_x species formed during potential sweeps in MnO_4^- solutions and to characterize the structure formed at +0.9 V (vs RHE) which provides highest selectivity, SEM, XPS and Raman were performed on films electrodeposited for 20 minutes at the desired potentials. SEM was used to investigate the morphology of MnO_x films. An image of the bare, polished Au substrate is shown in Figure A6.9 for comparison. All films were prepared in a manner similar to that of films used to determine selectivity towards hypochlorite reduction. The resulting SEM images are shown in Figure 6.4.

Figure 6.4: SEM images showing films deposited at +1.1 V, +0.9, +0.6, and -0.7 V for 20 minutes in 5 mM NaMnO_4 , pH 14. The scale bars show 1 μm .

SEM clearly reveals potential dependent changes in film morphology indicating a complex growth process. At a deposition potential of +1.1 V a dense film covered with caterpillar-like particles was observed. A dense, smooth film has been previously reported for permanganate deposition at this potential [80]. The caterpillar-like chains of particles have been observed [113], but the presence of particles on top of a film has not been previously reported. Cracks are due to drying of the film, and so exposure of the Au in the cracks on the SEM images does not necessarily mean that Au is exposed *in situ*. Indeed monolayer coverage of the Au surface was confirmed by energy-selective backscattering (ESB), shown in Figure A6.10, suggesting the film is continuous when in contact with the electrolyte.

At +0.9 V, highly porous spheres made of platelets are observed on top of a cracked, continuous film, also made of bladed plates. This bladed morphology has been reported and is hypothesized to be caused by partial dissolution of the dense film initially formed while the potential is dropping. This dissolved film is re-deposited through a cycling reaction [80]. A similar platelet structure was found for a film that was cathodically deposited at +0.88 V in an

alkaline solution, although the large dense spheres that cover the bladed film were not reported [79]. These structures are on the order of a few hundred micrometers in diameter. ESB revealed minimal areas of bare Au are formed (Figure A6.11).

Only minor structural changes are observed after deposition at +0.6 V, except that the structures are larger, measuring up to several micrometers, and the substrate is completely covered by platelet structures with no visible Au. Given that similar spherical platelet structures have also been found for chemical permanganate reduction [76], in our case, it seems likely that dense spheres are initially deposited before partial re-dissolution occurs, leaving spherical structures made of platelets.

After deposition at a very reductive potential (-0.7 V) a thick film measuring 2 micrometers is formed. It is made up of alternating layers of dense material with a porous platelet structure in between. It is connected to the substrate by finger-like extrusions made of platelets. These finger-like structures have also been found in films deposited in neutral conditions, though no explanation was given as to their formation [86]. The formation of the outermost dense layer appears to be induced by the alkaline conditions used here. Even in cracks in the film, the substrate is covered in platelets. After oxidation, as expected, the film was decidedly less homogeneous and many types of structures could be observed (Figure A6.12). In cracks in the film, the substrate was once again free of deposits, as seen in the film deposited at +1.1 and +0.9 V. As is known, a wide variety of morphologies can be made depending on deposition conditions [77]. Nevertheless, as film coverage seems to be homogeneous, and despite drying induced crack formation, a bare Au surface is not detected, and a clear correlation between selectivity and morphology cannot be obtained.

As all films appear to be X-ray amorphous, *ex situ* Raman measurements were performed to obtain additional information (Figure A6.13). The spectra show differences. At the highest applied potential, the spectrum is relatively featureless, suggesting associated currents are predominantly caused by formation of soluble species, in agreement with the cyclic voltammetry and QCM results. At less positive potential, spectra are dominated by a feature between 570 and 630 cm^{-1} of variable, potential dependent, intensity and

broadness. The identification of the composition of the film by these Raman features is very challenging. Bands in this region have been assigned to Mn-O vibrations of MnO_2 [55], [114], although these are typically quite weak. Furthermore, the broadness of the feature indicates that there is not a well-defined single phase, but instead a mixture of various MnO_2 phases might be present, for which the breadth of the peak has been assigned to a diversity of Mn-O environments [115]. Since the Raman signals of the *ex situ* measurements were relatively weak, likely due to the extended thickness minimizing surface enhancement of the signals, *in situ* Raman was performed to determine time resolved film formation during electrolysis at different potentials, applying roughened Au to induce surface enhanced Raman spectroscopy (SERS) [92]. The resulting spectra are shown in Figure 6.5. Excellent agreement was found between the voltammograms obtained from measurements performed in the different cells (Figure A6.4), allowing a direct comparison of the Raman data with the cyclic voltammograms obtained by QCM measurements.

Figure 6.5: Raman spectra recorded during cyclic voltammetry of a roughened Au electrode in 5 mM NaMnO_4 pH 14 at 1 mV s^{-1} . Recorded using 10 seconds integration times, at +1.4 V, +1.0 V, and +0.25 V vs RHE.

At open circuit potential, *i.e.* +1.4 V, a broad, asymmetrical peak appears in the Raman spectrum at 578 cm^{-1} (Figure 6.5, orange) upon addition of MnO_4^-

to the electrolyte. This peak persists during the cathodic sweep down to +1.0 V (Figure 6.5, mint), when a second, larger peak appears at 597 cm^{-1} , coinciding with a peak in reductive current on the electrode, and the start of deposition as evident in QCM (Figure 6.1b). At even more negative electrode potentials the signal intensity decreases due to increasing film thickness. A third change can be observed at +0.25 V (Figure 6.5, black), at which potential the signal maximizing at 597 cm^{-1} decreases sharply, leaving only a small peak at 583 cm^{-1} , concomitant with two new bands appearing at 402 and 661 cm^{-1} . Negative of -0.35 V the signal intensity decreases to zero, again due to increasing film thickness. The changes in Raman features are irreversible (these cannot be recovered when a consecutive oxidative sweep is performed), in agreement with continuous mass gain in the scan to more positive potential (Figure 6.1b). As the formation of gas bubbles will also interfere with the Raman measurement [116] the cathodic sweep was limited to -0.35 V.

Given the similarity between the spectrum at open circuit and that in the potential range between +1.4 and +1.0 V (Figure 6.5, orange), and the minimal mass gain (Figure 6.1b, only $0.11\text{ }\mu\text{g cm}^{-2}$), we tentatively assign the peak at 578 cm^{-1} to adsorption of MnO_4^- ions onto the Au surface. The $0.11\text{ }\mu\text{g cm}^{-2}$ is on the order of a monolayer of adsorbed permanganate (Figure A6.14). However, literature values place aqueous MnO_4^- bands at 921, 828, and 429 cm^{-1} [117], [118], although it is also noted that the solution is not easy to investigate due to permanganate's very efficient absorption of visible light [117], [118]. The different signature might be due to interactions with the Au surface, and/or reduction to MnO_4^{2-} ions, which is thermodynamically feasible (see Pourbaix diagram, Figure A6.17).

At a polarization of +1.0 V (Figure 6.5, mint), the band at 578 cm^{-1} has narrowed, and maximizes around 597 cm^{-1} , with two residual shoulders at $\sim 450\text{ cm}^{-1}$ and $\sim 520\text{ cm}^{-1}$. Deposition (as evidenced by QCM) is significant at this potential, and might occur through different oxidation states (Figure A6.17). The band at 597 cm^{-1} bears a similarity to a broad band observed at 585 cm^{-1} for *ex situ* electrochemically deposited MnO_2 films at open circuit potential in a highly alkaline environment, as reported by Gosztola *et al.* [115], and the *ex situ* spectrum shown in this study in Figure A6.13. [115]. At +1.0 V

our spectrum also resembles the features observed during polarization of metallic Mn in alkaline media, which were attributed to the formation of α - MnO_2 [119]. The narrowing of the band at decreasing positive potential has also been previously observed [23], and has been assigned to lattice distortions *en route* to MnOOH .

At lower oxidative potential, the bands at 402 cm^{-1} and 667 cm^{-1} closely resemble the bands observed by Gosztola *et al.* [115]. The band at 667 cm^{-1} has been assigned to $\text{Mn}^{\text{III}}\text{-OOH}$ involving Mn-O-Mn bonds. This band is not indicative of Mn-OH vibrations, since isotopic shifts were not observed upon exchange in D_2O . The band at $\sim 400\text{ cm}^{-1}$ is sensitive to Deuterium exchange [23], and therefore assigned to a Mn-OH vibration in $\text{Mn}^{\text{III}}\text{OOH}$. The formation of $\text{Mn}^{\text{II}}(\text{OH})_2$ cannot be observed by Raman spectroscopy. A band for $\text{Mn}(\text{OH})_2$ should be present at $\sim 470\text{ cm}^{-1}$, which is clearly not observed.

However, likely not all modes are enhanced to the same extent by surface plasmon resonance and charge transfer [120]. A phase with a strong Raman response may dominate a more numerous phase with a weaker response [119]. Finally, the SERS effect enhances the signal from the part of the film close to the electrode, not that at the film-electrolyte interface, so spectra may not fully correspond to voltammetric features [115]. This might explain the relatively wide range of potentials for which MnO_2 phases are evident in Raman, even though surface reduction might have formed MnOOH (eventually visible) or $\text{Mn}(\text{OH})_2$.

Finally, we used XPS to derive the elemental composition of the surface of the film. Given that drying and exposure to vacuum likely changes oxidation states we have not determined the oxidation states. Still it is worth noting that all films showed Mn 2p signals resembling the structure expected for MnO (Figure A6.16). The composition analysis revealed that for all films, independent of the deposition potential used, Mn and O are present at a 2:1 ratio (Mn:O ratio) on the surface, but sputtering for 1 minute (equivalent to a removal of 11 nm of material) reveals a 1:1 sub-surface ratio.

6.3.4 DFT Modeling

Having evaluated the structural and electrochemical properties of the manganese oxides in the following we will discuss the outcome of a DFT

modeling study to rationalize the origin of the observed blocking of hypochlorite reduction. On the basis of the XPS data, and considering the applied potential during hypochlorite reduction, it is likely that the film present at the surface displays a Mn^{II} oxidation state [121], as is also evident from the Pourbaix diagram (Figure A6.17) [122]. Building on this assumption, two candidate $\text{Mn}(\text{II})$ oxide structures, constructed from the $\text{Mn}:\text{O}$ stoichiometry obtained from XPS, were considered. In the bulk phase, the only Mn oxide to satisfy the 1:1 stoichiometry between Mn and O is MnO , while a large number of different oxides with 1:2 stoichiometry exists. From these oxides, only Brucite type layered $\text{Mn}(\text{OH})_2$ possesses the correct +II oxidation state. Indeed, indications for such a structure were also visible in the Raman data.

Having developed two suitable test systems, the surface configuration under experimental conditions ($E = -0.1 \text{ V}$; $\text{pH } 14$) can be determined from computed phase diagrams (Figure A6.18). In the case of MnO , our calculations indicate that a fully OH covered (100) surface must be expected in the absence of any reconstructions. Interestingly, a reconstructed fully O covered surface was also observed when screening different surface configurations (Figure A6.18). This surface was found to be significantly more stable than the corresponding unreconstructed OH covered surface and, accordingly, should prevail under thermodynamic control. As a part of the reconstruction, the octahedral ligand field spanned by the 6 O and OH groups surrounding Mn in the rock salt MnO structure was converted to a tetrahedral ligand field whereby each Mn ion is coordinated by 4 O groups. The surface O atoms on the other hand moved from a *cus* $\text{Mn}=\text{O}$ position into a bridged $\text{Mn}-\text{O}-\text{Mn}$ configuration. This reconstruction has been proposed earlier based on experiments [123]. Both surface terminations fulfill the 1:2 stoichiometry predicted by XPS. Considering that the reconstruction, albeit thermodynamically favorable, might still be hindered by an activation barrier, both a fully OH and a fully O covered surface were considered when modelling the HOCl reduction reaction.

Hypochlorite reduction over $\text{Mn}(\text{OH})_2$ was studied assuming a (100) (threefold terrace sites) and a (110) surface (bridged and *cus* edge sites). Building on the computed surface phase diagram, a fully OH covered (110)

surface was found to be most stable under experimental conditions. Similarly, the (100) facet was also predicted to be OH terminated.

The ability to reduce hypochlorite was tested using the recently proposed HOCl reduction mechanism [40]. This reaction route assumes that HOCl reduction is initiated by the adsorption of OCl⁻ at the catalytic site to form an $\ast\text{-OCl}$ intermediate. This is followed by the breaking of the O-Cl bond resulting in the formation of $\ast=\text{O}$. Both steps are purely chemical in nature and thus not affected by changing the electrochemical potential. The catalytic site is then recovered through the electrochemical reduction of $\ast=\text{O}$ to water via $\ast\text{-OH}$. The resulting free energy diagram is shown in Figure 6.6.

Figure 6.6: Summary of the energetics of HOCl reduction over MnO and $\text{Mn}(\text{OH})_2$. All reactions have been computed assuming pH 14 and electrochemical steps are stated versus NHE.

Assuming this mechanism, we found the initial adsorption of OCl^- to be only slightly exergonic for $\text{Mn}(\text{OH})_2(110)$ while it is strongly exergonic in all other cases (Figure 6.6). Similarly the O-Cl bond breaking is also found to be strongly exergonic for all considered $\text{Mn}(\text{OH})_2$ surfaces. On the other hand, in the case of MnO we observed significant differences between the reconstructed O covered and the unreconstructed OH covered surfaces. While the bond breaking is strongly exergonic for an O covered surface, it is approximately thermoneutral (e.g. the change in Gibbs Free energy is below 0.1 eV) when only OH is present (Figure 6.6). The significant difference between the 2 surface terminations is not surprising when considering the high energy gain from shifting to a reconstructed O covered surface. Independent of the less favorable energetics, this reaction is likely to occur in both cases.

Recovery of the catalyst is achieved through stepwise reduction of $\ast=\text{O}$ to water. At a potential of -0.1 V versus NHE this reaction is already blocked at the stage of $\ast=\text{O}$ for the two considered $\text{Mn}(\text{OH})_2$ surfaces. Lowering the potential further, the reduction of $\ast=\text{O}$ to $\ast\text{-OH}$ becomes activated: for $\text{Mn}(\text{OH})_2(110)$, a potential lower than -0.3 V is required for this step; the $\text{Mn}(\text{OH})_2(100)$ facet on the other hand remains poisoned by $\ast\text{-OH}$ until a potential lower than -2.2 V is applied. To complete the recovery of the surface through reduction of $\ast\text{-OH}$ to water at $\text{Mn}(\text{OH})_2(110)$, potentials below -0.7 V are needed.

Similarly, MnO does not support the direct electrochemical reduction of hypochlorite under experimental conditions, i.e. both surface terminations are poisoned by $\ast\text{-OH}$ or $\ast=\text{O}$, respectively.

It is worth noting that the OH covered surface activates below a potential of -0.4 V for HOCl reduction through enabling the reductive release of water. The $\ast=\text{O}$ covered surface on the other hand remains blocked until a potential of -1.7 V is reached. Overall, both the $\text{Mn}(\text{OH})_2$ and the MnO surfaces can explain the experimentally observed blocking at a potential of -0.1 V. Assuming that either $\text{Mn}(\text{OH})_2(110)$ or OH covered MnO is present at the surface, the experimentally observed HER onset may also be accompanied by some hypochlorite reduction.

The incomplete blocking observed experimentally can be rationalized when considering that the release of *-OH may alternatively also proceed through a ligand exchange following Equation 6.1:

In contrast to Cr(III), this reaction is not blocked kinetically [40], [124]. A requirement for this reaction to proceed is the presence of OH groups at the surface. Accordingly, OH covered MnO may, to a minor extent, be active for OCl⁻ reduction through this mechanism. Note that reduction cycles stopping at *=O should, however, still display complete blocking. Additionally, the possibility to access varying amounts of the Au underlayer through pores cannot be excluded and may also contribute to the observed incomplete blocking.

6.4 Conclusions

We have deposited MnO_x films from alkaline permanganate solutions on Au electrodes. Morphology ranges from thin films, to polycrystalline films with distinct platelet morphology, and thick MnO_x films at the least positive potentials. We discovered a remarkable deposition potential window wherein a stable thin film is formed on the Au substrate, with exceptional selectivity of 98% in formation of H₂ as compared to reduction of hypochlorite (OCl⁻), corresponding to the polycrystalline films with distinct platelet morphology. XRD and Raman identification of the composition of the most effective MnO_x film is difficult, while XPS analysis suggests the surface is most likely composed of Mn(OH)₂ and MnO. DFT modeling confirms that significant barriers for decomposition of OCl⁻ exist using models for these surface compositions. The present results suggest that MnO_x films are very promising for selective hydrogen evolution in the chlorate process.

Appendix 6

Figure A6.1: Cyclic voltammograms at pH 14 (a) RRDE with Au disc working electrode and Pt ring at constant potential, $E_{\text{ring}} + 1.5$ V vs RHE, at 4000 rpm and 100 mV s^{-1} . The red line shows the current on the Pt ring electrode, inverted from positive to negative and corrected for the collection efficiency to allow for direct comparison to the disc current. (b) Δm vs E on QCM electrode at 50 mV s^{-1} .

Figure A6.2: Cyclic voltammograms in 5 mM NaMnO_4 pH 14, second cycles. (a) RRDE with Au disc working electrode and Pt ring at constant potential, $E_{\text{ring}} + 1.5$ V vs RHE, at 4000 rpm and 100 mV s^{-1} . The red line shows the current on the Pt ring electrode, inverted from positive to negative and corrected for the collection efficiency to allow for direct comparison to the disc current. (b) Δm vs E on QCM electrode at 50 mV s^{-1} .

Similarly to the RRDE results, major differences in the current response during potential cycling are observed in the second cycle (Figure A6.2). The mass gain onset has shifted from +0.75 V to +1.1 V, coinciding with the suppression of the ring current at +1.1V in the second cycle of the RRDE experiments. The shift in onset suggests the product of the redox process peaking at +1.1 V, which produced primarily soluble products in the first cycle, is now contributing to film growth instead. Its shoulder at +1.3 V has all but vanished, suggesting that the reactions leading to the formation of soluble products are suppressed and primarily film-forming reactions at +1.1V and below remain. In addition, the mass loss in the oxidative region has become more pronounced. However, on the QCM the current is only diminished slightly in the second cycle, whereas the RRDE shows virtually no current. The reason for this may be kinetic, as the film may only delay the reactions, thus showing more current at 50 mV s⁻¹ on the QCM than at 100 mV s⁻¹ on the RRDE.

Figure A6.3: Cyclic voltammograms at 4000 rpm and 100 mV s⁻¹, RRDE with Pt disc working electrode and Pt ring, $E_{\text{ring}} +1.5$ V vs RHE, in 5 mM NaMnO₄ pH 14. The blue line shows the current on the Pt ring electrode, inverted and corrected for the collection efficiency. (a) First cycle, (b) second cycle.

Figure A6.4: Comparing cyclic voltammetry in the different cells in 5 mM NaMnO₄, pH 14, Au electrode.

Figure A6.5: Staircase voltammetry and corresponding μm , on Au at pH 14, 5 mM NaMnO_4 . Colored bands indicate potentials of specific interest, specifically +1.4 V, +1.1 V, +0.9 V, +0.6 V, and -0.3 V.

Figure A6.5 shows the current and mass response at a given potential. Each potential was applied for 1 minute in a staircase voltammetry experiment, so the steady state current could be observed for the different potential regimes (Figure A6.5). This shows that the initial mass change rates are indeed a function of potential and not an artefact introduced by mass transfer limitations. The colored bands indicate potentials of particular interest, and match the colored arrows in Figure 6.1a. All four graphs in Figure A6.1 show the same experiment with progressively more time shown. This is because initial mass changes are small and easily obscured by the deposition at very negative potentials, which is orders of magnitude larger. The blue line in the last image indicates a linear fit. The slope of the linear fit was used in combination with the charge, integrated from the current, to calculate the mass change per charge for deposition at very negative potential, where it is mass transfer controlled and thus independent of overpotential.

Figure A6.6: Cyclic voltammograms in 80 mM NaClO, pH 14, at 4000 rpm for Au electrode with Mn film, deposited for 20 minutes in 5 mM NaMnO₄, pH 14.

Figure A6.7: Chronoamperometry in 80 mM NaClO, pH 14, at 4000 rpm for Au electrode with Mn film, deposited for 20 minutes in 5 mM NaMnO₄, pH 14.

Figure A6.7 investigates the stability of an electrode coated by a film deposited at +0.9 V. Chronoamperometry was performed for 1 hour in a solution containing 80 mM hypochlorite. The potential was +0.02 V, within the hypochlorite reduction regime but not so negative as to produce H₂. The current density, j_{film} was used as a measure of film stability, with more current indicating a loss of selectivity. The current density of this experiment on bare Au, j_{Au} , is shown as a dotted line for reference. The inhibition was calculated using:

$$\text{inhibition} = \left(1 - \frac{j_{\text{film}}}{j_{\text{Au}}}\right) \times 100\% \quad (\text{A6.1})$$

Figure A6.8: Cyclic voltammograms in 80 mM NaClO, pH 14, at 4000 rpm for Au electrode with Mn film, deposited for 20 minutes in 5 mM NaMnO₄, pH 14, at +0.9 V. (b) shows the current at +0.02 V as a function of cycle number. The red dashed line is bare Au as a reference.

Figure A6.8 investigates the stability of the film deposited at +0.9 V under an alternating voltage in a solution containing hypochlorite. Again, the current at +0.02 V can be used as a measure of inhibition. Cycling does not impact the inhibition when the anodic vertex is below +0.85 V, but exposure to higher potential decreases the inhibition linearly with each repetition.

Figure A6.9: SEM image of polished Au substrate

Figure A6.10: SEM showing surface coverage in cracks, +1.1 V.

Figure A6.11: SEM showing surface coverage in cracks, +0.9 V.

Figure A6.12: SEM images of a film deposited at -0.7 V after oxidation to $+1.8$ V.

Figure A6.13: *Ex situ* Raman spectroscopy of films deposited for 20 minutes at different potentials onto polished Au.

Figure A6.13 shows *ex situ* Raman spectra for films deposited at different potentials. With the exception of the $+1.4$ V sample, which was only polarized

very close to OCP, all films show bands around between 560 and 680 cm^{-1} characteristic of MnO_2 .

Figure A6.14: QCM of addition of NaMnO_4 to NaOH , adsorption of monolayer.

Figure A6.15: Raman spectra recorded during cyclic voltammetry of a roughened Au electrode in 5 mM NaMnO_4 pH 14 at 1 mV s^{-1} . Recorded using 10 second integration times, at +1.4 V, +1.0 V, and +0.25 V vs RHE.

Deposition potential (V)	Mn 2p (%)	O 1s (%)
-0.7	35.0	65.0
+0.4	35.2	64.8
+0.9	33.6	66.4
+1.1	22.1	77.9

Figure A6.16: XPS of Mn films deposited for 20 minutes in 5 mM NaMnO₄ pH 14 at potentials indicated.

FIG. 1. Potential-pH equilibrium diagram for the system manganese-water, at 25°C.
[Considering β - MnO_2 (pyrolusite).]

Figure A6.17: Pourbaix diagram of Mn [122].

Figure A6.18: Computed phase diagrams.

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Summary

The topic addressed in this thesis was to ameliorate the use of the carcinogenic chromate additive in the chlorate process. This process employs chromate as a solution additive to create a selective cathodic film. The performance of the films was measured by determining the selectivity towards the hydrogen evolution reaction (HER) over the reduction of hypochlorite. The goal was to understand these films, and by doing so, to allow the rational search for non-toxic, high performing cathodes. In this context we studied films formed by the reduction of chromate, molybdate and permanganate. Deposition was studied on electrodes of Au, Pt and Ti. **Chapter 1** provides background information concerning the chlorate process, and an overview of the existing literature.

To investigate the film formation several dedicated techniques were used. **Chapter 2** provides an overview of the methods and equipment used, as well as theory on electrochemical potentials and the two most important techniques used: the rotating ring disc electrode (RRDE) and the electrochemical quartz crystal microbalance (QCM or eQCM). Chapter 2 also provides schematics for the pilot reactor and the self-designed cell for *in situ* Raman experiments.

The first step, described in **Chapter 3**, was to study the deposition mechanism of oxides formed by reduction of (di)chromate. This was done using a model system consisting of a Au electrode and a highly alkaline electrolyte to mimic the environment near the cathode in an industrial cell. The RRDE was used to detect soluble intermediates, and to investigate the kinetics of the deposition process. The QCM was used to determine the mass of the electrode, and so track the growth of the $\text{Cr}^{\text{III}}\text{O}_x$ film. By combining these two techniques, the transfer of charge throughout the deposition process could be monitored. Of the charge related to chromate reduction, only a minor component resulted in film formation, which terminates at a thickness of merely 1.85 nm. The remaining charge was dispersed into the solution in the form of soluble CrVO_4^{3-} and $\text{Cr}^{\text{III}}(\text{OH})_4^-$. This explains the large discrepancy between reductive (deposition) and oxidative (dissolution) charge observed in the cyclic voltammogram. We then disentangled the two concomitant reduction processes in detail, through peak deconvolution followed by a

Levich analysis. This demonstrates that a multi-step process occurs. Finally, we propose a mechanism based on our results, illustrated in Figure S1, in which the formation of the first monolayer inhibits the reduction of chromate, meaning only one or two additional layers can form until growth is inhibited.

Figure S1: An illustration of the growth of CrO_x on Au (left) and Pt (right). The approximate onset potential (in V vs RHE) for each step is indicated in each figure. Solid arrows indicate reactions; dashed arrows are molecules moving away from the electrode surface.

In **Chapter 4**, a similar study to the one in Chapter 3 was performed, only now exchanging Au for Pt. The use of the more stable Pt instead of Au also allowed the introduction of concentrated NaCl to the electrolyte, bringing us one step closer from our model system to industrial conditions. Interestingly,

the presence of Cl^- did not have any influence on the film deposition or oxidation process. Deposition occurs differently on Pt than on Au, with the exact potential of the redox processes being different, and the quantity of soluble intermediates being two orders of magnitude lower. We hypothesize that on Pt, a CrO_x film is formed of different composition than on Au, with a significantly lower charge permeability. This explains the lower quantity of soluble reduced species formed in the reductive scan in comparison to Au, the smaller film thickness, and the different, bottom-up mechanism of re-oxidation of the film for Pt.

Figure S2: An illustration of the Pt cathode surface immediately before HER onset, in solutions containing chromate and/or molybdate additive. (a) and (d) show a single additive. (b) and (e) show those same electrodes after the second additive is introduced. In (c) and (f) both additives were present in high and low concentrations, respectively, before potential was applied. The exact concentration is indicated in each figure. * denotes a film that continues to grow uninhibitedly.

The differences are illustrated in Figure S1. Finally, we introduce molybdate as a co-additive, and find that a) it activates the Pt-CrO_x cathode for the HER; b) improves the hypochlorite reduction inhibition; and c) the stability of the film, making it a highly promising co-additive.

In **Chapter 5**, we investigate film deposition on the industrially used electrode material Ti. We find a less defined deposition process on this material, especially as we extend our search into μM concentrations of chromate. We revisit the molybdate co-additive in order to facilitate the use of μM amounts of chromate, which by itself is not sufficient to reach an industrially viable energy efficiency. We confirm that molybdate is detrimental at high concentrations due to its catalysis of the homogeneous decomposition of hypochlorite to oxygen. We also find its activating effect is negated in the presence of too much chromate. We demonstrate that the two additives can display synergy, but only in a narrow concentration regime, as illustrated in Figure S2. The exact concentrations are affected by the mass transport and surface-to-volume ratio of the reactor used, and so do not translate well from one cell to another. In order to show that the combination of molybdate and chromate truly is a promising approach, we scale up the experiment to a pilot plant scale. We increase the size of the reactor and electrode, the temperature, and the current density. These results match the trends from the lab-scale experiments, and we demonstrate that the energy consumption for chlorate production is reduced by 4% through the addition of 0.8 mM molybdate to 27 μM chromate.

In **Chapter 6**, we eliminate chromate completely and apply our methods instead to the study of permanganate. Because it results in uninhibited film growth, permanganate cannot be used *operando*. Instead, we transferred the films to an Mn-additive-free solution and tested the selectivity in suppressing the reduction of hypochlorite as a function of the deposition potential. In general, thicker films deposited at more negative potential are more effective in minimizing oxychloride reduction, but most importantly we show that deposition in a narrow potential window around +0.9 V results in a film with exceptional properties. It fully inhibits the hypochlorite reduction for at least 1 hour, despite being relatively thin. The properties of the deposited films are strongly dependent on the deposition potential. From scanning electron microscopy (SEM), we find a wide array of morphologies, and *in situ* Raman

spectroscopy reveals reduction of permanganate to form likely defective MnO_2 , MnOOH and $\text{Mn}(\text{OH})_2$, depending on the applied redox potential. Based on Raman and XPS compositions, DFT modeling demonstrates that reduction of hypochlorite involves significant energy barriers, and might be inhibited by surface O and OH termination. In general, these results demonstrate that *ex situ* cathodic alkaline permanganate deposition is a suitable technique for creating selective films for the chlorate process.

Perspective and outlook

The aim of this thesis was to ameliorate the use of the carcinogenic chromate additive in the chlorate process. The overarching research question was: how does the formation of a selective cathode film from chromate proceed, and how can we replicate this functionality using a non-toxic alternative? The approach was centered around identifying the key properties that make chromate-based films so successful in the chlorate process, with the goal of finding a non-toxic alternative.

The first part of the research question, regarding the deposition of chromate, was answered thoroughly in Chapter 3, where we proposed a deposition mechanism. We expanded this knowledge to ultra-low chromate concentrations in Chapter 4, and it was only by using this understanding that we were able to investigate the interactions between chromate and molybdate.

Of the results in this thesis, molybdate stands out as a promising co-additive, especially as we have shown it to increase performance not only on a lab scale but also in a larger pilot cell. A 2000-fold reduction in chromate concentration while maintaining a significant fraction of its functionality certainly suggests a promising direction, and additional fine-tuning may decrease this even more. However, further large-scale optimization will be required before molybdate addition is truly an option for application, as the energy efficiency achieved in Chapter 5 is infeasible for operation. In addition, even though it represents a major reduction of Cr^{VI} use, it does not and will not by itself achieve the goal of a chromate-free chlorate process.

In terms of a truly chromate-free solution, films deposited *ex situ* from permanganate show more promise. However, these experiments have not yet been scaled up. A major challenge for *ex situ* films is stability, not on the 1 hour

timescale tested here, but on the order of 10 years. This proved to be an insurmountable problem for *e.g.* polymer and Zr-based coatings that had shown promise on the lab scale. Not only must the film itself maintain its function, leaching of permanganate into the electrolyte would cause problems due to its uncontrolled deposition. This may be challenging considering the rich redox chemistry of manganese oxides and permanganate, and the variable circumstances in the plant during operation, startup and shutdown. In short, manganese-based films, although promising, are still very far removed from application.

To bring either of these solutions closer to application still requires more understanding of the electrode-electrolyte interface. We achieved an understanding of CrO_x film growth in Chapters 3 and 4, but the exact structure of the film remains unclear. Knowledge of the film is needed to understand the mechanism by which selectivity is realized, a topic on which there is still debate in the community. The lack of definitive identification of the molecules involved is a problem encountered throughout this thesis. Instead, assumptions have been made regarding the nature of the Cr^{V} and Cr^{III} species. All mechanisms here are proposed based on indirect evidence: peaks in cyclic voltammetry, Pourbaix diagrams, and mass on an electrode surface. Rarely were we able to state with certainty that a specific molecule is present. This is the result of the recalcitrant nature of the species involved, as most are IR-inactive and amorphous, meaning common techniques such as XRD and FTIR could not be applied. Raman spectroscopy was effective for manganese species but produced spectra with a strong bias near the roughened Au surface. The composition of the Au- MnO_x interface was therefore detectable, rather than the surface layers in contact with the electrolyte. Although *ex situ* measurements such as SEM-EDX and XPS worked well, the results remain ambiguous because they most likely do not represent the materials as they are in their highly alkaline, cathodically protected environment.

The future work to resolve this issue is already in progress in the form of collaborations. These collaborations aim to support our experiments in two ways: first, providing direct evidence using *in situ* X-ray techniques; second, providing further DFT calculations to show the plausibility of our conclusions. In this context, it may then seem that this work states its conclusions with undue confidence, but this is not the case. We have performed carefully

designed experiments, investigated edge cases and designed experiments that strongly support our conclusions: indirectly but nevertheless rigorously. Our approach reveals itself in the extensive supplementary information provided with each chapter.

In addition to our collaborations, work in the chlorate field also continues with a focus on the mechanism of selectivity, both through experiments and calculations. Knowledge from this kind of work may be combined with our results regarding film formation and the interaction of different additives to direct research towards a combination of additives that can replace chromate. The drive to continue this research towards a slot-in replacement is very strong, because alternative solutions for the chlorate process would change the process on a fundamental level. These are options like lanthanides, whose deposition behavior is radically different and whose influence on the process is harder to predict. Another solution is to operate in a two-compartment cell by introducing a membrane, but this requires a costly redesign of the entire plant and introduces additional cell potential. Even further removed from the current process is a proposal to utilize a different chemical pathway altogether, eliminating the HER in favor of an oxygen consuming electrode. However, this technology still faces many major problems even on the lab scale.

Overall, the 2000-fold reduction of chromate we realized using the molybdate co-additive still seems a highly promising short-term solution, worthy of further investigation. Authorization from the EU for use of sodium dichromate relies partially on the amount of chromate used, so a decrease of this magnitude may provide an extension of chlorate plant operation until fully chromate-free technologies can reach the required technology readiness level.

Finally, the results described in this thesis can be applied more broadly than only to the chlorate process. Our society is changing from one dependent on fossil fuels to one that utilizes renewable energy. One of the major obstacles on the way to electrification of the chemical industry is the lack of selective electrodes. The understanding gained in this work contributes to that issue, too, as protection of metal by transition metal oxides is also applied in photocatalysis and water electrolysis. As the development of electrochemical processes continues, there will be much more to learn about selective

electrochemistry. Already, new terminology such as the “buried interface” is emerging to describe films such as the ones studied in this work, signaling that this field is maturing. Once the field gets to the required technology readiness level, electrochemistry could prove to be one of the major drivers for the energy transition.

Samenvatting

Het doel van deze thesis was het uitsluiten van het gebruik van kankerverwekkend chroom-6 in het chloraat proces. Daar wordt chroom gebruikt als toevoeging aan het elektrolyt, om een selectieve laag te vormen op de kathode. De maatstaaf voor de prestatie van deze laag was de verhouding waarin een laag de waterstof evolutie reactie de voorkeur geeft ten opzichte van de reductie van hypochloriet. Het doel was om de lagen te begrijpen, en daarmee de zoektocht naar een veilig en effectief alternatief richting te geven. We hebben lagen bestudeerd die gevormd werden door de reductie van chromaat, molybdaat en permanganaat. We bestudeerden de depositie op Au, Pt en Ti elektrodes. **Hoofdstuk 1** biedt een overzicht van het chloraat proces en de beschikbare literatuur over dit onderwerp.

Om de lagen te onderzoeken hebben we verschillende methodes gebruikt. **Hoofdstuk 2** biedt een overzicht van de gebruikte technieken en materialen, alsook de relevante concepten achter de elektrochemie en de twee belangrijkste technieken die gebruikt zijn in dit proefschrift. Dat waren de roterende elektrode (*rotating ring disc electrode* of RRDE) en de kwarts microweegschaal (*quartz crystal microbalance* of QCM). Hoofdstuk 2 bevat ook diagrammen voor de grootschalige pilot opstelling en de zelfgemaakte reactor voor *in situ* Raman experimenten.

De eerste stap, die te vinden is in **Hoofdstuk 3**, was het onderzoeken van het depositiemechanisme van de oxides die gevormd worden van dichromaat. Een versimpeld model met een Au elektrode en sterk alkalisch elektrolyt werd gebruikt om de omstandigheden bij de kathode in de industriële reactor te benaderen. De RRDE werd gebruikt om vloeibare tussenproducten te detecteren, en de kinetiek van de depositiereactie in kaart te brengen. De QCM gebruikten we om de massa van de elektrode te meten, en zo de groei van de $\text{Cr}^{\text{III}}\text{O}_x$ laag bij te houden. Door de twee technieken te combineren kon de balans opgemaakt worden van alle ladingsoverdracht in het proces. Hieruit bleek dat slechts een klein deel van de lading betrokken was bij de depositie van de laag, waardoor deze slechts 1.85 nanometer dik werd. De overige lading verdween in de oplossing in de vorm van oplosbaar $\text{Cr}^{\text{V}}\text{O}_4^{3-}$ en $\text{Cr}^{\text{III}}(\text{OH})_4$. Dit verklaart het grote verschil tussen reductieve (depositie) en oxidatieve (oplossing) lading in het cyclische voltammogram. We konden twee

verschillende reacties onderscheiden door een piek deconvolutie uit te voeren, gevolgd door een Levich analyse. Daarmee tonen we aan dat de depositie bestaat uit verschillende stappen. Tot slot stellen we een mechanisme voor, geïllustreerd in Figuur S1, gebaseerd op onze resultaten, waarin de vorming van de eerste monolaag de verdere reductie van chromaat blokkeert, waardoor slechts één of twee extra lagen gevormd kunnen worden voordat de groei van de laag geheel stopt.

Figuur S1: Een illustratie van CrO_x laaggroei op Au (links) en Pt (rechts). De potentiaal (in V vs RHE) van elke stap is aangegeven per figuur. Dichte pijlen geven reacties aan, gestreepte pijlen de beweging van molecule van het elektrodeoppervlak weg.

In **Hoofdstuk 4** voeren we een vergelijkbare studie uit, alleen deze keer gebruiken we een Pt in plaats van een Au elektrode. Omdat Pt stabiel is dan Au kunnen we ook geconcentreerd NaCl toevoegen aan het elektrolyt, om zo de daadwerkelijke industriële omstandigheden beter te benaderen. Opmerkelijk is dat Cl⁻ geen invloed bleek te hebben op de depositie of oxidatie van de laag. Wel blijkt dat de depositie op Pt anders plaatsvindt dan op Au, aangezien de potentialen van de verschillende redox reacties anders zijn, en de hoeveelheid oplosbare producten twee ordes van grootte kleiner is. Onze hypothese stelt dat dit komt omdat de laag een andere compositie heeft op Pt, en daardoor ook een andere ladingsdoorlaatbaarheid. Hiermee verklaren we ook dat de laag dunner is dan op Au, en dat de oxidatie van de laag vanaf de onderkant begint in plaats van de bovenkant. Tot slot introduceren we molybdaat als tweede toevoegmiddel in het elektrolyt. We concluderen dat molybdaat a) de Pt-CrO_x elektrode activeert voor de waterstofevolutie; b) de blokkade van hypochloriet reductie verbeterd; en c) de stabiliteit van de laag verbeterd. Al met al is molybdaat dus een veelbelovend toevoegingsmiddel.

In **Hoofdstuk 5** onderzoeken we de depositie van lagen op Ti elektrodes, zoals gangbaar zijn in de industrie. Depositie is hier minder gedefinieerd, vooral wanneer we onze zoektocht uitbreiden naar µM chromaat in plaats van mM. Wederom voegen we molybdaat toe om elektrolyse mogelijk te maken met zo weinig chroom, wat *an sich* niet toereikend is om een acceptabele energetische efficiëntie te bereiken. We bevestigen dat molybdeen bij hoge concentraties een nadelig effect heeft omdat het de decompositie van hypochloriet naar zuurstof katalyseert. We concluderen dat het voordelige effect van molybdaat op de activering van de waterstofevolutie teniet wordt gedaan door de aanwezigheid van te veel chroom. We laten zien dat beide toevoegingsmiddelen een synergetisch effect kunnen hebben bij een specifieke combinatie van concentraties, zoals geïllustreerd in Figuur S2. Deze concentraties worden beïnvloed door het massatransport en de elektrode-tot-elektrolyt ratio van de reactor, waardoor deze niet universeel gedefinieerd kunnen worden. Om te demonstreren dat de combinatie van molybdaat en chromaat echt een veelbelovende benadering is voeren we grootschaligere experimenten in een pilot opstelling. Daarbij verhogen we de grootte van de reactor en het elektrolyt, de stroomdichtheid, en de temperatuur. Deze resultaten hiervan laten dezelfde trends zien als de modelexperimenten, en

we laten zien dat de energetische efficiëntie voor de productie van chloraat met 4% verbetert door de combinatie van 0.8 mM molybdaat en 27 μM .

Figuur S2: Een illustratie van het Pt cathode oppervlak, direct voor het begin van waterstofevolutie, in oplossingen die chromaat en/of molybdaat bevatten. (a) en (d) bevatten één van twee, waarna (b) en (e) dezelfde elektrodes tonen nadat het tweede additief ook is toegevoegd. In (c) en (f) waren beide additieven aanwezig vóór een potentiaal werd aangebracht, in hoge respectievelijk lage concentraties. De exacte concentratie is per figuur aangegeven. De * geeft aan dat deze laag zonder belemmering door aan groeien was.

In **Hoofdstuk 6** vervangen we chroom-6 in zijn geheel door permanganaat, en we passen wederom dezelfde methodes toe om de depositie hiervan de bestuderen. Omdat oxide lagen van permanganaat depositie oneindig door blijven groeien kan permanganaat niet *operando* gebruikt worden. In plaats daarvan brachten we vooraf gedeponeerde lagen over naar oplossingen

zonder permanganaat, en testten we daar hun prestatie met betrekking tot het blokkeren van de hypochloriet reductie. In het algemeen zijn lagen die bij negatievere potentiaal gedeponereerd zijn beter, maar we ontdekken een opmerkelijke laag bij +0.9 V met uitzonderlijke eigenschappen. Deze laag blokkeert de hypochloriet reductie volledig, en ondanks dat de laag relatief dun is blijkt deze tenminste 1 uur stabiel. De eigenschappen van de mangaanoxide lagen blijken sterk afhankelijk te zijn van de depositiepotentiaal. Met elektronenmicroscopie vinden we een variëteit aan morfologieën, en *in situ* Raman spectroscopie laat zien dat er defectrijke MnO_2 , MnOOH en $\text{Mn}(\text{OH})_2$ gevormd kunnen worden. Op basis van de composities die we halen uit Raman en XPS voeren we *density functional theory* berekeningen uit. Deze laten zien dat de reductie van hypochloriet significante energetische barrières bevat en volledig geblokkeerd kan worden door O en OH groepen aan het oppervlak bij de potentialen die wij bestudeerden, maar dat deze omzeild kunnen worden door een ligandverwisseling. Deze resultaten tonen aan de *ex situ* kathodische depositie in alkalisch milieu een veelbelovende benadering is om selectieve lagen te vormen voor toepassing in het chlooraat proces.

List of publications

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